Assessment of pollution potentials and chemical interaction of polybrominated diphenyl ethers on soil and bitter leaf around dumpsite in Abraka, Nigeria.

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ABSTRACT

Background: This study was carried out in order to evaluate the pollution potential and chemical interaction levels of PBDEs congeners in relation to positive or negative reactions in soil and bitter leaf around e-waste dump site.
Method: The soil and plant samples around e-waste dumpsite were evaluated via integration after ultrasonic extraction with the use of ultra-sonication and the quantification of the individual persistent organic pollutants, for each sample with the aid of gas chromatography. The statistical analysis was conducted using window 10 version Microsoft.
Result: The results showed that positive pollution potential were high up to 5.250 at depth 20 – 30 cm (BDE- 25). Below detectable pollution potential and chemical interaction was detected for soil, leaf and root across months. The total BDE congeners for studied soil ranged from 29.84 – 3,049.34 ng/g and that for control and impacted plant ranged from 12.48 – 99.21 ng/g. The concentration of PBDEs across depth showed no definite trends, but there was a significant difference when the control and studied soil were compared. The pollution potential and chemical interaction of control and plant around e-waste showed no remarkable difference. The positive pollution potential and chemical interaction were dominated at the lower polybrominated diphenyl ethers congener than the higher congeners.

Keywords: Pollution potential, chemical interaction, e-waste, PBDEs, bitter leaf, soil.

1. INTRODUCTION
Polybrominated diphenyl ethers (PBDEs) along with other halogenated compounds are grouped among the persistent and bio accumulative organic compound known to be major pollutant in our environment. They are used as additive brominated flame retardants (BFRs) in many products used in our homes such as electronic equipment, plastics, textiles, etc [1]. PBDEs in some of these product amount to about 5% to 30% by weight [2]. Their production annually is about 67,125 metric tons (13% Penta-, 5.7% octa- and 82% deca- PBDEs) [2,3]. The commercial availability of PBDEs is in three technical combinations as penta-, octa- and deca- PBDEs, which are not only pure mixture of the above combination, but still contain either high or low quantities of brominated congeners [2]. Soil is a major depot for the deposition of e-waste, specifically Nigeria soil is a major dumping ground of e-waste from the neighboring countries in a significant amount. PBDEs deposited on land from e-waste dumping activities may enter into the food chain through plant uptake and serve as a potential health risk [4]. They can accumulate easily in the body fat, thereby leading to serious effects on neural development disruption in endocrine function. Therefore, it is important to assess the pollution potential and chemical interaction of PBDEs in the soil contaminated with e-waste dumping activities. So far there are none or little studies that dealt with the pollution potential and chemical interaction of PBDEs in soil due to e-waste dumping activities. According to [5, 6], PBDEs in soil can be taken up by plant. The major constituent in PBDEs generation are limited to Penta-, Octa- Deca- PBDEs [4,7], PBDEs degradation in environment can lead to lower brominated isomers that might serve as a source of abundant of PBDEs in our environment. Electronic waste (e-waste) can be described as obsolete electrical and electronic equipment found in our environment as a result of indiscriminate dumping. This has become a major environmental issue particularly in developing country like Nigeria.

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The risk of e-waste to human generally and our environment steeply rises with inability to guide against our health, safety and all the methods employed by humans to pollute the environment with e-waste, such as improper recycling, illegal dumping, roasting, burning, dismantling e.t.c. This inability to monitor the dumping activities of this e-waste have led to the release of different hazardous substances like flame retardants, nickel (Ni), lead (Pb), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) e.t.c, into our environment, of which PBDEs is of a major concern, due to the substantial level of flame retardants generated from it [4,8]. Studies have shown that plants influence the action of persistent organic pollutants in soil and promote the degradation of PBDEs in soils [6]. Chlorlfluorocarbon (CFCs), perfluorctane sulfonates (PFOS), polychlorinated (or brominated) diphenyl ethers (PCDEs/PBDEs), polychlorinated (or brominated) biphenyls (PCBs/PBBs), polyvinyl chloride (PVC) and tetrabromo bisphenol-A (TBBPA) are the major hazardous flame retardants and halogenated hydrocarbons that are present in e-waste. PBDEs are considered toxic to human due to their structural similarity to PBBs that has been classified as group 2A, which are probably carcinogenic to humans. Negligent to the control of e-waste dismantling and dumping activities and even treatment might lead to leaching of PBDEs which may linger into serious soil pollution [4,9]. Long term residing of pollutants in the human body can damage different systems, such as respiratory system, endocrine system, reproductive system and nervous system with a genetic toxicity, e.g lead that accumulate in the body for a long time can affect the digestive system, long term accumulation of cadmium can affect damage organ like kidney and liver, with apparent chronic toxicity. This study aimed to present the pollution potential and chemical interaction of PBDEs on soil contaminated with e-waste by applying an integral equation to the environment receiving the pollution.

1.1 Theory

According to [10], but in modified form. When a reactive compound from e-waste material A_g generate a change in an environment where it was found, i.e the sample of soil B_g. The Pollution potential (γ) of A and B depends on the concentration of [A] deposited on soil, the amount of B used for analysis and the chemical interaction of A and B (σ_{AB}). The pollution potential of A on B display the extent to which A can cause change in physicochemical properties of B.

Considering the above analogy,

$$dB= \int ([A], 1/M_B, \sigma_{AB}) \text{----------------------------}(1)$$

The applicable derivatives is the rate of change of B with change in concentration of [A], which can be defined as

$$\frac{dB}{dA} = \ln\frac{\Delta B}{\Delta A} \text{ --------------------------------------}(2)$$
$$\text{As } \Delta A = 0$$

When a positive derivative is observed, the amount of B function increase with the amount of A and when a negative derivative is noticed, the amount of B function decreases as A increases. Putting this into consideration, A therefore is an independent variable and B is the dependent variable.

$$\frac{dB}{dA} = \frac{dB}{dA} \text{ --}(3)$$

Rewriting equation (3) ,

$$dB = \frac{dB}{dA}. dA\text{----------------------------------}(4)$$

This equation shows that as B varies in values, dB is equal to the rate of change with respect to A, dB/dA, multiplied by dA, the change in A. An integration of A gives a finite change from A_1 to A_2, and also an integration of B to obtained a total change of B.

