



Occurrence, depth distribution and risk assessment of PAHs and PCBs in sediment cores of Lagos lagoon, Nigeria

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediment cores of the microtidal coastline of Lagos lagoon were investigated for the occurrence, sources and depositional contamination history. Sediment core samples were collected using the Wildco @ hand corer (50 cm) SS kit and extracted using a 40 mL mixture of hexane and acetone (1:1), and cleaned-up using 10 mm ID chromatographic column before the concentration of aliquots. In this investigation, 16 US EPA priority PAHs and PCB congeners were analysed in aliquots of sediment cores using Agilent 7820A gas chromatograph coupled to a 5975C inert mass spectrometer (with triple-axis detector) with an electron-impact source. PAHs and PCBs were detected at varying concentrations across the 50 cm depth of each sediment core. The total PAH concentrations ranged from 1.43–5.90 mg/kg, and were more widely distributed than the total PCBs. The total PCB concentrations ranged from BDL – 6.41 mg/kg. The PAH diagnostic ratios used identified the sources of the PAHs as pyrogenic rather than petrogenic. About 52% of the samples had concentrations above the ERM limit for total PCBs, suggesting that adverse effects on biota may occur in the long term. In general, the PAHs and PCBs concentrations detected in sediment cores of the Lagos lagoonal system may pose a considerable ecotoxicological risk to estuarine organisms.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants of concern, and they mostly enter the aquatic environment through anthropogenic inputs and adsorb to bottom sediments (Benson et al., 2014). Sediments are known to serve as an important reservoir for organic and inorganic pollutants discharged into the aquatic environment (Benson et al., 2014; Benson and Essien, 2009; Benson et al., 2007; Denis et al., 2012; Benson et al., 2018; Sampei et al., 2019; Giuliani et al., 2017; Benson et al., 2008). Some PAHs, PCBs and heavy metals are known carcinogenic, mutagenic and toxic substances that are capable of adsorbing onto aquatic sediments (Mouton et al., 2009; Xu et al., 2014; Benson et al., 2017a,b). Among several persistent organic contaminants, PAHs are semi-volatile organic compounds with two or more benzene rings attached. Low molecular weight (LMW) PAHs possess 2–3 fused rings and are volatile and more soluble in water than the 4–6 ringed high molecular weight (HMW) PAHs, making

them readily bioavailable for uptake and degradation. The HMW PAHs are denser, more stable and lipophilic hence, they tend to sink and adsorb onto sediments and remain adsorbed for long periods (Benson et al., 2014; Clayden et al., 2012). The stable structure of PAHs is due to the presence of delocalized π -electrons which account for their long half-lives and persistence in the environment (Clayden et al., 2012). PAHs are derived from natural sources like forest fires and eruptions from volcanoes and also from anthropogenic origins such as incomplete combustion of wood, grass, coal, petroleum products, automobile and diesel exhausts, and burning of municipal waste. They are ubiquitous environmental pollutants and have been identified in many sample matrices including air (Lin and Zhu, 2004), surface water (Denis et al., 2012; Hong et al., 2016), soil (Mouton et al., 2009; Lau et al., 2014), sediment (Benson et al., 2008; Hong et al., 2016; Udosen et al., 2007), and also in food products like tea (Fred-Ahmadu and Benson, 2019), coffee (Duedahl-Olesen et al., 2014), fish (Benson et al., 2008; Nwaichi and Ntorgbo, 2016), edible oils (Hao et al., 2016), and grilled and smoked meat (Li et al., 2016). Some PAH congeners are carcinogenic and mutagenic, even at low concentrations, and their occurrence in sediments have been used as surrogates to characterize aquatic ecosystem

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impacts that are associated with human-mediated activities (Boa et al., 2020).

Polychlorinated biphenyls are polychlorinated aromatic compounds consisting of 209 possible congeners. PCBs are a ubiquitous complex mixture of synthetic chemicals with no known natural sources, and they are known to be persistent in the environment. They have one to ten chlorine atoms attached to different positions on the two carbon-carbon linked benzene rings and their toxicity increases with the number of chlorine atoms (USEPA, 2007). The International Agency of Research on Cancer (IARC) has categorized them as “probable carcinogens”. PCBs have endocrine-disrupting ability and are known to cause skin acne, rashes, anaemia and liver problems. Humans can be exposed to PCBs through the use of old electrical devices, eating contaminated food like fish, drinking contaminated well water, releases from industrial incineration and contact with leaks from transformers and old capacitors (ATSDR, 2014). Due to increasing scientific evidence that PCBs are persistent and can accumulate in the environment leading to multiple deleterious effects on terrestrial and marine biota as well as humans, there is a worldwide prohibition of the use and production of PCBs.

More so, PAHs and PCBs are lipophilic compounds that can bioaccumulate in the food chain. They are chemically stable, resistant to degradation in the environment, and persistent. In the aquatic ecosystems, the evaluation of the depth-wise distribution of these organic pollutants in sediments could provide information about the temporal variations in their deposition. The objectives of this study, therefore, were to determine the concentrations and distribution patterns of PAHs and PCBs at different depths of the Lagos lagoon core sediment, to identify the possible sources of PAH pollution and to evaluate the ecological risks associated with PAHs and PCBs exposure.

2. Materials and method

2.1. Study area

The Lagos lagoon is located within the Lagos metropolis. It empties directly into the Atlantic Ocean at the Lagos harbour. The lagoon serves as a major harbour where ships dock to deliver commercial goods and petroleum products. It is a hub of fishing activities, marine transportation, and recreation. The presence of industrial and residential urban establishments along the shoreline contributes significantly to the introduction of pollutant-laden wastes and effluents into the lagoon. Point sources of effluent discharge from petroleum product depots, disposal of waste pesticides and pesticide washings, and sawdust from sawmills, wastewater from Ijora power plant, run-off from nearby markets and roads, and discharges from vessels are principal sources of pollution in the area. Large creeks like Agboyi, Ogudu, Majidun and other smaller creeks and drainages are also channelled into it. The sample sites coordinates (06° 28'00.9"N, 003° 22'13.5"E; 06° 28'07.8"N, 003° 22'16.6"E; 06° 28'03.9"N, 003° 22'15.9"E; 06° 28'02.7"N, 003° 22'11.2"E; 06° 27'57.7"N, 003° 22'17.4"E; and 06° 27'42.5"N, 003° 22'14.1"E) were ascertained using a hand-held global positioning system (GPS) (see Fig. 1).

2.2. Sample collection and treatment

Sediment core samples were collected from six designated locations in the Lagos lagoon using Wildco® hand corer 50 cm SS kit equipped with a liner tube of 5 cm diameter, egg shell core and a 1.5 m extension handle. The 50 cm sediment core was cut into 2 cm slices using a pre-washed spatula, giving a total of 25 sediment subsamples per core. The aliquot of each sediment sample was then wrapped properly using aluminium foil, and

placed in a labelled Ziploc bag. The polyethylene bags were stored in an ice-packed cooler maintained at about 4 °C and then later transported to the laboratory for further preparation and analysis. A total of 150 sediment subsamples from six cores were collected and processed for PAHs and PCBs analyses.

