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Polychlorinated Biphenyl Contamination in Water and Sediment Samples in Upper River Ogun, Lagos State, Nigeria

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A B S T R A C T

Polychlorinated biphenyls (PCBs) are a health risk for high trophic level predators and the Stockholm Convention requires measures to reduce or eliminate their release into the environment. The study was conducted an ecological survey on River Ogun, Lagos, Nigeria, quarterly over a period of two years (March 2013-February 2015). Water physicochemistry and the levels of nine PCB congeners were analyzed in water and sediment samples from five river zones: Agboyi, Maidan, Owode Elede, Kara, and Akute. Water physicochemistry showed significant ($p<0.05$) increases in conductivity, turbidity, temperature, salinity, total dissolved solids, and dissolved oxygen in the dry season compared to rainy season across the zones, while there was an increase in pH, transparency and depth in the rainy season across the zones. Mean temperature in the range of 28.53 -28.95°C, the mean pH ranged between 5.58-7.74, mean total dissolved solid ranged between 0.67 -1.69 g/L, mean conductivity ranged between 0.77 mS/cm -0.94 mS/cm, mean salinity ranged between 0.05 -0.42%, mean turbidity ranged between 29.30-30.50NTU, mean Secchi-disc transparency ranged between 2.88-3.16m, mean depth ranged between 3.21-3.65m while meaning dissolved oxygen ranged between 14.54- 22.65mg/L.PCB congeners were analyzed in sediment and water samples. The analyzed categories were the IUPAC numbers: non-*ortho* PCBs (CBs 8, 18 and 58), mono-*ortho* PCBs (CBs 87, 128,170 and 195) and dl-PCBs (CBs 206 and 209). The mean concentrations of PCBs in the sediment samples for all zones ranged from 0.000078-0.01µg/kg, while the mean concentrations of PCBs in the water samples for all the sampled zones ranged from 0.00006-0.006mg/L. The total PCBs concentrations in all water samples in this study for the rainy and dry seasons were 0.0296 mg/L and 0.0299 mgL^{-1}, respectively. The hazard quotient (HQ) values for the rainy season ranged from 0.0039 - 0.014 and between 0.0047 - 0.013571 for the dry season. The cancer risk for the rainy season ranged from 3.90×10^{-6} - 9.82×10^{-6}, while that of the dry season ranged from 1.57×10^{-7} - 3.17×10^{-7}. There was no significant difference between the congeners when the samples were subjected to descriptive (mean and standard error) and analysis of variance statistics and P<0.05 was considered to indicate statistical significance. Means were separated using Bonferroni's multiple comparison tests, p<0.05). PCB concentrations in all the zones were above US EPA limits in surface waters (0.0005 mg/L), which is a cause for environmental concern for River Ogun.

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INTRODUCTION

There is increasing concern over the fate of chemicals both natural and synthetic, which find their way into the environment. Urbanization and industrialization have brought these chemicals closer to a greater proportion of animal and human populations and this raises important conservation questions with regards to the possibility of species extinction and sustainable fish farming. These chemicals find their way into nearby freshwater and estuarine environments through industrial waste treatment facilities, agricultural runoff and uncontrolled industrial effluents such as veterinary services.[1,2,3,4]. Many industrial and agricultural wastes have contributed to the contaminated freshwater systems thereby causing adverse effects on aquatic biota and human health [5].

The Stockholm Convention defines Persistent Organic Pollutants (POPs), such as polychlorinated biphenyls; (PCBs) as being persistent, bioaccumulative and toxic. Polychlorinated biphenyls are listed under the Stockholm Convention which requires parties to take measures to eliminate or reduce the release of these contaminants in the environment. Beginning in 1929, PCBs were used as electrical transformer and capacitor fluids, flame retardants, hydraulic lubricants, sealants, and paints because of their heat resistance and insulating capacity. There are 209 congeners of PCBs with varying degrees of chlorination. PCBs are ubiquitous environmental contaminants, their physicochemical properties allow them to be transported over great

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distances through environmental processes, deposited, and incorporated into aquatic food webs.

Polychlorinated biphenyls are a group of nonflammable chemicals that have extremely high boiling points and primarily used in transformers capacitors paints and printing inks as well as other industrial applications [6, 7]. PCBs are amongst a group of industrial chemicals that have no known natural sources in the environment. They enter the aquatic environment through accidental spills, transportation leaks and from PCB containing transformers fires, river input, unregulated industrial and municipal wastewater discharge [8, 9, 10, 11].

Although the use of PCBs has been banned or restricted for many years; they are still found all over the world even where they have never been manufactured.Soils serve as an important reservoir for PCBs and play an important role in the global cycling and food chain transfer of PCBs [12,13, 14]. PCBs bioaccumulate up the food chain and can induce a variety of short and long-term toxic responses. They are therefore a concern for the health of high trophic level predators [15].Some authors have reported that soil particles are important reservoirs for PCBs [16,17,18,19]. Due to their slow biodegradability, and very high partition coefficient (insoluble in water) they settle into water and sediments resulting in an increased load of highly chlorinated PCBs for the deep-water habitat [20].

