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Research article

Organochlorine pesticides and polychlorinated biphenyls in city drains in Makurdi, central Nigeria: Seasonal variations, source apportionment and risk assessment

Sylvester M. Tongu [a,*], Rufus Sha'Ato [a], Geoffrey A. Wase [a], Jonathan O. Okonkwo [b], Rebecca N. Vesuwe [a,c,1]

[a] Department of Chemistry, Joseph Sarwuan Tarka University, Makurdi, PMB 2373, Makurdi, Benue State, Nigeria
[b] Department of Environmental, Water and Earth Sciences, Tshwane University of Technology, Pretoria, 0001, South Africa
[c] WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, United Kingdom

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ABSTRACT

A study of seasonal variation, sources and potential risks of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in open city drains in Makurdi, Central Nigeria was carried out. OCPs and PCBs were quantified using gas chromatograph-mass spectrometer. The total ($\sum_8$OCPs) concentrations (ngL^{-1}) of OCPs in water was 2.99 with a mean ± SD of 0.75 ± 0.12 during wet season, while during dry season, the values were 11.43 and 2.86 ± 1.54 respectively. In sediment, the total concentration (ngg^{-1}) of OCPs was 5270.66 with a mean ± SD of 1756.89 ± 450.01 during wet season and a total concentration of 5837.93 and the mean ± SD of 1945.98 ± 646.04, during dry season. Source apportionment of OCPs suggested historic application of the pollutants. The total ($\sum_7$PCBs) concentration (ngL^{-1}) of PCBs in water was 0.24 with a mean ± SD of 0.03 ± 0.02 during wet season and a total concentration of 0.61 with a mean ± SD of 0.09 ± 0.11 during dry season. The total concentration (ngg^{-1}) of PCBs in sediment was 37.88, mean ± SD of 5.41 ± 5.93 during wet season and a total of 47.07 and mean ± SD of 6.72 ± 7.27 during dry season. Ecological risk assessment based on effect range low (ERL) and effect range median (ERM) or threshold effect level (TEL) and probable effect level (PEL) that ecological risks were possible for some OCPs in this study, which calls for source control and remediation of the affected sites. Toxicity equivalency (TEQ) of PCB-118, the dioxin-like congener, indicated that it was most harmful to humans/mammals followed by birds, then fish.

1. Introduction

City drains are channels for conveying runoff or stormwater in cities or urban areas. Therefore, city drains serve as conveyor belts for city pollutants. Runoffs are known to be major vectors of pollutants disposed in cities; hence, they are among major contributors to deteriorating qualities of receiving water bodies [1]. Agriculture and residential use constitute the major sources of pesticides in urban stormwater runoff [2,3], the other source is leaching from municipal waste dump sites [4,5].

* Corresponding author.
E-mail addresses: tongusyl@gmail.com, tongu.sylvester@uam.edu.ng (S.M. Tongu).
Current address.

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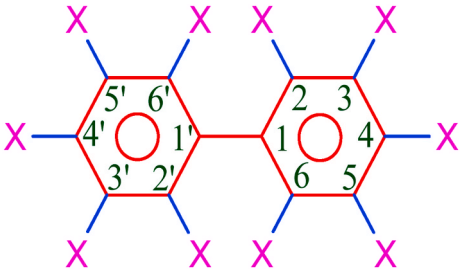

Fig. 1. Generic chemical structure of a PCB showing the ring numbering system with Xs representing chlorine Atoms [19].

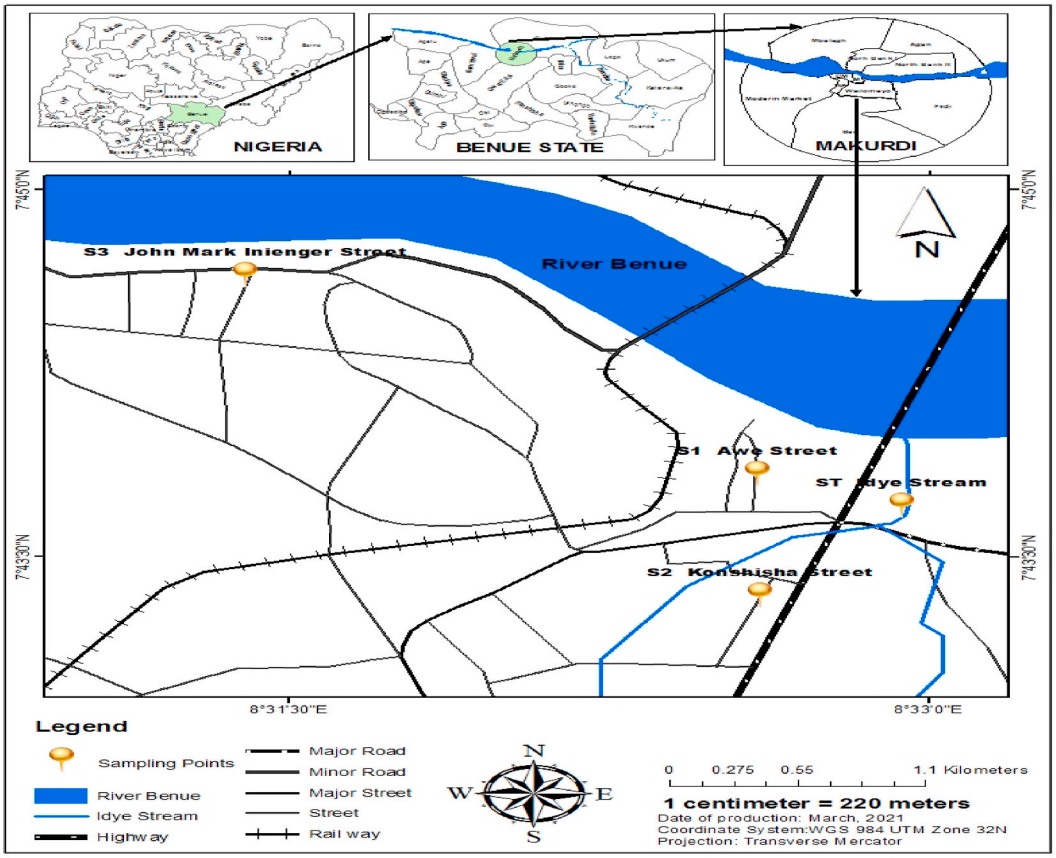

Fig. 2. Location map of Makurdi metropolis showing sampling sites.

