ISSN: 2642-9020

Research Article

Journal of Marine Science Research and Oceanography

Environmental Dominance and Potential Impacts of Endocrine Disruptors On the Surficial Sediments of Calabar River, South Eastern Nigeria

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Submitted: 28 Aug 2020; **Accepted:** 03 Sept 2020; **Published:** 14 Sept 2020

Abstract

Endocrine disrupting chemicals (EDCs) are persistent toxic organic and inorganic chemicals that enter the aquatic environment through point and non-point sources and alter the physico chemical nature of water and the physiology of aquatic organisms. Of significance are the organochlorine pesticides (OCPs) and the polychlorinated biphenyl (PCBs) contamination of aquatic ecosystems. The study was conducted to provide baseline data and information on the extent of surface sediments contamination by the EDCs in the Calabar river, Nigeria. Surficial sediments from five in equidistant locations were sampled using the Van Veen sediment sampler in the dry and wet seasons of 2014 and 2015. The TOC in the surface sediments for the dry and wet seasons were 33.84 ±0.21 and 54.44±0.14 % respectively. The EDCs were highest during the wet season than the dry season suggesting the desorption and re-mobilization of organochlorines from contaminated soils into the riverine system. The ∑OCP residues ranged from 12.93±0.06µg/kg dry wt in the dry season to 23.50±0.01µg/kg dry wt in the wet season. The ∑PCB concentrations, 4.02± 0.2µg/kg dry wt (dry season) and 7.26± 0.11µg/kg dry wt (wet season) were however lower than the OCPs during the study period. Most of the EDC values were above the permissible limits and maximum contaminant levels of USEPA, indicating that the Calabar river sediments are potentially contaminated as a result of anthropogenic activities entering the system. The implications of the observed seasonal trend with respect to contamination of sea foods and posing of ecological risks to humans are discussed. This study forms part of the ongoing environmental assessment of the pollution status of Nigeria's marine and coastal ecosystems.

Keywords: OCPs, PCBs, Surface Sediment Contamination, Potential Health Risks, Calabar River, Nigeria

Introduction

There is a growing concern on environmental safety worldwide in recent times than in the past few decades due to the generation of large volumes of uncontrollable effluent streams from point and non-point sources by industrial and municipal outfits. The discharged effluents most often consist of contaminants that are highly toxic even at low concentrations. Studies of fluxes and pathways of toxic environmental substances such as endocrine disrupting chemicals principally organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), involving organism- water exchange, sediment-water interaction and organisms-sediment flows have become contemporary global issues due to their impacts on human health as well as the aquatic and terrestrial ecosystems. Emanating from their suitability and efficacy in combating insect pests and quest for increased food production by the agricultural sector especially in the developing economies like Nigeria, the application of OCPs is almost irresistible despite regulatory restrictions. These toxic substances being highly persistent in the environment, posed serious threat to life because of their chronic, acute, lethal and sublethal and sometimes mutagenic nature, and are also carcinogenic on exposure to animals and humans. Their non-degradability, have been detected in a wide range of environmental matrices, such as water, soil, suspended particles, and organisms as well as the coastal and deep ocean [1-3, 5-8]. Inspire of the numerous researches done worldwide, information regarding OCPs and PCBs emissions, bioaccumulation and bio-concentrations especially in the coastal areas of Nigeria is extremely limited. This study is aimed at providing scientific data and information on the abundance of OCPs and PCBs and the extent of spread in the surface sediments of Calabar river, Nigeria. It will also establish any seasonal trend and associated climate change influence on the contaminants distribution.

Methodology Study Area

The area of study is Nigeria, with Calabar located in the South East region. Calabar River lies geographically between Lat. 04^0 54$^{'}$ 15N and Long. 08^0 16$^{'}$ 08E; and Lat. 04^0 56$^{'}$ 40N and Long 08^{0}16'14E (Fig.1). The area is influenced by the tropical equatorial climate of dry season (November – March) and wet season (April – October) each year.

