CO-EXISTENCE OF POLYBROMODIPHENYL ETHERS AND TRACE METALS IN INDOOR DUST: COMPLEX FORMATION IMPLICATIONS

K K. Kefeni[,†], AP Daso, OJ Okonkwo*[†],

[†]Environmental Chemistry Research Group, Department of Environmental, Water & Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, South Africa.

Keyword: PBDEs, Trace metals, Indoor dust, Implications, Complex formation

Introduction

Of all the BFRs, PBDEs have been applied extensively to a host of products in order to reduce the rate at which the products catch fire[1]. Consequently, PBDEs in household and office products can easily be released into the environment during product use or disposal. PBDEs are of particular concern because of their impact on human health[1]. Toxicity studies have reported PBDEs as endocrine disruptors [2,3]. Due to their widespread use, they have been detected in human hair[4,5] domestic animals[,5]; wildlife[6,7,8,9,], indoor dust[10,11], tree bark[13], seawater [14,], sediments[14,15], landfill leachate[16]. Dust and particularly indoor dust is known to contain different types of hazardous substances[17]. Toxic metals such as As, Cd, Cr, Cu Mn and Pb have been reported[18]. Therefore, exposure to dust via inhalation, skin contact and ingestion can lead to serious health problems[19]. Considering the fact that trace metals and PBDEs are known to be persistent in the environment, bioaccumulate in food chains and toxic; the influence of one group of contaminant on the other in indoor dust samples needs to be investigated. A number of the aforementioned toxic metals have low energy level empty d-orbitals which are suitable for the formation of complex compounds. On the other hand, many organic compounds such as PBDEs have the potential to act as ligands and, therefore, can interact with metals to form complex compounds. Therefore, the co-existence of trace metals and PBDEs in a sample may lead to the formation of complex compounds. Consequently, this can lead to unavailability of PBDEs and hence low detection. To date, the impact of some trace metals on the levels of PBDEs in indoor dust has not been given adequate attention. The main objectives of this study, therefore, were (1) to identify and quantify PBDEs and selected trace metals in indoor dust, (2) to predict the potential to form complex compounds if there is significant correlation between the concentrations of PBDEs and trace metals.

Material and method

For PBDEs analysis the chemicals and reagents were as described in Kefeni and Okonkwo (2012)[18]. For trace metal analysis, pure standards containing 1000 mg/ L of trace metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, As and Pb), were purchased from C.C IMELMANN (Pty) Ltd, South Africa. Collection of office and home dust samples were as described.[18]. All dust samples were sieved using stainless steel sieves with aperture size less than 250 µm. For PBDEs, the extraction was carried out using Soxhlet extractor as described by Kefeni and Okonkwo (2012).[18]. For the extraction of total trace metals, all collected dusts were dried at ambient temperature and about 1.0 g of dry dust sample was socked in 15 mL of 1M HNO_3 (prepared by ultrapure water) and shaken for 5 min, kept for 12 h, heated at 95^{o}C for 1 h and then sonicated for 40 min in an ultrasonic bath (Elmasonic S 40H, Germany) at 50 ^{o}C. The samples were filtered on Whatman filter paper and washed using 20 mL 1% HNO_3 and finally diluted to 50 mL mark in a volumetric flask. Analysis was carried out using Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES, model: ARCOS FHS). PBDEs analysis was carried out using an Agilent technologies 7890A GC system (China). One µL solutions of the extracted sample were injected by Agilent Technologies 7693 Autosampler and injector into split/splitless injection port on HP-5MS GC column (30 m, 0.25 mm ID, 0.25 µm d_f). Other chromatographic conditions used were as described in previous study[18]. Identifications were carried out using selected ion monitoring (SIM) mode. Each congener was quantified against five level external standard calibration curves and internal standards (BDE-77, $^{13}C_{12}$-BDE-139). The standards for calibration were prepared from ultrapure stock solutions metals described above. Unless otherwise stated, all the descriptive statistics were computed to characterize the concentration of trace metals and PBDEs in the dust sample using Microsoft office excel 2007. For correlation and *P*-value determination, Pearson correlation test and 2-tailed student's t-test were used. After injection of three samples, solvent blank and standards were run to ensure that the samples and the analysis process were free of contamination as well as to control deviation of the retention time.

Results and discussion

The overall recovery of the spiked internal standards BDE-77, $^{13}C_{12}$- BDE-139 and $^{13}C_{12}$-BDE-209 varied between 84-112%, 76-96% and 72-84%, respectively, and corresponded to the average recovery of 95%, 86% and 78% in the same order. The validation of the method was done through analysis of SRM-2585 in triplicate. A good linearity was obtained with $r \geq 0.99$. The mean concentrations detected from office and home dust are shown in Figure1.

