



## **Determination of the Contamination of Groundwater Sources in Okrika Mainland with Polynuclear Aromatic Hydrocarbons (PAHs)**

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### **ABSTRACT**

In this study, we examined the presence and concentrations of six polynuclear aromatic hydrocarbons (PAHs) in groundwater sources of Okrika mainland impacted by effluent discharges from a petroleum refinery into her surrounding Creeks. Sterile amber coloured bottles were used to collect 10 replicate borehole water samples from the mainland and fixed with concentrated H<sub>2</sub>SO<sub>4</sub>. Samples were transferred to the laboratory in iced coolers and analyzed using Gas chromatography coupled with Flame Ionization Detector (GC-FID). The interactions of the PAH components detected was determined using the Pearson product moment correlation coefficient (r) while spatial variance equality in means of concentrations was explored with the One-way ANOVA. Structure detection of observed inequalities was made with means plots. Concentrations of the PAHs were high and exceeded the WHO maximum permissible limit of 0.002mg/l in drinking water. Benzo(b)fluoranthene, with the highest mean concentration varied between 0.00037-0.51266 (0.08117±0.03330159)mg/l, fluoranthene varied between 0.00060-0.32890 (0.0473946±0.01769877)mg/l, while benzo(k)fluoranthene with the least mean concentration varied between 0.00017-0.08478 (0.0237385±0.00610045)mg/l. However, pyrene concentration ranged between 0.00015 and 0.24757 (0.0508440±0.01859716)mg/l, benzo(a)anthracene between 0.00020-0.21972 (0.0512660±0.01688275)mg/l, and chrysene between 0.00013 and 0.16571 (0.0488975±0.01090264)mg/l. Strong associations were observed between all the PAH components measured at P<0.01. Significant heterogeneity in mean variance of the PAHs [ $F_{(211,9502)} > F_{crit(3,921478)}$ ] was recorded across the sampling locations at P<0.05. Structure detection of mean difference revealed that the inequalities were most contributed in BH1, BH 2, BH 5 and BH 10, while

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equality in mean concentrations were observed between BH 1 and BH 4, and BH 5 and BH 6. BH 8 recorded the highest contamination level of the various PAHs due basically to its proximity to the refinery's effluent channel. The most probable source of these PAHs is therefore the nearby Port Harcourt Refinery Company's effluent discharges into the surrounding creeks of the mainland. This contamination is of public health concern as several PAHs are known carcinogens. It is recommended that advanced technological engineering be applied to contain the presence of these pollutants in drinking water sources of residents of the area.

*Keywords: Polynuclear aromatic hydrocarbons; carcinogens; Okrika mainland; Nigerian delta; refinery effluents;*

## 1. INTRODUCTION

Petroleum refining contributes solid, liquid, and gaseous wastes in the environment. Some of these wastes could contain toxic components such as the polynuclear aromatic hydrocarbons (PAHs), which have been reported to be the real contaminants of oil and most abundant of the main hydrocarbons found in the crude oil mixture (El-Deeb and Emara, 2005). However, other sources of PAHs such as incomplete combustion of coal, gas, wood, tobacco and charbroiled meat (ATSDR, 1995), as well as from uncontrolled disposal sites (Mahmood, 1989) also exist.

Once introduced in the environment, PAHs could be stable for as short as 48 hours (e.g. naphthalene) or as long as 400 days (e.g. fluoranthene) in soils (Martens and Frankenberger, 1995). They thus, resist degradation and thus, remain persistent in sediments and when in organisms, could accumulate in adipose tissues and further transferred up the trophic chain or web (Decker, 1981; Boehm et al., 1981).

Groundwater sources of PAH contamination could be from seepages from waste disposal sites, oilspills, surface and underground storage tank leakages, agro-activities, effluents discharges, and deliberate dumping (Sharma and Al-Busaidi, 2001). Contaminated groundwater sources pose potential risk to the local water consumers as well as the natural environment (Forstner and Wittmann, 1993; Abolfazi and Elahe, 2008).

Several PAHs have been classified by the World Health Organization (WHO, 1997), the Agency for Toxic Substances and Disease Registry (ATSDR, 1995), and Dionex (2009) as carcinogenic, while others have been confirmed to be at least, mutagenic to mammals.

For some time, residents of the Okrika mainland have raised complaints bordering on oil-tainted and odoriferous waters, as well as formation of oil films on left-over waters from ground sources. This complain raises concern, given the fact that some of the groundwater sources in the area are gotten from shallow hand-dug wells, soils are porous, and water table high. Worse still, the Port Harcourt Refining Company in the neighbourhood discharges her poorly treated effluents into the surrounding creeks; a practice inhabitants of the area reported have been ongoing for over a decade now.

