Polybrominated diphenyl ethers (PBDEs) in indoor and outdoor window organic films in Izmir, Turkey

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ABSTRACT

Polybrominated diphenyl ether (PBDE) concentrations of outdoor and indoor organic films on window glasses were measured at different locations (offices, laboratories, and homes in urban, suburban, rural, and industrial sites) in Izmir, Turkey. $\sum_7$PBDE concentrations were dominated by technical penta and deca-BDE mixture components. Average total outdoor PBDE ($\sum_7$PBDE) concentrations for suburban, urban, and industrial sites were 43.5, 45.5, and 206 ng m^{-2}, respectively. This spatial gradient (industrial > urban > suburban concentrations) was similar to one observed for ambient air concentrations recently in Izmir, Turkey. The highest concentrations measured in the industrial area were attributed to the significant PBDE emissions from several steel plants located in the area. Air-organic film partitioning modeling results have suggested that organic films can be used in conjunction with the dynamic uptake model to approximate the gas-phase ambient air concentrations. Modeling results have also indicated that congeners in the gas-phase with very large octanol–air partition coefficients (i.e., BDE-154, -153, and -209) will require several months to approach equilibrium with the surface films. This finding may have important implications for gas-particle and gas-film partitioning, transport, and photolytic degradation of atmospheric PBDEs.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants used in a wide variety of commercial and industrial products to reduce their flammability potential. Recent concern over the use of PBDEs is mainly related to their environmental fate and human exposure, whereby these compounds have been characterized as being persistent, bioaccumulative organic pollutants [1]. It is widely understood that the environmental fate of the PBDEs will be strongly influenced by their chemical properties. In particular, their low aqueous solubility combined with their high octanol–water and octanol–air partition coefficients, suggests a strong potential for PBDEs to partition to organic matter [1,2].

Organic films are derived through the condensation of gas-phase chemicals onto impervious surfaces such as window glasses. This condensation constitutes a sticky layer that particle and gas-phase compounds can be wet and dry deposited to this surface. Thus, the composition of organic film is representative of ambient air quality and the organic film can be used to evaluate contaminant deposition [3,4]. Film can act as sorption/desorption medium for gas-phase organic compounds and may grow through particle agglomeration and gas-phase condensation [5]. Surface films undergo temperature-dependent cycles of condensation-volatilization, making them sinks and sources of persistent organic pollutants (POPs) to the atmosphere [5]. Therefore, determination of POP levels in organic films on impervious surfaces is crucial to evaluate their environmental fate and transport.

Indoor air is an important route of exposure to PBDEs as a result of several indoor sources of PBDEs (i.e., thermoplastics, specifically high-impact polystyrene for electronic equipment housings such as computers, TV sets, electric components and cables, foam padding in furniture and upholstery textiles). In the indoor environment, PBDEs are less prone to atmospheric dilution and photolysis resulting in increased air concentrations [6–8]. PBDEs are also used in several parts of cars [9]. However, PBDEs that are known to break down when exposed to the sun and UV light [10], may break down at much higher rates in solar-exposed cars than in other indoor environments.

Other pollutants including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), n-alkanes, metals and trace elements were recently examined in window organic films [3–5,11–13]. However, window organic film studies on PBDEs are very scarce [11,14]. The objectives of this study were (1) to investigate the spatial variation of PBDE concentrations in organic films from window surfaces

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and to determine their congener profiles and, (2) to investigate the partitioning of PBDEs between surface films and air. Indoor and outdoor films were sampled at 15 different locations between June and October, 2004. Samples were analyzed for seven PBDEs (BDE-28, -47, -99, -100, -153, -154, and -209). Gas-phase air concentrations were predicted using the equilibrium partitioning model and the dynamic uptake model developed recently for passive samplers, and they were compared to recently measured concentrations in the study area.

2. Materials and methods

2.1. Sampling program and collection

Organic film samples from indoor and outdoor window surfaces were collected between June and October, 2004. In total, 38 samples were collected from suburban (7 indoor and 7 outdoor samples, Kaynaklar Campus of Dokuz Eylul University, Izmir, Turkey), urban (6 indoor and 6 outdoor samples, five residential sites and one TV repair shop), rural (1 indoor and 1 outdoor samples, remote site), and industrial sites (1 indoor and 1 outdoor samples) (Fig. 1). The last window cleaning time was not precisely known but was between 3 and 4 months at all sites. Indoor organic film samples from the windshields of four different cars were also collected for winter (February) and summer (July) periods (8 indoor samples). The last windshield cleaning time for the sampled cars was two weeks.

Organic films were collected from indoor and outdoor window surfaces with laboratory Kimwipes pre-cleaned with dichloromethane (DCM) by Soxhlet extraction. Prior to sampling, Kimwipes were wetted with GC-grade DCM. To prevent possible contamination from window-frame material, a measured 10-cm bound was left around the window area. The average sampling area was 4160 ± 1765 cm^2. Three duplicate samples were also taken to determine the sampling error. After sampling, Kimwipes were stored at $-20\,^\circ$C in their containers.

2.2. Sample preparation and analysis

Organic film samples were ultrasonically extracted for 60 min with a mixture of 1:1 acetone:hexane. Prior to extraction, all samples were spiked with surrogate standard (3,3′,4,4′-tetrabromodiphenyl ether, BDE-77) to monitor the analytical recovery efficiency. The volume of extracts were reduced and transferred into hexane using a rotary evaporator and a high purity N$_2$ stream. After concentrating to 2 mL, samples were cleaned up and fractionated on an alumina–silicic acid column containing 3 g silicic acid (deactivated with 4.5% deionized water) and 2 g alumina (deactivated with 6% deionized water). The column was pre-washed with 20 mL DCM followed by 20 mL petroleum ether (PE). Then, the sample in 2 mL hexane was added to the column and PBDEs were eluted with 35 mL PE [15]. The final extracts were solvent exchanged into hexane and were concentrated to 1 mL under a stream of N$_2$.