2.3. PAHs, PCBs extraction, clean-up and GC-MS analysis

In the laboratory, one aliquot of each sample was mixed with anhydrous sodium sulphate to remove moisture and then extracted with 40 mL of hexane:acetone (1:1). Extracts were subsequently sonicated for 20 min, decanted and cleaned up on column chromatography packed with alumina. The eluates were collected and concentrated to 2 mL using a Buchi R215 rotary evaporator. For the extract clean-up, a slurry of 10 g activated silica gel in methylene chloride was prepared and placed in a 10 mm ID chromatographic column with 8 mL anhydrous sodium sulphate added to the top of the silica gel. The column was purged with 40 mL of pentane, and then eluted with 25 mL of methylene chloride into a flask for concentration. The collected extract was concentrated to 2 mL using the rotary evaporator prior to gas chromatography mass spectrometry analysis.

Determination of the target PAHs in the core sediment samples were carried out using GC-MS by operating MSD in selective ion monitoring (SIM) and scan mode to ensure low level detection of the target constituents. The Agilent 7820A gas chromatograph coupled to a 5975C inert mass spectrometer (with triple axis detector) with an electron-impact source was used. The stationary phase used for separation of the compounds was HP-5 capillary column coated with 5% phenyl methyl siloxane (30 m length × 0.32 mm diameter × 0.25 μm film thickness). The carrier gas was Helium used at constant flow of 1.48 mL/min at an initial nominal pressure of 1.49 psi and average velocity of 44.22 cm/s. 1 μL of the samples were injected in splitless mode at an injection temperature of 300 °C. Purge flow to split vent was 15.0 mL/min at 0.75 min with a total flow of 16.67 mL/min; gas saver mode was switched off. Oven was initially programmed at 40 °C (1 min) then ramped at 12 °C/min to 300 °C (10 min). Run time was 32.67 min with a 3 min solvent delay. The mass spectrometer was operated in electron-impact ionization mode at 70 eV with ion source temperature of 230 °C, quadrupole temperature of 150 °C and transfer line temperature of 300 °C. After calibration, the samples were analysed and corresponding PAHs concentration obtained. The PAHs determined included acenaphthene (AC), acenaphthylene (ACL), anthracene (AN), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(g,h,i)perylene (BghiP), fluoranthene (FA), benzo(k)fluoranthene (BkF), chrysene (Chr), indeno(1,2,3cd)pyrene (IP), phenanthrene (PHE), naphthalene (NA), fluorene (FL), and pyrene (PY).

For the PCBs analysis, the GC-MS analysis was carried out by splitless injection of 1 μL of the samples at an injection temperature of 250 °C. The chromatographic separation was performed using HP-5 capillary column coated with 5% phenyl methyl siloxane (30m×0.32 mm×0.25 μm). The carrier gas was helium used at constant flow of 1.2 mL/min at an initial nominal pressure of 26 psi and average velocity of 40.00 cm/s. The injection oven was initially programmed at 110 °C (1 min), then ramped at 15 °C/min to 310 °C (5 min). The run time was 19 min with a 3 min solvent delay. The mass spectrometer was operated in electron-impact ionization mode at 70eV with ion source temperature of 230 °C, quadrupole temperature of 150 °C and transfer line temperature of 300 °C. The acquisition of ions were through the scan mode (scanning from m/z 35 to 550 amu at 2.0 s/scan rate) and selective ion mode (SIM). After calibration, the samples were analysed and corresponding PCB

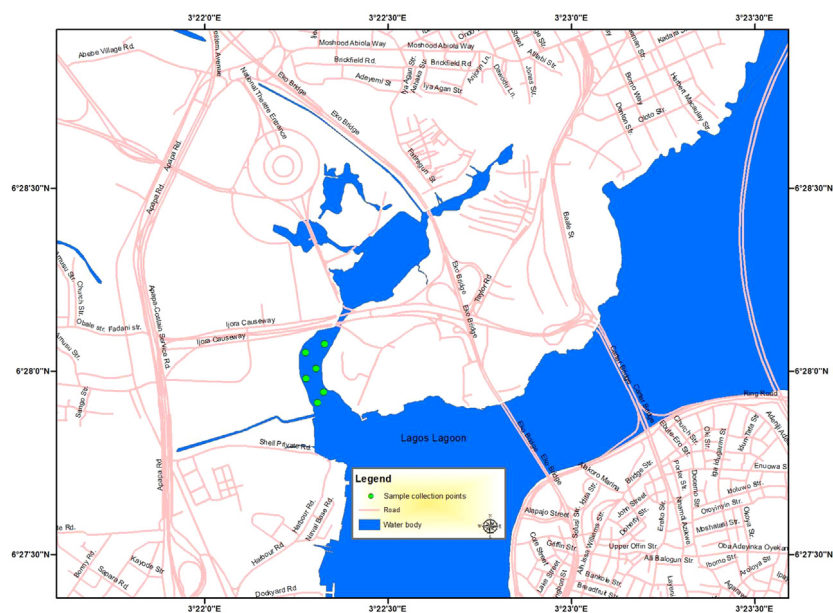


Fig. 1. Map showing the sampling points and surrounding areas.

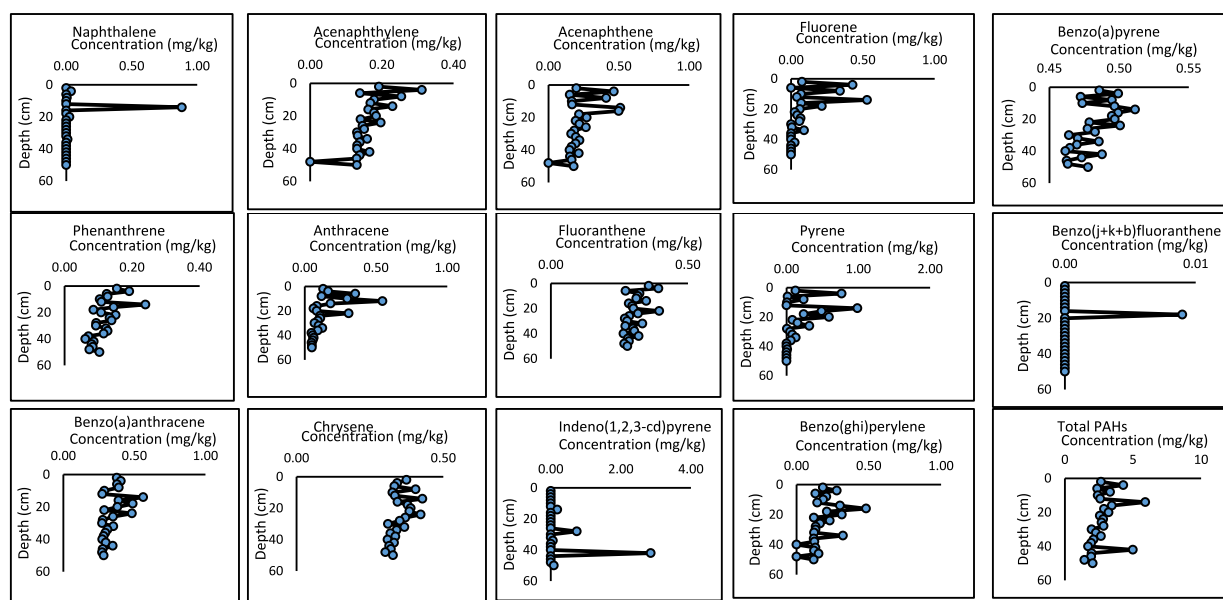


Fig. 2. Vertical profiles of concentrations (mg/kg) of PAH congeners and \sum_{16} PAHs in sediment cores of Lagos lagoon.

