

AFS2020002/21103

Polycyclic aromatic hydrocarbon (PAHs) and polychlorinated biphenyl (PCBs) profiles of sediments from Falcorp mangrove swamp, Warri, Delta State

O. Odigie^{1*} and J.O. Olomukoro²

¹Department of Biological Sciences, Faculty of Science, Benson Idahosa University, Benin City, Edo State, Nigeria

²Department of Animal and Environmental Biology, Faculty of Life Sciences, University of Benin, Benin City, Edo State, Nigeria

*Corresponding author; Email: oodigie@biu.edu.ng, Tel: +2348106234990

(Received March 12, 2020; Accepted in revised form March 20, 2020)

ABSTRACT: The Falcorp mangrove swamp has and is still been exposed to various forms of anthropogenic polluting activities which include; Vandalization of oil pipelines which transverse sections of the swamp. The PAHs and PCBs profile of swamp sediments was investigated. The sediments were subjected to routine PAH and PCB analyses which included; extraction, use of sonicator, GC-ECD and GC-FID analysis. The data were subjected to statistical and multivariate analysis using Microsoft Excel, SPSS version 16.0 and PAST respectively. The difference in the mean acenaphthene, florene, fluoranthene, pyrene, chrysene, benzo (k) fluoranthrene, benzo (k) pyrene and dibenzo (a,h)anthracene values across the five stations was statistically insignificant ($P>0.05$). According to the combinations of the clusters, the PAH characteristics in all the stations were dissimilar with value < 1 . There was a significant difference ($P<0.05$) in the seasonal concentrations of the PCBs; 2,2',3,3',4,5,5',6'-Octachlorobiphenyl, and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl. Despite the on-going anthropogenic pollution of the swamp, sediment borne PAHs and PCBs concentrations were low. There is a need to conduct more studies pertaining to evaluating the possible concentrations of these pollutants in some native animal sentinels such as molluscs present in the Falcorp mangrove swamp.

Keywords: Pipelines, PCBs, PAHs, Sediment, Falcorp

Introduction

Estuarine regions have being described as been of considerable substantial ecological, environmental, and economic value to the coastal and inland inhabitants (Shilla and Routh, 2018). Freshwater and sediment inputs from fluvial systems draining the upper reaches of the catchment are known to play an important part in the definition of the physical and chemical characteristics in these estuarine habitats (Shilla and Routh, 2018). The most characteristic vegetation present in the estuarine region is mangrove (Dudani *et al.*, 2017). The authors described mangroves as woody plant communities situated in the intertidal zone of tropical, subtropical coasts, and play a very critical role as biological resources in the coastal ecosystems. They are also known to provide various vital ecosystem services such as shoreline protection, sheltering and provide nutrients to a large diversity of organisms (Dudani *et al.*, 2017). However, this unique ecosystem is constantly under the brunt of anthropogenic activities such as agricultural run-off, urban sewage industrial effluents, mining and port activities respectively (Dudani *et al.*, 2017). Tao *et al.* (2003) reported that aquatic sediments are large reservoirs of physical and biological debris and act as sinks for a wide variety of hydrophobic organic pollutants.

Polycyclic aromatic hydrocarbons (PAHs) have been described as organic pollutants that are persistent and ubiquitously distributed in the environment (Shilla and Routh, 2018). These compounds can be easily traced in

air, water, soil, sediments, plants, animals, and human beings. Their presence in the aquatic environment is closely linked to anthropogenic sources (Soclo *et al.*, 2000). Generally, PAHs are mostly of anthropogenic origin (Yunker *et al.*, 2002) except perylene, which forms naturally in the course of sediment diagenesis (Silliman *et al.*, 1999). Environmental distribution of PAHs is mainly linked with anthropogenic activities such as fossil fuel combustion, waste incineration, coal gasification, liquefaction processes, petroleum cracking, and production of coke, black carbon, coal tar, pitch and asphalt (Yunker *et al.*, 2002). These compounds are released into the aquatic environment through industrial wastewater, sewage, runoff from roads, street dust, oil spills and vehicular/maritime traffic (Bouloubassi and Saliot, 1993; Soclo *et al.*, 2000; Yunker *et al.*, 2002; Ranjan *et al.*, 2012).

Polychlorinated biphenyls (PCBs) have been described as persistent organic compounds linked with a broad spectrum of negative human health effects due to their bioaccumulation and bio magnification in food chains (Salem *et al.*, 2014; Grimm *et al.*, 2015). Aquatic sediments contaminated by PCBs may pose potential risks to fish, and in turn to humans and wildlife that consume fish (Sorell and McEvoy, 2013). PCBs are among the organochlorine compounds that typically reside in soils and sediments (Ge *et al.*, 2013). When PCBs are discharged into the aquatic environment, either they are adsorbed onto the suspended particulate matter in the water column or deposited onto the surface sediment (Mechlińska *et al.*, 2010). Sediment-bound contaminants are transported in an ecosystem by means of trophic transfer, such as consumption of benthic organisms by fish (Clark *et al.*, 1990). These pollutants tend to bind to sediments for a long period, hence sediments act as a natural sink for a variety of organic as well as inorganic contaminants (Alkhatib and Weigand, 2002).

The water channel of the Falcorp mangrove swamp interphase with other water bodies of neighboring creeks. The swamp has/is been impacted directly by several anthropogenic activities which include; farming, fishing activities and most importantly illegal oil bunkering/pipeline vandalization. Several oil pipelines transverse the vicinity of the swamp which connect the nearby Warri refinery with other oil facilities in Delta State, Nigeria. These pipelines are often targeted by vandals resulting in periodic oil spillages into the swamp and nearby water bodies. These activities pose a great danger to the environmental integrity of both the swamp ecosystem and the resident villagers who depend on the swamp for their livelihoods as artisanal fishermen. Occasional spillage of petroleum or its refined products as a result of bunkering activities conducted within the swamp would indicate that the swamp area is being deliberately polluted with high concentrations of discharged environmental pollutants such as petroleum sludge residues, PCBs and PAHs. In line with this situation, this research was aimed at investigating the PCB and PAH profiles associated with sediments sourced from some sampling points on the Falcorp mangrove swamp and the Ifie canal, Delta State.

Materials and Methods

Study area: Falcorp mangrove swamp is located in Warri South Local Government Area of Delta State, Nigeria. It is situated off the Warri refinery and petrochemical company jetty road, just behind the refinery (Fig. 1). It falls within the mangrove swamp ecological zone but also has direct interphase with the rainforest ecological zone. It lies on longitude (005⁰ 41.1E, 005⁰ 57.4E) and latitudes (05⁰18.3N, 05⁰84.5N) (Fig. 1). 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.

Sampling stations: Five (5) stations were designated for this study. Each of this station was approximately 600 meters apart from each other. Stations 1, 2 and 3 were located within the 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). Sediments were collected from the five sampling points once a month for a period of 18 months; February 2013- July 2014, using a grab dipped into the water with the aid of a rope.