All the samples were analyzed for PBDEs with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD) working at electron capture negative chemical ionization (ECNI) mode. A capillary column (DB-5 ms, 15 m, 0.25 mm, 0.1 μm) was used. Pulsed-splitless injection was used to maximize the transfer of the PBDEs into the capillary column and minimize their degradation in the injector liner. The carrier gas (helium) was used at constant flow mode (1.8 mL min^{-1}) with a linear velocity of 70 cm s^{-1}. The initial oven temperature was held at 90 $^\circ$C for 1 min, raised to 340 $^\circ$C at 20 $^\circ$C min^{-1}, and held for 2 min. The injector, ion source, quadrupole, and interface temperatures were 280, 230, 150, and 320 $^\circ$C, respectively. High purity methane was the reagent gas. The MSD was run in selected ion monitoring mode. For the six analyzed BDEs, the surrogate (BDE-77) and internal standard (BDE-128), the two bromine ions at m/z 79.1 and 81.1 and for BDE-209 ions at m/z 488.5 and 486.5 were monitored. Compounds were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure.

2.3. Quality control

All samples were spiked with BDE-77 prior to extraction to determine analytical recovery efficiencies. Average recovery of BDE-77 was $75 \pm 13\%$ ($n=23$) and $76 \pm 15\%$ ($n=15$) for indoor and outdoor window film samples, respectively. The recoveries of target compounds were also tested by matrix spiking experiments ($n=6$) and average recovery efficiencies were between $86 \pm 9\%$ (BDE-28) and $110 \pm 7\%$ (BDE-154) with the average recovery for all 7 PBDEs measured from all 6 samples being $99 \pm 12\%$.

The relative standard deviation of the three duplicate samples taken to assess the sampling error ranged between 7.1 and 11.3%.

Instrumental detection limits (IDL) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. The quantifiable PBDE amounts were between 0.05 (BDE-28) and 0.35 pg (BDE-209) for 1 μl injection. Pre-cleaned and DCM-wetted Kimwipes were used as blanks ($n=4$) to determine if there was any contamination during sample handling and preparation. The limit of detection of the method (LOD, ng) was defined as the mean blank mass plus three standard deviations (LOD = mean blank value + 3SD). Instrumental detection limit was used for the compounds that were not detected in blanks. LODs for six BDE congeners including BDE-28, -47, -99, -100, -153 and -154 ranged from 0.05 to 0.33 ng and for BDE-209 it was 3.46 ng. Blank amounts were $7 \pm 12\%$ and $9 \pm 12\%$ of the sample amounts, for indoor and outdoor samples, respectively. Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

3. Results and discussion

3.1. Comparison of indoor and outdoor films

The summary of average concentrations of individual PBDEs are presented in Table 1. Average total outdoor PBDE ($\sum_7$PBDE) concentrations for suburban, urban, and industrial sites were 43.5, 45.5, and 206 ng m^{-2}, respectively (Table 1). This spatial gradient was similar to one observed for ambient air concentrations recently in Izmir (8.1, 12.2 and 36.3 pg m^{-3} for suburban, urban, and industrial sites, respectively) [15]. The highest concentrations measured in the industrial area are due to the significant PBDE emissions from several steel plants located in the area. Outdoor films collected from ambient air Sampling Cabin 2 near an industrial site (steel plants with electric arc furnaces) had relatively high $\sum_7$PBDE concentrations (206 ng m^{-2}). Steel plants with electric arc furnaces are significant PBDE sources as was recently shown by very high concentrations measured in the nearby soil samples [16], in stack gases of five plants, and in ambient air near these plants [17]. These findings support the high outdoor film concentrations measured near steel plants in the present study. Urban environments are characterized by many different PBDE sources relative to rural areas. The higher concentrations measured in urban sites of the present study may be attributed to these urban sources. Another factor could be the relatively closer distance of urban sites that are affected by the emissions from to the industrial region carried by the prevailing northwesterly winds (Fig. 1).
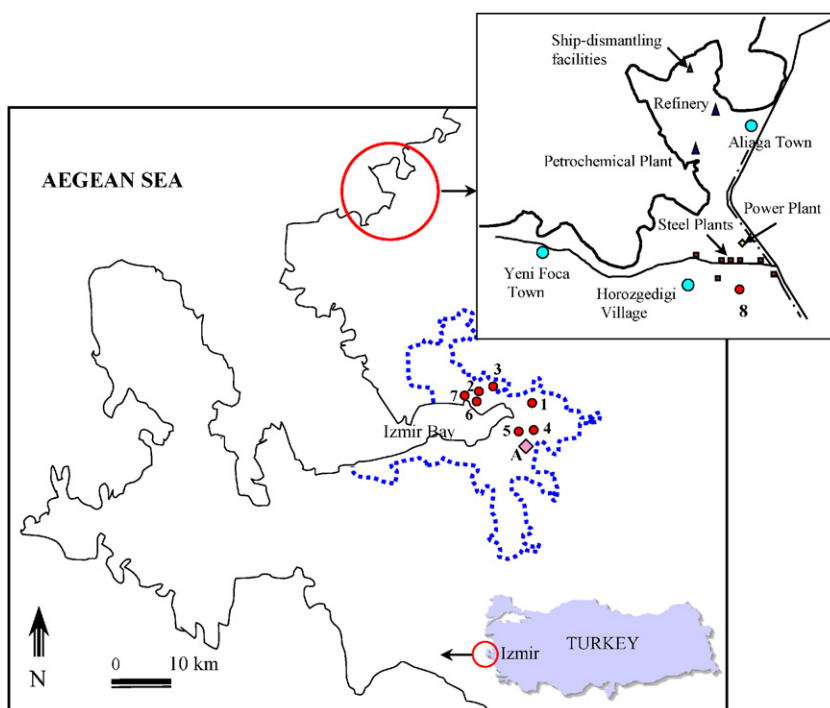
Fig. 1. Map of Izmir showing the window organic film sampling sites. A: Dokuz Eylul University (Lab. 1, 2, 3, Server, Office 1, 2, and Cabin 1), 1, 2, 3, 4, 5, 6: Residential sites, 7: TV repair shop, 8: Cabin 2. Dashed line is the border of densely populated areas.

