DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE DISTRIBUTION AND CYCLING OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN ENVIRONMENTAL COMPARTMENTS AT IZMIR AREA

by
Banu ÇETİN

December, 2006
İZMİR

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"THE DISTRIBUTION AND CYCLING OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN ENVIRONMENTAL COMPARTMENTS AT IZMIR AREA"** completed by **Banu ÇETİN** under supervision of **Assoc. Prof. Mustafa ODABAŞI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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THE DISTRIBUTION AND CYCLING OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN ENVIRONMENTAL COMPARTMENTS AT IZMIR AREA

ABSTRACT

Seven PBDE congeners including BDE-28, -47, -99, -100, -153, -154 and -209 were investigated in ambient air, soil, organic films and water samples in Izmir. Ambient air studies were carried out at four sampling sites a suburban, an industrial and two urban sites and their spatial and seasonal variations were investigated. BDE-209 was the most abundant congener at all sites, and all samples were dominated by penta and deca mixtures. Gas-particle partitioning of PBDEs were examined using Junge-Pankow and K_{OA}-based models. Dry deposition samples were collected in suburban and urban sampling sites concurrently with ambient air samples. Particle dry deposition velocities were calculated using particle concentrations and fluxes. Soil samples were collected at 13 different sites. A bag filter dust from electric arc furnace of steel production was also examined. Generally, industrialized and urbanized regions have higher soil concentrations while Suburban soils have relatively low PBDE concentrations. PBDEs in organic film samples were also collected from different sites with different characteristics. Indoor windshield film samples from 4 different types of vehicles were also collected for winter and summer periods. Concurrent ambient air and water concentrations were measured at a coastal site of Izmir bay. The gas and dissolved-phase concentrations of PBDEs were significantly correlated indicating that even in a coastal environment the atmosphere controls the surface water PBDE levels. This suggests that sediment may not contribute significantly to surface water concentrations. The net air-water exchange BDE fluxes were also examined using Henry's law constants of PBDEs measured in present study. The BDE-28 fluxes were found to be mainly volatilization while other congeners generally deposited to water during the sampling periods.

Keywords: Polybrominated diphenyl ethers (PBDEs), dry deposition, deposition velocity, air/water exchange, soil/air exchange, organic films.

İZMİR BÖLGESİNDE BROMLU DİFENİL ETERLERİN (PBDEler) ÇEVRESEL ORTAMLARDA DAĞILIMI VE DOLANIMI

ÖZ

İzmir bölgesinde yedi adet bromlu difenil eter (PBDEler) (BDE-28, -47, -99, -100, -153, -154 ve -209) dış havada, toprakta, organik filmlerde ve su örneklerinde incelenmiştir. Dış hava çalışmaları dört örnekleme bölgesinde gerçekleştirilmiş (Yarıkentsel, 2 Kentsel ve Endüstriyel) ve PBDE'lerin mevsimsel ve yerel değişimleri incelenmiştir. Tüm bölgelerde en çok BDE-209 bulunmuş ve penta ve deka teknik karışımlarının baskın olduğu gözlenmiştir. Junge-Pankow ve K_{OA}-tabanlı modeller kullanılarak PBDE'lerin gaz-partikül dağılımları incelenmiştir. Kuru çökelme örnekleri Yarıkentsel ve Kentsel örnekleme bölgelerinde dış hava örnekleriyle eş zamanlı olarak ölçülmüş ve partikül kuru çökelme hızları partikül konsantrasyonları ve akıları kullanılarak hesaplanmıştır. Toprak örnekleri on üç farklı bölgeden alınmıştır. Ayrıca çelik endüstrisinin filtre tozu da incelenmiştir. Genel olarak endüstriyel ve kentsel bölgelerde daha yüksek konsantrasyonlar gözlenirken yarıkentsel bölgelerden alınan topraklarda daha düşük PBDE konsantrasyonları bulunmuştur. Organik filmlerdeki PBDE'ler de farklı özelliklerdeki iç ve dış camlarda incelenmiştir. Dört farklı tip otomobilin iç camları da yaz ve kış aylarında örneklenmiştir. Dış hava ve su konsantrasyonları İzmir Körfezi kıyısındaki bir noktada eş zamanlı olarak ölçülmüştür. Her bir PBDE için gaz ve çözünmüş konsantrasyonların birbirleriyle önemli ölçüde ilişkili olduğu görülmüştür. Bu da, atmosferin yüzeysel sulardaki PBDE konsantrasyonlarını kontrol ettiğini ve sedimentin yüzey sularına ciddi bir katkısı olmayabileceğini göstermektedir. Hava-su arakesitindeki net akı bu çalışmada ölçülen Henry kanunu sabitleri kullanılarak hesaplanmış ve BDE-28'in genel olarak buharlaşma, diğerlerinin ise havadan suya çökelme eğiliminde olduğu bulunmuştur.

Anahtar Kelimeler: Bromlu difenil eterler (PBDEler), kuru çökelme, çökelme hızı, hava-su değişimi, toprak-hava değişimi, organik filmler.

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CHAPTER ONE
INTRODUCTION

1 Introduction

PBDEs are flame retardants used in polymers, paints, textiles, building materials and plastic housings of electronic products such as TV sets and computers, car parts, electrical components and cables in order to progress their fireproof properties (Chen et al., 2006; De Wit, 2002; Hyötylainen, & Hartonen, 2002; Strandberg, Dodder, Basu & Hites, 2001).

There has been great interest on these persistent organic pollutants (POPs) in last decade due to their high toxicity and persistence and thus, their toxic and carcinogenic/mutagenic human health effects such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Due to their relatively low water solubilities and vapor pressures, relatively large octanol-water and octanol-air partition coefficients, PBDEs are likely to partition to solids (i.e., sediment, soil, atmospheric particles) and bioaccumulate when they are released into the environment (D'Silva, 2004). Primary emissions of POPs into the atmosphere have changed over the past decades. PCB emissions for example have declined since 1960s/1970s (Jaward, Barber et al., 2004). However, as a result of their current use, PBDE concentrations are increasing in the environment (Hites, 2004).

Recently, PBDEs have been investigated throughout the world in air, precipitation, sediment, sewage sludge, fish tissue, bird eggs, whale, dolphin and seal fat, mussels and sediment and in human serum, milk and tissue (De Wit, 2002; Hites, 2004; Hyötylainen, & Hartonen, 2002; Nylund et al., 1992; Strandberg et al., 2001; Sellström, Kierkegaard, de Wit, & Jansson, 1998; ter Schure & Larsson, 2002). The studies suggest that especially tetra to hexa-congeners are likely to be carcinogens, endocrine disrupters and neurodevelopment toxicants (Hyötylainen, & Hartonen, 2002). Some BDEs can affect the liver enzyme activity, negatively influence the regulation of the thyroid hormone system, induce immunotoxicity and affect neurological development at a sensitive period of brain growth (De Wit, 2002).

Removal of the PBDEs from the atmosphere can occur by dry deposition of particles, wet deposition of gasses or particles, and by gas exchange across the air-water interface. Atmospheric levels of PBDEs were studied previously (Harner, Shoeib, Diamond, Ikanomou, & Stern, 2006; Hoh & Hites, 2005; Hayakawa, Takatsuki, Watanabe, & Sakai, 2004; Farrar et al., 2004; Lee, Thomas, & Jones, 2004; Jaward, Farrar, Harner, Sweetman, & Jones, 2004; Agrell et al., 2004). However, there are only a few studies on their partition between gas and particle phases (Chen et al., 2006; Shoeib, Harner, Ikonomou, & Kannan, 2004; Strandberg et al., 2001), their concentration in window organic films (Butt, Diamond, Truong, Ikonomou, ter Schure, 2004; Butt, Diamond, Truong, Ikonomou, Helm, ter Schure, 2004) and their soil (Harrad & Hunter, 2006; Hassanin et al., 2004; Wang et al., 2005) and water concentrations (Jaward et al., 2004; Oros, Hoover, Rodigari, Crane, & Sericano, 2005; Wurl, Lam, & Obbard, 2006). However, environmental levels of PBDEs have not been investigated in Turkey. Also, there has not been any previous studies on air-water and soil-air exchange of PBDEs.

The specific objectives of this study are as follows:

1. To measure the ambient particle and gas phase concentrations of PBDEs and to determine their temporal and seasonal variations and gas-particle partitioning.

2. To measure the PBDE concentrations in soil, to evaluate the congener profile and their soil-air exchange.

3. To determine particle phase dry deposition fluxes and compare them with gas flux to soil.

4. To measure the concentrations of PBDEs and evaluate the congener profile in organic films collected from indoor and outdoor window surfaces.

5. To determine the Henry's Law constants of PBDEs as a function of temperature that is used to evaluate their transport, environmental behavior and fate.

6. To determine the magnitude and direction of air-water exchange fluxes of PBDEs at a coastal site in Izmir Bay and to investigate their dynamic air-water coupling.

The PBDE congeners that have been extensively detected in the environment and reported in the literature were investigated in this study: 2,4,4′-tribromodiphenyl ether (BDE 28), 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE 99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE 100), 2,2′,4,4′5,5′-hexabromodiphenyl ether (BDE 153), 2,2′,4,4′5,6′-hexabromodiphenyl ether (BDE 154), and decabromodiphenyl ether (BDE 209) (the PBDE congeners are numbered according to IUPAC system established for PCBs).

This study consists of five chapters. An overview and objectives of the study were presented in Chapter 1. Chapter 2 reviews the concepts and previous studies related to this work. Experimental work is summarized in Chapter 3. Results and discussions are presented in Chapter 4. Chapter 5 includes the conclusions drawn from this study.

CHAPTER TWO
LITERATURE REVIEW

This chapter presents information on structures and general properties of PBDEs, sources, their health effects, and previous studies on PBDEs in different matrices including air, water, soil and window organic films.

2.1 Chemical Structures and Properties of PBDEs

The most common brominated flame retardants (BFRs) are polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) and polybrominated biphenyls (PBB).

According to their use, the flame retardants can be reactive and additive. The reactive chemicals are less prone to leach out to the environment until the product is decomposed or burnt due to their covalent bond to the polymer. However, the additive compounds are only mixed with or dissolved in the material and can more easily migrate out of the product (Hyötylainen & Hartonen, 2002).

PBDEs are typically additive type of flame retardants mainly used in plastics, textiles and electronics. The chemical structure of PBDEs is presented in Figure 2.1; x and y refer to the number of bromine atoms substituted on the aromatic rings. The total value of x and y can be up to 10, i.e. a PBDE molecule can have between one and ten bromines.

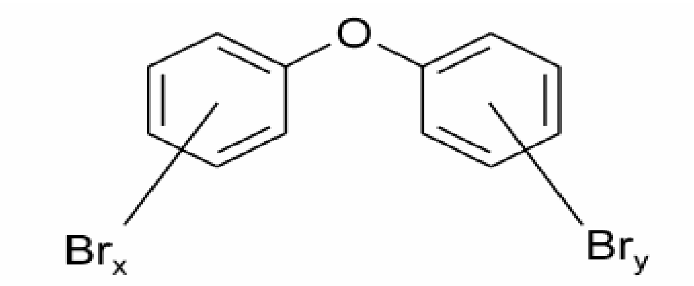

Figure 2.1 The chemical structure of PBDEs.

PBDEs are long-lived, bioaccumulating, environmental pollutants such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs). The water solubilities and vapor pressures of PBDEs are relatively low while they have relatively large octanol-water and octanol-air partition coefficients. Therefore, they are likely to adsorb onto solid particles (i.e., sediment, soil, atmospheric particles) when they are released into the environment. Because of their high lipophilicity and resistance to degradative processes, PBDEs are expected to bioaccumulate easily (D'Silva, 2004) and some congeners undergo long-range transport to remote ecosystems (Strandberg et al., 2001; ter Schure et al., 2004).

Table 2.1 shows the important physical-chemical properties of selected PBDEs that were investigated in this study. K_{OW} and K_{OA} are octanol-water and octanol–air partition coefficient, respectively. K_{OW} is the ratio of the solubility in water to that in octanol which acts as a lipid surrogate, and it is used to estimate sorption and bioaccumulation (Palm et al., 2002). The octanol-air partition coefficient, K_{OA}, is the ratio of the solute concentration in air versus octanol when the octanol-air system is at equilibrium. This value can be used to predict the transport and fate of PBDEs in the environment.

The physicochemical properties of PBDEs vary considerably from congener to congener. The commercial PBDEs are rather stable compounds with boiling points ranging between 310 and 425 °C (D'Silva, 2004).

Table 2.1 Structure and Important Properties of Selected PBDEs

Congener[a]	MW	Log K_{OA}	Log K_{OW}	Log $P_{L,25}$ (Pa)	Log $S_{L,25}$ (mol m^{-3})
BDE-28	406.9	9.41[b], 9.50[b]	5.80[b], 5.94[d]	-2.66[e], -2.80[f]	-4.15[e]
BDE-47	485.8	10.44[b], 10.53[c]	6.39[b], 6.81[d]	-3.73[e], -3.50[f]	-4.82[e]
BDE-99	564.7	11.26[b], 11.31[c]	6.76[b], 7.32[d]	-4.75[e], -4.17[f]	-5.03[e]
BDE-100	564.7	11.02[b], 11.13[c]	7.24[d]	-4.54[e]	-5.40[e]
BDE-153	643.6	11.89[b], 11.82[c]	7.08[b], 7.90[d]	-5.68[e], -5.07[f]	-6.06[e]
BDE-154	643.6	11.92[c]	7.82[d]	-5.42[e]	-6.06[e]
BDE-209	959.2	15.73[h], 15.11[j]	10.33[i]	-9.50[g]	

[a] 2,4,4′-tribromodiphenyl ether (BDE 28), 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE 99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE 100), 2,2′,4,4′5,5′-hexabromodiphenyl ether (BDE 153), 2,2′,4,4′5,6′-hexabromodiphenyl ether (BDE 154), and decabromodiphenyl ether (BDE 209).

[b] Wania & Dugani (2003)

[c] Harner & Shoeib (2002)

[d] Braekevelt, Tittlemier, & Tomy (2003)

[e] Tittlemier, Halldorson, Stern, & Tomy (2002)

[f] Wong, Lei, Alaee, & Wania (2001)

[g] Calculated from the equations based on bromine content given by Tittlemier et al., (2002)

[h] Xu et al. (2006)

[i] Calculated based on the data from Braekevelt et al. (2003) and molar volume of PBDEs (log K_{OW} = 0.0275Molar volume - 0.837)

j Calculated based on equations of K_{OW} obtained from Braekevelt et al. (2003) and H′ from Cetin, & Odabasi (2006).

2.2 Sources of PBDEs

In the mid 1990s the annual word production of brominated flame retardants was 150 000 tonnes and about one third of them was PBDEs (Hyötylainen & Hartonen, 2002). The annual global production of PBDEs was estimated to be 40 000 tons in 1992. In 1999, the world demand was 67 000 tons (de Wit, 2002). These results indicate the increasing trend of PBDE usages in global scale. They are marketed as three technical mixtures including pentabromodiphenyl ether, octabromodiphenyl ether and decabromodiphenyl ether. The estimated world market demand for penta-, octa-, and deca-BDE technical products in 2001 was 7500, 3790 and 56100 metric tons, respectively (Table 2.2) (Law et al., 2006). They can enter the environment during their production and migrate from the treated products over their entire lifetimes (Strandberg et al., 2001).

Table 2.2 The estimated market demand of PBDEs in different areas of the world in 2001 (in tones)

	America	Europe	Asia	Others	Total
Deca-BDE products	24500	7600	23000	1050	56150
Octa-BDE products	1500	610	1500	180	3790
Penta-BDE products	7100	150	150	100	7500
Total	33100	8360	24650	1330	67440

Because they are used as an additive, PBDEs are not chemically bound to the product, and can escape into the air or leach out over time. They can evaporate from the casings of computers and televisions, especially when the product heats up. They also end up in landfills when products are disposed of, and in soil, air, and surface water.

Recently, PBDEs have been investigated throughout the world in air, sediment, sewage sludge, fish tissue, bird eggs, whale, dolphin and seal fat, mussels and sediment and in human serum, milk and tissue (De Wit, 2002; Hites, 2004; Hyötylainen & Hartonen, 2002; Nylund et al., 1992; Sellström et al. 1998; Strandberg et al., 2001; ter Schure & Larsson, 2002).

In the study performed by Strandberg et al. (2001), PBDEs were compared to those of other organohalogen compounds such as PCBs and OCPs. According to them, the levels of PBDEs have been increasing drastically while the levels of PCB and DDT found in fish, birds, marine mammals, sediments, air and human blood have been decreasing. Temporal studies have also shown their increasing trend in the environment (Ikonomou, Rayne, & Addison, 2002) or biota at an exponential rate (Ikonomou et al., 2002; Luross et al., 2002; Ryan, Patry, Mills, & Beaudoin, 2002).

For example, PBDE concentrations measured in human milk in Sweden have increased exponentially from 1972 to 1997 (Darnerud, Eriksen, Johannesson, Larsen, & Viluksela, 2001). Similarly, concentrations of PBDEs in human samples collected from Japan, Norway and North America also showed an increasing trend (Ikonomou et al., 2002; Sjödin et al., 2004; Thomsen, Lundanes, Becher, 2002).

