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Evaluation of polybrominated diphenyl ethers in sediment of Lagos Lagoon, Nigeria

Adewuyi, G. O.[1]* and Adeleye, A. O.[2]

[1]Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria.
[2]Department of Physical and Chemical Oceanography, Nigerian Institute for Oceanography and Marine Research Victoria Island, Lagos State, Nigeria.

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Certain pollutants, particularly synthetic organic compounds have given rise to important environmental concerns. New organic pollutants especially polybrominated diphenyl ether (PBDEs) employed in electronic equipment and in some household items as flame retardants are now finding their way into the aquatic environment as components of waste discharge into the water body. These highly hazardous organic pollutants of concern are persistent, can bioaccumulate and biomagnify in aquatic organism especially fish, and there appears to be no clear strategy for managing them. In this study, levels of polybrominated diphenyl ethers were determined in sediments collected from Lagos lagoon with the aim of generating a database which can be employed for management options. Sediment samples were collected using Van Veen grab for a period of one year from randomly selected sites in Lagos lagoon. The samples were soxhlet extracted with dichloromethane to obtain PBDEs extracts which were later cleaned up in a column of silica gel using hexane as eluant. The cleaned extracts were analyzed using gas chromatography coupled with electron capture detector. The total concentrations of PBDEs in sediments ranged from 0.11 to 23.33 mg/kg. In all the studied locations, BDE-28, BDE-153, BDE-154 and BDE 205 were detected in all sediment samples at concentration range of 0.22 to 23.33 mg/kg. Among the PBDEs congeners, sum of tri to hepta BDEs contributed 61.32%, while BDE-205 contributed 38.68% to the total PBDE in the sediment samples. Brominated congeners BDE-47, BDE-153 and BDE-154 (tetra and hepta BDEs) were abundant which contributed 18.31, 12.06 and 34.75%, respectively to the sum of tri to hepta BDE in the sediment. The composition patterns of PBDEs in Lagos Lagoon sediment samples revealed that technical deca-BDE mixture was the major pollutant sources with a minor contribution of penta-BDE mixture.

Key words: Gas chromatograph, polybrominated diphenyl ether (PBDEs), sediment, Lagos Lagoon.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are additive flame retardants that are present in many commercial and house products such as electronics (computers, televisions, electronic circuit boards, etc) plastics, furniture, carpets, toys, paints, textiles, foam and rubber (Alaee et al., 2003). PBDEs composed of three comercial mixtures of decabromodiphenyl ether (decaBDE), octabromodiphenyl ether (octaBDE) and pentabromodiphenyl ether (pentaBDE). These additive PBDEs are the highest produced group of brominated flame retardants (BFR). The penta- and octa-products contain several BDE congeners, and the deca-product is composed of

*Corresponding author. E-mail: adewuyio@gmail.com.

entire BDE-209 (Guocheng et al., 2010). The European Union banned production of both pentaBDE and octaBDE in 2004; however PBDEs have been listed as persistent organic pollutants (POPs) under the treaty of Stockholm Convention in 2009. PBDEs enter the environment through direct and indirect urban domestic/industrial sewage discharges and atmospheric deposition. These chemicals are among emerging organic pollutants of concern as they are persistent, can bioaccumulate, biomagnify and have the potential for long-range atmospheric transport (Hities, 2004). PBDEs are also toxicants of particular significance to human health since they affect thyroid hormones, endocrine system and neurobehavioral development as well as possibly causing cancer (Viberg et al., 2006; Brigden et al., 2005; Darnerud, 2008). PBDEs are likely not produced in Nigeria but contamination arises from importation of consumer products and house textiles containing PBDEs from developed countries such as United State of America, Europe, Korea and Japan (Osibanjo and Nnorom, 2007; Aniyie, 2009). Yogui and Sericano (2009) reported that United State produced 50% of the total global demand of these manmade chemicals in 2001. In Korea, total use of PBDEs in 2002 was 49,050 tons; deca-BDE accounted for the major proportion (25%; 12,324 tons), while penta- and octa-BDEs together accounted for only a minor proportion (0.2%; 84 tons) of total usage (Moon et al., 2002). The domestic demand of PBDE has increased at a rate of 8% annually in China (Mai et al., 2005). In 2006, the productions of the technical deca-BDE mixture and decabromodiphenyl-ethane (DBDPE) in China were 15,000 and 11,000 tons, respectively (Guocheng et al., 2010).

