Brominated flame retardants in a computer technical service: Indoor air gas phase, submicron (PM$_1$) and coarse (PM$_{10}$) particles, associated inhalation exposure, and settled dust

Mesut Genisoglu [a], Aysun Sofuoglu [b], Perihan B. Kurt-Karakus [c], Askin Birgul [c], Sait C. Sofuoglu [a,*]

[a] Izmir Institute of Technology, Dept. of Environmental Engineering, Urla, Turkey
[b] Izmir Institute of Technology, Dept. of Chemical Engineering, Urla, Turkey
[c] Bursa Technical University, Dept. of Environmental Engineering, Bursa, Turkey

HIGHLIGHTS

- Dominant PBDE and NBFRs in PM$_1$, PM$_{10}$, and settled dust are BDE-209, BEH-TEBP, BTBPE.
- BFRs in PM$_1$ constitute ~50% of those in PM$_{10}$ in studied computer repair service.
- BFRs measured with passive samplers higher than active sampling but similar to PM$_{10}$.
- Similar gaseous and PM$_1$-associated BFR exposures at ~50% of PM$_{10}$-associated levels.
- The results point out that health risks for the employees may be considerable.

ARTICLE INFO

ABSTRACT

Brominated flame retardants (BFRs) are found in multi-media indoors, therefore, may pose serious risks to human health. This study investigated the occurrence of BFRs in particulate matter (PM$_1$ and PM$_{10}$) and gas phase by active and passive sampling, and settled dust to estimate potential exposure in a computer technical service. Polybrominated diphenyl ethers (PBDEs) and their alternatives (novel BFRs, NBFRs) were studied. PM and gas phase were collected on glass fiber filters and polyurethane foam plugs, respectively, and analyzed with a GC/MS after extraction, clean-up, and concentration. Inhalation exposure of the staff was estimated based on the measured concentrations using Monte Carlo simulation. BDE-209 was the dominating PBDE congener in all media while bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate and 1,2-bis(2,4,6-tribromophenoxy)ethane were those of NBFRs. Submicron particulate matter (PM$_1$) BFR levels constituted about one half of the PM$_{10}$-associated concentrations, while average PM$_{10}$ mass concentration (69.9 μg m^{-3}) was nine times that of PM$_1$ (7.73 μg m^{-3}). Calculated log$_{10}$ dust-gas and PM-gas partitioning coefficients ranged from -5.03 to -2.10, -2.21 to -0.55, and -2.26 to -1.04 for settled dust, PM$_{10}$, and PM$_1$, respectively. The indoor/outdoor concentration ratios were >1 for all compounds indicating the strength of indoor sources in the service. The estimated potential inhalation exposures, for future chronic-toxic and carcinogenic risk assessments, indicated that the levels of gas-phase and PM$_1$-associated exposures were similar at approximately one half of PM$_{10}$-associated levels. Results of this study indicate that the occurrence of BFRs in all studied media should be taken into consideration for occupational health mitigation efforts.

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1. Introduction

Flame-retardant chemicals have been added to furniture foam and upholstery, mattresses, curtains, plastics, and electronic devices such as computers and televisions due to requirements of fire regulations (Ali et al., 2012). Most flame retardants are

characterized by their long lifetime in nature due to their persistency, accumulation in the food chain, and toxicity (Darnerud, 2003). Flame retardants are found in all environmental media such as soil (Drage et al., 2016), vegetation (Morris et al., 2018), water sources (Gottschall et al., 2017), and air (Tao et al., 2016; Vorkamp et al., 2015). Bromine is one of the most used chemicals in production of flame retardants. Brominated flame retardants (BFRs) can be divided into three subgroups: additive, reactive, and polymeric BFRs. Stability of reactive BFRs is higher compared to that of additive ones due to chemical bonding to the materials. On the other hand, polymeric BFRs are much more stable than the others because they are incorporated into the framework of materials. Additive BFRs do not form a chemical bond with the material and thus increase the risk of exposure due to easier release to indoor air, where they are partitioned to dust/particulate and gas phases. Consequently, due to their lower physical stability, the contribution of additive BFRs to environmental persistent organic pollutant (POP) contamination is higher than that of the other types (Guerra et al., 2011).

Polybrominated diphenyl ethers (PBDEs) are a class of brominated hydrocarbons, that have been used as flame retardant chemicals for a long time (USEPA, 2012). They may be released to the environment via volatilization, abrasion and dissolution from PBDE-containing products (Kemmlein et al., 2003; Marklund et al., 2003), recycling of electronic wastes, burning of residential waste dump (Gullett et al., 2010), and steel production processes (Cetin and Odabasi, 2011; USEPA, 2012). Production of certain PBDEs has been banned in Europe and the US (Kurt-Karakus et al., 2017; Meeker et al., 2009). The commercial penta and octa-BDE mixtures were added to the Stockholm Convention list of POPs (SC, 2009), then commercial deca-BDE was added in 2016 (SC, 2017). Because of their persistence and lipophilicity (Toms et al., 2009), which result in bioaccumulation in the environment and the food chain, exposure to PBDEs are of the utmost importance. Animal and *in vitro* studies show that thyroid disorders, reproductive health effects, and neurobehavioral and developmental anomalies are some of the associated health effects (Bramwell et al., 2017).

PBDEs are classified as semi-volatile organic compounds (SVOCs), which may be more persistent indoors because of their partitioning to particle phase and lower degradation rates compared to that in ambient air (Li et al., 2015a). PBDEs present higher health risks since they are mainly associated with submicron particles (Besis and Samara, 2012), which have higher deposition rates in the respiratory airways and lungs compared to the coarse particles (Li et al., 2015a). In this context, determination of submicron particulate matter (PM_1) — bounded concentrations is important for the assessment of exposure to PBDEs.

