Journal of Environmental Sciences

JOESE 5

Polybrominated Diphenyl Ethers in Sediments and their Bioaccumulation in tissues of the sessile Bivalves, *Crassostrea tulipa* from some selected area of Lagos Lagoon, Nigeria

*** Fidelia Ijeoma Osuala[1], Olushola Ayoola Abiodun[2], Morounranti Yusuf Olalekan [3]**

[1&3] Department of Zoology, Faculty of Science, University of Lagos, P.M.B. 101017, Lagos, Nigeria

[2.] Biological Oceanography Departments, Nigerian Institute for Oceanography and Marine Research, Lagos State, Nigeria

Reprint

Volume 48, Number 1: 44 - 54
(2019)

http://Joese.mans.edu.eg

P-ISSN 1110-192X
e-ISSN 2090-9233

Journal of Environmental Sciences, 2019; Vol. 48, No.1: 44- 54

Journal of Environmental Sciences
JOESE 5
ISSN 2090-9233

Journal homepage http://Joese.mans.edu.eg

Original Article

Polybrominated Diphenyl Ethers in Sediments and their Bioaccumulation in tissues of the sessile Bivalves, *Crassostrea tulipa* from some selected area of Lagos Lagoon, Nigeria

*** Fidelia Ijeoma Osuala[1], Olushola Ayoola Abiodun[2], Morounranti Yusuf Olalekan[3]**

[1&3] Department of Zoology, Faculty of Science, University of Lagos, P.M.B. 101017, Lagos, Nigeria
[2.] Biological Oceanography Departments, Nigerian Institute for Oceanography and Marine Research, Lagos State, Nigeria

Article Info

Article history:
Received 12/2/2019
Received in revised form 14/3/2019
Accepted 25/3/2019

Keywords:
Bottom-dwelling,
Filter-feeding,
Chromatography,
Accumulation,
Contaminants,
Lagos Lagoon

Abstract

Bioaccumulation of Polybrominated Diphenyl Ethers (PBDEs) was investigated in sediment and tissues of the Oyster (*Crassostrea tulipa*) from Unilag Lagoon Front, Makoko and Oworonshoki sampling stations within the Lagos Lagoon, Nigeria using Gas Chromatography coupled with Electron Capture Detector (GC-ECD). The samples collected were analyzed for PBDEs congeners of BDE 28, 47, 99, 100, 153, 154, 183 and 209. The results of the mean concentration of PBDE congeners detected in sediment and Oyster tissue were BDE 28, 47,183 and BDE 28, 47, 153 respectively, in all sampled stations, which was significantly higher ($P < 0.05$) comparing with Canadian Federal Environmental Quality Guidelines for PBDEs. Oworonshoki station had the highest concentration of total PBDEs (600.07 ng/g dry weight) while Unilag (386.43 ng/g dry weight) had the least concentration. BDE 28 was detected highest in all stations while congener BDE 183 was lowest in concentration. BDE 28 (70%) was the only congener distributed in the Oyster and sediment samples collected from all the stations and was significantly higher when compared with the Federal Environmental Quality Guidelines for PBDEs. Total PBDE concentration in Oysters showed that Oworonshoki had the highest concentration (615.44 ng/g) while Makoko showed the least (336.22 ng/g). The Biota Sediment Accumulation Factors for BDE 28 (1.181) and BDE 47 (4.990) were greater than 1, an indication of bioaccumulation. The present study established a reflection of the environmental health of the selected sampled areas and therefore, a useful tool for monitoring of PBDEs pollution.

1. Introduction ·

Polybrominated diphenyl ethers (PBDEs) has emerged as a major environmental pollutant belonging to a class of synthetic organic halogenated, recalcitrant compounds with the ability to bioaccumulate. PBDEs are used as a flame-retardant in materials such as coatings, construction materials, electrical equipment, furniture padding, and textiles. Rapidly increasing levels of PBDEs has been detected in the different strata of the environment owing to their continuous use since its existence in 1960s and 1970s. Thus, residue of PBDEs in the environmental matrix has also increased drastically (Ramu *et al.,* 2010; Kang *et al.,* 2002). Presently, the increase in levels of PBDEs in aquatic organisms and sediment becomes alarming globally due to their toxicity, persistence and bioaccumulative effect in the ecosystem (Darnerud *et al.*, 2001; Martin *et al*., 2007).

* **Corresponding author**: fhilosu@yahoo.com;
fosuala@unilag.edu.ng;
Telephone: 08056226064

Reports have shown that Nigeria is one of the African countries that serve as dumping ground for e-waste importation. This also serves as an important source of PBDEs in the environment (Wang *et al.*, 2005; Leung *et al.*, 2007). It has been established that PBDEs possess a wide spectrum of toxicity in laboratory animals, and they are present in every level of the food chain (Wang *et al.*, 2005). PBDEs displayed a molecular structure similar to that of polychlorinated biphenyls (PCBs). Therefore, would probably exhibit slightly different spectrum of toxicity among the 209 possible congeners.