2.3 Health Effects of PBDEs

According to the studies on health impact of PBDEs, the lower PBDE congeners including tetra to hexa-BDEs are likely to be carcinogens, endocrine disrupters and neurodevelopment toxicants (Hallgren & Darnerud, 2002). Deca-BDE which is the predominant commercial product, is supposed to be a less active congener than the lower BDEs due to its lower bioavailability and poor gastrointestinal adsorption (Hooper & McDonald, 2000).

Some BDEs can affect the liver enzyme activity, negatively influence the regulation of the thyroid hormone system, induce immunotoxicity and affect neurological development at a sensitive period of brain growth (De Wit, 2002).

In general, chemical, biological, toxicological, environmental, and aquatic properties of PBDEs are similar to those of PCBs, and DDT (Darnerud et al., 2001). Therefore, the environmental toxicity of PBDEs can be serious, thus they may pose potential environmental and human health problems, similar to that of PCBs, and DDT.

2.4 Removal Mechanisms of PBDEs

Despite efforts to characterize the extent of PBDE contamination in the environment, little is known about the atmospheric chemistry of them. It is essential for accurate predictions about persistence and health threats from exposure to PBDEs and their potentially harmful degradation products.

Both gas and particle phase PBDEs are expected to undergo photolysis and reactions with atmospheric oxidants, such as hydroxyl (OH) and nitrate (NO_3) radicals and O_3 (Calvert et al., 2002). These processes and reaction may shorten the atmospheric lifetimes of PBDEs (Raff & Hites, 2006). PBDEs may also release to the atmosphere by thermal-breakdown. Previously, the formation of polybrominated dibenzodioxins (PBDDs) and dibenzofurans (PBDFs) from PBDEs has been studied (Luijk, Govers, & Nellssen, 1992). Buser (1986) have reported the formation of PBDDs and PBDFs during thermolysis (510–630 °C) of the penta, octa and deca-BDE technical mixtures and other break-down products such as polybrominated benzenes, phenols and naphthalenes were also identified. The replacement of Br by Cl was also observed in study conducted by Rupp & Metzger (2005) and they have mentioned about the importance of this replacement since it takes place even in the presence of trace amounts of Cl. In real thermal processes such as controlled/uncontrolled combustion processes, recycling processes, Cl is always present in excess. Thus, it can be expected to find mixed halogenated reaction products in all kinds of thermal processes.

However, photolytic debromination of PBDEs is of great importance rather than above reactions. Many researchers believe that in the environment deca-BDE can break down by UV light and sunlight to lower congeners. Norris et al. (1973) have found that both deca-BDE and octa-BDE were degraded down to hexa-BDEs. Söderström, Sellström, De Wit, & Tysklind (2004) have also proved that photolytic debromination of BDE 209 is a possible pathway for the formation of more bioavailable, lower brominated BDEs using five different matrices: toluene, silica gel, sand, soil and sediment. Nona and octa-BDEs were readily formed on all matrices. The photolytic half-life for BDE-209 is longer on more complex matrices including sediment and soil. The most commonly found PBDEs in environmental samples such as BDE-47, BDE-99 and BDE-100 were only formed to a minor degree from the photolysis of BDE-209. This result indicates that the origin of these congeners may be from emissions of technical penta-BDE products and/or possibly from other degradation pathways of deca-BDE.

2.5 PBDEs in Air

Recently, studies on PBDEs in air including their concentrations and distributions are increasing (Table 2.3). In Osaka, BDE-209 was found up to 3060 pg m^{-3} on airborne dust collected between 1993 and 1994 (Watanabe, Kwano, & Tatsukawa, 1995). In North America, PBDEs were investigated in urban, rural and remote sites near the Great Lakes in 1997-1999 and all the compounds, including BDE-47, -99, -100, -153, -154, -190, and -209 were found in all samples investigated. Among the BDE congeners, BDE-47 accounted for 50-65 % of the total mass of PBDEs and BDE-99 accounted for 35-40 %. The other five congeners found as accounted for less than 10% of the total (Strandberg et al., 2002). In a study conducted by Hoh & Hites (2005) in the atmosphere of the East-Central United States, it was found that the PBDE concentration obtained from Chicago was 3-6 times higher than that at the other sites. As their results, BDE-47 was the dominating congener and 80% of ∑PBDE concentrations were composed of BDE-47, -99, -100 and -209.

In South China, 11 PBDE congeners were detected; additionally BDE-66, -85, -138, and -183 were also investigated with these 7 congeners (Chen et al. 2006) and relatively higher PBDE concentrations were obtained in industrial sites. Jaward et al. (2004) performed a study on passive sampling of PBDEs across Europe including 25 urban locations and 46 rural/remote locations. As a result, higher PBDE concentrations were found in the United Kingdom because it has known as a major user of PBDE-based flame retardants due to severe fire regulations. Urban centers in mainland Europe including Milan, Bilthoven (Netherlands), Geneva, Athens and Seville have also high values. In Ontario, Canada, relatively high PBDE concentrations were found in the early spring prior to bud burst and it was suggested that this high PBDE concentrations were the result of an early spring pulse (Gouin et al., 2002). Relatively lower PBDE concentrations were found in England and Ireland (Lee et al., 2004) and in Great Lakes (Strandberg et al., 2001).

Table 2.3 Reported concentrations of PBDE in air samples (in pg m^{-3}).

∑PBDE (pg m^{-3})	BDE-209 (pg m^{-3})	$n_{cong.}$	Location	Area	Period	Reference
3673±2734	4200±4048	11	Guangzhou, China	industrial	June, 2004	Chen et al. (2006)
88.8±15.3	263.8±121.7	11	Guangzhou, China	urban	June, 2005	Chen et al. (2006)
4.5-65	ND-48	12	Kyoto, Japan	urban	Aug. 2000, Jan-Sept, 2001	Hayakawa et al. (2004)
0.4-78.5	ND	10	G. Sandön Island, Baltic Sea	remote	Sept-Nov, 2001	ter Schure et al. (2004).
2.0-6.6	100-340	10	Osaka, Japan		2001	Ohta et al. (2002)
2.2-21.3	ND-118.7	8	Malmö, Sweden	industrial	Oct-Nov, 2001 Feb-Mar, 2002	Agrell et al. (2004)
0-26.7	ND-190.9	8	Malmö, Sweden	urban	Oct-Nov, 2001 Feb-Mar, 2003	Agrell et al. (2004)
100±35[a]	6-31	26	Chicago	urban	2002-2003	Hoh & Hites (2005)
ND-53	ND-105	22	Ontario, Canada	rural	Jan-Jun, 2002	Gouin et al., (2005, 2006)
0.5-250		8	Europe	urban, remote	June-July, 2002	Jaward et al. (2004)[b]
2.8-37.0		21	Hazelrigg-Chilton, England	rural semirural	2001	Lee et al. (2004)
0.2-5.0		21	Mace Head, Ireland	remote	2000	Lee et al. (2004)
5.5±20	ND	7	Eagle Harbor, Great Lakes	remote	1997-1999	Strandberg et al. (2001)
7.2±13	ND	7	Sturgeon, Great Lakes	rural	1997-1999	Strandberg et al. (2001)
15±29	ND	7	S. Bear Dunes, Great Lakes	rural	1997-1999	Strandberg et al. (2001)
52±30	trace levels	7	Chicago, Great Lakes	urban	1997-1999	Strandberg et al. (2001)

[a] Including BDE-209

[b] Passive sampling

2.6 Gas-Particle Partitioning

Once released to the ambient environment, in the atmosphere PBDEs are entirely in the gaseous and particle phases. Lower brominated congeners are expected to be in the gas phase at a given temperature, whereas higher brominated PBDEs have a greater proportion in the particle phase (ter Schure, & Larsson, 2002).

Gas/particle partitioning is an important process affecting the deposition, degradation, transport and subsequent fate of PBDEs (Chen et al., 2004). Atmospheric levels of PBDEs were studied previously (Harner et al., 2006; Hoh & Hites, 2005; Hayakawa et al., 2004; Farrar et al., 2004; Lee et al., 2004; Jaward et al., 2004; Agrell et al., 2004). However, there have been only a few studies on their partition between gas and particle phases (Chen et al., 2006; Shoeib et al., 2004; Strandberg et al., 2001). Gas-particle partitioning is mainly controlled by atmospheric temperature and physical and chemical properties of the compound including vapor pressure and K_{OW} (Shoeib et al., 2004; Strandberg et al., 2001).

Chen et al. (2006) have found that BDE-28 was present mostly in the gas phase (96-98%) whereas the BDE-209 was found only in the particle phase. Model estimation of Harner, & Shoeib (2002) also shows that higher brominated congeners are expected to be particle bound >99% at 0°C. In southern Ontario, BDE-209 was found only in particle-phase (Gouin et al., 2006). It was suggested that the reason for not detecting BDE-209 in the gas-phase may be its sorption to the glass fiber filter during sampling (Gouin et al., 2006).

However, these predictions do not agree well with some previous studies. Contrary to model results, Agrell et al. (2004) have found that BDE-209 was mainly in gas phase (>90%) at an urban site while it was 100% in gas-phase at a rural site.

2.7 Particle Dry Deposition of PBDEs

PBDEs are found in the ambient air in gas-phase and as sorbed to aerosols. The fate, transport and removal of PAHs 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. Direct and indirect methods are used to measure particle-phase dry deposition flux. In the direct method, a surrogate surfaces are generally used. In the indirect method measured ambient concentrations (C_p) are multiplied by an assumed or modeled deposition velocity (V_p) to determine the dry deposition flux (F_p) (Odabasi, Sofuoglu, Vardar, Tasdemir, & Holsen, 1999):

$$F_p = V_p C_p \tag{2.1}$$

Deposition velocity is affected by the meteorological parameters, physical properties of the pollutant such as particle size, shape and density, and the type and roughness characteristics of the receptor surface (Vardar, Odabasi, & Holsen, 2002; Seinfeld, & Pandis, 1998). The selection of an appropriate deposition velocity is crucial since it may introduce large uncertainties in the calculation of dry deposition fluxes.

Ter Schure et al. (2004) performed a study on atmospheric deposition of PBDEs. They have found median dry deposition velocity values between 1.2 (BDE-154) and 49 (BDE-209) cm s^{-1} and their median values of dry deposition flux were between 0.3 (BDE-28) and 77.1 (BDE-209) ng m^{-2} day^{-1}. They have also found that PBDE fluxes increased at the industrial urban reference site when winds were blowing from the direction of the solid waste incineration plant suggesting that treatment of electronics recycling is a significant source of PBDEs to the environment. Ter Schure & Larsson (2002) conducted a study on PBDEs in precipitation in Southern Sweden. They have found that PBDE composition of the total (wet+dry) deposition was dominated by BDE-209, -47 and -99 and 65±18 % of the total PBDEs were particle associated.

2.8 PBDEs in Soil

Soil has a high capacity of store POPs such as PCBs and PBDEs where their degradation rates are very slow. All soils receive inputs of POPs via atmospheric deposition (Hassanin et al., 2004). Therefore, in atmospheric study of PBDEs, soil samples have a great concern in order to evaluate the rates of air-surface exchange and trend of congener patterns.

There have been a few studies on the levels of PBDEs in soils (Harrad, & Hunter, 2006; Cai, & Jiang, 2006; Hassanin et al., 2004; Wang et al., 2005). Hassanin et al. (2004) performed a study on PBDEs in background soils through the United

Kingdom (UK) and Norway. They have found that all PBDE concentrations ranged between 65 and 12000 ng kg^{-1} dry weight and BDE -47, -99, -100, -153 and -154 dominated the average congener pattern of the soils. Low concentrations were found in samples from both the UK and Norway, whereas the higher samples were only found in the UK (Hassanin et al., 2004).

Wang et al. (2005) investigated soil samples collected in the vicinity of electronic waste disposal and recycling facility located in Guiyu, China. They have found the PBDE concentrations varied from 0.80 to 824 ng g^{-1} (dry weight) and in all samples among 43 congeners with the mono- to hepta-brominated substitution, BDE-47, -100, -99, -154, -153 and -183 were the dominating congeners.

2.9 Soil-Air Exchange

Once deposited, POPs tend to accumulate in soil for a long period of time and subject to various partitioning, degradation and transport processes depending on their physical-chemical properties and microbiological stability (Park, Kim, & Kang, 2002). Soil-air exchange is an important diffusive process affecting the fate and transport of PBDEs into the environment. The direction and magnitude of the diffusion gradient is determined by the concentrations in air and soil, and by the soil-air equilibrium partition coefficient (K_{SA}) (Hippelein, & Mclachlan, 1998). K_{SA} values and soil-air equilibrium status for various POPs have been calculated previously (Bidleman, & Leone, 2004; Meijer, Shoeib, Jantunnen et al., 2003; Meijer, Shoeib, Jantunnen, Jones & Harner, 2003; Meijer, Harner, Helm, Halsall, & Jones, 2001; Harner, Green, & Jones, 2000; Hippelein & Mclachlan, 1998; Cousins, & Jones, 1998). However, soil-air partition coefficients and fugacities of PBDEs have not been investigated.

The main processes contributing to soil-air exchange of POPs are dry and wet deposition and volatilization from the soil. Atmospheric deposition of chemicals occurs directly to the soil surface or surfaces of vegetation. These chemicals onto the surfaces of the vegetation may either enter the soil or volatilize from the vegetation and re-enter the atmosphere (Cousins, Beck, & Jones, 1999).

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 (Meijer et al., 2001).

2.10 PBDEs in Window Organic Films

The organic films are derived through the condensation of gas-phase species and organic aerosols and form on impervious surfaces such as window glass. This condensation constitutes a sticky layer and particulate-associated compounds can be wet and dry deposited in 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 (Liu, Diamond et al., 2003). Film can act as sorption/desorption sites for gas-phase organic compounds and may grow through particle agglomeration (Lam et al., 2005). Surface films are supposed to undergo temperature-dependent cycles of condensation-volatilization, making them sinks and sources of POPs to the atmosphere (Lam et al., 2005).

Indoor air is an important route of exposure for environmental contaminants. In the indoor environment, contaminants are less prone to degradation and atmospheric dilution, resulting in increasing persistence of them. Main indoor sources of PBDEs are thermoplastics, specifically high-impact polystrene for electronic equipment housings such as computers, TV sets, electric components and cables, foam padding in furniture and upholstery textiles. PBDEs are also used in car interior fabric backing, wire insulation, electronic enclosures, arm rests, floor coverings and other plastic parts. Since automobiles have 360° windows, they can heat up to 90ºC; and PBDEs, that are known to break down when exposed to the sun and UV light (Söderström et al., 2004) and may break down at much higher rates in solar-exposed cars then in other indoor environments.

Other pollutants including PAHs, OCPs, PCBs, n-alkanes, metals and trace elements were recently examined in window organic films (Butt, Diamond, Truong, Ikonomou, Helm et al., 2004; Gingrich, Diamond, Stern, & McCarry, 2001; Kwamena, Clarke, Kahan, Diamond, & Donaldson 2006; Lam et al., 2005; Liu, Diamond et al., 2003; Liu, Chen et al., 2003). However, window organic film studies on PBDEs are very scarce (Butt, Diamond, Truong, Ikonomou, et al., 2004; Butt, Diamond, Truong, Ikonomou, Helm et al., 2004).

As a study conducted by Butt, Diamond, Truong, Ikonomou et al. (2004), the organic films collected from urban areas ranged from 2.5 to 14.5 ng m^{-2}, while the rural and suburban films ranged from 0.56 to 1.1 ng m^{-2}. Indoor films were 1.5 to 20 times greater than outdoor films related to the indoor sources of PBDEs and degradation loss in outdoor films. BDE-209, -99, -47, -100, -153 and -183 were the most dominating congeners accounted for 86-93% of total PBDE concentrations (Butt, Diamond, Truong, Ikonomou et al., 2004).

Gas phase compounds are capable of partitioning into the surface film dependent on the relative fugacity between the air and the film. It is possible to determine ambient air concentrations with the knowledge of film-air partition coefficient (K_{FA}) and sampling rate (Shoeib, & Harner, 2002).

2.11 The Henry’s Law Constants of PBDEs

Several approaches based on multimedia fate and transport models have been proposed to determine the long range transport potential of POPs (Palm et al., 2002; Wania, & Dugani, 2003). Recently, there has been a great interest in environmental fate of PBDEs. However, accurate physical-chemical property data on a congener specific basis are required in order to use multimedia fate and transport models (Palm et al., 2002; Wania, & Dugani, 2003).

The Henry’s law constant (H) is an important parameter that plays a fundamental role in predicting the transport, behavior and fate of POPs in the environment and it is required to model the chemical transfer between air and water. However, H values for PBDEs were not experimentally measured previously as a function of temperature, but they were estimated at only 25°C (Tittlemier et al., 2002, Wania, & Dugani, 2003). Since investigation of air-water exchange of PBDEs was within the objectives of this study, it was required to measure the Henry's law constants of these chemicals as a function of temperature.