$\sum_7$PBDE concentrations in organic films collected from residential sites ranged between 4.3–24.3 and 12.6–23.3 ng m^{-2} for indoor and outdoor film samples, respectively (Fig. 2). The indoor/outdoor concentration ratio could be used to identify the dominating sources of the pollutants [18]. Indoor/outdoor film concentration ratios ranged between 0.3 and 1.1 suggesting that residential sites were primarily affected by outdoor PBDE sources (Fig. 3). This may be due to the significant PBDE emissions by outdoor sources (several steel plants located to the north) that could be carried by the northerly prevailing winds to the study area [17].

$\sum_7$PBDE concentrations for the samples collected at Dokuz Eylul University Campus had in site variations (Fig. 2). For indoor films, Lab. 1 (air pollution lab) and Server room had the highest concentrations (up to 134 ng m^{-2}), while the concentrations in Lab. 2 (computer lab with computers produced in 2001) and Lab. 3 (GC lab) were relatively low (8.8 and 19.3 ng m^{-2}, respectively). Indoor/outdoor film concentration ratios for Lab. 1, Server room, Office 1 and ambient air sampling Cabin 1 were close or greater than 10 suggesting that these sites were primarily affected by indoor sources (Fig. 3). The common issue for those sites having high indoor concentrations was the use of old computers (produced before 1998). To confirm the measured high concentrations, indoor and outdoor sampling of the four windows (Lab. 1, Server room, Office 1 and ambient air sampling Cabin 1) were repeated (Fig. 4). For the second sampling period, their last cleaning time was ~19 months. The $\sum_7$PBDE concentrations increased ~2 times in the second samples except for Lab.1 (~13 times increase). Thicker organic films on window surfaces were shown to increase the accumulation of film-associated organic compounds [4]. Thus, this two-fold increase may be attributed to the longer exposure time. However, using an additional old computer within this period may have contributed to the observed significant increase in Lab. 1 ($\sum_7$PBDE concentrations of up to 696 ng m^{-2}). This observation suggests that old computers are likely to be significant indoor PBDE sources. Recently, Hazrati and Harrad [19] have also related the high indoor air PBDE concentrations to the use of old computers. The outdoor concentrations of these four windows (Lab. 1, Server room, Office 1 and ambient air sampling Cabin 1) were also relatively high, ranging from 22 to 141 ng m^{-2}. Their replicates were ~2 times higher than those obtained in their first sampling, parallel with indoor concentrations (except for Sampling Cabin 1) supporting the time-integrated increasing pattern of pollutants on thicker films. It was known that Cabin 1 was not cleaned for a long time (longer than 19 months) before its first sampling and thus, probably

Table 1
Average concentrations of individual PBDEs obtained from indoor and outdoor organic films (ng m^{-2}).

	Indoor ($n = 15$)		Outdoor ($n = 15$)		(Indoor/outdoor)		Suburban (outdoor)	Urban (outdoor)	Industrial (outdoor)
	AM ± SD	GM	AM ± SD	GM	AM ± SD	GM	AM ± SD	AM ± SD	AM
BDE-28	0.4 ± 0.4	0.3	0.4 ± 0.4	0.3	1.3 ± 0.6	1.1	0.3 ± 0.2	0.4 ± 0.2	1.9
BDE-47	9.0 ± 13	2.9	2.0 ± 2.6	1.2	7.4 ± 10	2.6	1.4 ± 1.1	1.0 ± 1.0	12
BDE-100	6.4 ± 16	1.4	0.9 ± 0.9	0.6	11 ± 19	2.9	0.6 ± 0.4	0.5 ± 0.4	4.2
BDE-99	34 ± 100	3.8	2.6 ± 3.6	1.5	13 ± 22	2.9	1.6 ± 0.8	1.1 ± 1.2	16
BDE-154	13 ± 19	4.5	0.7 ± 0.6	0.5	32 ± 38	12	0.3 ± 0.4	0.7	1.9
BDE-153	10 ± 21	1.5	0.7 ± 0.6	0.5	20 ± 34	4.0	0.47	0.7 ± 0.6	2.2
BDE-209	34 ± 63	14	57 ± 67	30	0.7 ± 0.6	0.4	39 ± 44	42 ± 65	168
$\sum_7$PBDE	99 ± 163	40	64 ± 72	37	2.0 ± 2.8	1.1	43.5 ± 43.2	45.5 ± 68.8	206

AM: arithmetic mean; GM: geometric mean; SD: standard deviation.

