Science of the Total Environment 622–623 (2018) 275–281

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Determination of legacy and novel brominated flame retardants in dust from end of life office equipment and furniture from Pretoria, South Africa

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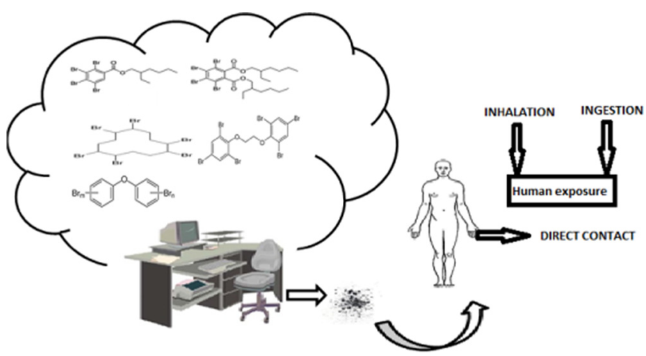
HIGHLIGHTS

- XRF was used to measure the levels of bromine in electronic equipment and furniture.
- GC–MS was employed in order to verify the presence of BFRs.
- Legacy and novel BFRs were detected in the dust samples analysed.
- The study provides first time concentrations of NBFRs and T-HBCDD in dust samples in South Africa.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 July 2017
Received in revised form 7 November 2017
Accepted 26 November 2017
Available online xxxx

Editor: Adrian Covaci

Keywords:
Br
XRF
T-HBCDD
PBDEs
NBFRs
GC–MS

ABSTRACT

Indoor dust is known to be a source of human exposure to brominated flame retardants (BFRs) and these consists of the legacy polybrominated diphenyl ethers (PBDEs), total hexabromocyclododecane (T-HBCDD) and the "Novel or alternate" Brominated flame retardants (NBFRs). In this study, x-ray fluorescence (XRF) analyser was employed to measure elemental bromine contents in office furniture and electronics as the first indication of the possible presence of BFRs. To investigate the possible BFRs present, a total of 21 dust samples were collected from surfaces of electronic equipment and office furniture and were analysed using gas chromatography–mass spectrometry (GC–MS). The concentrations of $\sum_7$ BDE- congeners ranged from 50 to 3346 ng ng^{-1}. Of the $\sum_7$ BDE congeners analysed, BDE-209, −183 and −99 were the most dominant congeners. The concentrations observed ranged from <LOD - 1758, <LOD - 401 and <LOD-543 ng g^{-1}, for BDE-209, −183 and −99, respectively. T-HBCDD and 2-ethyl-1-hexyl-2.3.4.5-tetrabromobenzoate (EH-TBB) were detected in 57 and 67% of the total dust samples analysed with concentrations ranging from <LOD - 673 and <LOD – 385 ng g^{-1}, respectively. However, Bis (2-ethylhexyl) tetrabromophthalate (BEH-TEBP) was only detected in 24% of the 21 samples exhibiting a concentration range of <LOD - 63 ng g^{-1}. The detection frequency of 1,2 Bis (2.4.6-tribromophenoxy) ethane (BTBPE) was 81% with concentrations of <LOD-1402 ng g^{-1}. Alongside the legacy BFRs, NBFRs were the most detected indicating probably increased usage as replacements for the banned commercial PBDEs products namely, penta-, octa-, and deca-BDE mixtures. No correlation was observed between

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https://doi.org/10.1016/j.scitotenv.2017.11.294

the bromine levels obtained using portable XRF and the BFRs detected using GC–MS ($r = 0.0073$, $p = 0.076$). The observed trend may be attributed to various factors including the sample matrix analysed and the number of BFRs analysed. The observed trend is consistent with those reported from other studies.

1. Introduction

Brominated flame retardants (BFRs) consists of a diverse group of bromine-containing compounds including polybrominated diphenyl ethers (PBDEs), total hexabromocyclododecane (T-HBCDD), tetrabromobisphenol A (TBBPA) and "novel or alternate" brominated flame retardants (NBFRs) (Muenhor et al., 2010; Santillo et al., 2001; Thomsen et al., 2002). These chemicals are intentionally incorporated into consumer products with the overall goal of preventing the ignition of fires thereby suppressing the burning process of materials (Alaee et al., 2003; Besis and Samara, 2012; Morf et al., 2005; Olukunle et al., 2015a). PBDEs were widely used and marketed as penta-, octa- and deca-BDE mixtures and have been applied to products such as electrical and electronic equipment and furniture (Abbasi et al., 2016; Daso et al., 2017; Muenhor et al., 2010; Ni et al., 2013). It has been reported that BFRs, when added into products additively, have the tendency to diffuse out from the surfaces of the treated products and subsequently can be released into the environment (Akortia et al., 2016; Daso et al., 2013; Harrad et al., 2016; Hassan and Shoeib, 2015; La Guardia et al., 2006). Furthermore, penta-BDE and octa-BDE and other BDEs have been found to be bioaccumulative and persistent with endocrine disrupting properties (Hooper and McDonald, 2000). Consequently, there was a call for the phasing out of these chemicals. For example, penta- and octa-BDE were voluntarily phased out in the USA in 2004; while the EU banned the use of penta- and octa-BDE in the same year (Besis and Samara, 2012; Eskenazi et al., 2011; Johnson et al., 2013; Katima et al., 2017; Li et al., 2014). Because of the phasing out of penta and octa-BDEs, the use of deca-BDE mixture increased in the EU (Söderström et al., 2004; Xu et al., 2016). The EU finally banned all technical mixtures of PBDEs by 2008 (Betts, 2008; Kemmlein et al., 2009; Directive 76/769/CEE, 1976; Directive 2003/11/EC, 2003; ECJ, 2008). Owing to their potential to persist in the environment, health concerns, bioaccumulation as well as their ability to undergo long-range atmospheric transportation, penta- and octa-BDE were added to the list of persistent organic pollutants (POPs) under the Stockholm Convention in 2009 (Vojta et al., 2017; Xu et al., 2015) and deca-BDE has recently been added to the list (Bramwell et al., 2017). Total hexabromocyclododecane is another class of BFR and they exist in three main diastereoisomers namely (<alpha>, <beta> and <gamma> HBCDD mixture) (Daso et al., 2017; Ni and Zeng, 2013; Olukunle and Okonkwo, 2015). T-HBCDD have also been classified as a POP under the Stockholm Convention (Zhu et al., 2016).