$$\int_{B_1}^{B_2} dB = \int_{A_1}^{A_2} \frac{dB}{dA} . dA \text{ --------------------------------------}(5)$$

$$B_2 - B_1 = \int_{A_1}^{A_2} B'[A] dA\text{------------------------------------}(6)$$

where B_2 and B_1 are the concentration of B obtained in the analysis corresponding to [A] deposited.
Resulting from this equation,

$$\gamma = \frac{dB}{[A]} = \sigma_{AB}.\frac{1}{M_B}\text{--}(7)$$

where dB is a change in physicochemical properties of B, W_B is the weight of polluted soil used for the analysis. The negative sign display a negative influence of A to reduce the quality of the soil, σ_{AB} is the chemical interaction parameter of A and B. Therefore γ display the capacity of A to reduce or affects the quality of the recipient soil. Rewriting equation (7), gives

$$\frac{dB}{1/M_B} \; \sigma_{AB} \;.[A] \text{---}(8)$$

$$dB.M_B = - \; \sigma_{AB} \;.[A]$$
$$M_B \,(B_2 - B_1) - \sigma_{AB} \;.[A]$$

$$\frac{B_2 - B_1}{[A]} = -\frac{\sigma_{AB}}{M_B} \text{--} (9)$$

$$\gamma = \frac{-(B_2 - B_1)}{[A]} = \frac{B_1 - B_2}{[A]} \; \sigma_{AB} \; (1/M_B)\text{------------------------------}(10)$$

δ_{AB} may be however obtained as the product of the pollution potential and the weight of the recipient soil used for the analysis ie $\sigma_{AB} = \gamma W_B$.

2. MATERIALS AND METHODS
2.1 Materials

2.1.1 Description of the Study Area:
Abraka is a University town which is one of the most popular towns in Ethiope East Local Government Area of Delta State, Nigeria. The town is bounded at the north by Obiaruku, at the south by Salubi in Eku. Abraka has low topography, the study area has a geographical location of Latitude $06.23'01\;45^0$ N and Longitude $007.73'09$ 80^0 E.

Figure 1 : Map showing the study sampling site.

Figure 2: E-waste dump site in Abraka.

2.2 Methods

2.2.1 Soil and Plant Sampling and preparation:
Soil and plant samples were collected from electronic waste dumpsite in the months of May and June, the dumpsite consists of television sets, DVD player, printed circuit boards, tape recorders and stabilizers, other electronic items from electronics workshop amounting to about 131kg and a controlled soil from a piece of land void of pollution with e-waste. The soils were taken from six different spots at three different depths (0 -10 cm, 10 – 20 cm and 20 – 30 cm) to form a composite sample of three each on both sites making a total of six samples. The soil were collected with soil auger into a black polythene bag in ice pack, properly labelled and conveyed into the laboratory immediately. The plant samples (leaf and root) were also collected and conveyed to the laboratory for further analysis. Both control soil and plant were taken from a remote area far away from the dump site. The soil samples were ground and sieved with 2 mm mesh, kept in a polythene bag prior to extraction. After the harvesting of the plant samples, they were thoroughly wash with tap water and rinsed with distilled water. Thereafter, they were cut into smaller particle and dry via freeze drying at 50°C for 48 hours and then pulverized into a fine powder ready for extraction.

2.2.2 Extraction and Clean-up of POPs from samples:
The soil and plant samples were prepared for analysis following the US EPA-3550C-ultrasonic extraction method [5,11] with little modification. A mass of 10.0 g of the soil and plant samples was mixed with same amount of Na_2SO_4. The resulting material was extracted by ultrasonication with 50 ml of hexane/dichloromethane (DCM) (1:1 v/v) at 30 °C for 30 minutes. The contents were filtered and the process was repeated three times by sonication of the residue with a fresh mixture of acetone/dichloromethane each time. The extracts were evaporated to 1 mL by using a rotary evaporator and purified by solid phase extractions with 2 g of aluminium oxide (5 % deactivated lower part). The POPs were subsequently eluted with 15 mL of hexane, 15 mL hexane and dichloromethane (9:1) and 20 mL of hexane and dichloromethane (4:1). The eluted fractions were combined and evaporated to approximately 0.5 mL using stream of nitrogen gas.

2.2.3 Gas Chromatographic Analysis:
The individual POPs was quantified using gas chromatography (Agilent 6890 Agilent Andante USA) equipped mass spectrometry. Seseparation was effected on a HP5 (cross-linked PHME siloxane) column with (0.25 µm film thickness and dimensions of 0.25 mm x 30 m). The carrier gas was helium with a linear flow rate of 30 cm/s. The mass spectrometer was operated in electron impact mode (70 eV). The column temperature was programmed at a rate 25 °C/min from initial temperature of 60 °C to a temperature of 180 °C (1- min hold), then at 3 °C/min to 280 °C (30 min hold). The injector, transfer line and ion source temperature were 280, 250 and 250 °C respectively.

The quantification was by the use of external calibrations which were obtained with POPs solutions at five concentration levels.

2.3 Statistical Analysis

The descriptive statistics of mean and standard deviation values were obtained via analysis with Microsoft Excel (Microsoft Inc.) and SPSS version 16.0 (SPSS Inc.).

3. RESULTS

The mean concentration of PBDEs congeners (BDE-I to BDE-209) for both control soil and soil around e-waste dumpsite, across depths and months are presented on Table 1.

Table 1: The mean concentrations of the detected PBDEs congeners of both control soil and soil around e-waste dumpsite.