It is against this suspicion and for the non-existence of research on the possible contamination of the groundwater aquifer of this area that the current investigation was

conducted with objectives aimed at the determination of the presence and levels, interactions, and spatial variations of some PAHs in groundwater sources of the Okrika mainland.

## 2. MATERIALS AND METHODS

### 2.1 Study Area

Okrika, is located between latitude  $04^{\circ}$  and  $50'N$ , and longitude  $07^{\circ}$  and  $10'E$  (Figs. 1 and 2) in the Niger Delta area of Nigeria. About 95% of the total area is wetland and is characterized by a network of creeks and small rivers which drain into short swift coastal rivers. The geology of the area is of the earlier deposits of the marine sediments of the Lower and Upper Cretaceous age, which constitutes the economically important structure where petroleum was formed and deposited. The soil type could be classified as coarse, loamy, highly weathered, and moderately acidic with low soluble salt content. Though urban and industrial developments have reduced the vegetation of the area to secondary growths, the pristine vegetation is characterized by thick mangrove forest of the red variety, which attains heights up to 50m and girth up to 27m. The climate is tropical, characterized by frequent precipitation that reaches up to 300-450cm annually. There is usually a long wet season that last from March to September, and mean monthly temperature ranges between  $24$  and  $27^{\circ}C$ . Humidity is about 80% (SPDC, 1998) and the major economic activity of the people is fishing.

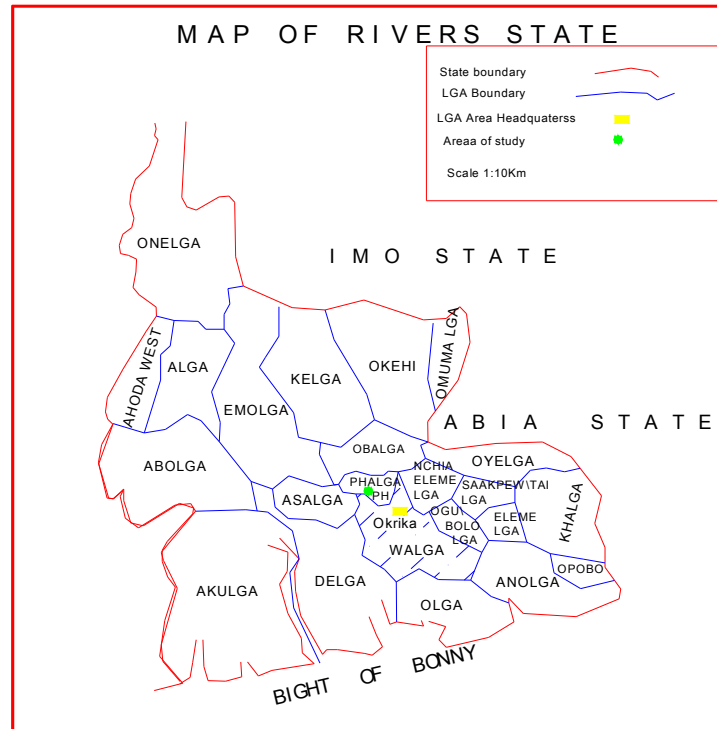
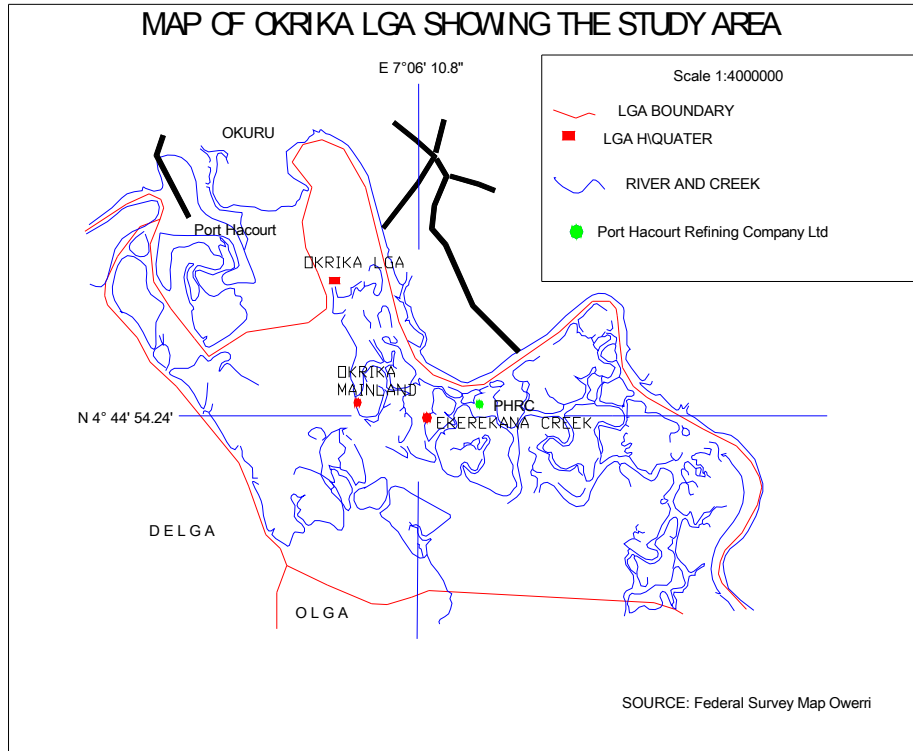