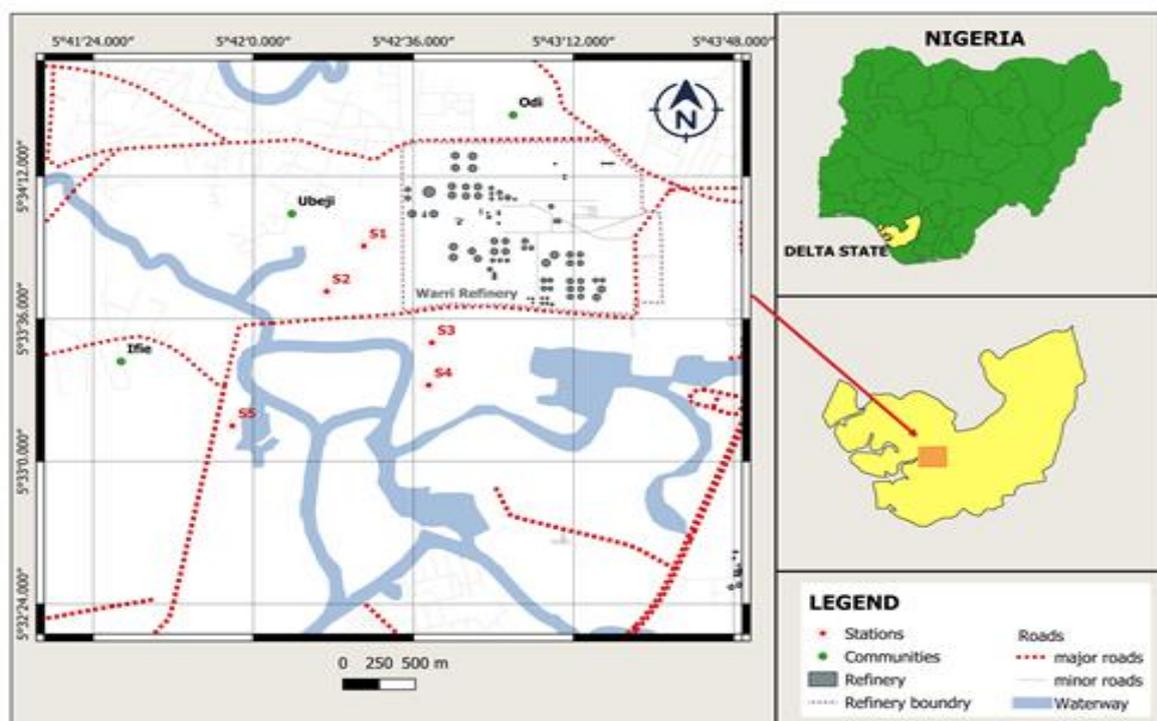


Figure 1: Map of the sampling locations

Sediment extraction and PCBs analysis using GC-ECD detector: The extraction method for sediment samples was adapted from method described by Fouial-Djebbar *et al.* (2010). Thirty (30) g of the air-dried, sieved sediment was placed into a solvent rinsed beaker. One milliliter (1 ml) of decachlorobiphenyl, was added and mixed thoroughly with the aid of glass rod. Thirty (30) g of Sodium sulphate was added to the mixture and mixed thoroughly. Fifty-fifty (50:50) solvent mix of acetone and n-Hexane was prepared and 50ml of the solvent mix was added to the sample mixture. The mixture was sonicated for about 10 – 15 minutes at about 60°C. The mixture was decanted and resultant extract placed into a round bottom flask. The procedure was then repeated once more with an additional 50ml of solvent mix, and the previously sonicated mixture. The mixture was decanted onto the same round bottom flask. The extract was further concentrated with the aid of a Rotary evaporator, to about 1-2mL. Five (5) ml of hexane was added to the concentrated extract, the mixture was evaporated to give a volume which ranged from 1 to 2 ml. The extract was made up to 15 ml by the addition of hexane. The extract was further cleaned up using H₂SO₄ and vortexed. The extract was concentrated under a gentle flow of nitrogen and transferred to 0.5 mL iso-octane. The solution was further re-concentrated to 0.05 mL in a conical injection vial. The same procedure was utilized for the blank sample which was run with every set of five sediment samples to check for secondary contamination.

The extract was analysed by GC-ECD on a Hewlett-Packard 5890 Series II gas chromatograph equipped with an electron-capture detector using a HP5 capillary column. The operating conditions of the GC column were; Split less injection (1 µL); injector temperature: 280 °C; detector temperature: 290 °C; initial oven temperature: 60 °C held for 2 min, heated to 120 °C at 6 °C/min and held for 5 min, then heated to 280 °C at 2 °C/min and held for 20 minutes. Helium was utilized as the carrier gas and the detection limit was 0.01 ng. The PCB congeners were analysed individually when possible, though in some cases the concentrations are reported as the sum of overlapping congeners due to co-elution on the GC column. The concentration of each PCB congener range in the sample was calculated directly from the instrument with the aid of Data Analysis Software.

Sediment extraction and PAHs analysis using GC-FID detector: Sediment extraction and clean up procedures was conducted as reported by Damas *et al.* (2009) with modifications. Thirty (30) g of the sieved sediment samples were freeze-dried (freeze-drier Model: OPR-FDB-5503, Korea) at -40 °C to a constant weight. Ten (10) g of each sample were mixed with 150 mL of n-hexane and dichloromethane mixture (1:1 ratio) for a period of 8 hours. The mixture was soxhlet -extracted for 8 hours and the extracts were concentrated to 1 mL with the aid of vacuum rotary evaporator (Buchi B-490). Five (5) g of activated copper powder was added to the concentrated extract for the elimination of sulphur and the concentrate was filtered through a folded filter paper (Whatman GF/C, 24micron) for 24 hours. The mixture was concentrated to 5 ml using the rotary evaporator. The extract (500 µL) was transferred to the top of a conditioned chromatographic column. Prior to the addition of the extract, the column was packed at the bottom with cotton wool and then filled with 7g of alumina, over 7g of silica gel and 1 cm of sodium sulphate was added at the top of the column. The first fraction (aliphatic

compounds) was eluted with 20 mL of n-hexane. The second fraction (aromatic hydrocarbons) was eluted with 20 mL of dichloromethane-hexane (50:50, v/v). The gas chromatographic analysis was conducted with a GC-FID on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a DB-5 fused silica capillary column and a splitless injector. Samples were separated in a DB-5 fused silica capillary column. Hydrogen was the carrier gas (1 mL/min). For PAH analysis the oven temperature program was: 45 °C held for 2 minutes, then ramped at 10 °C/min to 290 °C, and held for 8 minutes. Injector and detector temperature were 300 °C. The injection volume was 1 µL and the injection was in the split less mode, keeping the split valve closed for 1 min. PAH identification was reliant on GC retention times of authentic standards, injected and analysed under the same conditions as samples. A procedural blank was analysed periodically for each batch of 5 samples. It was prepared using the entire analytical procedure as well as the same reagents and solvents as utilized for the samples.

Statistical analysis: 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 exists. Statistical analysis was carried out on the data generated from each sampling station using general descriptive statistics.

Results and Discussion

Sediment associated PAH values: The results of the PAH congeners in sediments obtained from the 5 stations are shown in Table 1a. The monthly concentrations (mg/Kg) of naphthalene, acenaphthalene, benzo(a)anthracene, benzo(b)fluoranthrene, indeno(1,2,3-cd) perylene phenanthrene, anthracene and benzo(g,h,i) perylene were compared across the five stations. The results from the statistical analysis showed that there was a significant difference ($p < 0.005$) in the mean PAHs concentrations across the study stations. The results for the following PAH congeners; acenaphthene, florene, fluoranthene, pyrene, chrysene, benzo (k) fluoranthrene, benzo (k) pyrene and dibenzo (a,h)anthracene showed that there was no significant difference ($P > 0.05$) across the five stations. The result of the statistical analysis of PAHs values was shown in Table 1B. The results obtained from the statistical analysis showed that there was no significant difference ($P > 0.05$), across the five study stations. However, only florene displayed a divergence where there was a significant difference ($P < 0.05$) between wet and dry seasons across the stations (Table 1B).

The concentration of PAHs in aquatic sediments is dependent on several factors which include; sediment particles type, the physical and chemical properties of individual PAHs, soil temperature and moisture, redox-potential, availability of nutrients, and microbial activity (Okere and Semple, 2012). In this research, a very narrow range of summed concentrations of the 16 PAHs was detected in the sediments collected during the wet season across the stations followed by that of the dry season. The total amount of the 16 PAHs concentrations did not exceed the NOAA sediment quality guideline value for the effects range low (ERL) of 4022 ng/g and below the sediment threshold effect concentration (TEC) and the probable effect concentration (PEC) for summed PAHs of 1,610 and 22,800 µg/kg, respectively dry weight at the five sampling stations in Falcorp mangrove. In comparison with global contamination of PAHs in the sediment/soils, the results of this work were lower than the concentrations detected from different contaminated soil areas (297.4-458.0 µg/g for 16 PAHs) in the study conducted by Dean *et al.*, (1985). This range of concentrations of PAHs found in the wet and dry seasons were far lower than the range reported by Motelay-Massei *et al.* (2004) concerning soils collected from the Seine River basin, France respectively. The PAH fluxes in Falcorp mangrove swamp sediments ($0.09 \pm 0.03 \mu\text{g}/\text{cm}$) were higher in stations 1 and 2 than stations 3, 4 and 5 respectively. TOC and total nitrogen concentrations have been linked to influencing the sorption and distribution of PAH contaminants (Zhang *et al.*, 2004). However, there were no significant differences in the distribution of PAH congeners in the dry and wet seasons. This trend was also observed by Guinan *et al.*, (2001), Mucha *et al.*, (2003), Chindah *et al.*, (2004) and Kannan *et al.*, (2005). PAHs especially high molecular weight PAHs such as benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), dibenzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), chrysene (Chry), dibenzo(a,h)anthracene (DahA) and Indeno(1,2,3-cd)perylene (IndP) have been known to possess carcinogenic properties (Nwineewii and Kpee 2017). A major concern in animals is the ability of the reactive metabolites derived from PAH metabolism to bind cellular proteins and DNA, resulting in mutations, developmental malformations, tumours and cancer even at low concentrations. Purcaro *et al.* (2013) reported that most important metabolite of benzo (a) pyrene (BaP) metabolism was BaP-7,8-diol-9,10-epoxide which presented maximal tumor inducing activity, because it can form adduct with either proteins or DNA respectively.

Although, the recorded PAHs concentrations were low, however, the likely sources of PAHs in this aquatic environment were *via* industrial discharge, petroleum spills, combustion of fossil fuels, and various non-point source inputs such as agriculture, urban runoff, and atmospheric deposition. These PAHs sources have also been

reported by Benlahcen *et al.*, (1997), Yunker and McDonald, (2003), Christensen and Bzdusek, (2005), Ke *et al.*, (2005), Cavalcante *et al.*, (2009), Choudhary and Routh, (2010).

The PCA was based on the correlation matrix of the PAH congeners (Table 2). The PCA was performed on the data sets containing 16 components analysed in the sediment samples (Fig. 2). The PCA data sets yielded 23 variables under 16 components with Eigenvalues < 1 (PC1-PC16). These variables explained 99.56% 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: 42.60, 24.91, 12.80, 6.63, 4.40, 2.97, 1.75, 1.43, 0.95, 0.55, 0.50, 0.25, 0.17, 0.05, 0.03 and 0.02% respectively (Table 2). The parameters of importance in each component were: 1; Indeno (1, 2, 3-cd) perylene (0.93) 2; Chrysene (0.95) 3; Pyrene (0.75) and Benzo (k) fluoranthene (0.45) 4; Benzo (k) fluoranthene (0.73) 5; Acenaphthalene II (0.41), Phenanthrene (0.47) and Fluoranthene (0.38) 6; Anthracene (0.78) and fluoranthene (0.37) 7; Benzo (k) pyrene (0.39) and benzo (g, h, i) pyrene (0.70) 8; Acenaphthalene II (0.61) and anthracene (0.44) 9; None 10; Florene (0.51) and benzo (k) pyrene (0.66) 11; Florene (0.33), 12; Phenanthrene (0.62) 13; Benzo (a) anthracene (0.93) 14; Acenaphthlene II (0.93), 15; Dibenzo (a,h) anthracene (0.93) and 16; Naphthelene (0.94).

