

BROMINATED AND PHOSPHATED FLAME RETARDANTS IN INDOOR DUST FROM ISTANBUL: OCCURRENCE AND HUMAN EXPOSURE ASSESSMENT

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Introduction

Flame retardant chemicals (FRs) are additives that have been used for several decades to reduce flammability of resins and polymers found in various consumer products such as polyurethane foam, plastics, electronic equipment, textiles, furniture and others^{1,2} and even children's products including car seats, strollers, mattresses and clothing³⁻⁵. Of the many types of FRs such as hydroxy, brominated, organophosphorus, antimony oxide and chlorinated⁶, polybrominated diphenyl ethers (PBDEs) have historically been the most intensively used flame retardants. Global market demands were 56100 tonnes, 7500 tonnes and 3790 tonnes for decabromodiphenyl ether (deca-BDE), pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE), respectively in 2001⁷. However, due to their persistence, bioaccumulative nature and toxicity, commercial mixtures of PBDEs (i.e. pentaBDE and octaBDE) were added as persistent organic pollutants at the fourth meeting of the Conference of the Parties (COP4) to the Stockholm Convention⁸. This led to the development of alternate FRs formulations as well as an increase in use of existing non-PBDE brominated novel FRs (NBFRs)⁹ and non-brominated alternative FRs such as organophosphorus FRs (OPFRs)¹⁰ to meet flammability standards for consumer products¹¹.

A high Production Volume (HPV) chemical is defined as a chemical produced above 1000 tons/year¹². Considering that the BFR consumption had increased in 2008 to 410000 tons compared to 311000 metric tons in 2005¹³, it is most likely that many alternative FRs are in the HPV class. For example, total market demand for hexabromocyclododecane (HBCDD) in 2003 was estimated to be 22000 tons/year¹⁴. However, a report published by the Norwegian Pollution Control Authority (at the moment Norwegian Climate and Pollution Agency) states that it is difficult to determine the exact volume produced and used of NBFRs¹⁵. The organophosphorous compounds (OPFRs) are high production volume chemicals and are used as flame retardants but also as plasticizers, hydraulic fluids, lacquer, paint, glue and in cosmetics. According to the European Flame Retardants Association (EFRA, 2007 cited in der Veen and Boer¹⁶), the total consumption of OPFRs in 2006 was ~93,000 tonnes, which was equivalent to approx. 20% of total FRs consumption in Europe. Since FRs are normally employed as additives and are not chemically bonded to the polymers that they are used in, they can be released into the environment via volatilization, dissolution and abrasion. The phosphorus-containing compounds have vapour pressures that are orders-of-magnitude higher than most other halogenated flame retardants¹⁷ which increases the likelihood of release from a product¹⁸.

House dust is a repository medium for many contaminants that are transported from outside or that originate from indoor sources and is of increasing concern due to its probably being the main pathway of human exposure to various contaminants via ingestion, inhalation and dermal contact. PBDEs¹⁹, NBFRs²⁰ and OPFRs²¹ are categorized as semi-volatile compounds (SVOCs). Several SVOCs have been reported to be in indoor dust^{12,18} and these SVOCs are essentially adsorbed onto particulates²². Therefore, SVOCs associated with indoor dust is a potential risk for human health through oral ingestion and inhalation. This risk is increased for children due to their hand to mouth behaviour and increased dust ingestion rates compared to adults. Moreover, indoor exposure is a very important pathway since people spend approx. 80% of their time in indoor environments²³.

In this study, we investigated concentrations of Σ_{12} PBDEs, Σ_{12} NBFRs and Σ_{13} OPFRs in house and office dust collected in 2012 from Istanbul, Turkey. Target NBFRs were 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (ATE), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), octabromotrimethylphenyllindane (OBIND), hexabromocyclododecane (HBCDD), bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 1,2,5,6-tetrabromocyclooctane (TBCO), tetrabromoethylcyclohexane (TBECH) and dechlorane plus (DP). OPFRs of interest were tris-cresyl phosphate (TCP, ortho, meta and para-isomers), tris(2-chloroethyl) phosphate (TCEP),

tris-2-butoxyethyl-phosphate (TBEP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(2-chloroisopropyl) phosphate (TCPP), triphenyl Phosphate (TPhP), ethylhexyldiphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP), tris(2-isopropyl phenyl) phosphate (TPPP), tris(3,5-dimethyl phenyl) phosphate (TDMPP), tris(4-tert-butylphenyl) phosphate (TTBPP), tris(2,3-dibromopropyl) phosphate (TDBPP), bis(2-ethylhexyl) phosphate (BEHP)

Materials and methods

Study Location, Sample Collection, Extraction and Analysis

A total of 19 indoor dust samples were collected from homes (n=10) and offices (n=9) in Istanbul (Figure 1) located in urban (Besiktas), semi-urban (Bahcesehir) and rural (Gokturk) areas. Vacuum cleaner dust bags were provided by volunteers who were asked to change their bags at the beginning of the study and keep collecting dust samples as a result of their normal cleaning activities for a period of 8 weeks (February-March 2012). Dust samples were sieved through a 100 μm stainless steel sieve and kept at $-20\text{ }^{\circ}\text{C}$ in solvent rinsed amber bottles until analysis.