concentrations obtained. Fourteen of the PCB congeners were evaluated for each 2 cm depth, they are 2,2',5'-trichloro-1,1'-biphenyl (PCB 18), 2,4,4' + 2,4,5'-trichloro-1,1'-biphenyl (PCB 28, 29), 2,3,3'-trichloro-1,1'-biphenyl (PCB 20), 2,2',5,5'-tetrachloro-1,1'-biphenyl (PCB 52), 2,2',3,5'-tetrachloro-1,1'-biphenyl (PCB 44), 2,3,3',4,4'- pentachloro-1,1'-biphenyl (PCB 105), 2,2',3,4',5',6'-hexachloro-1,1'-biphenyl (PCB 142), 2,3',4,4',5'-pentachloro-1,1'-biphenyl (PCB 118), 2,2',4,4',5,5'-hexachloro-1,1'-biphenyl (PCB 153), 2,2',4,5,5'-pentachloro-1,1'-biphenyl (PCB 101), 2,2',3,4,4',5'-hexachloro-1,1'-biphenyl (PCB 138), 2,2',3,4,4',5,5'-heptachloro-1,1'-biphenyl (PCB 180), 2,2',3,3',4,4',5'-heptachloro-1,1'-biphenyl (PCB 170), and 2,2',3,3',4,4',5,5'-octachloro-1,1'-biphenyl (PCB 194).

2.4. Quality control

PAHs standard, 1000 ppm (catalog number: H-QME-01) containing 23 environmental PAHs components was purchased from AccuStandard, USA. Five (5) point serial dilution calibration standards (1.00, 5.00, 10.00, 50.00, 100.00 ppm) was prepared from the stock and used to calibrate the GC-MS. Also, PCBs standard, 2000 ppm (catalog number: M-8080) containing 14 PCBs components was purchased from AccuStandard. Prior to analyses of samples, five (5) point serial dilution calibration standards (0.5, 1.0, 2.0, 5.0 and 10.0 ppm) were prepared from the stock and used to calibrate the GC-MS. Before calibration, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of m/z 69, 219, 502 and other instrument optimal and sensitivity conditions. The

Table 1
Sources of PAHs based on diagnostic ratios.

PAH ratios	Assigned value range	Sources	Reference
LMW/ HMW	< 1 >1	Pyrogenic Petrogenic	Zhang et al. (2008)
Ant/Ant + Phe	<0.1 >0.1	Petrogenic Pyrogenic	Pies et al. (2008)
BaA/ BaA + Chr	<0.2 >0.35	Petrogenic Combustion	Yunker et al. (2002)
Fla/ Fla + Pyr	<0.4 0.4–0.5 >0.5	Petrogenic Fossil fuel combustion Grass, wood, coal combustion	De La Torre-Roche et al. (2009)

calibration curves of PAHs and PCBs had r^2 values ranging from 0.997 to 1.000 for all congeners. The recoveries of the PAHs from spiked sediment samples carried out for the recovery test ranged from 69.45 to 90.93%. Blank samples prepared without the core sediment aliquots were also analysed. In addition, a certified reference material (ERA #722, Low-level PAHs in Soil, A Waters Company, CO, USA) was used to check the quality of the method; measured and certified values are comparable.

2.5. Statistical analysis

The descriptive statistics and other parametric tests were performed using XLSTAT version 2018 (Addinsoft, USA). The Kaiser–Meyer–Olkin (KMO) test was employed to assess the sampling adequacy of the variables and the collected data, and the significance was set at $p < 0.05$. The total PAHs and PCBs KMO values were 0.755 and 0.547, respectively, indicating adequate and fairly adequate sampling data.

2.6. PAH diagnostic ratios

Diagnostic ratios are normally used to identify PAH sources in the environment. The sources depend on the types of human activities that are predominant in the sampled area. Low temperature processes like burning of wood generates LMW PAHs while high temperature activities such as combustion of engine fuels lead to the formation of HMW PAHs (Manoli et al., 2004). There are several diagnostic ratios in literature but this study employed the ratios given in Table 1.

2.7. Biological adverse effects of PAHs and PCBs using the SQG

Sediment quality guidelines (SQGs) are good predictors of ecological contamination and have been employed in many studies. Two-tier effect levels were used to estimate the potential biological effects and sediment quality. The effect range low (ERL) and effect range median (ERM) estimates the likely adverse effects on organisms with respect to individual PAHs as well as the cumulative toxic effects due to the sum of all the PAHs and also total PCBs (Long, 1992; MacDonald et al., 2012). Adverse biological effects are rare when the PAH or PCB concentrations are below ERL while adverse biological effects will occur occasionally where concentrations are above ERL but less than ERM. However, a concentration above ERM implies that adverse biological effects will frequently occur. For PCBs, only ERL and ERM values for total PCBs are provided in the SQG. The results of the comparison of PAH and PCB concentrations are illustrated in Table 2.

Table 2
Comparison of concentration (mg/kg) of PAHs with ERL and ERM.

PAHs	ERL	ERM	This study
Naphthalene	0.16	2.10	0.00–0.88
Acenaphthylene	0.04	0.64	0.00–0.31
Acenaphthene	0.02	0.50	0.00–0.51
Fluorene	0.02	0.54	0.00–0.53
Phenanthrene	0.24	1.50	0.062–0.24
Anthracene	0.085	1.10	0.047–0.55
Fluoranthene	0.60	5.10	0.26–0.39
Pyrene	0.66	2.50	0.00–0.98
Benzo(a)anthracene	0.26	1.60	0.27–0.56
Chrysene	0.38	2.80	0.30–0.43
Benzo(b)fluoranthene	0.32	1.88	0.0001–0.004
Benzo(k)fluoranthene	0.28	1.62	0.0002–0.0008
Benzo(a)pyrene	0.43	1.60	0.46–0.51
Dibenzo(a,h)anthracene	0.43	1.60	BDL
Indeno(123-c,d)pyrene	0	0	0.00–2.85
Benzo(g,h,i)perylene	0.063	0.26	0.00–0.48
Σ 16PAHs	4.02	44.79	1.43–5.89
LMW	0.55	3.16	0.12–2.57
HMW	1.70	9.60	1.31–4.43
Total PCBs	0.023	0.18	BDL–6.41

ERL – Effect Range Low; ERM – Effect Range Median Long (1992), Burton (2002).

