ABSTRACT

Aims: This study is aimed at determining the concentration of two widely used BFRs; Decabromodiphenyl Ether (BDE-209) and Tetrabromo Bisphenol-A (TBBPA) in sediment and leachate samples.

Place and Duration of Study: Field sampling were carried out from five major dumpsites around Warri Municipality, Delta State, Nigeria. Analyte extraction was done in 2017 at the Science laboratory, Federal University of Petroleum Resources, Effurun Delta State, Nigeria and quantification done in Switzerland by Bachema Analytical Laboratories in 2017.
1. INTRODUCTION

Brominated flame-retardants (BFRs) are compounds of bromine that are incorporated into flammable products to prevent or restrain fire. Brominated flame-retardants (BFR) are widely used in combustible materials due to facts that bromine is abundant; having a high performance with regards to ignition inhibition and is cost-effective [1]. The widely used BFR’s includes; Tetrabromobisphenol-A (TBBPA), Dibromophenols (2,4- and 2,6 DBP), Hexa-bromo-cyclo-dodecane (HBCDD) and Polybrominated diphenyl ethers (PBDEs). BFRs are used in commercial products such as electrical components, furniture, textile and plastics [2]. BFRs pose a serious threat to the environment and biota, due to their persistent nature in the environment, bioaccumulation and bio magnification properties [3,4], with different research raising concerns over the health impacts of the BFRs, they have been included in the Persistent Organic Pollutants (POPs) list from Stockholm Convention of 2009. An article by the European commission in 2006 holds that the use of BFRs greater than 0.1% by weight should be banned. Yet, the impact on the environment and biota have not been avoided because as of 2011 over 390,000 tons of products with brominated flame-retardants are already in use [5]. BFRs are introduced into the environment when consumer products including; textiles, plastics and electronics are incinerated in the open dumpsite when they are no longer fit for their intended use [6,7].

An increase in the molecular mass of organic compound results in increased sorption coefficient (Koc) and thus, preventing accumulation in the groundwater and leaching due to the attachment of the organics to the soil carbon [8]. Thus, groundwater has a lower possibility of being affected by BFRs because they are organobromine compounds. Literature study showed the exposure of humans to BFRs to be through ingestion of food, inhalation and Dermal contact [9]. Further study showed BFRs in the human system can affect neurological development [10], cause cytotoxicity [11], endocrine disruption [12] and carcinogenic effects [13]. There is not enough data to conclude any significant effects resulting from exposure of humans to TBBPA but when the impact was analysed on rats, it was said to be sexually dimorphic, as the male rats experienced behavioural changes at concentrations above 0.1mg/kg [14]. BFRs are released into the environment when products containing them are incinerated in open space to recover useful metals and reduce the waste size [14] and this is the predominant form of waste management in Nigeria. Approximately 32 million tons of waste is generated per year in Nigeria [15].

Increase in BFR contaminated waste in developing countries is due to import of waste from developed countries and with only a part of this being recycled, majority of these waste products are incinerated at the dumpsite [16]. Thus, BFRs are emerging pollutant in these countries, requiring regular monitoring because

Methods: Three soil samples were collected from each site 15cm from the soil surface. Also, three leachate samples from three different trial pits done for each site. Collected soil samples were stored in glass bottles and labelled. While the leachate samples are stored using glass containers and labelled. The BFRs were extracted using Aceton and cyclohexane for each soil matrix and cyclohexane for the leachate samples, then the extract was analysed using GC coupled with an ECD supplied by Thermo Trace GC Ultra, Italy.

Results: The results showed the average concentration for TBBPA in the sediments was 0.0234 g/kg and that of the BDE-209 was recorded as 0.1828 g/kg. Results from the leachate sample were below the detectable range of the analytical equipment, TBBPA (0.02 g/kg) and BDE (0.1 g/kg). There is no statistical difference between the mean concentration of TBBPA for the sediment in each of the locations (P>.05) and no difference (P>.05) for BDE-209 for the sediment in each of the locations (P>.05).

Conclusion: Findings from this study holds that the concentration of TBBPA and BDE-209 in sediment is higher when compared with concentrations presented in other literatures studied in this report and this calls for immediate action due to the health risk associated with exposure in these municipalities.

Keywords: Sediment; leachate; decabromodiphenyl ether (BDE-209); tetrabromobisphenol-A (TBBPA).
of its toxic effects. The concentrations of PBDE has previously been reported as 0.000303 g/kg [6] but there is no much information on the concentration of TBBPA in the environment in Nigeria and the study seeks to address this drawback.

The main objectives of this study therefore are:

1. Determine the concentration of BFRs: Decabromodiphenyl Ether (BDE-209) and tetrabromobisphenol-A (TBBPA) in the dumpsite around Warri metropolis using quantitative analytical methods.
2. Use statistics to show that there is no relationship between concentrations of the two BFRs in the soil.