In vivo, PBDEs have been shown to alter thyroid hormone homeostasis (Ellis-Hutchings *et al*., 2006). Sessile bivalves are bottom-dwelling, filter-feeding organisms used as indicators of pollutants in environmental monitoring programs throughout the world based on their abundance, wide spatial distribution, sessile behaviour, tolerance to salinity, resistance to stress, and tendency to accumulate a wide range of contaminants (Ramu *et al*., 2007). Thus, an organism such as bivalves; *Crassostrea tulipa* was examined in the present study. This animal is commonly as known as Western Africa Mangrove Oyster. It inhabits protected bays, estuaries and lagoons of Western Africa such as the Lagos Lagoon in Nigeria. The bivalves are integrator of contaminants in their dwelling place, and their use as indicators minimizes the problems inherent in comparing data from markedly different species (Oros *et al.*, 2005). They are good indicators of environmental quality because contaminant levels in their tissue respond to changes in the ambient environment and accumulate with little metabolic transformation (Sericano, 2003). The determination of contaminants in oysters gives a representative description of pollution patterns surrounding the area where it is collected (Negreira *et al*., 2015). The aim of this study was to determine the level of bioaccumulated PBDEs in sediments and in the tissues of the Oyster *Crassostrea tulipa*, (Lamarck, 1819) inhabiting selected areas of the Lagos Lagoon, Nigeria.

2.Materials and Methods

2.1 Study Area

Lagos Lagoon is among the major Lagoons in the Gulf of Guinea and it is located between longitude 30 10’ and 304’ SE and latitude 60 5’ and 60 36’ N (Figure 1). Several rivers empty into the lagoon among which are Yewa, Ogun, Oshun and Ona Rivers (Ayoola, 2016). The Lagoon is the ultimate sink of a number of industrial discharge/effluents and run off from surrounding metropolis. Three areas were selected for sampling based on the pollution dynamics of the Lagos lagoon (Table 1).

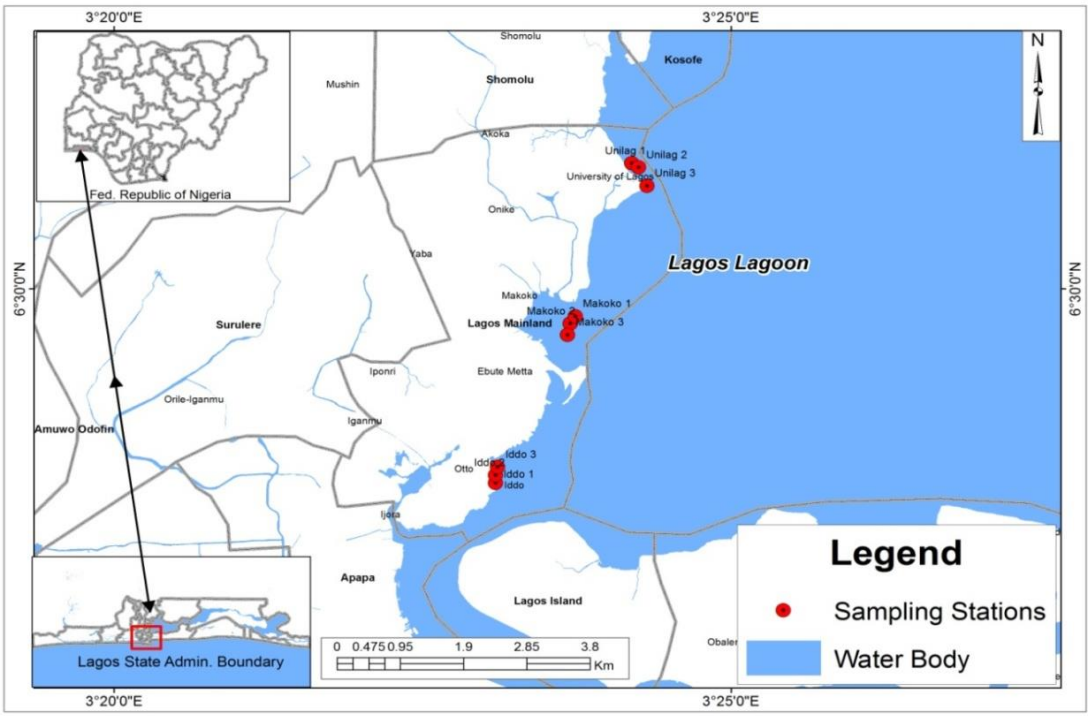

Fig. 1: Sampled study areas in the Lagos Lagoon

Table (1): Description of Sampled Locations

Sample Locations	Coordinates	Description of Site
Unilag Lagoon front	N 06º31. 057' E 003º 24. 113'	Characterised by natural fishponds built, boat transport and fishing activities.
Makoko	N 06º29. 457' E 003 º 23. 443'	Characterised by wooden residential buildings along the coast, fishing, sawmills and high boat transport density.
Oworonsoki	N 06º32. 035' E 003 º 24. 043'	Wooding/Bricks residential buildings lining the coastline, solid waste dumps in several locations along the coast, and sand mining activities.