Figures 3 and 4 showed the scatter plot and the relationship of the PAHs congeners in the sediment of Falcorp mangrove swamp. There were positive clusters of chrysene, benzo (a) anthracene and phenanthrene; and negative clusters of Indeno (1, 2, 3-cd) perylene, benzo (k) fluoranthrene and dibenzo (g,h,i) anthracene in components 1. Positive correlation exists between naphthalene, anthracene, benzo (a) anthracene, benzo (a) anthracene and ideno (1,2,3-cd) perylene. While a negative relationship exists between acenaphthlene I and II, fluoranthrene, chrysene, benzo (a) fluoranthrene, benzo (k) fluoranthrene, benzo (k) pyrene and dibenzo (g, h, i) perylene (Fig. 4). Table 3 showed the similarity and dissimilarity defined by Euclidean distance and the combination of cluster based on the Ward method are indicated in Fig. 5. According to the combinations of the clusters, the PAH characteristics in all the stations were completely dissimilar with values < 1 (Table 3 and Fig. 5).

In this study, PC1, PC2 and PC3 contributed the larger percentage (42.60, 24.91 and 12.80) >10, of the loadings in the PAHs of the sediment PCA respectively. The parameters of importance in each component PC1; Indeno (1, 2, 3-cd) perylene (0.93) PC2; Chrysene (0.95) PC3; Pyrene (0.75) and benzo (k) fluoranthene (0.45) respectively out of the 16 components.

The source distribution could be traced from hydrocarbon pollution. Hydrocarbon pollution as consequence of anthropogenic activities have also been reported in several ecosystems around the globe (Christensen and Bzdusek, 2005; Ke *et al.*, 2005; Cavalcante *et al.*, 2009; Choudhary and Routh, 2010). The Eigenvalues in this study were < 1 in PC1-PC16; in all the PCA components conversely 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 trend also revealed that the parameters in PC1-PC16 components had very poor influence in the ecosystem.

Sediment associated PCB readings: The concentration (mg/Kg) of PCB in sediments for the 5 sampling stations is shown in Table 4A. The PCB congeners, 4,4'-Dichlorobiphenyl, 2,2',3,3',4,5'-Hexachlorobiphenyl, were compared across the five stations and the results showed that there was high significant difference ($P < 0.01$), followed by 2,2',3,3',4,5,5',6'-Octachlorobiphenyl showed very highly significant difference ($P < 0.001$), whilst 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl and Decachlorobiphenyl displayed significant difference ($P < 0.05$) across the sampling stations. On the other hand, the following PCB congeners; 2,3,4,4',5'-Pentachlorobiphenyl, 2,2',3,4,4',5'-Hexachlorobiphenyl, 2,2',4,4',5,5'-Hexachlorobiphenyl, 2,2',3,3',4,4',6'-Heptachlorobiphenyl, 2,2',3,4,4',5',6'-Heptachlorobiphenyl, 2,2',3,4,5,5',6'-Heptachlorobiphenyl, 2,3,3',4,4',5,5'-Heptachlorobiphenyl, 2,3,3',4,4',5,5',6'-Heptachlorobiphenyl, 2,2',3,3',4,5',6,6'-Octachlorobiphenyl and 2,2',3,4,4',5,5',6'-Octachlorobiphenyl showed no significant difference ($P > 0.05$) in their level of concentrations across the five sampling stations.

The seasonal variation for concentration of PCB in sediment samples is shown in Table 4B. The PCB congeners 4,4'-Dichlorobiphenyl, 2,3,4,4',5'-Pentachlorobiphenyl, 2,2',3,3',4,5'-Hexachlorobiphenyl, 2,2',3,4,4',5'-Hexachlorobiphenyl, 2,2',4,4',5,5'-Hexachlorobiphenyl, 2,2',3,3',4,4',6'-Heptachlorobiphenyl, 2,2',3,4,4',5',6'-Heptachlorobiphenyl, 2,2',3,4,5,5',6'-Heptachlorobiphenyl, 2,3,3',4,4',5,5'-Heptachlorobiphenyl, 2,3,3',4,4',5',6'-Heptachlorobiphenyl, 2,2',3,3',4,5',6,6'-Octachlorobiphenyl, 2,2',3,4,4',5,5',6'-Octachlorobiphenyl and Decachlorobiphenyl were compared for their level of concentrations between the dry season and wet season respectively. The analysed results showed that there was no significant difference ($P > 0.05$). However, the difference among the seasonal concentrations of 2,2',3,3',4,5,5',6'-Octachlorobiphenyl, and 2,2',3,3',4,4',5,5',6'-Nonachlorobiphenyl was statistically insignificant ($P < 0.05$).

The sediment samples collected from Falcorp mangrove showed 15 specific PCB congeners. The list of PCB congeners detected were similar among all sites evaluated suggesting a redistribution of a common source of PCBs throughout the stations with the exception of PCB (2,2',3,3',4,4',6'-Heptachlorobiphenyl). This redistribution of a common PCB across the station is consequent of the fact that there was the possibility that some PCBs may be selectively degraded from the source areas on the Falcorp mangrove. Another possibility is

the dilution factor in the ecosystem. This trend has also been reported by Kumar *et al.*, (2012) which indicated similar sample results in some congeners, including the non-ortho PCBs, and revealed that the values were below detection limits in some cases. The source points of PCBs in this research may include sewage sludge and agriculture activities. There was no significant difference among the levels of chlorinated pollutants within the dry and wet seasons ($p < 0.05$). Although unsurprising, this result may be due to the very high rainfall in Falcorp mangrove during the wet season. This study showed that the low levels of PCBs in the sediments of Falcorp mangrove are also associated with higher levels of organic carbon and total nitrogen. These levels suggest insignificant pollution in Falcorp mangrove concerning PCBs.

The result of the PCA based on the correlation matrix of the PCB congeners is as shown in Table 5. The PCA was performed on the data sets containing 15 components analysed in the water samples (Fig. 6). The PCA of the data sets yielded 28 variables under 15 components with Eigenvalues < 1 (PC1-PC15). These variables explained 100.01% of the total variance in sediment 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: 24.14, 12.75, 9.75, 9.19, 8.72, 7.11, 5.60, 4.34, 4.28, 3.51, 2.81, 2.36, 2.30, 1.65 and 1.44% respectively (Table 5). The parameters of importance in each component were: 1; 4,4'-Dichlorobiphenyl (0.86) and 2,2',3,4,4',5'-pentachlorobiphenyl (0.38) 2; 2,2',3,3',4,5,-Hexachlorobiphenyl (0.43), 2,2',3,4,4',5'-Hexachlorobiphenyl (0.43) 2,2',4,4',5,5'-Hexachlorobiphenyl (0.31) and 2,2',3,3',4',5',6-Heptachlorobiphenyl (0.35) 3; 2,2',3,3',4,4',6-Heptachlorobiphenyl (0.48) 4; 2,3',4,4',5',6-Heptachlorobiphenyl (0.49) and 2,2',3,3',4,5,5',6-Octachlorobiphenyl (0.38) 5; 2,2',3,3',4,5-Hexachlorobiphenyl (0.60) 6; 2,3,4,4',5-Pentachlorobiphenyl (0.63) and 2,2',3,4,5,5',6-Heptachlorobiphenyl (0.37) 7; 2,2',3,4,5,5',6-Heptachlorobiphenyl (0.47) 8; 2,2',3,4,4',5'-Hexachlorobiphenyl (0.53), 2,3,3',4,4',5,5'-Heptachlorobiphenyl (0.52) and 2,2',3,4,4',5,5',6-Octachlorobiphenyl (0.34) 9; 2,2',3,4,5,5'-Heptachlorobiphenyl (0.35) and Decachlorobiphenyl (0.54) 10; 2,2',4,4',5,5'-Hexachlorobiphenyl (0.69) 11; 2,2',3,3',4,4',6-Heptachlorobiphenyl (0.44) 12; 2,3,3',4,4',5,5'-Heptachlorobiphenyl (0.54) and 2,2',3,3',4,5',6'-Octachlorobiphenyl (0.32) 13; 2,2',3,4,4',5',6-Heptachlorobiphenyl (0.74) 14; 2,2',3,4,4',5,5',6-Octachlorobiphenyl (0.46) Decachlorobiphenyl (0.33) and 15; 2,3,3',4,4',5',6-Heptachlorobiphenyl (0.49) and 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (0.55).

Figures 6 and 7 revealed the scatter plot and the relationship of the sediment borne PCB congeners. There were positive clusters of 2,2',3,4,4',5,5'-Hexachlorobiphenyl, Decachlorobiphenyl, 4,4' Dichlorobiphenyl, 2,3',4,4',5,6' 2,2',3,4,4',5-Hexachlorobiphenyl, 2,2',3,4,4',6'-Heptachlorobiphenyl, 2,3,3',4,4',5,5'-Heptachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl and 2,3,4,4',5-Pentachlorobiphenyl all in components 1 (Fig. 6).

