



POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND
POLYCHLORINATED BIPHENYLS (PCBs) PROFILE IN SURFACE WATER
OBTAINED FROM FALCORP MANGROVE SWAMP, WARRI, DELTA STATE



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Abstract: Surface water samples were regularly sourced for a period of 18 months; February 2013 – July 2014, from five (5) sampling stations on the Falcorp mangrove swamp and Ifie creek, respectively. The water samples were subjected to PAH and PCB analyses which were conducted in accordance with standard procedures which included; gas chromatography coupled with flame ionization or electron capture detector. The collated data were subjected to statistical analysis and multivariate analysis, respectively. The differences in the mean Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Fluranthene, Pyrene, Chrysene, Benzo[k]fluranthene, Benzo[k]pyrene and Dibenzo[a,h]anthracene values recorded across the five (5) stations was statistically insignificant ($P>0.05$). There were positive clusters of Benzo[b]fluranthene, Benzo[a]anthrene, Benzo[k]pyrene, Benzo[k]fluoranthrene, Pyrene, and negative clusters of Acenaphthylene, Benzo[g,h,i]pyrene, Acenaphthene, Phenanthrene, Naphthalene and Fluranthene in components 1. A positive correlation existed between Naphthalene, Acenaphthalene, Fluorene, Phenanthrene, Pyrene, Benzo[a]anthracene, Chrysene and Benzo(k)fluoranthrene. The differences observed in the PCB concentrations in the water samples across the five different stations for the following congeners; 4,4'-Dichlorobiphenyl, 2,3,4,4'-Pentachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl, Decachlorobiphenyl, 2,2',3,3',4,5,5',6'-Octachlorobiphenyl and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl was statistically insignificant ($P<0.05$). Source apportionment attributed the source of the water borne minimal PAHs and PCBs profiles to hydrocarbon and persistent organic pollution emanating from anthropogenic activities around the study area.

Keywords: Refinery, PCBs, PAHs, surface water, falcorp, mangrove swamp

Introduction

Natural water bodies such as mangrove channels that drain areas of industrial and agricultural activities have a high risk of being contaminated by a vast variety of chemicals, particularly hydrocarbons and pesticides. Polycyclic aromatic hydrocarbons (PAHs) are a collection of moieties that are generated in the course of the incomplete combustion of a variety of substances which include; coal, petroleum natural gas, wood, garbage, tobacco and charbroiled meat. There are more than 500 different PAHs in environment (Kumara *et al.*, 2016). Kumar and Kothiyal (2011) reported that PAHs normally exist as complex mixtures (i.e. combustion products such as soot and tar), not as single moieties. PAHs due to their parent origin from which they are derived (benzene ring), would naturally share certain basic characteristics with their parent compounds, one of which is the thermodynamic stability, possessed by benzene. With reference to their formation process, PAHs from both natural and anthropogenic sources can be grouped into three (3) groups: pyrogenic, petrogenic and biogenic respectively (Buczynska *et al.*, 2013). Pyrogenic PAHs culminate from incomplete combustion of fossil fuels and biomass under high temperatures. They are given off in the form of exhaust and solid residues, thereby being ubiquitous in edaphic habitats (Gao *et al.*, 2018). Petrogenic PAHs are derived from petroleum products such as crude oil and coal, and are formed under relatively low temperatures during fossil fuel formation processes (Gao *et al.*, 2018). Direct petroleum spillage has been documented as a prevalent source of petrogenic PAHs. In most cases, pyrogenic PAHs are dominant over petrogenic PAHs due to anthropogenic influences (Gan *et al.*, 2009; Duan *et al.*, 2015). Petrogenic PAHs are introduced into soils through accidental oil spills, release from tanker operations, and municipal runoff. Biogenic PAHs are formed in the course of the degradation of vegetative organic moieties by plants, algae and microorganisms respectively. Additionally, they are produced during the slow transformation of organic matter (OM) in soils by plants and microorganisms (Abdel-Shafy and Mansour, 2016).

PCBs have been described as synthetic organic chemicals that are widespread global environmental pollutants present in air,

water, sediments and soils and their physical and chemical properties permit their utilization for a wide range of industrial applications (Jing *et al.*, 2018). Their electrical insulating properties allow for their usage with electrical equipment, such as in cooling, for instance (Merkel *et al.*, 1999). PCBs are classified as persistent organic pollutants (POPs) with high toxicity, and have undesirable effects on the environment and on humans (Lallas, 2001). The PCB molecule is known to comprise of two (2) connected benzene rings and chlorine atoms that can attach to any or all of 10 different positions allowing for 209 different congeners and 10 different homologs (Alder *et al.*, 1993). High chlorinated PCB congeners are normally known to possess relatively high octanol-water partition coefficients (Kow), thus are often found in organic matter which include; soils and sediments (Jing *et al.*, 2018). As a result of low water solubility and vapor pressure, PCBs can partition between the aquatic and solid phase thus exist in multiple compartments culminating in widespread pollution (Tanabe, 1988).

Falcorp mangrove swamp is located behind the Warri Refinery and Petrochemical Company and the apparent close proximity between the swamp and the refinery complex has posed a plethora of questions as to a potential pollution linkage from both point and nonpoint sources. The aim of this study was to investigate the PAHs and PCB content of surface water collected from Falcorp Mangrove Swamp, Ijala, Warri, Delta State, Nigeria.

Materials and Methods

Study area

Falcorp mangrove swamp is located in Warri South Local Government Area, Delta State Nigeria. It is situated off the Warri refinery and petrochemical company jetty road, just behind the refinery. It falls within the mangrove swamp ecological zone but also has a direct interphase with the rainforest ecological zone. It lies on longitude (541'1" E, 557'4"E) and latitudes (5° 18' 3"N, 5° 84'5"N) (Odigie and Olumukoro, 2020). The water channel within the mangrove swamp is fed by water from surrounding creeks, rivers and surface runoffs from neighboring communities within the Ijala area.

Sample collection

Five (5) stations were utilized for this research. Each of these stations was approximately 600 meters apart from each other. Stations 1, 2 and 3 were located within the Falcorp mangrove swamp along the water channel, while Stations 4 and 5 were

located in Ifie creek which is linked to the water channel of the Falcorp mangrove (Fig. 1).

Water samples were collected from the five sampling points once a month for a period of 18 months; February 2013- July 2014, using 250 cm³ sterile sampling bottles dipped into the water with the aid of rope tied round it.