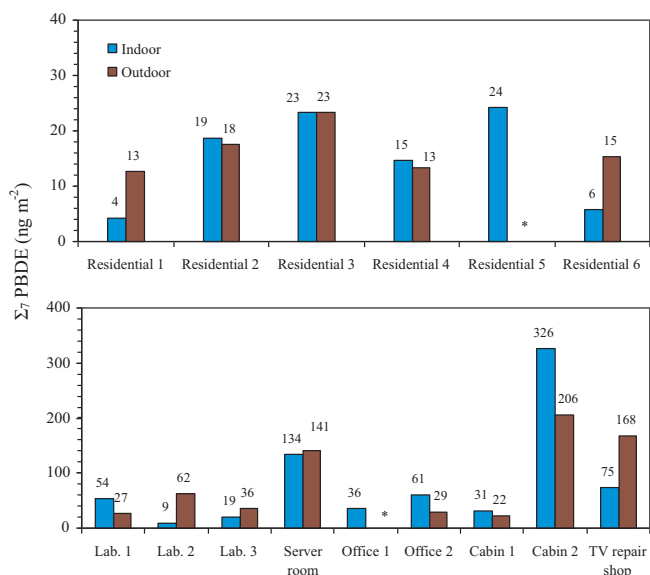**Fig. 2.** $\sum_7$PBDE concentrations of both indoor and outdoor organic films collected from different sites with different characteristics. (*) not analyzed.

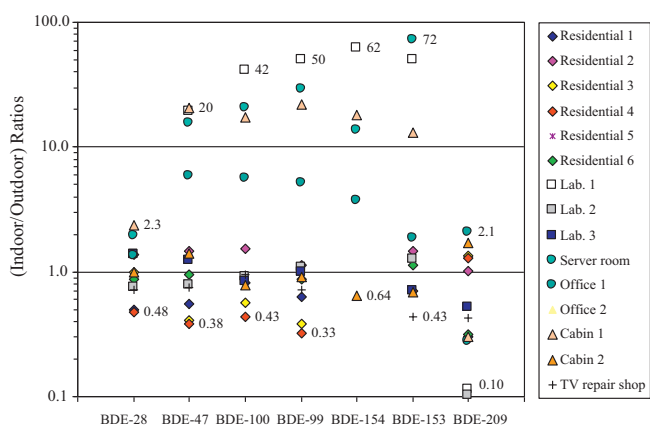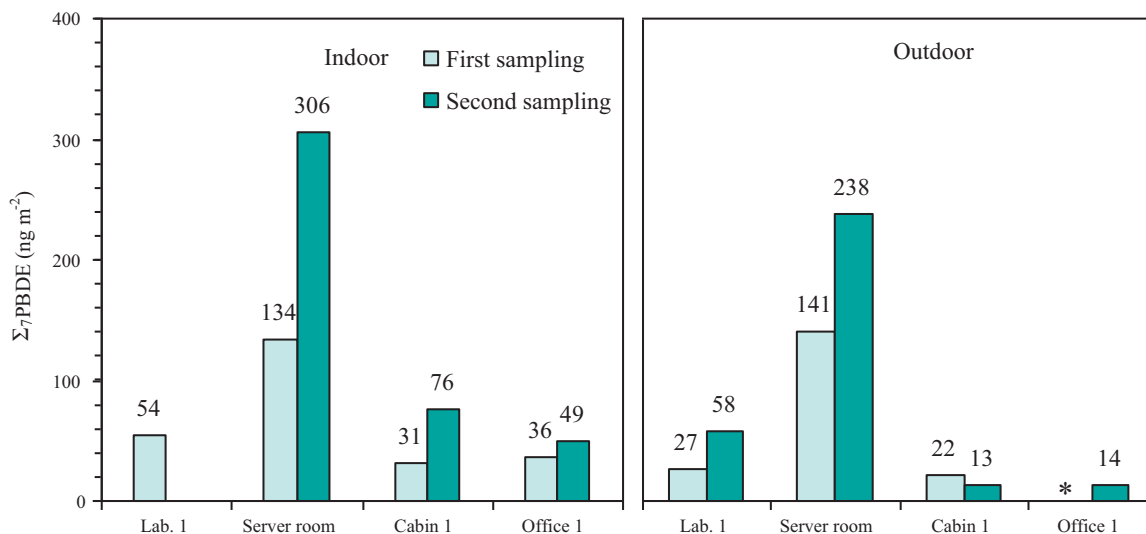**Fig. 3.** Indoor/outdoor window film concentration ratios for BDE congeners at different sites.

this resulted in lower film concentrations for the second sampling (Fig. 4).

Recently, in Southern Ontario, Butt et al. [11] found that the total PBDE concentrations (sum of the concentrations of 41 congeners) were between 0.6–14.5 ng m^{-2} for outdoor window films and 19–76 ng m^{-2} for indoor films. Total PBDE concentrations at an electronics recycling facility were 39 and 755 ng m^{-2} for outdoor and indoor films, respectively. Butt et al. [11] have also found that BDE-209, -99, -47, -100, -153, and -183 were the most abundant congeners (5 of them are the congeners measured in the present study) accounting for 86–93% of total PBDEs measured. Window film PBDE concentrations measured in the present study were within the ranges reported by Butt et al. [11].

