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Particle-Phase Dry Deposition and Air–Soil Gas-Exchange of Polybrominated Diphenyl Ethers (PBDEs) in Izmir, Turkey

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The particle-phase dry deposition and soil–air gas-exchange of polybrominated diphenyl ethers (PBDEs) were measured in Izmir, Turkey. Relative contributions of different deposition mechanisms (dry particle, dry gas, and wet deposition) were also determined. BDE-209 was the dominating congener in all types of samples (air, deposition, and soil). Average dry deposition fluxes of total PBDEs (Σ_7 -PBDE) for suburban and urban sites were 67.6 and 128.8 ng m⁻² day⁻¹, respectively. Particulate dry deposition velocities ranged from 11.5 (BDE-28) to 3.9 cm s⁻¹ (BDE-209) for suburban sites and 7.8 (BDE-28) to 2.8 cm s⁻¹ (BDE-154) for urban sites with an overall average of 5.8 ± 3.7 cm s⁻¹. The highest Σ_7 PBDE concentration (2.84 × 10⁶ ng kg⁻¹ dry wt) was found around an electronic factory among the 13 soil samples collected from different sites. The concentration in a bag filter dust from a steel plant was also high (2.05 × 10⁵ ng kg⁻¹), indicating that these industries are significant PBDE sources. Calculated net soil–air gas exchange flux of Σ_7 PBDE ranged from 11.8 (urban) to 23.4 (industrial) ng m⁻² day⁻¹ in summer, while in winter it ranged from 3.2 (urban) to 11.6 (suburban) ng m⁻² day⁻¹. All congeners were deposited at all three sites in winter and summer. It was estimated that the wet deposition also contributes significantly to the total PBDE deposition to soil. Dry particle, wet, and gas deposition contribute 60, 32, and 8%, respectively, to annual PBDE flux to the suburban soil.

Introduction

Polybrominated diphenyl ethers (PBDEs) are ubiquitous environmental pollutants. There has been great interest in these persistent organic pollutants (POPs) in the past decade because of their persistence and probable toxicity and carcinogenic/mutagenic human health effects. PBDEs are likely to partition to solids (i.e., sediment, soil, atmospheric particles) and they may bioaccumulate when they are released into the environment because of their relatively low water solubilities and vapor pressures, and relatively large octanol–water and octanol–air partition coefficients (1).

Atmospheric PBDEs are distributed between gas and particle phases. The fate, transport, and removal of POPs from the atmosphere by dry and wet deposition processes are strongly influenced by their gas–particle partitioning. Atmospheric deposition is a major source for PBDEs in soil.

Surrogate surfaces could be used to measure the particle-phase dry deposition flux. Also, measured ambient concentrations (C_p) multiplied by an assumed or modeled deposition velocity (V_p) could be used to determine the dry deposition flux (F_p) (2)

$$F_p = V_p C_p \quad (1)$$

Deposition velocity is affected by the meteorological parameters, physical properties of the particle (i.e., size, shape, and density), and the type and roughness characteristics of the receptor surface (3, 4). The selection of an appropriate deposition velocity is crucial since it may introduce large uncertainties into the calculated dry deposition fluxes.

Once deposited, POPs tend to accumulate in soil for a long period of time and are subject to various partitioning, degradation, and transport processes depending on their physical–chemical properties and microbiological degradability (5). Soil–air exchange is an important diffusive process affecting the fate and transport of PBDEs into the environment. The direction and magnitude of the gas-exchange is determined by the concentrations in air and soil, and by the soil–air equilibrium partition coefficient (K_{SA}) (6). K_{SA} values and soil–air equilibrium status for various POPs have been calculated previously (6–11). There have been a few studies on the levels of PBDEs in soils (12–14). However, soil–air partition coefficients and fugacities of PBDEs have not been investigated.

The objectives of this study were (1) to measure the particle-phase dry deposition fluxes of PBDEs and to determine their dry deposition velocities, (2) to investigate the levels of PBDEs in soil and their spatial variation in Izmir, Turkey, (3) to determine the magnitude and direction of soil–air exchange fluxes of PBDEs, and (4) to assess the relative importance of different deposition mechanisms (i.e., gas-exchange, particle deposition, and wet deposition).

Materials and Methods

Sampling Program and Collection. Izmir metropolitan city, with a population of 2.7 million, is the center of a highly industrialized area by the Aegean Sea shoreline of Turkey. Izmir is densely populated over two narrow flat basins between three series of mountains aligned perpendicular to the seashore.