Fig. 1. Map of Rivers State showing Okrika Local Government Area



**Fig. 2. Map of Okrika LGA showing the study area**

## 2.2 Field Sample Collection

Two replicate water samples were collected from each of 10 boreholes, using 1 liter amber glass bottles fitted with a screw cap and lined with foil and labeled BH1 to BH10. Samples were transferred to the laboratory in ice-packed cooler as soon as possible.

## 2.3 Laboratory Analysis

Glasswares were all washed with detergents and hot water and subsequently rinsed with distilled water. A gas chromatograph coupled with flame ionization detector (GC-FID model HP 5890); utilizing the column chromatograph for cleaning of sample extracts was used in the analysis of samples. Analytical grade reagents used include N-hexane as solvent, silica gel as desiccant, conc.  $H_2SO_4$  as preservative for samples, and reagent water that was prepared by passing tap water through a carbon filter bed containing about 0.5kg activated carbon, using a water purification system. A PAH standard mixture containing 1000 ppm each of fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene was used for calibration.

The GC parameters included a carrier gas (helium), fuel gases (air and hydrogen), back-up gas (nitrogen), detector temperature of  $35^\circ C$ , in-let temperature of  $25^\circ C$ , initial and final temperatures for oven of 5 and  $300^\circ C$ , respectively, hydrogen, air, nitrogen, and helium flow rates of 30, 300, 30, and 30 ml/minute, respectively.

For sample extraction, 50 ml of borehole water sample was measured into 1 liter separating funnel and a drop of concentrated H<sub>2</sub>SO<sub>4</sub> added to release the hydrocarbon components. 5ml of N-hexane was added to the sample, after which sample was vigorously shaken for 5minutes and allowed to stand for another 20minutes. Layers were formed that separated the extract at the top layer from the lower layer (which was discarded). Extract was collected for GC analysis in a glass vial.

In order to clean and remove biogenics from extracts, a column chromatography was set up using silica gel and a glass wool and extracts passed through the column.

With the use of a micro-GC syringe, cleaned extract was loaded and the GC prompted to run for about 41 minutes. At the end results containing the chromatograms were integrated and printed.

## 2.4 Statistical Analysis

The interaction of the PAHs was determined with the Pearson product moment correlation coefficient (*r*) and the test of homogeneity of variance in means across the sampling locations explored with the one-way ANOVA. Subsequent structure detection of mean difference was made with means plots.

## 3. RESULTS

### 3.1 PAHs Concentrations in Groundwater Sources

The PAHs detected showed wide variations in concentration. Fluoranthene, pyrene and benzo(a)anthracene varied between 0.0006-0.3289 (0.0474 ± 0.0177), 0.0002-0.2476 (0.0508 ± 0.0186), and 0.0002-0.2197 (0.0513 ± 0.0169) mg/l, respectively (Table 1).

