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PBDES AND TRACE METALS IN SOIL SAMPLES FROM AN ELECTRONIC WASTE RECYCLING AND DUMP SITE AT AGBOGBLOSHIE, ACCRA, GHANA

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Introduction
PBDEs are a group of industrial compounds used as flame retardants to inhibit the rate of accidental fires in order to save lives and properties from being gutted by flames. PBDEs have been used extensively as additives in many consumer and commercial products such as electrical appliances, textiles, polyurethane foam, furniture and various plastics. Unregulated e-waste dismantling and recycling has proved to be a significant source of environmental PBDEs. High concentrations of PBDE residues in areas greatly impacted by e-waste recycling have been detected in various abiotic and biotic environmental media 1, 2, 3. Soil is a significant environmental matrix that plays a very important role in the distribution and fate of organic and inorganic pollutants, as it is a major reservoir and sinks for environmental contaminants due to its large absorption capacity 4. Trace metals have received tremendous attention for many years because they exhibit similar adverse effects on the environment. Thus, trace metals and PBDEs can be deposited and accumulated in soil. To date, studies have been conducted on concentration of PBDEs in soil. However, information on possible relationship between trace metals and PBDEs when they co-exist in the environment, particularly in uncontrolled e-waste recycling environment is deficient. The objective of this study was to characterize soil samples from Agbogbloshie informal e-waste dump site with respect to the levels of PBDEs and trace metals and their possible sources.

Materials and methods
For PBDEs analysis, chemicals and reagents were as described by Olukunle et al.
5. For trace metal analysis, individual pure standards containing 1, 000 mg L
-1 of trace metals and 0.5 N nitric acid were purchased from C.C. Imelmann (Pty) Ltd, South Africa. All solvents used were of analytical grade and care was taken to avoid contamination. All standards and serial dilutions were prepared under fume hood and ultra-pure water (Labostar® Ultrapure, Siemens, Germany) was used throughout the experiment. Collection of soil samples and description of the study area were as described by Daso et al.
6. Surface soils (0 - 5 cm) and core samples (0 - 30 cm) were collected from five different locations in triplicates with a stainless steel hand trowel and mechanical Auger, respectively. The collected soil samples were air-dried and sieved separately using 250-μm stainless steel mesh sieves, homogenised thoroughly and stored at −20 ºC prior to extraction and analysis. Loss-on-ignition (LOI) method was employed for the determination of total organic carbon (TOC). Detailed analysis of TOC was as described by Daso et al.
6. PBDE concentrations were determined from ultra-sonication-assisted extraction solutions using Shimadzu model 2010 plus GC-MS, which was a slightly modified method reported in a previous study by Olukunle et al.
5. From each of the sieved samples, approximately 10 g sample was weighed into thoroughly cleaned 100 mL amber bottles. Each of the samples was spiked with 10 μL of surrogate standards (BDE-77 and C13-BDE-139) to monitor analytical recovery efficiencies. The extraction procedure is as described by Daso et al.
6, followed by a clean-up using a procedure described earlier
5. One μL solutions of the extracted sample each was injected by Shimadzu model 2010 plus GC equipped with model QP 2010 ultra-MS (Shimadzu, Japan) using electron ionization (EI) and injected by a Shimadzu A0C-20i auto sampler in selected ion-monitoring (SIM) mode. The capillary column used was DB 5 (15 m, 0.25 mm ID, 0.1 μm df). Other chromatographic conditions used were as described in a previous study
5. PBDE congeners were identified based on their retention times, target and qualifier ions, and quantification was done by monitoring the molecular and reference ions using external methods. Quantitative analysis was carried on the GC-MS using eight level calibration points. For each congener, good linearity was achieved with r

2 ≥ 0.998. The instrument LOD was defined as 3 times the signal-to-noise ratio and LOQ as 10 times signal-to-noise ratio. Statistical analysis was performed using Microsoft Office Excel 2010 package and STATISTICA.

For the acid digestion of soils for trace metals analysis, a modified method by Cetin

7 was applied. After digestion, the digestate was made up to 20 mL with double distilled water and assayed for the presence of Fe, Zn, Mn, Cu, Ni, Cd, Co, Cr and Pb by atomic absorption spectrometer (AAS) (VARIAN AA 240 FS) using air-acetylene flame for the measurements, at flow rates of 13.5 L min-1 and 2 L min-1, respectively.

Results and discussions

The TOC content determined for the surface soils ranged between (5.75 - 21.29%), with a mean of 12.43±6.12%.