Various PBDE congeners have been detected with significant levels in environmental matrices such as water, sediment and sewage sludge as well as biological samples such as biota, human blood, adipose tissue and breast milk. Due to the high octanol-water partition coefficient, PBDEs have a tendency to accumulate in sediments as well as bioaccumulate and biomagnify in biota (Erickson 1997; Guocheng et al., 2010 Woodwell et al., 1971; Eljarrat et al., 2004; Kierkegaard, 2007). Mai et al. (2005) reported that the total PBDEs concentrations in Pearl river Delta sediment were most <50 ng/g which is within the range for riverine and coastal sediments around the world while BDE-209 concentrations were at high end when compared with the worldwide figures. A study carried out by Hites et al. (2004) reported PBDEs to be present in both farmed and wild salmon. Although the levels of the contaminants were generally higher in farmed fish than wild fish, one species of wild salmon contained the highest level of PBDE found in the study. A previous study using green-lipped mussels from Hong Kong waters showed that PBDEs concentration were among the highest in the world (Zheng et al., 2004). A recent monitoring study conducted by United States Fish and Wildlife Service, Division of Environmental Contaminants in Carlsbad, CA reported that eggs of the sea birds nesting in south San Diego Bay contained not only PCBs and DDTs, but also the emerging contaminants, polybrominated diphenyl ethers (PBDEs), identified for the first time in the ecosystem of south San Diego Bay which is part of San Diego National Wildlife Refuge (Zeeman et al., 2008). Law et al. (2006) reported that there is about 60-fold increase of PBDEs level in human breast milk in Sweden.

Tlustos et al. (2007) also reported that PBDEs can have an effect on brain development in mice, slowing the learning process. As with PCBs, exposure to PBDEs may be particularly harmful during a critical window of brain development during pregnancy and early childhood. While the pentabromo compounds appear to be the most toxic, many of these persistent chemicals have not been extensively studied.

Nigeria's vast water resources especially Lagos lagoon are among those most affected by environmental stress imposed by human population growth, urbanization and industrialization. The disposal and management of wastes in Lagos Lagoon, Nigeria presents serious environmental problems as the usual methods of waste disposal such as land filling, dumping site and incineration lead to contamination of underground and surface water bodies.

Lagos lagoon is a multi-use re-source subject to fishing, recreational activities, dumping of solid wastes, non living resources (sand and coral) exploitation, effluent discharges and many other effects. Previous studies showed that the lagoon is highly polluted with various anthropogenic activities surrounding it (Adeyemi et al., 2011; Adedayo et al., 2012). The lagoon ecosystem is, however, vulnerable. The outcome of this study is therefore necessary for the evaluation of selected persistent organic pollutants (PBDEs) status of this lagoon. A precise idea about our coastal sediment is essential for evolving their rational exploitation and management strategies.

Study location

Lagos is located on the western side of Nigeria, and is bordered by Benin republic and Cameroun. Lagos lagoon has the estimated area of 150.56 km² (Figure 1). Figure 1 shows the sampling stations on Lagos lagoon while the coordinates and approximate depth for each sampling stations are recorded in Table 1. The lagoon receives a number of important large rivers namely: Yewa, Ogun, Osun and Ona. The brackish water lagoon surrounds the Lagos Island and empties into the Atlantic Ocean at Lagos harbour. The lagoon is generally shallow with a depth of between 0.3 and 3.2 m in most parts with the exception of some dredged parts, notably in the Lagos harbour, and where depth is > 10 m.

Lagos is 3,577 sq. km. in size with a maritime shoreline

Table 1. The study stations, their coordinates and approximate depth.