Compounds	Control soil (mean±S.D)			Dumpsite May (mean±S.D)			June (mean±S.D)		
	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm
BDE-1	0.03±0.03	0.58 ± 1.22	0.48 ± 1.12	0.83 ± 1,41	0.67 ± 1.28	0.85 ± 1.23	133.94 ± 238.66	226.95 ± 293.21	238.18 ± 263.69
BDE-2	0.00±0.00	0.00 ± 0.00	0.00 ± 0.00	0.81 ± 1.43	0.65 ± 1.29	0.84 ± 1.24	9.35 ± 10.98	127.28 ± 263.86	108.45 ± 240.47
BDE-3	0.05 ± 0.11	2.21 ± 4.83	1.84 ± 4.41	13.51 ± 24.58	11.01 ± 22.00	14.20 ± 21.17	77.94 ± 140.84	102.06 ± 133.37	113.89 ± 122.76
BDE-7	0.06±0.12	2.53 ± 5.51	2.10 ± 5.04	9.93 ± 18.08	7.95 ± 16.28	10.32 ± 15.67	134.48 ± 231.66	347.32 ± 516.48	337.49 ± 462.58
BDE-8	1.59±2.91	1.26 ±2.61	1.64 ± 2.52	4.35 ± 7.94	3.48 ± 7.15	4.52 ± 6.89	25.36 ± 45.82	26.37 ± 39.75	31.35 ± 37.59
BDE-10	1.84±3.37	1.70 ± 2.93	2.10 ± 2.81	6.31 ± 11.62	5.05 ± 10.45	6.58 ± 10.07	36.18 ± 63.97	67.13 ± 88.63	69.12 ± 79.43
BDE-11	1.87±3.35	3.05 ± 3.92	3.23 ± 3.53	0.93 ± 1.68	0.74 ± 1.51	0.96 ± 1.46	35.95 ± 64.13	57.50 ± 73.53	61.10 ± 66.35
BDE-12	2.82±5.11	3.22 ± 4.51	3.73 ± 4.22	7.88 ± 14.25	6.30 ± 12.83	8.17 ± 12.35	246.00 ± 448.11	255.78 ± 388.69	304.69 ± 367.72
BDE-13	2.72±5.01	2.18 ± 4.51	2.84 ± 4.34	7.89 ± 14.36	6.31 ±12.93	8.19 ± 12.45	15.03 ± 24.80	57.53 ± 97.43	53.14 ± 87.81
BDE-15	2.74±4.99	3.01 ± 4.37	3.53 ± 4.11	27.97 ± 51.36	23.11 ± 45.78	29.73 ± 44.04	46.54 ± 82.36	89.31 ± 119.31	91.38 ±106.83
BDE-17	0.24±0.46	0.41 ± 0.56	0.35 ± 0.53	8.98 ± 16.44	7.19 ± 14.79	9.34 ± 14.25	18.50 ± 25.53	163.30 ± 324.53	141.64 ± 295.07
BDE-25	0.02±0.04	0.77 ± 1.69	0.64 ± 1.54	4.36 ± 7.86	4.68 ± 6.84	5.51 ± 6.45	12.27 ± 22.43	10.08 ± 20.03	12.98 ± 19.27
BDE-28	0.01±0.02	0.40 ± 0.87	0.33 ± 0.79	5.11 ± 9.35	4.08 ± 8.41	5.31 ± 8.10	18.30 ± 33,02	24.89 ± 32.18	27.51 ± 29.49
BDE-30	0.09±0.17	0.07 ± 0.15	0.09 ± 0.14	0.89 ± 1.49	0.65 ± 1.34	0.84 ± 1.29	0,90 ± 1.63	1.11 ± 1.49	1.26 ± 1.38
BDE-32	0.00±0.00	0.00 ± 0.00	0.00 ± 0.00	1.63 ± 3.00	1.30 ± 2.69	1.70 ± 2.60	68.95 ± 124.05	98.07 ± 125.62	107.15 ± 114.54
BDE-33	0.03±0.06	1.25 ± 2.73	1.04 ± 2.50	10.08 ± 18.52	8.07 ± 16.66	10.50 ± 14.05	4.03 ± 6.97	10.35 ± 15.36	10.07 ± 13.76
BDE-35	0.01±0.02	0.38 ± 0.82	0.31 ± 0.75	8.78 ± 16.02	7.25 ± 14.29	9.31 ± 13.74	202.71 ± 366.10	274.51 ± 355.38	3o3.73 ± 325.82
BDE-37	0.03±0.06	1.17 ± 2.55	0.97 ± 2.33	10.48 ± 19.18	9.34 ± 18.49	11.46 ± 16.23	15.85 ± 28.97	15.85 ± 25.09	19.12 ±23.82
BDE-47	0.02±0.04	0.77 ± 1.69	0.64 ± 1.54	11.29 ± 20.75	9.34 ± 18.49	12.01 ± 17.79	20.90 ± 22.36	357.52 ± 752.95	302.54 ± 686.80
BDE-49	1.85±3.36	2.43 ± 3.17	2.71 ± 2.92	6.84 ± 12.56	5.47 ± 11.30	7.12 ± 10.88	17.54 ± 31.46	27.15 ± 34.71	29.08 ± 31.40
BDE-66	0.01±0.00	0.38 ± 0.82	0.31 ± 0.75	5.23 ± 9.59	4.19 ± 8.63	5.44 ± 8.31	11.04 ± 12.49	158.82 ± 330.63	135.06 ± 301.40
BDE-71	0.75±1.37	0.80 ± 1.19	0.95 ± 1.12	2.01 ± 3.66	1.61 ± 3.30	2.09 ± 3.17	2.75 ± 5.00	3.22 ± 4.45	3.71 ± 4.16
BDE-75	4.21±7.73	3.68 ± 6.80	4.64 ± 6.53	10.37 ± 18.88	8.30 ± 16.99	10.77 ± 16.36	31.66 ± 50.99	141.97 ± 250.59	129.07 ± 226.35
BDE-77	0.56±0.74	0.45 ± 0.70	0.44 ± 0.62	4.64 ± 8.41	3.71 ± 7.57	4.81 ± 7.29	8.14 ± 14.89	8.01 ± 12.90	9.71 ± 12.27
