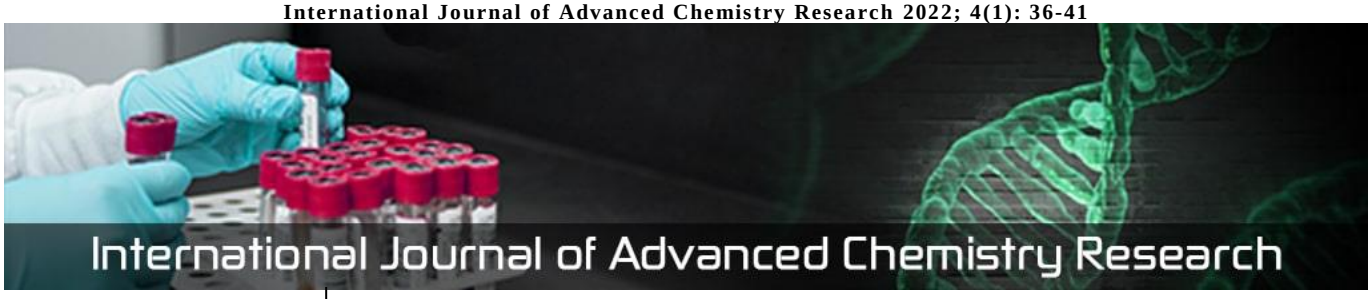

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Concentration, source apportionment and ring size analysis of polycyclic Aromatic Hydrocarbons (PAHs) in water from Kolo Creek, Niger Delta, Nigeria

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Abstract
Water samples were collected from Kolo Creek between the months of December to October and analyzed for the concentrations of polycyclic aromatic hydrocarbons (PAHs). The analysis for the PAHs was achieved through the use of gas chromatography-mass spectrometric analysis after extraction with dichlomethane and n-hexane solvents has been carried out. The result indicated that all the PAHs components were identified in the creek in the stations and the months. It was observed that the PAHs were more abundant in the dry months than the wet months. The values were December (11.140 mg/L) > February (9.130 mg/L) > April (4.06 mg/L) > August (2.310 mg/L) > (2.220 mg/L) > June (2.060 mg/L). Source Identification and apportionment gave both pyrogenic and petrogenic sources of PAHs contamination, although pyrogenic source was the dominant one. Ring size analysis indicated their abundance in the following order 2-3 rings (1.824±0.775 mg/L) > 4 rings (1.148±0.198 mg/L) > 5 rings (1.115±0.422 mg/L) >6 rings (0.875±0.951 mg/L). The concentrations of PAHs in Kolo Creek if allowed to continue will grow beyond threshold levels that may have detrimental consequences on man and the immediate environment in the near future. Therefore, regulatory efforts be put in place to curb such eventuality.

Keywords: Source apportionment, environment, polycyclic aromatic hydrocarbons, origin, water

Introduction
All over the world, the issue of discharge of effluents and contaminants into water bodies is now one of the most critical environmental problems in the present age. Even though natural sources of pollution also exist in the environment, yet higher contributions of pollutants within the environment arise from human continuous invasive activities in the surroundings. The pollution of water is known to have occurred when the water body has been undesirably affected as a result of the input of enormous quantities of constituents to the water and has made it unhealthy for its intentional usage (Klein, 1966) [13].

The harmfulness of polycyclic aromatic hydrocarbons (PAHs) and their extensive dissemination has steered up further curiosity into the occurrence of these constituents in water and soil environments**.** PAHs are known environmental contaminants which are appreciably present in different environmental media such as soils, water, air and sediments (Harris *et al*., 2011) [8]. These compounds (which are confirmed pollutants) are mostly produced from partial incineration of carbon based compounds of organic origin, which were either produced from homes or industries (Mastral and Callen, 2000) [14].

The arrangements of PAHs are characterized by bonded aromatic rings. The first member of the PAHs family is naphthalene, which is composed of two fused benzene rings placed side by side. PAHs are classified into two basic categories which are high molecular weight PAHs (HMWP) and low molecular weight PAHs (LMWP) (Helfrich and Armstrong, 1986) [9]. They usually found in polluted area, especially where oil exploration and exploitation activities are present and also where constant incineration of organic bound products are ubiquitous. The stability of the PAHs is based on the ability of the π electrons in the orbitals to delocalization between the carbon atoms. They are highly hydrophobic and therefore do not readily dissolve in water (Nasr *et al*., 2010). Besides human activities, (PAHs) also occur naturally in the environment.