Location	Coordinates	Approx. depth (m)
Oworosoki dumpsite	N 06°32.961” E 003°24.532”	0.40
Oko Baba	N 06°28.800” E 003°23.468”	1.25
Agboyin axis	N 06°33.655” E 003°24.275”	0.50
NEPA transformers depot Ijora	N 06°28.108” E 003°22.285”	2.60
Ijora NEPA Sub-station	N 06°27.916” E 003°22.622”	3.50
Mid Lagoon	N 06°30.770” E 003°28.212”	4.20

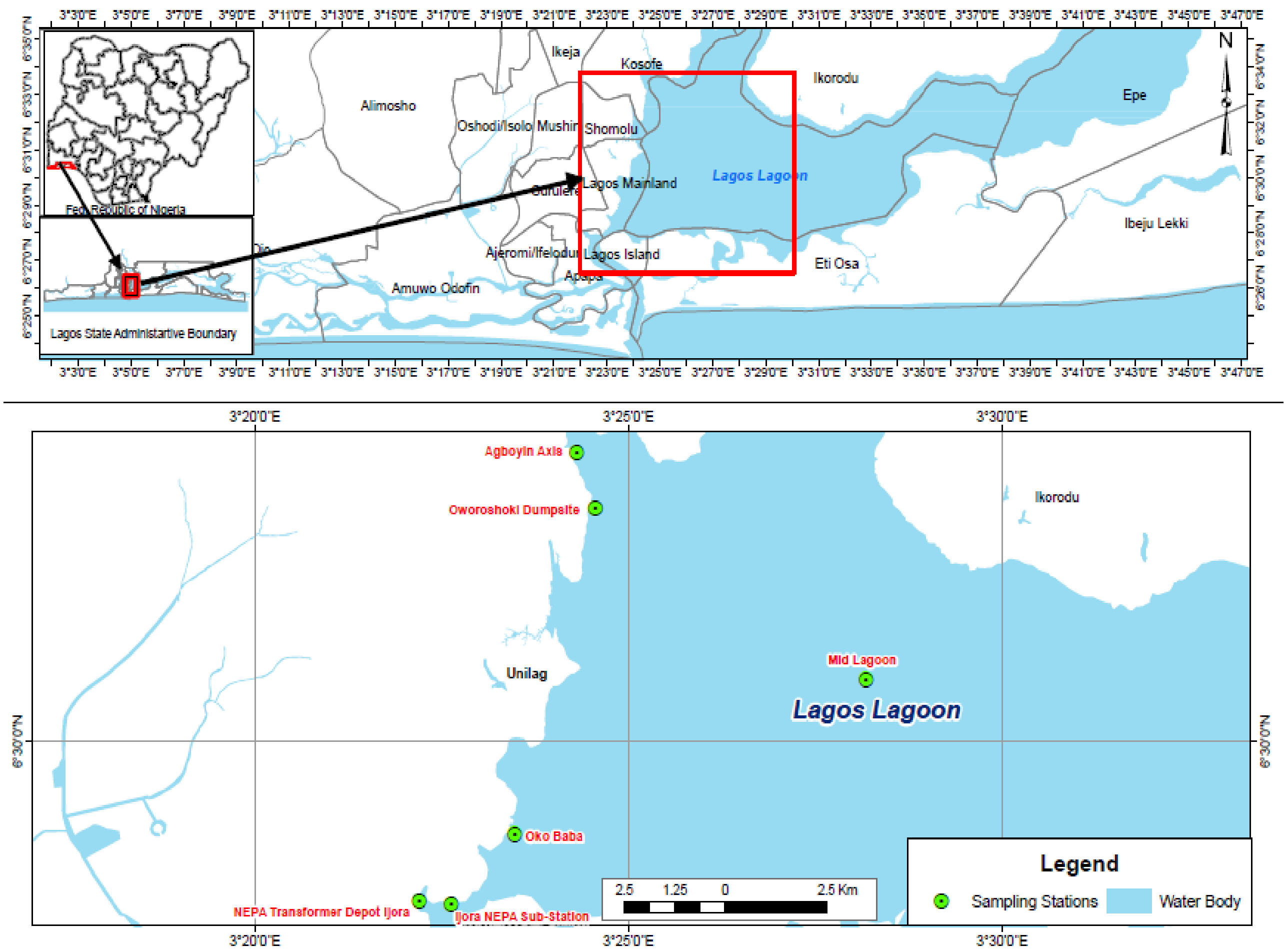

Figure 1. Map showing the sampling stations.