BDE-85	0.11±0.16	3.46 ± 7.51	2.89 ± 6.86	4.95 ± 9.09	3.96 ± 8.17	5.15 ± 7.87	67.01 ± 114.87	191.54 ± 295.70	183.48 ± 265.21
BDE-99	0.17±0.32	0.14 ± 0.28	0.18 ± 0.27	0.83 ± 1.50	0.66 ± 1.35	0.86 ± 1.30	2.82 ± 3.18	44.57 ± 93.40	37.81 ± 85.16
BDE-100	0.23±0.34	1.09 ± 1.93	0.98 ± 1.75	0.42 ± 0.70	0.34 ± 0.64	0.43 ± 0.61	9.03 ± 10.53	130.05 ± 270.76	110.63 ± 246.80
BDE-116	0.36±0.66	0.29 ± 0.60	0.38 ± 0.57	4.33 ± 7.96	3.47 ± 7.16	4.51 ± 6.90	1.95 ± 2.81	15.01 ± 29.30	13.11 ± 26.62
BDE-118	0.44±0.72	0.35 ± 0.65	0.44 ± 0.62	12.76 ± 23.42	10.20 ± 21.07	13.28 ± 20.29	4.96 ± 9.04	5.46 ± 7.91	6.40 ± 7.43
BDE-119	0.52±0.95	0.42 ± 0.87	0.55 ± 0.84	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.75 ± 1.39	0.60 ± 1.25	0.78 ± 1.20
BDE-126	0.00±0.00	0.00 ± 0.00	0.00 ± 0.00	0.32 ± 0.41	0.25 ± 0.38	0.30 ± 0.36	2.54 ± 4.68	2.04 ± 4.21	2.65 ± 4.06
BDE-137	2.29±4.19	1.84 ± 3.78	2.38 ± 3.62	0.19 ± 0.30	0.16 ± 0.28	0.19 ± 0.27	3.61 ± 6.59	3.79 ± 5.72	4.51 ± 5.41
BDE-153	0.80±1.39	0.64 ± 1.26	0.82 ± 1.21	0.02 ± 0.03	0.01 ± 0.03	0.01 ± 0.03	0.80 ± 1.37	2.40 ± 3.77	2.29 ± 3.38
BDE-154	0.04±0.08	0.03 ± 0.08	0.03 ± 0.07	0.05 ± 0.10	0.04 ± 0.09	0.03 ± 0.08	0.60 ± 1.08	0.72 ± 0.98	0.82 ± 0.91
BDE-155	1.20±2.18	0.96 ± 1.97	0.83 ± 1.79	0.17 ± 0.30	0.14 ± 0.27	0.18 ± 0.26	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
BDE-166	1.25±2.06	1.00 ±1.88	1.26 ± 1.80	0.03 ± 0.05	0.02 ± 0.04	0.02 ± 0.04	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
BDE-181	0.41±0.46	0.33± 0.44	0.34 ± 0.39	0.18 ± 0.29	0.15 ± 0.26	0.18 ± 0.25	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
BDE-183	0.14±0.26	0.38 ± 0.58	0.31 ± 0.54	0.01 ± 0.02	0.01 ± 0.02	0.01 ± 0.02	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
BDE-209	0.34±0.67	0.27 ± 0.60	0.22 ± 0.55	0.02 ± 0.04	0.02 ± 0.03	0.01 ± 0.03	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
TOTAL	29.84±46.92	43.87 ± 51.34	46.54 ± 46.38	195.28 ± 356.24	159.56 ± 318.68	205.71 ± 306.64	1288.34 ± 2240.98	3048.22 ± 4387.75	3003.87 ± 3926.02
Mono PBDEs	0.08±0.13	2.79 ± 6.05	2.32 ± 5.53	15.15 ± 27.42	12.32 ± 24.57	15.88 ± 23.64	221.23 ± 389.19	456.29 ± 624.39	460.52 ± 558.57
Di-PBDEs	13.64±24.70	16.95 ± 22.63	19.18 ± 20.96	65.26 ± 119.29	52.94 ± 106.91	64.46 ± 102.90	539.53 ± 960.66	900.92 ± 1159.81	948.27 ± 1042.83
Tri-PBDEs	0.42±0.37	4.45 ± 9.02	3.74 ± 8.25	50.23 ± 91.85	42.27 ± 81.51	53.97 ± 78.33	341.50 ± 607.91	598.15 ± 778.80	623.44 ± 699.33
Tetra-PBDEs	7.41±12.46	8.51 ± 11.07	9.69 ± 10.32	40.39 ± 73.85	32.62 ± 66.27	42.25 ± 63.80	92.01 ± 131.95	696.68 ± 1356.90	609.16 ± 1232.44
Penta-PBDEs	1.83±2.92	5.74 ± 9.11	5.40 ± 8.19	23.60 ± 43.05	18.88 ± 38.75	24.52 ± 37.31	89.06 ± 144.72	389.26 ± 682.87	354.86 ± 616.57
Hexa-PBDEs	5.58±7.36	4.46 ± 6.84	5.33 ± 6.48	0.46 ± 0.58	0.37 ± 0.54	0.43 ± 0.51	5.01 ± 9.04	6.92 ± 8.91	7.62 ± 8.15
Hepta PBDEs	0.55±0.67	0.70 ± 0.68	0.65 ± 0.62	0.19 ± 0.29	0.16 ± 0.26	0.19 ± 0.25	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Deca-PBDEs	0.34±0.67	0.27 ± 0.60	0.22 ± 0.55	0.02 ± 0.04	0.02 ± 0.03	0.01 ± 0.03	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