Polychlorinated biphenyls have a wide range of acute and chronic health effects in humans including cancer, neurological damage, reproductive disorders, immune suppression, birth defects and are also suspected endocrine disruptors [21]. The concentrations of PCBs found in the environment are generally in micrograms per liter (µg/L) or micrograms per kilogram (µg/kg) ranges and these might be considered to be below the necessary levels to result in acute toxicity or death [22]. These concentrations, however, are still at toxicologically relevant levels for sublethal effects to occur and alter important processes including growth, reproduction, behavior, and development. PCBs can be found in low concentrations in virtually every sphere of the environment. They are directly related to anthropogenic pollution. They can enter into the soil via waste emissions, oil leakage, volatilization, dry and wet deposition, etc. [23, 24, 25].Globally, the use of PCBs has been drastically curtailed and fortunately, they are not produced in Nigeria but contamination arises from the importation of electrical transformer oils containing PCBs from developed countries such as France, United Kingdom, and Japan. Between the 1970s and 1980s, these transformers were widely used in the energy-production sector, resulting in PCBs oil leakage into soil and ground waters [26]. PCBs have also been identified in water, sediments and fish in Niger Delta water, namely: Ethiope, Benin, and Warri Rivers [27]. Earlier studies by Osibanjo and Bamgbose [28] revealed the presence of PCBs in the Nigerian Environment. Risks associated with drinking PCBs contaminated surface and underground water supplies were highlighted [28]. The Objectives of this study are to determine the levels of PCBs contamination in water and sediment samples from River Ogun and to calculate a risk assessment in order to determine the degree of the pollution and its effects on the human health and the ecological system of Ogun River.

MATERIAL AND METHODS

Study site and sampling design

Ogun River is a perennial river in Nigeria, with characteristics typical of a tropical climate. It rises at $3^0 28''$E, $8^0 41''$N from its source in Oyo state near Shaki and ends at $3^0 25''$E, $6^0 35''$N where it enters the Lagos lagoon. The source is in the Igaran hills at an elevation of about 540m above the sea level and the river flows directly southward over a distance of 480km before it discharges. The major tributaries are Ofiki and Opeki rivers. The river is intersected by Ikere Gorge Dam in Iseyin local government area of Oyo State, with a reservoir capacity of 690 million m^3. The river serves as sources of drinking water, fishing, and other domestic uses; in densely populated areas the river is used directly for bathing, washing, and drinking. It also serves as a drain for organic waste from abattoirs along the river.

Sampling locations

The sampling locations were marked by GPS and recorded. We did the sampling in an open fiberglass boat with a 75hp Yahama outboard engine.

Sampling stations

Five sampling zones, with three stations in each zone, were selected based on their different environmental perturbations such as nearby pollution sources, urban settlements, domestic activities, abattoir effluent discharge, dredging etc. and suitability for comparative and future surveys, as a result of the effects of all the anthropogenic activities that are prevalent in these locations (Fig. 1).

Sampling periods

Sampling was carried out quarterly, at the peak of the dry and rainy seasons between March 2013 and February 2015. The coordinates of each sampling station were measured by GPS during the first sampling period to ensure the same locations were subsequently sampled. Water and sediment samples were collected during each sampling trip. *In situ* surface, water quality was assessed using hand-held probes (U-50 Series multi-parameter water quality meter, Horiba).The parameters were measured by dipping the Horiba into the water body and the parameters were taken when the readings remained stable.

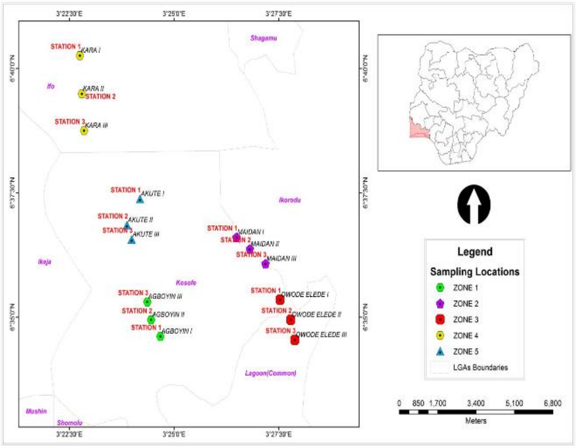

Figure 1. Map of River Ogun, the zones and sampling stations

Sediments samples:

Seven hundred gramme (700g) Sediment sample was collected from the river bottom using a Van Veen Grab Sampler. The sediments were immediately transferred into 13x16" zipper Storage Bags and transported to ecotoxicology laboratory at Department of Zoology, University of Lagos, after about two hours post-sampling period, where they were air-dried at room temperature, by laying them on the table, and covering up with foil papers in order to prevent them from other contaminants. The researchers utilized gloves while air-drying the sediment samples in order to for them to be protected against toxins or microbes. After drying, visible remains of organisms and debris were removed; then, the sediments were homogenized with a pestle and mortar to enable them to pass through a 200µm sieve to normalize for particle size. Mortars and pestles are constructed using hard materials—including ceramics, stones, basalt, and marble able to withstand repeated grinding.

Collection of water

Water samples were collected into 1-liter amber bottles within 0.5 meters of the surface, following the method of Nwankwo *et al*., [29]. The samples were carefully labeled with information about the date and time of collection, month and year, sampling location and quantity, and stored with ice packs in a cooler in which they were transported to the laboratory, where they were stored at 4^{o} C before analysis within 48 hours. The samples were chilled in order to retain its original status as same in the environment and prevent post-contamination.