of about 180 km as its southern border. About 22% of the total landmass is made up of a network of creeks, rivers and lagoons. The state is endowed with 147,877 hectares of swampland and utilizes about 61.3 hectares for aquaculture.

MATERIAL AND METHODS

Sample collection and preparation

The method employed is US EPA method 1614 (USEPA 2007) with slight modifications. These include: sample collection and storage;

Table 2. Gas chromatograph conditions.

Condition	Value
Carrier gas flow (Helium)	1.0 ml/min
Make up gas flow (Nitrogen)	29 ml/min
Oven program	100°C for 0.5min, 100 to 200°C at 30°C/min hold for 4 min, 200 to 300°C at 15°C/min hold for 4 min, 300°C hold for 5mins.
Injection temperature	250°C
Detector temperature	300°C

Table 3. Range and mean concentration of PBDES in sediment at various stations.

Location	Sediment (mg/kg)	
	Range	Mean
Agboyin	2.38 - 21.61	10.01
Oworonsoki Dumpsite	0.11 - 23.33	5.75
Oko Baba	1.12 - 19.88	9.68
Nepa Sub Station Ijora	0.70 - 19.56	11.47
Nepa Transformer Depot Ijora	0.19 - 9.54	2.90
Mid Lagoon	0.16 - 17.11	2.22

extraction; clean up, quality control (field replicate and recovery study); analytical determination using Gas Chromatograph coupled with Electron Capture Detector.

Sediment samples were collected each month from June 2011 – July 2012 using Veen van grab. The samples were placed in glass bottles and stored at –20°C until analyses.

After being air-dried at ambient temperature for 5 days, field sample replicates (3) for each station were pooled together, thoroughly mixed and ground with a mortar and pestle before being passed through a 250 µm sieve to obtain a homogeneous matrix. Ten grams (10 g) of each sample were precisely weighed, spiked with decafluorobiphenyl internal standard, and mixed with approximately 20 g baked anhydrous sodium sulphate. The prepared samples were transferred to the thimbles for Soxhlet extraction with dichloromethane for 18 h. The extract was concentrated to approximately 1 mL with rotary evaporator followed by evaporation under a gentle stream of nitrogen. The sample was then transferred to a glass chromatography column packed with 6 g of activated silica gel. PBDEs in the sample extract were eluted with 50 mL of hexane twice. The hexane fractions were concentrated to about 1 mL under a gentle stream of nitrogen.

Gas chromatograph analysis

A gas chromatograph model Agilent-7890 series equipped with ^{63}Ni Electron Capture Detector (µECD) of activity 15 mCi with an auto sampler and J and W 122 – 4732 DB-17ms: 30m x250µm x 0.25 µm fused Silica capillary column (50%Phenyl-methyl polysiloxane proprietary) was used for separation of the analytes. The GC temperature ramp is shown in Table 2 and 1 µL was injected in a splitless mode. All samples were run in triplicate.

Instrument calibration was performed from the analysis of 8 compounds of PBDEs (99% purity). Retention times were established by using five points calibration range of 0.01 µg/ml to 0.05 µg for BDE 28, 47, 100, 99, 154, 153, 183 and 205/ml PBDEs standard mixes obtained from Accustandard Inc. United State. The concentrations of PBDEs were determined by extrapolation of peak area using the calibration curves of the standards.