2.12 PBDEs in Water

The dynamics of air-ocean exchange and processes within the ocean are critical to the global fate and behavior of POPs. The capacity of surface waters to store POPs is spatially and temporarily variable, and influenced by the temperature, mixing depth, and biogeochemical processes (Jaward et al., 2004). POPs deposited to surface waters may be further subject to incorporation into the marine food chain, degradation, and eventually deposition into the deep sea. Surface waters may therefore act as "buffers" between the atmosphere and deep-sea (Jaward et al., 2004).

There is limited information on PBDEs in environmental water. Oros et al. (2005) have performed a study on levels and distributions of PBDEs in water, surface sediments and bivalves from the San Francisco Estuary. The sum of dissolved and particulate phase individual PBDE concentrations ranged between 0.2-180 pg L^{-1}. They have collected water samples from 33 sampling stations.

In North America, PBDE levels in Lake Ontario surface waters ranged from 4 to 13 pg L^{-1} in 1999 (Luckey, Fowler, & Litten, 2001) and BDE-47 and BDE-99 accounted for more than 90% of total PBDEs. Wurl et al. (2006) have conducted a study on occurrence and distributions of PBDEs in sea-surface microlayer and seawater in Hong Kong at five sampling locations and they have concluded that BDE 28, 47, 100 and 183 were dominating congeners while BDE-209 was detected only in trace amounts. However, in most locations they have found low PBDE concentrations or they were below detection limits. Their mean dissolved and particulate phase concentrations of seawater for eight congeners were 70.7 and 28.1 pg L^{-1}, respectively, and they were 149.2 and 38.2 pg L^{-1} for sea-surface microlayer.

Although scarce information on PBDE concentrations in water, PBDEs were extensively observed in aquatic ecosystems including fish, selfish, mussels, salmon and tuna and also in sediments of marine environment (Ikonomou et al., 2002; Nylund et al., 1992; Sakai, Hayakawa, Okamoto, & Takatsuki, 2002). This presence of PBDEs in marine environment confirms their bioaccumulation potential and their ability to disperse through aquatic ecosystems (Martin, Lam, & Richardson, 2004) and also represents the need of more studies on environmental waters.

2.13 Air-Water Exchange

There has been substantial investigation of the magnitude and direction of gas exchange of POPs in recent years due to their significant contribution to the cycling of POPs in the environment (Bamford, Poster, & Baker, 1999; Bamford, Ko, & Baker, 2002; Gigliotti et al., 2002; Gustafson & Dickhut., 1997; Helm, Jantunan, Ridal, & Bidleman, 2003; Hornbuckle, Jeremlason, Sweet, & Eisenreich, 1994; Hornbuckle, Sweet, Pearson, Swackhamer, & Eisenreich, 1995; Jantunen, & Bidleman, 2003; Nelson, McConnell, & Baker, 1998; Sundqvist, Wingfors, Brorstöm-Lunden, & Wiberg, 2004; Totten et al., 2001).

Paired or unpaired air and water concentration measurements in conjunction with the two-film model (Schwarzenbach, Gschwend, & Imboden, 1993) have been commonly used to estimate atmospheric loading of POPs to water bodies or their loss by volatilization (Odabasi, Sofuoglu, & Holsen, 2001; McConnell et al., 1997; Hoff et al., 1996; Hornbuckle et al., 1994). However, the air-water exchange of PBDEs has not been investigated using paired samples.

The stagnant two-film model has been commonly used to estimate air-water gas exchange of POPs. According to the two-film model, mass transfer is limited by the rate of molecular diffusion through thin films of air and water on either side of the surface (Schwarzenbach, Gschwend, & Imboden, 2003). The gas flux across a water surface is a function of Henry's law constant, the concentration gradient and the overall mass transfer coefficient (Hoff et al., 1996).

CHAPTER THREE
MATERIALS AND METHODS

Sampling techniques and the experimental methods used for the measurement of PBDEs during this study are discussed in this chapter.

3.1 Sampling Program and Collection

Izmir metropolitan city, with the 2.7 million of population 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 samples were collected at four sampling sites including a suburban, an industrial and two urban sites in Izmir. The Suburban samples were collected on a 4 m-high platform located on the Kaynaklar campus of the Dokuz Eylül University, 10 km southeast of Izmir’s center. It is relatively far from any settlement zones or Industrial facilities. There are residential areas located approximately 2 km southwest and a highway 0.5 km south of the sampling site. Land cover in the immediate area is a young coniferous forest. The nearest industrial facility is a cement work about 10 km at north and an open road gravel storage site nearly 3 km at the east. Urban samples were collected from Yesildere (Urban 1) site located near a main street with heavy traffic and residential areas (Figure 3.1). The other urban site (Urban 2) is located in Aliaga county at north of Izmir, approximately 50 km far from city center. There are many industrial plants (i.e., a petrochemical complex, petroleum refinery, and LPG storage plants) within a few kilometers. Finally, samples were collected at Horozgedigi village (Industrial) located at ~5 km south of Aliaga county. There are nearby steel plants with electric arc furnaces, a natural gas-fired power plant (1500 MW), a fertilizer factory, and a few small plants (Figure 3.2).

Concurrent ambient air and particle dry deposition samples were also collected at two sampling sites (Suburban and Urban 1).

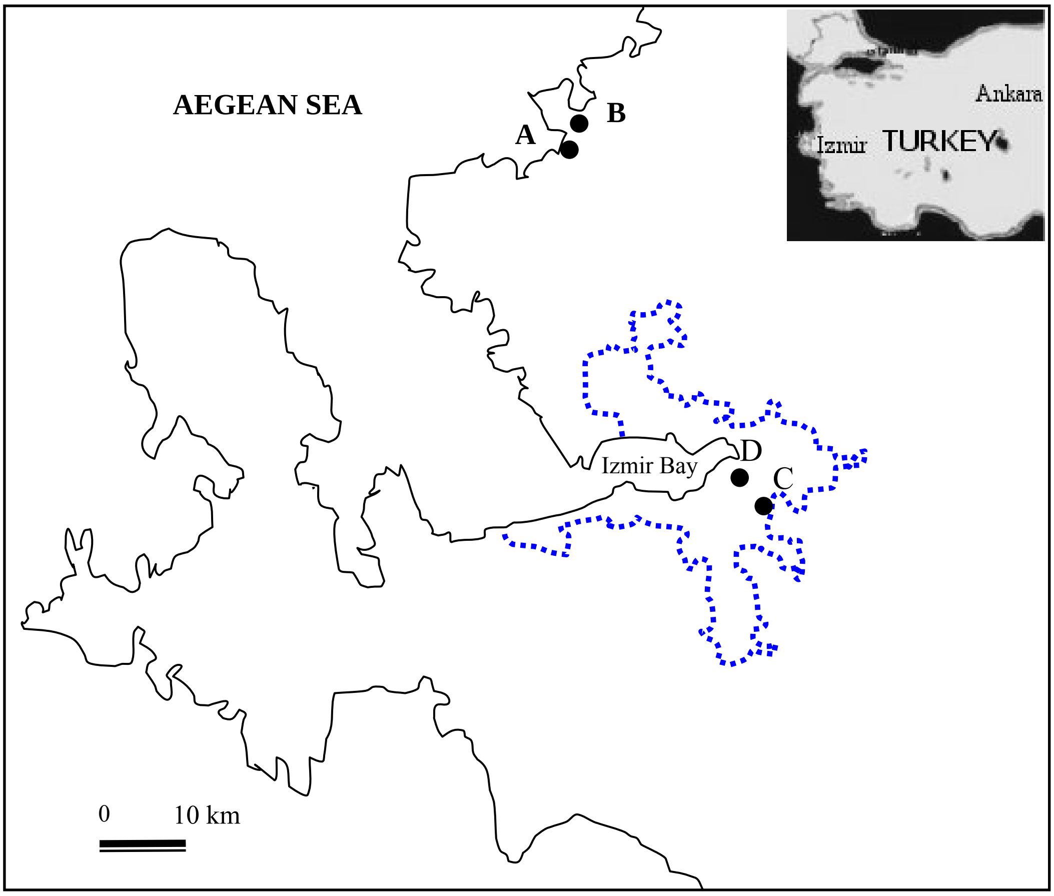

Figure 3.1 Map of Izmir showing the sampling sites. A-Industrial Sampling Site, B-Urban 2 sampling site C- Suburban sampling Site, D-Urban 1 Sampling Site. Dashed line is the border of densely populated areas.

Totally, 60 PBDE samples were collected during the sampling programs conducted at four sites during winter and summer periods. Detailed information on sampling is presented in Table 3.1-3.3. Samples were also collected to determine the total suspended particles (TSP) and their organic matter content (OM). However, OM content was not determined in Urban 2 and Industrial sites. Meteorological data for Suburban and Urban 1 sites were obtained from a 10 m high tower located at the suburban sampling site. For Urban 2 and Industrial samples, meteorological data was obtained from the air quality monitoring and weather station operated by the power plant located in Horozgedigi village (Industrial site) (Table 3.1-3.3).

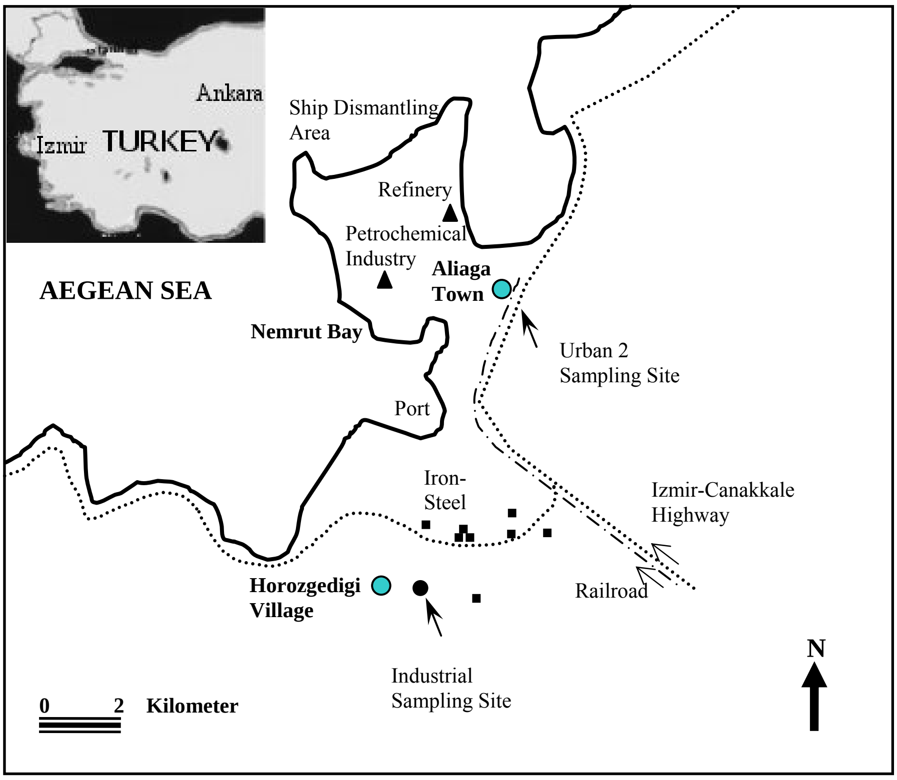

Figure 3.2 Map of Aliaga region showing the details of sampling sites

Table 3.1 Summary of sampling information, TSP and OM data collected from Suburban site.

SN	Date	T (°C)	RH (%)	WS ($m\ s^{-1}$)	WD	C (TSP) ($\mu g\ m^{-3}$)	C (OM) ($\mu g\ m^{-3}$)	OM (%)
1	09/07/2004	22.4	41.4	6.4	N	57.4	31.7	55.2
2	09/08/2004	20.1	58.4	5.0	WNW	37.5	24.4	65.0
3	09/09/2004	20.3	43.2	7.9	N	58.6	27.2	46.4
4	09/10/2004	16.8	41.8	8.2	N	48.0	26.7	55.6
5	09/11/2004	17.2	44.9	7.3	N	40.3	21.2	52.6
6	09/12/2004	18.1	49.0	3.7	NW	48.8	28.7	58.7
7	09/13/2004	19.2	51.7	2.3	NW	64.2	31.6	49.2
8	02/04/2005	3.5	71.1	8.3	N	114.4	52.7	46.1
9	02/05/2005	2.2	65.6	10.3	N	25.1	12.5	50.0
10	02/06/2005	-0.6	62.7	8.8	N	28.7	16.4	57.1
11	02/07/2005	0.5	59.3	8.1	N	31.7	17.1	53.8
12	02/08/2005	0.8	57.2	8.3	N	36.6	23.1	63.2
13	02/09/2005	2.2	44.1	8.0	N	37.8	23.1	61.1
14	02/10/2005	2.0	49.6	7.5	N	50.3	32.0	63.6
15	02/11/2005	1.5	56.7	3.7	N	60.0	40.7	67.7
16	02/12/2005	3.7	51.4	3.2	N	62.4	39.5	63.3

Table 3.2 Summary of sampling information, TSP and OM data collected from Urban 1.

SN	Date	T (°C)	RH (%)	WS ($m\ s^{-1}$)	WD	C (TSP) ($\mu g\ m^{-3}$)	C (OM) ($\mu g\ m^{-3}$)	OM (%)
1	09/15/2004	21.1	51.3	4.6	N	92.2	50.2	54.4
2	09/17/2004	23.9	41.0	9.0	NNW	137.4	48.3	35.2
3	09/18/2004	23.4	51.1	6.1	N	93.6	56.9	60.8
4	09/19/2004	20.8	65.1	2.8	N	92.8	50.8	54.7
5	09/20/2004	21.0	66.7	2.6	N	97.2	58.0	59.6
6	09/21/2004	21.6	62.7	2.4	N	106.1	60.1	56.6
7	09/22/2004	21.5	61.3	2.2	SE	71.0	44.8	63.2
8	09/23/2004	21.6	64.8	2.2	SSE	87.1	44.0	50.5
9	09/24/2004	23.6	64.5	4.2	S	73.5	34.1	46.3
10	03/03/2005	4.5	75.7	4.1	N	123.6	81.4	65.9
11	03/04/2005	7.6	69.4	2.0	NW	199.2	146.5	73.6
12	03/11/2005	0.9	71.2	3.4	N	143.6	66.1	46.0
13	03/15/2005	12.3	66.0	1.9	WNW	185.0	129.3	69.9
14	03/16/2005	13.4	45.9	4.9	N	96.5	50.3	52.1
15	03/17/2005	12.9	55.8	2.8	NNW	114.8	68.5	59.6
16	03/18/2005	13.6	56.8	2.2	WNW	115.0	79.2	68.9
17	03/19/2005	14.6	60.5	2.3	SE	87.5	52.9	60.5

Table 3.3 Summary of sampling information for Urban 2 and Industrial sites (2005).