Production of non-PBDE brominated alternative flame retardants (NBFRs) increased after the ban of certain PBDEs. Some widely-used NBFRs are 2,4,6-tribromophenyl allyl ether (TBP-AE), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), isomers of 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (α-, β-, γ- and δ-DBE-DBCH), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), isomers of dechlorane plus (syn- and anti- DP), 2,4,6-tribromophenyl 2,3-dibromopropyl ether (TBP-DBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), hexabromobenzene (HBB), hexabromocyclododecane (α- and γ-HBCDD), octabromo-1,3,3-trimethyl-1-phenylindane (OBTMPI), and 1,2,5,6-tetrabromocyclooctane (TBCO). They have been found at higher levels indoors compared to PBDEs reaching a median total Σ_{12}NFR dust concentration of 9.1 $\mu g\,g^{-1}$ in offices in Istanbul, Turkey with a maximum of 94 $\mu g\,g^{-1}$ measured in a computer room, while those values for Σ_{12}PBDEs were 1.9 $\mu g\,g^{-1}$ and 32 $\mu g\,g^{-1}$, respectively (Kurt-Karakus et al., 2017). The literature shows that PBDE and NBFR levels may be high for electronic device/computer rich occupational settings where house dust and submicron airborne PM may be important exposure pathways. However, studies on indoor submicron-PM-associated PBDEs and NBFRs are limited in general (Cao et al., 2014; Li et al., 2015b; Watkins et al., 2011), and absent for occupational settings such as computer repair services. The goal of this study is to investigate PBDE and NBFR concentrations of indoor air gas-phase, PM_1, PM_{10}, and settled dust in a computer repair service where exposure may be considerable.

2. Material and methods

Sampling was performed in a computer repair service at Izmir Institute of Technology (IzTech) between March 2016 and June 2016. Gas phase active sampling was conducted in parallel to passive sampling. Particulate phase was also collected along with the gas phase active sampling. Settled dust samples were collected in parallel to passive sampling. Active gas phase and particulate matter (PM_1 and PM_{10}) were sampled for 24 h every seven days (n = 12) while settled dust was collected once a month and passive gas-phase samples were collected monthly (n = 3). Impactors were used for PM_{10} (SKC Inc., PA, USA) and PM_1 (Harvard, Air Diagnostics & Engineering Inc.) sampling with flow rates of 14.4 $m^3\,d^{-1}$ and 28.8 $m^3\,d^{-1}$, respectively, on glass-fiber filters (GFF). Gas-phase samples were collected with PUF plugs along with PM_1. GFF were pre-cleaned before sampling (baked at 450 °C for 3 h in a furnace), wrapped in aluminum foil, and stored in glass Petri dish in a desiccator. Settled dust samples were collected from shelf surfaces (1 m^2 sampling area). Dust particles were brushed to pre-baked aluminum foils. Samples were wrapped in pre-cleaned aluminum foils, placed in zip-lock bags, and stored at −20 °C until extraction. PM and dust samples were extracted by ultrasonic extraction with 50 mL of acetone-hexane mixture (1:1) for 1 h. PUF plugs were extracted using a Soxhlet apparatus. All extracts were concentrated to 5 mL using a rotary evaporator, then to 1 mL under a gentle stream of nitrogen. Concentrated extracts were cleaned up by using a 1.1 cm i.d. glass column with deactivated alumina (3 g, at 400 °C overnight) activated by 6% ultrapure MilliQ water (w:w) and 1 cm anhydrous sodium sulfate. Analytes were eluted using 35 mL of dichloromethane (DCM)-hexane mixture (1:5), concentrated to ~2 mL, and extracts were collected in a final volume of 1 mL in isooctane. 50 ng of BDE-181 was added as internal standard. Instrumental analysis of target chemicals was conducted on Agilent 6890 GC-5973 MSD operated on electron capture negative ion mode (NCI). Methane was used as the reaction gas while helium was the carrier gas at 1.1 mL min^{-1}. The injector, transfer line, quadrupole, and source temperatures were 280 °C, 250 °C, 150 °C, and 150 °C, respectively. The column used was a DB-5 (J&W, 15 m, 0.25 mm i.d., 0.1 μm film thickness). The GC oven program was: 80 °C 2 min, 10 °C min^{-1} 285 °C 5 min, 25 °C min^{-1} 300 °C 5 min. 79 and 81 were the target and confirmation ions for BDE-28, -47, −99, −100, −153, −154, −183 while ions 486.5 and 488.5 were for PBDE-209. Target and qualifier ions for NBFRs were as follows: TBP-AE (79, 81, 290); BATE (79, 81, 160); α-, β-, γ-, and δ-DBE-DBCH (79, 81, 160); BEH-TEBP (79, 81, 160); BTBPE (79, 81, 249); syn- and anti-DP (652, 654); TBP-DBPE (79, 81, 160); EH-TBB (79, 81, 358); HBB (79, 81, 472); HBCDD (sum of α- and γ-isomers) (79, 81, 160); OBTMPI (79, 81, 159); α-TBCO (79, 81, 160).

2.1. Quality assurance/quality control

All glassware was baked at 450 °C and rinsed with solvent before use. Laboratory and field blanks were run along with the samples. Method detection limit (MDL) was calculated by sum of average concentration of a target chemical in blanks and 3 times of

standard deviation of average blank concentration. The instrument detection limit (IDL) was the lowest concentration of a target chemical that produced a signal distinguishable from a reagent blank at a 3:1 S/N ratio. If an analyte was not present in the blanks, IDL was equal to MDL (WDNRL, 1996). A sampling volume of 191.5 m^3 air and 0.145 g of dust weight was used in calculation of MDL and IDL for passive and settled dust samples, respectively. An air volume of 28.8 m^3 was used to calculate active air gas phase and PM samples. If an analyte was not determined in blank samples, IDL was employed to determine MDL. MDLs ranged from 4.16 to 7.46 pg m^{-3} for PBDE congeners except BDE-209 (41.7 pg m^{-3}), and 3.44–5.41 pg m^{-3} for NBFRs for active gas phase samples. For PM, MDLs ranged from 4.51 to 7.07 pg m^{-3} for PBDEs except BDE-209 (41.7 pg m^{-3}), and 4.16–7.06 pg m^{-3} for NBFRs. For settled dust samples, MDLs were 0.83 ng g^{-1} for NBFRs and PBDEs except BDE-209 (8.27 ng g^{-1}). For passive samples, MDLs were 0.63 pg m^{-3} for NBFRs and PBDEs except BDE-209 (6.26 pg m^{-3}). Recovery surrogate was BDE-77, and considering all recovery surrogate congener air samples, average recovery ranged between 68 and 109% with an average of 94%. In dust samples, these values ranged from 74% to 102% with an average of 86%. Blank correction was applied to all samples except for settled dust samples due to the absence of the dust blanks.