Measurement of physico-chemical parameters

Physicochemical parameters of the water were determined *in situ* with the Horiba U50G multi-sampler; the parameters were: salinity, temperature, dissolved oxygen (DO), pH, turbidity, conductivity, depth, total dissolved solids (TDS) and total suspended solids (TSS).

Analysis of PCBs in surface water and sediment samples

PCBs extraction in water samples

Sample extraction was carried out two days after sampling using liquid-liquid extraction. 500mL of the water sample was transferred into a 1-liter borosilicate separatory funnel and 60mL of redistilled dichloromethane (DCM) was added. The funnel was shaken vigorously for two minutes with periodic venting to release vapor pressure from the funnel. The organic layer was left to separate for l0 minutes and was recovered into a 250mL flask. The aqueous layer was re-extracted twice with 60mL of the extracted solvent. The combined extract was dried by passing through a Buckner funnel containing anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas following the method of EPA [30].

PCBS extraction in sediment

Twenty (20) g of the pulverized sample was weighed into a 250 mL borosilicate beaker and mixed with 2g anhydrous Na_2SO_4 until a completely dry homogenate was obtained, following the procedures described by USEPA [31]. This was then transferred into a Whatman (TM) cellulose extraction Soxhlet thimble and extracted with 300 mL of n-hexane – and l00 mL of redistilled hexane: DCM in a 3:1 ratio was added. All reagents utilized were purchased from Sigma- Aldrich (United Kingdom). Extraction was carried out with dichloromethane in cold extraction mode and extracting solvent was evaporated on a rotary evaporator. The beaker and its contents were placed in a sonicator to extract the lipids for about 8 hours. The organic layer was filtered into a 250 mL borosilicate beaker. The extract was dried by passing the filtrate through the funnel containing anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas. Extractions were done according to methods of ASTM 03328 and ASTM 03415.

PCBs separation and clean up

The clean-up of extracts was done using a 60mm x 0.32mm x 0.25µm column chromatography in accordance with the US EPA method 3630B. A 20 mL glass column was packed with glass wool to about 5 mL and activated silica gel (60-200 mesh size) from about 5 to 15 mL. 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 was 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 before gas chromatographic analysis.

Identification and quantification of selected PCB congeners

PCBs (8, 18, 58, 87, 128, 170, 195, 206 and 209) was determined in both sediment and water samples. Analyses were performed with a gas chromatograph. PCBS analyses were conducted using Hewlett Packard Gas Chromatograph 6890 with flame ionization detector and HP Chem Station Rev. A 09.01 (1206) software. The injection temperature was 250°C while the detection temperature was 325°C.

Risk assessment

Risk assessment of Ogun River water was assessed using the hazard quotient (HQ) and cancer risk assessment. HQ was calculated according to USEPA guidelines using the following equations:

$$HQ = ADD/RfD \quad (1)$$

ADD is the intake exposure level ($mgkg^{-1}day^{-1}$), and the reference doses are consistent (2×10^{-5} $mgkg^{-1}day^{-1}$) and calculated by the USEPA for Aroclor 1254 [32].

$$ADD = C \times (IR \times EF \times ED)/(BW \times AT) \times 10^{-3} \; [mgkg^{-1}\, d^{-1}] \quad (2)$$

Note: Conversion factor = 10^{-3} x μgL^{-1} to mgL^{-1}

Where C represents the average concentration of PCBs during the monitoring period (microgram per liter). For this study, IR represented the daily water intake rates in relation to the age groups according to the Exposure Factors Sourcebook for the European Population which was as follows: 0.3 L day-1 for ages 0-6; 1 L day^{-1} for ages 7-17; and 2 L day^{-1} for adults [33]. The exposure frequency (EF) was 365 days/year. The exposure duration (ED) varied by age group. It was 6 years for ages 0–6, 11 years for ages 7–17 and 30 years for adults. The average body weight was 15 kg for ages 0–6, 46 kg for ages 7–17, and 70 kg for adults [34**].** Averaging time (AT) was ED × 365 days. AT_{0-6} was 2190, AT_{7-17} was 4015 and AT_{Adult} was 10950 days.

$$Cancer\ risk = C \times (DI \times ED \times EF \times CSF)/(BW \times AT) \quad (3)$$

The cancer risk assessment of PCB congeners via water consumption was calculated according to the risk guidelines of the USEPA (*Equation 3*), where C was the concentration of PCBs in the water sample (mg L^{-1}); DI is the daily input of 2 L day^{-1}; ED was 30 years; body weight was 60 kg; average life span was 70 years × 365 days =25500 days; EF was 365 days/ year; cancer slope factor (CSF) was 0.07 ($mgkg^{-1}day^{-1}$) for low risk and persistent PCBs according to the USEPA [35,36].

Data analysis statistical analyses

The data were analyzed with Graph Pad Prism software (version 7; Graph Pad Software, Demo), using descriptive (mean and standard error) and analysis of variance statistics and $P<0.05$ was considered to indicate statistical significance. Means were separated using Bonferroni's Multiple Comparison tests, $p<0.05$).