3. Results and discussion

3.1. Concentrations of PAHs and PCBs

The mean concentrations of PAHs and PCBs in core sediments are presented in Figs. 2 and 3. In general, PAHs were detected at all depths of the sediment cores. The low molecular weight (2–3 rings) PAHs had concentrations ranging from 0.12 to 2.57 mg/kg while the corresponding high molecular weight (4–6 rings) PAHs which were found to be more dominant, ranged from 1.31 to 4.43 mg/kg. Benzo(b)fluoranthene and benzo(k)fluoranthene were not detected in most of the depths except in the sample collected at 20 cm depth. Total PAH concentrations ranged from 1.43 to 5.90 mg/kg, with the 14 cm depth having the highest concentration. Notably, the PAH depth-wise concentration distribution followed the order 14>42>4>16>8 cm. The least total PAHs concentrations were found at 48 and 40 cm depths with concentrations of 1.43 and 1.71 mg/kg, respectively. The dominance of the PAH congeners in sediment cores followed the sequence BaP>Chr>BaA>FL>ACL. This sequence agrees with the earlier indication of BaP, PAH2 (BaP and Chr) or components of PAH4 (BaP, Chr, BaA, BbF), being the most important biomarkers for PAHs toxicity, carcinogenicity and mutagenicity (Fred-Ahmadu and Benson, 2019; EFSA, 2004). The occurrence and detection of enhanced concentrations of PAHs in the studied sediment cores of the lagoonal system may be linked to the industrial development and related human activities in the area over the years. Other sources of PAHs may be associated with atmospheric deposition, fossil fuel emissions, as well as biomass combustion.

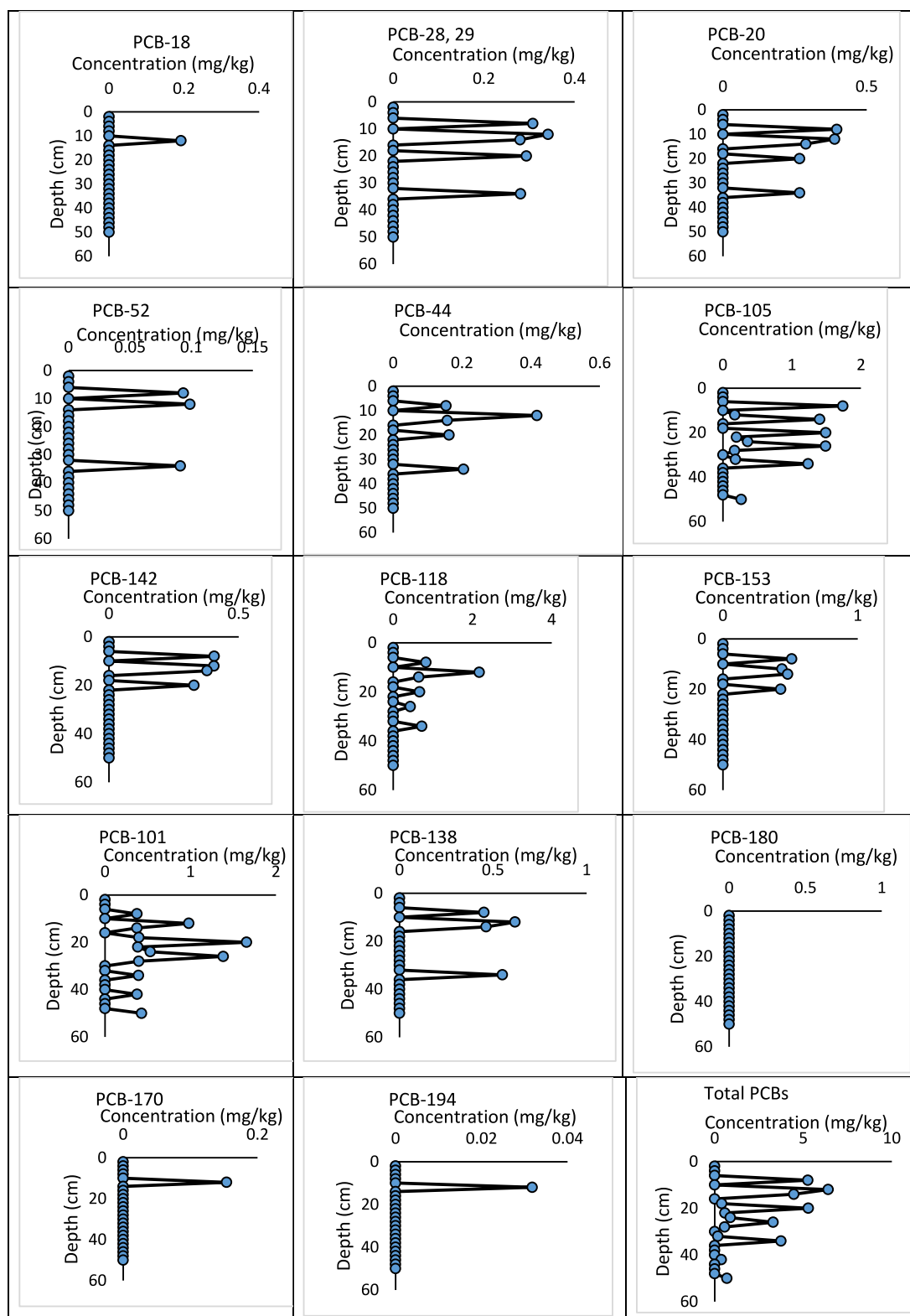


Fig. 3. Vertical profiles of concentrations (mg/kg) of PCB homologues and Σ PCBs in sediment cores of Lagos lagoon.