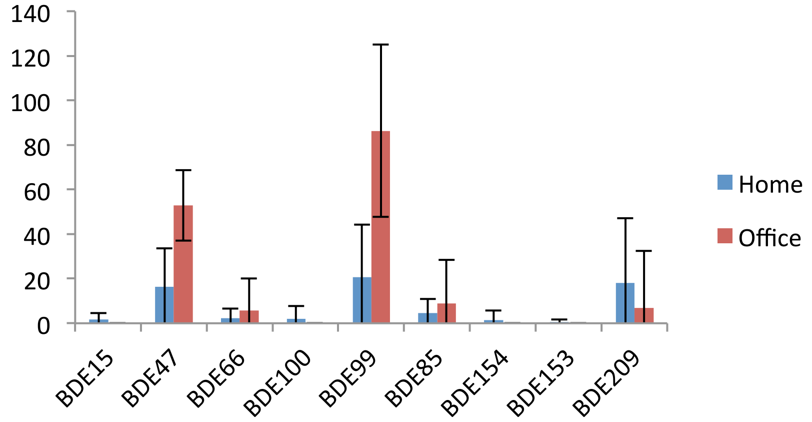

Figure **1:** Mean concentration of PBDEs detected in both offices and homes, error bars correspond to standard deviation

As can be seen in Figure 1, the order of mean concentrations was as follows: BDE-99 > BDE-47 > BDE-209 for both office home dust samples. The mean concentrations of PBDEs detected in office and home dust ranged between 5.8–86.3 and 1.5–20.6 ng g^{-1}, respectively. From Figure 1, BDE-100 and BDE-154 were not detected in office dust and BDE-15 and BDE153 not detected in either office or home dust samples. The results of six pooled analysed office dust samples for ten trace metals are summarized in Table 2. As can be seen in Table 2, all metals were detected in the sample except arsenic (As) which was detected only in one sample (OD2 = office dust number 2).

Table 2: Trace metal distribution in settled office dust (mg/kg)

sample No	Cr	Mn	Fe	Cu	Zn	Co	Ni	Cd	As	Pb
OD1 (n =1)	63.5	1100.0	5850.0	10700.0	245.0	140.3	31.4	0.9	ND	31.3
OD2 (n = 3)	164.0	583.0	27300.0	420.0	746.0	22.6	82.6	5.1	2.7	ND
OD3 (n = 20)	193.0	754.0	14300.0	1930.0	1910.0	16.2	77.0	1.9	ND	190.0
OD4 (n = 15)	164.0	709.0	16500.0	1240.0	1680.0	14.7	69.7	1.7	ND	164.0
OD5 (n = 26)	152.0	727.0	17300.0	290.2	1350.0	13.1	75.4	3.2	ND	190.0
OD6(n = 20)	223.0	760.0	21700.0	1870.0	1850.0	16.7	82.5	2.5	ND	182.0
Sum	960.00	4630.0	103000	16500	7780	224.0	418.5	15.2	2.7	757.0
Mean	160.0	772.0	17200	2740.0	1300.0	37.2	69.8	2.5	0.4	126.0
SD	53.8	173.0	7210.0	3960.0	670.0	50.6	19.4	1.5	1.1	86.6

The percentage concentration of Fe, Cu, Zn and Mn in office dust was 98%. The percentage concentrations were in the order of Fe (76.7%) >> Cu (12.3%) > Zn (5.8%) and Mn (3.45%). The elevated concentration of copper in dust sample OD1 was related to the presence of fine copper metals in the collected dust. During the dust collection, there was ongoing maintenance of electronic materials using copper wire in the office. On the other hand, metals such as Cr, Co, Ni, Cd, As and Pb were detected at lower concentrations and their percentage concentrations corresponded to 0.7%, 0.17%, 0.31%, 0.01%, 0.01% and 0.6%, respectively. Compared to the international standard concentrations for trace metals in soil for Zn, Cu, Pb, Cr and Cd are 25, 15, 5, 5 and 0.5 mg kg^{-1}, respectively. The values obtained in the present study were found to be highly polluted with toxic trace metals.. Leung *et al.*, (2008) reported extremely elevated levels of Pb, Cu and Zn in dust samples collected from printed circuit recycling workshop[19]. The reported Pb concentration ranged from 22,900 - 206, 000 mg kg^{-1}.