A recent study has reported that PBDEs are commonly found in windshields of cars [9]. To investigate their levels in cars, indoor windshield film samples from 4 different vehicles (i.e., Nissan Micra, Alfa Romeo, Ford Fusion and Ford Focus, all 2004 or 2005 model cars) were also collected in the present study during winter and summer periods. In winter, Nissan Micra had the highest window film PBDE concentration while the Ford Focus had the lowest one (Table 2). The indoor film PBDE concentrations were relatively low but comparable to concentrations observed at other indoor sites. Considering the significantly lower periods from last cleaning for car samplings (2 weeks vs. >12 weeks), the measured levels suggest that there are significant PBDE sources in cars. It is interesting that in summer, BDE-209, the most abundant congener measured in winter samples could not be detected in any of the vehicles. This could be explained by the photolytic debromination of deca-BDE in sunlight [7,8,10]. Since automobiles can heat up to 90 °C, PBDEs may break down at much higher rates in solar-exposed cars than in other indoor and outdoor environments. Photolytic debromination of BDE-209 result in lower brominated PBDEs. Since all brominated compounds give bromine ions at m/z 79.1 and 81.1 under the conditions used for the sample analysis in the present study (negative chemical ionization-MS), number of the observed peaks could be expected to increase in summer sample chromatograms as a result of the formation of less brominated PBDEs (including octa to nona-BDEs). However, examination of sample chromatograms did not show any additional peaks in summer, corresponding to less brominated PBDEs (other than those analyzed) or other brominated compounds that could be formed. A possible explanation for this observation is the complete debromination of BDE-209 to form diphenyl ether that does not undergo further photolysis [8].

Fig. 4. $\sum_7$PBDE concentrations of indoor and outdoor organic films collected from four sites in campus and their replicates. (*) not analyzed.

Table 2
Average concentrations and range of individual PBDEs collected from indoor organic films of vehicles[a] for summer and winter periods (ng m^{-2}).

	Winter ($n = 4$)				Summer ($n = 4$)				Literature[b]
	Min.	Max.	AM ± SD	GM	Min.	Max.	AM ± SD	GM	AM
BDE-28	0.2	0.3	0.2 ± 0.03	0.2	0.1	0.2	0.2 ± 0.1	0.2	3
BDE-47	1.3	2.5	1.9 ± 0.5	1.9	0.3	1.1	0.8 ± 0.4	0.7	65
BDE-100	0.3	0.7	0.5 ± 0.2	0.5	0.2	0.3	0.3 ± 0.03	0.3	53
BDE-99	1.4	3.3	2.3 ± 0.8	2.2	0.4	1.1	0.9 ± 0.3	0.9	158
BDE-154	0.1	0.2	0.2 ± 0.1	0.2	0.1	0.2	0.2 ± 0.1	0.2	32
BDE-153	0.1	0.3	0.2 ± 0.1	0.2	0.1	0.4	0.3 ± 0.1	0.3	41
BDE-209	2.8	93	26 ± 45	7.7	ND	ND	ND	ND	60
$\sum_7$PBDE	6.5	98	31 ± 45	16	1.3	3.3	2.7 ± 0.9	2.5	365[c]

AM: arithmetic mean; GM: geometric mean; SD: standard deviation; ND: not detected.
[a] Nissan Micra, Alfa Romeo, Ford Fusion and Ford Focus.
[b] Gearhart and Pooselt [9].
[c] Sum of 11 congeners.

The concentrations of other congeners were also generally lower in summer period. Film–air partition coefficient decreases as a function of temperature, favoring less partitioning into the film-phase. Therefore, a more likely contributing factor for lower summertime concentrations may be the decreased sorption of PBDEs to windshield film at higher temperatures. Gearhart and Pooselt [9] have conducted a similar and a more detailed study using the samples collected from windshields of 111 vehicles (excluding the 4 models investigated in the present study). They have found moderately high levels of $\sum_{11}$PBDEs ranging from 54 to 1772 ng m^{-2} (Table 2). Different vehicle models and/or different vehicle ages may have caused this wide range of concentrations. Hazrati and Harrad [19] have reported that indoor air PBDE concentrations measured in cars were correlated to the model year, newer cars having higher concentrations.

3.2. Congener patterns

In all outdoor film samples, BDE-209 was the most abundant congener with the average contribution of $87 \pm 11\%$ to total PBDE concentrations. However, indoor films had variable congener patterns. Excluding the four sites with very high indoor film concentrations (Lab. 1, Server room, Office 1 and sampling Cabin 1), BDE-209 was the dominating congener at other sites and average contribution of this congener was $83 \pm 8\%$ to total PBDE concentrations. In those four sites, BDE-99 (in Server room also BDE-153) was the dominant congener. Among the vehicles, the contribution of BDE-209 to total PBDE concentrations was 95% for Nissan Micra, and it was $39 \pm 5\%$ for the other 3 cars in winter period, while in summer BDE-99 and -47 were the dominating congeners. Recently, Butt et al. [11] have found a similar pattern that BDE-209 was the dominant congener with the 51% contribution to total PBDE concentrations followed by BDE-99 and -47. In Manhattan, the contributions of BDE-209, -99 and -47 to total concentrations were reported to be 60, 11 and 9%, respectively [14].

PBDEs are commercially produced and used as technical mixtures (i.e., penta, octa, and deca products). Penta-product composition is dominated by BDE-99 and -47 (followed by BDE-100, -254 and -153), octa-product contains mainly BDE-197, -183, and -207, and deca-product contains mainly BDE-209 [20]. Comparison of the congener profiles of technical products and samples collected from both outdoor and indoor films suggest that measured film concentrations were mainly affected by penta and deca-mixtures. However, this evaluation is only qualitative since congener fractionation may occur during the processes like emission from sources, transportation and partition to surface films due to different volatilities and partitioning characteristics of PBDE congeners (see Section 3.3).

