SELECTED ORGANOPHOSPHATE FLAME RETARDANTS IN TURKISH INDOOR DUST

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Introduction

Indoor dust is an important human exposure pathway to various environmental contaminants including persistent organic contaminants (POPs) and flame retardants (FRs). People spend the majority of their time indoors whether at home or at work. Many studies have reported that toddlers are subjected to higher exposure rates compared adults due to their hand to mouth behaviour and usage of FRs in baby products (Stapleton et al., 2011). Various household products are known sources of POPs and FRs to the indoor environment including building materials, paint, pest control activities, consumer products such as upholstery textiles and foam paddings in furniture and mattresses, thermoplastics in computers, TVs, electrical components and cables.

The organo-phosphorous compounds (OPFRs) are high production volume chemicals and are used as flame retardants but also as plasticizer, hydraulic fluids, lacquer, paint, glue and in cosmetics. According to the European Flame 30 Retardants Association (EFRA), the total consumption of OPFRs in 2006 was ~91,000 tonnes. Since OPFRs are normally employed as additives and are not chemically bonded, they can be released into the environment via volatilization, dissolution and abrasion. These phosphorus-containing compounds have vapour pressures that are orders-of-magnitude higher than most other halogenated flame retardants (Bergman et al. 2012; Brommer et al., 2014) which increases the likelihood of release from a product. As PBDEs and other brominated flame retardants are phased out due to national and international regulations, the use of OPFRs is expected in increase.

The few studies that looked at levels of OPFRs in house and office dust show very high levels compared to other flame retardants (Stapleton et al., 2009; Van den Eede et al., 2011). Amongst the highest concentrations of “new” flame retardants measured in indoor dust are the major replacements of penta-DBE, namely components of Firemaster 550 which includes several OPFRs, i.e. TPhP and TDCPP (Stapleton et al. 2008;2012; Dodson et al. 2012; Goosey et al. 2012a,b). Some of the highest concentrations of flame retardants measured indoors and outdoors are those of the phosphorus-containing FRs such as TDCPP and tri-cresyl phosphate (TCP) (Goosey et al. 2012a,b; Brommer et al. 2012; Marklund et al., 2003) and can be orders of magnitude higher than PBDEs. Studies on other flame retardants show that indoor dust is a main exposure route to PBDEs, with exposure models predicting highest exposures for toddlers and young children (Jones-Otazo et al. 2005; Frederiksen et al. 2009; Lorber 2008). This prediction was confirmed by data showing significant correlations between PBDE (penta-BDE to be specific) concentrations in dust and body burden, with inadvertent dust ingestion and possibly dermal exposure being the putative exposure pathway (Wu et al. 2007; Johnson et al. 2010; Watkins et al. 2011; Vorkamp et al. 2011). These studies indicate that humans are being exposed to FRs, including OPFRs from their indoor environment.

In this study we investigate OPFRs in indoor dust from houses and offices in Istanbul, Turkey. The chemicals 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). This is the first reported occurrence and level of OPFRs in dust from indoor environments in Turkey. Results of this study highlight the importance of exposure to OPFRs through indoor dust.

Materials and methods

Study Location, Sample Collection, Extraction and Analysis

A total of 51 indoor dust samples were collected from homes and offices in Istanbul (Figure 1). Samples were collected from different districts of Istanbul and locations are basically categorized as rural, semi-urban and urban.

