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SCREENING AND QUANTIFICATION OF BROMINE AND BFRS IN OFFICE EQUIPMENT IN PRETORIA, SOUTH AFRICA USING X-RAY FLORESCENCE AND GC-MS

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Introduction

Studies have confirmed the presence of PBDEs in several indoor and outdoor air^{1,2}, house and office dust^{3,4,5,6}, landfill leachates^{7,8} and sediments and soil⁸. It is, therefore, evident that PBDEs are present in a variety of environmental samples. Within the indoor environment, however, it is likely that exposure to PBDEs continues due to the presence of house and office equipment manufactured before the PBDEs was banned. According to Mcpherson et al (2004)⁹, about 40% of PBDEs are used in the outer casing of electronic equipment such as television, computers and printers and Deca-BDE been the mostly used BFR. The phasing-out of polybrominated diphenyl ethers has paved the way for the use of 'Novel' Brominated Flame Retardants (NBFRs) as their replacements. The NBFR formulations include, but limited to, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl-tetrabromophthalate (TBPH) and 1,2Bis(2, 4, 6- tribromophenoxy) ethane (TBPE). Penta-BDE being replaced with TBB and TBPH, while Octa-BDE and Deca-BDE replaced with TBPE and DBDPE respectively¹¹ Allen et al. (2008)¹² used X-ray fluorescence (XRF) to identify products containing bromine (Br) as an indicator of PBDEs. A correlation between Br and PBDE concentrations measured using XRF and GC-MS was observed. Furthermore, an association between Br levels in products and PBDE concentrations in house dust were observed. Kajiwara et al. (2011)¹³ also used XRF to screen for FRs in selected electronic products. Using XRF, Webster et al. (2009)¹⁴ outlined the possible mechanisms of BFRs, particularly PBDEs migration from PBDE-containing products and their distribution in house dust as follows: (1) through volatilization from the polymer followed by air-dust partitioning, (2) abrasion of the polymer surface causing the release of FR-enriched particles or fibres, and (3) direct transfer of FRs from the FR-containing polymer to dust. Volatilization is strongly suggested to be the main mechanism for the release of more volatile compounds whereas abrasion is considered more likely for less volatile compounds. The main goal of this study was, therefore, to understand which office products act as a source of BFRs to indoor office dust with respect to human exposure. In order to investigate this, a portable X-ray fluorescence (XRF) was used as a screening tool to determine the presence and levels of bromine and quantification of PBDEs and 'novel' BFRs in selected electronic and electrical equipment within the office environment.

Materials and methods

XRF (Olympus Innov-X DELTA portable XRF analyzer) was first used to identify and measure bromine levels in computers, laptops, printers and cell phones. Prior to use, the portable XRF was calibrated on the Delta docking station (DDS) and by using the 316 stainless steel coupon. Pure BDE standards (BDE-28, -47, -77, -99, -100, -118, -128, -183, -209 and 13C-BDE-77, -139, -209) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), Bis(2-ethylhexyl) tetrabromophthalate (TBPH), 1,2-Bis(2,4,6-tribromophenoxy) ethane (TBPE), were purchased from Cambridge Isotope Laboratories Inc (Andover, USA). Sodium sulphate (Purity 99.9%), Silica gel (100-200 mesh), glass wool, pesticarb and HPLC grade organic solvents (dichloromethane, hexane, acetone and toluene) were purchased from Sigma Aldrich (Chemie GmbH, Steinheim, Germany). Dust samples were collected from the aforementioned office equipment using pre-weighed glass wool by swiping on the surfaces of the equipment. After collection, the samples were wrapped with aluminium foil and kept in the refridgerator until extraction.

The extraction method used in this study was as described by Olukunle et al (2015). Briefly, about 100 mg of dust was weighed and extracted with 3 mL mixture of toluene: dichloromethane (1:1, v/v) for 15 min at 45oC using ultrasonic bath (Emalsonic S40H, Germany). Prior to extraction, dust samples were spiked with 3 µL mixture of labelled 10 ng µL⁻¹ BDE-77, -139 and -209 surrogate standards to monitor recoveries, and left to calibrate for 3 h. Extraction was repeated three times for each sample and the supernatants were transferred into clean tubes. Finally, the extracts were reduced under rotary evaporator and subjected to cleaning by column chromatography. The column was packed with 0.16 g silica gel, 0.06 g pesticarb, and finally with 0.5g sodium sulphate. Before introduction of the extract into the column, the packed column was eluted with 12 mL of toluene: dichloromethane (1:1, v/v). Thereafter,