2.2. Exposure assessment

Occupational inhalation exposure to BFRs in the gas and particle (PM$_1$ and PM$_{10}$) phases were modeled probabilistically using Monte Carlo simulation. Non-carcinogenic health effects are estimated using Equation (1) (USEPA, 1992). BFR concentrations were fitted to best suitable distribution using Crsytal Ball (V.4.0e) software (Supplementary Material (SM), Table S2). Distribution of IR and BW of Turkish people were adopted from our previous study (Cetin et al., 2018). The median annual working days in the last ten years in Turkey was calculated as 232 days (by excluding weekends, public and religious holidays, and annual leave), which was assumed to be the exposure frequency, while exposure duration and averaging time were assumed to be 30 years.

$$ADD = (C * IR * ET * EF * ED)/(BW * AT) \quad (1)$$

where, *ADD*: average daily dose (pg kg^{-1} d^{-1}), *C*: concentration (pg m^{-3}), *IR*: inhalation rate (m^3 d^{-1}); *ET*: exposure time; ratio of the working hours (8 h/24 h); *EF*: exposure frequency (d yr^{-1}); *ED*: exposure duration (yr); *BW*: body weight (kg); *AT*: averaging time (30 yr × 365 d yr^{-1}).

Lifetime ADD (LADD) was also estimated considering possible carcinogenic effects (USEPA, 1992). Averaging time (AT, 30 years) in ADD (Eq. (1)) was replaced with lifetime (LT, 70 years) to obtain Equation (2).

$$LADD = (C * IR * ET * EF * ED)/(BW * LT) \quad (2)$$

where, *C*: concentration (pg m^{-3}), *IR*: inhalation rate (m^3 d^{-1}); *ET*: exposure time ratio of the working hours (8 h/24 h); *EF*: exposure frequency (d/yr); *ED*: exposure duration (yr); *BW*: body weight; *LT*: lifetime (70 yr × 365 d yr^{-1}).

3. Results and discussion

3.1. PM concentrations

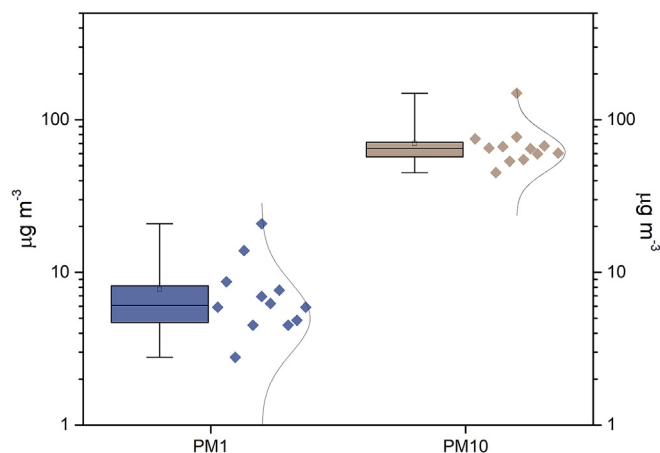Measured indoor air PM concentrations are shown in Fig. 1. The

Fig. 1. Indoor PM$_1$ and PM$_{10}$ concentrations in the computer technical service.

mean ± standard deviation PM$_1$ concentration was measured as 7.73 ± 4.77 μg m^{-3} with a range of 2.78–20.8 μg m^{-3}. Two and three-fold higher concentrations were observed on the 5th and 26th of April 2018, respectively, in comparison with the average of the remaining sampling days. These cases could have happened due to re-entrainment of the settled particles related to human activity and/or strong drafts, as well as disturbance of device parts with repair activity. Average concentration of the remaining PM$_1$ samples was 5.80 ± 1.62 μg m^{-3}. The mean PM$_{10}$ concentration was 69.9 ± 25.4 μg m^{-3}, with a range of 45.1–149 μg m^{-3}. The average PM$_1$/PM$_{10}$ concentration ratio was calculated as 0.12 ± 0.07, which is similar to indoor PM$_1$/PM$_{10}$ ratio values reported for Korean offices (0.17 ± 0.05) (Lim et al., 2005).