Ambient air and particle dry deposition samples were collected at two sampling sites (suburban and urban). Ambient samples were also collected at an industrial site (Figure S1 in the Supporting Information). The suburban samples were collected on a 4 m high platform located on the Kaynaklar campus of the Dokuz Eylul University, ~10 km southeast of Izmir's center. This site is relatively far from any settlement zones or industrial facilities. There are residential areas located approximately 2 km southwest and a highway located 0.5 km south of the sampling site. Urban samples were collected from Yesildere site located near a main street with heavy traffic and residential areas. Samples were also collected at Horozgedigi village (industrial) located ~5 km south of Aliaga county (~50 km north of Izmir). There are nearby steel plants with electric arc furnaces, a natural gas-fired power plant (1500 MW), a fertilizer factory, a few small plants, and other industrial plants (i.e., a petrochemical complex, petroleum refinery, and LPG storage plants) within a few kilometers.

Meteorological data for the suburban and urban sites were obtained from a 10 m high tower located at the suburban

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sampling site. Meteorological data for the industrial site was obtained from the air quality monitoring and weather station located at Horozgedigi village.

Concurrent ambient air and dry deposition samples from suburban and urban sites were collected during two sampling programs occurring September 6–25, 2004 (summer) and February 4–March 20, 2005 (winter). During the sampling programs 17 samples were collected in summer (8 suburban and 9 urban) and 17 samples were collected in winter (9 suburban and 8 urban). Air samples from the industrial site were also collected during two sampling programs occurring March 28–April 8, 2005 (winter) and June 13–20, 2005 (summer) (6 winter and 7 summer samples).

Air samples were collected using a modified high-volume sampler model GPS-11 (Thermo-Andersen Inc.). Particles were collected on 10.5-cm diameter quartz filters and the gas-phase compounds were collected in a cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF). The average sampling volume was $325 \pm 34 \text{ m}^3$ and the sampling duration was $\sim 24 \text{ h}$.

The particle dry deposition flux was measured using a smooth deposition plate ($22 \times 7.5 \text{ cm}$) with a sharp leading edge (with an angle $< 10^\circ$), mounted on a wind vane. Glass fiber filter (GFF) sheets mounted with cellulose acetate strips on the plates were used to collect the deposited particles. The dimensions of the GFF sheet's deposition surface were $5.5 \times 12 \text{ cm}$. Five plates and sheets with a total collection area of 330 cm^2 were used for sampling.

Prior to sampling, quartz filters and GFF sheets were baked at 450°C overnight. Then they were allowed to cool to room temperature in a desiccator. PUF cartridges were cleaned by Soxhlet extraction using an acetone/hexane mixture (1:1) for 24 h, dried in an oven at 70°C , and stored in glass jars capped with Teflon-lined lids. After sampling, air filters, GFF sheets, and PUF cartridges were stored at -20°C in their containers.

The soil samples were collected from 13 different sites (Figure S1). In total, 23 surface soil samples were collected manually at 0–5 cm depth between September 2004 and October 2005. The soil samples from urban, suburban, and industrial sites were collected during air sampling programs. For each site, equal amounts of 10 subsamples were taken over a $\sim 100 \text{ m}^2$ area and were homogenized for analysis. Large particles and organic debris were removed using a 0.5 mm mesh sieve. The samples were sealed with aluminum foil and stored at 4°C . A bag filter dust sample from a steel plant with electric arc furnaces was also taken to examine the sources of PBDEs.

Sample Preparation and Analysis. Ambient air and dry deposition samples were Soxhlet extracted for 24 h with a mixture of 1:1 acetone/hexane. Soil samples (10 g) were soaked overnight with the same solvent mixture and then they were ultrasonically extracted for 60 min. Prior to extraction, all samples were spiked with surrogate standard (BDE-77, 3,3',4,4'-tetrabromodiphenyl ether). The extract volumes were reduced and the solvent was exchanged into hexane using a rotary evaporator and a high-purity N_2 stream. After concentration to 2 mL, samples were cleaned up and fractionated on an alumina–silicic acid column containing 3 g of silicic acid (deactivated with 4.5% deionized water) and 2 g of alumina (deactivated with 6% deionized water). The column was pre-washed with 20 mL of dichloromethane (DCM) followed by 20 mL of petroleum ether (PE). Then, the sample in 2 mL of hexane was added to the column and PBDEs were eluted with 35 mL of PE. The final extracts were solvent exchanged into hexane and concentrated to 1 mL under a stream of N_2 .

Water content of soil was determined by weighing $\sim 30 \text{ g}$ of soil before and after drying at 103°C in an oven for

24 h, and the organic matter content was determined by loss on ignition in a muffle furnace at 600°C for 4 h.

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. Pulsed-splitless injection was used. The capillary column was DB-5ms (15 m, 0.25 mm , $0.1 \mu\text{m}$). The carrier gas (helium) was used at the 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°C for 1 min, raised to 340°C at $20^\circ\text{C min}^{-1}$, and held for 2 min. The injector, ion source, and quadrupole temperatures were 280, 230, and 150°C , respectively. High-purity methane was the reagent gas. The MSD was run in selected ion monitoring mode. For six BDEs, 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 on the basis of their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure.