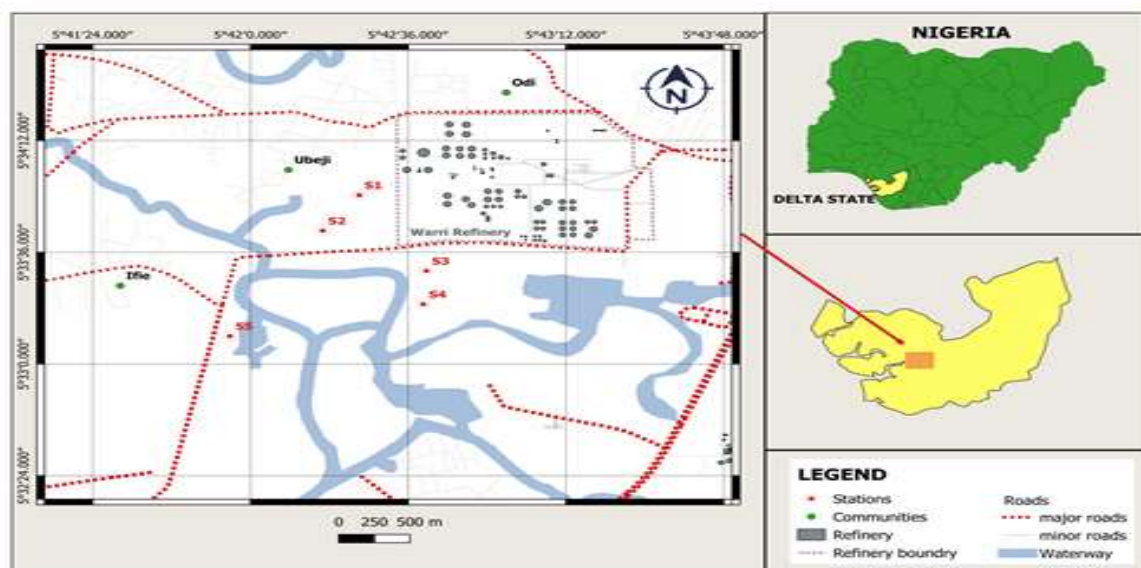


Fig. 1: Map of the respective sampling sites

Analysis of the surface water samples

Determination of PAHs in water

PAHs were extracted using liquid-liquid extraction (LLE) with 100 ml of n-hexane and dichloromethane mixture (1:1 v/v). Before extraction, the respective water sample (800 ml) was filtered with Whatman filter paper (i.d. 70 mm) to remove debris and suspended materials. The extract was concentrated to a final volume of 2 ml under a gentle stream of nitrogen using a rotary evaporator and then analyzed with Gas Chromatograph/Flame ionization Detector (GC-FID) according to a protocol detailed by Burton *et al.* (2005). N – Hexane and Dichloromethane (DCM) (90:10) was used for the extraction. The resultant solution was concentrated in iso-octane and submitted to PAH analysis. The respective PAH internal standards; 20 ng/cm³ each of naphthalene-D8, phenanthrene-D10, chrysene-D12 and perylene-D12 were gravimetrically added prior to the extraction and one extraction blank was performed with each series of extraction.

Determination of PCBs in water

PCB congeners in water were quantified and analyzed, using a Gas Chromatography Coupled to Electron Capture Detector (GC-ECD) according to the method described by Thompson and Budzinski (1999). The column contained alternating layers of neutral, basic, and acidic silica gel. The column was then pre-eluted with hexane, the sample was applied, and then PCBs eluted with hexane. Finally, the samples were concentrated to a final volume of 20 cm³. The GC conditions were: injector temperature, 270°C; initial temperature, 75°C; initial time, 2 min; temperature program, 75–150°C at a rate of 2°C min⁻¹ and then 150–270°C at a rate of 2.5°C min⁻¹; final time, 7 min. Helium was used as the carrier gas at 1.2 cm³ min⁻¹ at 200°C. Quantitation was performed on each chromatographic extract using the concentration of the labeled PCB (based on its response factor and the concentration of the internal standard).

Statistical analysis

Statistical analysis was carried out on the data generated from each sampling station using general descriptive statistics. The student T – test and Kruskal Wallis Test was also used to test

for significance at the 0.05 level of probability for the seasons and the different stations respectively. Multivariate analysis of the available data was done using the SPSS version 16.0 and PAST software whilst Duncan’s Multiple Range test (DMR) was used to locate significant difference(s) at 95% confidence Interval where one exist.

Results and Discussion

The results of the PAH congeners in surface water samples obtained from the 5 stations are shown on Table 1. The data obtained for all the PAHs were compared using analysis of variance ANOVA to test for significant difference among the parameters across the stations respectively. There was no significant difference ($P > 0.05$), in the PAHs; Napthlene, Acenaphthylene I, Acenaphthene II, Fluorene, Fluranthene, Pyrene, Chrysene, Benzo[k]fluranthene, Benzo [k] pyrene and Dibenzo [a,h] anthracene across the five study stations. However, there was a significant difference ($P < 0.05$) in the following PAHs; Phenanthrene, Anthracene, and Benzo[g,h,i] perylene, while there was a significant difference ($P < 0.001$) in the respective PAHs; Benzo[a]anthracene, Benzo [b] fluoranthrene, and Indeno[1,2,3-cd] perylene, in the water samples obtained from the 5 sampling stations.

The result obtained for the seasonal variation of PAHs in water samples is shown in Table 2. The seasonal mean PAH values were compared using unpaired t-test analysis to test if there any significant difference between the respective seasonal values. The results showed that there was significant difference ($P < 0.05$) for only Napthlene and Fluorene while the differences between the seasonal mean values of Acenaphthylene, Acenaphthene, Phenanthrene, Anthracene, Fluranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluranthene Benzo(k)fluranthene, Benzo(k) pyrene, Indeno [1,2,3-cd] perylene, Dibenzo(a, h) anthracene and Benzo(g,h,i) perylene was statistically insignificant ($P > 0.05$). In this study, there were significant differences ($P < 0.5, 0.01, 0.001$) in the occurrence of various congeners of PAHs across the sampled stations. This study revealed that the PAHs levels in Falcorp surface water contrasted with results reported by

Celino *et al.* (2018). Also, these ranges obtained in this study were at variance with PAH data reported by Zhang *et al.* (2004) which varied from 192 – 2651 ng/dm³ for 16 PAHs in respect of waters collected from Tonghui River in China. The total PAHs concentrations in the Falcorp mangrove water were similar to an earlier report by Maldonado *et al.* (1999) which indicated a range of PAH values; 0.11 – 0.49 ng/dm³ with a mean of 0.22 ng/dm³ which is very close to the result obtained in this research. PAHs concentrations lower than those found in the Falcorp mangrove have also been reported in Niger Delta, Nigeria where total PAHs concentrations were averaged at 0.18 mg/dm³ was documented in selected water

bodies in Niger Delta and 1.95 to 10.9 µg/dm³ determined in Ekpan Creek, Effurun, Delta State, Nigeria (Anyakora and Coker, 2006). A probable reason for the low levels of PAHs obtained for the water samples obtained from the sampled area could be the effect of dilution caused by high precipitation experienced in the study area. The Nigerian wet season is usually characterized by heavy rainfall and warm weather, which increases runoff from the surrounding area into the river system. This event could lead to increased water volume and dissolution of many pollutants such as PAHs in aquatic systems.