Studies on the quality of city runoff started since mid 20th century [6]. The United States Nationwide Urban Runoff Program (USNWURP) was the most extensive of all the large scale programmes which directed its research on the quality of city runoff and later culminated into developing the National Stormwater data base [7]. The European Union Water Frame Work Directive (Directive 2000/60/EC) addressed the need to mitigate diffuse pollution and its amending priority pollutant directive (Directive 2013L39lEU) contributed in broadening the list of substances included in runoff quality studies [8,9]. This confirmed earlier findings concerning trace metals, total suspended solids and polycyclic aromatic hydrocarbons (PAHs) [10], and produced new data on emerging pollutants in runoff such as phthalates [11,12], Alkylphenol ethoxylates (APEs) and Alkylphenols (APs) [13,14], bisphenol-A (BPA), pesticides and polychlorinated biphenyls (PCBs) [10,15].

OCPs are among the most widely used organic compounds, which generated global concern due to their resistance to environmental decay [16]. They belong to the group of chlorinated hydrocarbon derivatives, which have vast applications in the chemical industry and in agriculture [17]. The production and usage of these pesticides were stopped or restricted between the 1970s and 1980s in developed countries; however, some OCPs, especially dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), are still used in some developing countries in agriculture due to their high efficiency, low cost, and broad spectrum pest killing efficacy [18].

PCBs are artificial organic compounds formed by a biphenyl with variable numbers of chlorine atoms alternating on two benzene rings. The compounds have 10 homologues and 209 congeners differentiated based on the number and position of the chlorine atoms (Fig. 1).

These contaminants are lipophilic chemicals that were commonly used in many products including electronics and electrical gadgets and hardware such as high voltage transformers, heat-transfer fluids, hydraulic fluids, plasticizers, inks and dyes, adhesives, wood preservatives, fluorescent light fixtures and pesticides, Refs. [20,21] with a global production estimated to be over 1.3 million tons. However, because of their toxicity and danger to human health, the use of PCBs was banned in the U.S. and in most industrialized countries since 1970s [16].

In Nigeria, the use of OCPs was banned in 2008 by the National Agency for Food and Drug Administration and Control [22,23]. Prior to the ban, Nigeria was reported to had marketed a total of 15, 000 metric tons of pesticides under 200 different local brands and formulations annually between 1983 and 1990 [5]. Like other developing countries, Nigeria is also a major market for old, reconditioned and second-hand electrical and electronic appliances, which eventually end up as e-waste in open city dumpsites [24]. The 2009 inventory on persistent organic pollutants (POPs) conducted by Nigeria's Federal Ministry of Environment (FME) reported large amounts of PCBs in the Nigerian environment [24]. Persistent Organic pollutants accumulate in fatty tissue and are toxic to aquatic organisms as well. Ecological risk assessment is a useful tool for analyzing and evaluating adverse ecological effects caused by environmental contaminants to benthic organisms because benthos form the basis for food chain [25].

Wide scope of research on OCPs and PCBs have been reported on the Nigerian environment [18,24,26–34], nevertheless, data is scarce on OCPs and PCBs in water and sediment from city drains in Nigeria. To the best of our knowledge, there is no reported research on OCPs and PCBs from open city drains in Makurdi, located in Nigeria's vibrant agricultural belt.

2. Materials and methods

2.1. The study area

Makurdi city is located on latitude 7° 44′ N and longitude 8° 32′ E [35] with a population of about 292,645 inhabitants [36]. The city is divided into two halves by River Benue (Fig. 2) which is the major source of water for agricultural, domestic, industrial and recreational uses throughout the city. It experiences two seasons; the wet season (April to October), and dry season (October to March), and it is both the headquarters of Makurdi Local Government Area and Benue State. Due to the poor waste disposal system in the city, wastes of various compositions are discarded into open drains and by the road side [37]. Moreover, many of the drains in the city empty their contents directly into River Benue, the second largest river in Nigeria [38].

Direct waste dump into drains is a common characteristic of all the studied sites. Site 1 is located along Awe street; clustered residences, hotel and metal scrap market are characteristics of this site. Site 2 located along Konshisha street is characterized by clustered residences, hospital, eateries and pharmaceutical shops. Site 3 is located along John Mark Inienger street; common activities around the site are: car wash, block laying, provisions shops and vegetable gardens. Meanwhile, site 4 is Idye Stream. Motor park, fuel filling station, provisions shops and agrochemical shops are found around it.

2.2. Sample collection

Water samples were collected bimonthly at four (4) sampling sites from open city drains in the study area (Fig. 2) for 12 months of six months each during dry and wet seasons except at site 2 where only four months were covered during dry season due to dryness of the sampling site. Sediment samples were also collected at the same sites and times but not at site 4 due to de-silting of drain at the site. In all, 22 water samples and 15 sediment samples were collected. Water samples were collected at about 5 cm below the surface into well-washed and pre-labelled 2.5 L Winchester brown bottles and an aliquot of 10 mL of concentrated sulphuric acid was added to the water samples as preservative.

Sediment samples were collected between 0 cm and 5 cm below the benthic, into pre-labelled wide-mouth 500 mL Winchester brown glass sampling bottles using a stainless steel sampler. Both water and sediment samples were taken to the laboratory and kept in the refrigerator at about 4 °C until removed for extraction and analysis.

2.3. Sample extraction

Water and sediment samples were extracted by solid phase extraction (SPE) and Soxhlet method respectively, followed by SPE clean-up according to Refs. [39,40] with some modifications.

The SPE column was packed with 0.5 g C18-reversed phase Silica gel on top of glass wool and conditioned using 6 mL each of the eluting solvent and distilled water. 1000 mL water sample, already spiked with 100 ng 2,4,5,6-tetrachloro-m-xylene and kept overnight to equilibrate, was passed through it under gentle suction at the rate of 10 mL min^{-1}. The suction continued for 15 min after passage of water to dry the column and the compounds were eluted with 20 mL of 3:7 DCM/hexane mixture.

Before Soxhlet extraction, sediment was air dried at ambient temperature for 5–6 days in a wash glass, ground with pestle and mortar, sieved through a 500 μm pore mesh. 10 g of the sample was thoroughly mixed with 20 g anhydrous sodium sulphate, spiked with 100 ng 4,4′-dichlorobiphenyl and kept overnight to equilibrate. It was then extracted for OCPs with 200 mL DCM/hexane mixture (1:2) in 500 mL round bottom flask at 55 °C for 24 h. The extraction for PCBs was with 200 mL acetone/hexane (1:2) at the same temperature for 16 h. The extracts were cleaned by SPE as already described for water samples. The eluates were passed through 0.2 g

Table 1
Concentrations of OCPs (ngL^{-1}) in water during wet and dry seasons.