Quality assurance and quality control

The quality assurance and quality control (QA/QC) samples included solvent blank, procedural blank and matrix spiked samples, all of which were analyzed together with the collected sediment samples. Solvents injected before and after the injection of standards showed negligible contamination or carryover, the blanks did not contain quantifiable amounts of any target compounds. The percent recoveries of decafluorobiphenly was 78.6 ± 7.2% in matrix spiked samples. A procedural blank and spiked sample consisting of all reagents was run to check for interference and cross-contamination. Instrumental QC was performed by injecting solvent blanks and standard solutions. The relative percent difference were less than 20% for all targets analyses. The limit of detection range from 5 to 9.7 ng/g. Relative errors and standard deviations obtained from the analyses of four spiked samples were used to evaluate the accuracy and precision of the analytical method.

RESULTS AND DISSCUSION

Table 3 present the quantitative results of those identified PBDE congeners whose standard were available. Figure 2 shows the Chromatogram of PBDEs analysis of mid lagoon sediment sample. The obtained data indicated

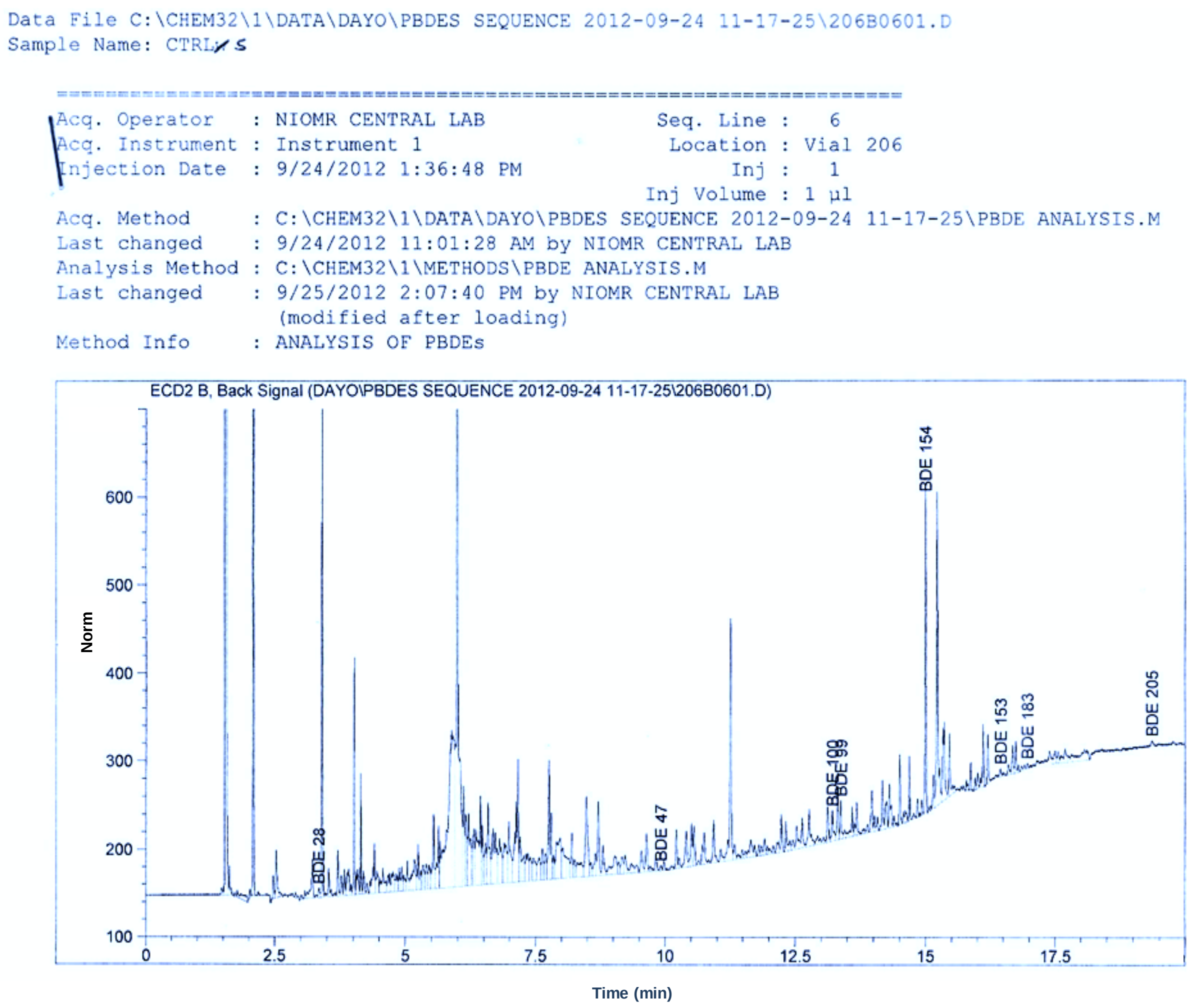

Figure 2. Chromatogram of PBDEs analysis of mid lagoon sediment sample.

that the PBDEs existed in the sediment samples with concentration ranging from 0.11 to 23.33 mg/kg with median value of 7.23. Total $\sum_8$ PBDEs level in surface sediments in the present study (254.35 mg/Kg) were generally comparable to those in surface sediment samples collected in Pearl river estuary of south China (150.11 to 230.13 mg/kg, Zheng et al., 2004), those