Table 1: Mean Concentrations (mg/dm³) of PAHs in water samples of falcorp mangrove

Parameter	Station 1	Station 2	Station 3	Station 4	Station 5	P-value	Significant-Level
	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$		
Napthalene (Min-Max)	0.028±0.01 (0.00-0.09)	0.02±0.01 (0.00-0.10)	0.02±0.01 (0.00-0.10)	0.06±0.02 (0.00-0.18)	0.05±0.01 (0.02-0.10)	0.09	P>0.05
Acenaphthylene I (Min-Max)	0.01±0.01 (0.00-0.06)	0.02±0.01 (0.00-0.05)	0.02±0.01 (0.00-0.05)	0.04±0.01 (0.00-0.10)	0.04±0.01 (0.00-0.08)	0.20	P>0.05
Acenaphthene II (Min-Max)	0.02±0.01 (0.00-0.09)	0.03±0.01 (0.00-0.10)	0.03±0.01 (0.01-0.06)	0.02±0.01 (0.00-0.08)	0.03±0.01 (0.00-0.07)	0.99	P>0.05
Fluorene (Min-Max)	0.03±0.01 (0.00-0.08)	0.02±0.01 (0.00-0.08)	0.01±0.00 (0.00-0.04)	0.033±0.01 (0.00-0.09)	0.03±0.01 (0.00-0.06)	0.28	P>0.05
Phenanthrene (Min-Max)	0.05±0.01 ^a (0.01±0.11)	0.010±0.01 ^c (0.00-0.02)	0.03±0.03 ^b (0.00-0.06)	0.03±0.00 ^b (0.02-0.04)	0.03±0.01 ^b (0.00-0.07)	0.05	P<0.05*
Anthracene (Min-Max)	0.06±0.01 ^a (0.01-0.20)	0.03±0.01 ^b (0.00-0.07)	0.03±0.00 ^b (0.01-0.06)	0.03±0.01 ^b (0.00±0.06)	0.03±0.01 ^b (0.00-0.06)	0.02	P<0.05*
Fluranthene (Min-Max)	0.06±0.01 (0.02-0.19)	0.04±0.00 (0.02-0.07)	0.04±0.01 (0.01-0.12)	0.04±0.01 (0.01-0.09)	0.05±0.00 (0.01-0.07)	0.09	P>0.05
Pyrene (Min-Max)	0.05±0.01 (0.01-0.27)	0.04±0.02 (0.01±0.27)	0.04±0.00 (0.01-0.66)	0.08±0.03 (0.01-0.32)	0.04±0.00 (0.01-0.06)	0.42	P>0.05
Benzo(a)anthracene (Min-Max)	0.02±0.072 ^a (0.00-0.06)	0.00±0.00 ^b (0.03-0.03)	0.00±0.00 ^b (0.00-0.01)	0.03±0.00 ^a (0.01-0.04)	0.04±0.01 ^a (0.00-0.07)	0.00	P<0.001**
Chrysene (Min-Max)	0.08±0.04 (0.03-0.61)	0.05±0.00 (0.02-0.07)	0.05±0.00 (0.02-0.07)	0.05±0.00 (0.03-0.08)	0.11±0.03 (0.00-0.41)	0.20	P>0.05
Benzo(b)fluoranthrene (Min-Max)	0.04±0.01 ^a (0.00-0.09)	0.03±0.00 ^b (0.02-0.05)	0.05±0.01 ^a (0.03-0.06)	0.01±0.01 ^b (0.00-0.03)	0.00±0.00 ^c (0.00-0.00)	0.00	P<0.001**
Benzo(k)fluoranthrene (Min-Max)	0.039±0.01 (0.00-0.14)	0.04±0.00 (0.02-0.08)	0.06±0.02 (0.02-0.42)	0.10±0.00 (0.09-0.09)	0.00±0.00 (0.00-0.00)	0.42	P>0.05
Benzo(k)pyrene (Min-Max)	0.04±0.03 (0.00-0.11)	0.01±0.00 (0.00-0.04)	0.03±0.01 (0.00-0.04)	0.02±0.01 (0.00-0.04)	0.02±0.01 (0.00-0.04)	0.56	P>0.05
Indeno(1,2,3-cd) perylene (Min-Max)	0.09±0.03 ^c (0.00-0.23)	0.03±0.00 ^c (0.01-0.04)	0.03±0.00 ^c (0.00-0.04)	0.22±0.03 ^a (0.03-0.42)	0.13±0.04 ^b (0.03-0.40)	0.00	P<0.001**
Dibenz(a,h)anthracene (Min-Max)	0.00±0.00 (0.00-0.01)	0.01±0.01 (0.00-0.03)	0.00±0.00 (0.00-0.00)	0.00±0.00 (0.00-0.00)	0.00±0.00 (0.00-0.01)	0.93	P>0.05
Benzo(g,h,i) perylene (Min-Max)	0.05±0.01 ^a (0.00-0.20)	0.03±0.00 ^b (0.00-0.05)	0.03±0.00 ^b (0.02-0.02)	0.02±0.00 ^c (0.001-0.05)	0.03±0.00 ^b (0.00-0.04)	0.06	P<0.05*

All similar alphabets with superscript in the same row shows mean that are not significantly difference; P>0.05 - There is no significant difference; P<0.001 - There is very highly significant difference***; P<0.05 - There is significant difference*

Table 2: Summary of the concentrations (mg/dm³) of PAHs in water samples of falcorp mangrove, dry and wet seasons