OCP	Wet Season			Dry Season		
	Total	Range	Mean ± SD	Total	Range	Mean ± SD
P,P′-DDE	0.04	0.00–0.02	0.001 ± 0.01	0.05	0.01–0.02	0.01 ± 0.00
P,P′-DDT	0.07	0.01–0.02	0.02 ± 0.00	0.10	0.00–0.05	0.02 ± 0.02
P,P′-DDD	0.07	0.01–0.02	0.02 ± 0.00	0.20	0.01–0.0	0.02 ± 0.02
$\sum_3$DDTs	0.17	0.03–0.06	0.04 ± 0.01	0.25	0.03–0.11	0.06 ± 0.03
α-Endosulfan	1.22	0.12–0.41	0.31 ± 0.13	4.07	0.21–2.12	0.02 ± 0.87
Endosulfan S.	0.05	0.01–0.01	0.01 ± 0.00	1.14	0.01–0.80	0.28 ± 0.37
$\sum_2$Endosulfan	1.27	0.13–0.42	0.32 ± 0.13	5.21	0.22–2.44	1.30 ± 0.91
Heptachlor	0.06	0.01–0.03	0.01 ± 0.01	0.08	0.00–0.06	0.02 ± 0.02
Dieldrin	0.12	0.01–0.06	0.03 ± 0.02	1.83	0.03–1.41	0.46 ± 0.65
Lindane	1.38	0.19–0.47	0.35 ± 0.13	4.05	0.46–1.81	1.01 ± 0.61
$\sum_8$OCPs	2.99	0.65–0.92	0.75 ± 0.12	11.43	0.92–4.59	2.86 ± 1.5

$\sum_8$OCPs = P,P′-DDE + P,P′-DDD + P,P′-DDT + α-Endosulfan + Endosulfan sulphate + Heptachlor + Dieldrin + Endrine. $\sum_3$DDTs = P,P′-DDE + P,P′-DDT + P,P′-DDD. $\sum_2$Endosulfan = α-Endosulfan + Endosulfan sulphate.

anhydrous sodium sulphate packed in a column, collected and reduced to incipient dryness under gentle stream of nitrogen.

Before GC-MS analysis, the eluates were reconstituted in 500 μL hexane, 10 μL solution (10 μg/mL) of pentachloronitrobenzene (PCNB) internal standard was added and vortexed on a Lasec mixer (BV 100). The content was then transferred into 1.5 mL GC vial for analysis.

2.4. GC–MS analysis

The sample eluates were analyzed for OCPs and PCBs using Shimadzu GC model 2010 plus coupled with Shimadzu MS model QP2010 mounted with auto sampler (AOC-20i) and operated in electron ionization mode. A DB5 30 m × 0.25 mm ID × 0.1 μm column was used for separation. The initial oven temperature of 90 °C was increased at the rate of 10 °C/min to 290 °C with a 10 min hold time, and injection temperature was 280 °C. Splitless injection mode, linear velocity of 44.4 cm/s and 87.8 kPa pressure were used. Helium (purity 99.999%) was used as a carrier gas at a constant flow of 1.5 mL min^{-1}. The mode of operation was selected ion monitoring (SIM). The analytes were quantified by external standard method. External calibration of the GC–MS was done using ten level calibration points, and compound tables were obtained for the analytes. Identification of each congener was made by monitoring its mass spectra at the elution retention time produced by the sample extracts in relation to the mass to charge ratio, retention time, and the reference ion obtained from the standard solution.

2.5. Quality assurance

Quality assurance measures adopted include collection of triplicate samples at each site and homogenizing them, duplicate analysis of the samples, transporting samples in ice box, gentle and incipient drying of extracts, and monitoring chromatographic conditions to check variations during analysis. Surrogate standards were used for accuracy during extraction. External calibration of the GC–MS was done using ten level calibration points with adequate linearity ($R^2 = 0.99$). The limits of detection (LOD) of the method, obtained through curve parameters, ranged from 0.02 to 0.25 ng μL^{-1} for water samples and 0.07–0.33 ng g^{-1} for sediment samples. The instrumental quality control (QC) was performed by injecting solvent blanks and standard solutions. None of the analytes was detected in the solvent blanks. The spiked recoveries ranged from 75% to 101% for OPCs and from 77% to 98% for PCBs.

2.6. Source apportionment

DDT biodegrades into DDE under aerobic conditions via dehydrochlorination and oxidation processes, and into DDD via reductive dechlorination under anaerobic conditions [41]. To ascertain whether the levels of DDT reported in this study were due to current or past applications, the ratio of p,p′-DDE and p,p′-DDD metabolites to p,p′-DDT, (DDD + DDE)/DDT), was applied. A ratio of >0.5 suggested historic use while a ratio of <0.5 suggested current use. On the other hand, the ratio of *p,p′*-DDD/*p,p′*-DDE > 1, shows that the main degradation product is *p,p′*-DDD under anaerobic condition; while the ratio of *p,p′*-DDD/*p,p′*-DDE < 1, shows that the main degradation product is *p,p′*-DDE under aerobic condition [42].

2.7. Ecological risk assessment

Sediment quality guidelines (SQGs) for aquatic environments were used to evaluate the risk implication by OCPs and PCBs contaminants in sediment from the open city drains. Two sets of SQGs known as: (i) effect range low (ERL) and effect range median (ERM), and ii) the threshold effect level (TEL) and probable effect level (PEL), were used. ERLs and TELs refer to chemical concentrations below which the probability of toxicity and other effects would rarely occur. ERMs and PELs denote mid-range above which adverse effects would frequently occur [43,44]. Toxicity equivalency factor (TEF) approach established by WHO [45,46] was adopted to

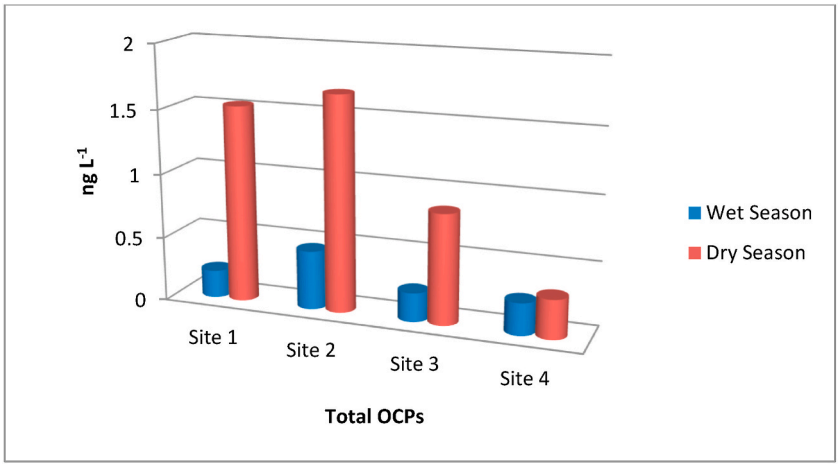

Fig. 3. Variations of total OCPs in water per site across seasons.