3.2. Particle-phase BFR concentrations

Levels of PM$_1$ and PM$_{10}$-associated NBFR and PBDE congeners are shown Fig. 2. BEH-TEBP and BTBPE were the highest concentration PM$_1$-NBFR compounds in all samples with averages of 19299 ± 430 and 3662 ± 96 pg m^{-3}, respectively, indicating the abundance of their sources in the study site. Average concentrations of PM$_1$-bounded α-, β-, γ-, and δ-isomers of DBE-DBCH were determined to be 85.82 ± 38.64, 63.69 ± 32.29, 61.87 ± 7.03, and 70.83 ± 12.24 pg m^{-3}, respectively, with an average Σ$_4$DBE-DBCH of 289 ± 81 pg m^{-3}. The concentrations of α- and β-isomers of DBE-DBCH were more variable, with coefficient of variation (CV) values of 0.45 and 0.51, respectively, than γ- and δ-isomers (CV = 0.11 and 0.17). Average concentrations of the other NBFR compounds, α-TBCO, TBP-DBPE, HBB, EH-TBP, α+γ-HBCDD, syn-DP, and anti-DP, were 137 ± 136, 52.3 ± 3.01, 14.9 ± 1.25, 90.2 ± 83.2, 171 ± 115, 16.8 ± 20.7, and 14.8 ± 18.2 pg m^{-3}. PM$_{10}$-associated NBFR concentrations in indoor air of the technical service are shown in Fig. 2. The mean concentrations of BEH-TEBP and BTBPE were determined as 25388 ± 1275 and 7425 ± 187 pg m^{-3}. PM$_{10}$-bounded α-, β-, γ-, and δ-isomers of DBE-DBCH concentrations were 215 ± 87, 161 ± 61, 157 ± 23, and 120 ± 2 pg m^{-3}, respectively, with an average Σ$_4$DBE-DBCH of 614 ± 159 pg m^{-3}. PM$_{10}$-associated concentrations of α- and β-isomers of DBE-DBCH were more variable than γ- and δ-isomers. Average concentrations of the other NBFR compounds, α-TBCO, TBP-DBPE, HBB, EH-TBP, α+γ-HBCDD, syn-DP, and anti-DP, were 259 ± 58, 114 ± 7.80, 31.0 ± 2.40, 262 ± 192, 615 ± 303, 28.3 ± 41.5, and 24.3 ± 35.8 pg m^{-3}, respectively.
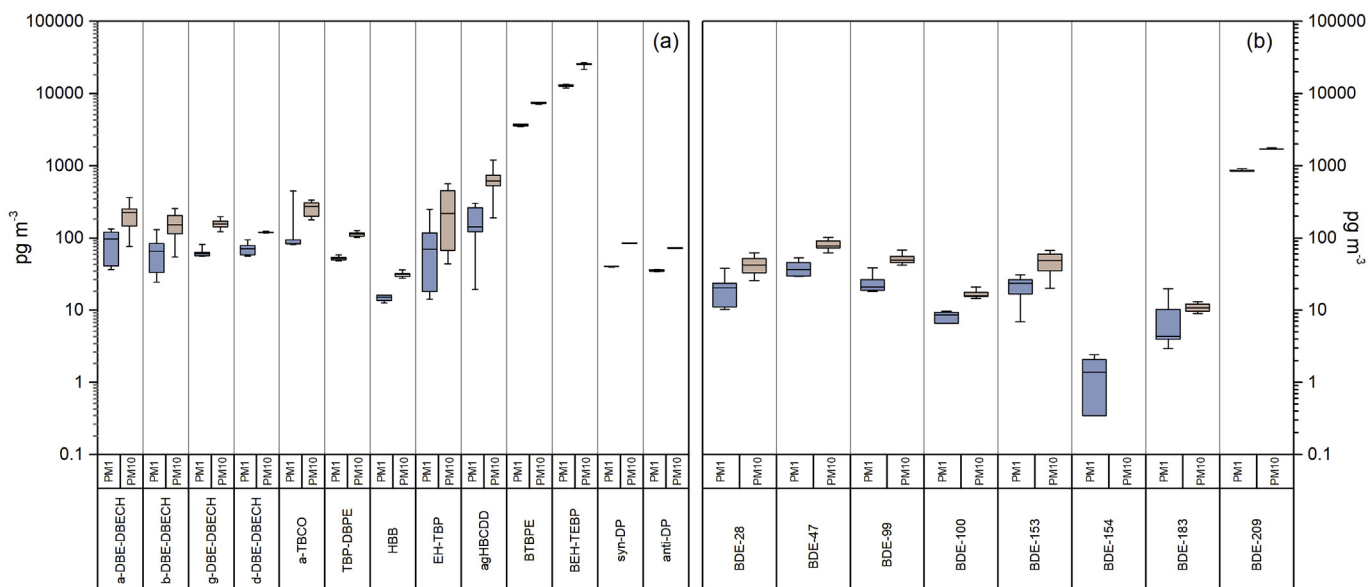
Fig. 2. PM-bounded flame retardants (a) NBFRs and (b) PBDEs.

Among PBDEs, BDE-209 was the dominant congener with an average concentration of 864 pg m^{-3}. Average concentrations of the other PBDE congeners, BDE-28, -47, −99, −100, −153, and −183 were 19.5, 38.3, 23.5, 8.26, 21.0, and 7.44 pg m^{-3}, respectively. In general, variation in the concentrations was not large during the three-month sampling period, especially for BDE-209 with a CV of 0.029. BDE-28, -47, −99, and −153 were the other abundant PBDE congeners distantly following BDE-209. The mean particle-phase PBDE concentrations measured in this study (SM, Table S1) are compared with those reported by Li et al. (2015a) in offices and Guo et al. (2015) in a workshop where waste printed wiring boards were heated. The comparison indicates that higher molecular weight congeners were generally measured at higher concentrations in this study. This discrepancy may be due to differences in source strengths and profiles. BDE-209 was found to be the dominant PBDE congener similar to that in PM$_1$. Average concentration of PM$_{10}$-bounded BDE-209 was 1719 pg m^{-3}. PM$_{10}$-bounded average concentrations of the other PBDE congeners, BDE-28, -47, −99, −100, −153, and −183 were 42.6, 80.3, 51.5, 16.6, 47.1, and 11.0 pg m^{-3}, respectively. PBDE concentrations associated with PM$_{10}$ are only about twice as high as those associated with PM$_1$, whereas the difference in the average PM mass concentration is 9-folds, indicating that submicron PM constitute a considerable fraction of particle-phase PBDE exposure. The concentrations of NBFRs are dominant as shown in Fig. 2, probably due to their abundance in new electronic devices. As determined in PBDEs, half of the particle-bounded concentrations of NBFRs are associated with PM$_1$.

PM-associated BFR concentrations in indoor air were segregated to submicron (PM$_1$) and coarse (PM$_{10-1}$) fractions to estimate their particle size distributions. The SM, Fig. S1 shows that all the BFR compounds are about equally segregated into the submicron and coarse fractions, whereas mass concentrations of coarse particles were 9-times higher than those of submicron particles. It has been determined that even though submicron fraction particle concentrations are low compared to those of coarse fraction, submicron-fraction BFRs may pose higher health risks because of their potential to penetrate deep into the lungs, while more than 90% of the larger particles (>5 μm) deposit before reaching the alveoli (Pražnikar and Pražnikar, 2012).