However, their rate of production is usually increased where there are incessant anthropogenic activities (Kadafa, 2012) [11]. They can be bio- magnified to appreciably high levels in the food web (Nacci *et al*., 2002) [2]. The leading origins of PAHs in the environs consist of wood fire, natural crude oil leakages, burning of fossil fuel, burning of coal, discharged waste from industries, workplaces and homes, used water and manure. PAHs
are amongst the tenacious organic noxious waste in the water environment (Andrea *et al*., 2012; Dosunmu *et al*., 2012; Olayinka *et al*., 2018) [12, 5].
This work therefore was done to determine the concentrations of polycyclic aromatic hydrocarbon in Kolo Creek, and important water body in the Niger Delta, Nigeria and also sought to define the sources or origin of the polycyclic aromatic hydrocarbons

Materials and Methods Sampling Procedure

Water samples were collected from a depth of 35 cm below the surface from Kolo creek. Triplicate samples were collected at three points between December 2018 – October 2019 bi-monthly. Previously washed amber coloured bottles were rinsed with water from the point where the samples will be collected before collection of the samples were done. Samples were transported to the laboratory in an ice-pack container and stored at a temperature of 4°C in a refrigerator.

Extraction of Polycyclic Aromatic Hydrocarbons from Water Samples

The water samples were extracted for polycyclic aromatic hydrocarbons in the laboratory following standard laboratory methods. A measured volume of 250 cm3 of the untreated samples were transferred into a 500 cm3 flask and 25 cm3 of C2H4Cl2 (DCM) was further added to the flask. The contents were agitated and the pressure in the vessel freed intermittently. Thereafter the content of the flask (sample and extracting solvent) were allowed undisturbed for some time to allow the formation two phases. The phases were separated using a separatory funnel. The organic phase which contained the extract was further treated with anhydrous sodium sulphate and the extracting solvent. The final extract was allowed to evaporate freely for twelve hours at 25 oC in a fume cupboard. The top of the vessel containing the extract was covered with aluminum foil. Sample clean-up was achieved in a column of 600 × 19 mm, where the open top was tightly covered with a glass wool. Precisely, a known mass of 3 g of activated silica gel was added and along with sodium sulfate sodium sulphate and the column eluted with 15 cm3 of n-hexane**.**
The final concentrated extract was put into a column and was eluted with 25 cm3 n-hexane as the eluent solvent. The obtained eluates were further concentrated by reducing it to 1 cm3 with the aid of with a mild flow of uncontaminated nitrogen as the carrier gas. Thereafter, the 1 cm3 extract was put into a labeled container and kept at a temperature of 4 °C until analysis was done with a gas chromatograph mass spectrometry (GC-MS)**.**

Analysis of Sample Extract for PAHs

The Polycyclic aromatic hydrocarbons were analyzed by gas chromatography, using Agilent model 6890N chromatograph, serial No US 10530055 (Agilent Technologies Avondale, USA). The gas chromatographic equipment was connected to a selective mass detector, model 5975 series MSD, Agilent, Avondale, USA. The column used was a fused silica capillary with dimensions (30 m × 0.25 mm × 0.25 µm film thickness) to separate the PAHs. The carrier gas was He, which was operated at a flow rate of 1.2 mL/min.
The injector for the sample was fixed at a temperature 250 oC and 300 oC respectively and the samples injected at a volume of 1 cm^3 in a split less approach. The mass spectrometry (MS) conditions were set as follows: ionization source: electron ionization at – 70 eV: ion source temperature: 200 oC (19-22): store mass range m/z 47- 400 µm. Identification of individual PAHs was based on comparison of retention time between samples and standard solutions.

