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Abstract. The concentrations of polychlorinated biphenyls (PCBs) were determined in samples of surface seawater collected from five (5) different locations along the coastline of a tropical lagoon. The surface water samples were analysed using gas chromatography coupled with electron capture detector (GC-ECD) with fifteen (15) PCB congeners detected across the studied area. The chlorobiphenyls levels are in the order Ebute Ero > Oko Baba > Ijora > Lagos Island > Unilag lagoon front with levels 107.89, 53.15, 34.90, 27.78, and 2.15 mg/L, respectively. The enhanced average concentration of PCBs at the Ebute Ero site is due to the predominance of PCB-180 and PCB-185. A negative correlation was found between the total PCB concentration and the level of dissolved oxygen. Although, the results indicated fairly high levels of PCBs, the anthropogenic contributions from industrial releases and domestic activities may be largely associated with the detected concentrations of the di-, tetra-, penta-, hexa-, hepta-, and octa-chlorobiphenyls.

1. Introduction

Over the years, there have been heightened concerns over the profound toxicity and potential human and ecosystem risks associated with the presence of polychlorinated biphenyls (PCBs) in the environment. PCBs are man-made organic environmental pollutants made up of carbon, hydrogen and chlorine atoms, and are generally known to be persistent, bioaccumulative and toxic (PBT) chemicals [1]-[5]. The level of toxicity exhibited by each PCB congener is a function of the pattern of chlorine substitution. Coplanar PCBs, particularly (PCB-77, 81, 126 and 169) and mono-ortho PCBs (PCB-105, 114, 118, 123, 156, 157, 167 and 189) are the most toxic congeners [6].

They are high boiling; chemically stable and non-flammable compounds hence their application as coolants, electrical insulators, plasticizers, transformer lubricants, and in capacitors etc. PCBs enter the environment during their manufacture process, use, and disposal. They emerge from accidental spills and leaks during their transport, and from leaks from disposed capacitors and transformer or burning of PCB products. Exposure to PCBs is known to cause skin rashes, acne, and liver damage [7]. They have been classified as probable carcinogens by the USEPA. Although the use of PCBs was banned in the US and most European countries in the 1970s, they still enter the marine environment through disposed PCB-containing materials, disposal of obsolete electrical equipment, and industrial discharge [8]. Due to their slow biodegradability, they settle into seawater and sediments resulting in increased load of highly chlorinated PCBs for the deep-water habitat [7], [9]. The role of floating plastic resin microparticulates in the transportation of contaminants within the marine environment resulting in

their accumulation in the surface microlayer has been reported [10]. This may pose a considerable toxic risk to the marine ecosystem and commercial fishing.
In Nigeria, coastal lagoons and lacustrine ecosystems have witnessed increasing physical, biological and chemical pollutions that emanate mostly from human mediated sources [11]-[13]. The major anthropogenic PCBs input into water resources include biomass burning, leakages from transformers and shipwreck, and illegal disposal of PCB-laden end-of-life electronic items [14]. In aquatic ecosystems, humans can be exposed to PCBs through oral ingestion, dermal contact and inhalation. Surface water constitutes a primary pathway transportation of particulate bound and water loosely absorbed PCBs. Thus, the concentration of PCBs in aquatic ecosystem is largely influenced by the quantity of the particulates suspended in the water column that actually adsorbs chlorobiphenyls [3], [15]. This study presents the concentration of PCBs in surface water collected from Lagos lagoon, a tropical inland aquatic ecosystem.

2. Materials and methods

2.1. Study area

The study area is the Lagos lagoon which lies between latitude 6^{o} 27' N and longitude 3^{o} 23' E with a maximum length of 50 km, and about 13 km width. The lagoon is located in the Southwestern part of Lagos State, Nigeria. The Lagos lagoon has large surface area of about 6,354.7 km^2 and extends to various parts of the Lagos Island. It is mainly plied by small boats and canoes, which are used as means of commercial transportation and fishing. Activities carried out on the lagoon and along its coast include fishing, manufacturing plants, wood constructions, transportation, saw milling, plank markets, other markets and hundreds of wooden shacks. Apart from the domestic and economic activities carried out on the lagoon, large amount effluents and other pollutants such as nutrient runoff from agricultural lands, sewages, wood preservatives and waste disposed of nearby markets are discharged into the lagoon regularly. The upsurge of industrial effluent in addition to the various discharges has resulted in intense pollution of the lagoon, enhancing health risks posed to humans and the seawater environment. The coordinates of the sampling locations were taken using a Garmin-GPSMAP 76S handheld global positioning system (GPS). The specific sampled sites are Ebute Ero, EBE, (6^{o}28'10" N, 3^{o}23'04" E), Ijora, IJR, (6^{o}27'55" N, 3^{o}22'36" E), Lagos Island, LGL, (6^{o}27'47" N, 3^{o}23'01" E), Oko Baba, OKB, (6^{o}28'50" N, 3^{o}23'29" E), and the University of Lagos lagoon front, UWF, (6^{o}30'18" N, 3^{o}24'01" E).