**Table 1. Variations in PAH concentrations (mg/l) in groundwater samples**

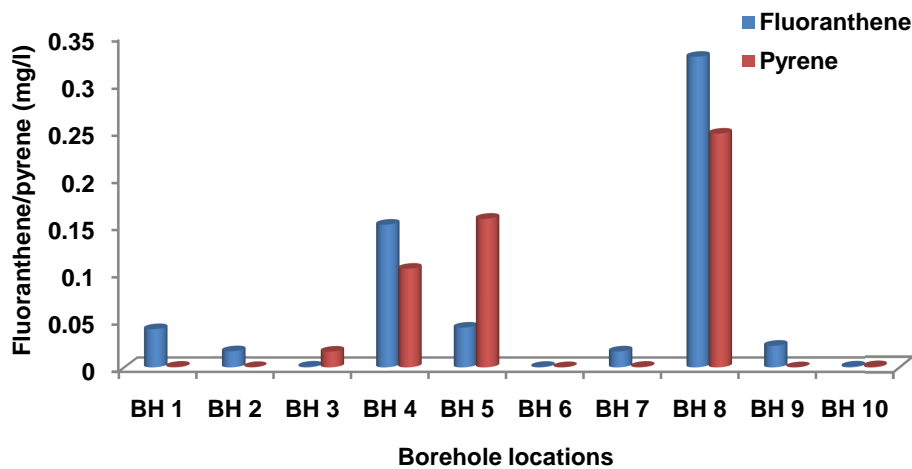
| PAH                  | Minimum | Maximum | Mean      | SE         |
|----------------------|---------|---------|-----------|------------|
| Fluoranthene         | 0.00060 | 0.32890 | 0.0473946 | 0.01769877 |
| Pyrene               | 0.00015 | 0.24757 | 0.0508440 | 0.01859716 |
| Benzo(a)anthracene   | 0.00020 | 0.21972 | 0.0512660 | 0.01688275 |
| Chrysene             | 0.00013 | 0.16571 | 0.0488975 | 0.01090264 |
| Benzo(b)fluoranthene | 0.00037 | 0.51266 | 0.081170  | 0.03330159 |
| Benzo(k)fluoranthene | 0.00017 | 0.08478 | 0.0237385 | 0.00610045 |

*SE = standard error*

Chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene varied from 0.0001-0.1657 ( $0.0489 \pm 0.0109$ ), 0.0004-0.5127 ( $0.0812 \pm 0.0333$ ), and 0.0002-0.0848 ( $0.0237 \pm 0.0061$ ) mg/l, respectively.

### 3.2 Spatial Variation in PAHs

BH8 recorded the highest levels of all the PAH components in the study. However, least concentrations of 0.00062 and 0.00028 mg/l were recorded in BH6 for fluoranthene and pyrene, respectively (Fig. 3), 0.00016, 0.00037, and 0.00017 mg/l recorded in BH10 for chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene, respectively, while 0.00021 mg/l was recorded for benzo(a)anthracene (Figures 4 & 5).



**Fig. 3. Spatial variation in fluoranthene and pyrene concentrations in groundwaters of Okrika Mainland**

The test of homogeneity of mean variance using the one-way analysis of variance (ANOVA) showed high significant spatial inequality in means of the PAH concentrations [ $F_{(211,95)} > F_{crit(3,92)}$ ] at  $P < 0.05$ . Using means plots for structure detection of mean differences, the inequalities were revealed to be contributed by all the PAH components measured, especially in BH1 and BH5 (Fig. 6), BH2 and BH10 (Figure 7), BH1 and BH2 (Fig. 8), BH2 and BH10 (Fig. 9), BH1 and BH10 (Figure 10) and BH2 and BH10 (Figure 11), while equality (homogeneity) was observed between BH5 and BH6 (Figures 6, 7, 8, 9, 10 and 11) and BH1 and BH4 (Figures 7 & 8).

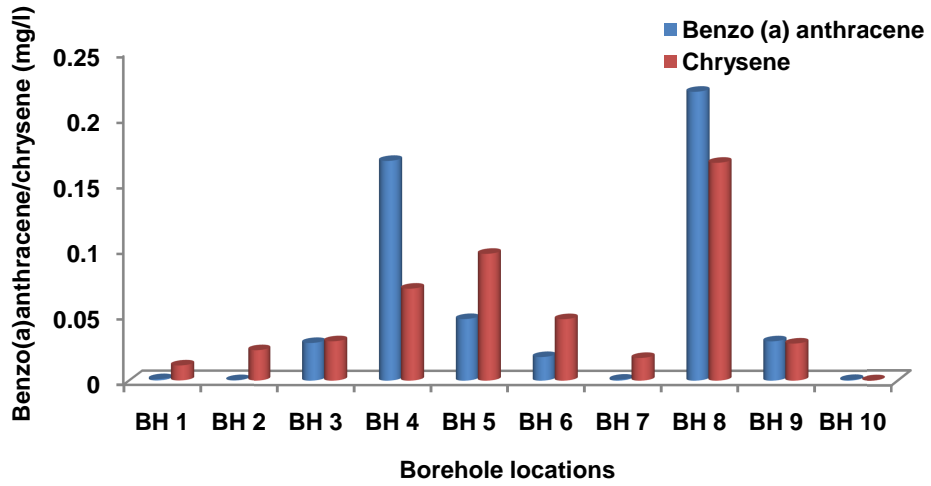


Fig. 4. Spatial variation in benzo(a)anthracene and chrysene concentrations in groundwaters of Okrika Mainland