The PCB concentrations in sediment cores across the sampling sites are presented in Fig. 3. In this study, the most dominant PCBs were the higher molecular weight PCBs (PCB-105, PCB-101, PCB-118 and PCB-138 with average concentrations of 8.70, 7.67, 5.46 and 2.08 mg/kg, respectively. The highest average concentrations of PCBs in sediment cores were 6.41, 5.29, 5.26, 4.47, and 3.74 mg/kg at 12, 20, 8, 14, and 34 cm depths, respectively, which

indicates that anthropogenic activities and human development over the years might have influenced the pollution levels. Besides, our results also indicated that sediments are important sinks for PCBs (Neira et al., 2018). The PCB-101 congener was the most widely detected PCB while PCB 118 had the highest concentration (2.17 mg/kg) of all PCB congeners across all the depths. On the other hand, PCB congeners were not detected at 2, 4, 6, 10, 16,

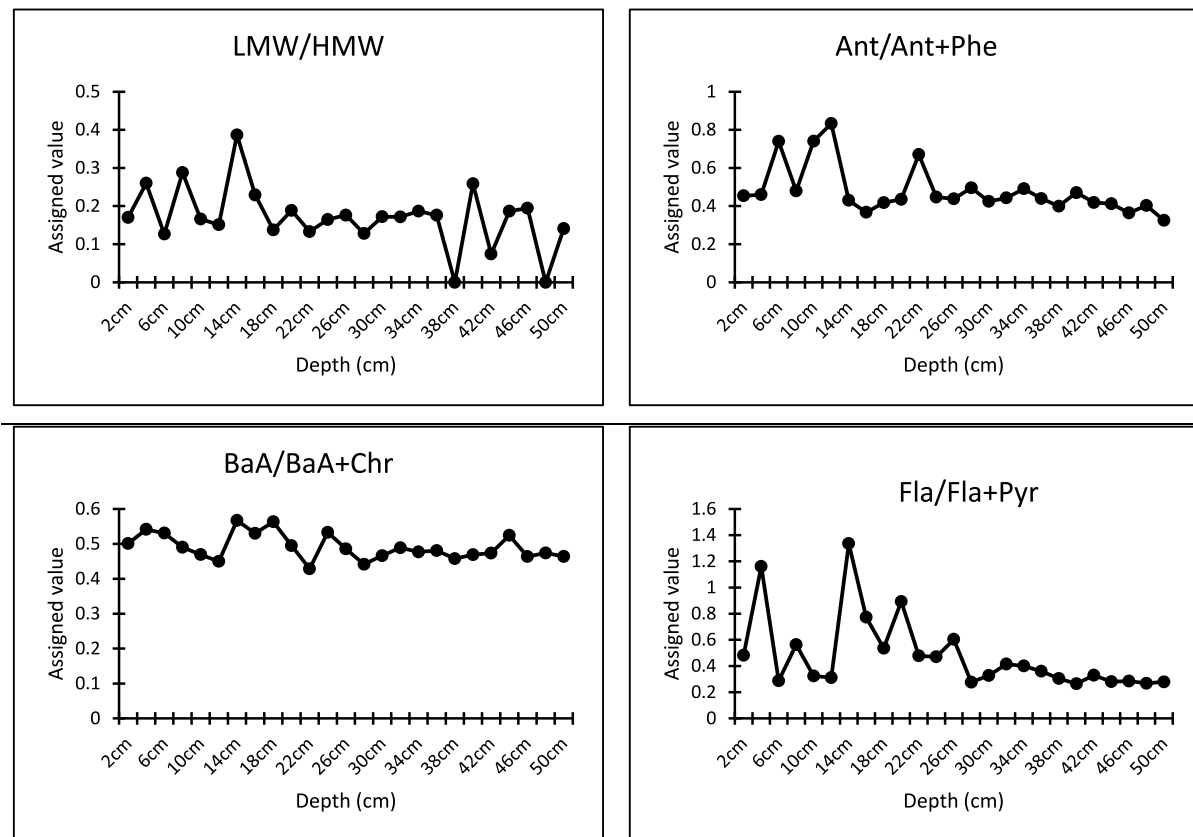


Fig. 4. Variations of PAH ratios with depth profile of sediment cores.

30, 36, 38, 40, 44, 46, and 48 cm depths, representing about 48% of the sampled cores. The non-occurrence and detection of PCBs in the top sediment cores suggests a discontinuation of PCBs-laden effluents discharge into the environment in recent times. In this study, 2,2',3,4,4',5,5'-heptachloro-1,1'-biphenyl (PCB-180) was not detected at any of the depths. High molecular weight PCBs has been reported at enhanced levels in sediments of San Diego bay of Southern California (Neira et al., 2018). Our result showed that PCB-20, which is a lightweight PCB had the highest concentration of 1.61 mg/kg.

PAHs were widely distributed across the various depths of the sediment cores compared with the PCB homologues. PAH and PCB concentrations at depths 2–50 cm had a Pearson moment correlation coefficient of 0.35, which indicates a weak positive correlation between the congeners of both pollutants. However, depths 14 cm and 8 cm had relatively higher contaminations of the combination of both PAHs and PCBs. However, a critical examination of the trends of PAHs and PCBs concentration profiles recorded in this study from the topcore to downcore sediments indicated a long-term history of contamination that might be associated with the rapid socio-economic and industrial development around the lagoonal ecosystem.

3.2. Diagnostic ratios

The PAHs detected were found to be largely from sources such as combustion of wood, coal and grass, which are pyrogenic while petrogenic sources produced about 16% of the PAHs. The concentrations of PAHs and their distributions fluctuated with the depth of the sediment core. Generally, the surficial depths (2 – 16 cm) showed relatively higher ratios of PAHs than the downcore subsamples (18–50 cm). This suggests that anthropogenic release of PAHs from pyrogenic sources may have increased in

recent years. The diagnostic ratios followed the order Fla/Fla+Pyr > Ant/ Ant+Phe > BaA/BaA+Chr > LMW/HMW (Fig. 4). Souza et al. (2018) reported similar observations as obtained in this study for the PAH sources in Proxim River in Brazil where HMW PAHs were dominant and sources being mainly pyrogenic. This is in agreement with many published works on PAHs in sediments (Benson et al., 2008; Yunker et al., 2002; Tobiszewski and Namieśnik, 2012; Yang et al., 2018).

3.3. Correlation between total concentrations of PAHs and PCBs

For the purpose of evaluating the distribution interrelationship between the total concentrations of the 16 priority PAHs (\sum_{16} PAHs) and \sum PCBs in sediment cores of the study area, a Pearson correlation coefficient was computed according the total depth-based concentrations of each contaminant. The \sum_{16} PAHs and \sum PCBs distribution concentrations as well as the Pearson correlation value indicating the strength of the associated between PAHs and PCBs at the six designated sites is presented in Fig. 5. From the result, a relatively low correlation value of 12.47% ($p < 0.05$) was derived. This could suggest that the PAHs and PCBs depositional sources over the years may have originated from different non-point human-mediated activities. However, in order to assess the spatial homogeneous variability of the PAHs and PCBs with respect to their depositional history, the percent variation coefficient (%CV) were computed for each total contaminant. Thus, the % correlation coefficient for \sum_{16} PAHs and \sum PCBs were 37.16% and 160.69%, respectively. Therefore, \sum_{16} PAHs indicated a relative spatial homogeneity when compared to \sum PCBs (Thurston et al., 2011; Tian et al., 2013).