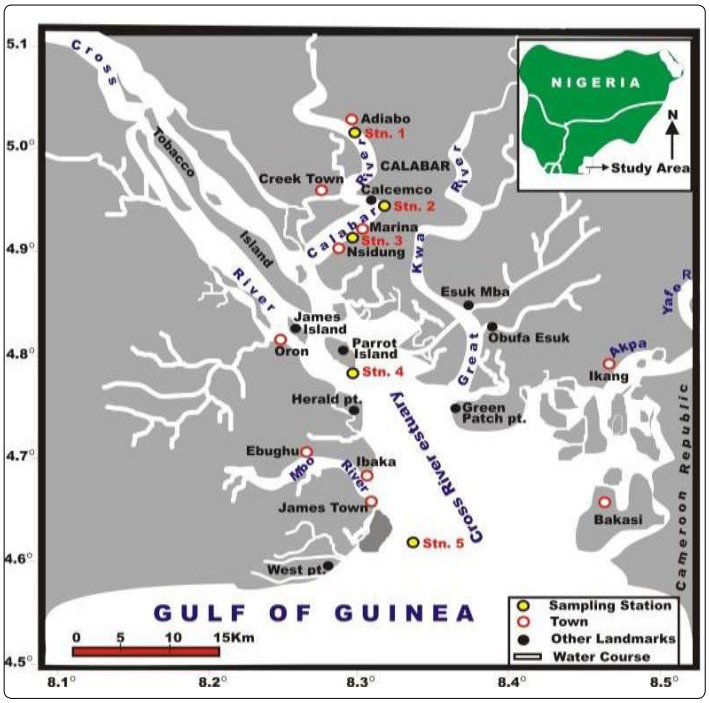

Figure 2: Map of the study location showing the sampling stations

The river is semi-diurnal with average depth of 6m at navigational channels and a current speed of < 1.0m/s especially at ebb tide [9]. Five sampling locations stretching from area of low human activity to the estuarine mouth viz Stn 1: Adiabo 25km upstream, Stn. 2: Nigerian Ports Authority Jetty 15km downstream, Stn.3: Unicem Jetty 10km downstream, Stn. 4 Parrot Island – middle Cross river estuary and Stn. 5: Cross river estuary (near the mouth), were monitored (Fig. 1).

Sediment Sampling and GC-FID, GC-ECD Analyses

Surface sediment samples (0-10cm) were obtained from each station between Jan – March (Dry season) and June – Sept (wet season) 2014 at low tide using the Van Veen Grab sampler. Samples were kept frozen in ice chase and taken to the laboratory. Sediments were oven-dried at 80ºC for 4-6 hours and extracted with hexane/acetone mixture, precleaned in a florosil column and the contaminants analysed using GC-FID and Helium gas as the carrier gas. The chromatographic procedure is as reported by Fatoki and Awofolu [1-3]. The concentrations of the PCB congeners were determined using a Perkin Elmer Auto Gas Chromatograph equipped with a splitless injector and Electron Capture Detector (GC- ECD). Chromatographic details are as reported by Froese *et al*. [10].

Results and Discussion

The TOC for each of the sampling stations for the dry and wet seasons were Stn. 1, 37.2 and 41.2 %; Stn. 2, 24.0 and 75.4 %; Stn. 3, 55.6 and 71.2 %; Stn. 4, 21.6 and 43.2 % and Stn. 5, 30.8 and 71.2 %; respectively. High TOC observed at the Jetties compared to the river channels, is attributed to increased human activity and close proximity to coastal farmlands located few kilometers away from the jetties upstream**.** The study revealed the presence of ten PCB congeners and 14 OCP derivatives viz α-HCH, β-HCH, γ-HCH, Aldrin, Endrin, p,p'-DDD, p,p'- DDT, γ-Chlordane, methoxychlor and others in the surface sediment samples. The high TOC inputs during the wet than the dry season contributed to observed trend of higher OCPs than PCBs. The most dominant OCPs were Aldrin (3.39 µg/kg dry wt) and Endrin (3.53 µg/kg dry wt) observed during the wet season. The most dominant PCBs were PCB 101 (1.45 µg/kg dry wt) and PCB 180(1.70 µg/kg dry wt). The increased rainfall from 2400 mm/yr in 2012 to 4011mm/yr in 2014, due to climate change, resulted in the flooding of coastal farmlands upstream which aided the desorption and re-mobilization of organochlorines from contaminated soils [11]. The ∑OCPs, 23.50 µg/kg dry wt were higher than ∑PCBs, 7.26 µg/kg dry wt an indication of more agricultural impact than industrial contamination.