Positive correlation exists between 2,3,4,4',5-Pentachlorobiphenyl, 2,2',3,4,4',5-Hexachlorobiphenyl, 2,2',3,4,4',5',6-Heptachlorobiphenyl and 2,2',3,3',4,5,5',6'-Octachlorobiphenyl. While a negative relationship exist between 4,4'-Dichlorobiphenyl, 2,2',3,3',4,5-Hexachlorobiphenyl, 2,2',4,4',5,5'-Hexachlorobiphenyl, 2,2',3,3',4,4',6-Heptachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl, 2,3,3',4,4',5,5'-Heptachlorobiphenyl, 2,3,3',4,4',5',6-Heptachlorobiphenyl, 2,2',3,3',4,5',6'-Octachlorobiphenyl and Decachlorobiphenyl (Fig. 8). Table 6 revealed the similarity and dissimilarity defined by Euclidean distance and the combination of cluster based on the Ward method are shown in Fig. 8 According to the combinations of the clusters, the PCB characteristics in all the stations were completely dissimilar with values < 1 (Table 6 and Fig. 8).

PC1-PC7 contributed the larger percentage (24.14, 12.75, 9.75, 9.19, 8.72, 7.11 and 5.60) > 5 , of the loadings in the sediment PCBs PCA respectively. The parameters of importance in each component PC1; 4,4'-Dichlorobiphenyl (0.86) and 2,2',3,4,4',5-pentachlorobiphenyl (0.38) PC2; 2,2',3,3',4,5,-Hexachlorobiphenyl (0.43), 2,2',3,4,4',5'-Hexachlorobiphenyl (0.43) 2,2',4,4',5,5'-Hexachlorobiphenyl (0.31) and 2,2',3,3',4',5',6-Heptachlorobiphenyl (0.35) PC3; 2,2',3,3',4,4',6-Heptachlorobiphenyl (0.48) PC4; 2,3',4,4',5',6-Heptachlorobiphenyl (0.49) and 2,2',3,3',4,5,5',6-Octachlorobiphenyl (0.38) PC5; 2,2',3,3',4,5-Hexachlorobiphenyl (0.60) PC6; 2,3,4,4',5-Pentachlorobiphenyl (0.63) and 2,2',3,4,5,5',6-Heptachlorobiphenyl (0.37) and PC7; 2,2',3,4,5,5',6-Heptachlorobiphenyl (0.47) respectively out of the 15 components.

The source distribution could be traced to persistent organic pollution. Organic pollution as a consequence of anthropogenic activities in sediment- water has also been reported in several ecosystems globally (Lannuzi *et al.*, 1995; Allen-Gill, 1997; Doong *et al.*, 2002; Ezemonye 2005).

The Eigenvalues in this study were < 1 in PC1-PC15; in all the PCA components conversely 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 trend also indicated that the parameters in PC1-PC15 components had very poor influence in the ecosystem.

The relationship of the parameters as shown in the scatter plot also indicate similar cluster between the following PCBs parameters; positive clusters of 2,2',3,4,4',5,5'-Hexachlorobiphenyl, Decachlorobiphenyl, 4,4' Dichlorobiphenyl, 2,3',4,4',5,6' 2,2',3,4,4',5-Hexachlorobiphenyl, 2,2',3,4,4',6'-Heptachlorobiphenyl, 2,3,3',4,4',5,5'-Heptachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl and 2,3,4,4',5-Pentachlorobiphenyl all in components 1. Positive correlation existed between 2,3,4,4',5-Pentachlorobiphenyl, 2,2',3,4,4',5-Hexachlorobiphenyl, 2,2',3,4,4',5',6-Heptachlorobiphenyl and 2,2',3,3',4,5,5',6'-Octachlorobiphenyl. While a

negative relationship existed between 4,4'-Dichlorobiphenyl, 2,2',3,3',4,5-Hexachlorobiphenyl, 2,2',4,4',5,5'-Hexachlorobiphenyl, 2,2',3,3',4,4',6-Heptachlorobiphenyl, 2,2',3,4,5,5',6-Heptachlorobiphenyl, 2,3,3',4,4',5,5'-Heptachlorobiphenyl, 2,3,3',4,4',5',6-Heptachlorobiphenyl, 2,2',3,3',4,5',6,6'-Octachlorobiphenyl and Decachlorobiphenyl (Fig. 8). This trend could indicate that there is a strong interrelationship between the chemical constituents and the aquatic environment. The dendrogram for cluster analysis indicated that the prevailing physical and chemical conditions in all the stations were completely dissimilar with values < 1. However, a similarity was noticed between stations 1, 2, 3 4 and 5 respectively (Fig. 9).

Table 1a: Summary results of PAH analysis of the sediments sampled from the five stations

Parameter	Station 1 $\bar{X} \pm S.E$	Station 2 $\bar{X} \pm S.E$	Station 3 $\bar{X} \pm S.E$	Station 4 $\bar{X} \pm S.E$	Station 5 $\bar{X} \pm S.E$	P-value	Significant-Level
Napthalene (Min-Max)	0.01±0.00 ^a (0.00-0.01)	0.00±0.00 ^c (0.00-0.00)	0.00±0.00 ^b (0.00-0.00)	0.00±0.00 ^b (0.00-0.00)	0.01±0.00 ^a (0.00-0.01)	0.00	P<0.001**
Acenaphthalene (Min-Max)	0.07±0.00 ^a (0.07-0.07)	0.00±0.00 ^c (0.00-0.00)	0.02±0.00 ^b (0.02-0.02)	0.00±0.00 ^c (0.00-0.00)	0.00±0.00 ^c (0.00-0.00)	0.00	P<0.001**
Acenaphthene (Min-Max)	0.04±0.03 (0.00-0.17)	0.01±0.01 (0.00-0.01)	0.015±0.01 (0.00-0.16)	0.00±0.00 (0.00-0.00)	0.00±0.00 (0.00-0.00)	0.60	P>0.05
Florene (Min-Max)	0.05±0.01 (0.00-0.14)	0.04±0.01 (0.00-0.05)	0.04±0.00 (0.01-0.08)	0.04±0.00 (0.01-0.06)	0.04±0.00 (0.02-0.09)	0.76	P>0.05
Phenanthrene (Min-Max)	0.0466±0.0095 ^a (0.01±0.11)	0.01±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±0.00 ^b (0.00-0.07)	0.05	P<0.05*
Anthracene (Min-Max)	0.056±0.01 ^a (0.01-0.2)	0.03±0.01 ^b (0.00-0.07)	0.03±0.01 ^b (0.01-0.06)	0.03±0.01 ^b (0.00-0.06)	0.03±0.01 ^b (0.00-0.02)	0.02	P<0.05*
Fluoranthene (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±0.02 (0.01-0.27)	0.04±0.02 (0.01-0.27)	0.04±0.00 (0.01-0.01)	0.07±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±0.01 ^a (0.00-0.06)	0.03±0.00 ^a (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)	0.12±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±0.00 ^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)	0.04±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 (0.10±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)	0.03±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 ^d (0.01-0.04)	0.03±0.00 ^d (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**
Dibenzo(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 (0.02-0.04)	0.02±0.00 ^c (0.00-0.05)	0.03±0.009 ^c (0.00-0.04)	0.05	P<0.05*

Note: All similar alphabets with a superscript in the same row showed that there was an insignificant difference amongst the mean values, $P>0.05$ -There is no significant difference, $P<0.01$ -There is a highly significant difference**, $P<0.001$ - There is a very highly significant difference***, $P<0.05$ -There is a significant difference*

Table 1b: Summary results of PAH values of the sediments sampled from the five stations

Parameter	Dry season	Wet season	P-value	Significance Level
	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$		
Naphthalene	0.01±0.00	0.00±0.00	0.09	P>0.05
Acenaphthalene	0.01±0.01	0.00±0.00	0.23	P>0.05
Acenaphthene	0.04±0.02	0.00±0.00	0.07	P>0.05
Florene	0.05±0.00	0.03±0.00	0.00	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
Fluoranthene	0.05±0.01	0.04±0.00	0.37	P>0.05
Pyrene	0.05±0.01	0.05±0.01	0.76	P>0.05
Benzo(a)anthracene	0.03±0.00	0.02±0.00	0.49	P>0.05
Chrysene	0.07±0.02	0.06±0.00	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±0.01	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
Dibenzo(a,h)anthracene	0.02±0.02	0.00±0.00	0.09	P>0.05
Benzo(g,h,i) perylene	0.03±0.03	0.03±0.00	0.66	P>0.05

Note: $P>0.05$ -indicated no significant difference and $P<0.05$ -indicated a significant difference

Table 2: Eigenvectors and Eigenvalues of the various PAH components in the sediment parameters of Falcorp mangrove swamp