2.2 Samples Collection

- ***Oysters samples***

Crassostrea tulipa (Oyster) samples were also collected through the three consecutive months; September, October and December 2016. These months were selected based on information regarding the abundance and availability of the animals sampled in the Lagoon. The oyster samples were collected from the three different stations along the lagoon using a stainless steel Van Veen Grab of 0.1 m^2. Oyster samples were sieved using 0.5 mm mesh stainless steel sieves and the collected samples were kept in aluminium foil,and stored in a cooler at a temperature of 4°C until transported to the laboratory. Scoops, sieves and buckets used in the collection of the sample were made from stainless steel because avoid interference in the organic sample analyzed for persistent organic pollutant.

- ***Samples of sediment***

Sediment samples were collected through the same months and stations in the Lagoon using a stainless steel Van Veen Grab of 0.1 m2. The sediments were collected in three (3) replicates and homogenized to produce a single composite sample for each station. The homogenized samples were kept in aluminum foil and stored in a cooler until conveyed to the laboratory.

2.3 Extraction of PBDEs In Oysters and Sediment Sampled

Exactly 5 g of crushed samples of sediment and oyster's tissues, each were mixed with sodium sulphate anhydrous separately, in ratio 1:1, and homogenized using an agate mortar and pestle to remove any residual moisture (Fatoki and Awofolu, 2003). Each dry sample (sediment and Oyster tissues) were then extracted separately using 50 ml n-Hexane as a solvent and vigorously shaked for 1 hour with the aid of an electronic shaker and filtered using Whatman filter paper. The extracts were concentrated and solvent-exchanged to n-hexane using a rotary evaporator. Concentrated extracts were cleaned and fractionated on an 8 mm i.d. silica column packed, from the bottom to top, with neutral silica gel (3 cm, 3% deactivated), 50% (on a weight basis) sulfuric acid silica (2 cm), and anhydrous sodium sulfate (1 cm). The PBDE fraction was eluted with 50 mL of acetone/n-hexane (1:1), and solvent-exchanged to n-hexane and concentrated to 0.5 mL under a gentle nitrogen stream. A known quantity of BDE-28 was added as an internal standard prior to instrumental analysis (Fatoki and Awofolu, 2003).

2.4 Gas Chromatography- Electron Capture Detector (GC-ECD) Analysis

Detection, identification and quantification of Polybrominated diphenyl ethers (PBDEs) congeners in cleaned-up extracts were done using a gas chromatography coupled electron capture detector (GC-ECD) PBDE recovery standards at known concentrations were analyzed, after which the samples were also analyzed using Agilent GC 7890A (ECD) with column (DB-17) (30m x 0.25mm x 0.25 micron).

2.5 Total Organic Carbon (TOC) and Grain Size Analysis of Sediments

Potassium dichromate ($K_2Cr_2O_2$) and concentrated sulphuric acid (H_2SO_4) were added to 1 g of sediment. The solution was swirled and allowed to cool. The solution was gently boiled, to enable complete digestion. Water was then added to halt the reaction. After sample digestion, the solution was centrifuged to remove any suspended particles and then placed in a calorimeter set to measure the light absorbance at a wavelength of 601. Colorimetric quantitative of TOC was then performed through the measurement of the colour change that results from the presence of Cr^{3+} in solution. The particle sizes were <4 mm for clay, 63 mm for silt and > 63 mm for sand. The relative error of the duplicate samples was > 3% (n ¼ 6).

2.6 Biota-Sediment Accumulation Factor (BSAF)

In this study, BSAF was considered as a measure of the biotic fate of PBDEs and defined using the following equation:

$$\textbf{BSAF} = \frac{\text{Concentration of PBDEs in Oyster Tissue}}{\text{Concentration of PBDEs in Sediment}}$$

2.7 Statistical Analysis

Data analysis was done using Statistical Package for Social Sciences (SPSS) version 16.0 and Excel Statistical Tool pack. The physicochemical parameters for each sample station were subjected to oneway Analysis of Variance (ANOVA) and Pearson correlation. The PBDEs concentration for each sample station and sample type (sediment and oysters) was subjected to two-way analysis of variance (ANOVA) and Duncan Multiple Range Test. The Grain size analysis, TOC and ∑PBDEs were subjected to Pearson correlation.

Results

3.1 Occurrence of PBDES in Sediments and Oyster

Eight numbers of PBDEs congeners were analysed such as BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183 and BDE 209 in both Oyster and sediments.