Table 1: Levels of OCPs in sediment samples from Calabar river, Nigeria

OCPs	Dry Season (µg/kg dry wt)		Wet Season (µg/kg dry wt)	
	Mean ± SD	Range	Mean ± SD	Range
Heptachlor	1.15 (0.21)	0.83 – 1.76	2.03 (0.11)	1.87 – 2.34
Aldrin	2.16 (0.01)	1.53 – 2.44	3.39 (1.03)	1.75 – 4.21
∑BHC	0.16 (0.10)	0.01 – 0.40	1.20 (0.2)	1.03 – 3.02
Heptachlor Epoxide	0.06 (0.01)	0.01 – 0.21	2.10 (0.3)	1.56 – 2.89
α-Chlordane	0.12 (0.1)	0.02 – 0.62	0.45 (0.01)	0.15 – 0.81
γ-Chlordane	0.22 (0.03)	0.12 – 0.54	2.08 (0.04)	0.68 – 3.10
∑DDT	0.11 (0.02)	0.08 – 0.17	1.92 (0.14)	1.03 – 2.63
Endosulfan 1	3.01 (0.12)	1.76 – 3.85	0.09 (0.01)	0.05 – 1.74
Endosulfan 11	0.01	nd – 0.01	1.17 (0.20)	0.04 – 1.92
Endrin Aldehyde	0.01	nd – 0.01	2.11 (0.04)	1.32 – 2.88
Endrin Ketone	0.08 (0.02)	0.06 – 1.2	1.80 (0.21)	1.08 – 2.65
Methoxychlor	0.01	nd – 0.01	1.87 (0.03)	1.33 – 2.69
Dieldrin	3.23 (1.1)	1.62 – 4.41	1.56 (0.32)	1.0 – 2.30
Endrin	2.60 (0.22)	1.47 – 2.86	3.53 (1.05)	2.66 – 4.84

nd-not detected

Table 2: Levels of PCBs in sediment samples from Calabar river, Nigeria

PCBs	Dry Season (µg/kg dry wt)		Wet Season (µg/kg dry wt)	
	Mean ± SD	Range	Mean ± SD	Range
PCB 28	0.33 (0.01)	0.17 – 0.76	0.54 (0.01)	0.21 – 0.93
PCB 52	0.01	nd – 0.01	0.63 (0.20)	0.08 – 1.98
PCB 101	0.47 (0.03)	0.16 – 1.10	1.45 (0.01)	0.74 – 2.23
PCB 105	0.11 (0.002)	0.03 – 0.45	0.56 (0.11)	0.26 – 1.30
PCB 118	0.78 (0.02)	0.13 – 1.25	0.25 (0.01)	0.08 – 0.61
PCB 138	0.86 (0.04)	0.29 – 1.47	0.56 (0.10)	0.10 – 0.92
PCB 156	0.52 (0.13)	0.28 – 1.26	0.87 (0.02)	0.45 – 1.32
PCB 158	0.06 (0.01)	0.03 – 1.0	0.60 (0.10)	0.08 – 1.11
PCB 180	0.56 (0.10)	0.31 – 0.85	1.70 (0.12)	1.05 – 2.55
PCB 187	0.32 (0.01)	0.07 – 1.97	0.24 (0.02)	0.13 – 0.81