Parameter Unit – mg/L	Dry season	Wet season	P-value	Significance Level
	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$		
Napthalene	0.02±0.01	0.05±0.01	0.03	P<0.05*
Acenaphthylene	0.02±0.01	0.03±0.01	0.24	P>0.05
Acenaphthene	0.02±0.00	0.03±0.00	0.09	P>0.05
Fluorene	0.02±0.00	0.03±0.00	0.02	P<0.05*
Phenanthrene	0.03±0.01	0.03±0.00	0.54	P>0.05
Anthracene	0.03±0.00	0.04±0.00	0.81	P>0.05
Fluranthene	0.05±0.01	0.04±0.00	0.37	P>0.05
Pyrene	0.05±0.01	0.045±0.01	0.76	P>0.05
Benzo(a)anthracene	0.03±0.00	0.03±0.00	0.49	P>0.05
Chrysene	0.07±0.02	0.06±0.01	0.56	P>0.05
Benzo(b)fluoranthrene	0.03±0.00	0.03±0.00	0.81	P>0.05
Benzo(k)fluoranthrene	0.06±0.02	0.04±0.00	0.20	P>0.05
Benzo(k)pyrene	0.03±0.00	0.03±0.01	0.90	P>0.05
Indeno(1,2,3-cd) perylene	0.09±0.02	0.09±0.02	0.97	P>0.05
Dibenz(a,h)anthracene	0.02±0.02	0.00±0.00	0.09	P>0.05
Benzo(g,h,i) perylene	0.03±0.00	0.03±0.00	0.66	P>0.05

P>0.05; Indicated no significant difference, P<0.05; Indicate significant difference*

Table 3: Eigenvectors and Eigenvalues of the various PAH components in the surface water parameters of Falcorp mangrove swamp

Parameters	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15	PC 16
Naphthalene	0.50	-0.32	0.13	0.53	-0.08	0.36	-0.17	-0.17	0.01	-0.21	-0.23	-0.02	-0.13	0.01	0.22	-0.01
Acenaphthylene I	0.02	0.22	0.40	-0.21	-0.30	0.35	0.48	0.33	-0.16	-0.14	0.03	-0.12	-0.31	-0.07	0.19	-0.01
Acenaphthene II	0.22	-0.07	-0.33	-0.34	-0.26	0.45	-0.16	0.19	0.23	0.47	-0.22	-0.15	0.08	0.11	-0.15	0.00
Fluorene	0.23	0.07	-0.24	-0.19	0.69	0.26	-0.10	0.34	0.00	-0.26	0.24	-0.07	0.03	-0.09	0.21	0.00
Phenanthrene	0.04	-0.15	0.39	-0.03	-0.01	0.19	-0.37	0.04	-0.33	0.38	0.54	0.32	-0.01	0.06	-0.05	-0.02
Anthracene	0.24	0.08	0.46	-0.29	0.12	-0.24	-0.34	0.23	-0.06	-0.15	-0.53	0.12	0.07	-0.08	-0.25	0.01
Fluranthene	0.12	-0.39	0.38	-0.13	0.38	-0.05	0.36	-0.27	0.15	0.30	0.03	-0.44	0.05	-0.03	-0.13	0.01
Pyrene	0.50	-0.27	-0.07	-0.22	-0.25	-0.33	0.25	0.10	0.33	-0.19	0.33	0.35	0.05	0.04	-0.03	0.00
Benzo(a)anthracene	0.34	0.34	-0.18	-0.15	0.15	0.12	0.27	-0.51	-0.31	0.16	-0.14	0.36	-0.08	-0.21	-0.12	0.00
Chrysene	0.01	0.28	0.19	-0.02	0.07	0.24	0.08	-0.20	0.13	-0.23	0.04	0.06	0.36	0.75	-0.10	0.00
Benzo(b)fluoranthrene	0.17	0.50	0.18	0.02	0.03	-0.20	-0.24	-0.15	0.49	0.26	0.11	-0.09	-0.33	0.02	0.36	-0.04
Benzo(k)fluoranthrene	0.01	0.27	0.16	0.26	-0.08	0.24	0.02	0.02	0.33	-0.07	0.20	-0.02	0.46	-0.55	-0.31	0.05
Benzo(k)pyrene	0.43	0.27	-0.11	0.27	-0.11	-0.33	0.05	0.23	-0.42	0.16	0.13	-0.43	0.21	0.14	-0.08	0.01
Indeno(1,2,3-cd)perylene	-0.02	0.05	-0.03	0.42	0.27	0.02	0.23	0.36	0.18	0.20	-0.07	0.26	-0.40	0.18	-0.47	0.00
Dibenzo(a,h)anthracene	-0.04	-0.03	0.06	0.12	0.09	-0.04	0.21	0.20	0.02	0.27	-0.20	0.25	0.37	-0.02	0.37	-0.66
Benzo(g,h,i)perylene	-0.03	-0.02	0.05	0.11	0.08	-0.04	0.16	0.16	0.01	0.25	-0.18	0.23	0.27	0.02	0.38	0.75
Eigenvalue	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
% variance	30.51	13.30	10.25	8.00	6.30	5.46	5.36	4.33	3.82	3.43	2.76	2.12	1.87	1.33	1.09	0.06

NB: Bolded values exceeded standards. According to Grimm and Yarnold (2000), loadings > 0.71 are typically regarded as excellent, and loadings < 0.32 very poor. However, Nair *et al.* (2010) stated that the component with the highest Eigenvalue is taken to be the most significant and should be one or greater for proper considerations during PCA. Factor loadings values of > 0.75, between 0.75–0.5 and 0.5–0.3 are classified as strong, moderate and weak respectively, based on their absolute values.

The results of the PCA based on the correlation matrix of the PAH congeners is shown in Table 3. The PCA was performed on the data sets containing 16 components analyzed in the water samples (Fig. 2). The PCA of the data sets yielded 39 variables under 16 components with Eigenvalues < 1 (PC1-PC16). These variables explained 99.99% of the total variance in water quality, respectively. The contributions were as followed - component 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, and 16 accounted for the proportion as follows: 30.51, 13.30, 10.25, 8.00, 6.30, 5.46, 5.36, 4.33, 3.82, 3.43, 2.76, 2.12, 1.87, 1.33, 1.09 and 0.06%, respectively (Table 2). The parameters of importance in each component were: 1; Naphthalene (0.50), Pyrene (0.50), Benzo [a] anthracene (0.34) and Benzo [k] pyrene (0.43), 2; Benzo [a]anthracene (0.34) and Benzo (k) pyrene (0.50), 3; Acenaphthylene I (0.40), Phenanthrene (0.39), Anthracene (0.46) and Fluranthene(0.38) 4; Naphthalene (0.53) and Indeno[1,2,3-cd]pyrene(0.42) 5; Fluorene(0.69) and Fluranthene(0.38) 6; Naphthalene (0.36), Acenaphthylene Iand II (0.35 and 0.45) 7; Acenaphthylene I(0.30) and Fluranthene(0.36) 8; Acenaphthylene I(0.33), Fluranthene(0.36) and Indeno[1,2,3-cd]pyrene(0.30) 9; Pyrene (0.33), Benzo[b]fluoranthene(0.49) and Benzo (k)Fluranthene(0.33) 10; Phenanthrene (0.38), Fluoranthene (0.30) and Acenaphthylene (0.47) 11; Phenanthrene (0.54) and Pyrene (0.33), 12; Phenanthrene (0.32), Pyrene (0.1) and Benzo [a] anthracene (0.36) 13; Chrysene (0.75), Benzo[k]fluranthene (0.46) and Dibenz[a,h]anthracene(0.37) 14; Chrysene (0.75), 15; Benzo[k]fluranthene (0.36), Dibenz(a,h)anthracene(0.37) and Benzo [g,h,i] perylene (0.38) and 16; Benzo [g,h,i] perylene (0.75).