2.2. Sample collection and treatment

Sampling was carried out using a boat. Surface seawater samples were collected using clean, and properly labelled amber glass bottles; physicochemical parameters were measured at the sampling sites using a pre-calibrated QPM – 7000 multi-probe analyser. Then samples were immediately stored in an ice-packed cooler and transported to the laboratory at the National Institute of Oceanography and Marine Research, Nigeria. They were then transferred into a refrigerator and stored at 4^{o}C.
Sample extraction was carried out 2 days after sampling using liquid-liquid extraction. 100 mL of water sample was introduced into a separatory funnel and 50 mL of solvent, dichloromethane (DCM) was added. The mixture was shaken vigorously and the stopper removed at intervals to release pressure from the funnel. The extract was the carefully drained into a conical flask and the process was repeated the second time with 50 mL of DCM [16]. This extraction was done in batches and the solvent extracts are concentrated using a rotary evaporator. The clean up of extracts was done using column chromatography in accordance with US EPA method 3630B [17]. The 20 mL glass column was packed with glass wool to about 5 mL and activated silica gel (60-200 mesh size) from about 5 mL to 15 mL of the glass column. 2 g of baked sodium sulphate (Na_2SO_4) was used to cap the sample; this was done to remove any trace of water present in the sample. The glass column was then conditioned with 20 mL of DCM to ensure that the silica gel is properly packed. The DCM was discarded and the concentrated sample was introduced into the glass column and eluted with 60 mL of DCM. The eluent was collected and concentrated using the rotary evaporator to about 2 to 3 mL. The

concentrated sample (1 µL) was then injected into the Perkin Elmer Autosystem XL Gas Chromatograph HP 5890 Series II, equipped with an electron capture detector (ECD) for analysis.

2.3. Quality assurance/control

Analytical quality control included the strict adherence to documented procedures, laboratory standard operating procedures and calibration of analytical instrument. The GC-ECD was calibrated using high quality analytical standards from the U.S. Environmental Protection Agency (US EPA). Standards were run to check for the column performance, peak height, resolution, and detection limit (LOD). The LOD were defined as 3 times the signal-to-noise ratio (S/N). Results from recovery studies for the chlorobiphenyls indicated recovery efficiency between 94% and 106%.

3. Results and discussion

The physicochemical properties and concentrations of PCBs determined in surface water samples collected from the Lagos lagoon are reported in Tables 1 and 2, respectively. The physicochemical parameters measured across the five sampling locations did not show large variations as presented in Table 1. The salinity values ranged between 20.1 and 23.6 PSU, while pH, conductivity, temperature and dissolved oxygen values ranged between 7.96 and 8.18, 32.6-37.3 µS, 30.1-30.6^{o}C, and 4.22-5.57%, respectively. A negative Pearson product-moment correlation, r (-5.71) was observed between the total concentrations of PCBs and dissolved oxygen (DO). This implies that higher concentrations of PCBs in seawater may likely contribute to the depletion of the amount of dissolved oxygen available for the biota in seawater environment. This trend may threaten the existence of sea creatures and plants. On the other hand, the salinity and conductivity values had a strong positive linear relationship (r = 0.99) as already established in literature. UWF recorded the lowest values of physicochemical parameters except for temperature (31^{o}C) and dissolved oxygen (5.13).

Table 1: Physicochemical properties of sampled seawater.