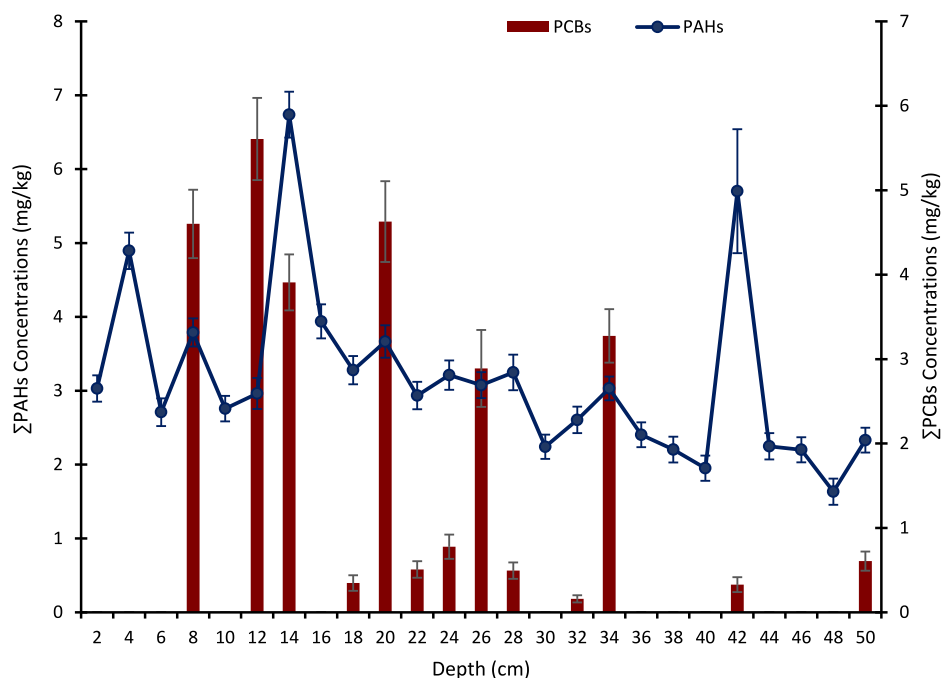


Fig. 5. Concentrations (mg kg^{-1} dw) of \sum_{16} PAHs and \sum PCBs in sediment cores of Lagos lagoon.

Table 3

Comparison of the total concentrations of PAHs and PCBs in sediments obtained in this study with those previously reported in other studies.

Location	Country	Analyte	Concentration (mg/kg)	Reference
Proxim River	Brazil	PAH	0.002–0.028	Souza et al. (2018)
Elizabeth River wetland	USA	PAH	1.20–22.00	Kimbrough and Dickhut (2006)
Hainan Island	China	PAH	0.067–1.97	Xiang et al. (2018)
Al Hawizah wetland	Iran	PAH	1.07–17.28	Janadeleh et al. (2018)
Cochin estuary	India	PAH	0.19–141.15	Ramzi et al. (2017)
North Pacific (Arctic ocean)		PAH	0.013–0.068	Ma et al. (2017)
Zhein bay	China	PAH	0.008–0.051	Gu et al. (2018)
Qatar marine environment	Qata	PAH	0.0031–0.014	Hassan et al. (2018)
Qin huangdao wetland	China	PAH	0.341–4.70	Lin et al. (2018)
Zhalong wetland	China	PAH	0.032–0.29	Liu et al. (2011)
This study		PAH	1.49–5.89	
Jobos bay	Puerto Rico	PCB	0.0004–1.23	Alegria et al. (2016)
San Diego bay, California	USA	PCB	0.023–1.39	Neira et al. (2018)
Haizhou bay	China	PCB	0.0013–0.0063	Zhang et al. (2014)
Pearl River	China	PCB	0.0032–0.022	Wang et al. (2011)
This study		PCB	BDL–6.41	

3.4. Comparison with ERL and ERM

The total PCB concentrations for the various depths varied from ND – 6.41 mg/kg, with depth 12 cm having the highest concentration. Thirteen various depths, representing 52% of the total number of depths sampled, had total PCB concentrations higher than the ERM value of 0.18 mg/kg. This indicates that biological adverse effects may frequently occur in that environment. The highly contaminated depths were 8 cm (5.26 mg/kg), 12 cm (6.41 mg/kg), 14 cm (4.47 mg/kg), 18 cm (0.39 mg/kg), 20 cm (5.29 mg/kg), 22 cm (0.58 mg/kg), 24 cm (0.89 mg/kg), 26 cm (3.30 mg/kg), 28 cm (0.56 mg/kg), 32 cm (0.18 mg/kg), 34 cm (3.74 mg/kg), 42 cm (0.38 mg/kg) and 50 cm (0.69 mg/kg). Other top- and down-core depths had concentrations that were below the ERL value (0.02 mg/kg), indicating no biological adverse effects are likely.

The total PAHs ranged from 1.43 mg/kg to 5.89 mg/kg at 48 cm and 14 cm depths, respectively. HMW PAHs were found to be more dominant than LMW PAHs at all the depths. This can be attributed to the higher stability, density and lipophilicity of the HMW PAHs hence they sorb strongly to sediment particles. Toxic effects due to the presence of C_1 -dibenzothiophene,

acenaphthene, indeno(123-cd)pyrene and benzo(g,h,i)perylene will likely occur in the long-term as their concentrations are above the recommended ERM. However, benzo(b)fluoranthene and benzo(k)fluoranthene were recorded at concentrations lower than the ERL, hence they may not pose any risk to marine organisms. However, our results indicated that the concentrations of other PAH congeners were above the ERL but lower than the ERM. The total concentrations of LMW, HMW and \sum_{16} PAHs in each of the depths were below the ERM value indicating that there could be occasional occurrence of toxic effects to organisms in the sampling site.

A comparison of the results of PAH and PCB concentrations from this study with reports from other parts of the world is presented in Table 3.

4. Conclusion

PAHs and PCBs occurrence were assessed in the sediment cores of the microtidal coastline of the Lagos lagoon. Generally, the maximum concentrations of PAHs and PCB concentrations appear to be higher in the upper depths (2 – 16 cm), suggesting

more recent anthropogenic input of the pollutants. A comparison of the levels of PAHs determined in this study with similar studies from other regions showed that the concentrations were significantly higher than most lagoonal and estuarine sediments. The PAHs were found to be widely distributed and in elevated concentrations from the topcore to downcore sediment samples relative to the PCBs levels. However, the total PCBs exceeded the ERM levels while total PAHs remained below the ERM. The sequence of PAHs occurrence was in agreement with the use of BaP, PAH2 or PAH4 as indicators of PAHs toxicity and carcinogenicity. A weak positive correlation was observed between \sum_{16} PAHs and \sum PCBs concentrations in the sediment. This interrelationship although not causal, could suggest that the PAHs and PCBs depositional sources may have originated from different non-point human-mediated activities. In general, the PAHs and PCBs concentrations detected in sediment cores of the Lagos lagoonal system may likely pose considerable ecotoxicological risk to estuarine organisms in the short term. However, in view of unabated pollution into the Lagoon, moderate to severe effects may occur with enhanced levels of the contaminants in the future.