3.3. Investigation of air-window film partitioning of PBDEs

Gas phase compounds partition into the surface film, depending on the fugacity difference between the air and film. It was suggested that the organic matter fraction in window films can be used as a time-integrated passive sampler to determine the gas-phase air concentrations [11] with the knowledge of film–air partition coefficient (K_{FA}) and sampling rate [21]. The octanol–air partition coefficient (K_{OA}) has been used to describe the partitioning between atmosphere and other organic phases (i.e., particles, soil, and vegetation) [22–24]. By analogy to K_{OA}-based absorptive gas/particle partitioning model [24], K_{FA} can be related to K_{OA} using the fraction of organic matter in the film (f_{om}) and assuming that gas-phase and film-phase compounds are at equilibrium, gas-phase air concentrations (C_A, pg m^{-3}) can be predicted using the concentrations in the film (C_F, pg m^{-3}):

$$K_{FA} = \left(\frac{C_F}{C_A} \right) = f_{om} K_{OA} \tag{1}$$

In the present study, C_F (pg m^{-3}) was calculated using the PBDE mass in sample (m, pg), sampled total film area (A_F, m^2), and film thickness (h_f, m) ($C_F = m/A_F h_f$).

Polyurethane foam (PUF) and polymer films coated on glass (POG) have been successfully used as passive sampling media [25,26]. Recently, advances in estimating the air concentration have been made by calculating the effective air volume needed to supply enough chemical to the POG to result in equilibrium between the air and the passive sampling medium [27]. As an analogy, we have adopted this uptake model as a tool to help better understand the kinetics of the gas-phase/organic film partitioning of PBDEs, with a particular emphasis of testing the assumption of equilibrium partitioning, which is implicit in the K_{OA}-based model described above (Eq. (1)). Thus we have assumed that the organic film on impervious surfaces can be treated as a passive sampling medium. The complete uptake profile for a passive sampling medium has been described as [25]:

$$C_F = K_{FA} C_A \left\{ 1 - \exp - \left[\left(\frac{A_F}{V_F} \right) \left(\frac{k_A}{K_{FA}} \right) t \right] \right\} \tag{2}$$

where K_{FA} is the film–air partition coefficient, C_F and C_A are the concentrations (mass cm^{-3}) of analyte in the passive sampling medium (organic film) and air, respectively, A_F and V_F are the planar surface area (cm^2) and volume (cm^3) of the organic film, k_A is the air-side mass transfer coefficient (cm day^{-1}), and t is the exposure time (day).

V_{AIR} was recently termed as "the effective air volume" that is required to exchange chemical with the film to establish equilib-

Table 3
Average calculated and measured ambient air gas-phase concentrations of individual PBDEs ($pg\,m^{-3}$).

	Suburban			Urban			Industrial		
	Estimated		Measured[a]	Estimated		Measured	Estimated		Measured
	M1[b]	M2[c]		M1	M2		M1	M2	
BDE-28	2.3	2.3	0.3	3.6	3.3	0.7	19.4	19.4	1.2
BDE-47	1.2	1.2	0.7	1.1	1.0	2.5	11.2	11.2	11.3
BDE-100	0.1	0.1	0.3	0.1	0.1	0.6	1.0	1.0	2.6
BDE-99	0.3	0.4	0.5	0.21	0.3	1.2	2.5	2.7	12.5
BDE-154	0.02	0.03	0.2	0.03	0.1	0.3	0.1	0.2	1.1
BDE-153	0.02	0.04	0.3	0.04	0.1	0.7	0.1	0.2	1.4
BDE-209	0.002	4.4	6.0	0.002	5.8	6.4	0.006	9.9	6.2
$\sum_7$PBDE	4.1	8.5	8.1	5.2	10.6	12.2	34.4	44.6	36.3

[a] Cetin [15]. Ambient air data obtained in the Suburban and Industrial sites that are located near the corresponding outdoor window-film sampling sites.
[b] M1: equilibrium model (Eq. (1)).
[c] M2: dynamic uptake model (Eq. (2)).

rium in the film–air system [25]:

$$V_{\text{AIR}} = K_{\text{FA}}V_{\text{F}}\left\{1 - \exp - \left[\left(\frac{A_{\text{F}}}{V_{\text{F}}}\right)\left(\frac{k_{\text{A}}}{K_{\text{FA}}}\right)t\right]\right\} \qquad (3)$$

The maximum uptake of a passive sampling medium is defined by its retention capacity or K_{FA}. For example, a compound having a high K_{OA} (and hence, a high K_{FA}) will have a greater chemical capacity in the organic film than a compound with a lower partition coefficient, and will therefore require a large volume of air to supply sufficient mass of chemical to the passive sampling medium. Recently, it was shown that compounds with lower K_{FA} values equilibrate in shorter periods of time [25].