Results and Discussion

Spatial and Monthly Concentrations of Polycyclic Aromatic Hydrocarbons

The spatial and monthly variations of PAHs in Kolo Creek is shown in Tables 1 and 2 and Figure 1. All the different priority PAHs were detected in station 1 except naphthalene, while at station 2, it was benzo (g,h,i) perylene and dibenzo (a,h) anthracene that were not detected and in station 3, naphthalene, acenaphthene, acenaphthylene and anthracene that were not detected.
The distribution of PAHs in surface water in Kolo Creek within the months of sampling showed that in December, all the PAHs investigated were detected except Indeno (1,2,3-cd) pyrene), while in February, the first three PAHs (naphthalene, acenephthene and acenaphthylene) and Indeno (1,2,3-cd) pyrene) were undetected. In April, August and December, all the PAHs were detected except the first three (naphthalene, acenaphthene and acenaphthylene) and in June, only naphthalene, acenaphthylene and anthracene were undetected. Naphthalene and acenaphthylene were only detected in the month of December.
Polycyclic aromatic hydrocarbon is one of the classes of tenacious and persistent pollutants. Their sources in the environment come from either natural or anthropogenic sources (Mastral and Callen, 2000) [14]. Polycyclic aromatic hydrocarbons were detected in varying degrees of concentrations in the creek and were higher in the dry season than the wet season, which disagrees with the findings of Moses *et al*. (2015) in Qua-Iboe River estuaries. The lower values of PAHs in the wet season when compared to the dry season is a result of dilution from flood water from rain and other adjoining water bodies.

The concentrations of PAHs observed in the present work, generally were higher than those observed in rivers of some oil producing communities in Delta State (Adeyemo and Ubiogoro, 2012), they were also higher than the observed values of total PAHs in estuaries of Qua-Iboe River (Moses *et al*., 2015) and the values of PAHs observed in Badagry Creek and Ologe Lagoon, Lagos, Nigeria (Aderinola *et al*., 2018).

The high presence of PAHs and their even distribution in the creek may not be unconnected with the different uncontrolled illegal oil activities present within the areas investigated. Secondly, the nature and activities around the Kolo at the specific sample stations contributed immensely to the distributive nature of the PAHs in Kolo Creek. Besides the artisanal refiners whose effluents are discharged directly into the creek, other sources of PAHs into the creek might be connected with agricultural activities and waste discharge system of the inhabitants. This is because wastes are directly discharged into the creek (a lifestyle of the rural dwellers in the study area). Another possible reason for the presence of PAHs in these environments is the continuous gas flaring (either by the approved operators or the unapproved operators) which is a common site in the area under investigation. Flared gases when precipitated into water bodies contribute to the total PAHs burden or content of that environment (Essumang *et al*., 2009).

Table 1: Polycyclic aromatic Hydrocarbons (PAHs) concentrations in Water samples from Kolo Creek at the different stations

PAHs (mg/L)	Stations		
	1	2	3
Na	ND	0.080 ± 0.004	ND
Ace	0.047 ± 0.004	0.139 ± 0.004	ND
Acy	0.307 ± 0.013	0.028 ± 0.013	ND
Fl	0.258 ± 0.122	0.046 ± 0.122	2.382 ± 0.122
Ph	0.900 ± 0.031	0.042 ± 0.031	0.256 ± 0.031
An	0.540 ± 0.018	0.446 ± 0.018	ND
Flu	0.181 ± 0.018	0.187 ± 0.018	0.288 ± 0.018
Py	0.412 ± 0.008	0.105 ± 0.008	0.006 ± 0.008
BaA	0.365 ± 0.013	0.568 ± 0.013	0.630 ± 0.013
Ch	0.361 ± 0.014	0.197 ± 0.014	0.332 ± 0.014
BbF	0.251 ± 0.10	0.688 ± 0.10	0.369 ± 0.10
BkF	0.079 ± 0.013	0.625 ± 0.013	0.341 ± 0.013
BaP	0.246 ± 0.024	0.292 ± 0.024	0.455 ± 0.024
BP	0.041 ± 0.01	ND	0.809 ± 0.01
DA	0.033 ± 0.032	ND	1.199 ± 0.032
IP	0.025 ± 0.00	0.313 ± 0.01	0.206 ± 0.01
Total	4.046	3.756	7.273

Table 2: Mean monthly variation of polycyclic aromatic hydrocarbons (PAHs) concentrations (Mean ± SD) in Water samples from Kolo Creek