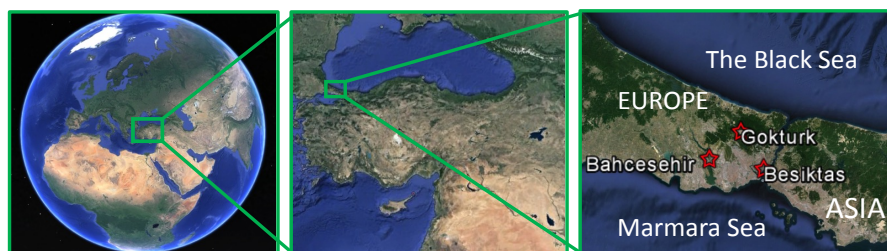


Figure 1. Sampling Areas in Istanbul, Turkey

PBDEs and NBFs analysis were done simultaneously while dust samples were re-visited in 2014 for OPFRs analysis. Extraction of PBDEs and NBFs were done using 1 g of dust with acetone:dichloromethane (10mL x 3 times) and $^{13}\text{C}_{12}$ PCB-28, -52, -101, -138, -138, -153, -180 (25 ng each) were used as recovery compounds. Extracts were cleaned up on 3-g 6% deactivated Alumina (baked at $450\text{ }^{\circ}\text{C}$ for 4 hours) and analytes were eluted using 35 mL of 20% DCM in hexane. Extracts were concentrated to 1 mL and solvent exchanged into iso-octane by rotary evaporation and N_2 blowdown. Extraction of OPFRs was done using 0.25-g using the same extraction procedure as above but 48 ng chlorpyrifos-oxon, 49 ng chlorpyrifos-methyl and 50 ng malathion were added as recovery standards and no further cleanup was done. $^{13}\text{C}_{12}$ PCB105 (5 ng) was the internal standard for volume correction.

PBDE, NBF and a few OPFRs were determined were on an Agilent 6890 GC - 5973 MSD operating in electron capture negative ion mode. Methane was the reaction gas (2.2 mL/min) and helium was the carrier gas at 1.1 mL/min. 2 μL inject pulsed split/splitless. The injector temperature, transfer line, quadrupole and source temperature were at $280\text{ }^{\circ}\text{C}$, $250\text{ }^{\circ}\text{C}$, $150\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$, respectively. The column used was a DB-5 (J&W, 30 m, 0.25 mm i.d., 0.1 or 0.25 (OPFRs) μm film thickness). The GC oven program was: $80\text{ }^{\circ}\text{C}$ 2 min, $10\text{ }^{\circ}\text{C}/\text{min}$ $285\text{ }^{\circ}\text{C}$ 5 min, $25\text{ }^{\circ}\text{C}/\text{min}$ $300\text{ }^{\circ}\text{C}$ 5 min. Most OPFRs were analysed on an Agilent 6890 gas chromatograph (GC) equipped with a mass selective detector (MSD) (Agilent 5975) operating in electron impact (EI) ionization mode. A capillary column (DB-5, 30 m, 0.25 mm, 0.25 μm) was used, injector $200\text{ }^{\circ}\text{C}$, transfer line $250\text{ }^{\circ}\text{C}$, quad $150\text{ }^{\circ}\text{C}$ and source $230\text{ }^{\circ}\text{C}$. Temperature programme was: initial $50\text{ }^{\circ}\text{C}$, $20\text{ }^{\circ}\text{C}/\text{min}$ to $160\text{ }^{\circ}\text{C}$, $2\text{ }^{\circ}\text{C}/\text{min}$ to $230\text{ }^{\circ}\text{C}$, $20\text{ }^{\circ}\text{C}/\text{min}$ to $310\text{ }^{\circ}\text{C}$.

Quality Control

Analytical recovery efficiencies were determined by spiking all samples with recovery compounds prior to extraction. Recovery of $^{13}\text{C}_{12}$ -PCBs were between 65% and 120% with an average recovery of $91\pm 15\%$. Recovery of chlorpyrifos-oxon, chlorpyrifos-methyl and malathion was between 48% and 88% with an average of $69\pm 8.6\%$. Relative standard deviation of concentrations detected in duplicate samples ranged between 9.6% and 27%. Blank samples were prepared using baked sodium sulphate, subjected to the same analytical procedure as dust samples. MDL values were 0.230 ng/g for PBDEs and NBFs (0.93 ng/g for PBDE-209) while this value ranged between 2 ng/g and 65 ng/g for OPFRs depending on analyte.