3.3. BFR concentrations in settled dust

NBFR and PBDE concentrations associated with settled dust are shown in Fig. 3. As in PM samples, the most abundant NBFR compound in settled dust was BEH-TEBP, with an average concentration of 994 ± 1474 ng g^{-1}. BTBPE concentrations, the second most abundant compound in PM, were relatively low with an average value of 34.2 ± 17.7 ng g^{-1} in settled dust. However, the mean α+γ-HBCDD concentration (813 ± 262 ng g^{-1}) was determined to be almost as high as the most abundant compound, BEH-TEBP. Our results show that fractionation of α+γ-HBCDD in PM increases with increasing particle size. The mean concentrations of the other NBFR compounds, α-DBE-DBCH, β-DBE-DBCH, γ-DBE-DBCH, δ-DBE-DBCH, α-TBCO, TBP-DBPE, HBB, EH-TBP, syn-DP, and anti-DP in settled dust were 25.2 ± 8.20, 27.6 ± 9.50, 19.6 ± 2.60, 19.4 ± 1.90, 51.6 ± 11.4, 17.8 ± 1.10, 32.6 ± 2.90, 136 ± 14.6, 15.4 ± 2.70, and 21.9 ± 2.90 ng g^{-1}, respectively. The same NBFRs were measured in Istanbul offices (Kurt-Karakus et al., 2017). Levels and profile of NBFR concentrations, except for α+γ-HBCDD, in settled dust in this study are different than those determined in Istanbul. In this study and generally in the literature (Table 1), α+γ-HBCDD concentrations in settled dust are higher than those of other NBFR compounds. Although, TBP-AE, BATE, and OBTMPI were reported at low levels in Istanbul (Kurt-Karakus et al., 2017), and TBP-AE was reported at low levels in Toronto offices (Abbasi et al., 2016), none were detected in this study.

As in the airborne PM samples, the most dominant PBDE congener in settled dust was BDE-209, constituting approximately 93% of total concentration of the total targeted PBDEs. The mean concentrations of BDE-28, -47, −99, −100, −153, −183, and −209 in settled dust were 4.69, 17.8, 18.1, 5.79, 71.0, 2.62, and 1802 ng g^{-1}, respectively. BDE-209 was similarly reported as the dominant PBDE congener in house dust collected from homes in Kocaeli, Turkey (Civan and Kara, 2016). BDE-47 was the second highest determined PBDE congener in the PM samples, but ranking of BDE-47 in settled dust is lower, the 4th. Comparison of the concentrations measured in this study to those measured in house dust of homes and offices in Istanbul, Turkey, and Lagos, Nigeria, and offices in Boston, USA, indicate that levels of all congeners fall within the range of the reported levels.
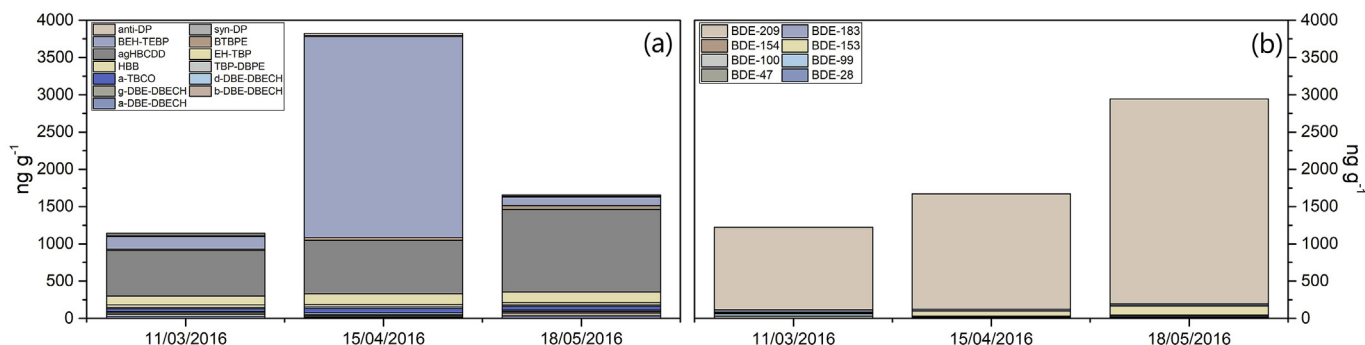
Fig. 3. BFR concentrations in settled dust: (a) NBFRs and (b) PBDEs.

Table 1
Comparison of settled-dust mean BFR concentrations with the literature (ng g^{-1}).

Location	İzmir, Turkey[a]	İzmir, Turkey[b]	İzmir, Turkey[c]	İstanbul, Turkey[b]	Lagos, Nigeria[b]	Boston, USA[c]	Toronto, Canada[a]	Shenzhen, China[a]	Cairo, Egypt[a]
BDE-28	4.69	4.62	4.62	0.12	1.1	7.5			
BDE-47	17.8	15.4	17.1	127	14	697			
BDE-99	19.3	18.1	16.5	76.1	7.7	915			
BDE-100	7.51	5.79	6.94	0.12	0.49	195			
BDE-153	67.7	71	43.3	31.3	0.84	138			
BDE-154	2.35	2.62	2.3	5.78	0.61	115			
BDE-183	23.9	23.5	23.6	18.9	2.2	81			
BDE-209	1802	1549	1677	615	419	4204			
α-DBE-DBCH	25.2	23.2	24.3	0.5[d]					
β- DBE-DBCH	27.6	27.7	26.4						
γ- DBE-DBCH	19.6	19.9	19.4						
δ- DBE-DBCH	19.4	19.4	19.3						
α-TBCO	51.6	53.6	50.7	0.13					
TBP-DBPE	17.8	17.8	17.7	0.13					
HBB	32.6	31.4	32.5	185			95		0.2
EH-TBB	136	143	135	543.4			1192		7.1
αγ-HBCDD	813	718	786	523.9				7276	19
BTBPE	34.2	35.0	30.8	420.8					2.4
BEH-TEBP	993	173	374	0.13			7676		
syn-DP	15.4	16.7	15.2				44		1
anti-DP	21.9	23.6	21.8				98		0.3
Reference	This Study			Kurt-Karakus et al. (2017)	Harrad et al. (2016)	Watkins et al. (2013)	Abbasi et al. (2016)	Ni and Zeng (2013)	Hassan and Shoeib (2015)

[a] Mean.
[b] Median.
[c] Geometric mean.
[d] Sum of α/β- and γ/δ-DBE-DBCH.