2. MATERIALS AND METHODS

2.1 Study Area and Sample Collection

A total of three (3) sediment and three (3) leachate samples were collected from each of the five government approved dumpsites around Warri metropolis in southern Nigeria (Fig 1); Agbarho (latitude:5\(^\circ\)36'33.918"N, longitude:5\(^\circ\)52'57.09"E)

Osubi (latitude:5\(^\circ\)34'3.918"N, longitude:5\(^\circ\)48'5.838"E)

Nigercat (latitude:5\(^\circ\)34'30.474"N, longitude:5\(^\circ\)44'53.52"E)

DSC (latitude:5\(^\circ\)34'22.332"N, longitude:5\(^\circ\)44'28.914"E)

Orhuworun (latitude:5\(^\circ\)50'1.944"E, longitude:5\(^\circ\)34'39.12"N).

Based on local information, the waste in these sites were not solely generated in these communities as other waste materials were transported from adjoining towns by the PSP (Private Sector Partnership) collection trucks. Sample collection points were selected strategically for each location based on the topography and the period of use. Soil samples were collected after the surface litter, mainly dead plant and leaves has been carefully removed at a 15cm depth using a clean auger, and stored directly into clean glass sampling bottles and labelled. Samples were taken to the laboratory for analysis preparation on the same day of collection. For the leachate samples to be taken, three (3) holes were dug in each location and then covered for 5 days and there after the samples were taken using a 1 liter glass container, sealed, labelled and taken to the laboratory for the purpose of analysis.

![Map showing the locations in the dumpsites investigated in the warri metropolis in Delta state, Nigeria](image)
The estimated waste generation in Nigeria per person is 0.65–0.95 kg/day [17]. The population for this study area has been estimated as; Okpe (128,398), Uvwie (188,728), Udu (142,480) by the National Population Commission of Nigeria [18]. Literature studies have shown that not all waste generated by the population are collected and taken to the dumpsite [17]. For each of the locations the main activities in the dumpsite were scavenging for recyclables including; metal scraps, plastics and electronic parts, which are then sold to recycling industries in the country while the others are burnt daily in the open, resulting in release of pollutants to the atmosphere.

2.2 Extraction of BFRs from Sediment samples

Soxhlet solid/liquid continues extraction for organics from air-dried sediment sample was carried out using the Soxhlet process [19,20,21]. For this study, the process included a 10 g of the soil mixed with 5 g of sodium sulphate to absorb the excess water. A filter paper containing the sample mixture was inserted into the Soxhlet extraction apparatus just below the condenser. Then, approximately 100 mL mixture of Cyclohexane and Aceton (1:1, v/v) was added before heating for 15 hours. Finally, aliquot extract were stored using a 10 ml vials with septum seal (Silicon/PTFE). Sample weight is 5 g in 100 ml Cyclohexane Extract.

2.3 Extraction of BFRs from Leachate Samples

A subsample (0.5 L) of 1 L was weighed into a calibrated Erlenmeyer flask of 1 L. To this is added 1 ml Cyclohexane internal Standard solution and then 9ml Cyclohexane. With the aid of a glass-coated magnet, the sample was then liquid/liquid intensively extracted for an hour. Using an upward delivery glass separating funnel, the solvent extract was then isolated in 10 ml vials. Sample volume is 0.5 L in 10 ml Cyclohexane Extract.

2.4 Blank Sample

This is done by the injection of the extracted blank at the beginning of all analytical series. A 10 g sea-sand sample and 1 L Osmose water treated exactly same as sample including exposure to all glassware, equipment and solvents. It is obligatory to run a blank sample alongside every sample series to prove and control the extraction process and the instrument for contaminations (European/German Norm DIN EN 62321).

2.5 Clean-up of Glassware and Reagent

Exhaustive clean-up of reagents and glassware was carried out to eliminate background signals that are not derived from the sample. Glassware was scrupulously cleaned. All glassware was clean as soon as possible after use by thoroughly rinsing with the last solvent used followed by washing with hot water and detergent and thoroughly rinsed with tap and reagent water. Dry and heat in an oven or muffle furnace at 400°C for one hour. The volumetric glassware was not heated. Thorough rinsing with Acetone was used to substitute for the heating. After cooling, the glassware was sealed with aluminium foil and stored in a clean environment to prevent accumulation of dust and other contaminants. The use of high purity reagents and solvents helped to minimize interferences observed during the analysis of BFRs. Purification of solvents by distillation in an all glass system was done. It is of necessity to note that matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary from source to source, dependent upon the nature and diversity of the samples.