the purified extracts were concentrated under the stream of nitrogen gas to about 100 μL , topped up with 150 μL of toluene and further reduced to about 160 μL . Prior to analysis, the reduced extracts were spiked with 10 μL of 2.0 $\text{ng } \mu\text{L}^{-1}$ of internal standard (BDE-118). One microlitre of the extract was injected into the GC-MS under optimized instrumental conditions. Analyses of PBDEs and NBFs were performed using Shimadzu model 2010 plus gas chromatography coupled with a model QP 2010 ultra-mass spectrometer (Shimadzu, Japan) using electron ionization and injected automatically by Shimadzu AOC-20i auto sampler. Operation mode was in the selected ion-monitoring (SIM). A 15 m column; DB5 (0.25mm ID, 0.1 μm df) was used for separation. The oven temperature program set at 90 $^{\circ}\text{C}$ (1min), 30 $^{\circ}\text{C min}^{-1}$ to 300 $^{\circ}\text{C min}^{-1}$ (5min) and 10 $^{\circ}\text{C min}^{-1}$ to 310 $^{\circ}\text{C min}^{-1}$ (10min). Helium (purity 99,999%) was used carrier gas and set at a constant flow of 1.5mL min^{-1} . The injector, transfer line, and ion source temperature were set at 290, 300 and 250 $^{\circ}\text{C}$, respectively.

All laboratory glassware were washed with soap water, rinsed and soaked overnight in 10% (v/v) nitric acid aqueous solution and finally rinsed with de-ionized water. Silica, glass wool and sodium sulphate were baked at 450 $^{\circ}\text{C}$ for 12 h to remove impurities. To avoid absorption of moisture, glass wool was wrapped with aluminium foil and kept in the desiccator. Silica gel and sodium sulphate were stored in separate glass jars, which were pre-cleaned and rinsed with a mixture of hexane: acetone (2:1, v/v), then sealed to protect them from moisture absorption and contamination. Samples were collected and wrapped with aluminium foil, to protect them from light. Extraction was performed in the absence of light (electricity). Retention times of the unknowns were matched with those of individual standards and quantification was done by monitoring the molecular ions using external methods.

Results and discussion

Bromine was detected in majority of the screened electronic products. Of these, keyboards had the highest concentrations which ranged from 174-4019 $\mu\text{g g}^{-1}$, while the lowest concentrations were found in cell phones, which ranged from ND-158 $\mu\text{g g}^{-1}$ with a mean of 33.5 $\mu\text{g g}^{-1}$. For the gas chromatography-mass spectrometry analysis, eight brominated diphenyl ether (BDE) congeners namely (BDE-28, -47, -99, -100, -154, -153, -128, and -183) and three novel brominated flame retardants (NBFs) TBB, TBPH and TBPE were identified in the collected dust samples. The Σ PBDEs ranged from 1814.7 - 5970.6 ng g^{-1} with a mean of 3456.3 ng g^{-1} , while that of NBFs ranged from <dl - 3376 ng g^{-1} with a mean of 1237.2 ng g^{-1} dry weight. The highest concentrations in electronic dust were observed for BDE-47 ranging from 1525.0 -3797 ng g^{-1} with a mean of 1442.6 ng g^{-1} . This is about 9 times greater than the mean of BDE-153 (154.0 ng g^{-1}) and six times more than the mean of BDE-28 (238.6 ng g^{-1}) and BDE-128 (219.8 ng g^{-1}). Penta-BDE represented the major congeners, in which BDE-47, BDE-99 and BDE-100 were detected in all dust samples analyzed. In the case of NBFs, a contribution of approximately 13 % to 38 % was observed. Of the sixteen dust samples analyzed, three were found to contain 2-ethylhexyl-2,3,4,5-Tetrabromobenzoate (TBB), bis (2-ethylhexyl) tetrabromophthalate (TBPH) and 1,2-bis(2,4,6-tribromophenoxy)ethane (TBPE). While keyboards were found to contain these compounds (NBFs) below detection limits. Printer (a) and (V) monitor contained only TBB and TBPE giving the total of NBFs 1237.2 ng g^{-1} for printer (a) and 665.1 ng g^{-1} for (V) monitor, respectively. The detection of NBFs in electronic dust may be due to their use as replacements for penta-, octa and deca-BDE. The presence of TBB and TBPH may have migrated through dust from the treated furniture which was stored at the same location with the screened electronics. With respect to keyboard, printers and monitors, the concentrations of Br determined using XRF exhibited the following trend: keyboard>printer>monitors. This trend was repeated in the GC-MS analysis of dust samples. With the novel BFRs, the concentration trend was: monitor>printer>keyboard. The observed trends suggest that the XRF can be used as a reliable screening tool for indirect measurement of PBDEs in dust samples.

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