3.4. Gas-phase BFR concentrations

3.4.1. Active sampling

Indoor air gas-phase concentrations of NBFRs and PBDEs are shown in Fig. 4. BEH-TEBP dominated the gas-phase concentrations of NBFRs with an average of 13155 pg m^{-3}. The second abundant NBFR was BTBPE with an average of 3707 pg m^{-3}. The mean concentrations of α, β, γ, and δ isomers of DBE-DBCH were determined to be 564, 375, 108, and 90.3 pg m^{-3}, respectively. Average concentration of the sum of α and γ isomers of HBCDD was 102 pg m^{-3}. Average concentrations of the other NBFR compounds were determined to be < 63 pg m^{-3} with a minimum concentration of 13.8 pg m^{-3}. Generally, variation in indoor air gas-phase NBFR concentrations were relatively low (CV = 0.3–0.7) except EH-TBB, α+γ-HBCDD, *syn*-DP, and *anti*-DP with CV > 1. A higher level variation, expressed herein with CV, could indicate the effect of some specific repair activities resulting in concentration fluctuations,

while lower CV levels could indicate shop-specific background levels, since passive sampling point to much lower outdoor levels compared to indoors (will be presented shortly) eliminating outdoor air from being a determining source. Therefore, BFRs with relatively large CV values could be considered to be dependent on specific indoor sources.

Gas-phase concentration ranges of BDE-28, -47, −99, −100, −153, −183, and −209 were determined to be 9–30, 28–41, 12–31, 6–16, 12–31, 2–17, and 542–786 pg m^{-3}, respectively. BDE-209 dominated the gas-phase concentrations. CV values of BDE-28, -47, −99, −100, −153, −183, and −209 were determined to be 31%, 34%, 39%, 25%, 84%, and 10%, respectively. CV value of BDE-183 was higher than the others, indicating that an indoor source had a strong effect. The fact that BDE-183 concentrations were high in the first two samples taken in May and then decreased to the previous levels supports this argument. The relatively high BDE-209 concentrations and low CV value indicate
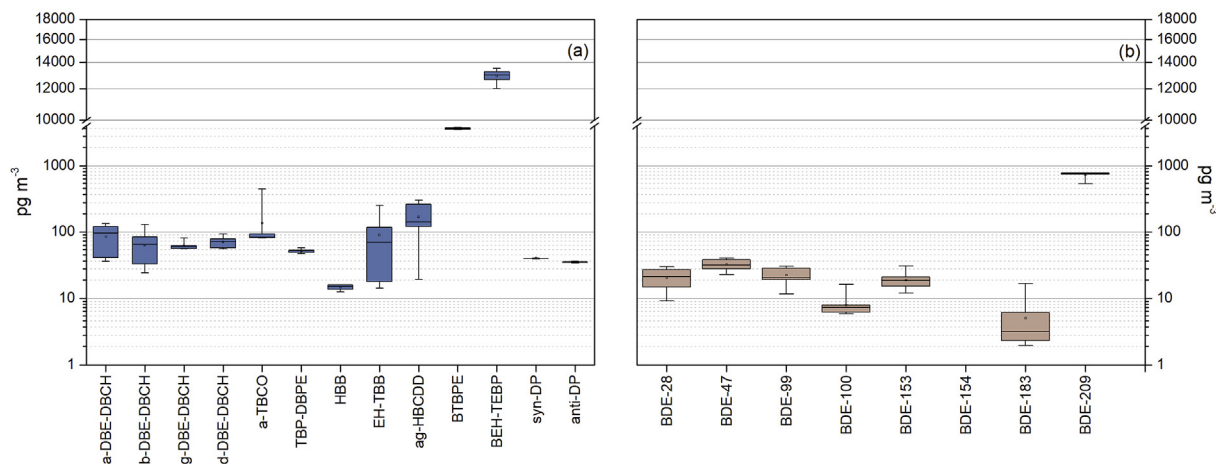
Fig. 4. Indoor air gas-phase concentrations; (a) NBFRs and (b) PBDEs.

strong, persistent indoor sources for this congener. Concentrations of BDE-209 were probably high because it is the most commonly used flame retardant in recent years. The ratio of BDE-47/BDE-99 in the commercial penta-BDE mixtures is generally in the range of 0.8–1.0 (Hazrati et al., 2010; Tian et al., 2010). The ratio was determined to be 0.88 in this study. This value indicates that commercial penta-BDE was an emission source in the technical service.

3.4.2. Passive sampling and I/O ratios

Indoor air concentrations of PBDEs and NBFRs measured by passive sampling are presented in the SM, Figs. S2 and S3, respectively. The ranges for BDE-28, -47, −99, −100, −153, −183, and −209 were determined to be 16–29, 18–32, 12–18, 4.0–5.0, 13–20, 0,8-2.0, and 1077–1487 pg m^{-3}, respectively. Passive samplers are also known to collect suspended particles in ambient air (He and Balasubramanian, 2012). It may also play a role indoors depending on the air velocities and movement of people that would result in re-entrainment of settled PM. In fact, indoor air PBDE concentrations measured by passive sampling were higher than those measured by active sampling, indicating PM collection. CV values of BDE-28, -47, −99, −100, −153, −183, and −209 were calculated as 23%, 23%, 17%, 11%, 20%, 41%, and 15%, respectively. The CV values obtained from the passive sampling data are similar to those obtained with active sampling but are relatively low due to the relatively long sampling times. The BDE-47/BDE-99 ratio from passive sampling (1.73) was determined to be relatively higher than the active sampling (0.88). However, the BDE-47/BDE-99 ratio of passive sampling was similar to those of PM$_1$ (1.63) and PM$_{10}$ (1.56), supporting the argument that the passive samplers used in this study collected PM indoors. Consequently, indoor air gas-phase concentrations determined by passive sampling should be considered with care, as they may not simply be gas-phase levels. This characteristic of the passive samplers may also be inferred from Fig. S2(b), which shows BDE-209 levels measured by active and passive sampling.