Table 3 shows the concentrations of trace metals in home dust samples. As can be seen in Table 3, all target metals were detected in all samples except As and Cd, which was detected only in sample HD5, and not detected in sample HD8, respectively. Similar to office dust samples, trace metals accounted for 97.7%, which was distributed as follows: Fe (87.3%) >> Zn (5.3%) > Mn(3.6) > copper (1.5%). However, As, Cd and Co were found at very low concentrations and they accounted for 0.01%, 0.01% and 0.08%, respectively.

Table 3: Trace metal distribution in settled home dust (mg kg–1)

Sample No	Cr	Mn	Fe	Cu	Zn	Co	Ni	Cd	As	Pb
HD1	111.0	468.0	9800.0	158.0	719.0	7.0	44.7	3.5	ND	86.6
HD2	87.0	354.0	8980.0	178.0	686.0	8.3	61.8	1.2	ND	79.4
HD3	111.0	608.0	10500.0	169.0	748.0	8.4	54.0	3.1	ND	89.5
HD4	127.0	457.0	21400.0	183.0	430.0	15.4	61.0	1.2	ND	56.7
HD5	172.0	469.0	11700.0	253.0	672.0	9.4	86.9	0.9	14.2	302.0
HD6	117.0	594.0	14400.0	179.0	692.0	12.7	57.2	0.9	ND	119.0
HD7	71.0	234.0	4910.0	173.0	493.0	5.4	52.9	1.1	ND	62.1
HD8	73.5	470.0	6080.0	192.0	911.0	9.9	57.4	ND	ND	79.4
Total	870.0	3650.0	87800.0	1490.0	5350.0	76.4	476.0	11.7	14.2	875.0
Mean	109.0	457.0	11000.0	186.0	669.0	9.5	59.5	1.5	1.8	110.0
SD	32.8	121.0	5170.0	29.0	149.0	3.2	12.3	1.19		80.2

The observed differences of trace metal concentrations in office and home dust samples were attributed to different sources to the indoor dust. It is possible that the paints used on the walls of offices may have contained Pb, Cr, Zn, Cd and Co as pigments. For instance, for white pigment a mixture of $PbCO_3$, $Pb(OH)_2$, lithopone (a mixture of $BaSO_4$ and ZnS), and ZnO; for yellow pigment: CdS, $PbCrO_4$ and litharge (PbO); for red pigment: Pb_3O_4; blue pigment: cobalt oxide; green pigment: Cr_2O_3 is the main pigment. For home dust, statistical significant ($p < 0.01$) strong positive correlations ($r = 0.85 - 0.96$) were observed between the following pairs: Cr:Ni, Cr:Zn, Mn:Co, Fe:Ni, and Fe:Cd. Furthermore, no statistical significance with strong positive correlations were noted between the following pairs: Mn:Cu, Co:Cu and Cd:As. On the other hand, strong negative correlations ($r = -0.80$ to -0.96) with a statistical significant ($p < 0.01$) were observed for the pairs: Cr:Co, Mn:Fe, Mn:Ni, and Fe:Cu, and without statistical significance for the pairs: Cr:Cu, Co:Ni, and Ni:Cu for office dust. Generally, for those having strong positive correlations they may have originated from common sources. Overall, the result showed more common sources of trace metals in homes than offices. The association of trace metals with PBDEs congeners detected in both office and home dust were evaluated. The result showed statistical significance correlation ($r = 0.77$, $p = 0.00$) between summation of concentration of PBDEs and trace metals from the home dust while no correlation ($r = -0.11$, $p = 0.00$) was observed for office dust. Using the valence theory model, formation of a complex compound between the trace metals determined in the present study and PBDEs is possible since such reactions involve Lewis bases (ligands) and Lewis acids (metal or metal ion) with the formation of a complex compound covalently bonded as illustrated below:

$$\mathbf{M^+ + L^- \;=\; M\text{-}L}$$

where
M = metal ion; L = ligand and M-L = complex compound.
The model utilizes hybridization of metal *s*, *p*, and *d* valence orbitals to account for the observed structures of complexes. For example, Co which is one of the metals determined in this study has the outer electronic structure $3d^7 4s^2$. Thus a Co^{3+} ion will have the structure $3d^6$. If this ion forms a complex compound with six PBDEs, then six empty atomic orbitals are required on the metal ion to receive the coordinated lone pairs of

electrons. The orbitals that can be used for the bonding are the 4*s*, three 4*p* and two 4*d*. Such reaction as stated above depends on, *inter alia*, (1) the nature of the ligand, (2) charge on the metal ion (3) whether the metal is in the first, second or third row of the transition elements and pH. Since PBDEs contains electronegative element (oxygen) with two lone pair of electrons and phenyl rings that contain pi-bonds, there is a possibility of formation of complex compounds with the suitable trace metal ions as illustrated above. Consequently, PBDEs may not be available for detection during analysis. It should be noted that the presence or absence of statistical correlations neither confirm the formation of complex compounds nor provide the presence of any chemical interaction. However, the statistical evaluation can help to observe the trends of their concentrations within the same environment. Work is currently in progress in our laboratory to investigate the possible formation of complex compounds between metal ions and PBDEs.