The mean concentration of PBDEs congener of plant parts for both control and contaminated plant samples are presented on Table 2

Table 2**:** The mean concentrations of the detected PBDEs congeners of both control and plant around e-waste dumpsite

Compunds	Control Leaf & Root (mean±S.D)		Dumpsite Leaf & Root (mean±S.D)			
	Leaf	Root	Leaf (May)	Root (May)	Leaf (June)	Root (June)
BDE-1	0.00 ± 0.00	0.00 ± 0.00	0.93 ± 0.01	0.45 ± 0.15	0.68 ± 1.19	0.08 ± 0.13
BDE-2	0.00 ± 0.00	0.00 ± 0.00	0.28 ± 0.00	0.40 ± 0.13	0.67 ± 1.20	0.06 ± 0.10
BDE-3	0.00 ± 0.00	0.00 ± 0.00	0.58 ± 0.01	0.18 ± 0.06	0.65 ± 1.21	0.04 ± 0.07
BDE-7	0.00 ± 0.00	0.00 ± 0.00	0.54 ± 0.01	0.33 ± 0.11	0.67 ± 1.34	0.01 ± 0.01
BDE-8	11.91 ± 8.59	0.00 ± 0.00	0.74 ± 0.01	0.24 ± 0.08	2.16 ± 2.74	1.48 ± 2.83
BDE-10	0.00 ± 0.00	0.00 ± 0.00	17.72 ± 0.20	1.24 ± 0.41	2.40 ± 3.17	1.72 ± 3.30
BDE-11	0.00 ± 0.00	0.00 ± 0.00	0.39 ± 0.00	0.50 ± 0.17	2.40 ± 3.17	1.72 ± 3.30
BDE-12	0.00 ± 0.00	0.22 ± 0.31	1.05 ± 0.01	0.09 ± 0.03	1.30 ± 1.52	0.59 ± 1.12
BDE-13	0.00 ± 0.00	0.01 ± 0.02	3.38 ± 0.04	0.49 ± 0.16	0.62 ± 1.24	0.64 ± 1.23
BDE-15	3.78 ± 2.72	0.04 ± 0.03	1.29 ± 0.02	1.39 ± 0.46	0.65 ± 1.31	0.67 ± 1.3o
BDE-17	13.51 ± 9.74	0.08 ± 0.12	9.72 ± 0.11	0.13 ± 0.04	0.24 ± 0.37	0.04 ± 0.05
BDE-25	0.00 ± 0.00	1.56 ± 2.38	12.78 ± 0.15	3.45 ± 1.15	0.84 ± 1.54	0.06 ± 0.10
BDE-28	6.25 ± 4.50	0.03 ± 0.03	10.53 ± 0.12	0.40 ± 0.13	0.93 ± 1.27	0.27 ± 0.51
BDE-30	6.10 ± 4.40	1.25 ± 1.90	1.66 ± 0.02	0.70 ± 0.23	5.07 ± 10.04	0.08 ± 0.09
BDE-32	11.33 ± 8.17	0.20 ± 0.29	1.02 ± 0.01	0.56 ± 0.18	1.12 ± 1.34	0.70 ± 1.33
BDE-33	0.00 ± 0.00	0.23 ± 0.23	0.25 ± 0.00	0.53 ± 0.17	0.95 ± 1.76	0.06 ± 0.10
BDE-35	0.00 ± 0.00	18.09 ± 26.54	1.42 ± 0.02	0.24 ± 0.08	0.41 ± 0.77	0.02 ± 0.03
BDE-37	3.63 ± 2.62	3.77 ± 5.76	1.69 ± 0.02	0.98 ± 0.33	2.94 ± 5.65	0.11 ± 0.16
BDE-47	5.38 ± 3.88	0.00 ± 0.00	3.76 ± 0.04	0.28 ± 0.09	5.37 ± 10.59	0.10 ± 0.11
BDE-49	5.23 ± 3.77	1.16 ± 1.60	0.56 ± 0.01	0.02 ± 0.01	1.86 ± 2.15	1.00 ± 1.90
BDE-66	0.00 ± 0.00	0.98 ± 1.49	0.21 ± 0.00	0.02 ± 0.01	0.53 ± 1.07	0.55 ± 1.06
BDE-71	2.91 ± 2.09	0.54 ± 0.85	0.35 ± 0.00	0.62 ± 0.21	0.00 ± 0.00	0.00 ± 0.00
BDE-75	0.00 ± 0.00	0.01 ± 0.02	0.85 ± 0.01	0.09 ± 0.03	1.91 ± 3.55	1.87 ± 3.72
BDE-77	0.00 ± 0.00	0.89 ± 1.42	3.00 ± 0.03	1.68 ± 0.56	10.77 ± 11.10	2.94 ± 3.77
BDE-85	0.00 ± 0.00	0.83 ± 1.25	0.75 ± 0.01	0.26 ± 0.09	11.62 ± 11.97	3.21 ± 4.16
BDE-99	0.00 ± 0.00	0.10 ± 0.16	1.19 ± 0.01	0.21 ± 0.07	0.33 ± 0.65	0.34 ± 0.65
BDE-100	0.00 ± 0.00	0.29 ± 0.47	0.47 ± 0.01	0.12 ± 0.04	0.98 ± 1.96	1.01 ± 1.94
BDE-116	0.00 ± 0.00	0.19 ± 0.27	0.00 ± 0.00	0.01 ± 0.00	0.07 ± 0.09	0.02 ± 0.03
BDE-118	0.00 ± 0.00	0.17 ± 0.27	1.41 ± 0.02	0.37 ± 0.12	7.41 ± 12.50	0.91 ± 1.55
BDE-119	0.00 ± 0.00	3.10 ± 4.61	2.28 ± 0.03	0.18 ± 0.06	0.39 ± 0.66	0.36 ± 0.89
BDE-126	0.00 ± 0.00	0.00 ± 0.00	0.71 ± 0.01	0.25 ± 0.08	0.43 ± 0.44	0.24 ± 0.40
BDE-137	0.00 ± 0.00	0.00 ± 0.00	3.01 ± 0.03	2.76 ± 0.92	3.46 ± 6.60	3.45 ± 6.60
BDE-153	0.00 ± 0.00	0.00 ± 0.00	7.89 ± 0.09	1.31 ± 0.44	0.37 ± 0.42	0.25 ± 0.43
BDE-154	0.00 ± 0.00	0.00 ± 0.00	0.83 ± 0.01	0.20 ± 0.07	2.41 ± 2.46	1.26 ± 2.07
BDE-155	0.00 ± 0.00	0.00 ± 0.00	0.91 ± 0.01	0.53 ± 0.17	2.00 ± 2.05	1.04 ± 1.70
BDE-166	0.00 ± 0.00	0.00 ± 0.00	0.97 ± 0.01	3.24 ± 1.08	2.31 ± 2.64	1.55 ± 2.73
BDE-181	0.00 ± 0.00	0.00 ± 0.00	1.57 ± 0.02	0.55 ± 0.18	0.30 ± 0.34	0.11 ± 0.16
BDE-183	0.00 ± 0.00	0.00 ± 0.00	2.57 ± 0.03	1.22 ± 0.41	0.26 ± 0.26	0.14 ± 0.23
BDE-209	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.63 ± 0.65	0.34 ± 0.56
TOTAL	70.03±50.48	33.73±45.12	99.21±1.12	12.48± 4.17	78.09±43.84	29.03±45.55
Mono PBDEs	0.00 ± 0.00	0.00 ± 0.00	1.79 ± 0.02	1.03 ± 0.35	2.00 ± 3.60	0.18 ± 0.30
Di-PBDEs	15.69 ± 11.31	0.27 ± 0.31	24.57 ± 0.28	3.94 ± 1.32	10.19 ± 12.76	6.83 ± 13.07
Tri-PBDEs	40.82 ± 29.43	25.21 ± 37.21	39.07 ± 0.44	6.98 ± 2.34	8724.93 ± 12033.00	2100.76 ± 3774.77
Tetra-PBDEs	13.51 ± 9.74	3.58 ± 2.72	8.72 ± 0.10	2.70 ± 0.90	20.43 ± 11.84	6.46 ± 10.15
Penta-PBDEs	0.00 ± 0.00	4.68 ± 5.70	6.80 ± 0.08	1.40 ± 0.47	21.23 ± 24.04	6.09 ± 7.85
Hexa-PBDEs	0.00 ± 0.00	0.00 ± 0.00	13.60 ± 0.15	8.04 ± 2.69	10.55 ± 12.84	7.55 ± 13.52
Hepta PBDEs	0.00 ± 0.00	0.00 ± 0.00	4.12 ± 0.05	1.77 ± 0.59	0.56 ± 0.58	0.25 ± 0.39
Deca-PBDEs	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.63 ± 0.65	0.34 ± 0.56