Quality Control. Average recovery of BDE-77 was $83 \pm 17\%$, $60 \pm 9\%$, $87 \pm 20\%$, and $98 \pm 22\%$ for PUFs, dry deposition, air filter, and soil samples, respectively. The recoveries of target compounds were also tested externally and average recovery efficiencies were between $86 \pm 9\%$ (BDE-28) and $110 \pm 7\%$ (BDE-154) (overall average $\pm \text{SD}$, $99 \pm 12\%$).

Instrumental detection limits (IDL) were determined from linear extrapolation from the lowest standard in calibration curve 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 $1 \mu\text{L}$ injection. Blank PUF cartridges, air filters, and dry deposition filters were routinely placed in the field. The limit of detection of the method (LOD, ng) was defined as the mean blank mass plus three standard deviations ($\text{LOD} = \text{mean blank value} + 3\text{SD}$). 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 for PUFs, from 0.05 to 0.28 for air filters, and from 0.05 to 0.33 ng for dry deposition samples. LODs for BDE-209 were 1.26, 1.40, and 1.87 ng for PUFs, air filters, and dry deposition filters, respectively. PBDE amounts in blanks were $20 \pm 12\%$, $14 \pm 10\%$, $27 \pm 14\%$, and $8 \pm 9\%$, of the amounts found in PUF, air filter, dry deposition, and soil samples, respectively. Sample quantities exceeding the LOD were quantified and blank-corrected.

The analytical reproducibility of the method was determined by replicate analysis of a soil sample collected from the suburban sampling site. The relative standard deviation was less than 10% ($n = 6$). Results from the analysis of pre-cleaned matrix blanks ($n = 3$) spiked with 15 ng of each target compound indicated that the method had a good precision with a relative standard deviation less than 10%. Soil samples ($n = 3$) taken from the same location (within a 100 m^2 area) were also analyzed to check if there was a short-scale spatial variation in BDE concentrations. The relative standard deviation was less than 20% and ranged between 4% (BDE-209) and 19% (BDE-28).

It was suggested that the GC column should be tested for possible coelution of target and interfering compounds (15, 16). Therefore, six congeners excluding BDE-209 were also analyzed using a longer column (HP5-ms, 30 m, 0.25 mm) with a thicker stationary phase ($0.25 \mu\text{m}$) that provides a relatively better peak separation. Coelution with any other compounds and systematic differences in PBDE concentrations were not observed during the two different GC measurements. The agreement between the two sets of analyses was very good (statistically the same at 95%

confidence level, two-tailed *t*-test) confirming the reliability of GC techniques used in this study.

Air–Soil Exchange Modeling. Air/soil exchange of gas-phase PBDEs is also an important process due to significant partition of PBDEs to gas phase. Fugacity is a measure of chemical potential or partial pressure of a chemical in a particular medium that controls the transfer of chemicals between media. Chemicals try to establish an equal fugacity (equilibrium) in the soil–air system (9). The equilibrium partitioning of a chemical between air and soil is described by the dimensionless soil–air partition coefficient, K_{SA} as follows:

$$K_{SA} = \frac{C_S \rho_S}{C_A} \quad (2)$$

where C_S is the soil concentration (ng kg⁻¹, dry weight), ρ_S is the density of soil solids (kg m⁻³), and C_A is the gas-phase air concentration (ng m⁻³).

K_{SA} is dependent on temperature, humidity, and the chemical and soil properties (8). Partitioning of POPs to soil occurs via absorption to the organic carbon fraction. The octanol–air partition coefficient (K_{OA}) is a key descriptor of chemical partitioning between the atmosphere and organic phases (10). Hippelein and McLachlan (6) formulated a linear relationship that relates K_{SA} to K_{OA} and the organic carbon fraction of the soil:

$$K_{SA} = 0.411 \rho_S \phi_{OC} K_{OA} \quad (3)$$

where ρ_S is the density of the soil solids (kg L⁻¹) and ϕ_{OC} is the fraction of organic carbon on a dry soil basis. The factor 0.411 improves the correlation between the K_{SA} and K_{OA} (6, 7). In calculation of K_{SA} , it is assumed that the fugacity capacity of soil is due to entirely the organic carbon fraction (7, 9).

The net air/soil gas exchange flux is driven by the fugacity difference between air and surface soil (17). The gas flux is a function of dimensionless soil–air partition coefficient, the concentration gradient, and the overall mass transfer coefficient. The instantaneous net flux (F_g , ng m⁻² day⁻¹) is

$$F_g = \text{MTC} \left(C_A - \frac{C_S \rho_S}{K_{SA}} \right) \quad (4)$$

where C_S is soil concentration (ng kg⁻¹, dry weight) and C_A is air concentration (ng m⁻³), MTC is the overall mass transfer coefficient (cm s⁻¹), ρ_S is the density of the soil solids (kg m⁻³), and K_{SA} is soil–air partition coefficient.