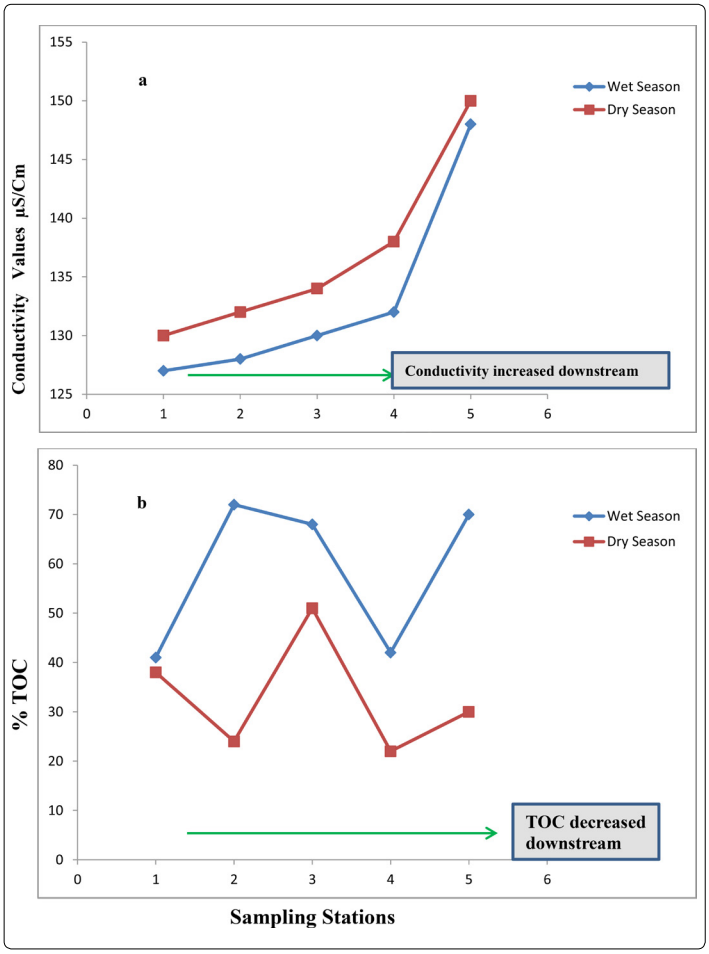

Figure 3a & b: Conductivity and TOC variations in wet and dry seasons in Calabar river, Nigeria

The amount of organic matter in an ecosystem is a reflection of the extent of ecosystem contamination and the proportion of organics deposited in the system. In this study, the TOC decreased downstream especially at locations very close to estuary. Estuarine sedimentation is modified to a great extent depending on the volume of river discharge and the texture of transported sediments from the upstream. The sedimentation rate may increase since the outflowing river velocity is impeded by sea incursion, coupled with flocculation and coagulation of the particles (predominantly mud and silt) by ionic species (Al, Cu, Fe etc.). Surface runoffs from coastal agricultural farms are major sources of inputs of organic and particulate materials since most farming activities involve incineration of deforested areas before cultivation commences. Artisanal farming thrives due to the practice that burning before planting increases nutrients in such areas. This is practically true since combustion products include white ash (CaO, K_2O, MgO etc.) which on reaction with water produces alkaline solutions that neutralizes the acidic tropical soils. The neutralization process releases micronutrient elements which were already bound in the acidic soils. In the absence of sanitary engineered landfill sites, domestic and municipal solid wastes are often disposed of at government approved dumpsites. Wastes incineration at the dumpsites destroy every combustible material including plastics and cellophanes which have been reported to be the most abundant component of commercial and house hold wastes in the municipality [12]. The sedimentary materials, nutrients and EDCs are transported into nearby coastal waters from the hinterland during flooding regimes.