PAHs (mg/L)				Months		
	December	February	April	June	August	October
Na	0.16 ± 0.01	ND	ND	ND	ND	ND
Ace	0.22 ± 0.02	ND	ND	0.158 ± 0.01	ND	ND
Acy	0.67 ± 0.02	ND	ND	ND	ND	ND
Fl	2.91 ± 0.17	1.34 ± 0.18	0.02 ± 0.00	0.41 ± 0.11	0.38 ± 0.13	0.32 ± 0.17
Ph	1.01 ± 0.04	0.57 ± 0.04	0.48 ± 0.05	0.02 ± 0.04	0.05 ± 0.04	0.29 ± 0.04
An	0.53 ± 0.03	0.56 ± 0.03	0.68 ± 0.03	ND	0.11 ± 0.03	0.10 ± 0.03
Flu	0.01 ± 0.03	0.35 ± 0.03	0.12 ± 0.03	0.01 ± 0.03	0.03 ± .025	0.03 ± 0.03
Py	0.53 ± 0.01	0.29 ± 0.01	0.17 ± 0.01	0.0 2 ± 0.01	0.02 ± 0.01	0.04 ± 0.01
BaA	0.82 ± 0.01	1.56 ± 0.03	0.42 ± 0.02	0.01 ± 0.00	0.13 ± 0.01	0.19 ± 0.02
Ch	0.82 ± 0.31	1.56 ± 0.02	0.42 ± 0.25	0.01 ± 0.00	0.13.± 0.11	0.19 ± 0.04
BbF	0.75 ± 0.02	0.44 ± 0.01	0.17 ± 0.00	0.20 ± 0.00	0.15 ±0.03	0.08 ± 0.00
BkF	1.01 ± 0.03	0.52 ± 0.01	0.53 ± 0.02	0.27 ± 0.02	0.18 ± 0.00	0.12 ± 0.01
BaP	0.39 ± 0.03	0.33 ± 0.02	0.40 ± 0.02	0.49 ± 0.04	0.22 ± 0.01	0.26 ± 0.00
BP	0.98 ± 0.03	0.68 ± 0.04	0.29 ± 0.03	ND	0.03 ± 0.04	0.02 ± 0.04
DA	0.33 ± 0.02	0.93 ± 0.02	0.32 ± 0.04	0.07 ± 0.02	0.03 ± 0.03	0.02 ± 0.01
IP	ND	ND	0.04 ± 0.00	1.01 ± 0.05	0.85 ± 0.05	0.56 ± 0.06
Total	11.140	9.130	4.06	2.060	2.310	2.220

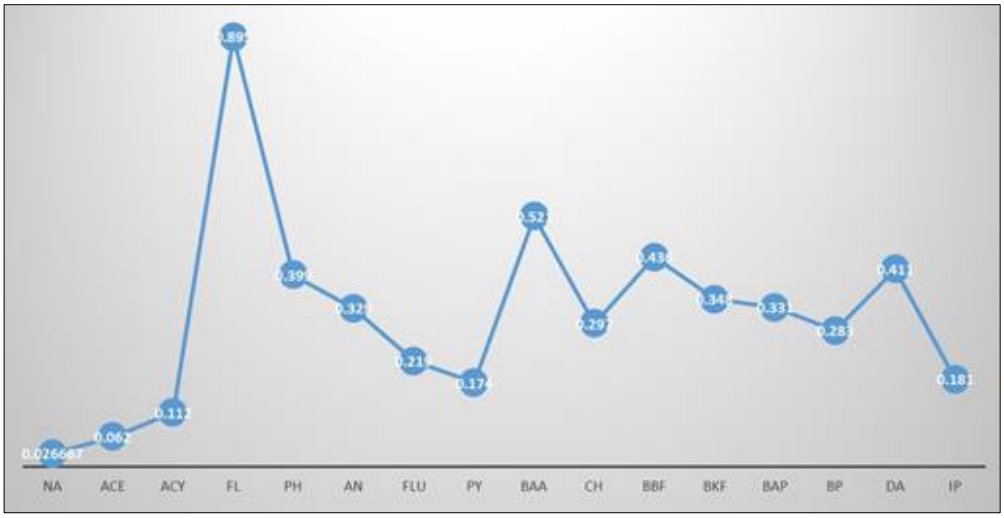

Fig 1: Mean values of polycyclic aromatic hydrocarbons in surface water of Kolo Creek during the sample period

Source Apportionment and Origin of Polycyclic Aromatic Hydrocarbons

The spread or distribution pattern of polycyclic hydrocarbons in any environment has a far reaching effect on the nature and sources of the PAHs and can be used in the assessment of their overall detrimental effects to the environment (Wang and Fingas, 1999). The behavioural characteristics in relation to the ratio of PAHs have is of great importance in the diagnoses, identification and prediction of sources of PAHs within the environment and also to separate their different sources of input (Zemo, 2009).