Figure 1 shows mean concentration of all PBDEs detected and error bars represent standard deviations. The mean concentration of PBDEs in the surface soils ranged from 1.76 to 16.82 ng g-1. Contrary to some studies, BDE-209 was not the dominant congener detected in this study,

8, 9. This can be ascribed to the fact that highly brominated congeners are susceptible to debromination to lower brominated congeners under ultraviolet light (UV)10. This may explain the relatively low concentration of BDE-209 detected in the present study. The concentrations of ∑

8PBDEs for a collection of eighteen composited samples ranged from 15.6 to 96.8 ng g-1 dry weight (dw), with an overall mean value of 54.8 ng g-1 dw. All targeted PBDE congeners were detected in the samples except BDE-183, which was least detected or below the detection limit in most of the samples. As can be seen in Figure 1, BDE-28 was the dominant congener in sampling site RP (Computer repairs shop), followed by BDE-209 and BDE-47. The order of mean concentration is as follows: BDE-28> BDE-209> BDE-47, while BDE-99 and BDE-100 exhibited relatively similar mean values respectively. Mean concentrations of a total of nine trace metals detected in the e-waste dump site soils are presented in Table 1, along with their standard deviations, coefficient of variations (CV) and minimum and maximum values.

The order of mean concentrations of the abundant metals is as follows: Fe> Cu> Pb>> Mn and the means ranged from 0.5 to 288.8 mg kg-1. All trace metals were detected in the soil samples except Cd, which was below the detection limit. Of the nine trace metals detected, Fe, Cu, and Pb appeared to be quite elevated, and Fe being the most elevated concentration ranged from 3.87 to 918.3 mg kg-1, suggesting the anthropogenic enrichment of Fe, as it falls in the category of crustal elements

7. Subsequently, the percentage concentrations in the e-waste soils also showed that 91% of the contaminants in the soils were attributed to Fe, Mn, Cu, and Pb. These were distributed in the following order: Fe (40.7%)> Cu (21.2%)> Mn (15.4%)> Pb (13.5%). However, Zn, Ni, Cd, Co, and Cr were detected at lower concentrations and their mean percentage concentrations accounted for 6.4, 1.1, 0, 0.3, and 0.3% respectively. Consequently, the metal concentrations were compared with the international standard concentrations for the following trace metals in soil: Zn=25 mg kg

-1, Cu=15 mg kg

-1, Pb=5 mg kg

-1, Cr=5 mg kg

-1 and Cd=0.5 mg kg

-1

11. In comparison, the levels obtained in the present study suggest that the e-waste dump site soils were found to be highly polluted with toxic trace metals. Differences and similarities among PBDEs and trace metal profiles of the dump site soils were also examined using principal component analysis (PCA) to evaluate environmental behaviour and source characteristics. In congruence with the results described, the multivariate analysis shows a 1 x 2 factor plot of PBDEs and trace metals content of the dump site soils in Figure 2.

The first principal component accounted for 67% of the total variance, while the second accounted for 16.7% of the total variance. In the factor plot (Figure 2), two distinct groupings were determined. The first group (factor 1) is characterized by strong groupings of BDEs (-28, -47, -100, -99, -154, -153, -183) and trace metals (Mn, Zn, Ni, Cd, Co, Cr), suggesting that these contaminants may derive from a common source, i.e. e-waste recycling activities such as open burning and crude combustion of electronic items. The factor 1 loadings also indicate the influence of major components of the penta-BDE and some octa-BDE products

2. This suggests that commercial penta- and octa-BDEs are the major commercial PBDE products incorporated in most of the obsolete consumer items. BDE-209 had a different loading from other

congeners in the plot. A moderately high positive loading for factor 1 indicates some contributions from commercial deca-BDE formulated products

2. Consequently, BDE-209 loading in factor 1 indicated that transformation to less brominated PBDEs has occurred

12 giving rise to environmentally abundant lower mass PBDEs. As can be seen from the factor plot, Cu and Pb had relatively high loadings in factor 2, hence bearing identical sources related to e-waste recycling activities. Fe loading in the PCA was also different from other metals and has relatively high loading in factor 2, suggesting that Fe pollution is also related to crude e-waste recycling activities. Given however, that Fe is a crustal element; its enrichment may be attributed to the different parent materials in the study area as well as anthropogenic causes.

Conclusion
The inappropriate dumping and recycling of e-waste was identified as an important source for a number of toxic chemicals, including PBDEs and trace metals. Soil samples from e-waste recycling site at Agbogbloshie were characterized with respect to PBDEs and toxic trace metals. This study is one of the few researches that assess the co-contamination of PBDEs and trace metals in e-waste dump site soils in Ghana. Consequently, the co-existence of PBDEs and toxic trace metals in the same matrix may engender complex formation under chemically favorable conditions, and as such, the interplay of trace metals and PBDEs requires further attention.