The results of the mean concentration of PBDE congeners detected in sediment sample were BDE 28, BDE 47, and BDE 183 (TABLE 2) which were not significantly ($P > 0.05$) different in the three (3) sampling stations but were significantly higher when compared with the Federal Environmental Quality Guidelines for PBDEs (Environment Canada, 2006). Oworonshoki station had the highest concentration of total PBDEs, while Unilag had the least concentration (Table 2). PBDE congener (BDE 28) had the highest concentration of the congeners detected in all stations while congener BDE 183 had the lowest concentration. Only BDE 28 was detected in all the sampling stations in significantly higher concentrations.

Table 2: Mean occurrence of PBDEs (ng/g dry weight) in Sediment Sampled

Homologue	PBDE congeners	Unilag Lagoon Front	Makoko	Oworonshoki	Canada FEQG
TriBDE	BDE 28	379.83 ± 0.02	475.35 ± 0.01	491.55 ± 0.05	44
TetraBDE	BDE 47*	ND	ND	108.52 ± 0.17	39
PentaBDE	BDE 100*	ND	ND	ND	0.4
PentaBDE	BDE 99*	ND	ND	ND	0.4
	BDE 154	ND	ND	ND	44
HexaBDE	BDE 153*	ND	ND	ND	440
HeptaBDE	BDE 183	6.60 ± 0.06	ND	ND	-
DecaBDE	BDE 209	ND	ND	ND	19
	TOTAL ∑PBDE	**386.43**	**475.35**	**600.07**	**586.8**

* denote that: Tetra-, penta- and hexa BDEs were identified as persistent, bioaccumulative, and inherently toxic (PBiT) (Environment Canada, 2006; FEQG, 2013); ND: Not detected; ∑PBDE: the total concentration of PBDE in sediments from all the sampling stations

3.2 Occurrence of PBDES in *C. Tulipa* (Lamarck 1891)

Three congeners were detected in the oyster sample (BDE 28, BDE 47, BDE 153) of all the BDE congeners analysed. BDE 28 was the only congener distributed in the oyster samples collected from all the stations and was significantly higher when compared with the Federal Environmental Quality Guidelines (FEQG) for PBDEs. However, BDE 153 was found in two (2) station (Unilag and Oworonshoki), while PBDE 47 was found within one (1) sampling station (Oworonshoki). There was no significant ($P > 0.05$) difference in the PBDE concentration in oysters collected from the sampling stations, although Oworonshoki showed the highest concentration of the total PBDE (615.44 ng/g), while Makoko showed the least concentration (336.22 ng/g) (Table 3).

Table 3: Mean concentration levels of PBDEs (ng/g dry weight) occurrence in *C tulipa*

HHomologue	Congeners	Unilag Lagoon front	Makoko	Oworonshoki	FEQG
TriBDE	BDE 28	448.75 ± 0.31	336.22 ± 0.66	424.82 ± 0.73	46
TetraBDE	BDE 47	ND	ND	180.35 ± 0.03	24
PentaBDE	BDE 100	ND	ND	ND	3.9
PentaBDE	BDE 99	ND	ND	ND	0.23
	BDE 154	ND	ND	ND	-
HexaBDE	BDE 153	14.49 ± 0.01	ND	10.27 ± 0.02	-
HeptaBDE	BDE 183	ND	ND	ND	-
DecaBDE	BDE 209	ND	ND	ND	19
	∑PBDE	463.24	336.22	615.44	

ND- Not Detected; ∑PBDE: the total concentration of PBDE in oyster's tissue from all the sampling stations ± error bar Federal Environmental Quality Guidelines (FEQG)

3.3 Distribution Pattern of PBDE Congeners in Samples and Sampled Stations

The distribution of the BDE congeners analysed in sediments and oyster samples (Figure 2) showed that BDE 28 has the highest concentration in both sediments and oysters collected in all the sampling stations. The highest concentration detected in sediments samples was collected from Oworonshoki. In all the sampling locations the concentrations of PBDE in sediments were higher than concentration detected in Oyster samples. BDE 183 was found in low concentration in sediments collected in only Unilag Station, and BDE 153 was also detected in low concentrations in Oyster's samples from Unilag as well as Oworonshoki stations. Conversely, BDE 47 was found only in samples collected from Oworonshoki sampling stations, with the highest concentration detected in Oyster samples.

3.4 Particle Distribution of Sediments and Total Organic Carbon (TOC) Content

The sediments collected from Makoko had the highest TOC, while sediments from Oworonshoki had the lowest rate. The particle distribution of sediments showed the highest amount of clay particles from Oworonshoki while sediments from Unilag Lagoon front had the highest sand particles. There was no significant ($P > 0.05$) difference in the silt particles composition of the sediments collected within all sampling stations (Table 4).