Recent reports suggest that the bans and restrictions of some "legacy" BFRs have resulted in an increase in the use of NBFRs as replacements (Al-Omran and Harrad, 2016; Covaci et al., 2011; Fromme et al., 2014; Poma et al., 2014). These include 2-ethyl-1-hexyl-2,3,4,5 tetrabromobenzoate (EH-TBB), bis(2-ethyl-1-hexyl)-2,3,4,5 tetrabromophthalate (BEH-TEBP) and 1,2bis(2,4,6- tribromophenoxy) ethane (BTBPE) and many others (Dodson et al., 2012; Olukunle and Okonkwo, 2015; Saunders et al., 2013). EH-TBB and BEH-TEBP were introduced as replacements for penta-BDE, while octa-BDE and deca-BDE were replaced with BTBPE and DBDPE, respectively (Ali et al., 2011a; Covaci et al., 2011; Peng et al., 2017).

In sub-Saharan Africa, particularly in South Africa, information with respect to the production and industrial usage of these chemicals is scarce. The few reports that have emerged so far from the African continent on BFRs have indicated that the presence of BFRs in the African environment is most likely to stem from the importation of brominated flame retarded consumer products (Kefeni and Okonkwo, 2012; Olukunle et al., 2012). As mentioned earlier, these chemicals have the tendency to diffuse out of materials and consequently, can be discharged into different environmental media including dust. Since BFRs treated consumer products are found within the indoor environment, dust becomes an important medium where these chemicals can reside. Therefore, in order to determine the presence and levels of BFRs in an indoor environment, dust offers one of the best medium for indoor estimation of POP chemicals and this has been confirmed by several reports (Kefeni and Okonkwo, 2012; Rauert et al., 2014).

X-ray fluorescence analyser is a quick and easy to use tool that is generally employed for qualitative measurement of various elements in soil, rocks, and ores. The application of XRF has been extended to the identification of elements in products. Therefore, the main objective of this study was to (i) use X-ray fluorescence analyser as a screening tool to measure bromine in electronic equipment and furniture which may suggest the presence of brominated flame retardants and (ii) use GC–MS to quantitatively determine the concentrations of PBDEs, T-HBCDD and some NBFRs in dust samples collected from the items screened for bromine.

2. Materials and methods

2.1. Materials and reagents

About 1.2 mL of 50 μg mL^{-1} pure BDE standards (BDE-47, -99, -100, -118, -153, -154, -183, -209 and $^{13}C_{12}$ BDE-77, -139), hexabromocyclododecane (α, β, and γ T-HBCDD), 2-ethyl-1-hexyl-2.3.4.5-tetrabromobenzoate (EH-TBB), bis(2-ethy-1-lhexyl) tetrabromophthalate (BEH TEBP) and 1,2 bis(2.4.6-tribromophenoxy) ethane (BTBPE), were purchased from Cambridge Isotope Laboratories Inc. (Andover, USA). Sodium sulphate (purity, 99.9%), silica gel (100–200 mesh, with pore size 60 Å and particle size of 75–150 μm), dichloromethane, *n*-hexane, acetone, and toluene (all HPLC grade) and glass wool were all purchased from Sigma-Aldrich (Chemie GmbH, Steinheim, Germany). Pesticarb (120–400 mesh) was supplied by Agela Technologies (Stargate Scientific, Wilgeneuwel, South Africa). Nitrogen and helium gases were of high purity (99.999%) and were bought from Afrox (Pty) Ltd. in Pretoria, South Africa.

2.2. X-ray fluorescence (XRF) product testing

Accessible electronic equipment and furniture at the Tshwane University of Technology, Arcadia campus were subjected to XRF (Olympus Innov-X DELTA XRF analyser) screening to identify and measure bromine which may suggest the presence of brominated flame retardants in the identified products. Prior to use, the XRF was calibrated using calibration check (pass/fail) 316 stainless steel coupon, followed by the measurement of polymeric check standards (ERM-EC680 and -EC681) through the Mylar window of the plastic cup. The instrument was triggered for 120 s in order to verify the instrument's reliability and accuracy. In total, 49 electronic equipment and furniture were randomly selected and tested for bromine using the portable XRF in the RoHS/WEEE mode and triggered for 60 s during each measurement. Screening covered the outer surface of components, except for the system unit where screening was performed on the interior components and thus, the motherboards and the cooling fans. It is important to note that all items screened were no longer in use. Table S2 summarizes the results obtained from the tested electronic equipment and furniture.