

Distribution and levels of polybrominated diethyl ethers (PBDEs) in sediment and biota of Lagos Lagoon, Nigeria

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Introduction

Polybrominated diphenyl ethers (PBDEs) have become ubiquitous in the environment. PBDEs represent one of the sub-groups of brominated flame retardants (BFRs). When incinerated, PBDEs have a share in formation of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), having similar effects as PCDD/Fs. PBDEs are persistent, bioaccumulative and can be found everywhere in the surrounding environment – in soil, water, sewage, in tissues of fish, birds, seals, whales and polar bears, in human blood, as well as in mother's milk [1]. PBDEs concentrations in the environment are steeply rising and they double each 3 - 5 years [2]. PBDEs are endocrine disruptors and neurotoxins. They are believed to cause liver tumors, neurodevelopmental and thyroid dysfunctions [1].

Lagos lagoon is a crucial marine environment in the city of Lagos. The lagoon is the largest tropical lagoon complex in the Gulf of Guinea, expanding to 250 km from Cotonou in the Republic of Benin to the borders of the Niger [3]. The lagoon system links the Atlantic Ocean (in the west and south) and Lekki lagoon (in the east) with an area of 6354.708 km² [4]. It is a brackish water environment that is fed in the north by a number of large rivers, including Ogun, Yewa, Ona, and Osun rivers as well as tidal creeks. Of which, the Ogun river discharges a large volume of water into the lagoon. During the rainy season, the lagoon empties in the south and opens into the Atlantic Ocean via the Lagos harbor [3,5]. It serves as a means of livelihood and transport, residential and recreation site for the surrounding Lagosian. It also functions as a dumpsite for residential wastes and receives a discharge from the surrounding industries that accounted for about 80-85% of the industries in Nigeria. Studies showed that sediment samples from Lagos lagoon contain higher concentrations of polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and heavy metals [4]. Also, different studies showed that fish species inhabiting the Lagos lagoon system suffer from severe intersex, developmental and reproductive effects and fish exposed to sediment extracts from the Lagos lagoon showed teratogenic, embryotoxic and genotoxic effects [5]. There is limited information on the distribution of PBDEs in Lagos lagoon sediment and accumulation in fish in the different discharge point and River Ogun tributary. Thus, this study assesses the levels and distribution of PBDEs in the sediment and fish of Lagos lagoon, Nigeria.

Materials and methods

Biota (one fish sample each was collected at the Ajah and Agboyi sampling locations as fish was not available at the other sampling location) and sediment samples (one composite sample consisting of 5 subsamples) making a total of 12 representative samples were collected at different locations of industrial effluent and sewage discharges into the Lagos lagoon. The sampling locations are Egbin, Ibeshe, Ajah, Majidun, Agboyin, Okobaba, Iddo, Ijora, Apapa, University of Lagos (Unilag) front, Makoko, and River Ogun tributary. Description of the activities at the different sampling locations is presented in Table 1. Samples were preserved and stored accordingly using standard procedures and transported to the Geo-Environmental Research Laboratory (GRC), BCCC-Africa, University of Ibadan, Nigeria. All chemicals and reagents used were of analytical grade and high purity. HPLC grade acetone and n-hexane used for the extraction were obtained from Merck (Germany). Approximately 5 g of the sediment and 5 g of anhydrous sodium sulphate were weighed and mixed until free flowing. 10 mL of dichloromethane/hexane (1:1, v/v) was added and the samples were extracted using ultrasonic bath for 10 minutes. The extraction was repeated with another 10 mL of the extracting solvent for another 10 minutes. All the extracts were combined and the volume evaporated to less than 1 mL, this was dissolved in 2 mL of n-hexane for clean-up using silica gel column. Extract on top of the column was eluted using 10 mL dichloromethane/hexane (1:1v/v). This was allowed to evaporate to less than 1 mL and re-dissolved in 2 mL n-hexane. The cleaned extracts were analyzed for PBDEs using GC- μ ECD (Agilent 7890A). An Agilent DB-XLB fused silica column (30 m x 250 mm x 0.25 μ m i.d) was used. The operating conditions was: injector temperature 250°C, detector temperature 300°C, oven temperature was initially at 100°C (1 min hold) and finally increased to 300°C at 25°C/min (10 min hold) to give the total run time of 19 mins. The carrier gas was nitrogen (99.99 % purity) and flow rate was 1 ml/min. One microliter of the extract was injected. 50 % duplicate analysis and blank determination were carried out. Calibration curve was obtained using PBDEs working standards (500, 250, 125, 62.5, 31.25 and 15.63 ng/g). The LODs ranged from 0.005 ng/g- 0.01 ng/g while the LOQs ranged from 0.02 ng/g to 0.03 ng/g.