Recently, organic carbon fraction of films on impervious surfaces (f_{OC}) was assumed to be 7.7% [3], 10% [11,13], 5% [5] and 20% [12]. Based on these values and assuming that $f_{\text{OM}} = 1.6f_{\text{OC}}$ [28,29] organic matter fraction of films (f_{OM}) was estimated to be 15% in the present study. Film thickness is of another concern in estimation of gas-phase air concentrations. The range of film thickness was reported to be from 2.5 nm to 1 μm [12]. Film thickness was assumed to be 0.5 μm in modeling studies to assess the reactions in surface films [13]. Recently, Wu et al. [30] have measured the growth rate of urban films as 1.6–2.6 nm day^{-1} in Toronto. Using a midrange value of 2 nm day^{-1} and a 100-day period (based on a 3–4 month period from the last cleaning to sampling), film thickness was estimated as 0.2 μm in the present study. A film thickness of 0.03 μm was also calculated for the car windshields for a 15-day accumulation period. The air-side mass transfer coefficient (k_{A}) was recently determined as 9500 cm day^{-1} for POG samplers [25]. This value was derived for passive air samplers enclosed in a sampling chamber that is designed to reduce the effect of wind-speed. This may differ from the uptake of contaminants from the bulk atmosphere to outdoor window films. The boundary layer for the outdoor window films will be subject to variability due to changes in wind speed, and as a result k_{A} may be higher than the assumed value. The average measured ambient air temperature was 25 °C during the sampling period for window organic films. Based on three daily measurements (at 7:00 am, 14:00 and 9:00 pm) conducted during the sampling periods (two weeks) in one car, interior temperatures were estimated as 15 °C and 45 °C for winter and summer sampling periods, respectively. Thus, the K_{OA} values at these temperatures were calculated using the regression parameters (A and B) given by Harner and Shoeib [5] ($\log K_{\text{OA}} = A + B/T$). The regression parameters were not available for BDE-209. Therefore, $\log K_{\text{OA}}$ values of BDE-209 were determined using its temperature dependent dimensionless Henry's law constant (H') [31] and $\log K_{\text{OW}}$ values calculated based on the data from Braekevelt et al. [32]. $\log K_{\text{OA}}$ values ranged between 9.51 (BDE-28) and 14.98 (BDE-209) at 25 °C.

A sensitivity analysis indicated that the dynamic uptake model is more sensitive to exposure time and K_{OA} values rather than other parameters (i.e., organic matter fraction, mass transfer coefficient, and film thickness). Decreasing the organic matter fraction 50% results in 50% increase in air concentrations of all BDEs predicted by the equilibrium model while the increase for the dynamic uptake model ranges between 0.01% (BDE-209) and 50% (BDE-28). Increasing k_{A} 50% results in 0% (BDE-28) to 33% (BDE-209) decrease in predicted gas-phase concentrations by the dynamic uptake model. Increasing film thickness 50% results in 33% decrease in gas-phase concentrations for all congeners predicted by the dynamic uptake and equilibrium models.

Average predicted gas-phase concentrations of individual PBDEs using Eq. (1) (equilibrium) and Eq. (2) (dynamic uptake) are presented in Table 3 along with the recently measured concentrations in ambient air representative for Suburban, Industrial, and Urban sites in Izmir, Turkey [15]. However, the comparison of measured and predicted concentrations is a semi-quantitative one due to the associated uncertainties with the estimated (i.e., possible particle-phase deposition that was not accounted in the model) and measured concentrations (i.e., not concurrent with film samples). Therefore, organic films can be used in conjunction with the dynamic uptake model only to approximate the gas-phase ambient air concentrations. Predicted $\sum_7$PBDE outdoor gas-phase concentrations using the dynamic uptake model ranged between 3.2 and 45 (average ± SD, 11 ± 12) $pg\,m^{-3}$, while indoor concentrations were between 2.1 and 150 (average ± SD, 25 ± 36) $pg\,m^{-3}$ (Table 4). $\sum_7$PBDE gas-phase concentrations in cars were estimated to range between 15 and 79 (average ± SD, 33 ± 31) $pg\,m^{-3}$ in winter, while they ranged between 126 and 283 (average ± SD, 215 ± 70) $pg\,m^{-3}$ in summer (Table 4). These concentrations were within the range of indoor and outdoor concentrations predicted in the present study and measured recently in the area. Calculated concentrations were

Table 4
Estimated indoor air gas-phase concentrations of individual PBDEs ($pg\,m^{-3}$) by the dynamic uptake model.

	Buildings				Cars			
	Min.	Max.	AM ± SD	GM	Min.	Max.	AM ± SD	GM
BDE-28	1.2	19	4.2 ± 4.1	3.3	5.9	135	51 ± 52	24
BDE-47	0.3	49	9.5 ± 13	3.0	3.4	120	49 ± 55	20
BDE-100	0.04	18	1.7 ± 4.2	0.4	0.4	11	4.9 ± 4.7	2.2
BDE-99	0.03	74	6.3 ± 17	0.9	1.3	18	8.5 ± 7.7	5.4
BDE-154	0.1	2.6	0.8 ± 1.0	0.4	0.1	1.0	0.4 ± 0.4	0.3
BDE-153	0.02	6.1	0.8 ± 1.7	0.2	0.1	2.4	0.9 ± 0.9	0.5
BDE-209	0.1	17	2.4 ± 4.0	1.0	2.0	65	18 ± 31	5.4
$\sum_7$PBDE	2.1	150	25 ± 36	13	15	283	124 ± 110	72