RESULTS AND DISCUSSION

The results of the physical parameters of the water sampling done quarterly during rainy and dry seasons are presented in table 1. Mean Temperature ranged between 28.53 -28.95°C, the mean highest values of 28.95°C recorded in zone 3 and 5 during dry season while mean highest value of 28.53°C, was recorded in zone 3 during the rainy season. The mean pH ranged between 5.58-7.74, the mean highest value of 7.74 was recorded in zone 2 during rainy season while the mean lowest value of 5.58 was recorded in zone 2 during the dry season. Mean total dissolved solid ranged between 0.67 -1.69 g/L, the mean highest value of 1.69g/L was obtained in zone 4 during dry season while mean highest value of 0.67g/L was recorded in zone 2 during the rainy season. Mean conductivity ranged between 0.77 -0.94 mS/cm, the mean highest value of 0.94 mS/cm was obtained in zone 3 during dry season while mean highest value of 0.77 mS/cm was recorded in zone 2 during the rainy season. Mean salinity ranged between 0.42 - 0.05%, the mean highest value of 0.42% was obtained in zone 3 during dry season while mean highest value of 0.05% was recorded in zone 2 during the rainy season. Mean turbidity ranged between 18.6-305, with a mean highest value of 29.30 obtained in zone 1 during dry season while mean highest value of 30.50 was recorded in zone 2 during the rainy season. Mean Secchi-disc transparency ranged between 2.88-3.16m, the mean highest value of 2.88 m was obtained in zone 1 during rainy season while the mean highest value of 3.16m was recorded in zone 1 during the dry season. Mean Depth ranged between 3.21-3.65m, with a mean highest value of 3.21m obtained in zone 3 during dry season while the mean highest value of 3.65m was recorded in zone 1 during the rainy season. Mean dissolved oxygen ranged between 14.54- 22.65mg/L, the mean highest value of 14.54 mg/L was obtained in zone 4 during dry season while mean highest value of 22.65mg/L was recorded in zone 2 during the rainy season. The results of PCB congeners in water and sediment samples done quarterly during rainy and dry seasons are presented in tables 2 and 3. PCB congeners were analyzed in water; the analyzed categories were the indicator (IUPAC numbers; non-*ortho* PCBs (CBs 8, 18 and 58), mono-*ortho* PCBs (CBs 87, 128,170 and 195) and dl-PCBs (CBs 206 and 209). The mean concentrations of PCBs in the water samples for all the

TABLE 1. Mean values of seasonal variation in physicochemical properties of surface water of Ogun River, Lagos, Nigeria.

		Sampling Points					
Properties	Season	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	WHO
Surface Water Temperature (°C)	Dry	28.21± 0.6	28.13 ± 0.8	28.95±1.2	28.46 ± 0.6	28.96 ± 1.0	<40
	Rainy	27.21 ± 0.9	27.54 ± 0.9	28.53 ±1.8	27.83 ± 1.7	28.45 ±1.7	
pH	Dry	6.89 ± 0.32	7.0± 0.2	7.2 ± 0.3	7.1± 0.2	.2 ± 0.16	6.5-8.5
	Rainy	7. 6 ±0.5	7.7± 0.2	7.5 ± 0.4	7.5 ± 0.3	7.7 ± 0.3	
Total Dissolved (mg/L)	Dry	0.29±0.14	0.34 ± 0.13	0.50 ± 0.17	1.7 ±1.5	0.3± 0.14	1000
	Rainy	0.44± 0.23	0.67 ± 0.36	0.46 ± 0.29	0.21 ± 0.15	0.19 ±0.13	
Conductivity (mS/cm)	Dry	0.50 ± 0.27	0.80± 0.64	00.94±0.49	0.18± 0.06	0.16±0.04	NS
	Rainy	0.58±0.3	0.77 ± 0.58	0.60±0.47	0.13 ± 0.04	0.16±0.04	
Salinity ((‰)	Dry	0.29±0.21	0.39± 0.31	0.43 ± 0.23	0.03 ±0.02	0.11± 0.05	NS
	Rainy	0.03±0.02	0.05±0.0	0.00 ± 0.00	0.03±0.03	0.03± 0.03	
Turbidity((NTU)	Dry	29.3 ±10.01	19.73±11.2	18.6 ±11.05	28.48±11.1	27.0± 11.16	10
	Rainy	19.88 ±7.85	30.5± 8.16	27.95 ±9.50	28.78±8.67	22.6 ± 7.54	
Transparency	Dry	3.16±0.21	2.98 ± 0.09	2.52 ± 0.16	2.83 ± 0.222	45 ± 0.12	
	Rainy	2.88± 0.42	2.21 ± 0.59	2.60 ± 0.44	2.40 ± 0.41	2.15 ± 0.30	
Depth (m)	Dry	2.53 ± 0.72	2.35 ± 0.73	3.2 ± 0.86	3.0 ± 0.86	3.02 ± 0.98	
	Rainy	3.70 ± 0.56	3.2 ±0.10	2.68 ± 0.19	2.80 ± 0.36	3.00 ± 0.43	
Dissolved Oxygen (Mg/L)	Dry	9.34 ± 4.99	13.24 ± 7.25	12.81 ±7.22	14.54 ±9.20	9.943 ±5.80	5.0
	Rainy	14.33± 4.58	22.66 ± 11.54	9.56 ± 2.98	14± 4.92	11.37±3.51	