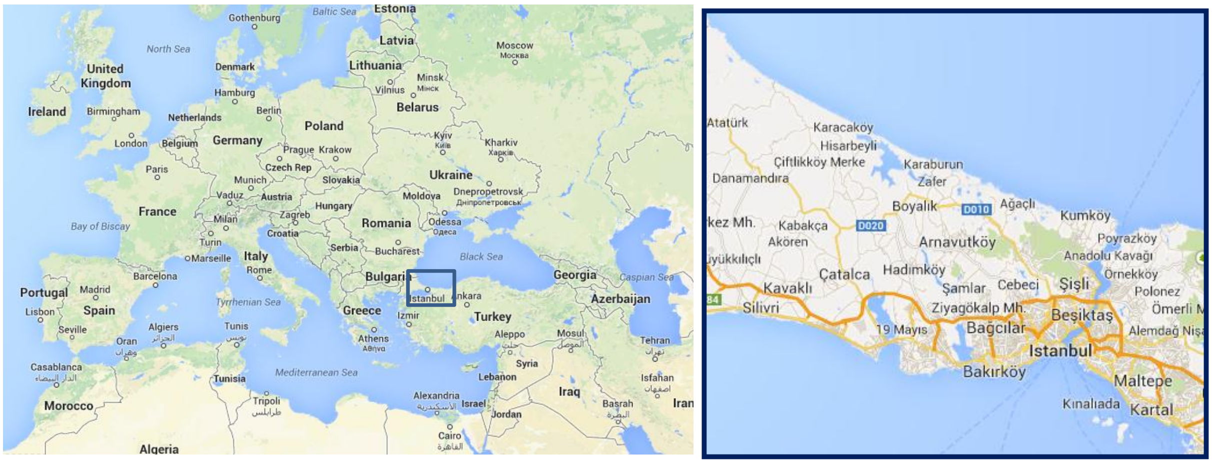

Figure 1. Sampling Area

Dust samples investigated in this study were obtained from in use vacuum cleaner bags Therefore, different makes and models were employed in this study. Simply, the participants were asked to change their bags at the beginning of the study and to continue cleaning their homes/offices as normal over the 8-week study period (February-March 2012). At the end of the 8-week period, the bags were sealed and returned to the laboratory for analysis. Dust samples were sieved through a 100 µm stainless steel sieve on to a solvent rinsed stainless steel tray. Following the removal of hair, debris and other large particles, the samples were transferred to the baked and solvent rinsed amber bottles and kept at -20ºC until the analysis.

Briefly, following the addition of recovery compounds (malathion, chlorpyrifos methyl and chlorpyrifos oxon, 25 ng each) to 0.25 g dust sample, 10 ml of 1:1 acetone:dichloromethane solvent mixture was added and vortexed for 5 minutes. Dust samples were kept in solvent overnight and were ultrasonically extracted for 60 minutes in the following day. After sonication, samples were centrifuged and the aliquot was transferred into a round bottom flask. The procedure was repeated three times and aliquots were combined. The volume of the extracts were reduced and transferred into hexane using a rotary evaporator and further reduction to 1 mL in isooctane was done under a high purity N_2 stream. No further cleanup was done.

Analysis of target compounds were done on an Agilent 6890 gas chromatograph (GC) equipped with a mass selective detector (MSD) (Agilent 5975) working in electron impact (EI) ionization and electron capture negative ionization (ECNI) modes. A capillary column (DB-5, 30 m, 0.25 mm, 0.25 µm) was used, 2uL inject pulsed split/splitless, injector 200C, transfer line 250C, quad 150C and source 230C(EI) and 150C (ECNI). Temperature programme was: initial 50ºC, 20ºC/min to 160ºC, 2ºC/min to 200ºC, 20ºC/min to 270ºC.

Quality Control

Analytical recovery efficiencies were determined by spiking all samples were with recovery compounds prior to extraction. Average recovery was 69±10 % (44-93%). 4 samples were analyzed as duplicate and relative standard deviation of duplicate samples for the target chemicals ranged between 9.6% and 13%. Instrument detection limit was the method detection limit and for (TCP, , TCEP, TBEP, TDCPP were 2ng/g, 4ng/g, 20ng/g and 4ng/g respectively. Blank samples were prepared using baked sodium sulphate, subjected to the same analytical procedure as dust samples and no target chemicals were detected in blank samples.

Results and discussion

Concentration of Σ_6OPFRs in house dust ranged between 180 and 21000 ng/g with an average value of 1900±3600 ng/g while concentration range for office samples was from 1001 to 9711 ng/g with an average value of 2200±2400 ng/g.

Table 1. Concentrations of OPFRs in indoor dust from Istanbul

Compound	Detection n/N	Min.	Max.	Average	STD	Geometric mean	Median
	House Dust (N=39)						
TCP2 meta	25/39	13	190	58	37	49	50
TCP3 para	3/39	16	21	18	2.3	18	19
TCEP	39/39	15	2600	390	590	200	190
TBEP	2/39	1800	8300	5000	4600	3800	5000
TDCPP	39/39	16	17000	1200	260-	650	610
Σ_6OPFRs		180	21000	1900	3600	1100	1100
	Office Dust (N=12)						
TCP2 meta	11/12	28	200	88	61	71	70
TCP3 para	0	na	na	na	na	na	na
TCEP	12/12	88	2500	590	690	390	320
TBEP	1/12	6400	6400				
TDCPP	12/12	610	1700	1000	370	956	890
Σ_6OPFRs		1000	9700	2200	2400	1700	1400

TDCPP and TCEP were detected in all samples, where TDCPP had higher concentraitons. Stapleton et al. (2011) also found high concentrations of TDCPP in house dust. TBEP detection rate was low but had high concentrations when found and median concentrations of TBEP in house and office dust were much higher than concentration of indoor dust (66 ng/g) collected from Pakistan (Ali et al, 2011) but lower than samples from New Zealand (4020 ng/g) (Ali et al, 2012), Belgium (2030 ng/g) (Van den Eede et al., 2011), Spain (9400 ng/g) (Garcia et al., 2007) and Japan (1570000 ng/g) (Kanazawa et al., 2010). Office dust samples mean values detected in this study were lower compared to dust concentrations from three different office environments in China (128000 ng/g, 17300 ng/g and 17200 ng/g) (Cao et al., 2014).

Research Gaps

This is the first study reporting OPFRs in Turkish environment and 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 but 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 2013 (Kurt-Karakus, 2014). 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.