CRedit authorship contribution statement

Nsikak U. Benson: Conceptualization, Formal analysis, Investigation, Supervision, Writing - original draft, Writing - review & editing. **Omowunmi H. Fred-Ahmadu:** Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Simeon I. Eckett:** Data curation, Investigation, **Mercy O. Basil:** Data curation. **Adedamola D. Adebowale:** Data curation. **Adeyemi G. Adewale:** Writing - original draft. **Olusegun O. Ayejuyo:** Supervision, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Alegria, H., Martinez-Colon, M., Birgul, A., Brooks, G., Hanson, L., Kurt-Karakus, P., 2016. Historical sediment record and levels of PCBs in sediments and mangroves of jobos bay puerto rico. *Sci. Total Environ.* 573, 1003–1009.
- ATSDR (Agency for Toxic Substances and Diseases Registry), 2014. Polychlorinated biphenyls - ToxFAQs™ polychlorinated biphenyls. Retrieved from <https://www.atsdr.cdc.gov>.
- Benson, N.U., Adedapo, A.E., Fred-Ahmadu, O.H., Williams, A.B., Udosen, E.D., Ayejuyo, O.O., Olajire, A.A., 2018. New ecological risk indices for evaluating heavy metals contamination in aquatic sediment: A case study of the Gulf of Guinea. *Reg. Stud. Mar. Sci.* 18, 44–56. <https://doi.org/10.1016/j.rsm.2018.01.004>.
- Benson, N.U., Essien, J.P., 2009. Petroleum hydrocarbons contamination of sediments and accumulation in *tympantonus fuscatus* var. *radula* from the qua iboe mangrove ecosystem, Nigeria. *Current Sci.* 96 (2), 238–244.
- Benson, N.U., Essien, J.P., Asuquo, F.E., Eritobor, A.L., 2014. Occurrence and distribution of polycyclic aromatic hydrocarbons in surface microlayer and subsurface seawater of lagos lagoon, Nigeria. *Environ. Monit. Assess.* 186, 5519–5529.
- Benson, N.U., Essien, J.P., Ebong, G.A., Williams, A.B., 2008. Petroleum hydrocarbons and limiting nutrients in macrura reptantia, *procambarus clarkii* and benthic sediment from Qua Iboe Estuary, Nigeria. *The Environmentalist* 28 (3), 275–282. <http://dx.doi.org/10.1007/s10669-007-9140-6>.
- Benson, N.U., Essien, J.P., Williams, A.B., Ebong, G.A., 2007. Petroleum hydrocarbon accumulation potential in shellfishes from littoral waters of the bight of bonny, niger delta (Nigeria). *Res. J. Environ. Sci.* 1, 11–19.
- Benson, N.U., Fred-Ahmadu, O.H., Adedapo, A.E., Anake, W.U., 2017b. Characterisation of polychlorinated biphenyls in coastal inland seawater Nigeria. In: 3rd International Conference on Advances in Environment Research. In: IOP Conf. Series: Earth and Environmental Science, vol. 68(1), 012007. <http://dx.doi.org/10.1088/1755-1315/68/1/012007>.
- Benson, N.U., Udosen, E.D., Essien, J.P., Anake, W.U., Adedapo, A.E., Akin-tokun, O.A., Fred-Ahmadu, O.H., Olajire, A.A., 2017a. Geochemical fractionation and ecological risks assessment of benthic sediment-bound heavy metals from coastal ecosystems off the Equatorial Atlantic Ocean. *Int. J. Sediment Res.* 32 (3), 410–420.
- Boa, K., Zaccone, C., Tao, Y., Wang, J., Shen, J., Zhang, Y., 2020. Source apportionment of priority PAHs in 11 lake sediment cores from Songnen Plain, Northeast China. *Water Res.* 168, 115158. <https://doi.org/10.1016/j.watres.2019.115158>.
- Burton, G.A., 2002. Sediment quality criteria in use around the world. *Limnology* 3, 65–75.
- Clayden, J., Greeves, N., Warren, S., Wothers, P., 2012. *Organic Chemistry*. Oxford University Press, <https://doi.org/10.1086/278635>.
- De La Torre-Roche, R.J., Lee, W.Y., Campos-Díaz, S.I., 2009. Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: Analysis of a potential problem in the United States/Mexico border region. *J. Hazard. Mater.* 163 (2–3), 946–958.
- Denis, E.H., Toney, J.L., Tarozo, R., Anderson, R.S., Roach, L.D., Huang, Y., 2012. Polycyclic aromatic hydrocarbons (PAHs) in lake sediments record historic fire events: validation using HPLC-fluorescence detection. *Org. Geochem.* 45, 7–17.
- Duedahl-Olesen, L., Navaratnam, M.A., Jewula, J., Jensen, A.H., 2014. PAH in some brands of tea and coffee. *Polycycl. Aromat. Compd.* 35, 74–90.
- EFSA, 2004. Opinion of the scientific panel on contaminants in the food chain on a request from the commission related to mercury and methylmercury in food. *The EFSA Journal* 1–14.
- Fred-Ahmadu, O.H., Benson, N.U., 2019. Polycyclic aromatic hydrocarbons (PAHs) occurrence and toxicity in *Camellia sinensis* and herbal tea. *Polycycl. Aromat. Compd.* 39 (4), 383–393. <https://doi.org/10.1080/10406638.2017.1335216>.
- Giuliani, S., Bellucci, L.G., Çağatay, M.N., Polonia, A., Piazza, R., Vecchiato, M., Pizzini, S., Gasperini, L., 2017. The impact of the 1999 Mw 7.4 event in the İzmit Bay (Turkey) on anthropogenic contaminant (PCBs, PAHs and PBDEs) concentrations recorded in a deep sediment core. *Sci. Total Environ.* 590–591, 799–808. <https://doi.org/10.1016/j.scitotenv.2017.03.051>.
- Gu, Y.-G., Ke, C.-L., Liu, Q., 2018. Characterization, sources, and ecological hazards of polycyclic aromatic hydrocarbons in the intertidal sediments of Zhelin Bay the biggest mariculture area on the eastern Guangdong coast of China. *Mar. Pollut. Bull.* 130, 192–197.
- Hao, X., Li, J., Yao, Z., 2016. Changes in PAHs levels in edible oils during deep-frying process. *Food Control* 66 (835), 233–240.
- Hassan, H.M., Castillo, A.B., Yigiterhan, O., Elobaid, E.A., Al-Obaidly, A., Al-Ansari, E., Obbard, J.P., 2018. Baseline concentrations and distributions of polycyclic aromatic hydrocarbons in surface sediments from the Qatar marine environment. *Mar. Pollut. Bull.* 126, 58–62.
- Hong, W.J., Jia, H., Li, Y.F., Sun, Y., Liu, X., Wang, L., 2016. Polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs in the coastal seawater, surface sediment and oyster from Dalian, Northeast China. *Ecotox. Environ. Saf.* 128, 11–20.
- Janadeleh, H., Kameli, M.A., Boazar, C., 2018. Seasonal variations of metal pollution and distribution, sources, and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in sediment of the al hawzah wetland, Iran. *Hum. Ecol. Risk Assess.* 24 (4), 886–903.
- Kimbrough, K.L., Dickhut, R.M., 2006. Assessment of polycyclic aromatic hydrocarbon input to urban wetlands in relation to adjacent land use. *Mar. Pollut. Bull.* 52, 1355–1363.
- Lau, E.V., Gan, S., Ng, H.K., Poh, P.E., 2014. Extraction agents for the removal of polycyclic aromatic hydrocarbons (PAHs) from soil in soil washing technologies. *Environ. Pollut.* 184, 640–649.
- Li, J., Dong, H., Li, X., Han, B., Zhu, C., Zhang, D., 2016. Quantitatively assessing the health risk of exposure to PAHs from intake of smoked meats. *Ecotox. Environ. Saf.* 124, 91–95.
- Lin, F., Han, B., Ding, Y., Li, Q., Gao, W., Zheng, L., 2018. Distribution characteristics, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in sediments from the qinhuangdao coastal wetland, China. *Mar. Pollut. Bull.* 127, 788–793.
- Lin, D., Zhu, L., 2004. Polycyclic aromatic hydrocarbons: pollution and source analysis of a black tea. *J. Agric. Food Chem.* 52 (26), 8268–8271.
- Liu, J.-W., Xie, Q.-L., Wang, Y., Xu, Y., Li, J., Zhang, G., 2011. Characterization of polycyclic aromatic hydrocarbons contaminations in surface sediments from zhalong wetland, China. *Huan Jing Ke Xue* 32 (8), 2450–2454.
- Long, E.R., 1992. Ranges in chemical concentrations in sediments associated with adverse biological effects. *Mar. Pollut. Bull.* 24, 38–45.