BEH-TEBP and BTBPE were the dominating NBFRs indoors with average concentrations of 3588 and 12997 pg m^{-3}, respectively, measured by passive sampling. The mean indoor air concentrations of the other NBFRs were determined to be 1204, 790, 74, 67, 93, 58, 15, 46, 303, 41, and 36 pg m^{-3} for α-DBE-DBCH, β-DBE-DBCH, γ-DBE-DBCH, δ-DBE-DBCH, α-TBCO, TBP-DBPE, HBB, EH-TBP, (α+γ) HBCDD, s-DP, and a-DP, respectively. Indoor air passive sampling NBFR concentrations were also higher than those of the active gas-

phase sampling.

Outdoor air was simultaneously sampled using the passive sampler. Outdoor BFR levels (C$_{out}$) were lower than those of indoors (C$_{in}$) (SM, Figs. S2 and S3). The indoor/outdoor (I/O) ratio was generally much higher than '1', indicating the strength of indoor BFR sources compared to outdoor sources. The lowest I/O ratio values based on overall average concentrations were about 2 (1.88 for α+γHBCDD and 1.94 for BDE-153). In addition, sample-based I/O ratio values were calculated, for which the mean I/O values were 1.41 for α+γHBCDD and 3.34 for BDE-153.

3.5. Dust-gas and particulate-gas phase partitioning

Dust-gas phase partitioning (K$_D$) and particulate-gas phase partitioning (K$_P$) coefficient values were calculated using Equations (3) and (4), respectively (Li and Jia, 2014; Wei et al., 2016). Table 2 shows the average K$_D$ values for BFRs. The average log$_{10}$K$_D$ values calculated on the basis of active sampling were similar to those calculated from passive sampling. K$_D$ values calculated for PBDEs using the levels reported by Watkins et al. (2013) in Boston are consistent with the data obtained in this study. However, the calculated log$_{10}$K$_D$ value for BDE-209 in this study is lower than the value reported by Wei et al. (2016) in France. The difference may have originated from the difference in types of indoor environments studied: houses by Wei et al. (2016) and offices by Watkins et al. (2013).

$$K_D = X_d/C_g \tag{3}$$

where; K$_D$ (m^3 µg^{-1}): Dust-gas partitioning coefficient; X$_d$ (µg µg^{-1}): BFR concentration in settled dust; C$_g$ (µg m^{-3}): BFR concentrations in gas phase.

$$K_P = (C_p/C_{PM})/C_g \tag{4}$$

where; K$_P$ (m^3 µg^{-1}): Particulate-gas partitioning coefficient; C$_p$ (pg m^{-3}): BFR concentration in particulate matter; C$_{PM}$ (µg m^{-3}): particulate matter concentration; C$_g$ (pg m^{-3}): BFR concentrations in gas phase.

3.6. Occupational exposure to BFRs

Occupational inhalation exposure levels of BFRs were estimated probabilistically with Monte Carlo simulation (n = 10,000 trials) using active sampling gas and particulate (PM$_1$ and PM$_{10}$) phase

Table 2
Dust-gas and PM-gas partitioning of brominated flame retardants.

BDE congener	This study[a]	This study[b]	Watkins et al. (2013) [c]	Wei et al. (2016)	Torre et al. (2018)
BDE-28	-3.65^d, -0.92^e, -1.53^f	-3.71^d	-3.88^d	-3.62^d	
BDE-47	-3.26^d, -0.82^e, -1.45^f	-3.15^d	-2.58^d	-2.70^d	-2.00^g
BDE-99	-3.07^d, -0.87^e, -1.48^f	-2.88^d	-1.95^d	-1.74^d	-0.14^g
BDE-100	-3.02^d, -0.88^e, -1.52^f	-2.77^d	-1.99^d	-1.89^d	
BDE-153	-2.45^d, -0.85^e, -1.45^f	-2.36^d	-1.62^d	-0.90^d	
BDE-154	-3.01^d, -1.22^e		-1.60^d	-1.09^d	
BDE-183	-2.32^d, -0.72^e, -1.51^f	-1.79^d	-3.39^d		
BDE-209	-2.55^d, -0.76^e, -1.42^f	-2.83^d	-2.62^d	5.34^d	0.68^g
α-DBE-DBCH	-4.35^d, -1.71^e, -2.26^f	-4.68^d			
β- DBE-DBCH	-1.66^e, -2.21^f				
γ- DBE-DBCH	-3.74^d, -1.13^e, -1.68^f	-3.58^d			
δ- DBE-DBCH	-3.67^d, -0.99^e, -1.72^f	-3.54^d			
α-TBCO	-3.08^d, -0.55^e, -1.23^f	-3.25^d			
TBP-DBPE	-3.49^d, -0.91^e, -1.53^f	-3.52^d			
HBB	-2.66^d, -0.89^e, -1.52^f	-2.66^d			-3.27^g
EH-TBB	-2.49^d, -0.55^e, -1.04^f	-2.53^d			
α+γ-HBCDD	-2.10^d, -0.67^e, -1.06^f	-2.57^d			
BTBPE	-5.03^d, -0.89^e, -1.54^f	-5.02^d			-0.03^g
BEH-TEBP	-4.12^d, -0.90^e, -1.56^f	-4.12^d			
syn-DP	-3.01^d, -0.86^e, -1.59^f	-3.42^d			
anti-DP	-2.80^d, -0.86^e, -1.60^f	-3.21^d			

[a] Active sampling.
[b] Passive sampling.
[c] Derived using reported concentrations.
[d] $\log_{10}K_D$.
[e] PM_1 associated $\log_{10}K_p$.
[f] PM_{10} associated $\log_{10}K_p$.
[g] Modeled $\log_{10}K_p$.