Table 1. Waste composition in dumpsites in Delta State, Nigeria [22]

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>18</td>
</tr>
<tr>
<td>Metals</td>
<td>10</td>
</tr>
<tr>
<td>Plastics</td>
<td>21</td>
</tr>
<tr>
<td>Vegetative Materials</td>
<td>37</td>
</tr>
<tr>
<td>Ceramics</td>
<td>6</td>
</tr>
<tr>
<td>Textile Materials</td>
<td>5</td>
</tr>
<tr>
<td>Others</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 2. Limit of quantification for PBDEs

<table>
<thead>
<tr>
<th>Flame Retardant and Class</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE (47,99,100,153,154,183 and 197)</td>
<td>0.02 g/kg</td>
</tr>
<tr>
<td>DeBB (TBBPA)</td>
<td>0.02 g/kg</td>
</tr>
<tr>
<td>BDE (28 and 209)</td>
<td>0.1 g/kg</td>
</tr>
<tr>
<td>HBCD</td>
<td>0.2 g/kg</td>
</tr>
</tbody>
</table>

2.6 Analysis using GC-ECD

The Extract is then concentrated with nitrogen stream or compressed air to almost dryness for exchange to toluene. The Toluene extract is then diluted and derivatised using 4,4'-Dibromooccafluorobiphenyl (DBOFB). The derivatised extract is then injected splitless into the GC and separated using a column (HP-1 Agilent :10m x 0.25mm x 0.1µm) with an oven temperature program (100°C, Hold 3 min., Rate 20°C/min., 320°C. Hold 3 min., Cool.) then detected according to retention time with the aid of an electron capture detector (ECD). The calibration of the analyte and the Surrogates was done using a linear or quadratic curve over the peak areas in ng / ml. The calibration was done with 1,11-Dibromundecane as an internal standard (ISTD). The limit of quantification according to the analytical method used follows: Bachema method and standard operating procedure (SOP) Flame retardants in Soil and Electronic waste using GC-ECD as modified from the European/German Norm DIN EN 62321 [23].

2.7 Quality Control

As a routine measure, spiking using surrogate recovery percentage in each sample to get information on losses of analyte from the extraction step through to analysis. However, no single PBDE can be a representative of all of the flame-retardants being determined and thus recovery correction was performed with caution. Blank correction was carried out for all samples using a robust method based on a blank known to be representative of a batch of samples. The methodology adopted in this study for PBDEs in soil is in line with European/German Norm DIN EN 62321 [23].

2.8 Data Analysis

Data were sorted and analysed using the R statistical software. Descriptive statistics of the data set was presented using Mean, Minimum, Maximum and Standard deviation. The unit for final results is given in g/kg. The statistical tests carried out includes a Pearson’s correlation test and a one-way ANOVA, after the homogeneity of the variance was verified. Data visualisation were presented using Bar chart, Box plot and a scatter plot. All the graphs were done using ‘R’.

3. RESULTS

3.1 Results for the Sediment

Fifteen (15) samples were analysed and the summary of the concentrations of Tetrabromobisphenol-A (TBBPA) and Decabromodiphenyl Ether (BDE-209) are presented in the Table 3 and Table 4 below and the results show that for each of the locations the concentration for each of the BFRs differs. Based on observations it can be said that the concentrations of BDE-209 is greater than TBBPA [24] in all the other locations apart from Osubi which could not be ascertained due to the concentration being less than detectable range of the GC-ECD (TBBPA <0.02 g/kg and BDE<0.1 g/kg).

Table 3. Concentration of Tetrabromobisphenol-A (TBBPA) from the five (5) locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Mean Result (TBBPA), [g/kg]</th>
<th>Minimum [g/kg]</th>
<th>Maximum [g/kg]</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agbarho</td>
<td>0.0393</td>
<td>0.03</td>
<td>0.06</td>
<td>0.017</td>
</tr>
<tr>
<td>Osuibi</td>
<td>0.0000</td>
<td>0.00</td>
<td>0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>Nigercat</td>
<td>0.0237</td>
<td>0.01</td>
<td>0.05</td>
<td>0.024</td>
</tr>
<tr>
<td>DSC</td>
<td>0.0373</td>
<td>0.00</td>
<td>0.07</td>
<td>0.034</td>
</tr>
<tr>
<td>Orhuworun</td>
<td>0.0170</td>
<td>0.01</td>
<td>0.02</td>
<td>0.004</td>
</tr>
</tbody>
</table>
Table 4. Concentration of decabromodiphenyl Ether (BDE-209) from the five (5) locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Mean Result (BDE-209) [g/kg]</th>
<th>Minimum [g/kg]</th>
<th>Maximum [g/kg]</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agbarho</td>
<td>0.0590</td>
<td>0.00</td>
<td>0.10</td>
<td>0.052</td>
</tr>
<tr>
<td>Osubi</td>
<td>0.0000</td>
<td>0.00</td>
<td>0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>Nigercat</td>
<td>0.4183</td>
<td>0.22</td>
<td>0.73</td>
<td>0.276</td>
</tr>
<tr>
<td>DSC</td>
<td>0.1650</td>
<td>0.00</td>
<td>0.38</td>
<td>0.195</td>
</tr>
<tr>
<td>Orhuworun</td>
<td>0.2717</td>
<td>0.21</td>
<td>0.37</td>
<td>0.083</td>
</tr>
</tbody>
</table>