Zone 1 =Agboyi, Zone 2= Maidan, Zone 3= Owode Elede; Zone 4= Kara**;** Zone 5 =Akute
Each value represents the mean of four determinations ± standard error.
WHO represents stipulated limits [37]

TABLE 2. Mean concentration of PCBs in water during the dry season

	Sampling Locations				
PCBs	1	2	3	4	5
PCB 8	0.0012 ± 0.0004	0.0027 ± 0.002	0.0001 ± 0.0000	0.0007 ± 0.0003	0.0006 ± 0.0001
PCB 18	0.0009 ± 0.0005	0.003 ± 0.0022	0.0008 ± 0.0002	0.0007 ± 0.0002	0.0007 ± 0.0004
PCB 58	0.0007 ± 0.0002	0.0005 ± 0.0002	0.0006 ± 0.0002	0.0006 ± 0.0002	0.0011 ± 0.000
PCB 87	0.0012 ± 0.0002	0.0022 ± 0.0017	0.0009 ± 0.0001	0.0009 ± 0.0001	0.0010 ± 0.0003
PCB 128	0.0002 ± 0.0000	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0000
PCB 170	0.0012 ± 0.0005	0.0007 ± 0.0003	0.0007 ± 0.0003	0.0013 ± 0.0004	0.0010 ± 0.0004
PCB 195	0.0003 ± 0.0001	0.0003 ± 0.0001	0.0002 ± 0.0001	0.0003 ± 0.0001	0.0003 ± 0.0001
PCB 206	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000	0.000 ± 0.0000
PCB 209	0.0001± 0.0000	0.0001 ± 0.0000	0.0002 ± 0.0000	0.0001 ± 0.0000	0.0001 ± 0.0000
Mean	0.0007 ±0.0002	0.0011±0.0007	0.0005±0.0001	0.0005± 0.0001	0.0006±0.0002

Zone 1 =Agboyi, Zone 2= Maidan, Zone 3= Owode Elede, Zone 4= Kara**;** Zone 5 =Akute. Each value represents the mean of three determinations ± standard error.

TABLE 3. Mean Concentration of PCBs In Water During The Rainy Season

	Sampling Locations				
PCBs	1	2	3	4	5
PCB 8	0.0021 ± 0.0009	0.0027 ± 0.0009	0.0020 ± 0.0009	0.0025 ± 0.0006	0.0017 ± 0.0007
PCB 18	0.0030 ± 0.0008	0.0028 ± 0.0009	0.0024 ± 0.0008	0.0012 ±0.0002	0.0019± 0.000
PCB 58	0.0009 ± 0.0003	0.0011 ± 0.0002	0.0022 ± 0.0013	0.0007 ±0.0001	0.0012± 0.0002
PCB 87	0.0013 ± 0.0002	0.0017 ± 0.0004	0.0015 ± 0.0005	0.0017 ± 0.0007	0.0012± 0.0002
PCB 128	0.0002 ± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0000	0.0002 ± 0.0000	0.0017 ± 0.0005
PCB 170	0.0027 ± 0.0008	0.0026 ± 0.0009	0.0019 ± 0.0010	0.0017 ± 0.000	0.0022 ± 0.0010
PCB 195	0.0003 ± 0.0001	0.0004± 4.525E -07	0.0003 ± 0.0001	0.0003 ± 0.0001	0.0006 ± 0.0003
PCB 206	0.0002± 0.0001	0.0004 ± 0.0000	0.0003 ± 0.000	0.0004 ± 0.000	0.0004 ± 0.0002
PCB 209	0.0001± 0.0000	0.0003 ± 0.0002	0.0001 ± 0.0000	0.0001 ± 0.000	0.0022 ± 0.0010
Total PCBs	***0.0059***	***0.0098***	***0.0039***	***0.0049***	
Mean	0.0007 ± 0.0003	0.0011 ± 0.0007	0.0004 ± 0.0001	0 .0005 ± 0.0001	0.0006 ± 0.0003

Zone 1 =Agboyi, Zone 2= Maidan, Zone 3= Owode Elede, Zone 4= Kara**;** Zone 5 =Akute
Each value represents the mean of three determinations ± standard error.

TABLE 4. Individual Average Daily Dose (mgkg^{-1}day $^{-1}$) Hazard Quotients of Investigated PCBs Across Age Groups

Water sampling site	Total PCBs(μgL^{-1})		ADD/HQ_{0-6}		ADD/HQ_{0-17}		ADD/HQ_{Adult}		Cancer Risk	
	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season
1	0.0059	0.0058	0.000000118/0.0059	0.000000116/0.0058	1.28E-07/0.0064	1.261E-07/0.0063	1.69E-07/0.0084	1.66E-07/0.0083	5.91157E-06	1.93712E-07
2	0.0098	0.0095	0.000000196/0.0098	0.00000019/0.0095	2.13E-07/0.0107	2.07E-07/0.0103	0.00000028/0.014	2.71E-07/0.0136	9.81922E-06	3.17288E-07
3	0.0039	0.0047	0.000000078/0.0039	0.000000094/0.0047	8.48E-08/0.0042	1.02E-07/0.0051	1.11E-07/0.0056	1.34E-07/0.0067	3.90765E-06	1.56974E-07
4	0.0049	0.0048	0.000000098/0.0049	0.000000096/0.0048	1.07E-07/0.0053	1.04E-07/0.0052	0.00000014/0.007	1.37E-07/0.0069	4.90961E-06	1.60314E-07
5	0.0051	0.0051	0.000000102/0.0051	0.000000102/0.0051	1.11E-07/0.0055	1.11E-07/0.0055	1.46E-07/0.0073	1.46E-07/0.0073	0.00000511	1.70333E-07
TOTAL	*0.0296*	*0.0299*								