Sample No	Date	Time (min)	WS ($m\ s^{-1}$)	WD	T (°C)	RH (%)
1	03/28	1158	2.5	W	16	62
2	03/29	1429	2.7	NW	13	74
3	03/30	1323	9.4	NW	12	77
4	04/05	1410	1.6	WNW	7	60
5	04/06	1363	1.5	WSW	8	63
6	04/07	1522	1.7	W	10	60
7	06/13	1414	4.4	NW	20	61
8	06/14	1399	5.1	NW	20	68
9	06/15	1256	3.8	NW	22	63
10	06/16	1416	2.5	WNW	24	62
11	06/17	1366	3.2	NW	25	58
12	06/18	1658	2.0	WNW	24	66
13	06/19	1114	3.2	NW	22	68

The soil samples were collected from 13 different sites (Figure 3.3). In a total, 23 soil samples were collected from September, 2004 to October, 2005. Soil samples for Kaynaklar Campus were collected at the beginning and end of the ambient air sampling period both for summer (n=3) and winter (n=2) seasons. Soil from electronic industry (TV set production) (n=5) expected to be possible PBDE source, Yamanlar (remote site), different sites of Aliaga (n=8) expected to be influenced from heavy industrial area (Horozgedigi, Bozkoy, Petkim, Sehit Kemal, Steel production industry), Torbali (industrial), Kemalpasa (industrial), Konak (urban), Yesildere (urban) and a bag filter dust from electric arc furnace of steel production were also collected (Figure 3.3)

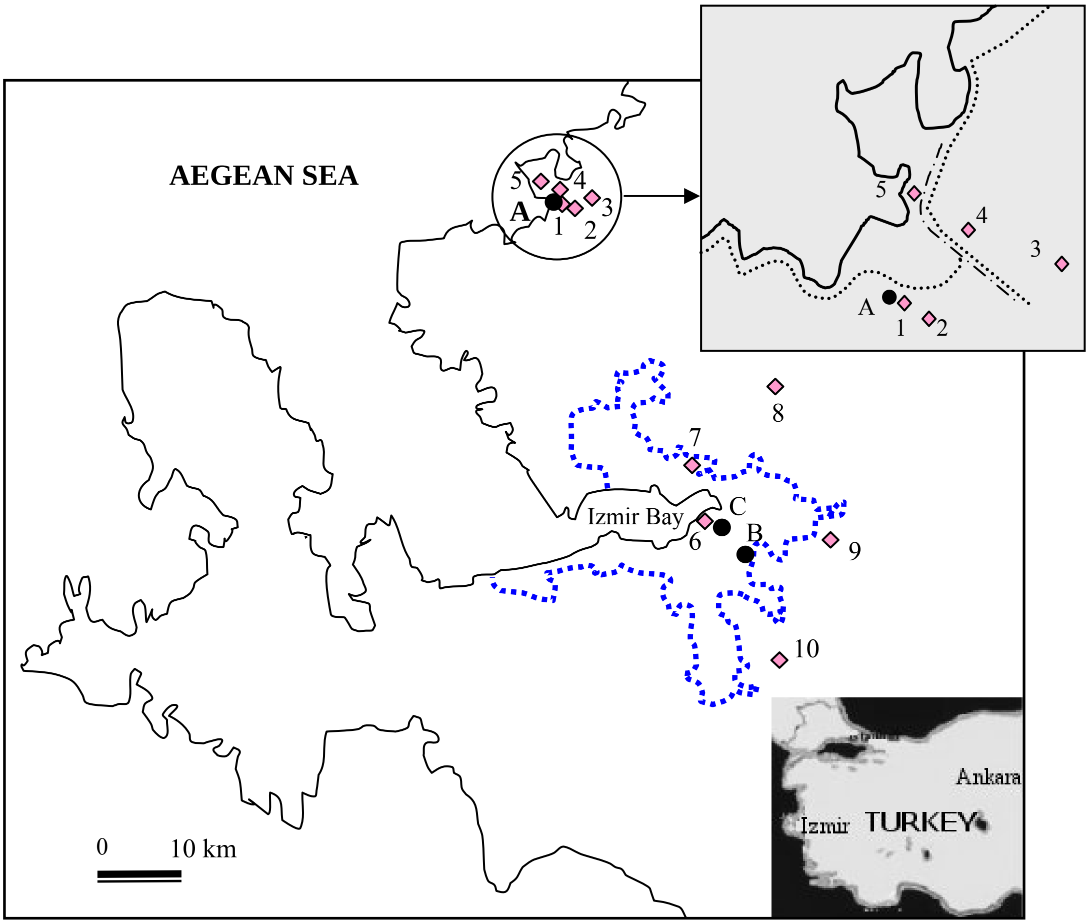

Figure 3.3 Map of Izmir showing the soil sampling sites. A-Industrial Sampling Site, B- Suburban sampling Site, C-Urban 1 Sampling Site, 1- Steel Production Industry, 2- Bozkoy, 3- Sehit Kemal, 4- Aliaga commercial site, 5- Petkim Housings, 6-Agora, 7- Yamanlar, 8- Electronic Industry, 9- Kemalpasa, 10-Torbali. Dashed line is the border of densely populated areas.

Surface water and concurrent air samples (n=15) from Guzelyali Port were collected during two sampling programs in July and December, 2005. Guzelyali Port is an urban site located at the south of Izmir Bay (Figure 3.4). Sampling data and meteorological conditions are given in Table 3.4. Meteorological data (air temperature, wind speed and direction, and relative humidity) was taken from Guzelyali station located ~500 meters from the sampling site while surface water temperatures were measured on-site. Long-term observations indicate that the prevailing wind direction in the area is NW. During the sampling programs generally northerly winds were prevailed (except the last two days of winter sampling). These wind directions indicate that sampled air was off the bay water but also affected by the urban plume since there are densely populated areas around the Izmir Bay (Figure 3.4).

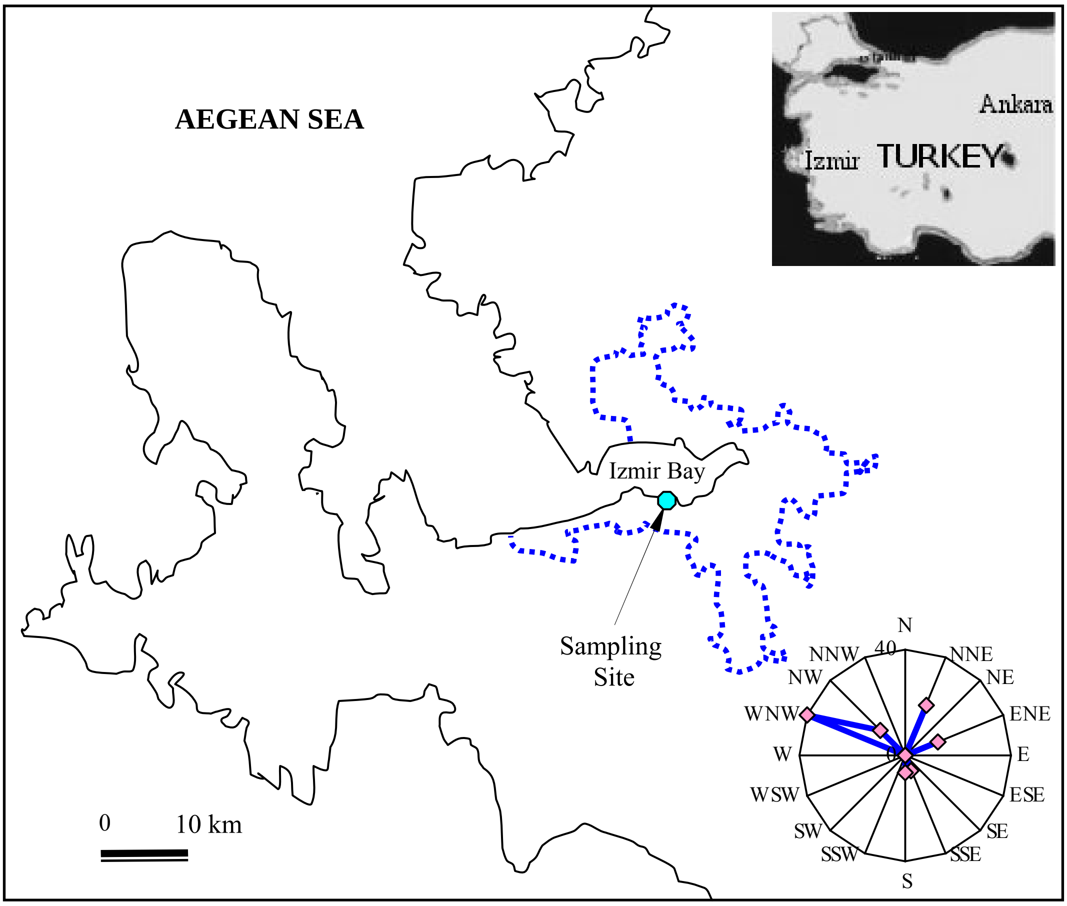

Figure 3.4 Map of Izmir Bay showing Guzelyali Port sampling site. Dashed line is the border of densely populated areas. Wind rose shows the frequency (%) of prevailing wind directions during the sampling programs.

Organic film samples from indoor and outdoor window surfaces were collected between June and October, 2004. In a total, 30 samples were collected, 14 from Kaynaklar Campus of Dokuz Eylul University (7 indoor and 7 outdoor) and 16 other were from Izmir region having different characteristics (five residential, one TV repair shop, one remote and one industrial site). The average outside air temperature during the sampling period was higher than 30°C. The last window cleaning time was not precisely known but was longer than three months at all sites. Indoor organic film samples from the windshields of 4 different cars were also collected for winter (February) and summer (July) periods. Vehicles having windshields that were not cleaned within the last two weeks were sampled.

Table 3.4 Summary of sampling information (Guzelyali, 2005)

Sample No	Date	Time (min)	WS (m s^{-1})	WD	Water Temp. (°C)	Air Temp. (°C)	RH (%)
1	7/6	360	5.2	WNW	26	29	38
2	7/7	272	2.7	NNE	26	32	39
3	7/8	442	3.3	WNW	27	33	42
4	7/9	574	5.1	WNW	27	32	48
5	7/10	490	5.0	WNW	28	32	47
6	7/11	376	3.3	NW	28	33	39
7	7/12	362	2.7	NNE	27	33	48
8	7/13	401	4.0	NW	27	30	54
9	12/20	455	4.4	ENE	13	5.1	48
10	12/21	448	1.8	WNW	13	5.0	52
11	12/22	225	2.2	WNW	12	3.9	72
12	12/23	498	2.5	ENE	12	4.9	63
13	12/24	411	5.5	NNE	12	4.2	58
14	12/25	473	3.9	SSE	11	3.9	61
15	12/26	527	4.6	S	11	9.7	53

The Henry's law constants of PBDEs were measured for seven PBDE congeners as a function of temperature. Henry's law constants were measured at five different environmental temperatures including 5, 15, 25, 30 and 40°C by a commonly used gas-stripping technique.

3.2 Sampling Method

3.2.1 Ambient Air Samples

Air samples were collected by 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 modified cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF).

Concurrently, particle samples were collected on 11-cm diameter glass fiber filters using another high volume sampler to determine total suspended particulate matter (TSP) and its organic matter (OM) content. The average sampling volumes were 317±37 m^3 and 72±29 m^3 for PBDE and TSP samples, respectively. Sampling duration was ~24h.

3.2.2 Dry Deposition Samples

The particle dry deposition flux was measured using a smooth deposition plate (22x7.5 cm) with a sharp leading edge (<10°), 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 5.5x12 cm. Five plates and sheets with a total collection area of 330 cm^2 were used for sampling.

3.2.3 Soil Samples

The soil samples were collected manually in 0-5 cm depth and sieved through a 0.5 mm mesh to remove large particles and organic debris, sealed with aluminium foil and stored at -4 ^{0}C. A bag filter dust sample from a steel plant with electric arc furnaces was also collected to examine the sources of PBDEs. About 30 g of soil and dust samples were used to determine their water and organic matter content and the 10 g was used for PBDE analysis.

3.2.4 Organic Film Samples

Organic films were collected from indoor and outdoor window surfaces with laboratory Kimwipes precleaned with dichloromethane (DCM) in a Soxhlet apparatus. Prior to sampling, Kimwipes were wetted with GC-grade DCM. To prevent possible contamination from building material, a 10-cm bound was left around the window area. After sampling, Kimwipes were stored at -20°C in their containers.

3.2.5 Water Samples

Water samples from Güzelyalı Port were collected along with the concurrent air samples for both summer and winter seasons. Air samples were collected using above mentioned procedure with PS-1 sampler. Water samples were collected at the beginning of each air sampling (at 9.00 a.m.) manually from a depth of 30 cm using high density polyethylene containers without leaving a headspace. For each sampling period, 55 liters of water were collected. All the samples were collected when there was no rain during daytime. The average sampling duration was 7 hours for ambient air samples.

3.3 Laboratory Experiments (Henry’s Law Constant)

In addition to field studies, Henry’s Law constant measurements were conducted in the laboratory at five different temperatures, using gas stripping technique that was previously applies by Bamford, Poster, & Baker (2000) for PCBs.

The gas-stripping apparatus (Figure 3.5) consisted of a 75 cm by 5 cm diameter water-jacketed glass reactor filled with 1 L deionized water at a depth of 50 cm. The water depth was selected based on previous studies indicating that the equilibrium between gas and water-phases is achieved at less than 50 cm of water depth (Sahsuvar, Helm, Jantunen, & Bidleman, 2003; Harrison, Cape, Mathew, & Heal, 2002; Jantunen & Bidleman, 2000; Bamford et al., 2000, Bamford et al., 1999).

BDE 209 has the lowest water solubility among the seven congeners and it is followed by BDE 153. Preliminary calculations concerning instrumental detection limits (0.5 pg for BDE 209) and durations of experiments necessary to obtain detectable gas-phase concentrations indicated that using a certain percent solubility of BDE 209 as the initial water concentration is not practical since the required experimental duration is >30 days. Therefore, the initial water concentrations were set to 4% solubility of BDE 153. The PBDEs were prepared in 1 ml methanol and spiked into the water in the reactor to obtain concentrations less than 4% of the solubility of BDE 153 (650 ng L^{-1}) which is 0.0166 mg L^{-1} (Wania & Dugani, 2003). Then, 200 ml min^{-1} compressed chromatographic grade N_2 was passed through a 40-µm fritted glass diffuser from the bottom of the reactor. Pure N_2 was passed through an impinger filled with deionized water to saturate it with water vapor before introduced into the reactor. Flow rates of N_2 were measured using a flow meter and the temperature was controlled by a constant-temperature circulated water bath.

A 5-cm section of the tube exiting the inner chamber was plugged with pre-baked silanized glass wool to prevent the escape of the water droplets that may be produced during the bubbling process. Vapor phase PBDEs were captured by an XAD-2 resin filled glass column. Water samples (5 ml) were drawn through a valve located at the base of the reactor at the start and end of each experimental period (~ 24 h). Above mentioned procedure was applied at five different temperatures including 5, 15, 25, 30 and 40°C and replicated three times for each temperature.

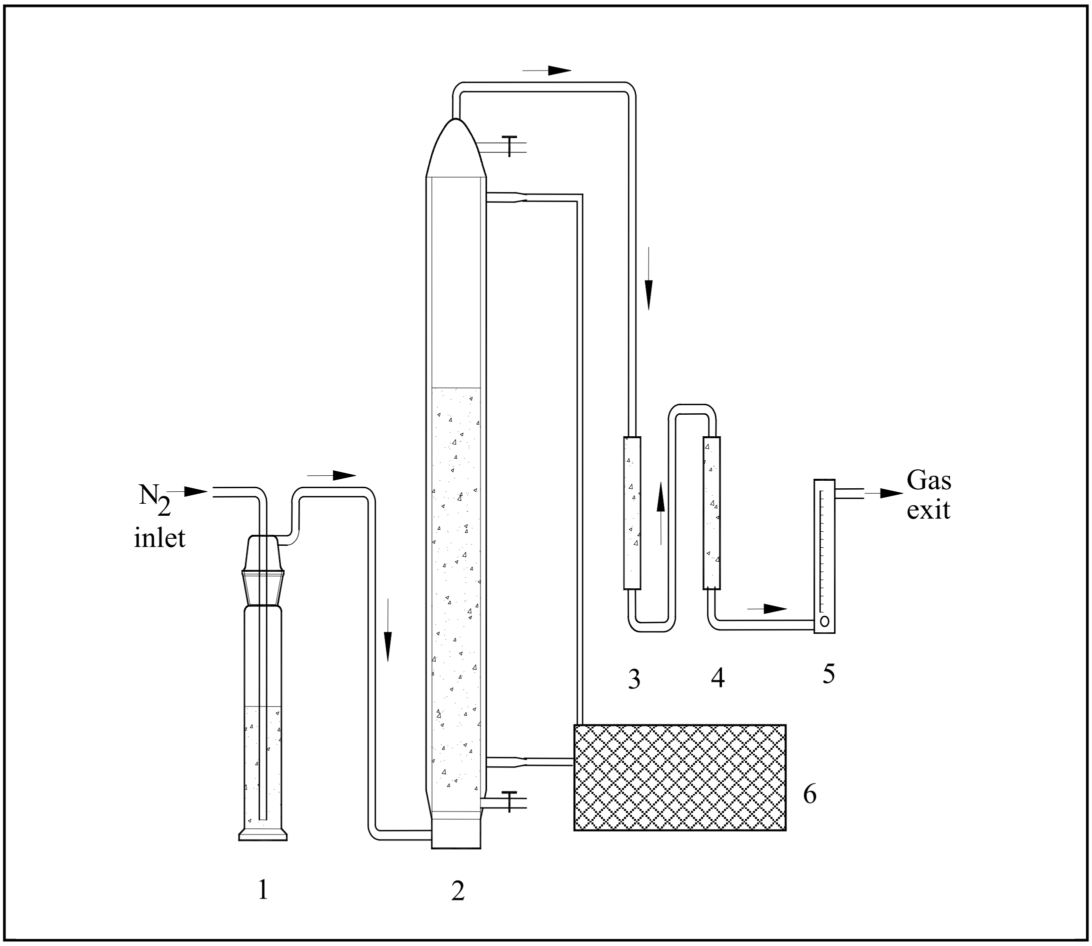

Figure 3.5 Schematic layout of Henry's law constant's experimental train. (1) Impinger containing DI water for gas conditioning, (2) water jacketed stripping column, (3) adsorbent (XAD-2) column, (4) backup column, (5) rotameter, (6) circulating constant temperature water bath

3.4 Preparation for Sampling

3.4.1 Glassware

Glassware was washed with detergent and tap water and deionized water. After rinsing with acetone and hexane, then they were dried in an oven at 105°C for overnight. The openings of the glassware were covered with aluminum foil.

3.4.2 Glass Fiber and Quartz Filters

Glass fiber and quartz filters were wrapped loosely with aluminum foil and baked in a muffle furnace at 450 °C overnight. Then they were allowed to cool to room temperature in a desiccator.

3.4.3 PUF Cartridges

PUF and resin cartridges were cleaned by Soxhlet extraction using acetone hexane mixture (1:1) for 24 h. After extraction, the cartridges were wrapped loosely with aluminum foil and dried in an oven at 70°C. Cleaned cartridges were stored in glass jars capped with Teflon-Lined lids.