	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	0.00	0.00	0.00	-0.01	0.02	0.02	0.03	-0.06	0.05	0.00	0.07	-0.04	0.10	0.00	0.31	0.94
Acenaphthalene 1	0.00	-0.01	-0.02	0.00	0.11	-0.11	0.02	0.19	0.10	-0.02	-0.02	-0.17	0.18	0.93	-0.07	0.00
Acenaphthene II	-0.02	-0.04	-0.06	0.06	0.41	-0.41	0.07	0.61	0.27	-0.18	0.00	-0.01	0.26	-0.31	0.02	-0.01
Florene	0.01	0.00	0.11	0.17	0.35	-0.08	0.20	0.05	-0.40	0.51	0.55	-0.22	-0.13	-0.01	0.01	-0.03
Phenanthrene	0.10	-0.01	0.00	0.01	0.43	0.04	0.29	-0.05	0.09	-0.14	-0.05	0.62	-0.53	0.16	0.01	0.05
Anthracene	0.07	-0.03	-0.09	-0.04	0.05	0.78	-0.15	0.44	0.17	0.20	0.17	0.17	0.14	0.00	-0.03	-0.01
Fluoranthene	-0.01	-0.05	0.21	0.21	0.38	0.37	0.22	-0.02	-0.28	-0.15	-0.57	-0.38	0.04	-0.06	0.05	0.00
Pyrene	-0.16	-0.16	0.79	-0.55	-0.01	0.00	0.02	0.10	0.03	-0.05	0.09	0.02	-0.01	0.00	0.00	-0.01
Benzo(a)anthracene	0.08	0.00	0.01	-0.03	0.26	0.12	0.29	-0.52	0.20	-0.13	0.26	0.13	0.61	-0.04	-0.16	-0.09
Chrysene	-0.21	0.95	0.17	0.07	-0.02	0.05	0.05	0.07	0.03	-0.07	0.04	0.03	0.01	0.01	0.01	0.00
Benzo(b)fluoranthrene	-0.09	-0.08	-0.02	0.10	-0.26	0.00	0.18	0.25	-0.67	-0.33	0.10	0.39	0.29	0.06	0.01	0.03
Benzo(k)fluoranthrene	-0.15	-0.18	0.45	0.77	-0.14	0.01	-0.16	-0.03	0.26	-0.07	0.12	0.11	-0.01	0.03	0.00	0.00
Benzo(k)pyrene	-0.06	0.00	0.07	0.05	-0.22	-0.14	0.39	0.07	0.10	0.66	-0.44	0.28	0.22	-0.01	-0.08	0.04
Indeno(1,2,3-cd) perylene	0.93	0.15	0.25	0.07	-0.14	-0.07	0.00	0.09	-0.04	-0.03	-0.02	-0.01	0.04	-0.01	0.01	0.00
Dibenzo(a,h)anthracene	0.00	0.00	-0.01	-0.01	0.01	0.00	0.03	-0.05	0.05	0.06	0.01	0.08	0.11	0.07	0.93	-0.32
Benzo(g,h,i) perylene	-0.01	-0.07	-0.09	0.02	-0.38	0.13	0.70	0.14	0.26	-0.21	0.21	-0.31	-0.22	-0.02	0.03	-0.04
Eigenvalue	0.01	0.01	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	42.60	24.91	12.80	6.63	4.40	2.97	1.75	1.43	0.95	0.55	0.50	0.25	0.17	0.05	0.03	0.02

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.

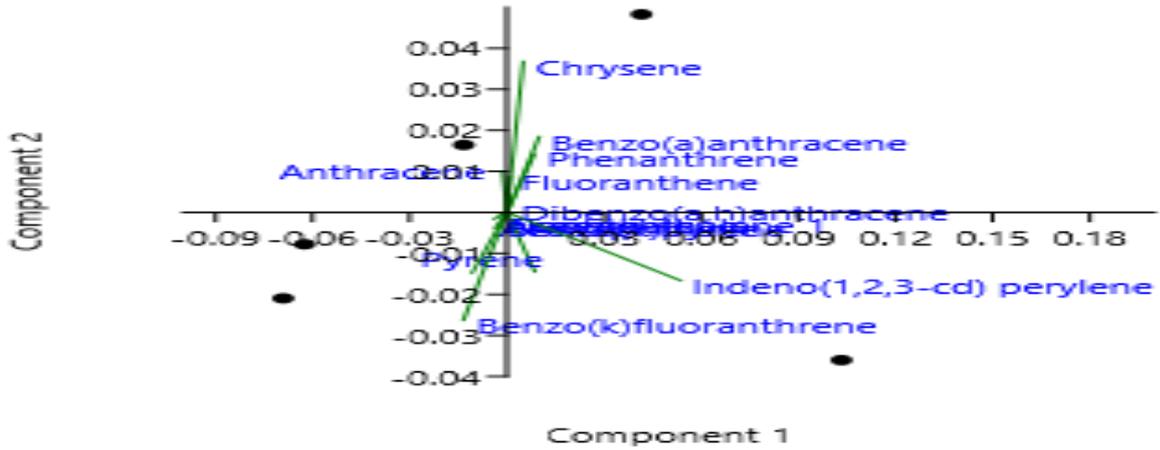


Fig. 2: Scatter plot for PAHs in the sediments collected from the Falcorp mangrove swamp

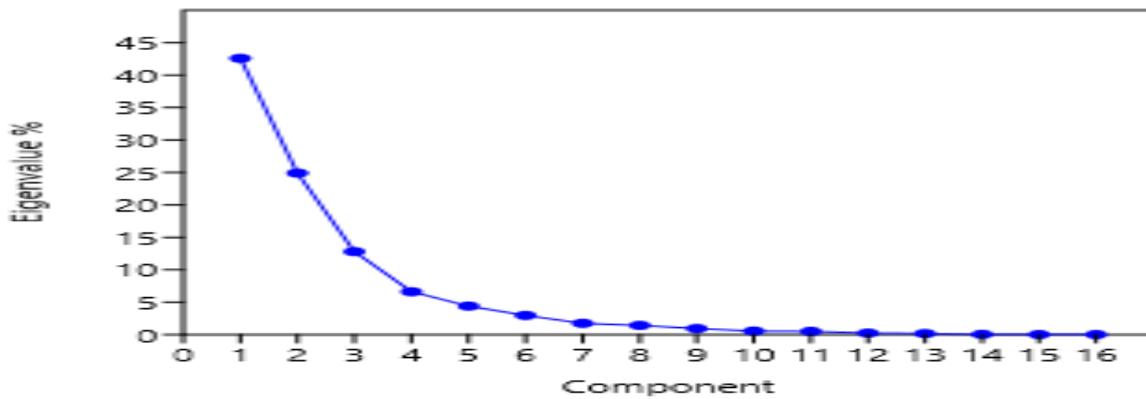


Fig. 3: Screen plot for PAH in the sediments collected from the Falcorp mangrove swamp

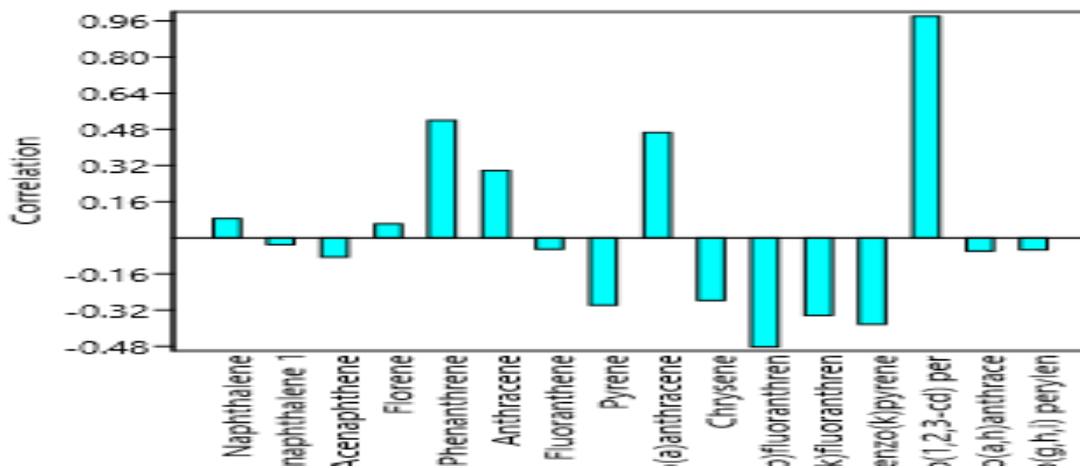


Fig. 4 Correlation of PAH in the sediments sourced from the Falcorp mangrove swamp

Table 3: Euclidean similarity and distance indices of the five PAHs congeners in the sediments collected from the Falcorp mangrove swamp

Stations	1	2	3	4	5
	0.00				
2	0.06	0.00			
3	0.07	0.03	0.00		
4	0.13	0.17	0.17	0.00	
5	0.07	0.12	0.13	0.10	0.00

Ward-Euclidean: 0 and < 1; complete dissimilarity, ≥ 1 ; complete similarity, critical level of significance (C) = 0.05. The bolded values indicated similarity.

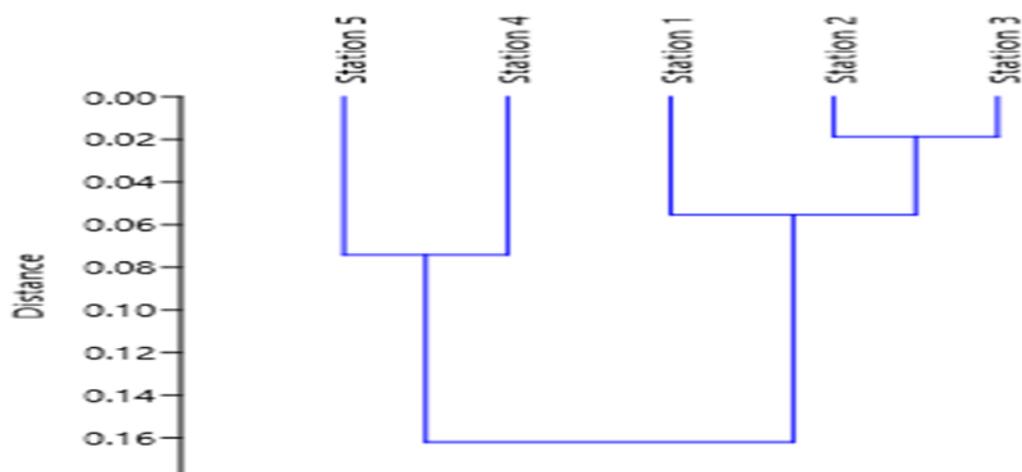


Fig. 5: Cluster analysis for PAH in the sediments

Table 4a: Summary results of PCB analysis of the sediments sampled from the five stations