The soil pollution potential of PBDEs congeners (BDE-1 to BDE-209) in relation to depths are presented on figure 3
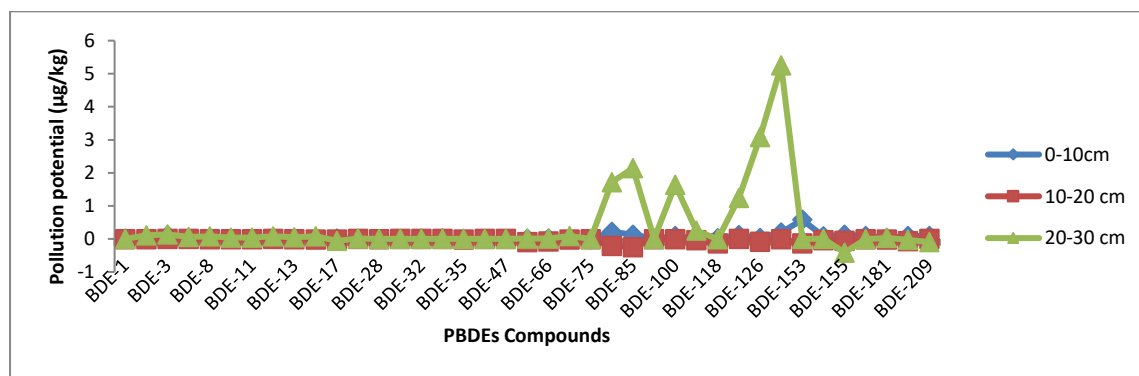

Figure 3**:** Pollution potentials of PBDEs congeners on soil around e-waste dumpsite across depths.

The soil chemical interaction of PBDEs congeners (BDE-1 to BDE-209) in relation to depths are presented on figure 4.
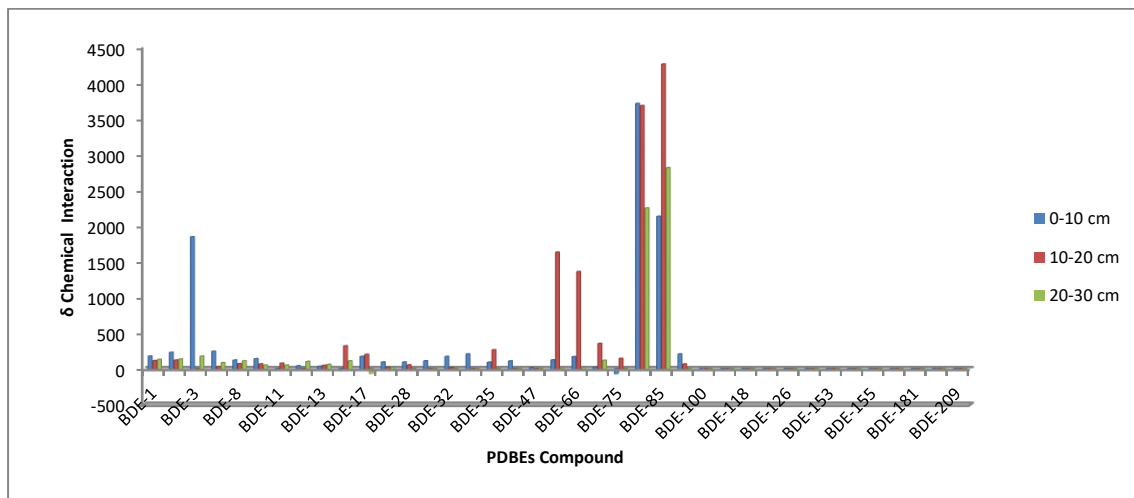

Figure 4 **:** Chemical Interactions of PBDEs congeners on soil around e-waste dumpsite across depths.