From the results of the Analysis of variance for the different locations, even though the mean value for each of the location differs, the output shows that there exists no statistical difference between the mean concentrations of TBBPA for each location ($P > .05$) and likewise no difference for the mean concentration for BDE-209 ($P > .05$). An indication that the same effect can take place in all the locations since there is no significant difference in the concentration.

![Boxplot](image1)

**Fig. 2.** Boxplots showing the median concentration of BFRs in each location: (a) Median concentration of BDE-209 for each of the locations as well as the 25th and 75th percentiles, and the range (b) Median concentration of TBBPA for each of the locations as well as the 25 and 75 percentiles, and the range of values.
3.2 Relationship between BDE-209 and TBBPA

The results from the Pearson correlation test between the concentration of TBBPA and BDE-209 shows that there exists no linear relationship between the two types of flame retardants ($R^2=0.3879$, $P$-value = 0.15, $n=15$). This implies that neither of the two BFRs has an influence on the other, which is a confirmation of the null hypothesis as stated in the objective of this study.

3.3 Results for the Leachate

The concentration of Brominated flame retardant (BFR’s); decabromodiphenyl ether (BDE-209) and tetrabromobisphenol-A (TBBPA) extracted from leachate samples collected from five major dumpsites in Warri metropolis was found to be less than the limit of detection (LOD) of 0.1 g/kg and 0.02 g/kg respectively which made them undetectable using the GC-ECD analytical technique. Furthermore, there are also general scientific notions and research findings that analysis of TBBPA in water will yield no results because they are lipophilic and have a poor water solubility [25]. Based on these I would say theoretically the same can be said for the BDE-209 concentration in leachate samples.

4. DISCUSSION

From the results of this study carried out using a total of 15 samples from five different locations in Warri metropolis, both BDE-209 and TBBPA were detected in each site as a result of open incineration carried out as a form of waste management in Nigeria [7]. The statistical results also show no relationship between these compounds. Surprisingly the concentration of BDE-209 and TBBPA in the sediment in Osubi location was recorded <0.1 g/kg and 0.2 g/kg respectively. This could be because the site was newly opened and there has been no open burning of waste in this location. Ultraviolet light is said to be a major cause of proliferation of BDE-209 and TBBPA in the environment [14], but this study presents a contrary view. Based on the results from the analysis, it was noted that the concentration of BDE-209 is above the TBBPA concentration in the soil and this is because the TBBPA is more volatile, having the capacity to bind to suspended particles or dust in the atmosphere [26]. Comparing the results from different literature in Nigeria [16,6], the concentration is noted to be higher which is an indication that not much has been done with regards to recycling and the waste generation that has increased compared to previous years. Apart from the acute health challenges associated with exposure of humans to these compounds, recent studies carried out in the NYU Grossman School of medicine in 2019 notes that not only lead (Pb) has an impact on the IQ of children but also based on their findings the same impacts resulted from exposure to flame retardants with the bromine additive. The daily exposure limit for TBBPA recommended by the UK for the environment is set as 0.0001g/kg per day [27] and the results obtained from this
Fig. 4. The diagram above is a scatter plot showing the relationship between BDE-209 and TBBPA.

report shows the mean concentration of TBBPA to be 0.023 g/kg, which is an indication that the environment has been heavily contaminated. There is no set limit for the concentration of BDE-209 because it has been banned in many countries but the results from this study show its dominance in our environment.

5. CONCLUSION

Considering the poor waste management system and the rapid generation of waste in Nigeria, the concentration of PBDEs in the environment has increased significantly. Although, there is almost a zero percent chance for groundwater contamination due to dumpsite incineration, other exposure routes must be addressed, otherwise the health of people around these locations will start deprecating as the concentrations of BFRs in the environment continue to increase with continuous open incineration. This study has reports for the concentration of BFRs in the year 2018.

7. RECOMMENDATIONS

Dumpsites in Nigeria should be surrounded with protective walls to limit or rather control human access to these sites. If incineration becomes the only available option for us as a country, then proper technology should be put in all the government approved dumpsite so the refuse can be incinerated, and the gases trapped as biogas for alternative energy source. This will reduce attenuation through volatilisation and same time help reduce our country CO₂ emission. Furthermore, we advise that government should fund more research in this area of waste management for monitoring purpose in other to reach more informed decisions.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES


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