in the coastal areas of Korea (180.56 to 260.38 mg/kg, Moon et al., 2002), and those in the river and coastal areas of Portugal (185.50 to 277.20 mg/kg, Lacorte et al., 2003), but were generally lower than those in Osaka Bay of Japan (8.80 to 13.52 mg/kg, Ohta et al.,2002) and those in San Francisco Estuary of US (ND to 2.12 mg/kg, Oros et al., 2005). PBDEs levels in sediment of Lagos lagoon were generally at low-intermediate ranges in the world. In all the samples, BDE-47, BDE-154, BDE-153, BDE-183 and BDE 205 were dominant congeners. The results indicate that 79.17% of samples analyzed recorded positive response for the presence of PBDEs. Tri BDEs (BDE-28) was detected at concentration varying from 0.70 mg/kg to 10.36 mg/Kg in Lagos lagoon sediment. Detection of Tri-BDEs (BDE-17 and BDE-28) has been previously reported in crab tissue and in air samples whereas only trace levels of BDE-28 were found in ringed seals serum samples (Dongli *et al.,* 2005). Penta-BDEs, (BDE-99 and BDE-100) were only detected in Agboyin and Oworonsoki sampling stations..

BDE-153 and BDE-154 were detected in all the sediment samples at concentration range of 0.22 mg/Kg to 16.66 mg/Kg (Figure 3). The concentration ratio of the hexa-BDE to hepta-BDE congeners was similar to that reported in the octa-PBDE based flame retardant (Dongil et al., 2005).

The levels of total PBDEs in the sediment collected near commercial centre (comprising automobile, textiles, building materials, electronic products manufacturing factories) Oworonsoki and Agboyin stations were apparently higher than those in sediment taken from the mid lagoon and NEPA transformer depot which possibly related to be far from industrial and urban activities.”