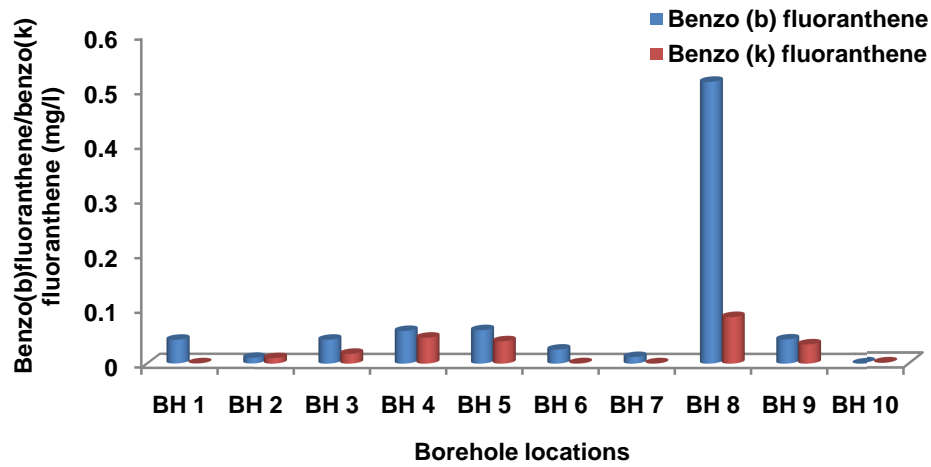


Fig. 5. Spatial variation in benzo(b)fluoranthene and benzo(k) fluoranthene concentrations in groundwater of Okrika Mainland

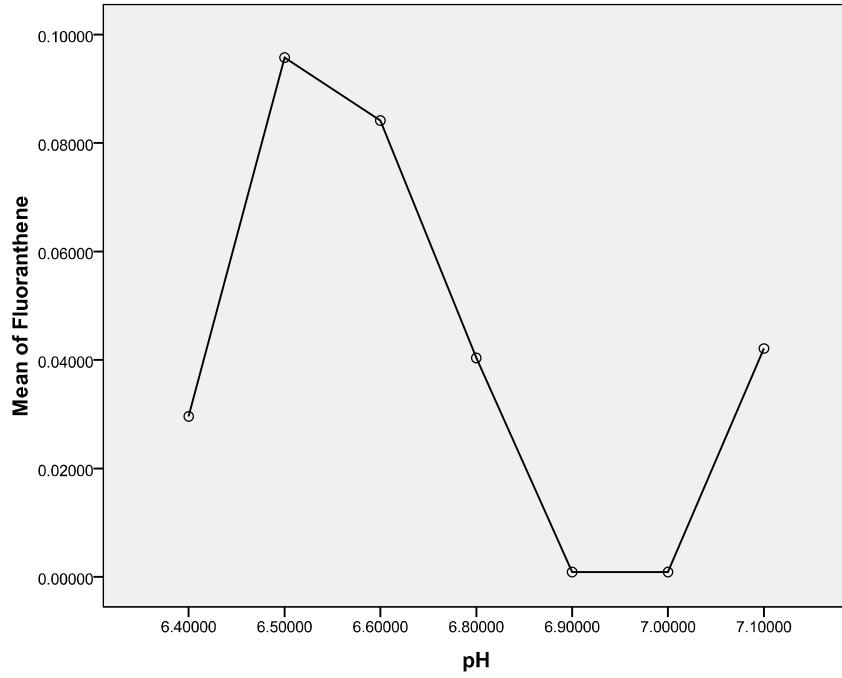


Fig. 6. Structure of group means in concentrations of fluoranthene using means plot