Table 3: Seasonal Distribution of Total OCPs, Total PCBs and Hydrographic Factors of Calabar river, Nigeria

Environmental Components	Dry Season	Wet Season
%TOC	33.84 ±0.21	54.44±0.14
∑OCPs µg/kg dry wt	12.93±0.06	23.50±0.01
∑PCBs µg/kg dry wt	4.02± 0.2	7.26± 0.11
Water Temp °C	22.03± 0.2	21.34± 0.1
pH	6.23 ± 0.1	6.16 ± 0.4
Conductivity µS/cm	136.0 ± 0.01	133.8 ± 0.002

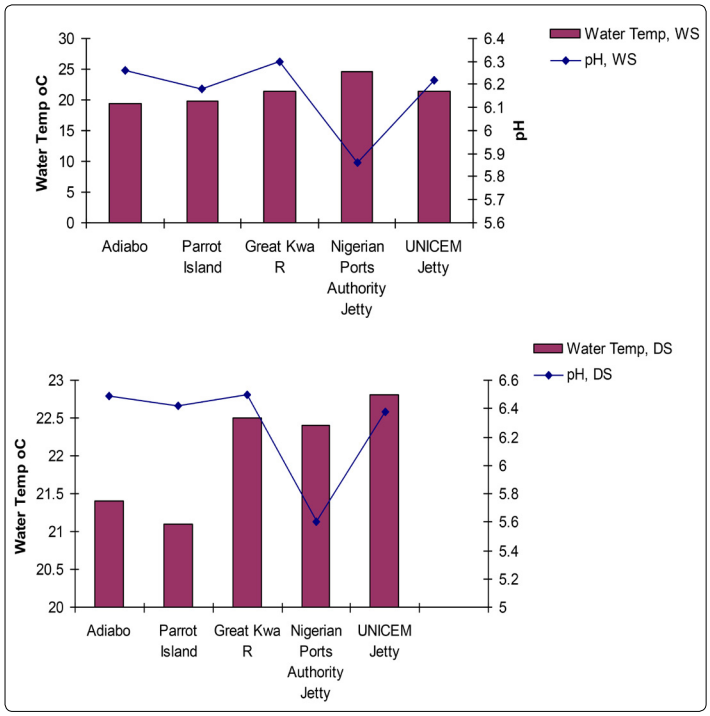

Figure 4: Spatial variation in water Quality factors during wet (WS) and dry seasons (DS) in Calabar river, Nigeria

There were minimal variations in water quality factors measured between the seasons and with respect to the stations (Fig. 4). The water temperature, conductivity and pH measurements during the period were pH 6.23 ±0.1, conductivity 136.0 ± 0.01µS/cm and water temperature 22.03± 0.2°C in the dry season; and pH 6.16 ±0.4, conductivity 133.8 ± 0.002µS/cm and water temperature 21.34± 0.1°C in the wet season (Table 3). The availability of good quality water is very essential for unhindered primary production in the aquatic ecosystem.

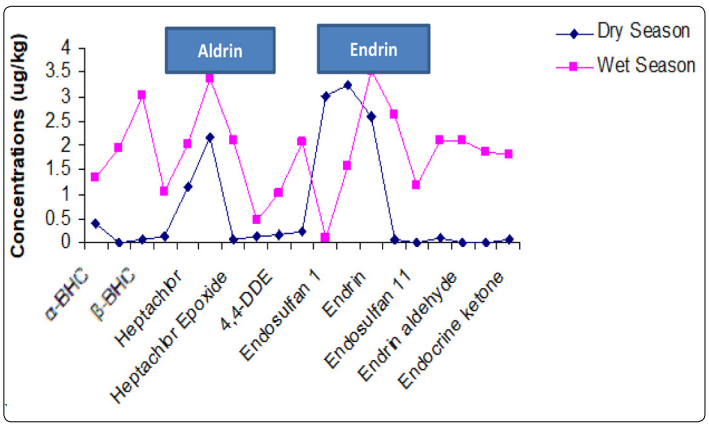

Figure 5: Distribution of OCP residues in dry and wet seasons in Calabar river, Nigeria