Table 3
Average occupational exposure levels of BFRs.

	ADD (pg kg^{-1} d^{-1})			LADD (pg kg^{-1} d^{-1})		
	Gas phase associated	PM$_1$ associated	PM$_{10}$ associated	Gas phase associated	PM$_1$ associated	PM$_{10}$ associated
BDE-28	13.2	12.2	27.3	5.63	5.2	11.7
BDE-47	20.7	24.4	52.4	8.87	10.4	22.6
BDE-100	4.47	4.76	10.3	1.88	2.04	4.41
BDE-99	14.1	14.5	33.1	6.09	6.22	14.3
BDE-153	11.8	13.6	29.6	5.06	5.82	12.8
BDE-183	2.41	3.64	6.56	0.99	1.58	2.82
BDE-209	503	565	1124	214	242	483
α-DBE-DBCH	372	55.9	138	158	23.9	58.6
β- DBE-DBCH	245	41.1	105	104	17.7	45.4
γ- DBE-DBCH	70.3	39.6	103	29.9	17	44.0
δ- DBE-DBCH	57.3	45.8	78.2	24.5	19.7	33.6
α-TBCO	58	74.7	168	24.7	32.1	72.8
TBP-DBPE	35.2	33.7	73.9	15	14.5	31.7
HBB	9.31	9.15	19.8	3.89	3.92	8.51
EH-TBB	32.5	55.7	172	13.8	24.8	74.5
α+γ-HBCDD	168	139	404	71.3	59.8	174
BTBPE	2439	2400	4873	1039	1028	2092
BEH-TEBP	8647	8480	16702	3683	3633	7170
syn-DP	24.3	25.8	54.8	10.8	11.1	23.5
anti-DP	25.3	22.6	47.4	9.49	9.69	20.4

BFR concentrations (Table 3), all of which were fitted with probability distributions. Distributions of the remaining two variables (body weight and inhalation rate) of the exposure model (Eq. (1)) were taken from our previous study (Cetin et al., 2018). Parameter values of the probability distributions are listed in the SM, Table S2. Generally, PM$_1$ and one-half of PM$_{10}$-associated BFR inhalation exposure levels were similar to those of gas-phase exposure levels. In contrast, gas-phase exposure dominated those of particulate phase for α and β isomers of DBE-DBECH. The average gas-phase associated ADD and LADD levels of BDE-209 through inhalation route were estimated at 503 and 214 pg kg^{-1} d^{-1}, respectively, which were similar to the PM$_1$-associated ADD and LADD levels (565 and 242 pg kg^{-1} d^{-1}, respectively). PM$_{10}$-associated average

ADD and LADD levels of BDE-209 were estimated at 1124 and 483 pg kg^{-1} d^{-1}, respectively. The average gas-phase-associated ADD and LADD levels of the other BDE congeners ranged from 2.41 to 20.7 pg kg^{-1} d^{-1} and from 0.99 to 8.87 pg kg^{-1} d^{-1}, respectively. PM$_1$-associated exposure levels were similar to those of gas phase, whereas those of PM$_{10}$ were approximately twice as high. The exposure levels of BEH-TEBP were estimated to be considerably higher than the other BFR compounds due to the relatively high concentrations in all phases. The average gas-phase, PM$_1$ and PM$_{10}$-bounded ADD levels of BEH-TEBP were estimated to be 8647, 8480, and 16702 pg kg^{-1} d^{-1}, respectively, while LADD of gas, submicron, and PM$_{10}$ phases were estimated to be 3683, 3633, and 7170 pg kg^{-1} d^{-1}, respectively. The inhalation exposure levels

of BTBPE were estimated relatively higher than other BFRs except for BEH-TEBP. The average ADD levels of BTBPE through gas, PM_1 and PM_{10} phases were estimated at 2439, 2400, and 4873 pg kg^{-1} d^{-1}, respectively. On the other hand, LADD of BTBPE through the inhalation gas phase, PM_1 and PM_{10} were estimated at 1039, 1028, and 2092 pg kg^{-1} d^{-1}, respectively. Parameters of the fitted distributions to the estimated ADD and LADD values are listed in the SM, Tables S3 and S4.

4. Conclusion

Results of this study indicate that (1) BDE-209 is the dominant BDE congener in airborne PM (both PM_1 and PM_{10}) and settled dust, while BEH-TEBP is the dominant NBFR compound followed by BTBPE, and (2) BFRs associated with PM_1 constitute about one half of those with PM_{10} in the studied computer repair service. Accordingly, all studied particle phases (settled dust, PM_1, and PM_{10}) are important sources of exposure to BFRs, implicating that all should be considered for a realistic exposure assessment. BFR concentrations measured with the passive samplers yielded higher levels compared to those of active sampling but similar to those of PM_{10}, indicating they collected PM indoors, similarly to outdoors. The BDE-47/BDE-99 ratio in gas-phase and settled dust samples (0.6−1.0) pointed to commercial penta-BDE as a source of the emissions, while its value was higher in passive (1.73), PM_1 (1.63) and PM_{10} (1.56) samples. These differences in the ratio values probably arose due to the fact that the more volatile BDE-47 is partitioned more to submicron particles with larger surface area, while BDE-99, with a larger molecular weight, is partitioned more to coarse particles. Consequently, gas phase and submicron particles that have higher concentrations of lower molecular weight compounds, and coarse particles and settled dust that have higher concentrations of higher molecular weight compounds are all exposure-risk relevant phases for BFRs. The measured concentrations in all three phases and estimated inhalation exposures indicate that associated occupational risks for computer repair service employees may be significant.

Conflicts of interest

None.

CRediT authorship contribution statement

Mesut Genisoglu: Formal analysis, Writing - original draft. **Aysun Sofuoglu:** Formal analysis, Writing - original draft. **Perihan B. Kurt-Karakus:** Formal analysis, Writing - original draft. **Askin Birgul:** Formal analysis, Writing - original draft. **Sait C. Sofuoglu:** Writing - original draft.

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Appendix A. Supplementary data

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