3.4.4 Dry Deposition Plates

Plates and cellulose strips were cleaned with detergent and hot water, rinsed with tap water several times and with DI water. Then, they were rinsed with acetone and hexane and wrapped with aluminum foil. Glass fiber filter sheets (7.5 x 12 cm) were mounted on dry deposition plates and both sides covered with cellulose acetate strips (1 x 12 cm).

3.4.5 Sample Handling

All prepared materials for sampling such as dry deposition plates, glass fiber filters, PUF cartridges etc. were transported to the field in their closed containers without allowing exposure to ambient air in order to protect from any contamination. After sampling, PS-1 filters and PUF and resin cartridges were placed into their containers, brought back to the laboratory and stored in a freezer until they were analyzed.

3.5 Preparation for Analysis

3.5.1 Sample Extraction and Concentration

Ambient air samples were Soxhlet extracted for 24 hours with 50% acetone in hexane. Prior to extraction, all samples were spiked with surrogate standard (BDE-77, 3,3′,4,4′-tetrabromodiphenyl ether) to monitor the analytical recovery efficiency that was suggested to be used as surrogate standard by Covaci, Voorspoels, & de Boer (2003). The extract was reduced in volume by rotary evaporator. The sample extracts was concentrated to approximately 5 ml, and transferred into hexane by addition of 10 ml hexane and concentrating the mixture to approximately 5 ml, and again adding 5 ml of hexane and concentrating the mixture approximately 5 ml. The temperature of water bath was maintained at approximately 30°C during sample concentration and solvent exchange. The sample in 5 ml hexane was transferred into a 40 ml vial. The flask used for evaporation was rinsed with 5 ml hexane. Approximately 10 ml sample was blown down to 2 ml with a high purity stream of nitrogen (~ 150-200 ml min^{-1}).

Samples collected from window surfaces and soils were extracted in an ultrasonic bath for 60 minutes with 50% acetone in hexane with an addition of recovery standard, BDE-77. Prior to extraction, the mixture left overnight at room temperature. The extract was concentrated and solvent exchanged into hexane using a rotary evaporator using the above mentioned procedure for air samples

For Henry’s Law constant, water and gas-phase samples were spiked with 20 ng of BDE-77 (surrogate standard) prior to extraction. Gas-phase samples were extracted into DCM in an ultrasonic bath for 30 min. Water samples were liquid-liquid extracted three times with 5 ml DCM using a separatory funnel. Then, the solvent for all samples was exchanged into hexane and sample volumes were reduced to 1 ml under a gentle stream of pure nitrogen. Clean-up and fractionation procedure was not applied to these samples.

3.5.2 Sample Clean-up and Fractionation

Clean-up and fractionation experiments for 9 PBDE congeners were conducted using the procedure as Strandberg et al. (2001) summarized in their paper in which silica gel have been used. In that study it was stated that all PBDEs were eluted in fraction 2 (1:1 DCM in hexane) and the recoveries were close to 100% except for PBDE 209. In present study, BDE-77, -99, -100, -154 and -153 were mostly in fraction 1, as opposed to their results, BDE-28 and -47 were distributed between two fractions and BDE-128 was poorly recovered only in fraction 2. The results of this recovery experiments were presented in Table 3.5.

Table 3.5 Recovery results for 30 ng/sample spikes using silica gel.

Congeners	Fraction 1	Fraction 2
BDE-28	37 ± 15	38 ± 10
BDE-47	42 ± 12	41 ± 10
BDE-77	62 ± 11	22 ± 8
BDE-99	69 ± 7	5 ± 1
BDE-100	57 ± 10	10 ± 4
BDE-154	67 ± 7	3 ± 0.3
BDE-153	64 ± 12	6 ± 0.3
BDE-128	0	26 ± 10

After these results, alumina-silicic acid cleanup and fractionation procedure was carried out. In this procedure, cleanup and fractionation were performed on a column containing 3% w/w water-deactivated silicic acid and 6% deactivated alumina, using 25 ml of petroleum ether (PE) (fraction 1) and 20 ml of DCM (fraction 2). The procedure was not acceptable that the highest recovery ratio was about 25%. Therefore, elution of different volumes of PE was worked on including 40, 50 and 60 ml. Only different volumes of PE elution were tested as the PBDEs were eluted in the first fraction. The results of these experiments were depicted in Figure 3.6. Sharp increase on percent recovery as a function of eluent volume (especially from 25 ml to 40 ml) can be clearly seen in this figure.

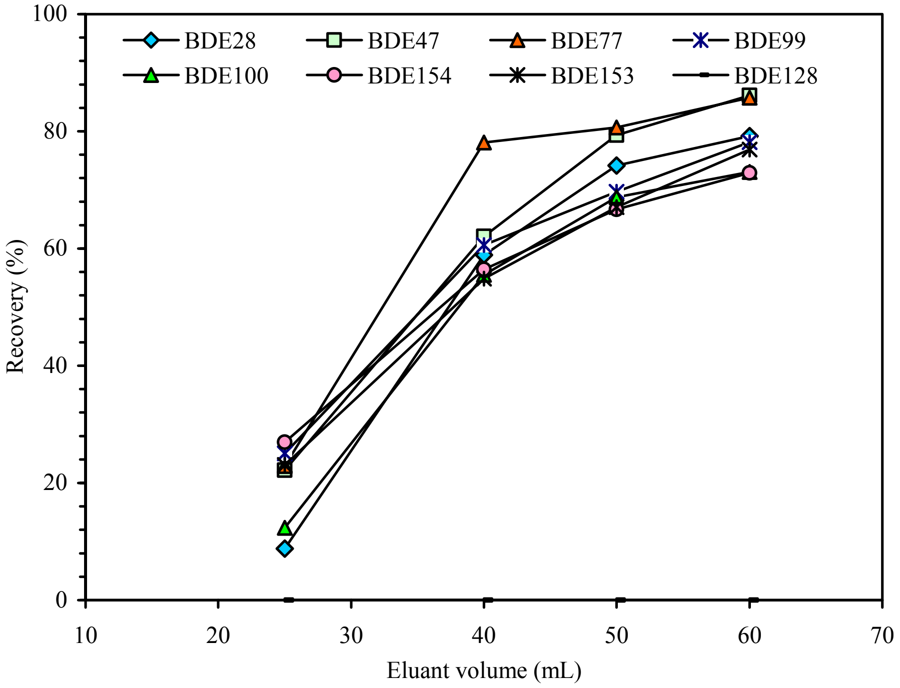

Figure 3.6 The recovery experiments with the elution of different volumes of PE including 25, 40, 50 and 60 ml for 8 congeners.

The percent recovery of 60 ml eluent volume should be acceptable, but this volume is very high (mostly 20-25 ml eluent was used in literature), thus it needs further experiment comprising different deactivation of silicic acid. Based on these findings, 3.5, 4.0 and 4.5% deactivation of silicic acid were tested for 25 ml of PE. The results of these experiments were illustrated in Figure 3.7. As can be seen from the figure, there is not considerable increase on percent recovery from 3.5% to 4% deactivation of silicic acid. But in 4.5% deactivation, some increase was obtained.

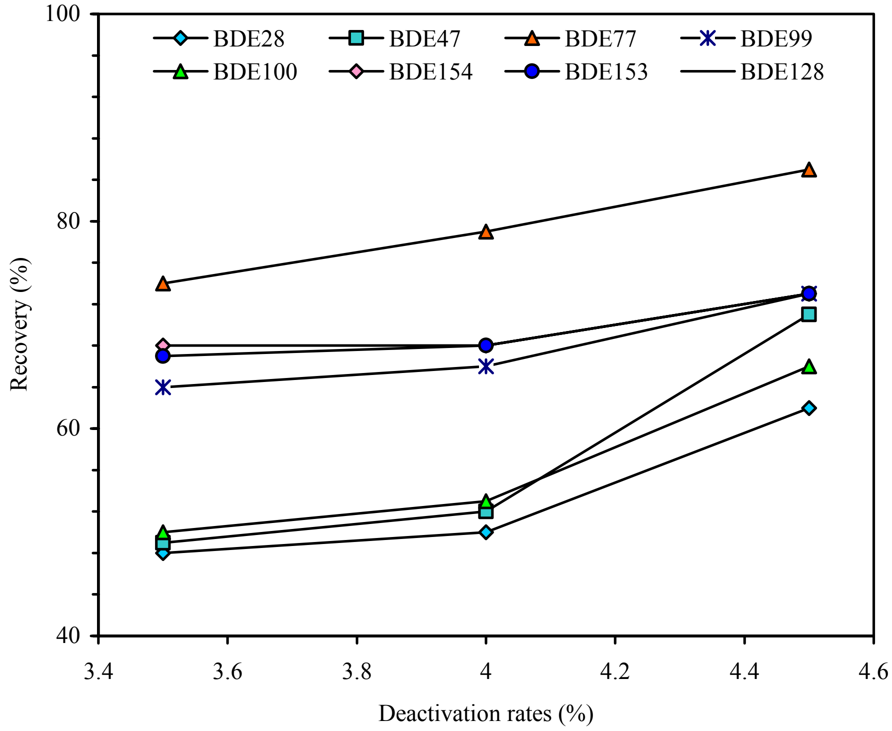

Figure 3.7 The recovery experiments for different deactivation rate of silicic acid including 3.5%, 4.0% and 4.5% for 25 ml of PE.

Nevertheless, this result was not acceptable as the recovery of most congeners was about or under 70%. Combining two matrices; deactivation rate and eluent volume, the optimum result was obtained by 4.5 % deactivation of silicic acid with the elution of 35 ml of solvent (PE) and the results were depicted in Figure 3.8. As can be seen, the results were excellent, especially the recovery of BDE-77 was about 100%. These results were proved the consistency of BDE-77 as an internal standard.

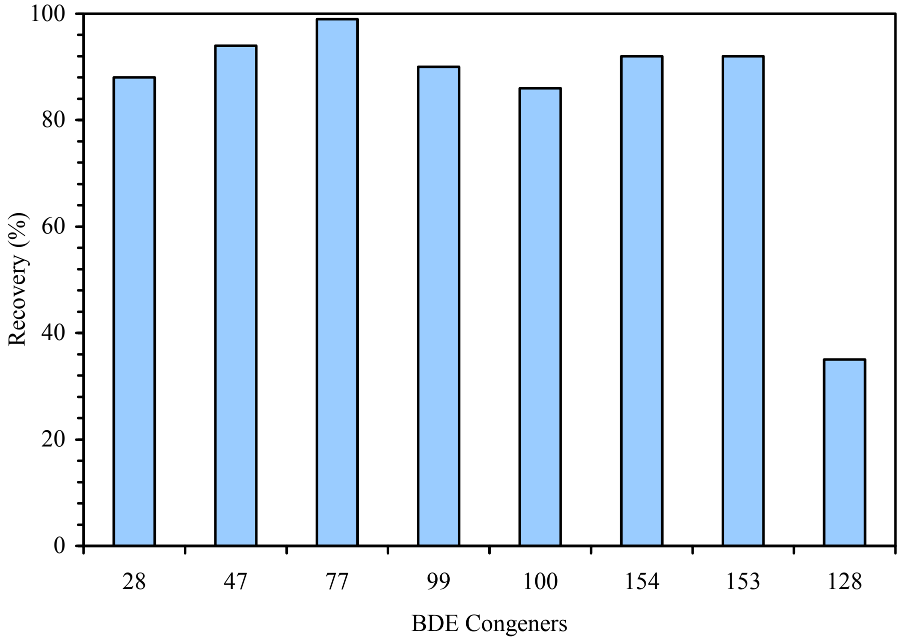

Figure 3.8 The recovery experiment for 4.5% deactivation of silicic acid with the elution of 35 ml of solvent (PE) for 8 congeners.

During recovery studies, the samples were analyzed with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 µm) was used. Björklund, Tollbäck, Hiärne, Dyremark, & Östman, (2004) have investigated the influence of the column system on Gas Chromatographic determination of PBDEs. Finally, they have found that there was no significant difference in yield of the low molecular weight PBDEs for any columns. However, for PBDEs with a higher degree of bromination, a significant difference between the column brands was observed. The HP-5ms column was also investigated and they have noticed that the degradation increased with the degree of bromination, as well as BDE-209 vanished almost completely as occurred in this study. They have recommended DB-5ms column to overcome this problem. Therefore, the samples were re-analyzed using DB-5ms column for BDE 209. Finally, the recovery of BDE 209 was obtained as 75%.

Finally, after the results of different deactivation rates, different eluent volumes and 2 different column experiments, it can be concluded that the best result was obtained from 4.5% deactivation of silicic acid with the elution of 35 ml of PE using DB-5 ms column on GC analysis.

All samples were cleaned up and fractionated on an alumina-silicic acid column containing 3 g silicic acid and 2 g alumina. Silicic acid was prepared by oven drying at ~100°C for overnight in a flask loosely covered with aluminum foil to remove moisture. It was cooled in a desiccator. Three grams of silicic acid was deactivated adding 140 μL of deionized water (DI) (4.5 % deactivation rate). The mixture was sat at room temperature al least 1 h before use, and used within 12 hours. Alumina was prepared by oven drying at 450°C for several hours. After cooling to room temperature, 2 g of alumina was deactivated by addition of 120 μL DI water (6% deactivation rate). The column was prewashed with 20 ml DCM followed by 20 ml PE. The sample in 2 ml hexane was added into the column with a 2 ml rinse of PE and eluent was collected in a vial at a rate of two drops per second. After letting the sample passed through the column, 35 ml PE was added and eluent was collected in the same vial. This was Fraction 1 and contained PBDEs and PCBs. Then, 20 ml DCM was added into the same rate and eluent was collected into another vial (Fraction 2). Fraction 2 is containing PAHs and pesticides.

For both fractions the solvent was exchanged into hexane. The sample was blown down to appr. 5 ml with a high purity stream of nitrogen (~ 150-200 ml/min). The 10 ml hexane was added into a sample vial and then the sample was blown down to appr. 5 ml with a high purity stream of nitrogen. Then, again 10 ml hexane was added into a sample volume and it was adjusted to 1 ml by nitrogen blown-down.

3.6 Determination of TSP and Its Organic Matter (OM) Content

Prior to sampling for TSP, baked and cooled glass fiber filters were weighed using a micro balance capable of weighing 0.1 mg. After collection of sample, they were kept in a desiccator overnight and reweighed. TSP can be obtained by subtracting the initial weight from the final weight. Filters were baked in a furnace for 1 hour at 450 °C, then allowed to cool to room temperature in a desiccator and weighed to determine the organic matter content of the particles. Organic matter content was determined by subtracting these weight from the initial weight before baking at 450 °C. Concurrent blank filters were used for each sample to obtain the weight loss of filters at high temperatures and OM contents were corrected using the weight loss in blank filters during baking.

3.7 Determination of Water and OM content of Soil Samples

Soil samples were put in a crucible that was dried in an oven at 105 °C and allowed to cool room temperature in a desiccator and weighed. Then the sample was dried in an oven at 105 °C at 24 h and cooled to room temperature and reweighed. The subract was water content of samples. Organic matter content was determined by loss on ignition in a muffle furnace at 600ºC for 4 h. Soil concentrations were corrected using water content to obtain dry weight concentrations.

3.8 Analysis of Field Samples

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-5ms, 15 m, 0.25 mm, 0.1 µm) was used. The column selection and instrumental parameters were based on recent studies on the effect of the injection technique and the column system on gas chromatographic determination of PBDEs (Björklund, et al., 2004; Tu & Prest, 2005). 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°C for 1 min and raised to 340ºC at 20ºC 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 used as the reagent gas. The MSD was run in selected ion monitoring mode. For 6 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 based on their retention times, target and qualifier ions, and quantified using the internal standard calibration procedure.

3.9 Analysis of Henry's Law Constant Samples

The samples were analyzed using a gas chromatograph (GC) (Agilent 6890N) equipped with a micro-electron capture detector (µECD). A capillary column (DB-1, 15 m, 0.25 mm, 0.1 µm) was used. The column selection and instrumental parameters were based on a recent study on the effect of the injection technique and the column system on gas chromatographic determination of PBDEs (Björklund et al., 2004). The initial oven temperature was held at 50°C for 1 min and raised to 300 °C at 25 °C min^{-1}, and held for 9 min. The injector and detector temperatures were 290 and 320 °C, respectively. Pulsed-splitless injection was used to maximize the transfer of the PBDEs into the capillary column and minimize their degradation in the injector liner. High purity helium and nitrogen were used as carrier and detector make-up gases, respectively. The carrier gas was used at constant flow mode with a linear velocity of 35 cm s^{-1} and the flow rate for the make-up gas was 40 ml min^{-1}. Compounds were identified based on their retention times (within ±0.02 min of the retention times for calibration standards).

3.10 Quality Control and Assurance

3.10.1 Field Measurements

All samples were spiked with BDE-77 prior to extraction to determine analytical recovery efficiencies. Average recoveries of BDE-77 and blank/sample amounts were presented in Table 3.6. Average recovery was between 60±9% (for dry deposition filters) and 98±22% (for soil samples) and blank/sample amounts were between 8±5% (for water filters) and 27±14% (for dry deposition filters). The recoveries of target compounds were also tested externally for PUF and air filter samples and presented in Table 3.7. The overall average recovery efficiency was 99±12% (average±SD).