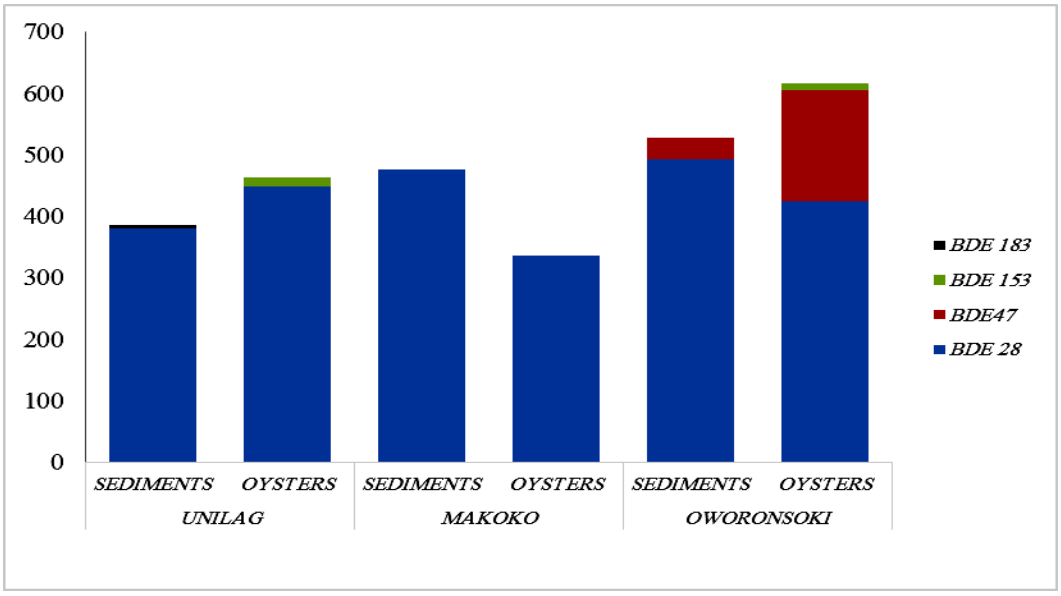

Fig. 2: Distribution pattern of PBDE congeners in Sediment and *C. tulipa*

Table 4: Sediments Grain size and Total Organic Carbon (TOC) content

Sampling Stations	TOC (mg/g)	Sand (%)	Silt (%)	Clay(%)	Sediments description
Unilag Lagoon Front	7.5	45	24	31	Dark Grey Organic Sandy Clay
Makoko	8.65	40	29	31	Dark Grey Organic Sandy Clay
Oworonshoki	2.6	14	29	57	Dark Grey Organic Silt and Sandy Clay

3.5 Correlation between sediment ∑PBDEs, grain size and total organic carbon (TOC)

The correlation between particle sizes, total organic carbon (TOC) and ∑PBDEs in sediment showed that ∑PBDEs had a strong correlation with the silt and clay particle composition (R= 0.93494; 0.77475). Total PBDEs and TOC had a significant negative correlation (R= -0.64908). TOC also significantly correlated with silt, while clay and TOC were negatively correlated (Table 5).

Table 5: **Correlation between sediment ∑PBDEs, grain size and total organic carbon (TOC)**

Parameter	TOC	Sand (%)	Slit (%)	Clay (%)	∑PBDEs
TOC	0	0.21054	0.78122	0.11455	0.55031
Sand %	0.94581	0	0.57068	0.09599	0.33976
Slit%	-0.33694	-0.62441	0	0.66667	0.23091
Clay%	-0.98385	-0.98865	0.5	0	0.43575
∑PBDEs	-0.64908	-0.86093	0.93494	0.77475	0

3.6 Biota- Sediment Accumulation Factor (BSAF)

The BSAF of BDE 28 in Unilag Lagoon Front was higher than 1, while it was less than 1 in other sampling stations. BDE 47 was significantly greater than 1 in Oworonshoki while it was lower in the Unilag Lagoon Front and Makoko (Figure 3)