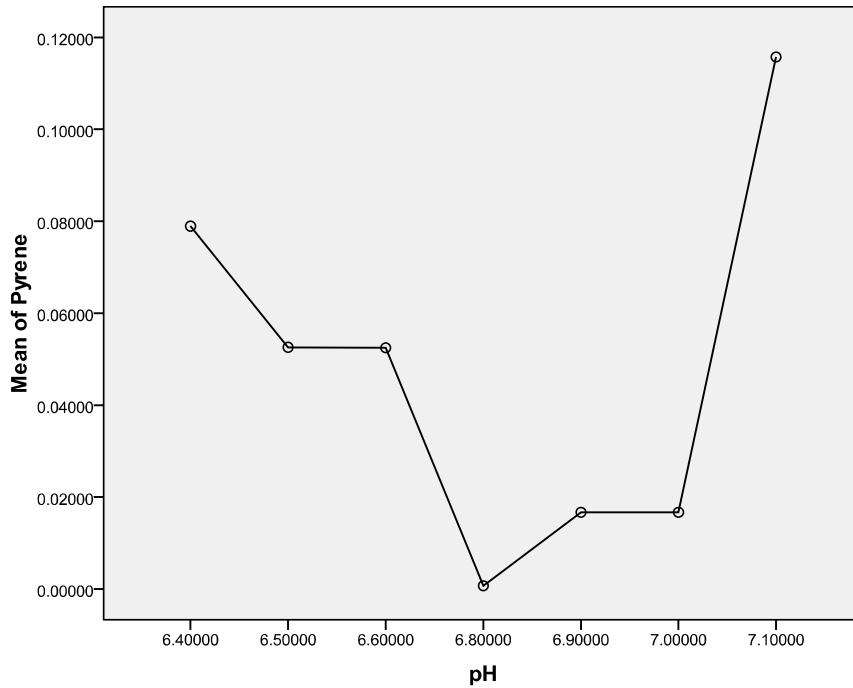


Fig. 7. Structure of group means in concentrations of pyrene using means plot



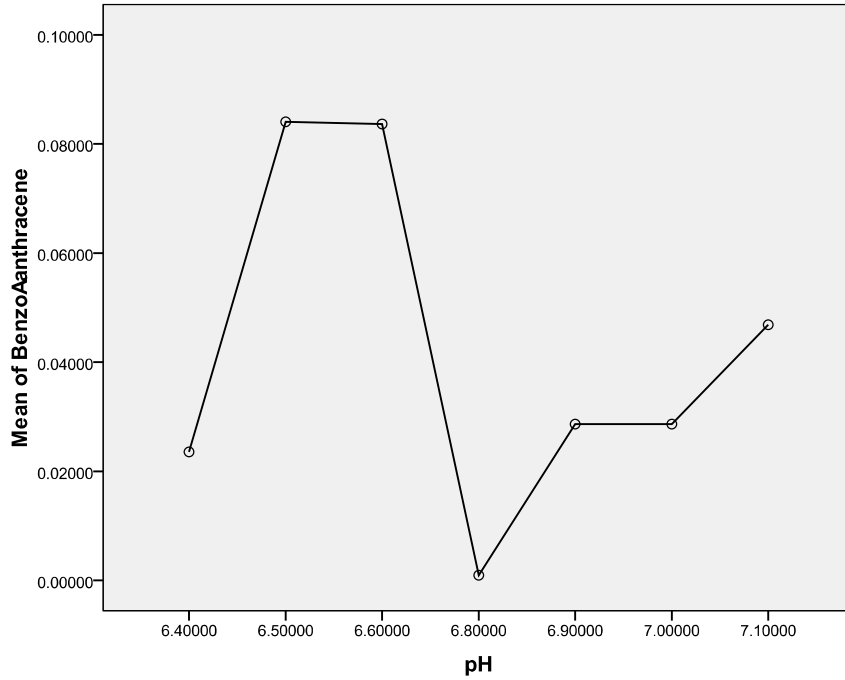


Fig. 8. Structure of group means in concentrations of benzo(a)anthracene using means plot