Water Sampling Station 1 =Agboyi, Water Sampling Station 2= Maidan, Water Sampling Station 3= Owode Elede, Water Sampling Station 4= Kara**,** Water Sampling Station 5 =Akute sampled zones ranged from 0.00006-0.006mg/L while the mean concentrations of PCBs in the sediment samples for all the sampled zones ranged from 0.000078-0.01mg/kg.The individual average daily dose and hazard quotients of investigated PCBs across age groups is presented in table 4.

There was uniformity with water temperature readings which may be linked to the shallowness and regular complete mixing of the river water. The relatively small mean ranges in water temperature observed in the zones are in accordance with various works of. [38, 39]. The pH range shows that zone 5 is highly alkaline during dry and rainy seasons. Aquatic organisms are affected by pH because most of their metabolic activities are pH dependent [40]. Optimal pH range for sustainable aquatic life is pH 6.5 - 8.2. The pH variation in zone 5 was 5.58-7.74. The results showed that pH was above normal levels, pH levels in zone 5 are above the range of 6.9-9.6, recorded pH values by [41], and pH range of 6.2-8.5 reported by[42]as values most suitable for fish production for maximum productivity level. This suggests that zone 5 will be a good breeding site for fish production [42]. The mean total alkalinity of 5.58-7.74 agreed with the range values documented by Moore *et al*., [43] for natural waters which is indicative of hard water and buffering from carbonates or bicarbonate dissolved in the water. [43, 44].

The variation in mean total dissolved solids (TDS) of 0.67 g/L recorded for zone 2 during the rainy season, mean 1.69 g/L value obtained in zone 4 during dry season. The EPA Secondary Regulation advises a maximum contamination level (MCL) of 500 mg/L for TDS. When TDS exceeds 1000mg/L, it is generally considered unfit for human consumption. High TDS indicates hard water and it results in undesirable taste which could be salty, bitter or metallic. Some dissolved solids come from organic sources such as leaves, silts, plankton, industrial wastes and sewage and all these could add a variety of ions or salts to a river. The salts act to dehydrate the skin of animals, which affect many forms of aquatic life. This is in agreement with report of [45]. Adeosun et al., also reported a high TDS in lower Ogun River. The mean value of 0.77 -0.94 mS/cm (conductivity levels below 50 mS/cm are regarded as low [46]), conductivity recorded in zones 2 and 3 shows that the conductivity level is low. This is in agreement with report of Adeosun *et al.*,[38] at Akomoje in lower Ogun River, Ogun State, Nigeria. Conductivity of water depends upon the concentration of ions and its nutrient status and variation in dissolved solid content. Seasonal variation in the conductivity is mostly due to increased concentration of salt because of evaporation. Dilution of water during the rainy season causes a decrease in electrical conductance due to the addition of rainwater that might contain other organic compounds which do not break down into ions (dissolve into ionic components) when washed into the water [47]. Heavy rainfall can also decrease the conductivity of a body of water as it dilutes the current salinity concentration. Mean salinity level recorded was low in the two zones that had highest values during the dry and rainy seasons. This is in agreement with the report of Aguayo *et al*,. [1].Salinity was low and it is an indication that the river is a freshwater body. The mean Turbidity ranged between 18.60-30.50 NTU (nephelometric turbidity unit) recorded in zone 1 during dry season and zone 2 during the rainy season may associated with waste discharge activities occurring around the zones. Turbidity of water is actually the expression of optical property in which the light is scattered by the particles present in the water. Clay, slit, organic matter, phytoplankton and other microscopic organisms cause turbidity in lake water [48]. High turbidity shows presence of large amount of suspended solids and affects the life indirectly by cutting off light utilized by the plants for photosynthesis [49, 50]. Mean Secchi-disc transparency ranged between 2.88-3.16 m, the mean highest value of 3.16 m was obtained in zone 1 during dry season while mean highest value of 2.88m was recorded in zone 1 during the rainy season. The decrease in transparency from dry season to rainy season may be due to the increase in turbidity of the water as a result of run-off carried into the river. This agrees with Ssebugere et al., [50] who reported that the pattern of change of transparency varies inversely with that of turbidity and rainfall and that higher transparency leads to deeper light penetration. The higher dry season Secchi-disc transparency mean value compared to that of the rainy season could be due to absence of floodwater, surface run-offs and settling effect of suspended materials that followed the cessation of rainfall. Low Secchi-disc transparency recorded during rainy season in this study agrees with the findings of Adebisi, who observed that onset of rain decreased the Secchi-disc visibility in two mine lakes around Jos, Nigeria [51]. Lower transparency recorded during rainy season when there was turbulence and high turbidity, has a corresponding low primary productivity, because turbidity reduces the amount of light penetration, which in turn reduces photosynthesis and hence primary productivity [52,53]. Mean Depth ranged between 3.21-3.65m, with mean highest value of 3.21m obtained in zone 3 during dry season while mean highest value of 3.65m was recorded in zone 1 during the rainy season. This agrees with Adeosun *et al.*, who reported that Lower depth was recorded in the dry season and higher depth during the rainy season in lower Ogun River; who opines that depth of water followed a seasonal pattern with an impact of ambient temperature and rainfall. Dagaonkar *et al.*,[54] also reported the maximum depth of Kailasagar in rainy season and minimum in dry season, low water depth was noticed due to water evaporation.