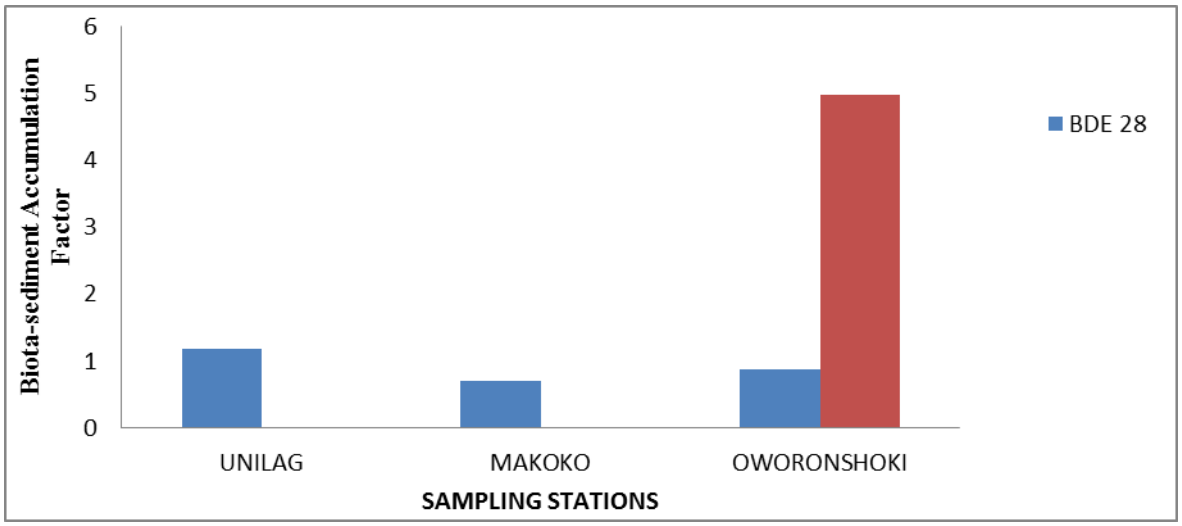

Fig 3: Biota-Sediment Accumulation Factor For Congeners

Discussion

This study evaluated the concentration levels of Polybrominated diphenyl ethers (PBDEs) concentrations in sediment and the Oyster; C. *tulipa* in Oworonshoki, Makoko and Unilag Lagoon front of the Lagos Lagoon. The mean concentration of the PBDE congeners detected in sediments was significantly higher than that of FEQG (Environment Canada, 2006). This was a similar finding to that of Adewuyi and Adeleye (2013) who studied several areas of Lagos Lagoon, including Oworonshoki. Mean concentration of PBDE congeners in the sediment in the present study compared with studies from other countries (Oros *et al.*, 2005; Song *et al*., 2005) showed relatively high concentration for PBDE 47 and 28. The dominating congeners as detected in the sediment that were Hepta-BDE, Octa-BDE and Nona-BDEs corroborated with the findings of Hassanin *et al.* (2004). However, the absence of BDE 209 in the sediments samples could probably be as a result of photodecomposition or photolytic debromination of large BDEs into smaller molecules BDEs. Fang *et al.* (2012) reported on the experimental photo degradation of BDE 47, BDE 99, BDE 100, BDE 153, and BDE 183 dissolved in hexane. According to the authors, higher brominated BDE congeners degraded at a faster rate than the lower brominated congeners. The authors concluded that the main decomposition mechanism induced by photolysis was reductive debromination resulting in lower brominated BDE congeners. Bezares-Cruz *et al.* (2004) postulated that the photochemical reaction would be expected to be attenuated by sorption of heavier BDEs onto colloidal particles in the water column, and by the light attenuation properties of humic materials in aquatic systems. This probably could explain the presence of BDE 183 in low concentration in Unilag Lagoon Front with high TOC. The ∑PBDEs in sediments from all the sampling locations were relatively higher than concentration reported from other studies with similar sample size (Mai *et al*., 2005; Pan *et al*., 2010; Li *et al.*, 2010; Jiang *et al*., 2011). The high concentration of BDE 47 in sediments collected within Oworonshoki sampling stations could be as a result of heavy dumpsite along the coast and that also receive municipal, electronic and organic wastes from the coastal community.

The concentration of PBDE congeners BDE 28 and BDE 47 detected in *C. tulipa* which exceeded the FEQGs for PBDEs was similar to the work of Sericano *et al.* (2003) and La-Guardia *et al.* (2007). The authors finding from their studies showed relatively high concentrations of Tri-BDE and BDE 28 compared to most studies on bivalves that have BDE 47 and other higher PBDE congeners as the dominating congeners. This could be attributed to *in vivo* metabolic debromination in the bivalve, *C. tulipa*. Certain shellfish species have the capacity to debrominate PBDE congeners *in vivo*. This involves the removal of bromine atoms in the para and meta-positions of a higher molecular weight PBDE congener to form lower-brominated PBDE compounds. It is not clear whether all aquatic species or even bivalves, both marine and freshwater, have the innate propensity for bio-transforming PBDE, but debromination of PBDEs has been observed some fish species and crustaceans (La-Guardia *et al*., 2007). However, the detection of BDE 153 congeners which were found in two of the sampling locations (Oworonshoki and Unilag Lagoon Front) and BDE 47 found only in Oworonshoki, similar to the sediments concentrations, was a clear indication of bioaccumulation of the congener from the sediment in the sampling station. To collaborate the findings, BSAF for BDE 47 was greater than 1 in Oworonshoki and BDE 28 in Unilag Lagoon Front, an indication that bioaccumulation of these congeners had occurred in these sampling stations (USEPA, 2008). This corroborates with the results of Bodin *et al.* (2011) who worked with C. *gasar* and Oros *et al.* (2005), who worked with *C. gigas*. A probable explanation could be hinged on the debromination of some of these PBDE congeners, or the fact that they are used as a food source.