Table 3.6 Average recovery of BDE-77 and blank amounts in samples (%) in all matrices (avg±SD)

	Recovery	Blank amount in sample
PUF	83±17	20±12
Air filter	86±19	14±10
Water filter	93±11	8±5
Water resin	89±9	17±10
Dry deposition filters	60±9	27±14
Soil	98±22	8±9
Organic films	76±13	22±14

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 μl injection. 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 were also presented in Table 3.7 for all sample matrices.

Table 3.7 Average recoveries and LODs of BDE congeners.

Congener	Recovery (%)		LOD (ng)						
	Filter	PUF	PUF	Filter	Water filter	Water resin	Organic films	Dry dep. filter	Soil
BDE-28	88±5	92±6	0.05	0.05	0.05	0.09	0.05	0.05	0.05
BDE-47	79±7	86±9	0.33	0.22	0.18	0.37	0.29	0.33	0.29
BDE-100	111±10	108±4	0.05	0.05	0.12	0.13	0.05	0.05	0.05
BDE-99	101±5	106±6	0.18	0.28	0.26	0.37	0.33	0.29	0.33
BDE-154	112±14	110±7	0.05	0.05	0.05	0.05	0.05	0.05	0.05
BDE-153	115±12	108±4	0.05	0.05	0.05	0.18	0.05	0.05	0.05
BDE-209	70±20	86±20	1.26	1.40	0.35	1.16	3.46	1.87	3.46

During TSP sampling, concurrent blank filters were run for each sample to determine if there was any contamination during sample handling and preparation and to account for probable interferences (i.e., weight loss of filters at high temperatures) in OM determination. Finally, TSP and OM contents were corrected using blank filters (5±5%) and the weight loss in blank filters during baking (6±5%), respectively.

Six congeners excluding BDE-209 were also analyzed using an HP5-ms column (30 m, 0.25 mm, 0.25 μm). Since BDE-209 could not be analyzed with this column, all samples were reanalyzed using a shorter DB5-ms column with a lower film thickness (15 m, 0.25 mm, 0.1 μm). Covaci et al. (2003) reported the co-elution of PBDEs with some other organic compounds in their study, especially co-elution of hexabromobiphenyl (PBB-153) and BDE-154, and BDE-153 and tetrabromobisphenol-A (TBBP-A). They have suggested that the column should be tested for possible co-elution of target compounds. Hites (2004) have suggested two different GC measurements to separate PBB-153 from BDE-154 (long column) and to measure BDE-209 (short column, preferably 10-15m) due to its susceptibility for degradation in the GC system. In present study, during the two different GC measurements, co-elution with any other compounds and systematic differences in PBDE concentrations were not observed. The agreement between the two set of analysis was very good (statistically the same at 95% confidence level-two-tailed t-test) indicating the reliability of GC techniques used in this study.

Five levels of calibration standards were used to calibrate the GC/MS system. In every case, the r^2 of the calibration curve was ≥0.999. System performance was verified by the analysis of the mid-point calibration standard for every 12 hours during the analysis period.

Possible artifacts associated with the high volume air sampling are the adsorption of gas-phase chemical to the filter and the breakthrough of the gas-phase compounds through the PUF. These artifacts were recently investigated for BDEs using sampling volumes ranging between 300-600 m^3 (outdoor) and 100-200 m^3 (indoor) (Shoeib et al., 2004) It was shown that the sampling artifacts were insignificant for the measured total BDE concentrations (gas+particle phases, sum of 9 congeners) ranging between 39 (outdoor)-2088 pg m^{-3} (indoor) (Shoeib, Harner, Ikonomou, Kannan, 2004). In the present study, since the sampling volume was within these ranges (averagely 336 m^3), and the maximum total BDE concentration was approximately an order of magnitude lower than the one reported by Shoeib et al. (2004), it was assumed that the PUF effectively captured the gas-phase fraction.

3.10.2 Laboratory Experiments (Henry's Law Constant)

Blank XAD-2 resin and water samples were prepared to determine if there was any contamination during sample handling and preparation for analysis. The average amounts of blanks ranged between 0.10 ± 0.08 ng (BDE 99) and 13.2 ± 6.2 ng (BDE 28) for XAD-2 resin samples and between 0.06 ± 0.02 ng (BDE 99) and 0.47 ± 0.22 ng (BDE 47, BDE 100) for water samples. Generally, blank amounts were significantly lower than the sample amounts. Sample amount/blank amount ratios ranged between 3.1±1.3 (BDE 154)-108±124 (BDE 99) and 3.0±1.1 (BDE 154)-9.4±3.8 (BDE 99) for gas-phase and aqueous samples, respectively.

LODs ranged from 0.29 ng (BDE-153) to 31.8 ng (BDE-28) for air samples and from 0.12 ng (BDE-99) to 1.98 ng (BDE-154) for water samples. In general, samples were substantially higher than LODs. Sample amounts exceeding LODs were quantified and blank corrected using the average blank amounts.

Five point calibration curves were used to calibrate the analytical system. In all cases the r^2 was >0.999. A mid-point calibration standard was used to confirm the GC performance for every 12-h period. The compounds were quantified using the internal standard calibration procedure. Recoveries of surrogate standard BDE 77 (95±9%) and those determined externally for other BDEs (n=3) were very good (86±11%, BDE 100-94±9%, BDE 47) indicating no significant loses occurred during sample preparation.

A backup column was also placed in series with first glass column in order to determine possible breakthrough of chemicals during the experiments at 40°C. The average amounts found on these backup columns were between 1.00 ± 0.01 % (BDE 47) and 26.0 ± 1.8 % (BDE 28) of the values found in first columns. These results indicated that the breakthrough of chemicals was not significant even at the highest gas-phase concentrations (at 40°C).

The comparison of the measured water-phase concentrations and the estimated solubility of BDE 209 suggested that the water concentrations were near or slightly above its solubility (117±10%). Therefore, it is possible that the measured H values for BDE 209 may be slightly biased. However, this is not conclusive since there are no experimentally determined solubility values for BDE 209.

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents the results of ambient concentrations of PBDEs, their gas particle partitioning, dry deposition fluxes, water concentrations and air-water exchange, soil concentrations and soil-air exchange and concentrations of PBDEs in window organic films. Experimental particle phase dry deposition velocities, overall gas phase transfer coefficients were calculated using measured fluxes and concentrations. Results of these measurements were compared to the values reported in the literature.

4.1 Ambient Air Concentrations

Total (gas+particle phases) concentrations of individual PBDEs at all four sites including Suburban, Urban 1, Urban 2 and Industrial sites, were presented in Table 4.1 for summer and Table 4.2 for winter seasons. Total PBDE ($\sum_7$PBDE) concentrations ranged from 11 (Urban 1) to 149 pg m^{-3} (Industrial) in summer, while in winter, they ranged from 6 (Suburban) to 81 pg m^{-3} (Industrial). Summer concentrations of Industrial site were relatively high ($\sum_7$PBDE, average±SD, 117±23 pg m^{-3}) followed by those found in Urban 2. As expected, Suburban samples have the lowest concentrations among the four sampling sites. However, winter concentrations of Urban 1, Urban 2 and Industrial sites were slightly different from each other. Among the urban sites, the PBDE concentrations at Urban 2 were higher than those obtained from Urban 1, probably due to the proximity of this site to Industrial site.

Table 4.1 Average concentrations of total (gas and particle phases) individual PBDEs for summer period (pg m^{-3}) (average±SD).

Congener	Suburban	Urban 1	Urban 2	Industrial
BDE-28	0.50±0.12	0.92±0.53	1.31±0.45	1.62±0.60
BDE-47	1.42±0.48	3.32±1.10	20.76±8.01	21.29±5.28
BDE-100	0.53±0.24	1.11±0.32	5.09±1.69	5.45±1.27
BDE-99	1.28±0.60	2.56±1.25	24.96±10.10	28.70±7.11
BDE-154	0.19±0.18	0.38±0.41	1.93±0.65	2.76±0.41
BDE-153	0.55±0.15	1.09±0.72	2.66±0.91	3.65±0.61
BDE-209	19.04±8.49	22.98±13.57	24.96±11.78	53.99±26.98
$\sum_7$PBDE	23.50±9.87	32.36±16.86	81.67±27.64	117.46±22.71

Table 4.2 Average concentrations of total (gas and particle phases) individual PBDEs for winter period (pg m^{-3}).

Congener	Suburban	Urban 1	Urban 2	Industrial
BDE-28	0.37±0.26	0.94±0.24	1.34±0.59	1.85±0.57
BDE-47	1.43±0.84	3.39±1.94	9.54±3.19	6.10±2.88
BDE-100	1.52±1.81	1.34±0.54	2.39±0.66	1.99±0.59
BDE-99	2.82±2.45	3.96±2.07	10.21±3.35	7.13±3.75
BDE-154	1.66±3.35	0.83±0.57	1.77±1.58	1.12±0.38
BDE-153	1.88±4.22	0.87±0.43	1.87±0.78	1.88±0.40
BDE-209	10.96±7.81	28.70±16.01	20.62±9.79	32.53±11.05
$\sum_7$PBDE	20.64±17.47	40.03±16.29	42.65±9.11	52.59±17.74

In Guzelyali Port, average gas-phase $\sum_7$PBDE concentrations were 189±61 and 76±65 pg m^{-3} (average±SD) and particle-phase PBDE concentrations were 83±37 and 68±48 pg m^{-3}, for summer and winter periods, respectively (Table 4.3).

Hoh & Hites (2005) have performed a study on brominated flame retardants in the atmosphere of the East-Central United States at five sites and they have reported the average atmospheric concentrations of $\sum_{26}$PBDEs as 100±35 pg m^{-3} at the Chicago site. In a study performed by Agrell et al. (2004), the median concentrations of

$\sum_7$PBDE and BDE-209 were found as 6.3 and 10.4 pg m^{-3}, respectively, near a solid waste incineration plant. In Gotska Sandön Island in Baltic Sea, median $\sum_{10}$PBDEs concentrations ranged between 0.4 to 78.5 pg m^{-3} (ter Schure et al., 2004). Ohta et al. (2002) conducted a study on PBDEs in Osaka atmosphere in 2001 and reported that the sum of tri- to hepta-BDEs was 2.0-6.6 pg m^{-3} while the concentrations of BDE-209 was 100-340 pg m^{-3}. In a study conducted by Chen et al. (2006), it was reported that the average $\sum_{11}$PBDE concentration in urban site of China was 352.6 pg m^{-3} (Table 2.3). In these studies the numbers of target compounds were variable. However, in all samples more than 80% of total PBDEs were composed of BDE-47, -99, 100 and 209. The concentrations of PBDEs measured in the present study were within the ranges of previously reported values.

Table 4.3 Ambient air concentrations of individual PBDEs for Guzelyali Port.

	Gas phase		Particle phase	
	Summer	Winter	Summer	Winter
Congener	(n=8)	(n=7)	(n=8)	(n=7)
BDE-28	3.4±1.7	1.0±0.4	1.1±0.7	0.6±0.6
BDE-47	49±20	6.9±5.9	12±7	6.7±4.8
BDE-100	11±3	2.9±2.0	4.5±2.0	2.7±1.7
BDE-99	63±22	11±7	23±11	9.7±5.9
BDE-154	5.2±1.7	1.1±0.6	2.7±1.1	1.0±0.8
BDE-153	7.3±1.7	1.2±0.5	3.4±1.5	1.0±0.9
BDE-209	49±15	52±52	36±19	46±34
$\sum_7$PBDE	189±61	76±65	83±37	68±48

4.1.1 Congener Profiles

BDE-209 was the most abundant congener at all sites, followed by BDE-99 or -47. Average contributions of BDE-209 to total concentrations were between 80.1±4.1% (Suburban)-30.3±10.0% (Urban 2) in summer and 68.3±15.2% (Urban 1)-42.6±9.1% (Urban 2) in winter samples (Figure 4.1).

BDE-209, 99 and 47 were the dominating congeners also in Guzelyali Port samples, contributing up to 85-92% to total PBDE concentrations. In summer, gas-phase PBDEs were dominated by BDE-99 (34%), followed by BDE-47 and 209 while in particle-phase, 42% of PBDEs were consisted of BDE-209. However, in winter, the contribution of BDE-209 to total concentrations was 59 and 67%, for gas and particle-phases, respectively (Table 4.3).

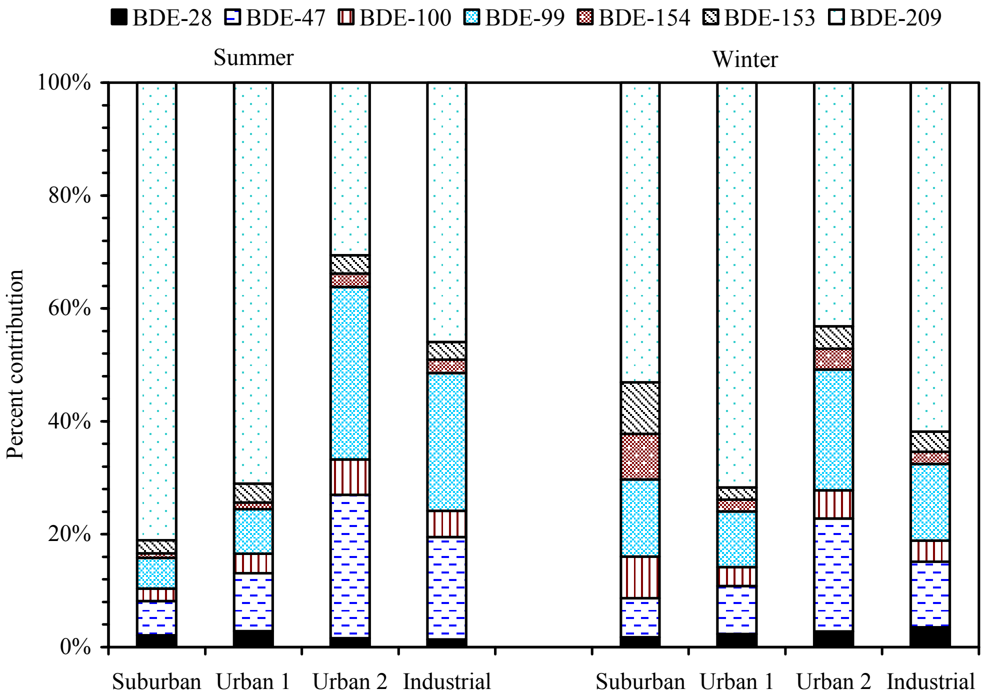

Figure 4.1 Percent contributions of individual congeners to PBDE concentrations for all sites and summer and winter periods.

The congener profiles were similar to those reported previously. Chen et al. (2006) reported that BDE-209 was the most dominating congener with the abundance of 40 to 99%. In southern Ontario, BDE-209 concentration was up to 105 pg m^{-3} (Gouin et al., 2006) while the concentrations of BDE-47 and -99 were up to 10 and 16 pg m^{-3} (Gouin et al., 2005), respectively. Hayakawa et al. (2004) and Ohta et al. (2002) have also reported the same trend. However, BDE-209 was found much lower in some studies. Hoh & Hites (2005) reported as BDE-47, the most dominating congener in the East-Central United States and followed by BDE-99, -100 and -209.

Unlike the results of the present study, the average fraction of BDE-209 was only 6 to 31%. In North America, Strandberg et al. (2002) have found BDE-209 at trace levels only in Chicago site while BDE-47 and -99 accounted for 50-65 % and 35-40 % of the total concentrations of PBDEs, respectively.

4.1.2 Effect of Meteorological parameters on Air Concentrations of PBDEs

The temperature dependence of gas-phase ambient concentrations of POPs has been investigated using Clausius-Clapeyron equation previously (Hoh & Hites, 2005; Lee & Jones, 1999; Sofuoglu, Cetin, Bozacioglu, Sener, & Odabasi, 2004).

$$\ln P = m\,(1/T) + b \tag{4.1}$$

where P is the gas-phase partial pressure (atm) of POPs, T is the average atmospheric temperature (K) and m and b are slope and intercept, respectively. The regression of ln P vs. 1/T should be linear with a negative m.

Inferences can be done using the slope (m) and coefficient of determination (r^2) with regard to the importance of temperature in controlling the gas phase ambient concentrations of POPs and the relative importance of other factors (Lee, Burnett, Harner, & Jones, 2000). Generally steep slopes and high r^2 values indicate that temperature-controlled air-surface cycling and short-term transport influences the ambient gas phase concentrations (Hoff, Brice, & Halsall, 1998; Wania, Haugen, Lei, & Mackay, 1998). Relatively shallow slopes and low r^2 values suggest that other factors (i.e., advection, ongoing sources, wet and dry deposition, atmospheric reactions) and long-range transport affect concentrations (Lee et al., 2000).