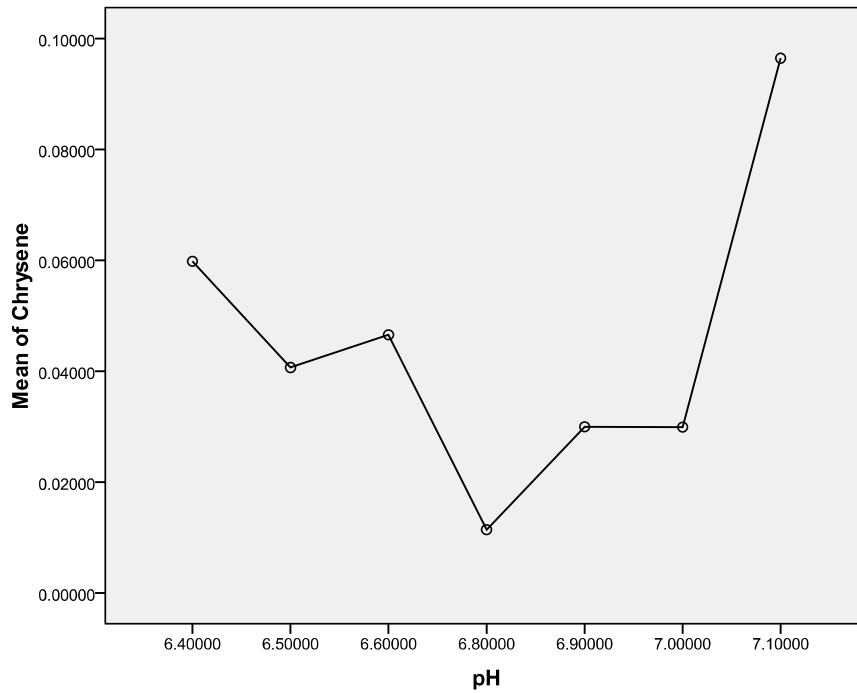


Fig. 9. Structure of group means in concentrations of chrysene using means plot

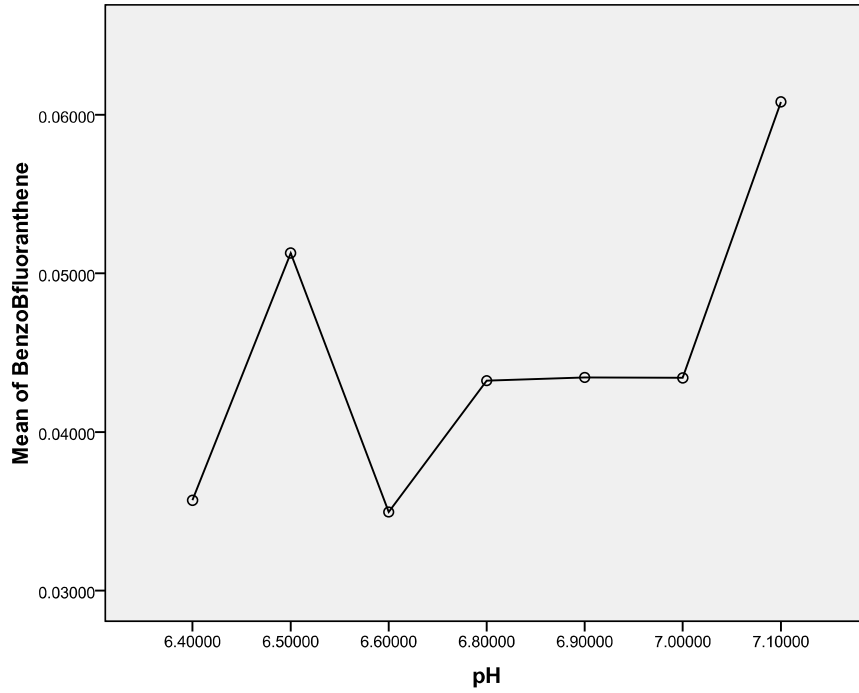


Fig. 10. Structure of group means in concentrations of benzo(b)fluoranthene using means plot

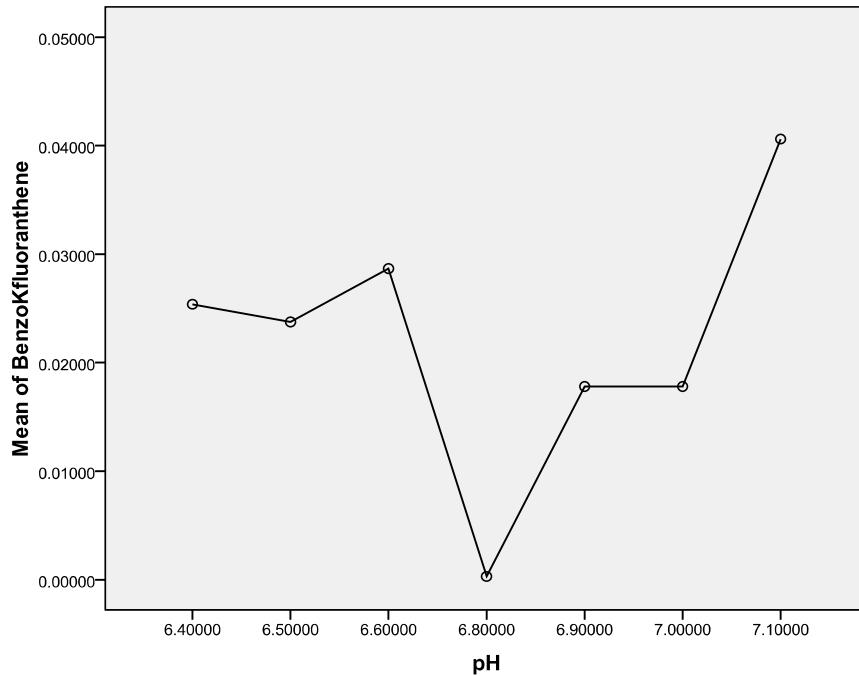


Fig. 11. Structure of group means in concentrations of benzo(k)fluoranthene using means plot

### 3.3 Relationships between the PAHs

Though pH had no significant influence on the PAHs, the polynuclear aromatics showed very strong significant influences on one another at  $P < 0.01$  (Table 2).