Recently, a research grant application was made to be able to investigate some other OPFRs in indoor dust samples from Istanbul. 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.

From a wider perspective, since OPFRs have higher volatility than brominated flame retardants (BFRs), these chemicals are distributed between settled dust and suspended dust. Therefore, it is recommended to assess the partition of OPFRs on different sizes of dust particles since exposure via inhalation and dermal exposure can become an important issue. PM 2.5 and smaller can be absorbed into the blood stream; this size can be suspended in the air longer than larger particles.

Acknowledgements

A part of the dust samples analyzed in this study was collected in frame of a previous study (TUBITAK Project # 112Y004). The authors would like to thank to The Scientific and Technological Research Council of Turkey (TUBITAK) for the financial support. We also would like to thank to all participants who provided dust samples and Autur Padja for help during analysis.

References

1. Stapleton HM, Klosterhaus S, Keller A, Ferguson PL, van Bergen S, Cooper E, Webster TF, Blum A. (2011); *Environ. Sci. Technol*. 45: 5323–5331
2. Bergman Å, Rydén A, Law RJ, de Boer J, Covaci A, Alaee M, Birnbaum L, Petreas M, Rose M, Sakai S, Van den Eede N, van der Veen I. (2012); *Environ. Int*. 49: 57-82.
3. Brommer S, Jantunen L, Bidleman T, Harrad S, Diamond M. (2014. *Environ. Sci. Technol.* in press.
4. Stapleton HM, Klosterhaus S, Eagle S, Fuh J, Meeker JD, Blum A, Webster TF. (2009); *Environ. Sci. Technol.* 43: 7490–7495
5. Van den Eede N, Dirtu AC, Neels H, Covaci A. (2011); *Environ. Int.* 37:454–461
6. Stapleton HM, Kelly SM, Allen JG, McClean MD, Webster TF. (2008); *Environ. Sci. Technol*. 42: 3329-3334
7. Stapleton HM, Sharma S, Getzinger G, Ferguson PL, Gabriel M, Webster TF, Blum A. (2012); *Environ. Sci.Technol*. 46: 13432-13439
8. Dodson RE, Perovich LJ, Covaci A, Van den Eede N, Ionas AC, Dirtu AC, Brody JG, Rudel RA. (2012); *Environ. Sci. Technol*. 46: 13056-13066
9. Goosey E, Diamond ML, Saini A, Chaudhuri SR, Abbasi G. (2012a); 13th Annual Workshop on Brominated and Other Flame Retardants. Winnipeg, June 4-5
10. Goosey E, Saini A, Abbasi G, Malymuk L, Diamond ML. (2012b); Proceedings of the 33rd SETAC North America Annual Meeting, pp. 215-216.
11. Brommer S, Harrad S, Van den Eede N, Covaci A. (2012); J. Env. Monit. 14: 2482-2487
12. Marklund A, Barbro A, Peter H. (2003); *Chemosphere* 53(9):1137
13. Jones-Otazo HA, Clarke JP, Diamond ML, Archbold JA, Ferguson G, Harner T, Richardson GM, Ryan JJ, Wilford B. (2005); *Environ. Sci. Technol*. 39:5121-5130.
14. Frederiksen M, Vorkamp K, Thomsen M, Knudsen LE. (2009); *Int. J. Hygiene and Environ. Health*. 212: 109-134
15. Lorber M. (2008); J. Exp. Sci. Env. Epidem. 18: 2-19
16. Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF. (2007); *Environ. Sci. Technol*. 41: 1584-1589.
17. Johnson PI, Stapleton HM, Slodin A, Meeker JD. (2010); *Environ. Sci. Technol*. 44:5627-5632
18. Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton HM, Sjödin A, Webster TF. (2011); *Environ. Health Perspect*. 119: 1247-1252
19. Vorkamp K, Thomsen M, Frederiksen M, Pedersen M, Knudsen LE. (2011); *Environ. Int*. 37: 1-10.
20. Ali N, Van den Eede, N, Dirtu, AC, Neels, H, Covaci, A. (2011), *Indoor Air*, 1-12
21. Ali N, Dirtu AC, Van den Eedea N, Goosey E, Harrad S, Neels H, Mannet A, Coakley J, Douwes J, Covaci A. (2012); *Chemosphere*, 88:1276-1282
22. Garcia M, Rodriguez I, Cela R.(2007);*J. Chromatogr. A*, 1152: 280–286.
23. Kanazawa A, Saito I, Araki A, Takeda M, Ma M, Saijo Y, Kishim R.(2010) *Indoor Air*, 20: 72–84.
24. Cao Z, Xu F, Covaci A, Wu M, Yu G, Wang B, Deng S, Huang J. (2014); *Env. Int.* 65: 100-106
25. Kurt-Karakus PB. (2014). National Implementation Plan Update Project, Ministry of Environment and Urbanization