The higher percentage of sand particle (Unilag Lagoon front and Makoko) and clay particles (Oworonshoki) with a significantly higher TOC content in sediments collected from Unilag and Makoko stations compared to that of Oworonshoki could be explained from the perspective of Hale *et al.* (2003). The authors reported that PBDE concentrations in sediments appeared to be a function of sediment organic carbon content. There was a strong positive correlation between the concentration of ∑PBDEs in sediments and the percentage of silt and clay particles. Rayne *et al.* (2003) proposed that PBDE congener concentration is expected to occur among sediment with smaller grains, being improved by the contribution of higher brominated congeners. TOC and ∑PBDEs concentration were also positively correlated, as the concentration of TOC increased with decreasing grain size due to the increase in surface area to volume ratio (Hedges and Keil, 1995). This also explains the positive correlation between TOC and smaller grain fractions such as clay and silt. The contaminants were detected in all the samples collected in concentrations above FEQGs. Additionally, there was a strong correlation between the percentage of smaller particles in sediments and the concentration of ∑PBDEs. The dominant PBDE congeners in sediments and Oyster's samples within the sampling locations was BDE 28. However, 28 BDE and 47 BDE congeners appeared to bioaccumulate and appeared to be environmentally persistent, as indicated by their

detection in sediments and oysters over spatial and temporal conditions.

These results suggested that occurrence and bioaccumulation level of PBDEs in sediment and Oyster's tissue respectively could reflect the contamination levels of benthic sediment are useful bioindicators of pollution in the environment. Additionally, being an edible animal, bioaccumulated pollutants could be harmful in the food web. Therefore, *C. tulipa* could be a useful bioindicator to identify pollution by hydrophobic chemicals, such as PBDEs.

Conclusion

This study provided findings on the concentration of PBDEs present in sediments and Oysters within selected sampling stations. The study provides information on the occurrence and environmental distribution of PBDEs in Oyster and sediment within selected Lagos Lagoon. It will also contribute to the global inventory and pave way for adequate risk assessment where necessary. This will go a long way to augment the efforts of Nigeria's environmental protection agencies towards the minimization of PBDEs in line with the Stockholm Convention**.**

Acknowledgements

The authors are grateful to Dr M. N. Ezikpe for editing the write up and for providing technical support.

Reference

Adewuyi, G.O. and Adeleye, A. O. (2013). Evaluation of Polybrominated Diphenyl Ethers in Sediment of Lagos Lagoon, Nigeria. *Afr. J. Environ. Sci Technol*. 7(7): 686-693.

Ayoola, O. A. (2016*).* Comparative Toxicity of Three Petroleum Products against Benthic Macroinvertebrate *Clibanarius africanus* of Lagos Lagoon. *J Sci Res Rep*. 9(2): 1-9.

Bezares-Cruz, J., Jafvert, C.T. and Hua, I. (2004). Solar photodecomposition of decabromodiphenyl ether: products and quantum yield. *Environ. Sci. Technol*. 38: 4149 - 4156.

Bodin, N., Abarnou, A., Fraisse, D., Defour, S., Loizeau, V., Le Guellec, A. and Philippon, X. (2007). PCB, PCDD/F and PBDE levels and profiles in crustaceans from the coastal waters of Brittany and Normandy (France). *Mar Pollut Bull***.** 54: 657-668.

Darnerud, P. O., Eriksen, G. S., Jóhannesson, T., Larsen, P. B. and Viluksela. M. (2001). Polybrominated diphenyl ethers: occurrence, dietary exposure, and Toxicology. *Environ Health Perspect.* 109 (suppl 1): 49–68.

Ellis-Hutchings, R. G., Cherr, G. N., Hanna, L. A. and Keen, C. L. (2006). Polybrominated diphenyl ether (PBDE)-induced alterations in vitamin A and thyroid hormone concentrations in the rat during lactation and early postnatal development. *Toxicol Appl Pharmacol.* 215**:** 135-145.

Environment Canada (2006). Canadian Environmental Protection Act, 1999 Ecological Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). 34 pp.

Fang, M., Choi, S., Baek, S., Jin, G. and Chang, Y. (2012). Deposition of Polychlorinated biphenyls and Polybrominated Diphenyl Ethers in the vicinity of a steel manufacturing plant. *Atmos. Environ.* 49: 206-211.

Fatoki, O.S. and Awofolu, R.O. (2003). Methods for selective determination of persistent organochlorine pesticide residues in water and sediments by capillary gas chromatography and electron capture detection. *J. Chromatogr. A.* 983(1-2): 225–236.

FEQG (2013). Federal Environmental Quality. Guidelines Polybrominated Diphenyl Ethers *(*PBDEs) *CEPA. 1999.*

Hale, R.C., La Guardia, M. J., Harvey, E. P., Mainor, T. M., Duff, W. H. and Gaylor, M.O. (2003). Polybrominated diphenyl ether flame retardants in Virginia freshwater fishes (USA). *Environ Sci Technol.* 35: 4585-4591.