Table 2
Concentrations of OCPs (ngg^{-1}) in sediment during wet and dry seasons.

OCP	Wet Season			Dry Season		
	Total	Range	Mean ± SD	Total	Range	Mean ± SD
P,P′-DDE	10.04	2.03–4.33	3.35 ± 1.18	10.47	3.01–4.12	3.50 ± 0.61
P,P′-DDT	5.58	1.45–2.38	1.86 ± 0.45	8.19	1.57–3.97	2.73 ± 1.20
P,P′-DDD	5.74	1.47–2.28	1.91 ± 0.41	8.82	1.44–3.74	2.94 ± 1.7
$\sum_3$*DDTs*	21.370	6.70–7.41	7.12 ± 0.37	27.48	7.19–11.72	9.16 ± 2.32
α-Endosulfan	268.53	58.52–110.82	89.51 ± 27.46	509.82	58.47–297.55	169.94 ± 120.36
Endosulfan S	8.12	1.45–3.51	2.71 ± 1.10	17.44	0.57–11.18	5.81 ± 5.7.25
$\sum_2$Endosulfan	276.65	60.-114.33	92.22 ± 28.56	527.26	59.04–308.73	175.75 ± 125.64
Heptachlor	1.47	0.39–0.68	0.49 ± 0.16	26.53	0.38–24.80	8.84 ± 13.83
Dieldrin	60.80	15.02–30.18	20.27 ± 8.59	67.82	8.76–31.63	22.61 ± 12.17
Lindane	4910.37	1245.08–2173.03	1636.79 ± 480.56	5188.84	1283.44–2433.86	1729.61 ± 617.11
$\sum_8$OCPs	5270.66	1382.09–2255.98	1756.89 ± 450.01	5837.93	1358.82–2638.06	1945.90 ± 654.19

estimate toxicity equivalency (TEQ) for PCB-118 for the risk assessment of humans/mammals, fish and birds since it was the only dioxin like PCB in the study.

$TEQ = \Sigma TEF_i \times C_i$,

where, C_i = concentration of dioxin like PCB (PCB-118) in water and sediment. TEF = values of PCB-118 for humans/mammals, fish and birds [46].

3. Results and discussion

3.1. Seasonal variation and source apportionment of OCPs in water and sediment

Concentrations (ngL^{-1}) of OCPs in water were in the range of 0.92–4.59 with mean ± SD of 0.75 ± 0.12 and total ($\sum_8$OCPs) of 2.99 during wet season, while $\sum_8$OCPs during dry season ranged from 0.92 to 4.59, with mean ± SD of 2.86 ± 1.54, and total of 11.43 (Table 1). In comparison with similar studies, Ref. [47] reported concentrations of total OCPs from the surface water of Wuhan, central China during dry season within the range of this study. Other studies reported higher total OCP values in water: [26,28,48,49]. The levels of OCPs in water was in the order: lindane > $\sum_2$endosulfan > dieldrin > $\sum_3$DDTs > heptachlor during wet season, and $\sum_2$edosulfan > lindane > dieldrin > $\sum_3$DDTs > heptachlor during dry season (Table 1). Total $\sum_8$OCPs in water in the open city drains per site was in the order of: site2 > site4 > site3 > site1 during wet season, and site2 > site1 > site3 > site4 during dry season (Fig. 3).

Concentrations of $\sum_8$OCPs in sediment (ngg^{-1}) were in the range of 1382.09–2255.98 with mean ± SD of 1756.89 ± 450.01 and total of 5270.66 during wet season. Meanwhile, the range, mean ± SD and total concentrations of $\sum_8$OCPs during dry season were: 1358.82 to 2638.06, 1945.96 ± 646.04 and 5837.93 respectively (Table 2).

Lower values of total OCPs in sediment from the Swartkops and Sundays river estuaries, Eastern Cape Province, South Africa than in this study have been reported [50]. Mean concentration of $\sum_8$OCPs in sediment in the open city drains from Makurdi were higher than water across the two seasons (Tables 1 and 2), which might be due to higher affinity of OCPs to bind into solid particles such as sediment than water, which conforms with reported studies [51,52]. Distribution of total OCPs in sediment occurred in the order:

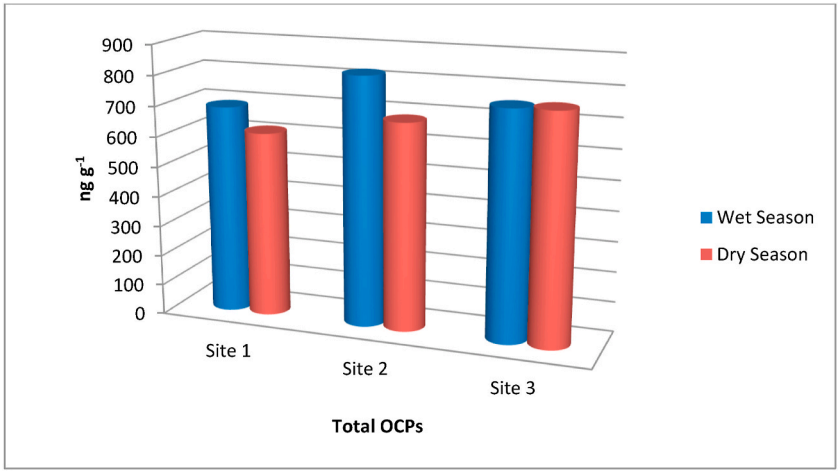

Fig. 4. Variations of total OCPs in sediment per site across seasons.

Table 3
Mean DDT and endosulfan isomer ratios in water and sediment.