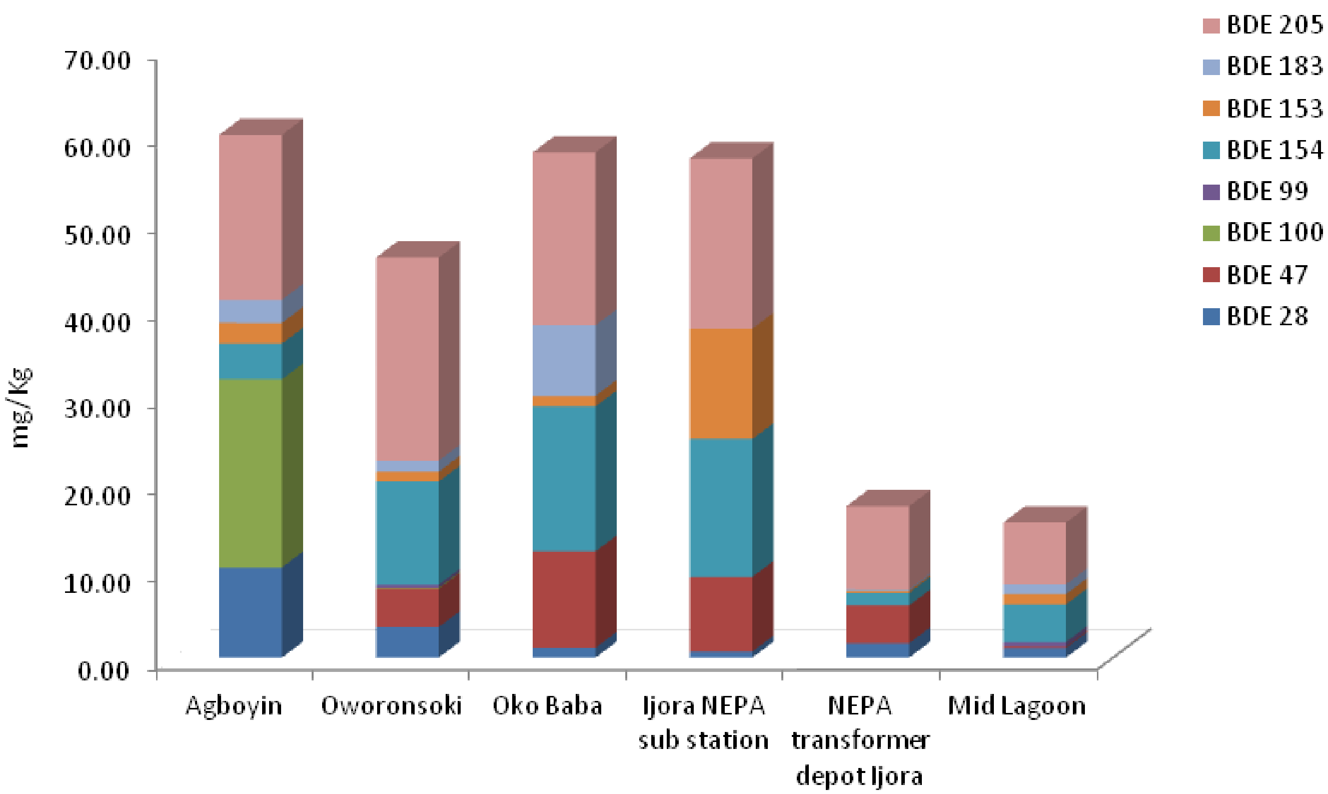

Figure 3. Mean value for PBDE congeners analyzed in sediment between June 2011 and July 2012.

Among PBDEs congeners, BDE-205 was the most predominant in the sediment samples. The average concentrations of BDE-205 were 1-2 orders magnitude higher than other PBDEs in sediments from Lagos lagoon. The findings were consistent with previous reported result, which indicated that BDE-205 was the dominant component of PBDEs detected in the sediments from Pearl River Delta, South China (Mai et al., 2005).

PBDEs in sediment samples likely originated from a combination of point and non point sources and atmospheric deposition. Larger amounts of industrial activities (such as dismantling electronic products, cables and wires, oils depot and chemical plants) were likely responsible for the high concentrations of PBDEs in sediment samples of Agboyin, Oko Baba and Oworonsoki (Table 3). The concentrations of PBDEs in sediment samples from Lagos lagoon were also compared with water bodies in other parts of the world as shown in Figure 4. 69.80% of samples analyzed recorded mean concentrations higher than European community allowable residual limits in aquatic system. The concentration levels of PBDEs recorded at locations could be an indication of pollution arising from various industries in the region. Good correlation coefficients ranging between 0.9953 and 0.9986 were achieved for the calibration curves of all tested PBDE congeners.