Hassanin, A., Breivik, K., Meijer, S.N., Steinnes, E., Thomas, G.O. and Jones, K.C. (2004). PBDEs in European background soils: levels and factors controlling their distribution. *Environ Sci Technol.* 38: 738-745.

Jiang, J.J., Lee, C.L., Fang, M.D., Ko, F.C. and Baker, J. E. (2011). Polybrominated diphenyl ethers and polychlorinated biphenyls in sediments of southwest Taiwan: regional characteristics and potential sources. *Mar Pollut Bull.* 62: 815-823.

Kang, Y. S., Yamamuro, M., Masunaga, S. and Nakanishi, J. (2002). Specific biomagnification of polychlorinated dibenzo-p-dioxins and dibenzofuransin tufted ducks (*Aythya f uligula*), common cormorants (*Phalacrocorax carbo*) and their prey from Lake Shinji, Japan. *Chemosphere*. 46: 1373−1382.

La Guardia, M. J., Hale, R. C. and Harvey, E. (2007). Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from wastewater receiving stream. *Environ Sci Technol.* 41 (19): 6663−6670.

Leung, A. O. W., Luksemburg, W.J., Wong, A.S. and Wong, M.H. (2007). Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China. *Environ Sci Technol.* 41: 2730-2737.

Li, Q. Z., Yan, C. Z., Luo, Z .X. and Zhang, X. (2010). Occurrence and levels of polybrominated diphenyl ethers (PBDEs) in recent sediments and marine organisms from Xiamen offshore areas, China. *Mar Pollut Bull.* 60: 464-469.

Mai, B. X., Chen, S. J., Luo, X. J., Chen, L.G., Yang, Q.S., Sheng, G.Y., Peng, P.G., Fu, J.M. and Zeng, E.Y. (2005). Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ Sci Technol*. 39: 3521-3527.

Martin, P. A., Mayne, G. J., Bursian, F. S., Tomy, G., Palace, V., Pekarik, C. and Smits. J. (2007). Immunotoxicity of the commercial polybrominateddiphenyl ether mixture De-71 in ranch mink (M*ustelavison*). *Environ Toxicol Chem.* 26 (5): 988–997.

Negreira, N., Cobas, J. and Carro, N. (2015). Optimization of Soxtec Extraction Procedure for Determination of Polybrominated diphenyl ethers in bivalve mollusc. *J Anal Chem.* 70(7): 804–813.

Oros, D. R., Hoover, D., Rodigari, F., Crane, D. and Sericano, J. (2005). Levels and distribution of polybrominated diphenyl ethers in water, surface sediments, and bivalves from the San Francisco Estuary. *Environ Sci Technol.* 39: 33–41.

Pan, X. H., Tang, J. H., Li, J., Guo, Z. G. and Zhang, G. (2010). Levels and distributions of PBDEs and PCBs in sediments of the Bohai Sea, North China. *J Environ Monit.* 12 (6): 1234-1241.

Ramu, K., Isobe, T., Takahashi, S., Kim, E.Y., Min, B.Y., We, S.U., Tanabe, S. (2010). Spatial distribution of polybrominated diphenyl ethers and hexabromocyclododecanes in sediments from coastal waters of Korea. *Chemosphere*. 79: 713-719.

Ramu, K., Kajiwara, N., Isobe, T., Takahashi, S., Kim, E.Y., Min, B.Y. and We, S.U. and Tanabe, S. (2007). Spatial distribution and accumulation of brominated flameretardants, polychlorinated biphenyls and organochlorine pesticides in blue mussels (*Mytilus edulis*) from coastal waters of Korea. *Environ Pollut.* 148: 562–569.

Rayne, S., M. G. Ikonomou M. G. and Antcliffe B. (2003). Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. *Environ Sci Technol*. 37: 2847–2854.

Sericano, J.L., Wade, T. L., Brookes, J. M., (2003). Accumulation and depuration of organic contaminants by the American oyster (*Crassostrea virginica). Sci Total Environ.* 179: 149–160.

Song, W., Li, A., Ford, J. C., Sturchio, N. C., Rockne, K. J., Buckley, D. R. and Mills, W. J. (2005). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environ Sci Technol.* 39 (10): 3474-3479.

USEPA (U.S. Environmental Protection Agency). (2008). Emerging contaminants – polybrominateddiphenyl ethers (PBDE) and polybrominated biphenyls (PBB). Available at: http://www.epa.gov/tio/download/contaminantfocus/epa542f07007.

Wang, Z.Y., Zeng, X. L. and Zhai, Z. C. (2005). Prediction of supercooled liquid vapor pressures and n-octanol/air partition coefficients for Polybrominated Diphenyl Ethers by means of molecular descriptors from DFT method. *Sci Total Environ.* 389: 296-305.