Parameter Unit – mg/Kg	Station 1 $\bar{X} \pm S.E$	Station 2 $\bar{X} \pm S.E$	Station 3 $\bar{X} \pm S.E$	Station 4	Station 5	P-value	Significant -Level
4,4'-Dichlorobiphenyl (Min-Max)	0.0324±0.0090 ^b (0.0012-0.1328)	0.0262±0.0058 ^b (0.0012-0.0843)	0.0212±0.0048 ^b (0.0013-0.0643)	0.0655±0.0128 ^a (0.0176-0.1620)	0.0726±0.0162 ^a (0.0078-0.191)	0.002	P<0.01**
2,3,4,4',5'- Pentachlorobiphenyl (Min-Max)	0.0321±0.0079 (0.0007-0.0974)	0.0438±0.0086 (0.0084-0.0997)	0.0310±0.0067 (0.0011-0.0964)	0.0442±0.0071 (0.0111-0.0973)	0.0465±0.0090 (0.0023-0.1400)	0.488	P>0.05
2,2',3,3',4,5'- Hexachlorobiphenyl (Min-Max)	0.0178±0.0059 ^b (0.0011-0.0577)	0.0288±0.0063 ^b (0.0071-0.0741)	0.0269±0.0041 ^b (0.0134-0.0468)	0.0630±0.0143 ^a (0.0139-0.1934)	0.0343±0.0067 ^b (0.0007-0.0774)	0.006	P<0.01**
2,2',3,4,4',5'- Hexachlorobiphenyl (Min-Max)	0.0229±0.0065 (0.0039-0.0532)	0.0275±0.0122 (0.0035-0.1210)	0.0182±0.0047 (0.0003-0.0368)	0.0442±0.0085 (0.0101-0.0900)	0.0440±0.0079 (0.0107-0.0994)	0.141	P>0.05
2,2',4,4',5,5'- Hexachlorobiphenyl (Min-Max)	0.0240±0.0065 (0.0105-0.0452)	0.0333±0.0156 (0.0005-0.0928)	0.0256±0.0132 (0.0109-0.0652)	0.0353±0.0049 (0.0106-0.0603)	0.0502±0.0082 (0.0241-0.0980)	0.302	P>0.05
2,2',3,3',4,4',6'- Heptachlorobiphenyl (Min-Max)	0.0186±0.0053 (0.0007-0.0447)	0.0274±0.0093 (0.0003-0.0654)	0.0366±0.0155 (0.0136-0.0981)	0.0385±0.0104 (0.0118-0.0911)	0.0426±0.0106 (0.0046-0.0887)	0.411	P>0.05
2,2',3,4,4',5',6'- Heptachlorobiphenyl (Min-Max)	0.0139±0.0033 (0.0020-0.0333)	0.0360±0.0145 (0.0108-0.0885)	0.0222±0.0122 (0.0036-0.0559)	0.0261±0.0079 (0.0004-0.0603)	0.0234±0.0088 (0.0029-0.0512)	0.444	P>0.05
2,2',3,4,5,5',6'- Heptachlorobiphenyl (Min-Max)	0.0204±0.0050 (0.0014-0.0476)	0.0348±0.0072 (0.0049-0.0644)	0.0310±0.0162 (0.0036-0.1249)	0.0359±0.0089 (0.0080-0.0915)	0.0349±0.0105 (0.0045-0.0720)	0.715	P>0.05
2,3,3',4,4',5,5'- Heptachlorobiphenyl (Min-Max)	0.0207±0.0059 (0.0019-0.0661)	0.0293±0.0099 (0.0009-0.0863)	0.0223±0.0063 (0.0101-0.0587)	0.0305±0.0051 (0.0071-0.0613)	0.0310±0.0057 (0.0014-0.0507)	0.675	P>0.05
2,3,3',4,4',5',6'- Heptachlorobiphenyl (Min-Max)	0.0182±0.0064 (0.0035-0.0661)	0.0276±0.0078 (0.0006-0.0592)	0.0295±0.0092 (0.0065-0.0693)	0.0384±0.0059 (0.0065-0.0693)	0.0352±0.0094 (0.0052-0.0947)	0.381	P>0.05
2,2',3,3',4,5',6,6'- Octachlorobiphenyl (Min-Max)	0.0195±0.0104 (0.0003-0.0873)	0.0282±0.0054 (0.0009-0.0653)	0.0212±0.0059 (0.0073-0.0454)	0.0407±0.0077 (0.0024-0.0850)	0.0240±0.0054 (0.0014-0.0736)	0.207	P>0.05
2,2',3,3',4,5,5',6'- Octachlorobiphenyl (Min-Max)	0.0130±0.0032 ^d (0.0016-0.0266)	0.0202±0.0030 ^c (0.0013-0.0350)	0.0163±0.0063 ^c (0.0028-0.0623)	0.0434±0.0059 ^a (0.0040-0.0887)	0.0320±0.0063 ^b (0.0001-0.0676)	0.001	P<0.001** *
2,2',3,4,4',5,5',6'- Octachlorobiphenyl (Min-Max)	0.0209±0.0073 (0.0011-0.0432)	0.0293±0.0103 (0.0001-0.1029)	0.0267±0.0057 (0.0022-0.0619)	0.0286±0.0049 (0.0029-0.0694)	0.0280±0.0057 (0.0029-0.0694)	0.951	P>0.05
2,2',3,3',4,4',5,5',6'- Nonachlorobiphenyl (Min-Max)	0.0141±0.0034 ^c (0.0018-0.0279)	0.0250±0.0055 ^b (0.0072-0.0682)	0.0204±0.0035 ^b (0.0016-0.0391)	0.0321±0.0054 ^a (0.0008-0.0610)	0.0356±0.0063 ^a (0.0034-0.0980)	0.058	P<0.05*
Decachlorobiphenyl (Min-Max)	0.0116±0.0034 ^c (0.0003-0.0328)	0.0233±0.0045 ^b (0.0051-0.0502)	0.0227±0.0042 ^b (0.0006-0.0555)	0.0408±0.0069 ^a (0.0013-0.0913)	0.0324±0.0061 ^a (0.0019-0.0881)	0.017	P<0.05*

Note: All similar alphabets with a superscript in the same row showed that there was an insignificant difference amongst the mean values

- P>0.05 - There is no significant difference
- P<0.01 - There is a highly significant difference**
- P<0.001 - There is a very highly significant difference***
- P<0.05 - There is a significant difference*

Table 4b: Summary results of PCB values of the sediments sampled from the five stations

Parameter Unit – mg/Kg	Dry season	Wet season	P- value	Significance Level
	$\bar{X} \pm S.E$	$\bar{X} \pm S.E$		
4,4'-Dichlorobiphenyl	0.0476±0.0078	0.0417±0.0073	0.596	P>0.05
2,3,4,4'5- Pentachlorobiphenyl	0.0463±0.0057	0.0354±0.0044	0.137	P>0.05
2,2',3,3',4,5- Hexachlorobiphenyl	0.0415±0.0108	0.0314±0.0036	0.270	P>0.05
2,2',3,4,4',5- Hexachlorobiphenyl	0.0279±0.0060	0.0348±0.0053	0.443	P>0.05
2,2',4,4',5,5'- Hexachlorobiphenyl	0.0376±0.0098	0.0341±0.0045	0.719	P>0.05
2,2',3,3',4,4',6- Heptachlorobiphenyl	0.0219±0.0074	0.0364±0.0054	0.126	P>0.05
2,2',3,4,4',5',6- Heptachlorobiphenyl	0.0195±0.0048	0.0259±0.0055	0.399	P>0.05
2,2',3,4,5,5',6- Heptachlorobiphenyl	0.0282±0.0054	0.0320±0.0058	0.661	P>0.05
2,3,3',4,4',5,5'- Heptachlorobiphenyl	0.0290±0.0050	0.0250±0.0033	0.492	P>0.05
2,3,3',4,4',5',6- Heptachlorobiphenyl	0.0369±0.0056	0.0244±0.0042	0.075	P>0.05
2,2',3,3',4,5',6,6'- Octachlorobiphenyl	0.0337±0.0063	0.0249±0.0035	0.190	P>0.05
2,2',3,3',4,5,5',6'- Octachlorobiphenyl	0.0342±0.0047	0.0220±0.0032	0.031	P<0.05*
2,2',3,4,4',5,5',6- Octachlorobiphenyl	0.0267±0.0040	0.0277±0.0040	0.870	P>0.05
2,2',3,3',4,4',5,5',6- Nonachlorobiphenyl	0.0337±0.0044	0.0235±0.0030	0.059	P<0.05*
Decachlorobiphenyl	0.0327±0.0048	0.0255±0.0034	0.225	P>0.05

Note: $P>0.05$ indicated no significant difference and $P<0.05$ indicated a significant difference

Table 5: Eigenvectors and Eigenvalues of the various PCB components in the sediment parameters of Falcorp mangrove swamp