Isomers	Water				Sediment		
	Site1	Site2	Site3	Site4	Site1	Site2	Site3
(P,P′-DDE + P,P′-DDD)/DDT	1.52	1.50	1.36	1.73	2.86	3.39	1.81
P,P′-DDD/P,P′-DDE	0.15	2.12	2.12	1.32	0.54	0.44	1.39
α-Endosulfan:Endosulfan S	63:1	7:1	1:1	28:1	23:1	42:1	30:1

Lindane > $\sum_2$edosulfan > dieldrin > $\sum_3$DDTs > heptachlor during wet season, and $\sum_2$edosulfan > lindane > dieldrin > $\sum_3$DDTs > heptachlor during dry season respectively (Table 2), while $\sum_8$OCPs varied in sediment per site as follows: site2 > site3 > site1 during wet season, and site3 > site2 > site1 during dry season (Fig. 4).

Variation in physico-chemical properties and emission sources of OCPs might account for the variation in concentrations of these pollutants in water and sediment in the studied sites during wet and dry seasons [47,50].

Lindane, the gamma isomer of hexachlorocyclohexane (HCH) [53] is a highly toxic and persistent organochlorine pesticide that has caused serious environmental problems since its production began in the early 1940s [54]. Levels of lindane recorded in water (ngL^{-1}) from this present study during wet season ranged from 0.19 to 0.47 with mean ± SD of 0.35 ± 0.13), while its dry season levels ranged from 0.46 to 1.81 with mean ± SD of 1.01 ± 0.61. Sediment concentrations of these pollutants during wet season ranged from 1245.08 to 2173.03, mean ± SD of 1636.79 ± 480.56, whereas the range of 1283.44–2433.86 with mean ± SD of 1729.61 ± 617.11 were recorded during dry season respectively (Tables 1 and 2). Concentrations of lindane in water from this study were lower than the reported in urban runoff from: Beijing, China [2], River Benue at Buruku and Katsina-Ala, Nigeria [26], Ogbesse River, Nigeria [55] and Tarkwa Bay, Lagos Lagoon, Nigeria [56]. Mean values of lindane in sediment from this study were higher than the values reported from Illushi, Ogbesse and Owan Rivers, Nigeria [57]; Tarkwa Bay, Lagos Lagoon, Nigeria [56]. Higher concentrations of lindane in water during wet season than dry season could be attributed to re suspension of the pollutant from sediment into surface water as a result of turbulence [16]. Higher levels of lindane recorded in sediment than water in the city drains might be due to its low solubility in water, and its high affinity to solid surfaces like sediment, [52].

Concentrations of total DDTs ($\sum_3$DDTs) in water (ngL^{-1}) during wet season ranged from 0.03 to 0.06, with mean ± SD of 0.04 ± 0.01), while its dry season concentrations ranged from 0.03 to 0.11, mean ± SD of 0.06 ± 0.03). Their concentrations (ngg^{-1}) in sediment during wet season ranged from 6.67 to 7.41, mean ± SD of 7.12 ± 0.37), whereas its dry season concentrations ranged from 7.19 to 11.72, mean ± SD of 9.16 ± 2.32 (Tables 1 and 2). The generally low levels of DDTs might be due to evaporation. DDTs have high Henry's law constants, hence their high tendency to evaporate [58]. DDTs were banned for agricultural uses worldwide by the Stockholm Convention except for the control of malaria vectors [59], while Nigeria prohibited the use of DDTs for both agricultural and health purposes [23]. Mean concentrations of $\sum_3$DDTs in water from this study were lower than those reported by Zhang et al. [2], but in conformity with levels in rivers reported in other studies [60,61]. Values of DDTs in sediment from the open drains were higher than other reported values [57,62].

The mean values of (DDD + DDE)/DDT ratio in open city drains from Makurdi (Table 3) were all >0.5 which suggested historic use of the chemical in the studied sites. This study, therefore, gave an indication of the compliance with the ban on DDTs in the study area. Based on the ratios of *p,p′*-DDD/*p,p′*-DDE, aerobic degradation of DDT to P, P′-DDE was dominant in sites 1 (water), 1 and 2 (sediment), whereas, anaerobic degradation to P, P′-DDD was dominant in sites 2–4 (water), and 3 (sediment). The α-endosulfan to endosulfan sulphate (α:sulphate) ratios established in this study decreased in the sequence: site 1 > site 4 > site 2 > site 3 (for water), then, site 2 >

Table 4
Concentrations of PCBs (ngL^{-1}) in water during wet and dry seasons.

PCBs	Wet Season			Dry Season		
	Total	Range	Mean ± SD	Total	Range	Mean ± SD
PCB-28	0.0103	0.0005–0.0021	0.0099 ± 0.0005	0.3207	0.0007–0.1881	0.0292 ± 0.0638
PCB-52	0.0038	0.0000–0.0020	0.0023 ± 0.0006	0.0793	0.0001–0.0475	0.0072 ± 0.0156
PCB-118	0.0666	0.0001–0.0401	0.0061 ± 0.0121	0.0781	0.0000–0.0615	0.0071 ± 0.0182
PCB-138	0.0339	0.0022–0.0037	0.0031 ± 0.0005	0.0279	0.0006–0.0035	0.0025 ± 0.0011
PCB-152	0.0531	0.0040–0.0051	0.0048 ± 0.0003	0.0472	0.0002–0.0053	0.0043 ± 0.0015
PCB-155	0.0557	0.0001–0.0057	0.0051 ± 0.0017	0.0429	0.0000–0.0057	0.0039 ± 0.0026
PCB-180	0.0176	0.0011–0.0047	0.0016 ± 0.0010	0.0113	0.0000–0.0023	0.0010 ± 0.0006
$\sum_7$PCBs	0.2410	0.0038–0.0666	0.0344 ± 0.0246	0.6075	0.0113–0.3207	0.0868 ± 0.1061

$\sum_7$PCBs = PCB-: 28 + 52 + 118 + 138 + 152 + 155 + 180.

Table 5
Concentrations of PCBs (ngg^{-1}) in sediment during wet and dry seasons.

PCBs	Wet Season			Dry Season		
	Total	Range	Mean ± SD	Total	Range	Mean ± SD
PCB-28	16.5533	0.4250–10.89	2.36 ± 3.82	21.19	0.15–5.13	2.65 ± 1.68
PCB-52	10.6315	0.38–3.71	1.52 ± 1.10	10.27	0.47–2.38	1.28 ± 0.64
PCB-118	2.4270	0.16–0.64	0.35 ± 0.19	7.56	0.20–1.59	0.94 ± 0.58
PCB-138	1.6590	0.02–0.54	0.24 ± 0.17	0.90	0.01–0.20	0.11 ± 0.07
PCB-152	2.1295	0.07–0.47	0.30 ± 0.15	2.41	0.04–0.46	0.30 ± 0.13
PCB-155	3.8733	0.54–0.58	0.55 ± 0.01	3.80	0.01–0.56	0.47 ± 0.19
PCB-180	0.5988	0.01–0.17	0.09 ± 0.06	0.95	0.07–0.36	0.11 ± 0.10
$\sum_7$PCBs	37.87	0.60–16.55	5.41 ± 5.93	47.07	0.90–21.19	6.72 ± 7.27

site 3 > site 1 (for sediment) respectively. The dominance of the α-endosulfan isomer established in this study suggested slow degradation of the isomer or recent application of the pollutant around the studied sites.