**Table 2. Correlation matrix of the PAH components**

| Components   | pH     | Fluoranthene | Pyrene  | B(a)A   | B(b)F   | B(k)F   |
|--------------|--------|--------------|---------|---------|---------|---------|
| Fluoranthene | -0.328 |              |         |         |         |         |
| Pyrene       | -0.099 | 0.676**      |         |         |         |         |
| B(a)A        | -0.146 | 0.765**      | 0.883** |         |         |         |
| Chrysene     | 0.032  | 0.635**      | 0.965** | 0.861** |         |         |
| B(b)F        | 0.233  | 0.616**      | 0.858** | 0.813** | 0.869** |         |
| B(k)F        | -0.015 | 0.680**      | 0.914** | 0.911** | 0.907** | 0.827** |

\*\* = significant at  $P < 0.01$ , B(a)A = benzo(a)anthracene, B(a)F = benzo(b)fluoranthene, B(k)F = benzo(k)fluoranthene

## 4. DISCUSSION

The levels of the PAHs in the current study are generally believed to be of petrogenic origin and closely related, due to their molecular weights (Okoro, 2007). The high concentrations detected in the samples could therefore be traced to petroleum contamination of the groundwater aquifer from the poorly treated refinery effluents in the neighbourhood. The refinery operators have been discharging oil-contaminated wastewaters into the creeks surrounding the small mainland for over a decade now. The possibility of constituent pollutants seeping and subsequently contaminating groundwater aquifer proximally has also been identified by other authors such as Ogbonna et al. (2006; 2008), Narayanan (2007) and Kaufmann and Claveland, (2008). The high water table and porous soils of the area could aid contamination of groundwater aquifers. Anyakora et al., (2004) had already identified components of the PAHs in ground waters of some other Niger Delta region of Nigeria; wherein he detected high concentrations of benzo(a)pyrene, especially in water sources of some oil producing communities. The maximum permissible limit for total PAHs in drinking water by the World Health Organization (WHO, 1984) is 0.0002mg/l. Values from this study far exceed this standard for total PAHs. Undoubtedly, these results create a great cause for public health concerns, especially as certain PAHs have been confirmed to be carcinogenic (ATSDR, 1995), and are not only ingested by inhabitants through drinking contaminated waters, but also when the water is used to prepare their foods. This thus increases the risk of elevated concentrations in adipose tissues of man and other animals. Inevitably man suffers the greatest risk of bioaccumulation due to his position as tertiary consumer in the trophic chain, in addition to his predisposition to other route of entry into his body. Furthermore, carcinogenicity is transgenic, as oncogenes (cancer prone genes) could be inherited by filial generations (Evans, 1977; Cerna, 1996).

The absence of significant influence of pH on the PAHs imply that hydrogen ion concentration does not play a role in the biogeochemical availability of PAHs, rather their eco-availability, especially at high concentrations are anthropogenic in origin (ATSDR, 1995). The very strong significant association between the PAHs agrees with the work of El-Deeb and Emara (2005) and confirms their close relatedness in molecular weights (Okoro, 2007).

The observed spatial variations in their concentrations indicate differential levels and proximal inputs of contaminants in the boreholes. BH8, which had the highest concentration of all the PAHs measured is located closest to the refinery's effluent discharge channel to the Ekerekana Creek. Similarly, BH 4, which is situated few meters from the Ogan waterside; a highly contaminated slow flowing Creek, also had very high concentrations of fluoranthene, pyrene, and benzo(a)anthracene. Conversely, BH10 and BH6 which recorded most of least contaminations are located relatively far from the effluent discharge route and creeks. The source of these contaminations remains chronic seepages from the surrounding Creeks.

## **5. SUMMARY, CONCLUSION AND RECOMMENDATION**

The high concentrations of PAHs recorded in this study could be fingerprinted to inputs from the Port Harcourt Refining Company which has been discharging poorly treated oil effluents into the surrounding creeks of the small mainland. The reported porous nature of the soils as well as high water table of the area are twin accelerators to possible serious contamination of groundwater aquifers of the host community, resulting in potential, chronic detrimental health effects. The observed spatial variation in concentrations indicates proximal inputs, even as the PAH components exhibited very high relatedness. The presence of these polynuclear aromatic hydrocarbons in alarming concentrations, higher than the stipulated maximum contamination level (MCL) of regulatory agency (WHO, 1984) calls for intervention to save the ignorant residents from impending debilitating health problems.

The refinery's effluents should be properly treated with advanced technologies before environmentally friendly disposal methods that are in line with regulatory standards and guidelines. As a matter of urgency, the company should act to contain the expanding groundwater plume and further remediate contaminated aquifers. There is however the need for further research into the presence and levels of PAHs in soils impacted by oil activities, aquatic and macrobenthic organisms, plankton assemblages, as well as microbial biotypes of the area.

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