Results and discussion

There is variation in the concentrations of total PBDEs in the sediment of Lagos lagoon collected at different sampling location with different anthropogenic activities on the lagoon. The levels of PBDEs as well as the mean, standard deviation and coefficient of duplicate analysis in the sediment and fish of Lagos lagoon is presented in Table 1. The concentrations of the PDBEs ranged from 6.92-22.6 ng/g and 10.3-14 ng/g in the sediment and fish samples, respectively. The sediment samples collected at Ijora and Agboyi had the highest mean concentrations of 18.4 \pm 1.2 ng/g and 17.9 \pm 6.6 ng/g, respectively while Okobaba had the lowest, 7.39 \pm 0.7 ng/g. Fish showed bio-accumulative potential as the total concentrations were more than what was obtained in the sediment samples collected at the same location as the sediment. PBDE-17 and 28 had the highest concentrations of all the 8 congeners determined in this study. When compared with what was reported in the literature, the concentrations obtained in this study was more than 0.01 to 0.13 ng/g (DW) and 0.13 to 0.82 ng/g (WW) in the sediment and fish tissues, respectively reported by [2] and 0.11 to 23.33 mg/kg reported by [6] for Lagos lagoon. The results showed that PBDEs is present in the sediment collected at all the sampling points and fish of Lagos lagoon, which might be

attributed to the different activities going on at the sampling locations such as disposal of municipal solid waste. Municipal solid waste in Nigeria and most developing countries are co-disposed with other waste such as e-waste [7]. Thus, the presence of this toxic and endocrine disruptor in the sediment and fish of Lagos lagoon. To the best of our knowledge, this is the first study on Lagos lagoon on the distribution of PBDEs in all the major discharge points and the tributary.

Table 1: Mean concentrations, standard deviation (SD) (ng/g) and coefficient of variation of PBDEs in sediment and biota of Lagos Lagoon, Nigeria

S/N	Sample Locations	Description of different activities	Concentrations of PBDEs (Σ PBDEs)
	Sediment		
1	Ajah	Fishing, residential building, domestic waste discharge	11.0 \pm 4.4 (39.7)
2	Egbin	Power station, dredging, boat transportation	12.8
3	Ibeshe	Textile industrial effluent discharge, solid waste dump, boat transportation, fishing	14.4 \pm 7.1 (49.4)
4	Agboyi	Fishing, municipal waste discharge, public toilets, dredging	17.9 \pm 6.6 (36.7)
5	Majidun	Transportation of crude oil via pipelines, dredging, boat transportation	7.77
6	Makoko	Boat transportation, fishing, solid waste dump, residential building	10.3
7	Ijora	Abandoned power station, solid waste dump, boat transportation	18.4 \pm 1.2 (6.6)
8	Apapa	Industrial effluent discharge, boat transportation, petrol tanker loading	13,0
9	Iddo	Sewage discharge, public toilets, open defecation, solid waste dump	9.68
10	R. Ogun	Agricultural waste, industrial effluent discharge	13.2 \pm 6.1 (46)
11	Unilag front	Fishing, solid waste dump, boat transportation	8.21
12	Okobaba	Saw milling, open defecation, fishing, saw dust burning	7.39 \pm 0.7 (8.9)
	Fish		
1	Ajah		14.0 \pm 1.42 (10)
2	Agboyi		10.3

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