Figures 2 and 3 revealed the scatter plot and the relationship of the PAHs congeners. There were positive clusters of Benzo[b]fluoranthene, Benz[a]anthracene, Benzo (k) pyrene, Benzo[k]fluranthene, Pyrene, and negative clusters of Acenaphthylene I, Benzo [g,h,i] perylene, Acenaphthene II, Phenanthrene, Naphthalene and Fluranthene in components 1. Positive correlation existed between Naphthalene, Acenaphthene II, Fluorene, Phenanthrene, Pyrene, Benzo (a) anthracene, Chrysene and Benzo [k] fluranthene, while a negative

relationship existed between Indeno [1,2,3-cd] perylene, Dibenz[a,h]anthracene and Benzo [g,h,i] perylene (Fig. 2).

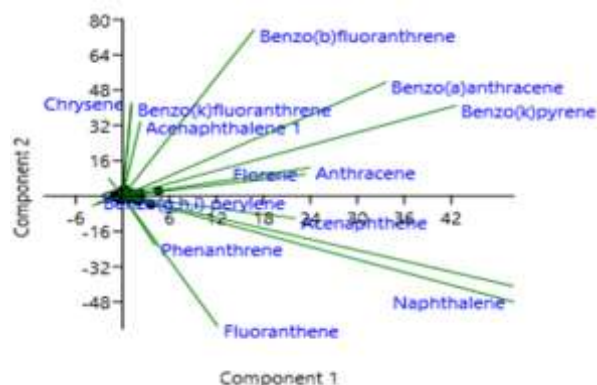


Fig. 2: Scatter plot for PAH values associated with the watersamples

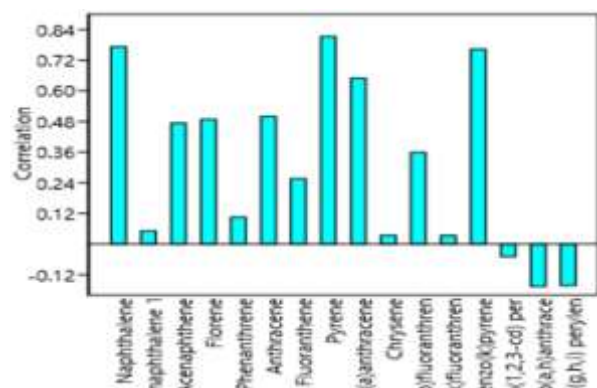


Fig. 3: Correlation for PAH values associated with the water samples

In this study, PC1, PC2 and PC3 contributed the larger percentage (30.51, 13.30 and 10.25) >10, of the PAHs loadings of the surface water PCA, respectively. The parameters of importance in each component were PC1; Napthalene (0.50), Pyrene (0.50), Benzo (a) anthracene (0.34) and Benzo (k) pyrene (0.43), PC2; Benzo (a) anthracene (0.34) and Benzo (k) pyrene (0.50) and PC3; Acenaphthylene 1 (0.40), Phenanthrene (0.39), Anthracene (0.46) and Fluranthene(0.38), respectively out of the 16 components. The source apportionment could be traced to hydrocarbon pollution. Hydrocarbon pollution as a result of anthropogenic activities in surface water has also been reported in several ecosystems around the world (Elder and Dresler, 1998; Oluseyi *et al.*, 2011; Qi *et al.*, 2013; Nekhavhambe *et al.*, 2014).

The Eigenvalues in this study were < 1 in PC1-PC16; in all the PCA components were in contrast to the threshold (>1) slated by Shrestha and Kazama (2007). By implication, the eigenvalues were not significant and should not be considered during PCA (Nair *et al.*, 2010). This also revealed that the parameters in PC1-PC16 components had very poor influence in the ecosystem.

The relationship of the parameters as shown in the scatter plot (Fig. 2) also indicated a similar cluster between the following PAH parameters; Benzo[b]fluoranthene, Benzo [a] anthracene, Benzo [k] pyrene, Benzo (k) fluranthene, Pyrene, and negative clusters of Acenaphthylene I, Benzo [g,h,i] perylene, Acenaphthylene II, Phenanthrene, Napthalene and Fluranthene in components 1. There was a positive correlation between Napthalene, Acenaphthylene II, Fluorene,

Phenanthrene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo(k)fluranthene and Benzo [k] fluranthene, while a negative relationship existed between Indeno [1,2,3-cd] perylene, Dibenz[a,h]anthracene and Benzo (g,h,i) perylene. This trend would indicate that is a strong interrelationship between the chemical constituents and the aquatic environment and their impacts negatively and positively.

The mean PCBs detected in the respective water samples is shown on Table 4. There was a significant difference ($P < 0.05$) in the PCBs; 4,4'-Dichlorobiphenyl, 2,3,4,4',5-Pentachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl, Decachlorobiphenyl, 2,2',3,3',4,5,5',6'-Octachlorobiphenyl and 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl concentrations in the water samples across the five different stations. Also the difference between the PCB; 2,2',3,3',4,5-Hexachlorobiphenyl and the other different PCBs was significantly different ($P < 0.05$). The seasonal variation of PCB in water samples is shown in Table 5. The result revealed a highly significant difference ($P < 0.001$) between the seasonal mean readings for 4,4'-Dichlorobiphenyl. Across the sampling stations, the differences in the PCB concentrations of 2,2',3,3',4,5-Hexachlorobiphenyl, 2,2',3,4,4',5,5',6-Octachlorobiphenyl, 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl, and 2,2',3,3',4,4',5,5',6'-Octachlorobiphenyl was significantly different ($P < 0.05$), while there was no significant difference ($P > 0.05$) between seasonal values of 2,2',3,3',4,4',6-Heptachlorobiphenyl, 2,2',3,4,4',5',6-Heptachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl and Decachlorobiphenyl, respectively.