Mean concentration (ngL^{-1}) of total endosulfan ($\sum_2$Endosulfan) in water from the open city drains ranged from 0.13 to 0.42with mean ± SD of 0.32 ± 0.13 during wet season, while its dry season concentrations ranged from 0.22 to 2.44, mean ± SD of 1.30 ± 0.91 (Table 1). Mean concentrations of endosulfan in water from this study was within the similar range in literature [63]. Conversely, Sediment concentrations (ngg^{-1}) of $\sum_2$Endosulfan ranged from 60 to 114.33, mean ± SD of 92.22 ± 28.56 during wet season, and 59.04 to 308.73 range with 175.75 ± 125.64 mean ± SD during dry season (Table 2). Concentrations of α-endosulfan and endosulfan sulphate in water and sediment from this study were lower than the values reported from River: Densu Basin, Ghana [49], a farming community in Ghana [64] and Warri River, Nigeria [65], but higher than those reported from Florida [66]. The greater tendency of endosulfan to bind to sediment than water could account for its higher concentration in sediment than water across the two seasons in this study). Total concentrations of α-endosulfan were higher than that of endosulfan sulphate in water and sediment across the two seasons (Tables 1 and 2). This phenomenon indicates slower degradability of α-endosulfan over endosulfan sulphate [42,49].

The concentrations of heptachlor in water (ngL^{-1}) in the open city drains from Makurdi ranged from 0.01 to 0.03, mean ± SD of 0.01 ± 0.01 during wet season, the range from 0.00 to 0.06, mean ± SD of 0.02 ± 0.02 were observed during dry season (Table 1). Higher levels of heptachlor were reported in water from catchments of River Benue [26,48], fish Pond in Sogbo, Osun [67], Tarkwa Bay, Lagos Lagoon [56]. Heptachlor concentrations in sediment (ngg^{-1}) from this study ranged from 0.39 to 0.68 with mean ± SD of 0.49 ± 0.16 during wet season while the range and mean ± SD of 0.38–24.80 and 8.84 ± 13.83 were recorded during dry season. A study on sediment from Lake Manyas, Turkey reported concentrations of heptachlor in similar range to this study [68]. Higher values of heptachlor in sediment have also been reported [69,70]. Affinity of heptachlor to solid surfaces such as sediment might be responsible for the higher levels of the pollutant in sediment than water in this study [71]. Since heptachlor has been banned in Nigeria [23], its presence in the environment might be due to either historic or illegal current use.

Levels of dieldrin in water (ngL^{-1}) from this study ranged from 0.01 to 0.06, mean ± SD were 0.03 ± 0.02 during wet season, and the range of 0.03–1.41 with mean ± SD of 0.46 ± 0.65 were obtained during dry season (Table 1). These results were similar to those reported from Taihu lake region, China [72], but lower than values reported from similar studies in Nigeria [26,28,48,55,67,68,73]. Sediment levels of dieldrin (ngg^{-1}) during wet season ranged from 15.02 to 30.18, mean ± SD of 20.27 ± 8.59, while the range of 8.76–31.63, and mean ± SD of 22.61 ± 12.17 were equally obtained during dry season. The results from this study were similar to other reports [68,74]. Although, dieldrin is highly effective insecticides for soil-dwelling pests and for the protection of wooden structures against termites and wood borers [75], its use has either been severely restricted or banned in many countries since the early 1970s, and Nigeria in 2008 [23]. Therefore, the high levels of dieldrin in water and sediment from the studied sites might be due to its illegal current use and/or historic applications of the insecticides.

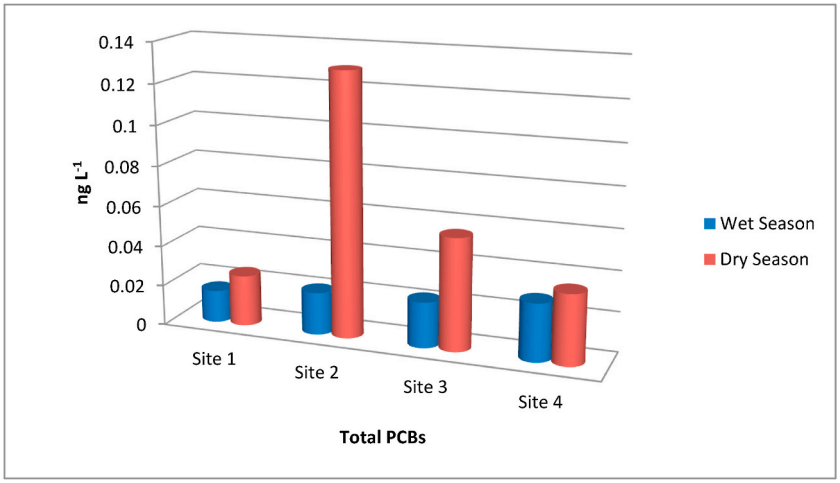

Fig. 5. Variations of total PCBs in water per site across seasons.

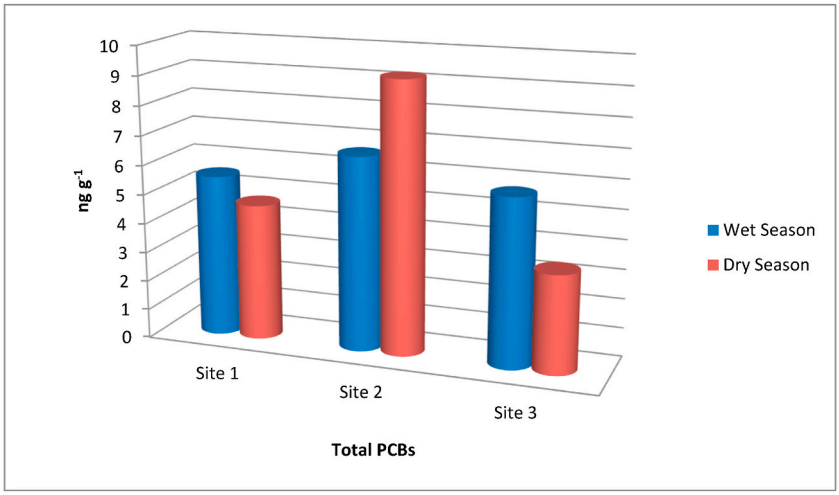

Fig. 6. Variations of total PCBs in sediment per site across seasons.