Acknowledgements

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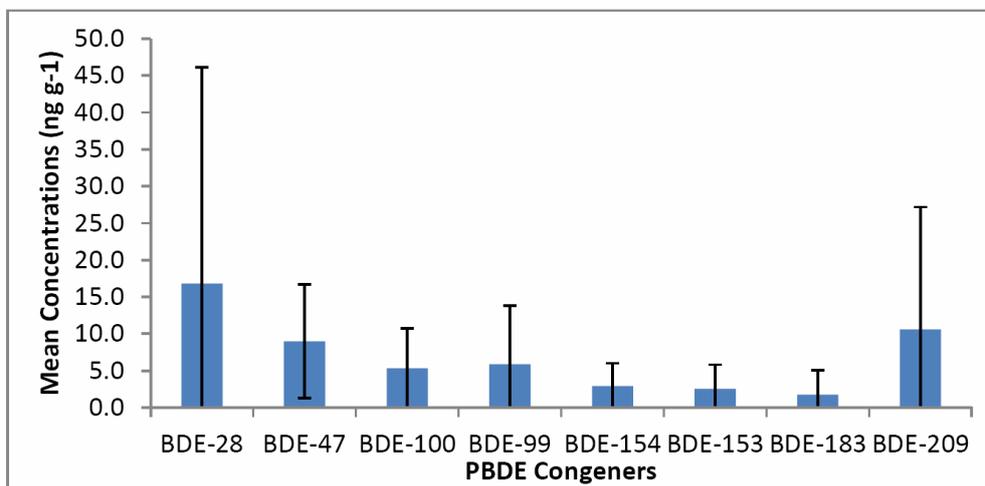
Figure 1 Mean concentration of PBDEs in e-waste dump site soils (error bars depict standard deviation)

Table 1 Descriptive statistics of trace metals concentration (mg kg^{-1}) in soil

Cation	Mean	SD	CV	Min	Max
Fe	288.8	329.6	1.1	4.0	918.3
Mn	46.8	32.4	0.7	6.2	103.1
Cu	222.0	327.1	1.5	0.6	869.3
Zn	34.7	39.3	1.1	1.8	112.0
Pb	206.6	291.7	1.4	15.3	709.7
Ni	7.6	8.2	1.1	0.1	23.2
Cd	0.5	0.7	1.4	0.1	1.8
Co	3.0	5.0	1.7	0.1	13.1
Cr	3.3	3.4	1.0	0.9	9.2

SD=Standard deviation, CV=Coefficient of variation, Min=minimum, Max=maximum
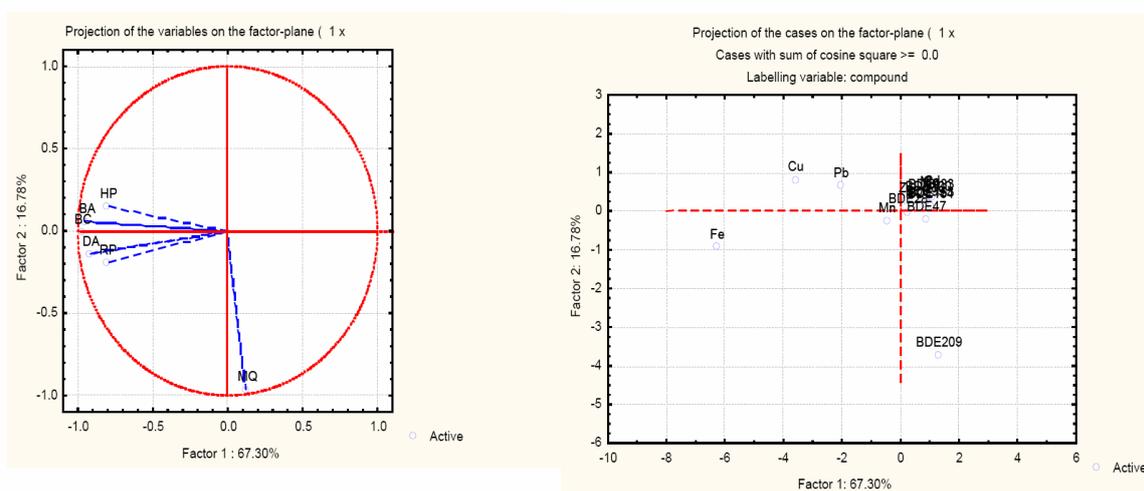
Fig 2 Principal Component analysis showing 1 x 2 factor coordinate plots for PBDEs and trace metals