Table 4: Mean concentrations (mg/dm³) of PCBs in water samples of falcorp mangrove

Parameter	Station 1	Station 2	Station 3	Station 4	Station 5	P-value	Significant Level
	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$		
4,4'-Dichlorobiphenyl (Min-Max)	0.0289±0.0006 ^c (0.0239-0.0342)	0.0296±0.0009 ^c (0.0261-0.0364)	0.0312±0.0003 ^c (0.0285-0.0334)	0.0820±0.0143 ^b (0.0095-0.1881)	0.1387±0.0205 ^a (0.0301-0.2871)	0.000	P<0.001***
2,3,4,4',5-Pentachlorobiphenyl (Min-Max)	0.0003±0.0002 ^c (0.0001-0.0021)	0.0026±0.0009 ^c (0.0001-0.0104)	0.0014±0.0008 ^c (0.0001-0.0101)	0.0068±0.0006 ^b (0.0035-0.0096)	0.0099±0.0009 ^a (0.0059-0.0198)	0.000	P<0.001***
2,2',3,3',4,5-Hexachlorobiphenyl (Min-Max)	0.0000±0.0000 (0.0000-0.0000)	0.0030±0.0000 (0.0030-0.0030)	0.0000±0.0000 (0.0000-0.0000)	0.0037±0.0002 (0.0033-0.0062)	0.0021±0.0005 (0.0012-0.0030)	0.015	P<0.05*
2,2',3,3',4,4',6-Heptachlorobiphenyl (Min-Max)	0.0000±0.0000 (0.0000-0.0000)	0.0001±0.0000 (0.0001-0.0001)	0.0000±0.0000 (0.0000-0.0000)	0.0012±0.0000 (0.0012-0.0012)	0.0010±0.0000 (0.0010-0.0010)	-	
2,2',3,4,4',5',6-Heptachlorobiphenyl (Min-Max)	0.0000±0.0000 (0.0000-0.0000)	0.0000±0.0000 (0.0000-0.0000)	0.0000±0.0000 (0.0000-0.0000)	0.0010±0.0000 (0.0010-0.0010)	0.0001±0.0000 (0.0010-0.0010)	-	
2,2',3,4,5,5',6-Heptachlorobiphenyl (Min-Max)	0.0000±0.0000 ^c (0.0000-0.0000)	0.0000±0.0000 ^c (0.0000-0.0000)	0.0000±0.0000 ^c (0.0000-0.0000)	0.0358±0.0002 ^a (0.0345-0.0366)	0.0244±0.0012 ^b (0.0214-0.0288)	0.000	P<0.001***
2,2',3,3',4,5,5',6'-Octachlorobiphenyl (Min-Max)	0.0000±0.0000 ^c (0.0000-0.0000)	0.0273±0.0027 ^b (0.0218-0.0300)	0.0000±0.0000 ^c (0.0000-0.0000)	0.0277±0.0012 ^b (0.0218-0.0318)	0.0320±0.0004 ^a (0.0300-0.0344)	0.004	P<0.01**
2,2',3,4,4',5,5',6-Octachlorobiphenyl (Min-Max)	0.0000±0.0000 (0.0000-0.0000)	0.0150±0.0013 (0.0130-0.0184)	0.0138±0.0008 (0.0130-0.145)	0.0176±0.0004 (0.0158-0.0206)	0.0205±0.0017 (0.0130-0.0299)	0.102	P>0.05
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (Min-Max)	0.0000±0.0000 (0.0000-0.0000)	0.0131±0.0108 ^b (0.0023-0.037)	0.0000±0.0000 (0.0000-0.0000)	0.0358±0.0002 ^a (0.0347-0.0368)	0.0225±0.0039 ^b (0.0023-0.0357)	0.002	P<0.01**
Decachlorobiphenyl (Min-Max)	0.0005±0.0002 ^c	0.0028±0.0013 ^b	0.0013±0.0002 ^b	0.0040±0.0004 ^a	0.0055±0.0008 ^a	0.000	P<0.001***

NB: Action level = 0.0005 mg/dm³ (FDA, 1992)

Table 5: Summary of the concentrations (mg/dm³) of PCBs in water samples of falcorp mangrove, dry and wet seasons

Parameter	Dry season	Wet season	P-value	Significance Level
	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$		
4,4'-Dichlorobiphenyl (Min-Max)	0.0353±0.0028	0.0791±0.0102	0.001	<i>P</i> <0.001***
2,3,4,4',5'-Pentachlorobiphenyl (Min-Max)	0.0055±0.0009	0.0053±0.0008	0.852	<i>P</i> >0.05
2,2',3,3',4,5'-Hexachlorobiphenyl (Min-Max)	0.0041±0.0004	0.0029±0.0002	0.018	<i>P</i> <0.05*
2,2',3,3',4,4',6'-Heptachlorobiphenyl (Min-Max)	0.0008±0.0003	0.0000±0.0000	-	-
2,2',3,4,4',5',6'-Heptachlorobiphenyl (Min-Max)	0.0001±0.0000	0.0000±0.0000	-	-
2,2',3,4,5,5',6'-Heptachlorobiphenyl (Min-Max)	0.0000±0.0000	0.0300±0.0015	-	-
2,2',3,3',4,5,5',6'-Octachlorobiphenyl (Min-Max)	0.0276±0.0012	0.0313±0.0007	0.008	<i>P</i> <0.01**
2,2',3,4,4',5,5',6'-Octachlorobiphenyl (Min-Max)	0.0156±0.0005	0.0206±0.0012	0.010	<i>P</i> <0.05*
2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl (Min-Max)	0.0235±0.0044	0.0328±0.0021	0.039	<i>P</i> <0.05*
Decachlorobiphenyl (Min-Max)	0.0032±0.0009	0.0026±0.0004	0.437	<i>P</i> >0.05

P>0.05; There is no significant difference, *P*<0.001 -There is very highly significant difference***, *P*<0.05; There is significant difference*

Table 6: Eigenvectors and Eigenvalues of the various PCB components in the surface water of Falcorp mangrove