	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	0.86	0.12	0.31	0.04	-0.07	-0.25	-0.14	0.02	-0.02	0.01	-0.18	-0.03	-0.05	0.09	-0.09
2,3,4,4'5-Pentachlorobiphenyl	0.38	-0.33	-0.42	-0.06	0.01	0.63	-0.08	-0.05	-0.36	-0.02	0.10	-0.10	0.03	0.06	0.02
2,2',3,3',4,5-Hexachlorobiphenyl	0.06	0.45	0.08	-0.53	0.60	0.14	-0.08	0.02	-0.05	0.19	0.19	0.03	-0.11	-0.10	0.14
2,2',3,4,4',5-Hexachlorobiphenyl	0.01	0.43	-0.18	-0.19	-0.27	0.27	0.03	0.53	0.25	-0.27	-0.30	-0.10	0.28	0.10	0.02
2,2',4,4',5,5'-Hexachlorobiphenyl	-0.10	0.35	0.04	0.12	-0.38	0.19	-0.19	-0.19	-0.17	0.69	-0.11	-0.03	0.15	-0.15	-0.17
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.03	0.11	0.48	-0.08	-0.46	0.33	0.18	-0.08	-0.01	-0.23	0.44	0.08	-0.19	-0.16	0.26
2,2',3,4,4',5',6-Heptachlorobiphenyl	0.00	-0.01	0.22	-0.02	0.13	0.12	-0.05	-0.32	0.04	-0.16	0.10	0.39	0.74	0.24	-0.13
2,2',3,4,5,5',6-Heptachlorobiphenyl	0.02	-0.22	0.31	0.02	0.19	0.37	0.47	-0.10	0.35	0.29	-0.44	-0.09	-0.08	0.17	0.11
2,3,3',4,4',5,5'-Heptachlorobiphenyl	0.05	-0.14	0.11	0.29	0.17	0.22	-0.08	0.52	0.11	0.12	0.09	0.54	-0.11	-0.30	-0.31
2,3,3',4,4',5',6-Heptachlorobiphenyl	-0.02	0.04	0.10	0.49	0.18	0.13	-0.49	0.11	0.25	0.06	0.17	-0.26	0.09	0.17	0.49
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	-0.13	0.35	0.01	0.31	0.11	0.17	-0.07	-0.21	-0.37	-0.32	-0.41	0.32	-0.34	0.19	0.08
2,2',3,3',4,5,5',6'-Octachlorobiphenyl	0.06	0.26	0.02	0.38	0.26	0.13	0.26	-0.17	0.02	-0.26	0.11	-0.46	0.13	-0.39	-0.38
2,2',3,4,4',5,5',6-Octachlorobiphenyl	0.02	0.16	0.00	0.24	0.05	-0.14	0.51	0.34	-0.39	0.23	0.31	-0.03	0.10	0.46	0.05
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.22	0.10	-0.35	0.16	0.00	-0.15	0.31	-0.12	0.07	0.08	-0.09	0.30	0.21	-0.45	0.55
Decachlorobiphenyl	0.14	0.24	-0.40	0.09	-0.09	0.05	0.07	-0.28	0.54	0.07	0.31	0.19	-0.29	0.33	-0.21
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	24.14	12.75	9.75	9.19	8.78	7.11	5.60	4.34	4.28	3.51	2.81	2.36	2.30	1.65	1.44

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.

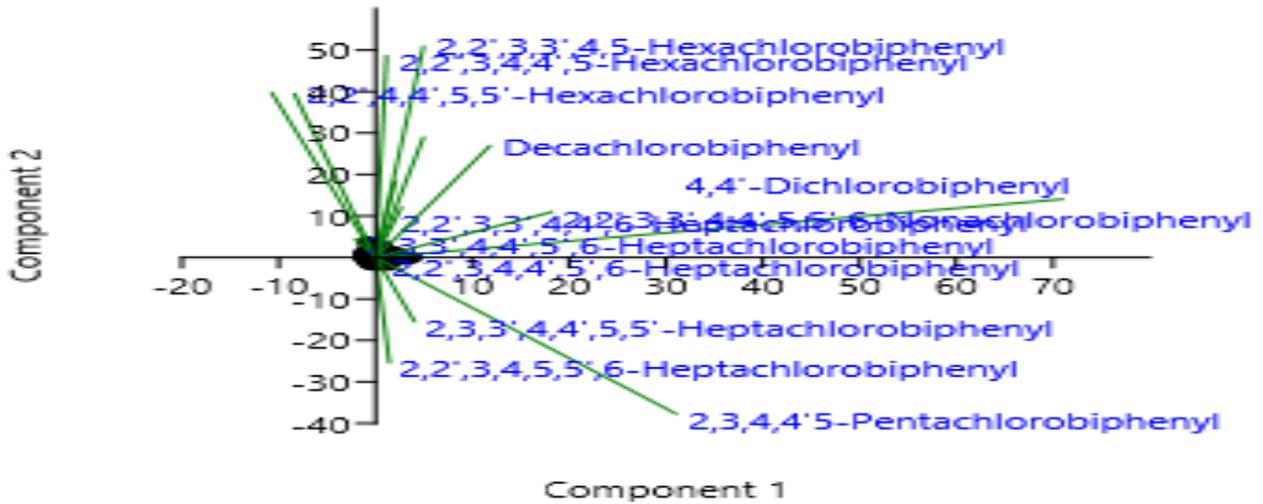


Fig. 6: Scatter plot for PCBs in the sediments collected from the Falcorp mangrove swamp

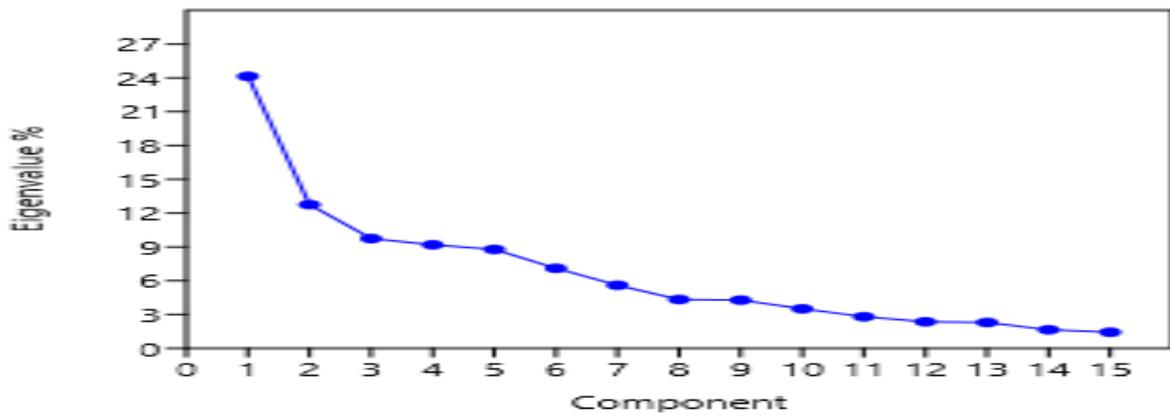


Fig. 7: Screen plot for PCBs in the sediment collected from the Falcorp mangrove swamp

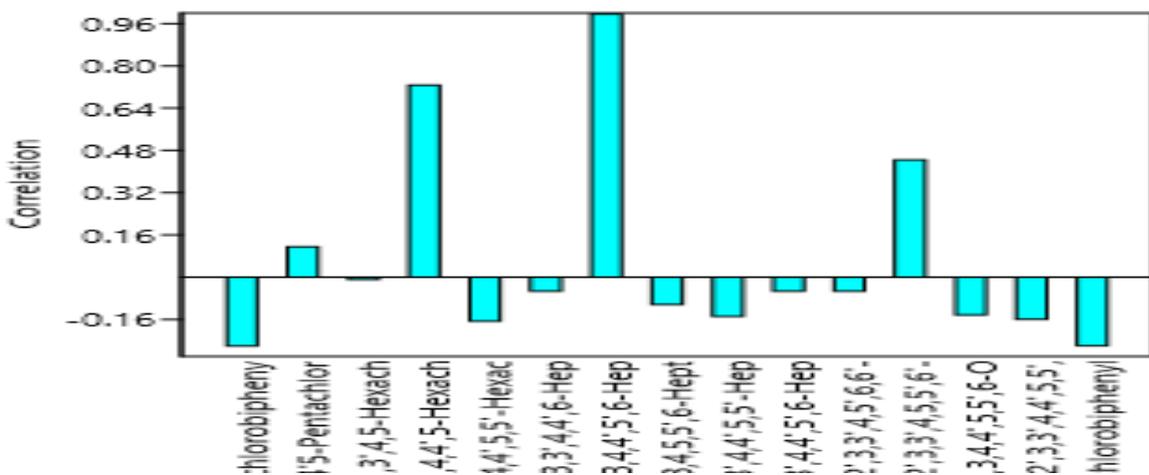


Fig. 8: Correlation of PCBs in sediments sourced from the Falcorp mangrove swamp

Table 6: Euclidean similarity and distance indices of the five PAHs congeners in the sediments collected from the Falcorp mangrove swamp

Station	1	2	3	4	5
1	0.00				
2	0.02	0.00			
3	0.02	0.02	0.00		
4	0.06	0.05	0.06	0.00	
5	0.06	0.06	0.06	0.03	0.00

Ward-Euclidean: 0 and < 1; complete dissimilarity, ≥ 1 ; complete similarity, critical level of significance (C) = 0.05. The bolded values indicated similarity.