The overall mass transfer coefficients (MTC) of gaseous pollutants can be predicted by the resistance model developed by analogy to electrical resistance (17). In this model, the atmosphere is considered to have three major resistances: aerodynamic (R_a), quasi-laminar boundary layer (R_b), and canopy (R_c). The overall MTC is the reciprocal of the overall resistance and can be expressed as

$$\text{MTC} = \frac{1}{(R_a + R_b + R_c)} \quad (5)$$

Aerodynamic resistance accounts for turbulent diffusion transfer from the bulk atmosphere to the canopy. It depends on the wind speed, atmospheric stability and surface roughness. The aerodynamic resistance for unstable atmospheres can be represented by (18)

$$R_a = \frac{9}{U_{10} \sigma_\theta^2} \quad (6)$$

where U_{10} is the wind speed 10 m above the surface, and σ_θ is the standard deviation of the wind direction in radians.

The atmosphere was determined to be unstable over the sampling periods, thus (eq 6) was used in the present study.

Boundary layer resistance is the resistance in the laminar sublayer and depends on the molecular diffusion. It can be calculated from the equation developed by Wesely and Hicks (19) and is given as

$$R_b = \left(\frac{2}{\kappa U^*} \right) \left(\frac{\text{Sc}}{\text{Pr}} \right)^{2/3} \quad (7)$$

where Pr is Prandtl number of air (~0.72), Sc is the Schmidt number (ν/D_A) (ν (cm² s⁻¹) is the kinematic viscosity and D_A (cm² s⁻¹) is the molecular diffusion coefficient of the contaminant in air), κ (~0.4) is the Karman's constant, and U^* (cm s⁻¹) is the friction velocity. Canopy resistance is not applicable to surface soils since it is associated with deposition to vegetated land.

Results and Discussion

Ambient Concentrations. Σ_7 PBDE concentrations refers to sum of air concentrations (gas + particle) of the seven BDE congeners covered in this study. Σ_7 PBDE concentrations ranged from 6.2 (suburban) to 148.8 (industrial) pg m⁻³. On the average, the association of PBDEs with gas-phase was between 27% (BDE-209) and 64% (BDE-28) in all samples. BDE-209 was the dominating congener followed by BDE-47 and/or -99 (Table 1). In the suburban site, the average contribution of BDE-209 to total ambient concentrations was up to 80% in summer, and in urban and industrial sites it was 68 and 44%, respectively. In winter, contributions of BDE-209 in suburban, urban, and industrial sites were 58, 68, and 62%, respectively. The congener profiles observed in this study were similar to those reported previously (20, 21).

A recent study conducted using passive samplers at a continental scale reported that Σ_8 PBDE concentrations (excluding BDE 209) ranged between 0.5 and 250 pg m⁻³ over Europe (22). Σ_6 PBDE concentrations (excluding BDE 209) on a rural–urban transect across a major UK conurbation ranged between 2.8 and 23.3 pg m⁻³ (12). In Gotska Sandön Island in the Baltic Sea, median Σ_{10} PBDEs concentrations ranged between 0.4 and 78.5 pg m⁻³ (23). In Chicago, atmospheric concentrations of Σ_{26} PBDEs were found at 100 ± 35 pg m⁻³ (21). In a study performed by Agrell et al. (24), the median concentrations of Σ_7 PBDE and BDE-209 were found as 3.5 and 6.5 pg m⁻³, respectively, at an urban site. In all these studies the number of target compounds was variable. However, the contribution of BDE-47, -99, -100 and -209 to Σ PBDEs was >80% in all samples. Ambient PBDE concentrations measured in the present study were within the ranges of previously reported values.

Particle-Phase Dry Deposition Fluxes and Velocities. The range for measured particle-phase fluxes of individual PBDEs was 1.8 (BDE-28) to 49.4 (BDE-209) ng m⁻² day⁻¹ at the suburban site and 2.2 (BDE-154) to 107.5 (BDE-209) ng m⁻² day⁻¹ at the urban site (Table 2). Average fluxes of Σ_7 PBDE for both sites were 67.6 and 128.8 ng m⁻² day⁻¹, respectively. Particulate fluxes were dominated by BDE-209, which accounted for 49 and 76% of Σ_7 PBDE fluxes in the suburban and urban sites, respectively. The average flux of BDE-209 was ~2 times higher at the urban site than the one measured at the suburban site. This result is consistent with higher TSP concentrations at the urban site (112.7 ± 36.0 μg m⁻³) compared to those measured at the suburban site (50.1 ± 21.2 μg m⁻³). The average fluxes of other target congeners were similar in both sites. Particle-phase concentrations in the urban site were approximately 2 times higher than those obtained in the suburban site, while the dry deposition velocities were lower in the urban site resulting in similar deposition fluxes in both sites for other six congeners. Particle-phase dry deposition of PBDEs has not been studied