In this study, partial pressures (atm) of individual PBDEs were calculated for each sample using gas-phase concentrations and ideal gas law. The resulting slope, intercept and r^2 values of Clausius-Clapeyron plots were presented in Table 4.4. Suburban samples were divided into two subgroups including summer and winter. Because the temperature difference was very high during both sampling periods, averaged as 19.7 and 1.8°C and resulting in two different trends in plots. The temperature dependence of gas-phase concentrations of PBDEs was statistically significant for Suburban summer and winter, Urban 1 and Industrial samples except for a few congeners and r^2 values were between 0.29 and 0.80 for statistically significant samples ($p<0.01$ or <0.1) (Table 4.4). For the most PBDE congeners the slopes were negative indicating that concentrations increased with temperature. Slopes were generally steep (up to -28957) suggesting that ambient gas-phase PBDE concentrations were influenced by short-range or regional transport (Lee and Jones, 1999; Sofuoglu et al., 2004). However, the temperature dependence of Urban 2 samples was not statistically significant for the most congeners. Relatively shallow or positive slopes and low r^2 values were observed for some BDEs especially in Urban 2 and Industrial sites. Considering the relatively high concentrations measured, low temperature-dependency suggested that the gas-phase PBDE concentrations at these sites were affected by local ongoing sources rather than long-range transport.

To investigate the effect of wind speed and direction on gas-phase atmospheric concentrations of individual PBDEs, multiple linear regression (MLR) analysis was also performed by adding these parameters into Equation (4.1) (Hillery, Basu, Sweet, & Hites, 1997; Sofuoglu et al., 2004):

$$\ln P = m_1\,(1/T) + m_2\,U + m_3 \cos \mathrm{WD} + b \tag{4.2}$$

where U is the wind speed (m s^{-1}), WD is the predominant wind direction during the sampling period (radians) m_1, m_2, m_3 and b are the regression parameters. However, the relationship with wind speed and direction was not statistically significant for any of the congeners suggesting that advection did not have a significant impact on atmospheric PBDE concentrations measured in sampling sites (Sofuoglu et al., 2004). Multiple linear regression analysis was also performed for Guzelyali Port samples. It was found that concentrations increased with temperature and the correlation was statistically significant for 6 BDEs excluding BDE-209 (Table 4.4) However, BDE concentrations were not correlated to wind speed and direction.

Table 4.4 Summary of Clausius-Clapeyron plots for all sites and individual congeners.

	slope	intercept	r^2	n
Suburban Summer				
BDE-28	-5326	-20.4	0.51^a	8
BDE-47	-2274	39.7	0.75^b	8
BDE-100	-12700	4.5	0.67^a	7
BDE-99	-22032	36.7	0.80^b	8
BDE153	-3701	-26.4	0.21	8
BDE-209	-28957	62.1	0.69^b	8
Suburban Winter				
BDE-28	-10868	0.54	0.57^a	8
BDE-47	-16569	22.5	0.46^a	8
BDE-100	-8515	-7.2	0.22	8
BDE-99	-18293	29.0	0.46^a	8
BDE153	-5789	-17.2	0.005	6
BDE-209	-28573	67.3	0.39^a	8
Urban 1				
BDE-28	-3000	-27.5	0.29^b	17
BDE-47	-7949	-9.7	0.77^b	17
BDE-100	-2219	-30.7	0.50^a	17
BDE-99	-3781	-24.8	0.50^b	17
BDE153	-6939	-14.8	0.57^b	14
BDE-209	-6621	-14.3	0.30^a	16
Urban 2				
BDE-28	188	-38.2	0.0008	12
BDE-47	-3425	-23.7	0.16	12
BDE-100	-5136	-19.5	0.33^a	12
BDE-99	-3642	-23.2	0.14	12
BDE154	-1799	-32.0	0.09	10
BDE-153	-1982	-31.0	0.11	12
BDE-209	-435	-34.9	0.002	12
Industrial				
BDE-28	-1107	-33.5	0.04	12
BDE-47	-6627	-12.9	0.41^a	12
BDE-100	-8808	-7.0	0.73^b	12
BDE-99	-13179	9.3	0.75^b	12
BDE154	-11174	0.03	0.68^b	10
BDE-153	-7814	-11.1	0.72^b	12
BDE-209	39	-36.8	0.0008	12
Guzelyali Port				
BDE-28	-2866	-26.3	0.69^b	15
BDE-47	-6347	-11.7	0.79^b	15
BDE-100	-4157	-20.5	0.75^b	15
BDE-99	-5413	-14.7	0.79^b	15
BDE154	-4311	-21.1	0.80^b	15
BDE-153	-5009	-18.5	0.87^b	15
BDE-209	-2322	-23.3	0.44	14

^{a} p<0.1, ^{b} p<0.01

4.1.3 Sources of PBDEs

PBDEs are commercially produced and used as technical mixtures (i.e., penta, octa, and deca products). To investigate the source profiles of measured PBDEs, they were fitted to a linear combination of the compositions of the technical products (Hoh & Hites, 2005). This was done by least squares procedure applied using the Solver feature of Excel, in which the following function was minimized (Zhu & Hites, 2006).

$$\xi_c = \sum[(f_P c_{i,P} + f_O c_{i,O} + f_D c_{i,D}) - c_{i,obs}]^2 \qquad (4.3)$$

where f_P is the fraction of the penta product in sample, $c_{i,P}$ is the percent of congener i in the penta product, f_O is the fraction of the octa product in sample, $c_{i,O}$ is the percent of congener i in the octa product f_D is the fraction of the deca product in sample, $c_{i,D}$ is the percent of congener i in the deca product, and $c_{i,obs}$ is the average observed percent of congener i in sample. The results of the fits are presented in Table 4.5, for summer and winter periods. Comparison of average and fitted congener profiles for all samples are also illustrated in Figure 4.2.

Table 4.5 Fractions of penta, octa and deca products in ambient air samples for summer and winter periods.

		f_P	f_O	f_D
Summer	Suburban	0.16	0.04	0.80
	Urban 1	0.27	0.04	0.69
	Urban 2	0.68	0.02	0.31
	Industrial	0.54	0.02	0.44
Winter	Suburban	0.35	0.09	0.56
	Urban 1	0.28	0.04	0.69
	Urban 2	0.53	0.04	0.43
	Industrial	0.33	0.05	0.62

The results of the fit show that samples collected from four different regions were dominated by penta and deca mixtures. In Suburban and Urban 1 samples, deca-BDEs were dominant while in Urban 2 and Industrial sites, samples were mostly composed of penta mixtures, especially in summer periods. In Industrial site, electric arc furnaces of steel plants are the likely PBDE sources. The bag filter dust from a steel plant and soil samples collected around these plants had significantly high amounts of PBDEs. The concentrations of $\sum_7$PBDEs in dust and soil were found as 204 and 21.7 µg kg^{-1}, respectively in present syudy. In these plants steel is produced from scraps, therefore penta-BDEs that were commonly used in the past are emitted. Since Urban 2 was also affected by these emissions, BDE profiles in this site were also dominated by penta-mixtures. Technical penta-mixtures containing mainly BDE-47 and -99 have no direct usage today (ter Schure et al., 2004), and therefore, BDE profiles at other two sites far from the steel plants (Suburban and Urban 2) contained less penta-mixture. All observed congeners except BDE-28 were fitted well to the commercial products ($p<0.01$) (Figure 4.2). However, this model tended to underestimate BDE-28. This may be due to higher volatilization tendency of low molecular weight congeners relative to higher ones and/or potential decomposition of higher congeners to lighters in the environment (Chen et al., 2006). For all samples, r^2 values were between 0.98 and 0.99 and slopes and intercepts are 0.91-0.98 and 0.22-1.25, respectively.

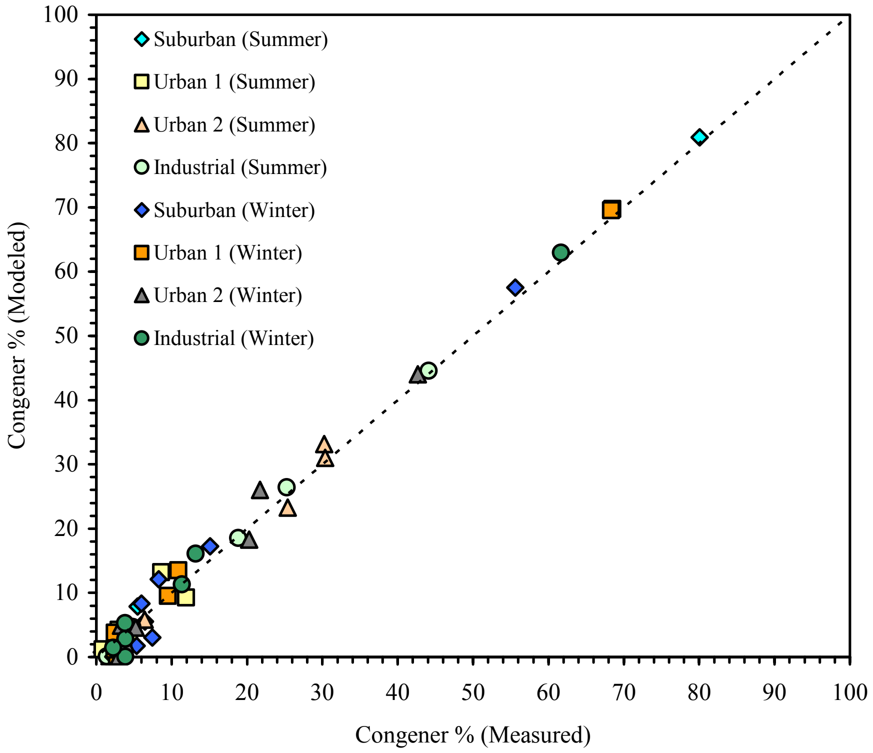

Figure 4.2 Comparison of average congener profiles for all ambient air samples and fitted congener profiles for summer and winter periods

4.1.4 Gas-Particle Partitioning

Partitioning of atmospheric organic compounds between the gas and particle phases is parameterized using the gas/particle partition coefficient, K_p (m^3 μg^{-1}) (Harner & Bidleman, 1998):

$$K_p = (C_p / C_{TSP}) / C_g \qquad (4.4)$$

where C_p and C_g are the organic compound concentrations in the particulate and gas phases, respectively (pg m^{-3}), and C_{TSP} is the concentration of total suspended particles in the air (μg m^{-3}).

The octanol-air partitioning coefficient (K_{OA}) can be used to predict K_p with the assumption of predominant distribution process is absorption (Harner and Bidleman, 1998). The relationship between K_P and K_{OA} is:

$$K_p = (f_{OM}\ MW_{OCT}\ \zeta_{OCT})\ K_{OA} / (\rho_{OCT}\ MW_{OM}\ \zeta_{OM}\ 10^{12}) \tag{4.5}$$

where f_{OM} is the fraction of organic matter phase on TSP, MW_{OCT} and MW_{OM} are the mean molecular weights of octanol and the organic matter phase (g mol^{-1}), ρ_{OCT} is the density of octanol (0.820 kg L^{-1}), ζ_{OCT} is the activity coefficient of the absorbing compound in octanol, ζ_{OM} is the activity coefficient of the compound in the organic matter phase. With the assumptions that ζ_{OCT}/ζ_{OM} and $MW_{OCT}/MW_{OM}=1$, Equation (4.5) can be written as:

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \tag{4.6}$$

Junge-Pankow Adsorption Model is also used in predicting the partitioning of POPs, associated with particles. In this model, aerosol surface area per unit volume of air(θ) and a compounds sub-cooled liquid vapor pressure (P_L) as a function of the ambient temperature control the fraction sorbed to airborne particles (Halsall, Sweetman, Barrie, & Jones, 2001). The Junge-Pankow model can be described as:

$$\phi = c\ \theta / (c\ \theta + P_L) \tag{4.7}$$

where ϕ is the fraction sorbed to aerosol, the parameter c (Pa cm) is related to the heat of desorption from the particle surface (J mol^{-1}), the heat of vaporization of compound (J mol^{-1}), and the moles of adsorption sites on the aerosol (mol cm^{-2}). c is usually taken as 17.2 Pa cm and θ is often assumed to be 1.1×10^{-5} cm^2 cm^{-3}. (Bidleman, & Harner, 2000; Chen et al., 2006). Particle fracrion, ϕ was then calculated from K_p and TSP through

$$\phi = (K_p\ C_{TSP})/(1+K_p\ C_{TSP}) \tag{4.8}$$

Temperature dependent K_{OA} values were calculated using the regression parameters (A and B) given by Harner & Shoeib (2002) ($\log K_{OA} = A + B/T$). The regression parameters were not available for BDE-209. Therefore, log K_{OA} values of BDE-209 were determined using its dimensionless Henry's law constant (H′) (Cetin and Odabasi, 2005) and log K_{OW} values calculated based on the data from Braekevelt et al. (2003). The temperature dependent P_L values of PBDE congeners were calculated using the regression parameters by Tittlemier et al. (2002). The influence of temperature on P_L values of BDE-209 could not be accounted. Therefore, a log P_L value of -9.50 (calculated for 25°C from the equations based on bromine content given by Tittlemier et al., 2002) was used for all samples. Organic matter contents of airborne particles in this study were averaged as 55±8 % and average TSP concentrations were in the range of 113 (Urban 1)-52 $\mu g\ m^{-3}$ (Urban 2). OM content was not determined at Urban 2 and Industrial sites. Therefore, the average f_{OM} value of 0.50 measured previously in Izmir region was used to calculate log K_p values.

Pankow (1987) have suggested that both adsorptive and absorptive partitioning mechanisms predict that at a given temperature K_p values will depend on the sub-cooled liquid vapor pressure (P_L) and it is expressed as:

$$\log K_p = m \log P_L + b \tag{4.9}$$

where m and b are constants. Plots of log K_p vs. log P_L for experimental gas/particle partitioning data are usually well correlated and m values should be near -1. However, slopes of these plots derived from ambient air sampling data often deviate from -1 possibly because of sampling artifacts and/or nonequilibrium conditions or thermodynamics factors (Bidleman, & Harner, 2000; Finizio, Mackay, Bidleman, & Harner, 1997). Similarly, plots of log K_p versus log K_{OA} have been used in field and laboratory studies to evaluate the gas-particle partitioning of POPs in urban and rural particulate matter (Shoeib & Harner, 2002; Falconer & Harner, 2000). A good correlation between log K_p and log K_{OA} and a slope near 1 indicates that octanol is a good surrogate for the partitioning of POPs into aerosol organic matter (Falconer & Harner, 2000).

The regressions between K_p and P_L were generally well correlated and the regression parameters, *m* and *b* were -0.17 to -0.48, and -2.7 to -4.3, respectively and the r^2 values were between 0.61 and 0.99 (Figure 4.3). Good correlations were also obtained for measured log K_p vs. log K_{OA} plots (Figure 4.3). The regression parameters, *m* and *b* were -0.17 to -0.61, and -3.7 to -9.0, respectively and the r^2 values were between 0.70 and 0.98. However, especially at lower ambient temperatures (<3°C), dependencies of log K_p values with P_L and K_{OA} decreased with lower r^2 and *m* values. Recently, the same trend was also observed for PCDD/Fs in an urban region in Japan at temperatures lower than 5°C (Kadowaki & Naitoh, 2005). It was suggested that this decrease in relationship with K_p and P_L in lower temperatures should probably be caused by the gas adsorption artifacts during sampling with filter/sorbent samplers. Mader & Pankow (2001) investigated this artifact in their measurements with quartz fiber filters and the results indicated that the gas adsorption artifact cause positive biases in measured K_p values. However, sampling artifacts result in curved plots which were not observed in the present study.

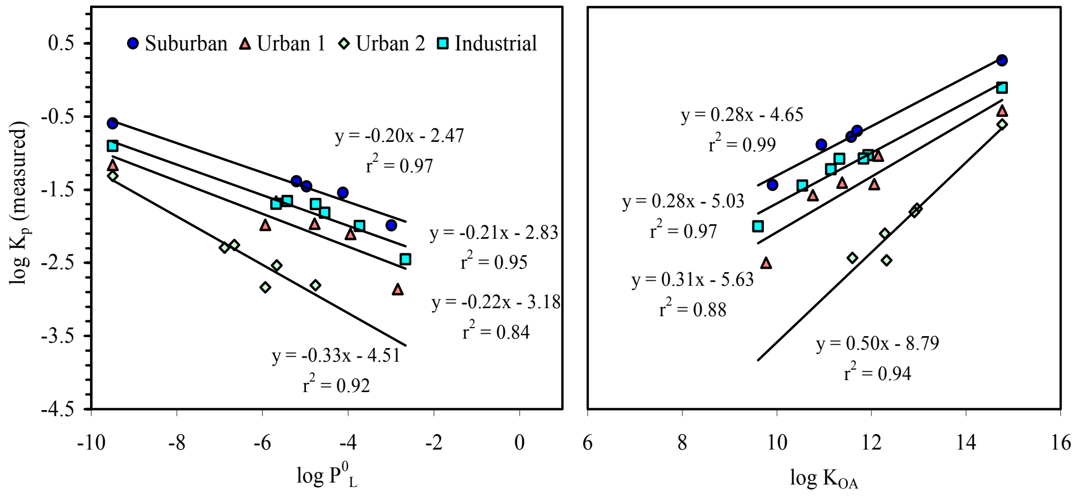

Figure 4.3 Plots of log K_p (m^3 μg^{-1}) measured in four sampling sites vs. log P°_L and log K_{OA} for selected days.