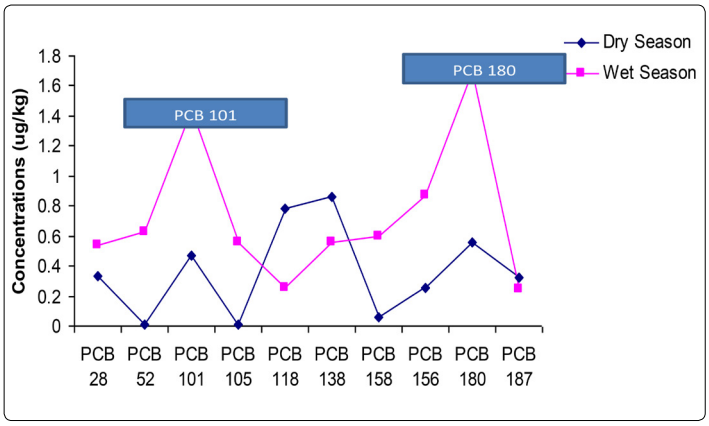

Figure 6: Distribution of OCP residues in dry and wet seasons in Calabar river, Nigeria

Distribution of OCPs and PCBs in Surface Sediments

The pattern of distribution of OCPs in the dry season follows the order: Endosulfan 11 ≤ Endrin Aldehyde ≤ Methoxychlor ≤ Heptachlor epoxide <Endrine ketone < ∑DDT <α-Chlordane <∑BHC <γ-Chlordane < Heptachlor <Aldrin<Endrin<Endosulfan 1<Dieldrin and for the Wet season: Endosulfan 1 <α- Chlordane <Endosulfan 11<∑BHC <Dieldrin<Endrine ketone<Methoxychlor< ∑DDT < Heptachlor <γ-Chlordane < Heptachlor epoxide <Endrin Aldehyde<Aldrin<Endrin. Fig. 5 shows that the concentrations of the OCPs were generally low in the dry than the wet season. The most dominant OCPs was Endrin closely followed by Aldrin. A similar trend occurred for the PCBs in the surface sediments. Concentrations were higher in the wet season than the dry season (Fig. 5). For the dry season, the distribution followed the order: PCB 52< PCB 158 <PCB 105 < PCB 187 <PCB 28 < PCB 101 < PCB 156 < PCB 180 <PCB 118 <PCB 138 and for the wet season, the pattern was PCB 187 < PCB 118 < PCB 28 < PCB 105 ≤ PCB 138 < PCB 158 < PCB 52 < PCB 156 <PCB 101 < PCB 180. The dominant PCBs were PCB 180 followed by PCB 101. The levels of these contaminants were highly variable, representing a contaminated ecosystem.

Comparison of EDCs (OCPs and PCBs) levels with permissible limits

Table 4: Comparative assessment of EDCs levels with USEPA MCL (2020)

EDCs µg/g	Seasonal levels (µg/g dry wt)		USEPA (2020) µg/g	Remarks
	Dry	Wet		
PCB 28	0.33	0.54	0.5	> MCL (wet season)
PCB 52	0.01	0.63	0.5	> MCL (wet season)
PCB 101	0.47	1.45	0.5	> MCL (wet season)
PCB 105	0.11	0.56	0.5	> MCL (wet season)
PCB 118	0.78	0.25	0.5	> MCL (dry season)
PCB 138	0.86	0.56	0.5	> MCL (dry and wet seasons)
PCB 156	0.52	0.87	0.5	> MCL (dry and wet seasons)
PCB 158	0.06	0.60	0.5	> MCL (wet seasons)
PCB 180	0.56	1.70	0.5	> MCL (dry and wet seasons)
PCB 187	0.32	0.24	0.5	< MCL (dry and wet seasons)
Heptachlor	1.15	2.03	0.4	> MCL (dry and wet seasons)
Aldrin	2.16	3.39	-	na
∑BHC	0.16	1.20	-	na
Heptachlor Epoxide	0.06	2.10	0.2	> MCL (wet season)
α-Chlordane	0.12	0.45	2	< MCL (dry season)
γ-Chlordane	0.22	2.08	2	> MCL (wet season)
∑DDT	0.11	1.92	-	na
Endosulfan 1	3.01	0.09	-	na
Endosulfan 11	0.01	1.17	-	na
Endrin Aldehyde	0.01	2.11	-	na
Endrin Ketone	0.08	1.80	-	na
Methoxychlor	0.01	1.87	40	< MCL limit
Dieldrin	3.23	1.56	-	-
Endrin	2.60	3.53	2	> MCL