PCB	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
4,4'-Dichlorobiphenyl	0.95	-0.28	-0.08	-0.10	0.00	-0.03	-0.05	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,4,4',5'-Pentachlorobiphenyl	0.05	0.07	-0.15	0.18	0.24	0.92	-0.14	-0.08	0.02	0.00	0.00	0.00	0.00	0.00	0.00
2,2',3,3',4,5'-Hexachlorobiphenyl	0.00	0.07	0.05	0.02	0.06	0.04	-0.18	0.98	-0.01	0.00	0.00	0.00	0.00	0.00	0.00
2,2',3,4,4',5'-Hexachlorobiphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.88	0.00	0.00	0.00
2,2',4,4',5,5'-Hexachlorobiphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.88	-0.47	0.01	0.00	0.00
2,2',3,3',4,4',6'-Heptachlorobiphenyl	0.00	0.00	0.00	0.00	-0.01	-0.01	0.02	0.01	0.86	-0.51	0.00	0.00	0.00	0.00	0.00
2,2',3,4,4',5',6'-Heptachlorobiphenyl	0.00	0.00	0.00	0.00	0.00	-0.01	0.01	0.01	0.51	0.86	0.00	0.00	0.00	0.00	0.00
2,2',3,4,5,5',6'-Heptachlorobiphenyl	0.16	0.08	0.79	0.57	-0.03	0.02	0.12	-0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,3',4,4',5,5'-Heptachlorobiphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	1.00	-0.04	0.00
2,3,3',4,4',5',6'-Heptachlorobiphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	1.00	0.00
2,2',3,3',4,5',6'-Octachlorobiphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00
2,2',3,3',4,5,5',6'-Octachlorobiphenyl	0.17	0.55	-0.44	0.53	-0.27	-0.21	-0.28	-0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,2',3,4,4',5,5',6'-Octachlorobiphenyl	0.12	0.32	-0.19	0.00	0.01	0.09	0.90	0.15	-0.02	0.00	0.00	0.00	0.00	0.00	0.00
2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl	0.17	0.70	0.33	-0.56	0.10	0.03	-0.19	-0.10	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Decachlorobiphenyl	0.02	0.06	-0.10	0.18	0.92	-0.31	-0.02	-0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eigenvalue	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
% variance	92.42	5.52	1.09	0.67	0.15	0.08	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00

NB: Bolded values exceeded standards. According to Grimm and Yarnold (2000), loadings > 0.71 are typically regarded as excellent, and loadings < 0.32 very poor. However, Nair *et al.*, (2010) stated that the component with the highest Eigenvalue is taken to be the most significant and should be one or greater for proper considerations during PCA. Factor loadings values of > 0.75, between 0.75–0.5 and 0.5–0.3 are classified as strong, moderate and weak respectively, based on their absolute values.

PCA based on the correlation matrix of the PCBs is shown on Table 6. The PCA was performed on the data sets which contained 15 components analyzed in the water samples (Fig. 4). The PCA of the data sets yielded 21 variables under 15 components with Eigenvalues < 1 (PC1-PC15). These variables explained 99.99% of the total variance in water quality, respectively. The contributions were as followed - component 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 accounted for the proportion as follows: 92.42, 5.52, 1.09, 0.67, 0.15, 0.08, 0.04, 0.02, 0.00, 0.00, 0.00, 0.00, 0.00, 0.00 and 0.00%, respectively (Table 6). The parameters of importance in each component were: 1; 4,4'-Dichlorobiphenyl (0.95) 2; 2,2',3,3',4,5,5',6'-Octachlorobiphenyl (0.53), 2,2',3,4,4',5,5',6'-Octachlorobiphenyl (0.32) and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl (0.70) 3; 2,2',3,4,5,5',6'-Heptachlorobiphenyl (0.75) and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl (0.33) 4; 2,2',3,4,5,5',6'-Heptachlorobiphenyl (0.57) and 2,2',3,3',4,5,5',6'-Octachlorobiphenyl (0.53) 5; Decachlorobiphenyl (0.92) 6; 2,3,4,4',5'-Pentachlorobiphenyl (0.92) 7; 2,2',3,4,4',5,5',6'-Octachlorobiphenyl (0.90) 8; 2,2',3,3',4,5'-Hexachlorobiphenyl (0.98) 9; 2,2',3,3',4,4',6'-Heptachlorobiphenyl (0.86) and 2,2',3,4,4',5',6'-Heptachlorobiphenyl (0.51) 10; 2,2',3,4,4',5',6'-Heptachlorobiphenyl (0.86) 11; 2,2',4,4',5,5',6'-Hexachlorobiphenyl (0.47) and 2,2',3,3',4,4',6'-Heptachlorobiphenyl (0.88) 12; 2,2',3,3',4,4',6'-Hexachlorobiphenyl (0.88) 13; 2,3,3',4,4',5,5',6'-Heptachlorobiphenyl (1.00) 14; 2,3,3',4,4',5,5',6'-

Heptachlorobiphenyl (1.00) and 15; 2,2',3,3',4,5',6,6'-Octachlorobiphenyl (1.00). Figure 4 showed the scatter plot and the relationship clusters of the PCBs. There were positive clusters of 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl, 2,2',3,3',4,5,5',6'-Octachlorobiphenyl, 2,2',3,4,4',5,5',6'-Octachlorobiphenyl, 2,2',3,3',4,5'-Hexachlorobiphenyl and negative cluster of 4,4'-Dichlorobiphenyl all in components 1. Positive correlation existed between 4,4'-Dichlorobiphenyl, 2,3,4,4',5'-Pentachlorobiphenyl, 2,2',3,3',4',5'-Hexachlorobiphenyl, 2,2',3,4,5,5',6'-Heptachlorobiphenyl, 2,2',3,3',4,5,5',6'-Octachlorobiphenyl, 2,2',3,4,4',5,5',6'-Octachlorobiphenyl and Decachlorobiphenyl, while a negative relationship existed between 2,2',3,3',4,4',6'-Heptachlorobiphenyl and 2,2',3,4,4',5',6'-Heptachlorobiphenyl. The PCB congeners in water samples exhibited significant difference (*P*<0.05) with respect to 4,4'-Dichlorobiphenyl, 2,3,4,4',5'-Pentachlorobiphenyl, 2,2',3,4,5,5',6'-Heptachlorobiphenyl, Decachlorobiphenyl, 2,2',3,3',4,5,5',6'-Octachlorobiphenyl and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl. However, for the congener 2,2',3,3',4,5'-Hexachlorobiphenyl there was significant difference (*P*<0.05) in its concentration of water samples across the five stations. All concentrations of 4,4'-Dichlorobiphenyl in all the stations were higher than the action level of PCBs (0.005mg/dm³) recommended for water (FDA, 1992). While all PCBs in station 4 and 5 were more than the slated value except Decachlorobiphenyl whose concentrations equates the action