3.2. Seasonal variation and source apportionment of PCBs in water and sediment

Total PCBs ($\sum_7$PCBs) in water (ngL^{-1}) from the open city drains in Makurdi was 0.2410, ranging from 0.0038 to 0.0666 with mean ± SD of 0.0344 ± 0.0246 during wet season, whereas the total of 0.6075, range of 0.0113–0.3207, mean ± SD of 0.0868 ± 0.1061 were obtained during dry season (Table 4). The higher levels of PCBs during the dry season than the wet season might be due to dilution and concentration during the respective seasons or the rate of transportation of the pollutants from the drains during dry season. The result of this study is in conformity with the study of total PCBs in stormwater runoff in Washington DC [76] and in surface water from Ethiope and Benin rivers [77].

The total, range and mean ± SD of $\sum_7$PCBs in sediment (ngg^{-1}) from the open city drains were 37.87,0.60 to 16.55 and 5.41 ± 5.93, respectively during wet season, while the total of 47.07, range of0.90–21.19 with mean ± SD of 6.72 ± 7.27 were obtained during dry season (Table 5). In comparison with similar studies, PCBs values have been reported in the range of this study [61,76–79].

Sources of PCBs in the studied sites could be attributed to runoff from old transformers located around the sites, PCBs containing waste materials, cartridges from waste dump sites or direct waste dump into the drains.

Mean concentrations of $\sum_7$PCBs for water varied per site in the order: site4 > site3 > site2 > site1 during wet season and site2 > site3 > site4 > site1 during dry season (Fig. 5).

In sediment the concentrations varied in the order of site2 > site3 > site1 during wet season and site2 > site1 > site3 during dry season respectively (Fig. 6).

Variation in concentrations of PCBs in water and sediment between sites could be due to differences in physicochemical properties of the media, activities around the sites and nature of discharges in the drains at the various sites. PCBs showed higher levels in

Table 6
Comparison of concentrations of OCPs and PCBs in water with regulatory standards.

Analyte	Site1		Site2		Site3		Site4		Regulatory Agent			
ng/L	Total	Mean ± SD	Total	Mean ± SD	Total	Mean ± SD	Total	Mean ± SD	WHO, 2011 [81] (ngL^{-1})	USEPA, 2004 [82] (ngL^{-1})	Australia [49] (ngL^{-1})	SON, 2007 [83] (ngL^{-1})
P,P′-DDE	0.02	0.0033 ± 0.0036	0.0321	0.0080 ± 0.0032	0.02	0.0033 ± 0.0039	0.0182	0.0030 ± 0.0030	2000	–	60	–
P,P′-DDT	0.03	0.0054 ± 0.0022	0.0669	0.0167 ± 0.0168	0.04	0.0075 ± 0.0038	0.0245	0.0041 ± 0.0005	2000	1	60	1000
α-Endosulfan	1.42	0.2371 ± 0.4250	2.4383	0.6096 ± 0.8026	0.82	0.2337 ± 0.0896	0.6173	0.1029 ± 0.0979	–	5.6	50	–
Endosulfan S	0.02	0.0065 ± 0.0016	0.3331	0.0833 ± 0.1144	0.81	0.1352 ± 0.2354	0.0219	0.0037 ± 0.0022	–	–	50	–
∑Endosulfan	1.45	0.2436 ± 0.4261	2.7714	0.6929 ± 0.1135	1.63	0.3689 ± 0.2356	0.6392	0.1059 ± 0.0021	–	–	–	1000
Heptachlor	0.02	0.0037 ± 0.0005	0.0107	0.0027 ± 0.0018	0.09	0.0145 ± 0.0139	0.0223	0.0037 ± 0.0003	30	3.8	50	1000
Dieldrin	1.44	0.2394 ± 0.5656	0.3879	0.0970 ± 0.1399	0.08	0.0139 ± 0.0221	0.034	0.0057 ± 0.0043	30	56	10	1000
Lindane	2.25	0.3754 ± 0.6614	0.9279	0.2320 ± 0.1480	1.35	0.2243 ± 0.2466	0.9036	0.1506 ± 0.1207	2000	950	50	–
∑PCBs	0.12	0.0206 ± 0.0104	0.2985	0.0746 ± 0.1153	0.23	0.0392 ± 0.3670	0.1912	0.0319 ± 0.0267	–	14	–	–

Table 7
Comparison of OCPs and PCBs in sediment with sediment quality guidelines.

	SQGs (ng/g)					Frequency (%)					
Analyte	ERL	ERM	TEL	PEL	Range	<ERL	ERL - ERM	>ERM	<TEL	TEL - PEL	>PEL
P,P′-DDE	2	15	2.07	374	0.24–3.10	73	27	0	73	27	0
P,P′-DDD	2	20	1.22	7.81	0.47–1.96	100	0	0	73	27	0
P,P′-DDT	1	7	1.19	4.77	0.44–1.77	73	27	0	80	20	0
$\sum_3$DDT	3	300	NG	NG	1.25–6.00	53	47	0	–	–	–
Dieldrin	0.02	8	0.71	4.3	2.67–16.72	0	60	40	0	13	87
Lindane	NG	NG	0.32	0.99	221.40–1378.90	–	–	–	0	0	100
$\sum_7$PCBs	50	400	21.5	189	1.34–13.74	100	0	0	100	0	0

NG = no guideline.

sediment than water during the wet and dry seasons (Tables 4 and 5). PCBs have higher affinity to solid surfaces and low solubility in water [76] which explains their higher concentrations in sediment than water from this study. Mean concentrations of PCB-28 (less chlorinated PCB congener) in water and sediment across the two seasons were consistently highest, while that of PCB-180 (highly chlorinated congener) were least (Tables 4 and 5). As semi-volatile persistent pollutants, the solubility and volatility of PCBs tend to decrease as the number of chlorine atoms increase. Light chlorinated congeners easily volatilize in air and accumulate in the aquatic environment by atmospheric deposition, whereas highly chlorinated congeners are poorly diffused. Reductive dechlorination of higher PCB congeners under anoxic conditions might be another reason for higher levels of lower PCB congeners in the water and sediment from this study. These findings were consistent with other reports [78,80]. Leakages of PCBs from PCB-containing materials such as capacitors and old transformers at various locations in the Makurdi city might enter the open drains through runoff during rains, constituting another important source of PCBs in the studied sites. Large quantities of e-wastes (locally called Tokumbo Electronics) found in the Makurdi city might contain PCBs and these e-wastes likely end-up as wastes that were either dumped directly into the open drains or in open waste dumpsites.