na – limit not available; MCL – Maximum Contaminant Levels

The EDCs concentration in the sediments of Calabar river, Nigeria varied spatially and seasonally, with absolute levels occurring highest in the wet than the dry season. The EDCs (OCPs and PCBs) in the sediments of Calabar river were markedly higher (0.05 – 4.48 µg/kg dry wt, 0.08 – 2.55 µg/kg dry wt) than values (6.63 to 206.13 ng g^{-1}- dry weight (dw), 0.85 to 26.56 ng g^{-1}-dw) for the sediments of the Awash River Basin, Ethiopia and 6.3 to 400 ng g (-1) dry weight (dw) for sediments from the East Lake, China [13, 14]. The EDC values obtained in this study were however lower than the amounts determined in the sediments from Nairobi River, Kenya, 0.01 to 41.9 µg kg^{-1} in sediment [15]. Most of the contaminant concentrations were higher than the maximum contaminant levels (MCLs) of USEPA, Table 7. These were observed for the PCB 101, 118,138, 156, and 180 while the OCPs were heptachlor, heptachlor epoxide and Endrin [16]. Only 3 of the EDCs were occurred below the MCLs namely PCB 181, α-Chlordane and Methoxychlor (Table 4). The study revealed that the EDCs were markedly abundant in the sediments especially in the wet season. Their occurrences suggest significant contribution and addition to the ecosystem from the erosive force of surface runoffs during the wet season. Large volumes of water flowing through municipal drainages estimated at 20, 000 to 30,000 cubic

centimeter of water are usually observed during heavy rainfall, which often result in occasional flooding and destruction of municipal facilities. The relatively high levels of the OCPs and PCBs are not desirable in the ecosystem since they could be absorbed by benthic species during their feeding regimes and subsequently transferred to humans upon consumption of sea foods. EDCs are known to cause liver damage, stomach pain, reproductive difficulties and an increased risk of cancer; and are responsible for the disruption of the central nervous system in humans [17]. A continuation of these studies on the bio-concentration of the EDCs by fish and shell fishes in the riverine ecosystem is recommended which shall reveal the extent of contamination of the organisms.

Conclusion

During the period of investigation, OCPs were more abundant than PCBs indicating possible anthropogenic input from agricultural sources and municipal/industrial sources. The water quality variables were lower than previous values of 28°C and 6.8 - 7.5 for water temperature and pH respectively [9]. The decreasing trend in water quality between the dry and wet seasons is attributed to increased volume discharges of the river. Coastal flooding from rainfall due to climate change may also contribute to the high abundance of OCPs and PCBs in the riverine sediments. Climate change also contributed to the temporal changes in OCPs between the dry and wet seasons. EDCs concentrations, which were higher in the wet than dry seasons, is attributed to the desorption of EDCs from surface soils. The temporal monitoring indicates that the sediment concentrations of OCPs are controlled largely by downstream transport of desorbed residues from coastal farmlands during ebb-tidal and flooding regimes of the river channel. An associated environmental risk may be possible due to the transportation of OCPs and PCBs over long distances in tidal systems, from target to non-target areas, predisposing the contaminants to bio-accumulation by the different ecological matrices and humans. Even though the surface sediments showed some degree of OCPs and PCBs accumulation, there were no reports of the coastal community exposure to significant health risks associated with consumption of benthic species in the region [18].

Therefore, in LMICs (low and medium income countries) such as in the Sub-Saharan Africa, continuous monitoring should be encouraged and strict regulations enforced on the export/import and ban on the sale of pesticides. These will ultimately lead to the reduction and availability of these contaminants in the coastal waters. The continuous and regular monitoring of the ecosystem is suggested in-order to create a data bank for future references.

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