Figure 4 presented that PBDEs concentrations in the study sites were approximately 20 to 80 times higher than those reported from other PBDEs contaminated locations in the Spain and United State of America except in contaminated sites in China. Uncontrolled disposal of electronic waste (e-waste) by simple dismantling, acid treatment and open burning of plastic, building materials, casing, etc have apparently resulted in water and sediment contamination and mitigation of PBDEs into river and lagoon sediment.

Conclusion

This study provided the levels of PBDEs in the sediment from Lagos lagoon, Nigeria. PBDEs were detected in all the sediment samples in the study area. The PBDEs concentrations in sediment Lagos lagoon were at intermediate levels when compared with those reports in other parts of the world. The high concentration of PBDEs found in sediment sample from Lagos lagoon could be attributed to the high industrial impact of this area and indiscriminate waste disposal such as land filling, open dumps and incineration.

The congener patterns of PBDEs in sediments from Lagos lagoon were similar, which indicated that BDE 205 was the most predominant among the congeners studied, accounting for 38.68% of the total targets PBDEs. The compositional patterns suggested that the major sources

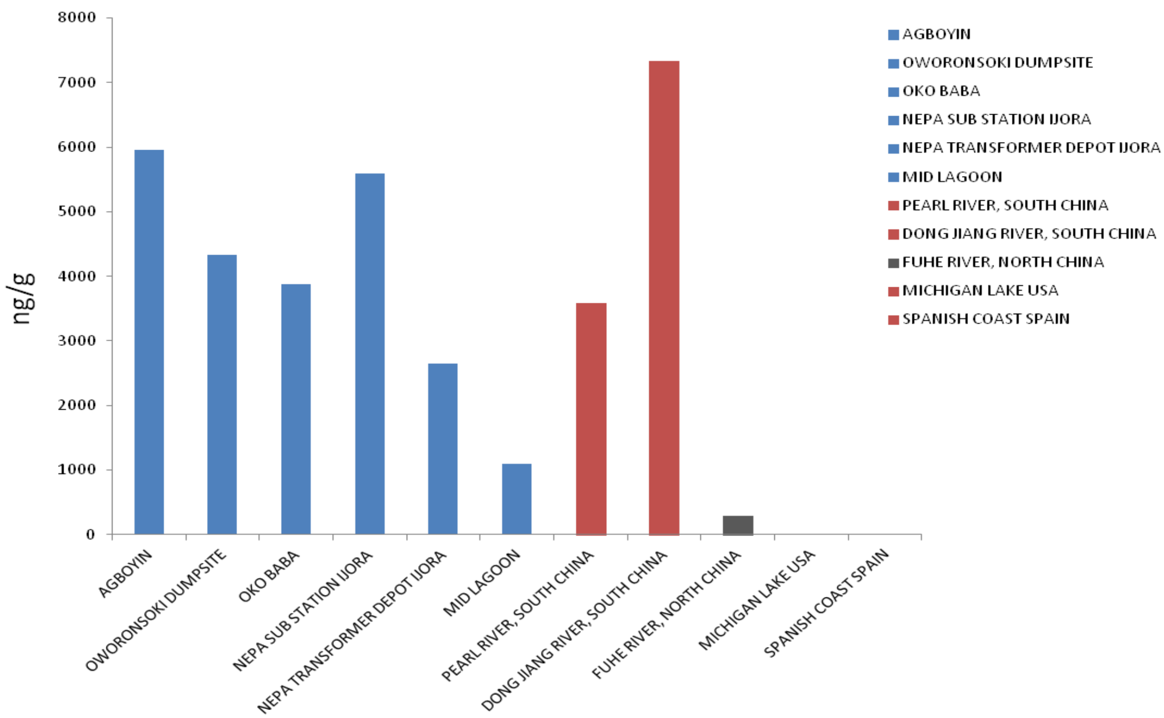

Figure 4. BDE-205 (ng/g) in sediments when compared with other locations from different regions worldwide.

of PBDEs were probably e-wastes and waste discharges from dump sites around Lagos lagoon.

To the authors' knowledge, this is the first study on PBDEs in West Africa. The result will serve as baseline data for future study.

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