The diagnostic ratio of 1.029 (LMW/HMW) obtained for station 1 in Kolo Creek suggested petrogenic source of PAHs, while stations 2 and 3 gave values of 0.263 and 0.569, respectively which were all less than 1, and therefore suggested pyrogenic sources of PAHs. Stations 1 and 2 when assessed with An / An + Ph ratio showed the input source to be pyrogenic since the determined values which were 0.375 and 0.914 were each greater than 0.1. The Flu / Flu + Py ratio analysis done in the three stations investigated showed that station 1 (0.304) fall into petrogenic source of PAHs contamination, while stations 2 (0.640) and station 3 (0.980) were greater than 0.5 and so are classified as pyrogenic enrichment sources of PAHs contamination. The BaA/ BaA + Ch ratio analysis indicated that all the stations had values greater than 0.35 which is in the category of pyrogenic sources of input.

The observed multiple sources of PAHs in the surface water from the creek is in agreement with the findings of other authors (Anyakora *et al*., 2004; Essumang *et al*.,2009; Edokpayi *et al*., 2016; Olayinka *et al*., 2018; Edori and Iyama, 2019), in different rivers within Nigeria and elsewhere. The variability of input sources as observed from the diagnosis implies the influence of natural and human factors as contributory factors to PAHs presence in the creek.

Table 3: Diagnostic Ratios and Sources of PAHs in water Sample from Kolo Creek

Stations	∑LMW PAHs	∑HMW PAHs	LMW/HMW	An/(An + Ph)	Flu /(Flu + Py	BaA/ (BaA + Ch)
1	2.052	1.994	1.029	0.375	0.304	0.503
2	0.781	2.975	0.263	0.914	0.640	0.742
3	2.638	4.635	0.569	-	0.980	0.655
Petrogenic			> 1	< 0.1	< 0.4	< 0.2
Pyrogenic			< 1	> 0.1	> 0.5	> 0.35

Ring Size analysis of Polycyclic Aromatic Hydrocarbons

The concentrations of the PAHs based on ring size classification is shown in Table 4. The distribution of the various ring sizes showed that in station 1, 2-3 rings (LMWH) was the most abundant species of PAHs, which was followed by the 4-ring category, then the 5-ringed members and the lowest was the 6-ringed members. In station 2, the occurrence and distribution concentrations of the different PAHs categories was in the order of 5-membered rings > 4-membered rings > 2-3-membered rings > 6-membered rings. In station 3, the nature of occurrence was 2-3-membered rings > 6 membered rings > 4 membered rings > 5-membered rings.

The concentrations of the lower molecular weight (2-3 rings) at higher levels than the other ring members in the present work disagrees with the observation of Kafilzadeh *et al*., (2011) in water samples of Kor River Iran, where the presence of the higher molecular weight PAHs (4-6 rings) where predominant over the low molecular weight PAHs. They observed that the most predominant class was the 4-membered rings, which was followed by the 5 and the 6-membered rings. The observation in the present work of more values of the LMWP is also at variance with the observation of Edori and Iyama (2019), in drainage discharge points into the New Calabar River, where HMWP predominated over the LMWP. The predominance of the lower molecular weight PAHs (LMWP) over the higher molecular weight PAHs probably arose from the incessant flaring of gases from the artisanal petroleum refining points (which is rampant within the area) and others from conventional flaring from nearby gas stations own by multinationals.

Table 4: Ring size Analysis of Polycyclic Aromatic Hydrocarbons in Water samples from Kolo Creek

Ring Size	Stations			Mean±SD
	1	2	3	
2-3	2.052	0.781	2.638	1.824±0.775
4	1.319	0.870	1.256	1.148±0.198
5	0.576	1.605	1.165	1.115±0.422
6	0.099	0.313	2.214	0.875±0.951

Conclusion

The concentrations of polycyclic aromatic hydrocarbons in superficial water of Kolo Creek was assessed within a period of twelve months (December –October). The results showed the presence of all the sixteen USEPA priority PAHs in the water body. The range of concentrations of the total PAHs within the period varied from 2.060 - 11.140 mg/L. The concentrations of PAHs was more in the dry months when compared to the wet months. This occurrence was attributed to the nature of the creek and discharge pattern of the illegal crude refiners. The high level presence of PAHs in the water body is a signal of impending danger with regard to health implications. So, efforts should be focused on ways of tackling the menace of illegal spills and refining of crude within the area.

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