AM: arithmetic mean; GM: geometric mean; SD: standard deviation.
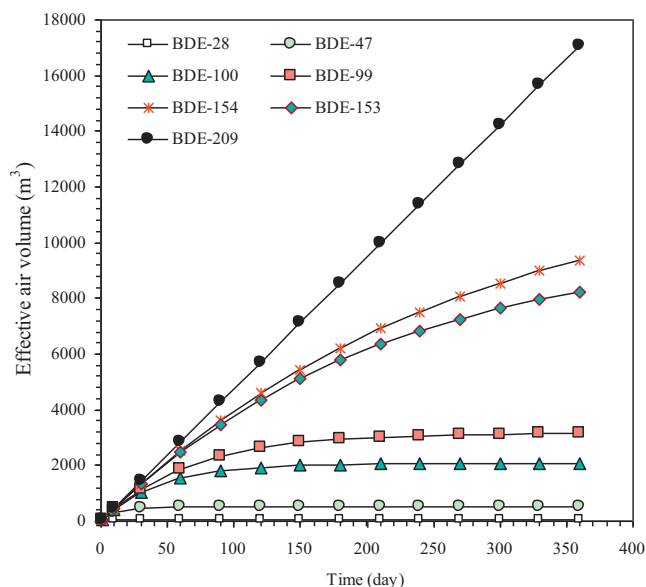
Fig. 5. Variation of effective air volume (Eq. (3)) with time for different BDE congeners. K_{FA} from Eq. (1), $f_{om} = 0.15$, $\log K_{OA} = 9.51$, 10.54, 11.14, 11.32, 11.93, 11.83, and 14.98 (at 25 °C) for BDE-28, -47, -100, -99, -154, -153, and -209, respectively, $A_F = 5000 \, cm^2$, film thickness $= 0.2 \, \mu m$, $k_A = 9500 \, cm \, day^{-1}$.

also comparable to those measured in cars recently by Harrad et al. [33] (11–8200 pg m^{-3}, median 41 pg m^{-3}) and Mandalakis et al. [34] (range 0.4–2644 pg m^{-3}, geometric mean 114 pg m^{-3}).

Recently, it was suggested that BDE-209 is transported in the environment primarily as particle-bound [35,36]. Also, in recent modeling efforts on the environmental fate of PBDEs (i.e., photochemical removal/conversion), atmospheric BDE-209 was assumed to be particle bound 99.1–99.98 [7] and 99.999% [8]. Gas-phase fraction of BDE-209 has a crucial importance since the photolysis rate is significantly (120 times) higher in this phase according to Schenker et al. [7] while no photolysis takes place on particles according to Raff and Hites [8]. Equilibrium partitioning gas-particle models estimate that higher brominated congeners like BDE-209 are expected to be particle bound >99.9% [2]. Although there have been several studies reporting atmospheric PBDE concentrations, the number of studies that included the BDE-209 is relatively small. There are an increasing number of studies reporting appreciable gas-phase BDE-209 fractions. Agrell et al. [37] have measured the BDE-209 mainly in gas-phase (>90%) at an urban site while it was 100% in gas-phase at a rural site. The average proportion of BDE-209 in gas-phase was 30 ± 11% at four sites in Izmir, Turkey [38]. Li et al. [39] have reported that on the average, 5% of BDE-209 was associated with gas-phase at three sites in southeast China. Furthermore, the average proportion of BDE-209 in gas-phase was 41 ± 28% in the stack gases from five scrap processing steel plants with electric arc furnaces [17]. The results of the study by Odabasi et al. [17] are very important since it was shown that contrary to common assumption, significant amounts of heavy congeners like BDE-209 could be emitted in the gas-phase. However, it is not possible to determine the net influence of being emitted in the gas-phase for the environmental fate of BDE-209. Modeling efforts taking into account the presence of emissions in the gas-phase, higher photolysis rates in this phase relative to particle-phase, and relatively slow gas-particle/organic film partitioning are required to better assess the environmental fate of PBDEs.

The effect of K_{FA} (or K_{OA}) on the uptake profiles for surface films is shown in Fig. 5, that is a plot of Eq. (3) over time for a range of K_{OA} values. BDE-28 ($\log K_{OA} = 9.51$) will equilibrate within 10 days in the film–air system while BDE-47 ($\log K_{OA} = 10.54$) will require 60 days

for equilibrium. BDE-100 and -99 ($\log K_{OA} = 11.14–11.32$) will reach equilibrium within ~180 days. Congeners with $\log K_{OA} > 12$ (BDE-154, -153, and -209) will not reach equilibrium even for a period of 1 year (Fig. 5). Predicted gas-phase ambient concentrations for BDE-28, -47, and -100 in the present study were identical for equilibrium and dynamic uptake models suggesting that for these congeners, the gas-phase and compounds in film may be close to equilibrium. However, equilibrium model significantly underestimated the air concentrations of BDE-153, -154 and -209 (Table 3). Cetin and Odabasi [38] have indicated that several months are required for these heavier congeners to reach equilibrium between the air and atmospheric particles. Similarly, the results of the present study obtained by the application of the dynamic uptake model indicated that several months are required for gas-phase BDE congeners with high $\log K_{OA}$ values (>12) to reach equilibrium with the surface films. As a result, surface films and atmospheric particles act mainly as sinks for these BDEs. Also, the gas-phase atmospheric transport and photolytic removal/conversion of congeners like BDE-209 may be as important as their fate in particle-phase.

4. Conclusions

Polybrominated diphenyl ether concentrations of indoor and outdoor organic films on window glasses were measured at different sites in Izmir, Turkey. $\sum_7$PBDE concentrations were dominated by technical penta and deca-BDE mixture components. Measured window film PBDE concentrations were within the ranges reported in the literature. Results of this study have supported some recently reported findings obtained using passive sampling techniques (i.e., the spatial concentration gradient between the urban and suburban areas). The results of the air-organic film partitioning modeling have suggested that PBDE concentrations in organic films can be used to approximate the gas-phase ambient air concentrations. Modeling results have also indicated that if congeners with very large octanol–air partition coefficients (i.e., BDE-154, -153, and -209) are emitted from their sources in the gas-phase, they will remain in that phase for several months before establishing an equilibrium with the organic films. This may also have important implications for atmospheric fate and transport of PBDEs.

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