TABLE 1. Ambient Air Concentrations ($\mu\text{g m}^{-3}$, Average \pm SD) of Individual PBDE Congeners for Suburban, Urban, and Industrial Sites

congener	suburban		urban		industrial	
	gas	particle	gas	particle	gas	particle
BDE-28	0.3 \pm 0.1	0.20 \pm 0.1	0.6 \pm 0.4	0.3 \pm 0.1	1.2 \pm 0.4	0.6 \pm 0.2
BDE-47	0.8 \pm 0.5	0.7 \pm 0.3	1.8 \pm 0.9	1.7 \pm 1.4	8.2 \pm 4.7	6.6 \pm 4.8
BDE-100	0.8 \pm 1.3	0.4 \pm 0.2	0.6 \pm 0.2	0.7 \pm 0.4	2.0 \pm 1.0	1.9 \pm 1.2
BDE-99	1.3 \pm 1.7	0.9 \pm 0.5	1.0 \pm 0.5	2.2 \pm 1.7	9.0 \pm 6.0	10.3 \pm 7.3
BDE-154	1.6 \pm 3.6	0.4 \pm 0.3	0.3 \pm 0.1	0.7 \pm 0.5	0.9 \pm 0.4	1.3 \pm 0.5
BDE-153	1.3 \pm 3.4	0.4 \pm 0.1	0.5 \pm 0.3	0.7 \pm 0.3	1.1 \pm 0.6	1.7 \pm 0.7
BDE-209	6.2 \pm 4.7	9.5 \pm 5.9	4.3 \pm 3.8	21.6 \pm 14.8	6.8 \pm 5.1	39.8 \pm 24.5
Σ_7 PBDE	11.9 \pm 12.3	12.1 \pm 6.6	8.6 \pm 5.3	27.3 \pm 16.9	28.9 \pm 14.7	62.2 \pm 28.8

TABLE 2. Particle-Phase Dry Deposition Fluxes and Velocities and Soil–Air Gas Exchange Fluxes (Average \pm SD) of Individual PBDEs

congener	dry deposition velocity (cm s^{-1})		dry deposition flux ($\text{ng m}^{-2} \text{day}^{-1}$)		soil–air gas exchange flux ($\text{ng m}^{-2} \text{day}^{-1}$)		
	suburban	urban	suburban	urban	suburban	urban	industrial
BDE-28	11.5 \pm 2.2	7.8 \pm 3.5	1.8 \pm 0.5	2.4 \pm 1.4	0.4 \pm 0.2	0.4 \pm 0.5	0.8 \pm 0.4
BDE-47	9.2 \pm 4.6	3.9 \pm 1.7	6.1 \pm 2.6	6.0 \pm 3.5	1.1 \pm 0.8	1.8 \pm 2.0	4.9 \pm 3.2
BDE-100	8.4 \pm 3.9	6.4 \pm 2.5	3.0 \pm 1.0	3.6 \pm 1.9	0.8 \pm 0.5	0.5 \pm 0.3	1.3 \pm 0.7
BDE-99	5.7 \pm 3.1	3.1 \pm 1.6	4.9 \pm 2.8	6.7 \pm 5.2	1.4 \pm 1.4	0.9 \pm 0.6	5.7 \pm 4.2
BDE-154	6.5 \pm 3.8	2.8 \pm 1.4	2.7 \pm 1.8	2.2 \pm 0.8	0.6 \pm 0.5	0.3 \pm 0.2	0.6 \pm 0.3
BDE-153	7.6 \pm 1.3	4.6 \pm 1.6	2.9 \pm 1.7	2.6 \pm 0.6	0.5 \pm 0.2	0.5 \pm 0.5	0.8 \pm 0.4
BDE-209	3.9 \pm 3.6	2.9 \pm 1.8	49.4 \pm 89.0	107.5 \pm 114.8	8.5 \pm 7.9	4.0 \pm 5.1	4.3 \pm 4.1
Σ_7 BDE			67.6 \pm 90.3	128.8 \pm 122.8	12.9 \pm 10.2	7.8 \pm 8.2	18.2 \pm 10.9

extensively. The measured median dry deposition fluxes by ter Schure et al. (23) for BDE-209 and Σ_6 PBDE flux (excluding BDE-209) were 77.1 and 18.4 $\text{ng m}^{-2} \text{day}^{-1}$, respectively, near a solid waste incineration plant. They measured BDE-209 and Σ_6 PBDE fluxes as 10.9 and 7.0 $\text{ng m}^{-2} \text{day}^{-1}$, respectively, at an urban reference site.

Particle-phase dry deposition velocities for PBDEs were calculated by dividing the particulate fluxes measured with dry deposition plates by ambient particle phase concentrations (eq 1) and are presented in Table 2. They ranged from 11.5 (BDE-28) to 3.9 cm s^{-1} (BDE-209) for the suburban site and 7.8 (BDE-28) to 2.8 cm s^{-1} (BDE-154) for the urban site with an overall average of $5.8 \pm 3.7 \text{ cm s}^{-1}$ for both sites. The particle-phase PBDE fluxes and ambient concentrations correlated well ($r^2 = 0.84$, $p < 0.01$, $n = 139$). The slope of a linear regression line (3620 m day^{-1} or 4.2 cm s^{-1}) is the apparent best-fit particulate overall dry deposition velocity, which is in good agreement with the average value of 5.8 cm s^{-1} .