The soil pollution potential of PBDEs congeners (BDE-1 to BDE-209) in relation to plant parts are presented on figure 5.
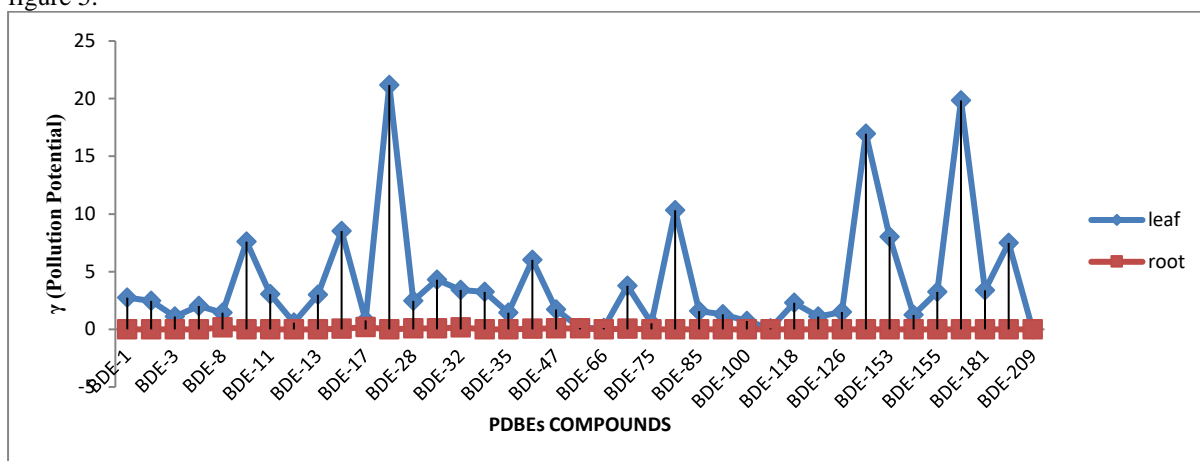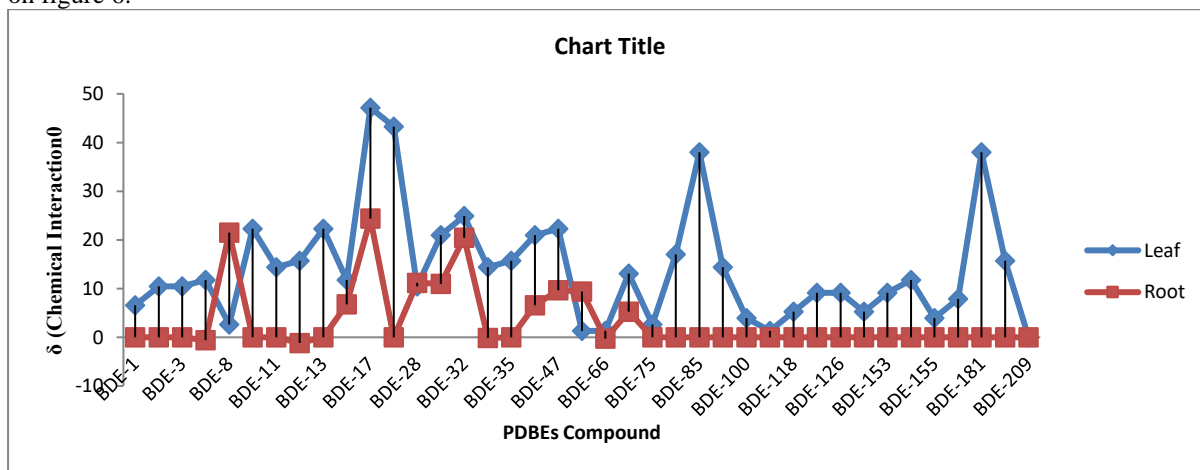

Figure 5**:** Pollution potentials of PBDEs congeners on plant partsl around e-waste dumpsite.

The soil chemical interaction of PBDEs congeners (BDE-1 to BDE-209) in relation to plant parts are presented on figure 6.

Figure 6: Chemical interaction of PBDEs congeners on plant parts around e-waste dumpsite

4. DISCUSSION

From Table 1, residual amount of each PBDEs congeners were detected in the soil across depths and months. In comparing the control soil data with the dumpsite soil, there is a significant difference in all the PBDEs congeners of the control in relation to the two months and there is also a significant difference between the first and the second month across depths. The data of the PBDEs congners in the control sample indicates concentration ranging from below detectable limit - 5.5 ng/g at depths 0 – 10 cm and 10 – 20 cm (BDE- 2, 32 and BDE- 8). While data of BDE at the first month ranged from below detectable limit – 29.74 ng/g at depth 10 – 20 cm and 20 – 30 cm (BDE-119 and BDE-15) and those of the second month ranged from below detectable limit – 357.52 ng/g across the depths (BDE-155, 166, 181, 183, 209 and BDE- 47) respectively. PBDEs concentrations in soil around e-waste dumpsite were generally higher than those of the control site and those reported by [12] (below detectable limit – 1.191) in a similar study. The levels of all the components of PBDEs (Mono-, Di-, Tri-, Tetra-, Penta-, Hexa-, Hepta-, and Deca-) determined were within detectable limit in all the sample collected from control and around e-waste dumpsite, except Hepta- and Deca- that fell below (< 0.01 ng/g) detectable limit at the second month across depths. This might be due to the fact that higher PBDEs congeners like BDE – 209 degrade to lower BDEs congeners by the absorption of light from the UV- spectra on the organic-bromine compound which might have led to the loss of bromine and possibly molecular rearrangement. This corroborates with the report of [12]. The summation of all the PBDEs congeners ($\sum$ PBDEs) of both the control and the studied site ranged from 29.84 – 3,048.34 ng/g across depths. The total PBDEs observed in this study were far lower than those reported by [13] (1.702 – 149,770.56 ng/g) in Ibadan and Aba, Nigeria. the concentration of PBDEs congeners across depths has no definite trend. The lower concentration observed in Deca- across depths and months may be attributed to the fact that highly brominated PBDEs degrade photolytically, and high temperature caused by fire lowers concentration of brominated PBDEs like Tetra-, Penta- and Hexa –BDE, in the environment [2]. The increase in concentration of PBDEs congeners across depths and months of soil around e-waste contaminated site above the control site might be due to the leaching ability of the e-waste contaminant to the surrounding soil and degradation through photolytic and high temperature by fire [2]. The concentrations of the control plant sample ranged from below detectable limit to 6.25 ng/g (BDE – 28) for leaf and below detectable limit to 18.09 ng/g (BDE - 35) for root. For plant around e-waste dumpsite in the month of May, it ranged from below detectable limit to 12.79 ng.g (BDE – 25) for leaf and below detectable limit to 3.45 ng/g (BDE – 25) for root. In July, it ranged from below detectable limit to 11.62 ng/g (BDE – 85) for leaf and below detectable limit to 3.45 ng/g (BDE – 137) for root. The concentrations showed minimal significant difference when the plant around e-waste is compared with the control. In the control plant, there is more of below detectable limit than those of plant around e-waste which are majorly of detectable PBDEs congeners. This might be due to transport and uptake by plant mechanisms (soil – air – plant versus soil – soil moisture in root – plant), which depend strongly on physical parameters of the compound like vapour pressure, plant distribution coefficient and meteorological parameters like wind velocity, rainfall, degradation through photolytic and high temperature by fire [2,14]. It was observed that Deca – BDE in the control sample in the month of May, fell below detectable limit across all the component of PBDEs calculated. This might be attributed to the fact that higher BDE- congeners degrade to less brominated PBDE like Tetra-, Penta- and Hexa-BDE in the environment and also, due to high molar mass and lipophilicity properties of high brominated BDEs [2, 6, 15]. The total ($\sum$ PBDEs) for control plant sample is 70.03 and 33.73 ng/g, while for plant around e-waste dumpsite ranged from 12.48 to 99.21 ng/g for both leaf and root samples. BDE-137 had the highest positive pollution potential (5.250) at depth 20 – 30 cm and BDE-25 has the lowest negative pollution potential at depth 10 – 20 cm. This could be attributed to weak ability of the soil binding to the PBDEs congener as a result of weak carbon-bromine bond that is thermally – labile from the e-waste contaminants, that leached out to the surrounding soil [2, 16, 17]. Due to some physicochemical properties like cation exchange capacity (CEC), rainfall and organic matter present in the soil, the soil binds strongly to PBDEs congeners at depth 20 – 30 cm, which led to positive pollution potential at that depth. The positive pollution potential are majorly observed at depth 20 – 30 cm, while negative pollution potential are found in depths 0 – 10 cm and 10 – 20 cm. This corroborates the findings of [18], who reported that concentration of lower BDEs congeners in the soil increases by soil depths and decreases with high brominated BDEs compound. It was also reported that photolytic degradation occur mostly at the upper surface of the soil, which degrade the Deca- BDE leading to negative pollution potential as a result of the weak binding capacity, which may also be attributed to the lower bio accumulative and biological activities of the Deca-BDE [2]. Lower brominated congeners are known to be more persistent in the environment and potentially migrate far in the soil and air leading to positive pollution potential at depth 20 – 30 cm. Positive chemical interaction was observed majorly at depth 20 – 30 cm with the lower PBDEs congeners and most of the negative chemical interactions were found in depths 0 – 10 cm and 20 – 30cm with the higher PBDEs congeners. This positive chemical interaction found at the lower BDE congeners, might be attributed to their high bio accumulative and biological activities, since there is high water retention capacity of the soil as a result of poor drainage system in the site [2, 17]. As such, photolytic degradation is lacking. The observed negative chemical interaction at the higher BDE might be ascribed to photolytic energy breaking the carbon-bromine bond to release bromine radical and also the low bio accumulative and biological activities exhibited by them [2,19]. This might weaken the