Results and discussion

Average concentrations of analytes were as follows: Σ_{12} PBDEs; 400-12500 ng/g for PBDEs in homes and 330-32000 ng/g for offices; Σ_{12} NBFs; 320-31400 ng/g for homes and 910-97900 ng/g for offices; Σ_{13} OPFRs; 1450-

As it is seen in Figure 3, Σ_{12} NBFRs contribution to the average total FRs concentration in house dust was from NBFRs (46%) followed by OPFRs (32%) and PBDEs (22%). NBFRs contribution was the highest (60%) in office dust as well. However, contribution of PBDEs (24%) was higher than that of OPFRs (16%).

11130 ng/g for homes and 2080 ng/g and 17300 ng/g for offices. A box and whiskers graph representing the 5th percentile, 95th percentile, median value of detected concentrations is given in Figure 2.

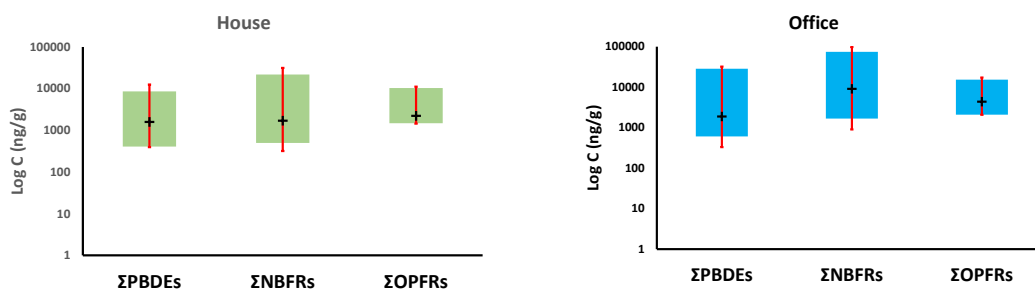


Figure 2. Log scale box-and-whiskers plots of Σ_{12} PBDEs, Σ_{12} NBFRs and Σ_{13} OPFRs in house dust (left panel) and office (right panel) dust in Istanbul. The center box is bounded by the 5th and 95th percentile, the black cross depicts the median value while vertical red line represents the range of the data.



Figure 3. Percent distribution of Σ_{12} PBDEs, Σ_{12} NBFRs and Σ_{13} OPFRs in house and office dust in Istanbul

Human exposure to Σ PBDEs, Σ NBFRs and Σ OPFRs via dust ingestion is calculated using the formula given below.

$$D_{ing} = C \times \frac{I}{BW} \times P \quad \dots\dots\dots 1$$

whereas

Ding = exposure to chemical via ingestion (ng/day/kg); C= concentration of chemical (ng/g) (Median and 95th concentration values were used for low exposure and high exposure scenarios, respectively; both office and house concentrations were taken into account for adults exposure while only house concentrations were taken into account for children's exposure); I= average dust ingestion (Low exposure scenario: 50 mg/day and 20 mg/day for children and adults respectively; High exposure scenario: 200 mg/day and 50 mg/day for children and adults, respectively)²⁴; BW: body weight (60 kg and 15 kg for adults and children, respectively)²⁵; P: percent of a day people spend indoors (64% and 86% for adults and children respectively).²³

Calculations showed that children in Istanbul were exposed to PBDEs approx. 4.8-20 times higher compared to adults while the ratio between children and adults exposure to NBFRs and OPFRs were 6.4-11 and 9.7-16 respectively (Table 1).

Table 1. Adult and Child exposure (ng/day/kg) to FRs chemicals in Istanbul

	Exposure (ng/day/kg)					
	Σ PBDEs		Σ NBFRs		Σ OPFRs	
	Adult	Child	Adult	Child	Adult	Child
Low exposure-Low Dust Ingestion	374	4541	768	4880	659	6378
Low Exposure-High Dust Ingestion	934	18166	1921	19519	1648	25512
High exposure-Low Dust Ingestion	4855	23410	8902	61206	2506	25311
High exposure-High Dust Ingestion	12137	93641	22255	244826	6265	101242

Research Gaps

The only flammability standard related to consumer products in Turkey is for construction materials (TSE EN ISO 1182 ve TS 1912) but there are no standards for other consumer products such as furniture, foam, electronics and upholstery. Although no production amounts of flame retardant chemicals in Turkey are reported, a recent inventory showed the import of 547 tonnes of diphenyl ether and 177 tonnes of penta / tetra bromo diphenyl ether in to the country, between 1996 and 2013²⁶. OPFRs are also imported through their use in

various consumer products. The results of this study indicate that Turkish people are being exposed to FRs released from their consumer products. It should also be noted that the size of the samples in this study is relatively small to be able to integrate the results to all over Turkey. However, it will serve a preliminary database to be used in future studies and it highlights that there is a need for further research on this area in Turkey.

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