Mean dissolved oxygen ranged between 14.54-22.65mg/L, the mean highest value of 14.54 mg/L was obtained in zone 4 during dry season while mean highest value of 22.65mg/L was recorded in zone 2 during the rainy season. This dissolved oxygen values of 14.54-22.65mg/L was similar to those reported for many other polluted Nigerian waters; including 6.9-8.8mg/L for Lagos Lagoon, 4.00-7.50mg/L for Luubera creek in Niger Delta Ogunwenmo CA, Kusemiju [55-56]. However, dissolved oxygen value which varied from 14.54- 22.65mg/L in the locations indicated a good aeration of water as a result of strong winds and sending of more oxygen into water [57].

In this study, PCB congeners were analyzed in sediment and water samples, the analyzed categories were the indicator (IUPAC numbers; non-*ortho* PCBs (CBs 8, 18 and 58), mono-*ortho* PCBs (CBs 87, 128,170 and 195) and dl-PCBs (CBs 206 and 209). However, there was no significant difference observed between the congeners analyzed while subjected to (Bonferroni's Multiple Comparison tests, $p < 0.05$). The concentrations of PCBs in all the zones sampled in River Ogun were above the guideline of USEPA PCBs limits in surface waters (0.0005 mg/L), through drinking water for some of the zones. Although low levels of PCBs were observed in the water and sediment samples, some stations, had values exceeding the USEPA PCBs limits in surface waters (0.0005 mg/L) and water quality criterion for chronic exposure (79 pgL) through drinking water which is a cause for environmental concern for Ogun River. The findings of this study are in agreement with the findings of Beyer and Biziuk, Lohmann et al., and Mai et al., who reported that PCBs can be found in low concentrations in virtually every sphere of the environment, which is directly related to anthropogenic pollution[58,59].A number of studies have reported PCB concentrations in sediments from water bodies in Nigeria. Ezemonye reported the PCBs levels of 1.50–1.5 μg l^{-1} (Ethiope River) and 0.03–2.93 μg l^{-1} (Benin River) surface water samples, and mean sediment concentration of PCBs ranging from 0.73–6.7 ng g^{-1} (Ethiope River) and 0.35–15.15 ng g^{-1} (Benin River). Hien et al., also reported lower concentrations of PCBs in mainstream water of Jiangsu section of the Yangtze River, China (<0.21–44.4 ng/L) [60].All these studies, however, support the findings in this current study. Anyasi and Atagana, Passatore *et al.*, stated that PCBs with lower chlorinated congeners tend to be more volatile and soluble in water, while adsorption to organic materials, sediments, and soils tends to increase with chlorination of PCB and organic content of the substrate [61, 62, 63]. Okeniya *et al.*, also reported higher PCBs levels ranging from 6721 mg/L for water samples from water bodies and Rivers in northern Nigeria [64,]. Aina *et al*., [65] also reported higher PCBs levels in sediment from lower Rivers Ogun.

Risk Assessment

The total PCBs concentrations in all water samples in this study for the rainy and dry seasons were 0**.**0296 mgL$^{\mathbf{-1}}$ and 0.0299 mgL$^{\mathbf{-1}}$, respectively (Table 4). The concentrations in rainy seasons were 148 fold higher times higher and 1fold higher in dry seasons than those obtained by Amdany et al., in an assessment of bioavailable fraction of POPS in surface water bodies in Johannesburg City, South Africa [66]. These values were within the USEPA set value of 500 ng L^{-1} for PCBs in drinking water. However, the values were much lower than those obtained by Olayinka *et al.,* in a study on the Assessment of the Pollution Status of Eleyele Lake, Ibadan, Oyo State, Nigeria [67]. Table 3 also shows individual average daily doses and hazard quotients of contaminated water with PCBs. The HQ values for the rainy season ranged from 0.0039 -0.014 and between 0.0047-0.013571 for the dry season. The HQ values were smaller than 1, which indicates a possibility of non-carcinogenic effects occurring. Cancer risk assessment of PCBs was calculated in the five sampling locations along Ogun River for the rainy and dry seasons. There were seasonal variations in the cancer risk calculated for all sampling locations. The cancer risk for the rainy season ranged from 3.90×10^{-6} - 9.82×10^{-6}, while that of the dry season ranged from 1.57×10^{-7} - 3.17×10^{-7}.Cancer risk in all the sampling sites for the rainy season was higher than the USEPA acceptable or tolerable risk level for regulatory purposes, which is within the range of 1×10^{-6} –1×10^{-4} [68,69**].** Meanwhile, cancer risks were within the limit at some sampling sites during the dry season, Generally, cancer risks were lower in the dry season compared to the rainy season. These results indicated that non–cancer hazards were greater than the cancer hazards. Consequently, these results imply that Ogun river water is unsafe for human consumption and poses a carcinogenic risk. The results indicate that Ogun River is impacted by anthropogenic activities which affect water quality as well as the entire aquatic life and the environment.