interaction of the PBDEs congener contaminants in the soil. It was also observed that BDE – 77 displayed the highest chemical interaction, which might be as a result of its high dominating level in the e-waste dumpsite that leached out to the surrounding soil. The positive pollution potential occurs in all lower BDE- congeners across the leaf except Deca- BDEs which is below detectable limit. This agrees with the finding of [20], who reported that low PBDEs concentration gradient was observed at the height of plant, while high brominated PBDEs displayed low mobility at root as a result of high lipophilicity of the compound. Across the root, minimal negative pollution potential was observed in some BDE congeners like BDE – 3, BDE- 11, BDE – 12, etc and also all BDE congener on the root sample displayed low concentration when compared to those of leaf samples. This implies that there is high rate of transfer of BDE congener from root to leaf due to sufficiency of water solubility which facilitated the transportation. The concentration of PBDE congeners on leaf range from below detectable limit (Deca – BDE) to 19.84 ng/g (BDE – 166), while across the root, the concentrations ranged from below detectable limit (BDE – 25) to 0.186 ng/g (BDE – 17). Furthermore, the higher concentrations observed on the leaf across all the BDE congeners except Deca - BDE might be due to the season of collection of samples which involve more water that helps in transportation or carriers of the contaminants from the root to leaf, which will not equilibrate because of plant-growth-effect [4]. Different PBDEs congeners having different physical properties and molecular structure might also affect the uptake by plant, hence Deca – BDE is known to degrade easily through photolytic degradation to Penta-, Hexa- etc, which fell below detectable limit in leaf and root. Figure 6 displayed a profile of chemical interaction of 39 PBDEs congeners on leaf and root samples. These range from below detectable limit of (Deca – BDE) to 47.160 ng/g (BDE – 17) and (BDE – 13) to 24,366 ng/g (BDE – 17) for leaf and root samples respectively. For the leaf, positive chemical interaction was observed. This might be as a result of high rate of transportation with the help of much water present in the plant that carries contaminants of BDE that leached out from e-waste and the water retention capacity exhibited by the leaf than the root which displayed negative chemical interaction in some of the BDE congeners. It was also observed that there were high chemical interactions in the leaf sample for lower BDE congeners than the higher BDE congeners. This might be due to the fact that lower brominated BDE congeners are more persistent in the environment and can as well move a long distance potentially when there is degradation of the higher BDE like Deca- as a result of high temperature by fire [2]. The leaching ability of the e-waste contaminants and the degradation reaction of PBDEs congeners in the environment enhance the positive chemical interaction and higher concentrations of the lower BDE congeners on the leaf sample [4].

5. CONCLUSION

Based on the fact that positive pollution potential and chemical interactions with regards to PBDEs are more prominent than negative pollution potential and chemical interactions in this study, it depicts that there was a substantial amount of PBDEs contaminants that leached out of the e-waste to the surrounding soil for plant uptake. This led to a lot of considerable reactions, leading to positive pollution potential and chemical interactions. Hence we are recommending that the dumping of e-waste in our environment should be checkmated concurrently for safety purposes, as a of the positive pollution potential and chemical interactions observed.

Conflict of Interest
The authors have declared that there is no conflict of interest.

Contribution of the Authors
Eyenubo and Apiamu contributed equally to this paper in terms of laboratory, statistical analysis and the writing of the manuscript, while Osakwe and Egarevba assisted in structuring the work and reviewing the write up.

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