Dry deposition velocities of PBDEs were lower in the urban site than those calculated for the suburban site (Table 2). The dry deposition velocities are the function of particle size distribution and the meteorological parameters (i.e., wind speed and temperature). The difference in deposition velocities may be due to different size distributions of urban and suburban particles. Since large particles dominate the atmospheric dry deposition, higher deposition velocities in the suburban site can be attributed to larger particles from re-suspension of polluted soil and dust particles from unpaved roads and non-vegetated areas. The deposition velocity increases with wind speed (25). The average wind speed was also significantly higher in the suburban site ($6.8 \pm 2.3 \text{ m s}^{-1}$) compared to the urban site ($3.5 \pm 1.9 \text{ m s}^{-1}$), favoring higher deposition velocities.

The particle-phase dry deposition velocity of PBDEs generally decreased with increasing molecular weight. The same trend was observed for PAHs and was attributed to association of the greater fraction of the high molecular weight compounds with fine particles (3). However, there is no size-segregated particle-phase data for PBDEs to support a similar conclusion. Recently, median dry particle deposition

velocities of BDEs ranging from 0.4 to 49 cm s^{-1} have been reported (23). Unlike the present study, the velocity of BDE-209 was the highest. Particle-phase dry deposition velocities of other POPs have been studied extensively and values ranging between 0.3 and 7.3 cm s^{-1} were reported for PCBs and PAHs (2, 3, 26). PBDE deposition velocities determined in this study were similar to those reported for other POPs.

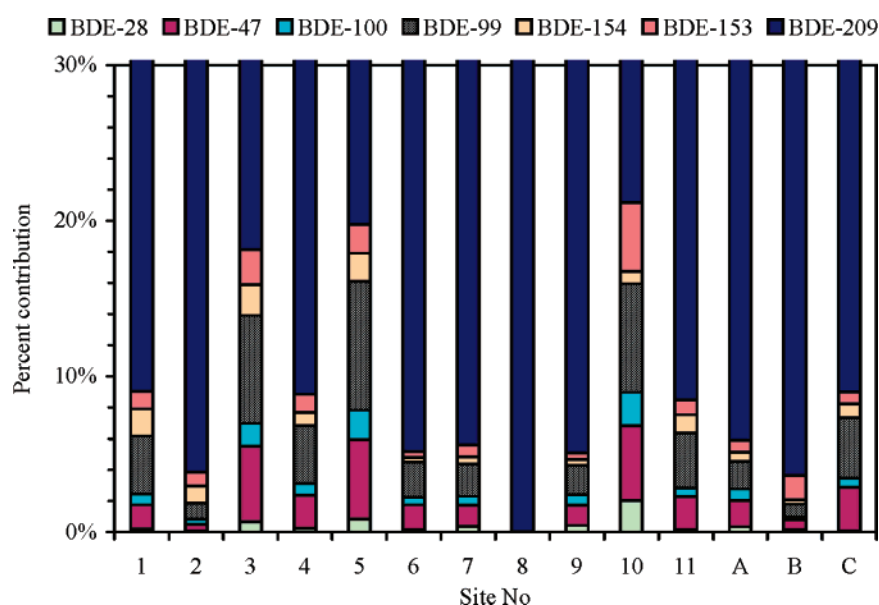
PBDE Concentrations in Soil and Air–Soil Exchange. Soil samples were collected at 13 different sites. Bag-filter dust from an electric arc furnace at a steel plant was also analyzed. Water and organic matter contents and Σ_7 PBDE concentrations measured in these sites are presented in Table 3. The highest Σ_7 PBDE concentration ($2.84 \times 10^6 \text{ ng kg}^{-1}$ dry weight) was measured around an electronic industry. Four additional soil samples around this electronic industry were collected and analyzed to determine whether this anomalously high concentration was caused by a sampling artifact. Nearly the same concentration ($2.63 \times 10^6 \text{ ng kg}^{-1}$) was found at soil collected from south of the industry and relatively high concentrations were also obtained from other sites (3.69×10^5 and $1.07 \times 10^5 \text{ ng kg}^{-1}$ for east and north sites, respectively). The concentration of Σ_7 PBDE obtained from bag-filter dust of the steel plant was also seriously high ($2.05 \times 10^5 \text{ ng kg}^{-1}$), indicating that these industries are very likely to be PBDE sources. BDE-209 was the dominating congener in both industries. Six congeners detected in soil collected near the electronic industry accounted for 0.8% of Σ_7 PBDE concentration. However, in steel plant dust, the concentrations of remaining six congeners were comparably high—an order of magnitude higher than those measured around the electronic industry. Other soil samples collected close to this steel plant also had high PBDE concentrations. Σ_7 PBDE concentrations were 21998, 44160, and 98381 ng kg^{-1} at soils around the steel plants, the industrial sampling site, and Bozkoy (affected by steel plant emissions due to its location and prevailing wind direction), respectively (Table 3, Figure S1). However, in the Torbali industrial site, Σ_7 PBDE concentration was found to be the lowest indicating that there is not any nearby PBDE source.