Conclusions

Characterization of dust samples from offices and homes with respect to PBDEs and toxic metals are very important in order to mitigate the health risk. In this study, the concentrations of organic and inorganic contaminants in indoor dust were determined and the correlation between the contaminants evaluated. The result showed statistical significance correlation (r = 0.77, p = 0.00) between summation of concentration of PBDEs and trace metals for dust samples obtained from homes; while no correlation (r = -0.11, p =0.00) was observed for office dust. Using the valence theory model, the chemical interaction between PBDEs and trace metals suggests possible formation of complex compounds. It should be noted that the presence or absence of statistical correlations neither confirm the formation of complex compounds nor provide the presence of any chemical interaction. However, this still needs to be explored.

Acknowledgments

The authors thank Tshwane University of Technology for all the research fund and instrumental facilities. We also would like to express our gratitude to Mr Haile for his support during the analysis of the metals using ICP-OES and to all those who allowed us to collect dust samples from their houses.

Reference

1. Haglund, P. L.; Zook, D. R.; Buser, H. R. (1997) . *Environ Sci Technol.,*,31,3281 - 3287.
2. Hwang, H.-M.; Park, E.-K.; Young, T. M.; Hammock, B. D. (2008a) *Sci Total Environ.* 404(1), 26-35.
3. Vonderheide, A. P. (2009) *Microchemical J.,* 92(1),49-57.
4. Anderson, H. A.; Imm, P.; Knobeloch, L.; Turyk, M.; Mathew, J.; Buelow, C.. (2008) *Chemosphere, ,* 73(2),187-194.
5. Covaci, A.; Dirtu, A. C. Brominated flame retardants: analytical, toxicological and environmental aspects. Proceeding of the NATO Advanced Research Workshop on Applications of Mass Spectrometry in Life Safety. Arad, Romania, 24–27 September 2008. pp. 153–184.
6. Polder, A.; Venter, B.; Skaare, J. U.;Bouwman, H. *Chemosphere*, **2008**, 73(2), 148-154.
7. Fromme, H.; Körner, W.; Shahin, N.; Wanner, A.; Albrecht, M.; Boehmer, S. (2009) *Environ Intern, ,* 35(8),1125-1135.
8. Roosens, L.; Abdallah, M.A.E.; Harrad, S.; Neels, H.; Covaci A (2009) A*Environ Sci & Technol***,** 43(10),3535-3541.
9. Johnson, P.I.; Stapleton, H.M.; Sjodin, A.; Meeker, J.D. (2010) *Environ Sci & Technol.,* 44(14), 5627-5632.
10. Harrad, S.; Ibarra, C.; Diamond, M.; Melymuk, L.; Robson, M.; (2008) *Environ Intern.,* 34(2), 232-238.
11. Harrad, S.; Ibarra, C.; Abdallah, A. E.; Boon, R.; Neels, H.; Covaci A. (2008a). *Environ Intern, ,* 34 (8),1170 -1175.
12. Venier, M.; Hites, R. A. *Environ Sci & Technol.***2011***,* 45(10),4602-4608.
13. Dye, J. A.; Venier, M.; Zhu, L.; Ward, C. R.; Hites, R. A.; Birnbaum, L. S.(2007). *Environ Sci & Technol.,* 41(18),6350-6356.
14. Daso, A. P.; Fatoki, O. S.; Odendaal, J. P.; Olujimi, O. O. (2012) *Arch. Environ. Contam. Toxicol.*, *62*, 391 – 40243.
15. Lindberg, P.; Sellström, U.; Häggberg, L.;De Wit, C. A. (2003) *Environ Sci & Technol., ,* 38(1),93-96.
16. Odusanya, D. O.; Okonkwo, J. O.;Botha, B. (2009) . *Waste Man.* **2009***,* 29(1),96-102.
17. Harrad, S.; Hazrati, S.;Ibarra, C. (2006) *Environ Sci & Technol.* 40(15),4633-4638.
18. Kefeni, K.K.; Okonkwo, J.O. (2004_*Chemosphere*, 87(9), 1070-1075.
19. Leung, A.O.W.; Duzgoren-Aydin, N.S.; Cheung, K.C.; Wong, M.H. (2008) *Environ Sci & Technol*,, 42(7)**,** 2674-2680.