- Ma, Y., Halsall, C.J., Xie, Z., Koetke, D., Mi, W., Ebinghaus, R., Gao, G., 2017. Polycyclic aromatic hydrocarbons in ocean sediments from the North Pacific to the Arctic Ocean. *Environ. Pollut.* 227, 498–504.
- MacDonald, D.D., Smith, S.L., Wong, M.P., Mudroch, P., (1992) The development of Canadian marine environmental quality guidelines. Ecosystem Sciences and Evaluation Directorate, Conservation and Protection, Environment Canada, Ottawa, Ontario, 32pg.
- Manoli, E., Kouras, A., Samara, C., 2004. Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* 56 (9), 867–878.
- Mouton, J., Mercier, G., Drogui, P., Blais, J.F., 2009. Experimental assessment of an innovative process for simultaneous PAHs and Pb removal from polluted soils. *Sci. Total Environ.* 407 (20), 5402–5410.
- Neira, C., Vales, M., Mendoza, G., Hoh, E., Levin, L.A., 2018. Polychlorinated biphenyls (PCBs) in recreational marina sediments of San Diego Bay, Southern California. *Mar. Pollut. Bull.* 126, 204–214.
- Nwaichi, E.O., Ntorgbo, S.A., 2016. Assessment of PAHs levels in some fish and seafood from different coastal waters in the Niger Delta. *Toxicol. Rep.* 3, 167–172.
- Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T., 2008. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Chemosphere* 72 (10), 1594–1601.
- Ramzi, A., Habeeb, K., Gireeshkumar, T.R., Balachandran, K.K., Jacob, C., Chandramohanakumar, N., 2017. Dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of cochin estuary, India. *Mar. Pollut. Bull.* 114 (2), 1081–1087.
- Sampei, Y., Uraoka, S., Ono, T., Dettman, D.L., 2019. Polycyclic aromatic hydrocarbons (PAHs) in sediment cores from lakes Shinji and Nakaumi, SW Japan: A proxy of recent fire events in the watershed. *Estuar. Coast. Shelf Sci.* 226, 106269, <https://doi.org/10.1016/j.ecss.2019.106269>.
- Souza, M.R.R., Santos, E., Suzarte, J.S., Carmo, L.O., Frena, M., Damasceno, F.C., Alexandre, M.R., 2018. Concentration, distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in proximal river sediments, Brazil. *Mar. Pollut. Bull.* 127, 478–483.
- Thurston, G.D., Ito, K., Lall, R., 2011. A source apportionment of U.S. fine particulate matter air pollution. *Atmos. Environ.* 45, 3924–3936.
- Tian, Y.-Z., Li, W.-H., Shi, G.-L., Feng, Y.-C., Wang, Y.-Q., 2013. Relationships between PAHs and PCBs, and quantitative source apportionment of PAHs toxicity in sediments from Fenhe reservoir and watershed. *J. Hazard. Mater.* 248249, 89–96.
- Tobiszewski, M., Namieśnik, J., 2012. PAH Diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162, 110–119.
- Udosen, E.D., Benson, N.U., Essien, J.P., 2007. Trends in heavy metals and hydrocarbon burdens in stubbs creek, a tributary of the Qua Iboe River Estuary, Nigeria. *Trends Appl. Sci. Res.* 2 (4), 312–319. <http://dx.doi.org/10.3923/tasr.2007.312.319>.
2007. USEPA Table of PCB species by congener number. <https://www.epa.gov/sites/production/files/2015/HYPHEN09/documents/congenertable.pdf>.
- Wang, H., Du, J., Leung, H., Leung, A.O.I., Wah, Liang, P., Giesy, J.P., ..., Wong, M.-H., 2011. Distribution and source apportionments of polychlorinated biphenyls (PCBs) in mariculture sediments from the pearl river delta, south China. *Mar. Pollut. Bull.* 63 (5–12), 516–522.
- Xiang, N., Jiang, C., Yang, T., Li, P., Wang, H., Xie, Y., .. Diao, X., 2018. Occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) in seawater, sediments and corals from Hainan island, China. *Ecotoxicol. Environ. Saf.* 152, 8–15.
- Xu, J., Guo, J.-Y., Liu, G.-R., Shi, G.-L., Guo, C.-S., Zhang, Y., Feng, Y.-C., 2014. Historical trends of concentrations, source contributions and toxicities for PAHs in dated sediment cores from five lakes in western China. *Sci. Total Environ.* 470–471, 519–526.
- Yang, Z., Shah, K., Crevier, C., Laforest, S., Lambert, P., Hollebone, B.P., Yang, C., Brown, C.E., Landriault, M., Goldthorp, M., 2018. Occurrence, source and ecological assessment of petroleum related hydrocarbons in intertidal marine sediments of the bay of fundy, New Brunswick, Canada. *Mar. Pollut. Bull.* 133, 799–807.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser river basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochem.* 33 (4), 489–515.
- Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., Wang, X., 2008. Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environ. Pollut.* 153 (3), 594–601.
- Zhang, R., Zhang, F., Zhang, T., Yan, H., Shao, W., Zhou, L., Tong, H., 2014. Historical sediment record and distribution of polychlorinated biphenyls (PCBs) in sediments from tidal flats of Haizhou bay, China. *Mar. Pollut. Bull.* 89 (1–2), 487–493.