In all soil samples, BDE-209 was the most abundant congener and accounted for 79–99% of the total soil

TABLE 3. Soil Properties and PBDE Concentrations

site no	description	water content (%)	organic matter (%)	Σ_7 BDE concentrations in soil ^a	
				(ng kg ⁻¹ dry wt)	(ng kg ⁻¹ OC) ^b
A	suburban sampling site	1.7	10.4	8.40×10^2	1.21×10^4
B	urban sampling site	0.7	5.0	1.86×10^4	5.64×10^5
C	industrial sampling site	7.7	7.6	4.41×10^4	8.70×10^5
1	steel plants (industrial)	3.4	7.3	2.20×10^4	4.53×10^5
2	Bozkoy (industrial)	5.2	17.7	9.83×10^4	8.35×10^5
3	Sehit Kemal (suburban)	5.9	10.3	3.11×10^3	4.54×10^4
4	Aliaga commercial site (suburban)	8.6	9.9	6.86×10^3	1.04×10^5
5	Petkim housings (residential-industrial)	6.6	7.6	1.01×10^3	2.00×10^4
6	Agora (urban)	3.7	9.1	8.74×10^3	1.44×10^5
7	Yamanlar (rural)	2.6	9.2	2.27×10^3	3.69×10^4
8	electronic industry	0.7	4.6	2.84×10^6	1.03×10^8
9	Kemalpasa (industrial)	0.9	3.1	3.11×10^3	1.51×10^5
10	Torbali (industrial)	1.3	4.0	5.04×10^2	1.90×10^4
11	filter dust	0.4	2.3	2.05×10^5	1.33×10^7

^a $n = 5$ for A, $n = 2$ for C, $n = 1$ for the other sites. ^b OC = OM/1.5.

FIGURE 1. Percent contributions of individual congeners to Σ_7 PBDE concentrations in soil (see Table 3 for site descriptions)

concentrations, followed by BDE-99 and -47 (Figure 1). Soil concentration of BDE-209 was 5 to 3615 times higher than the concentrations of Σ_6 PBDEs. PBDEs are commercially produced and used as technical mixtures (i.e., penta, octa, and deca-products). Technical penta-mixtures containing mainly BDE-47 and -99 are not currently used (23). In the steel plants, scrap metal is used for production. Therefore, penta-BDEs that have been commonly used in the past are emitted. The high contribution of BDE-209 to Σ_7 PBDE concentration in soils around the electronic industry is probably due to the current use of deca-product during production (Figure 1).

Generally, industrialized and urbanized regions had higher soil concentrations while suburban soils had relatively low PBDE concentrations (Σ_7 PBDE concentrations were found as 560 ng kg^{-1} at the suburban sampling site) (Table 3). This is consistent with a recent study reporting that concentrations of PBDEs in soil decrease with increasing distance from a city center in UK (12). In urban soil, it was found that Σ_6 PBDE concentration (excluding BDE-209) was up to 3890 ng kg^{-1} , while in rural areas it decreased to 73.2 ng kg^{-1} (12). Σ_6 PBDE concentrations (excluding BDE-209) observed in the present study ($49\text{--}3981 \text{ ng kg}^{-1}$) were comparable to this range.

Concurrent air and soil concentrations are ideally used to assess the fugacity gradients of individual PBDEs between the soil–air interfaces. The soil to air fugacity ratios $[(f_s/f_a) = (C_s \rho_s / K_{SA}) / C_A] > 1$ indicate that the soil is a source with net volatilization of compounds from soil, values < 1 indicate that the soil is a sink and net gas-phase deposition occurs from air to soil.

The uncertainty of the calculated fugacity ratios and fluxes was assessed using a propagated error analysis. For each congener, measurement errors in C_A and C_s , K_{SA} , and MTC values are taken into account. The uncertainties of C_A , C_s , and K_{OA} (used to calculate K_{SA}) were assumed to be 15% (8, 27) and uncertainty in the overall MTC was assumed as 40%.