level of PCBs (0.005mg/dm³). Fluctuations in the the seasonal variations in Decachlorobiphenyl and 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl were also observed in this study. When the levels of PCBs are way higher than the recommended action level, they could pose a potential health risk to people using this water for domestic and agricultural purposes. PCBs levels in different environmental media higher than those recorded in this current Study, have been reported from Poland: 60-440 ng/dm³(Sulej *et al.*, 2008); Pearl River, China: 91-1353 ng/dm³ (Chau, 2005); Northern Nigeria: 6721 ng/dm³ (Okeniyia *et al.*, 2009); the Warri River: 350-1300 ng/dm³ (Ezemonye, 2005a); Ethiopie River: 1500 ng/dm³ and the Benin River: 30-2930 ng/dm³ in Southern Nigeria (Ezemonye, 2005b); Turkey: 505-2377 ng/dm³ (Aydin *et al.*, 2004); the Minjiang River, Southeast China: 204-2473 ng/dm³ (Wan *et al.*, 2005); Southern Moravia, Czech Republic: 5.2 to 190.8 ng/dm³ (Lana *et al.*, 2008).

Both the PC1 and PC2 contributed the larger percentage (92.42 and 5.52) > 5, of the PCBs loadings in the surface water PCA, respectively. The parameters of importance in each component PC1; 4,4'-Dichlorobiphenyl (0.95) and PC2; 2,2',3,3',4,4',5,5',6'-Octachlorobiphenyl (0.53), 2,2',3,4,4',5,5',6'-Octachlorobiphenyl (0.32) and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl (0.70), respectively out of the 15 components (Table 6). The source distribution could be traced to persistent organic pollution. Organic pollution through anthropogenic activities in surface water has also been reported in several ecosystems around the world (Chui and Lam-leung, 1991; Brandli *et al.*, 2007; Dai *et al.*, 2011). The Eigenvalues in this study were < 1 in PC1-PC15; in all the PCA components which were in contrast to the threshold (>1) slated by Shrestha and Kazama, (2007). By implication, the eigenvalues were not significant and should not be considered during PCA (Nair *et al.*, 2010). This also revealed that the parameters in PC1-PC15 components had very poor influence in the ecosystem.

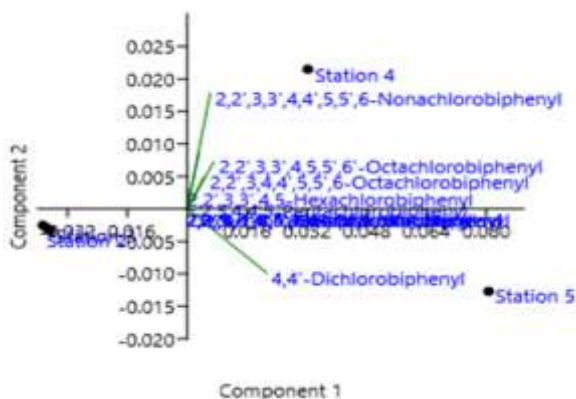


Fig. 4: Scatter plot for PCBs associated with the surface water samples

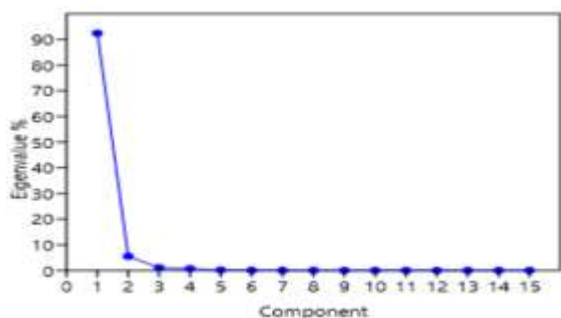


Fig. 5: Screen plot for PCBs values associated with the surface water samples

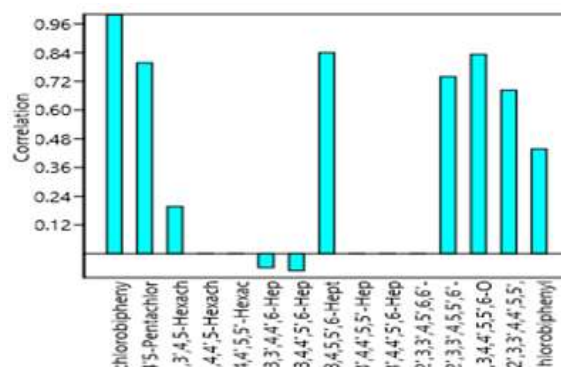


Fig. 6: Correlation of PCBs linked with the respective surface water samples

Relationship between the PCB parameters is shown in the screen plot (Fig. 5) and the correlation graph (Fig. 6) respectively. These results revealed similar cluster between the following PCBs parameters; positive clusters of 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl, 2,2',3,3',4,4',5,5',6'-Octachlorobiphenyl, 2,2',3,4,4',5,5',6'-Octachlorobiphenyl, 2,2',3,3',4,4',5,5',6'-Octachlorobiphenyl and negative cluster of 4,4'-Dichlorobiphenyl all in components 1. Positive correlation existed between 4,4'-Dichlorobiphenyl, 2,3,4,4',5-Pentachlorobiphenyl, 2,2',3,3',4',5-Hexachlorobiphenyl, 2,2',3,4,4',5,5',6-Heptachlorobiphenyl, 2,2',3,3',4,4',5,5',6'-Octachlorobiphenyl, 2,2',3,4,4',5,5',6-Octachlorobiphenyl, 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl and Decachlorobiphenyl, while a negative relationship existed between 2,2',3,3',4,4',6-Heptachlorobiphenyl and 2,2',3,4,4',5,5',6-Heptachlorobiphenyl. The implication of this trend is an indication of a strong interrelationship between the chemical constituents, the aquatic environment and their negative or positive impacts.

Conclusion

This study revealed low PAHs and PCBs concentrations for all the sampled locations and these low PAHs and PCBs values can be credited to the levels of industrial residues/wastes being discharged into the swamp and creek. Source apportionment attributed the source of the water borne minimal PAHs and PCBs profiles to hydrocarbon and persistent organic pollution emanating from anthropogenic activities around the study area. The recorded low values of these pollutants were surprising, given the multitude of anthropogenic activities which include; bunkering and vandalization of pipelines which transverse some sections of the swamp. However, there is an urgent need to conduct more research with respect to determining the tropic concentrations of these pollutants with reference to indigenous animal and plant species such as shrimps, molluscs and mangrove present in the Falcorp mangrove swamp and nearby aquatic/estuarine habitats.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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