CONCLUSION

Environmental contamination with PCB is generally related to point sources (industrial discharges and sewage treatment plant effluents) or diffuse sources such as atmospheric transport and deposition.This study identifies PCB congeners with IUPAC numbers; non-*ortho* PCBs (CBs 8, 18 and 58), mono-*ortho* PCBs (CBs 87, 128,170 and 195) and dl-PCBs (CBs 206 and 209), in Sediment and Water samples at a level above the USEPA limit, which calls for environmental concerns. The low PCBs concentrations can be found in this study could be directly linked to anthropogenic activities around the river. Exposure to PCB by young children could due to crawling on bare dirt surfaces, eating soil, and more hand-to-mouth activities or as a result of swimming or bathing in the river which could, in turn, impact their health. It will, therefore, be recommended that proper monitoring of wastes and effluents discharges into the river be monitored more effectively.

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چکیده

یفینیل های پلی کربنات (PCBs) یک خطر بهداشتی برای شکارچیان سطح بالا هستند و کنوانسیون استکهلم نیاز به اقداماتی برای کاهش یا رها کردن انتشار آنها در محیط زیست دارد. این مطالعه یک بررسی بر اساس اکولوژیکی در رودخانه اوگان، لاگوس، نیجریه، به صورت سه ماهه طی یک دوره دو ساله (مارس ۲۰۱۳ تا فوریه ۲۰۱۵) انجام شد. فیزیکوشیمی آب و سطوح ۹ ترکیبات PCB در نمونه های آب و رسوب از پنج منطقه رودخانه ای Agboyi، Maidan، Owode، Elede، Kara و Akute مورد بررسی قرار گرفتند. فیزیکوشیمی آب در زمان رسیدن، بارندگی، درجه حرارت، شوری، جامدات جامد محلول و اکسیژن محلول در فصل خشک در مقایسه با فصل بارانی در سراسر مناطق افزایش معنی داری (p <0.05) در حالی که افزایش pH، شفافیت و عمق در فصل بارانی در سراسر مناطق. دمای متوسط در محدوده ۲۸,۵۳- ۲۸,۹۵ درجه سانتی گراد، میانگین pH بین ۷۴,۵-۷۴,۵,۵۷، متوسط مقدار جامد محلول در فاصله ۰,۶۷-۱,۶۹ گرم در لیتر، هدایت متوسط بین ۰,۷۷ mS / cm-94.9 mS / cm، میانگین شوری بین ۰,۲۵-۰,۴۲٪، کربن متوسط بین ۳۰,۳۰-۳۰,۳۰ NTU، متوسط شفافیت Secchi–دیسک بین ۱,۶-m۲,۳۶، عمق متوسط بین ۳,۲۱-m۳,۶۵ بود، در حالی که معنی اکسیژن محلول در بین ۱۴,۵۴-۲۲,۶۵mg / L.PCB در نمونه های رسوب و آب تجزیه و تحلیل شد. مقادیر تجزیه و تحلیل شده عبارت بودند از شماره های IUPAC: PCB های غیر اورث (CBs 8، 18 و ۵۸)، PCB های مونو اورتو (CB 87، 128،170 و ۱۹۵) و dl-PCB ها (CBs 206 و ۲۰۹). غلظت متوسط PCB در نمونه های رسوب برای تمام مناطق در محدوده ۰,۰۰۰۰۷۸-۰,۰۱ µg / kg بود، در حالی که میانگین غلظت PCB ها در نمونه های آب برای تمام مناطق نمونه برداری از ۰,۰۰۰۰۶-۰,۰۰۶ mg / L بود. غلظت کل PCB در تمام نمونه های آب در این مطالعه برای فصل های بارانی و خشک به ترتیب ۰,۰۲۹۶ میلی گرم / لیتر و ۰۲۹۹۲ میلی گرم در لیتر بود. مقادیر خطر (HQ) برای فصل بارانی از ۰,۰۰۳۹ تا ۰,۰۱۴ و بین ۰,۰۰۴۷ تا ۰,۰۱۳۵۷۱ برای فصل خشک بود. ریسک ابتلا به سرطان در فصل بارانی از ۱۰-۹۰ / ۳-۶-۹ / ۸ × ۱۰-۶ متغیر بود، درحالیکه فصل خشک از ۷ / ۱-۵۷ / ۷-۷ / ۱ -۷ / ۱۰-۷ متغیر بود. بین نمونه های همجنسگرایان اختلاف معنی داری وجود نداشت که نمونه ها به صورت توصیفی (میانگین و خطای استاندارد) و تجزیه و تحلیل آمار واریانس و P <0.05 به عنوان معنای آماری معنی داری در نظر گرفته شد. معیارها با استفاده از آزمون مقایسه چندین Bonferroni، p <0.05) جدا شدند. غلظت PCB در تمام مناطق بالاتر از مقادیر EPA ایالات متحده در سطوح آب (۰۰۰۵ mg / L) است که باعث نگرانی زیست محیطی رودخانه اوگان می شود.