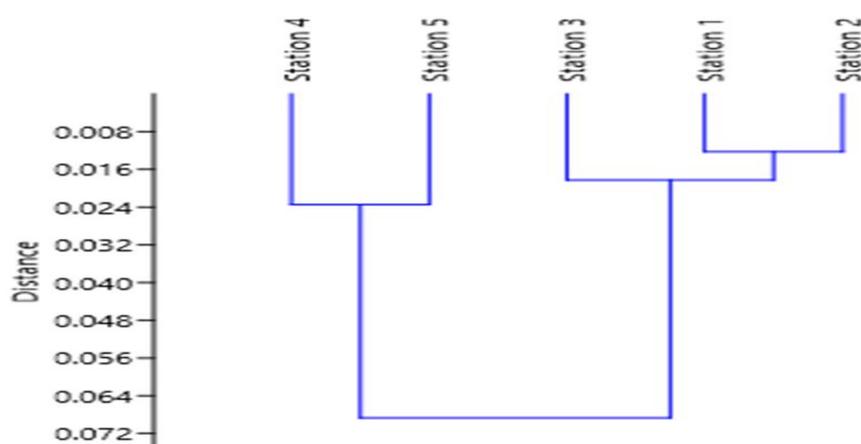


Fig. 9: Cluster analysis for PCBs in the sediments

Conclusion

This research examined the concentrations of PAHs and PCBs in sediments collected from Falcorp mangrove swamp and the Ifie canal. Despite the presence of an active petroleum refinery complex; The Warri petrochemical refinery within close proximity to the wetland and the plethora of other anthropogenic activities which include; bunkering and vandalization of pipelines which transverse some sections of the swamp, the sediment borne PAHs and PCBs concentrations were very low. This trend indicated that the examined sediments were minimally polluted. However, there is an urgent need to conduct more studies pertaining to evaluating the trophic concentrations of these pollutants with reference to native animal sentinels such as mudskippers, crabs, shrimps and molluscs present in the Falcorp mangrove swamp and nearby aquatic habitats.

References

- Alkhatib EA, Weigand C: Parameters affecting partitioning of 6 PCB congeners in natural sediments. *Environ Monit Assess* 78: 1–17. 2002.
- Allen-Gill SM: Organochlorine pesticides and polychlorinated biphenyl in sediments. *Environ Contam Toxicol* 33(4):378-387. 1997.
- Benlahcen KT, Chaoui A, Budzinsk H., Garrigues P: Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. *Mar Pollut Bull* 34:298-305. 1997.
- Bouloubassi I, Saliot A: Dissolved, particulate and sedimentary naturally derived polycyclic aromatic hydrocarbons in a coastal environment: geochemical significance. *Mar Chem* 42: 127–143. 1993.

- Cavalcante RM, Sousa FW, Nascimento RF, Silveira ER, Freire GSS: The impact of urbanization on tropical mangroves (Fortaleza, Brazil): Evidence from PAH distribution in sediments. *J Environ Manage* 91: 328-335.2009.
- Chindah AC, Braide SA, Sibeudu OC: Distribution of hydrocarbons and heavy metals in sediment and a crustacean (*shrimps-Penaeusnotialis*) from the Bonny/New Calabar River Estuary, Niger Delta, *Ajeam-Ragee* 9: 1 –17. 2004.
- Choudhary P, Routh J: Distribution of polycyclic aromatic hydrocarbons in Kumaun Himalayan Lakes, northwest India. *Org Geochem* 41: 891–894.2010.
- Christensen ER, Bzdusek PA: PAHs in sediments of the Black River and the Ashtabula River, Ohio: source apportionment by factor analysis. *Water Res* 39: 511–524. 2005.
- Clark KE, Gobas FAPC, Mackay D: Model of organic chemical uptake and clearance by fish from food and water. *Environ Sci Technol* 24 (8) 1203–1213. 1990.
- Countway RE, Dickhut RM, Canuel EA: Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary *Org Geochem* 34: 209–224.2003.
- Damas EYC, Medina COM, Clemente NCA, Diaz AM. Validation of an analytical methodology for the quantitative analysis of petroleum hydrocarbons in marine sediment samples. *Quim. Nova* 32 (4): 855-860.2009.
- Dean BJ: Recent findings on the genetic toxicology of benzene, toluene, xylenes and phenols. *Mutat Res* 154:153–181. 1985.
- Doong RA, Peng CK, Sun YC, Liao PL: Composition and distribution of organochlorine pesticide residues in surface sediments from the Wu-Shi River estuary Taiwan. *Mar Poll Bull* 45:246-253. 2002.
- Dudani SN, Lakhmapurkar J, Gavali D, Patel T: Heavy metal accumulation in the mangrove ecosystem of South Gujarat Coast, India. *Turkish J Fish Aqua Sci* 17: 755-766.2017.
- Ezemonye LLN: Polychlorinated biphenyls (PCBs) levels and distribution in Ethiope and Benin Rivers of the Niger Delta Nigeria: surface water and sediments. *Int J Environ Stud* 62:491-504. 2005.
- Fouial-Djebbar D, Ahmed AYB, Budzinski H: Determination of organochlorine compounds in coastal marine sediments from the southern west of the Mediterranean Sea. *Int J Environ Sci Tech* 7 (2): 271-280.2010.
- Ge J, Woodward LA, Li QX, Wang J: Distribution, sources and risk assessment of polychlorinated biphenyls in soils from the Midway Atoll, North Pacific Ocean. *PLoS One* 8 (8):e71521. 2013.
- Grimm FA, Hu D, Kania-Korwel I, Lehmler HJ, Ludewig G, Hornbuckle KC, Duffel MW, Bergman A, Robertson LW: Metabolism and metabolites of polychlorinated biphenyls. *Crit Rev Toxicol* 45 (3): 245–272. 2015.
- Guinan J, Charlesworth M, Service M, Oliver T: Sources and geochemical constraints of polycyclic aromatic hydrocarbons in sediments and mussels of two Northern Irish Sea Loughs. *Mar Poll Bull* 42(11): 1073-1081.2001.
- Kannan K, Johnson-Restrepo Y, Yohn S, Giesy J, Long D: Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan Inland lakes. *Environ Sci Technol* 39: 4700–4706. 2005.
- Ke L, Yu KSH, Wong YS, Tam NFY: Spatial and vertical distribution of polycyclic aromatic hydrocarbons in mangrove sediments. *Sci Total Environ* 340: 177-187.2005.
- Kumar B, Singh SK, Kumar S, Sharma CS: Distribution of polychlorinated biphenyls in surface waters of various sources from national capital region Delhi India. *J Nat Sci Res* 2:26-38.2012.
- Lannuzi TJ, Hantely SL, Bonnevie NL, Finley BL: Distribution and possible sources of polychlorinated biphenyls in dated sediments from Newark Bay New Jersey. *Arch Environ Contam Toxicol* 28:108-117.1995.
- Mechlińska A, Wolska L, Namieśnik J: Isotopelabelled substances in analysis in environmental samples. *Trends Anal Chem* 29 (8):820–831. 2010.
- Motelay-Massei AD, Ollivon B, Garban MJ, Teil MB, Chevreuil M: Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere* 55: 555–565.2004.
- Mucha AP, Vasconcelos MTSD, Bordalo AA: Macrobenthic community in the Douuro Estuary: relation with trace metals and natural sediment characteristics. *Environ Poll* 121: 169-180.2003.
- Nair IV, Singh K, Arumugam M, Gangadhar K, Clarson D: Trace metal quality of Meenachil River at Kottayam, Kerala (India) by principal component analysis. *World Appl. Sci. J.* 9 (10): 1100–1107.2010.
- Nwineewii JD, Kpee, F: Polycyclic aromatic hydrocarbon (PAHs) concentrations in roasted plantain and fish from Port Harcourt City, Rivers State, Nigeria. *Chem. Sci. Rev. Lett.* 6 (23):1356 -1362. 2017.
- Okere UV, Semple, KT: Biodegradation of PAHs in pristine soils from different climatic regions. *J Bioremed Biodegrad* 1:1-6.2012.
- Purcaro G, Moret S, Conte LS: Overview on polycyclic aromatic hydrocarbons: Occurrence, legislation and innovative determination in foods. *Talanta* 105:292-305. 2013.
- Ranjan RK, Routh J, Ramanathan AL, Klump JV: Polycyclic aromatic hydrocarbon fingerprints in the Pichavaram mangrove estuarine sediments, Southeastern India. *Org Geochem* 53:88–94. 2012.
- Salem DMA, EL Sikaily A, El Nemr A: Organochlorines and their risk in marine shellfish collected from the Mediterranean coast, Egypt. *Egypt. J. Aquat. Res* 40 (2):93–101.2014.
- Shilla DJ, Routh J: Distribution, behavior, and sources of polycyclic aromatic hydrocarbon in the water column, sediments and biota of the Rufiji Estuary, Tanzania. *Front Earth Sci* 6:70.doi:10.3389/feart.2018.00070.2018.
- Shrestha S, Kazama F: Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. *Environ Modell Softw* 22 (4): 464-475.2007.
- Silliman JE, Meyers P, Eadie JB: Perylene: an indicator of alteration precursor material? *Org Geochem* 29:1737–1744.1999.
- Soclo HH, Budzinski H, Garrigues P, Matsuzawa, S: Biota accumulation of polycyclic aromatic hydrocarbons in Benin coastal waters. *Polycycl. Arom Comp* 28:112–127.2008.
- Tao S, Cao HY, Liu, W.X: Fate modeling of phenanthrene with regional variation in Tianjin, China. *Environ Sci Technol* 37:2453-2459.2003.
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S: PAHs in the Fraser river basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515.2002.

O. Odigie & J.O. Olomukoro

- Yunker M.B., Macdonald RW: Alkane and PAH depositional history, sources and fluxes in sediments from the Fraser River Basin and Strait of Georgia, Canada. *Org Geochem* 34: 1429–1454.2003.
- Zhang Z, Huang J, Yu G, Hong H.: Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. *Environ Poll* 130:349–361.2004.