The average water and organic matter contents of soil samples were found as 5.2 and 7.4% (in dry sample), respectively. Site-specific OM contents (Table 3) were used in fugacity calculations. Organic matter fraction was assumed to be 1.5 times the organic carbon fraction. The measured average density of soil solids ($2.0 \pm 0.1 \text{ g cm}^{-3}$, $n = 6$) was used for all calculations. Temperature-dependent K_{OA} values of the PBDE congeners used in eq 3 were calculated using the regression parameters (A and B) given by Harner and Shoeib (27) ($\log K_{OA} = (A + B)/T$). The regression parameters were not available for BDE-209. Therefore, $\log K_{OA}$ values of

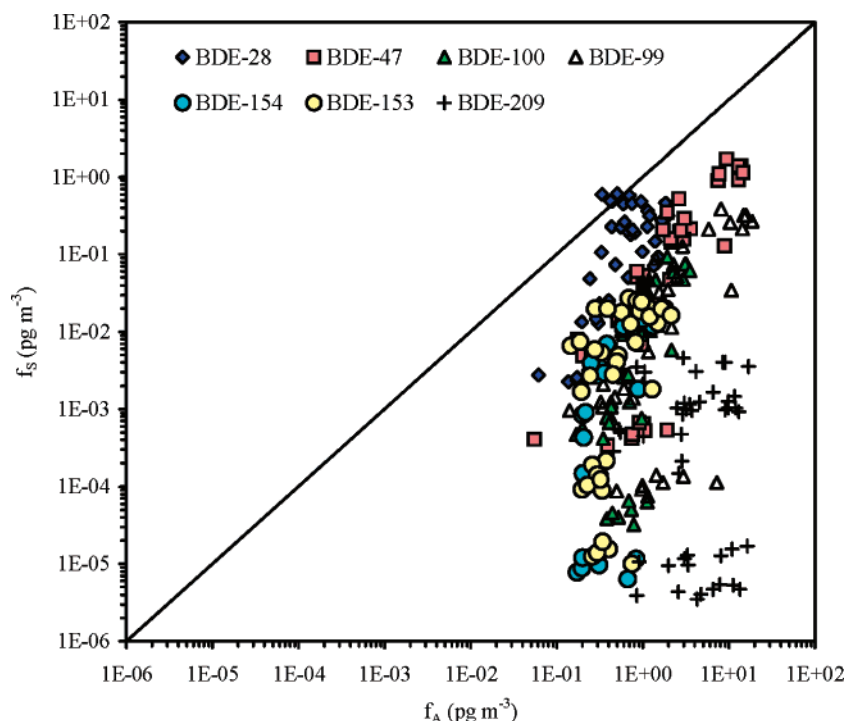


FIGURE 2. Relationship between the PBDE fugacities in soil (f_s) and air (f_A) (all sites). The solid diagonal line represents a 1:1 relationship (equilibrium).

BDE-209 were determined using its dimensionless Henry's law constant (H') (28) and log K_{OW} values that were calculated based on the data from Braekvelt et al. (29).

For a system in equilibrium, f_s/f_A value is ~ 1 (10). A propagation of the errors that are associated with the calculation indicated that the equilibrium is represented by an f_s/f_A of 1.0 ± 0.26 (i.e., a range of 0.74–1.26). The fugacity ratios of all congeners (except the ratios for BDE-28 for four samples) fell outside this uncertainty range and we can be confident that for all BDE congeners the soil and ambient air were not in equilibrium. Figure 2 shows the deposition tendency of congeners to the soil with fugacity ratios for all congeners < 1.0 (except the ratios for BDE-28 for a few samples). Figure 2 also shows the relationship between fugacities in soil and air ($r^2 = 0.13\text{--}0.79$, $p < 0.01$, except for BDE-209, $r^2 = 0.01$, $p > 0.01$). This close link between air–soil concentrations suggests that the atmosphere is a major source for the PBDEs in surface soil.

The instantaneous soil–air gas exchange PBDE fluxes were calculated using eq 4 (Table 2). The average net Σ_7 PBDE flux ranged from 11.8 (urban) to 23.4 (industrial) $\text{ng m}^{-2} \text{day}^{-1}$ in summer, while in winter it ranged from 3.2 (urban) to 11.6 (suburban) $\text{ng m}^{-2} \text{day}^{-1}$. Generally, summer fluxes were higher than winter fluxes except in the suburban site. Since the ambient gas-phase BDE concentrations were higher in summer in urban and industrial sites, higher depositional fluxes were observed during this period. However, in suburban site, due to the small seasonal variations in PBDE concentrations, summer and winter deposition fluxes were similar (Table S1).

The overall estimated uncertainty in the fluxes by error propagation was $\pm 43\%$. Uncertainty values for all congeners were nearly the same with a range of ± 42 to $\pm 45\%$. All congeners were very far from equilibrium resulting in relatively small and similar uncertainties.

Table S2 shows the annual deposition fluxes of PBDEs in the suburban site including the recently measured wet deposition fluxes (30). It was estimated that the contribution of wet deposition to the total PBDE deposition to soil was significant. Dry particle, wet, and gas deposition contribute

60, 32, and 8%, respectively, to annual Σ_7 PBDE flux to the suburban soil.

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Supporting Information Available

Soil–air gas exchange fluxes of PBDEs for summer and winter periods (Table S1), annual deposition fluxes of PBDEs in the suburban sampling site (Table S2), map of the study area (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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