Properties	EBE	IJR	LGL	OKB	UWF
Salinity (PSU)	23.4	23.3	23.6	22.2	20.1
pH	8.05	8.10	8.18	8.02	7.96
Conductivity (µS)	36.7	36.7	37.3	35.0	32.6
Temperature (^{o}C)	30.2	30.1	30.1	30.6	31.0
Dissolved Oxygen (%)	4.22	5.57	4.32	4.45	5.13

Table 2: Mean concentrations of PCB congeners in the seawater samples (mg/L).

PCB Congener	IUPAC name	EBE	IJR	LGL	OKB	UWF
PCB-8	2,4′-DiCB	2.69	1.16	ND	ND	ND
PCB-60	2,3,4,4′-TetraCB	ND	ND	ND	5.64	ND
PCB-81	3,4,4′,5-TetraCB	ND	1.26	4.46	ND	ND
PCB-105	2,3,3′,4,4′-PentaCB	5.34	1.35	ND	3.73	2.15
PCB-114	2,3,4,4′,5-PentaCB	9.98	1.38	ND	1.68	ND
PCB-126	3,3′,4,4′,5-PentaCB	ND	1.71	8.70	ND	ND
PCB-128	2,2′,3,3′,4,4′-HexaCB	ND	2.35	4.38	8.44	ND
PCB-138	2,2′,3,4,4′,5′-HexaCB	ND	2.52	3.19	9.48	ND
PCB-153	2,2′,4,4′,5,5′-HexaCB	ND	6.88	3.89	ND	ND
PCB-156	2,3,3′,4,4′,5-HexaCB	ND	7.58	3.17	3.13	ND
PCB-170	2,2′,3,3′,4,4′,5-HeptaCB	2.77	8.71	ND	ND	ND
PCB-180	2,2′,3,4,4′,5,5′-	25.46	ND	ND	ND	ND

	HeptaCB					
	2,2′,3,4,5,5′,6-					
PCB-185	HeptaCB	56.25	ND	ND	ND	ND
	2,3,3′,4,4′,5,5′-					
PCB-189	HeptaCB	ND	ND	ND	ND	ND
	2,2′,3,3′,4,4′,5,6-					
PCB-195	OctaCB	5.40	ND	ND	21.05	ND
∑PCBs		107.89	34.90	27.78	53.15	2.15

The total concentrations of PCBs ranged between 2.15 and 107.89 mg/L. Table 2 indicates that total concentration of chlorobiphenyls in the lagoon system followed the sequence Ebute Ero > Oko Baba > Ijora > Lagos Island > UniLagos lagoon front with levels 107.89, 53.15, 34.90, 27.78, and 2.15 mg/L, respectively. The UWF site had the lowest concentration due to the presence of PCB-105 as the only detected congener. This low concentration may be due to minimal pollution of the site being a relaxation spot for the University of Lagos community. No visible economic or industrial activities occur around the lagoon. The high average concentration of PCBs at the EBE site is due to the predominance of PCB-180 (25.46 mg/L) and PCB-185 (56.25 mg/L). However, the enhanced levels of these heptachlorobiphenyls at this may be attributed to the fact that the coastline of EBE is characterised by a beehive of heavy anthropogenic activities such as municipal waste burning, indiscriminate disposal of solid and liquid waste, industrial discharge, human faeces, and runoff from nearby markets into the sea water. In addition, the location also recorded the concentration of two pentachlorobiphenyls PCB-105 (5.34 mg/L) and PCB-114 (9.98 mg/L), which may suggest contributions from industrial and domestic sources. PCB-105 was the most prominent congener as it was detected in four of the sampled sites except LGL, followed by PCB-114, PCB-128, PCB-138 and PCB-156, which were detected in three sampled locations.

4. Conclusion

The concentration of PCBs in the Lagos lagoon was assessed by collecting samples from 5 different locations along the seawater course. PCBs were detected in all samples. The physicochemical properties of the seawater across the sampled locations were similar. A negative correlation was observed between the concentration of PCBs and the amount of Dissolved oxygen which indicates that PCB accumulation depletes DO levels in the sea water. Unilag water front recorded low level of PCBs while Ebute Ero sample had the highest concentrations of PCBs. It is recommended that human activities contributing to PCB accumulation in the seawater should be seriously controlled by environmental regulatory agency along the coastline, while a continuous monitoring program is instituted and conducted periodically to ensure that the low profile concentrations of PCBs in the lagoon system are kept within threshold levels.

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