3.3. Risk assessment

Data obtained from water and sediment were compared with water quality standards and sediment quality guidelines (SQGs) set by various regulatory agents in order to evaluate human and ecological risks. Values of OCPs and PCBs were compared with the water quality standards set by the WHO, USEPA, Australia and SON (Table 6). Total and mean concentrations of OCPs and $\sum_7$PCBs were below the regulatory limits of WHO, USEPA, Australia and SON water quality standards.

From Table 7, 100% samples gave $\sum_7$PCBs concentrations below ERL and TEL, while 100% of lindane samples had their concentrations above PEL. Dieldrin gave 40% and 87% of sample concentration above ERM and PEL. Concentrations of $\sum_3$DDT samples were 53% below ERL, and 47% within ERL-ERM. 73% of P,P′-DDE samples gave concentrations below ERL and TEL while 27% of its samples gave their concentrations within ERL-ERM, and TEL-PEL respectively. Concentrations of 73% and 80% of P,P′-DDT samples were less than ERL and TEL, while 27% of the samples had their concentrations within ERL-ERM, then 20% within TEL-ERL respectively. 100% of P,P′-DDD samples gave concentration less than ERL, 73% samples less than TEL, and 27% within TEL-PEL. Based on this analysis, it could be concluded that some of the OCPs analyzed could pose potential ecological risk.

Toxicity equivalency (TEQ) was calculated for PCB-118, because of its dioxin-like properties. PCB-118 was the only dioxin like congener that was analyzed in this study. TEQ concentrations for PCB-118 in water ranged from 6.90×10^{-8} to 3.20×10^{-6} ngL^{-1}, mean of 1.25×10^{-6} ngL^{-1} for humans/mammals, 5.95×10^{-8} to 5.27×10^{-7} ngL^{-1} with mean of 1.81×10^{-7} ngL^{-1} for fish, while the range of 2.30×10^{-8} to 1.05×10^{-6} ngL^{-1} with mean of 3.61×10^{-7} ngL^{-1} were obtained for birds respectively. Similarly, TEQ concentration for sediment ranged from 7.90×10^{-5} to 1.10×10^{-4} ngg^{-1} with mean of 8.97×10^{-5} ngg^{-1} for humans/mammals, 1.87×10^{-5} to 1.33×10^{-5} ngg^{-1} with mean of 1.51×10^{-5} ngg^{-1} for fish, and 2.64×10^{-5} to 3.74×10^{-5} ngg^{-1} with mean of 3.01×10^{-5} ngg^{-1} for birds (Table 8). It could deduced from the data in Table 8 that PCB-118 in water and sediment in the open city drains was most harmful to humans/mammals followed by birds, then fish. Another study has reported dioxin like effect to be most harmful to birds followed by humans and mammals [84].

4. Conclusion

This study was carried out on seasonal variation, source apportionment and risk assessment of OCPs and PCBs in water and sediment in open city drains in Makurdi, Nigeria. The mean values of (DDD + DDE)/DDT ratio in the city drains were all >0.5 which suggested historic use as source of the chemical in the studied sites. This indicated compliance with the ban on DDTs in the study area. Aerobic degradation due to P, P′-DDE and anaerobic degradation with respect to P, P′-DDD were established in water and sediment at various sites. The results also established varying concentrations of OCPs and PCBs in water and sediment during wet and dry seasons. Concentrations of the pollutants in water from all the sites were below the limits set by WHO, USEPA, Australia and SON respectively, which indicated safety. The concentrations of $\sum_7$PCBs were less than sediment quality guidelines (SGQs) at all the sites. However, some sediment samples gave concentrations of OCPs above SQGs, TEQ results of PCB-118 indicated various levels of harm to humans/mammals, fish and birds. It was also concluded that some of the OCPs analyzed could pose potential ecological risk. Further research

Table 8
Toxicity equivalency for PCB-118 in water and sediment.

Species	Water (ngL^{-1})					Sediment (ngg^{-1})					
	Site1	Site2	Site3	Site4	Range	Mean	Site1	Site2	Site3	Range	Mean
	TEQ	TEQ	TEQ	TEQ			TEQ	TEQ	TEQ		
Humans/ Mammals	6.90×10^{-8}	3.60×10^{-7}	7.50×10^{-7}	3.20×10^{-6}	6.90×10^{-8}- 3.20×10^{-6}	1.25×10^{-6}	7.90×10^{-5}	8.00×10^{-5}	1.10×10^{-4}	7.90×10^{-5}-1.10×10^{-4}	8.97×10^{-5}
Fish	1.15×10^{-8}	5.95×10^{-8}	1.26×10^{-7}	5.27×10^{-7}	5.95×10^{-8} - 5.27×10^{-7}	1.81×10^{-7}	1.32×10^{-5}	1.33×10^{-5}	1.87×10^{-5}	1.87×10^{-5} - 1.33×10^{-5}	1.51×10^{-5}
Birds	2.30×10^{-8}	1.19×10^{-7}	2.51×10^{-7}	1.05×10^{-6}	2.30×10^{-8} - 1.05×10^{-6}	3.61×10^{-7}	2.64×10^{-5}	2.66×10^{-5}	3.74×10^{-5}	2.64×10^{-5} - 3.74×10^{-5}	3.01×10^{-5}

on more dioxin like PCBs and on the pollutants in general is therefore recommended for better mapping of the study area with respect to the pollutants. Although, there is near absence of harm from OCPs in sediment from our study, there is a need for control and remediation measures at the sites where dieldrin and lindane levels are above the acceptable limits and to guide against a build up the studied pollutants in the environment.

Author contribution statement

Sylvester M. Tongu: Conceived and designed the experiments; Performed the experiments.
Rufus Sha'Ato: Conceived and designed the experiments.
Geoffrey A. Wase: Analyzed and interpreted the data; Wrote the paper
Jonathan O. Okonkwo: Contributed reagents, materials, analysis tools or data.
Rebecca N. Vesuwe: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interest's statement

The authors declare no competing interests.

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