Even though strong correlations were observed between log K_p and log P_L, and log K_p and log K_{OA}, the slopes were significantly different than -1 and 1, respectively. In a plot of log K_p vs. log K_{OA}, slope values of 0.45-099 for OCPs (Sofuoglu et al., 2004), 0.5 for PCBs and PCNs (Helm & Bidleman, 2005) and for log K_p and log P_L plots, slopes of -0.3 to -0.7 for PCBs (Lohmann, Harner, Thomas, & Jones, 2000) and -0.5 (Helm & Bidleman, 2005) for PCNs and PCBs were reported previously. Recently, Goss & Schwarzenbach (1998) questioned the necessity of a slope of 1 for equilibrium partitioning when log K_p is plotted vs. log K_{OA} and they concluded that the slope might deviate significantly from 1. Deviations from a unity slope further indicate that atmospheric particles have sorbing properties different from that of octanol.

The comparison of the average measured particle fraction (100 × ϕ) of PBDEs with the ones predicted by K_{OA}-based model (using Equation 4.6) is illustrated in Figure 4.4. A good agreement was obtained between the measured and predicted ϕ values for BDE-28 (Figure 4.4). However, K_{OA}-based model tends to overestimate the sorption of other congeners. Chen et al. (2006) have also performed a study on gas/particle partitioning of PBDEs. OM content of particles in their study was assumed to be 10 and 20% lower than those measured in the present study. Similarly, they have found that the absorption model overestimated the partitioning of PBDEs, but generally prediction was better with the assumption of 10% OM. Using the K_{OA}-based model Shoeib et al. (2004) observed a good predictability for all PBDE congeners (excluding BDE-209). However, they have performed this study in indoor air with the assumption of TSP concentrations of 30 μg m^{-3} and 20% organic matter content. In the present study, K_{OA}-based model calculations were repeated with the assumption of 10% OM (Figure 4.4). Lower OM content push the K_{OA}-based model lines right, resulting in better agreement between the modeled and measured values except for BDE-28 and -209. These results indicated that K_{OA} model is very sensitive to OM and TSP content. Thus, the relatively better agreement between the experimental and modeled partition coefficients observed in previous studies may be due to the assumed OM and TSP contents.

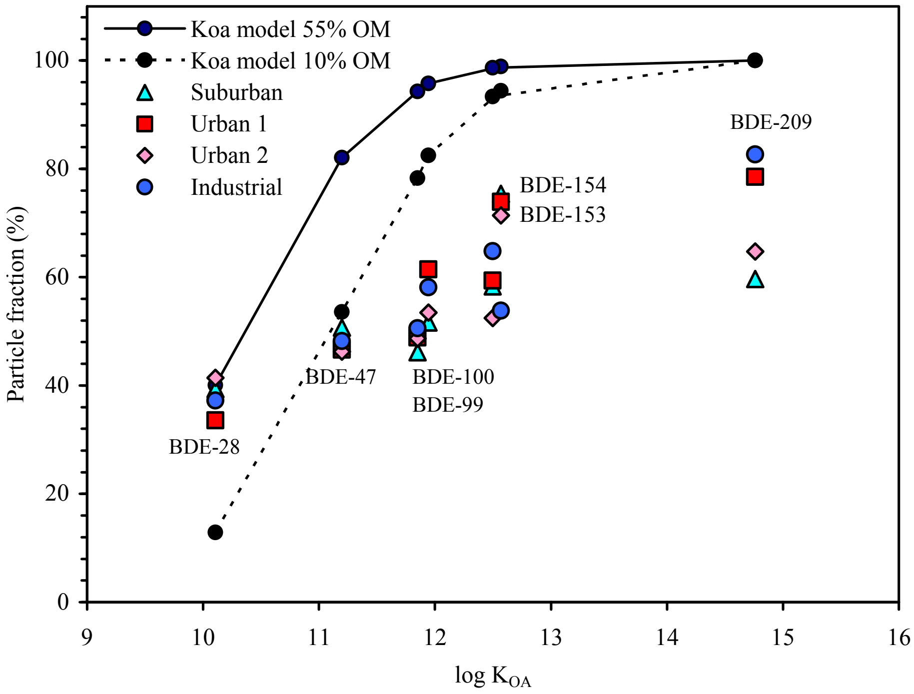

Figure 4.4 Comparison of the measured particle fraction of PBDEs with K_{OA}-based model results.

Figure 4.5 compares the average measured particle fraction (100×ϕ) of PBDEs (Equation 4.8) with those predicted by Junge-Pankow adsorption model (Equation 4.7). This model underestimated the particle fraction of BDE-28 and overestimated the values for other congeners. Chen et al. (2006) also found the similar results and mentioned the overestimating tendency of this model for other classes of POPs. Predictions of this model mainly depend on assumptions of parameters such as c value and θ. Although c value was often chosen as 17.2, Pankow (1987) suggested a value of 13.3 Pa cm based on field data. Junge-Pankow model calculations were repeated assuming a c value of 13.3 Pa cm (Figure 4.5). A better agreement was observed for BDE-47, -99 and -100. The estimated fraction of higher molecular weight PBDEs were changed slightly while the value for BDE-28 that was already underestimated became worse. Helm & Bidleman (2005) have also observed similar results for PCNs and PCBs and discussed the uncertainties of this model. Kadowaki & Naitoh (2005) have also mentioned the uncertainties in c and θ parameters and they suggested that appropriate values should be used to obtain a better predictability for Junge-Pankow model.

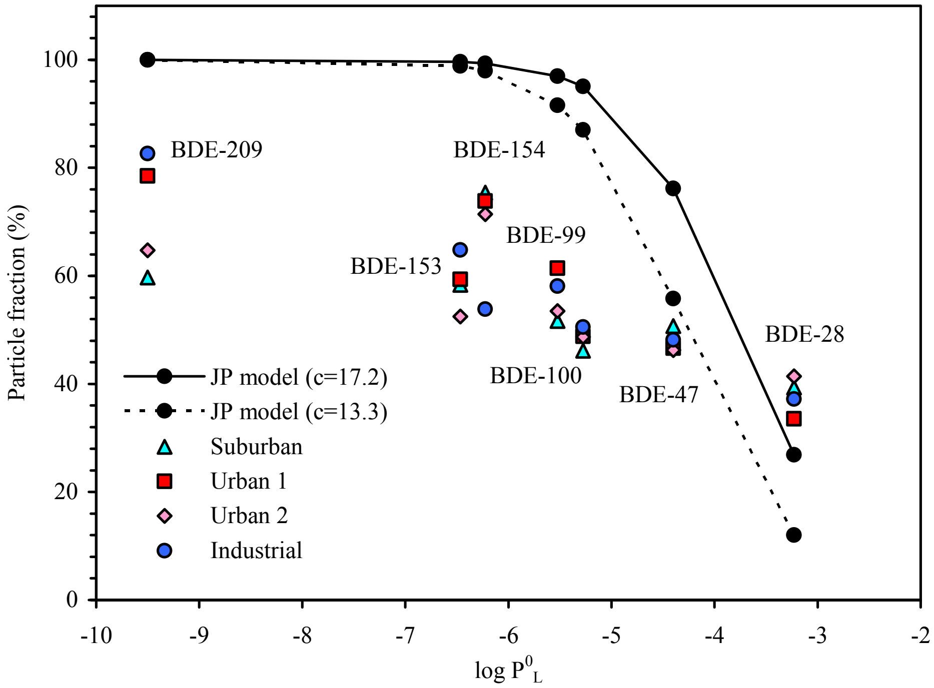

Figure 4.5 Comparison of the measured particle fraction of PBDEs with model results of Junge-Pankow.

Gas-particle partitioning models estimate that higher brominated congeners like BDE-209 are expected to be particle bound >99% (Harner & Shoeib, 2002). However, Agrell et al. (2004) have found that BDE-209 was mainly in gas phase (>90%) at an urban site while it was100% in gas-phase at a rural site. In southern Ontario, BDE-209 was found only in particle-phase (Gouin et al., 2006). It was suggested that the reason for not detecting BDE-209 in the gas-phase may be its sorption to the glass fiber filter during sampling (Gouin et al., 2006). The average proportion of BDE-209 in particle-phase was 70±22% at the four sites of the present study that lies between the extreme values (0-100% particle-phase) reported by Agrell et al. (2006) and Gouin et al. (2006). Since there are only a few studies, the phase partitioning of BDE-209 should be further investigated. Also, it may be necessary to recalibrate the existing models or to develop new empirical relationships to better describe the gas/particle partitioning of BDEs.

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4.2 Particle Phase Dry Deposition Fluxes and Velocities

The range for particle-phase fluxes of individual PBDEs measured with dry deposition plates was 1.8 (BDE-28) to 49.4 (BDE-209) ng m^{-2} day^{-1} in Suburban site and 2.2 (BDE-154) to 107.5 (BDE-209) ng m^{-2} day^{-1} in Urban site (Table 4.6). Average fluxes of $\sum_7$PBDE for both sites were 67.6 and 136.6 ng m^{-2} day^{-1}, respectively. Particulate fluxes were dominated by BDE-209 that accounted for 49 and 76% of $\sum_7$PBDE fluxes in Suburban and Urban sites, respectively. The average flux of BDE-209 was ~2 times higher at Urban site than those obtained for Suburban site. This result is consistent with higher TSP concentrations at Urban site (112.7±36.0 µg m^{-3}) compared to those measured at 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 Urban site were approximately 2 times higher than those obtained in Suburban site while the dry deposition velocities were lower in Urban site resulting in similar deposition fluxes in both sites for other six congeners.

Particle-phase dry deposition of PBDEs has not been studied extensively. ter Schure et al. (2004) have reported a median dry flux for BDE-209 as 77.1 ng m^{-2} day^{-1} and $\sum_8$PBDE flux (excluding BDE-209) as 18.4 ng m^{-2} day^{-1} near a solid waste incineration plant. They have measured BDE-209 and $\sum_8$PBDE fluxes as 10.9 and 7.0 ng m^{-2} day^{-1}, respectively at an urban reference site.

Table 4.6 Average particle phase dry deposition fluxes and velocities of individual PBDEs.

	Dry deposition flux (ng m^{-2} day^{-1})		Dry deposition velocity (cm s^{-1})	
Congener	Suburban	Urban	Suburban	Urban
BDE-28	1.8±0.5	2.4±1.4	11.5±2.2	7.8±3.5
BDE-47	6.1±2.6	6.0±3.5	9.2±4.6	3.9±1.7
BDE-100	3.0±1.0	3.6±1.9	8.4±3.9	6.4±2.5
BDE-99	4.9±2.8	6.7±5.2	5.7±3.1	3.1±1.6
BDE-154	2.7±1.8	2.2±0.8	6.5±3.8	2.8±1.4
BDE-153	2.9±1.7	2.6±0.6	7.6±1.3	4.6±1.6
BDE-209	49.4±89.0	107.5±114.79	3.9±3.6	2.9±1.8

Particle phase dry deposition velocities for PBDEs were calculated by dividing the particulate fluxes measured with dry deposition plates by ambient particle phase concentrations (Equation 2.1) and presented in Table 4.6. They ranged from 11.5 (BDE-28) to 3.9 cm s^{-1} (BDE-209) for Suburban site and 7.8 (BDE-28) to 2.8 cm s^{-1} (BDE-154) for Urban site with an overall average velocity of 5.8±3.7 cm s^{-1} for both sites. The particle-phase PBDE fluxes and ambient concentrations correlated well (r^2=0.84, p<0.01) (Figure 4.6). 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 that is in good agreement with the average value of 5.8 cm s^{-1} reported above.

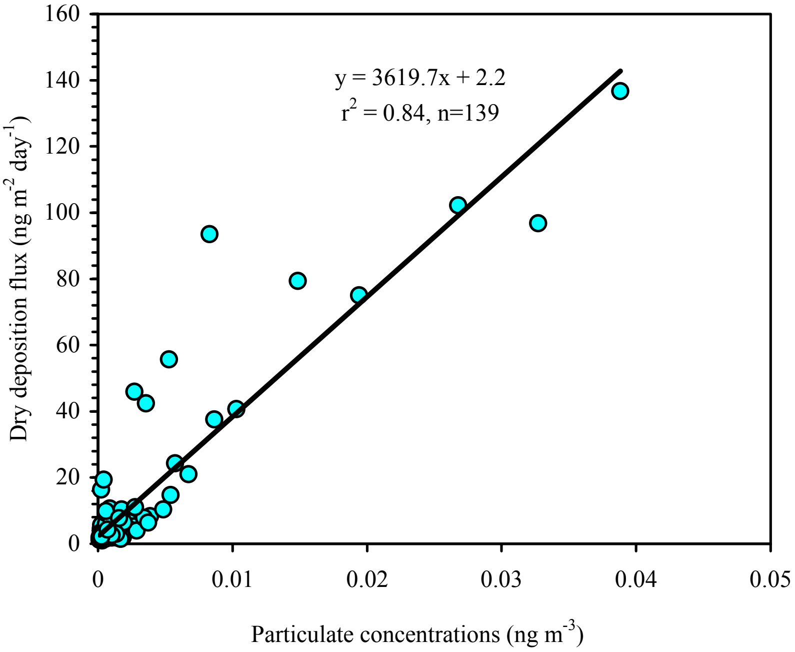

Figure 4.6 Relationship between ambient particle phase PBDE concentrations and particulate PBDE fluxes measured with dry deposition plates.

Dry deposition velocities of PBDEs were lower in Urban site than those calculated for Suburban site (Table 4.6). 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 can be attributed to larger particles from re-suspension of polluted soil and dust particles from unpaved roads and non-vegetated areas in Suburban site. The average wind speed was also significantly higher in the Suburban site (6.8±2.3 m s^{-1}) compared to Urban site (3.5±1.9 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 (Odabasi, Vardar, Sofuoglu, Tasdemir, & Holsen, 1999).

ter Schure et al. (2004) have recently reported that the median dry particle deposition velocities of BDEs ranged from 0.4 to 49 cm s^{-1}. 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 (Lee et al., 1996; Odabasi, Sofuoglu et al., 1999; Vardar, et al., 2002; Tasdemir et al., 2004). PBDE deposition velocities determined in this study were similar to those reported for other POPs.

4.3 PBDE Concentrations in Soil

Soil samples were collected at 13 different sites. A bag filter dust from an electric arc furnace of steel plant was also analyzed. Water and organic matter contents and $\sum_7$PBDE concentrations found in these sites were presented in Table 4.7. The highest $\sum_7$PBDE concentration (2.84×10^6 ng kg^{-1} dry weight) was found around an electronic industry. Four additional soil samples around the electronic industry were collected and analyzed to determine that whether this anomalously high concentration caused by a sampling artifact. Nearly the same concentration (2.63×10^6 ng kg^{-1}) was found at soil collected from the south of industry and relatively high concentrations were also obtained from other sites (3.69×10^5 and 1.07×10^5 ng kg^{-1} for east and north sites, respectively). The concentration of $\sum_7$PBDE obtained from bag filter dust of the steel plant was also seriously high (2.05×10^5 ng kg^{-1}), indicating these industries are very likely to be PBDE sources. BDE-209 was the dominant congener in both industries. Six congeners detected in soil collected near the electronic industry accounted for 0.8% of $\sum_7$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 had also high PBDE concentrations. $\sum_7$PBDE concentrations were 21998, 44160, and 98381 ng kg^{-1} at soils around the industry, Industrial sampling site, and Bozkoy (affected by steel plant emissions due to its location and prevailing wind direction), respectively (Table 4.7, Figure 3.3). However, in Torbali industrial site, $\sum_7$PBDE concentration was found to be the lowest indicating that there is not any nearby PBDE sources.

Table 4.7 Properties and concentrations of soil samples.

Site No	Description	Water content (%)	Organic Matter (%)	Soil conc. of $\sum_7$BDE (ng kg^{-1} dry wt)[a]
A	Industrial Sampling Site	7.7	7.6	44160
B	Suburban Sampling Site	1.7	9.3	840
C	Urban Sampling Site	0.7	5.0	18604
1	Steel Plants (Industrial)	3.4	7.3	21998
2	Bozkoy (Industrial)	5.2	17.7	98381
3	Sehit Kemal (Suburban)	5.9	10.3	3109
4	Aliaga commercial site (Suburban)	8.6	9.9	6861
5	Petkim Housings (Residential-Industrial)	6.6	7.6	1011
6	Agora (Urban)	3.7	9.1	8742
7	Yamanlar (Rural)	2.6	9.2	2272
8	Electronic industry	0.7	4.6	2840494
9	Kemalpasa (Industrial)	0.9	3.1	3108
10	Torbali (Industrial)	1.3	4.0	504
11	Filter Dust	0.4	2.3	204866

[a] n=2 for A, n=5 for B, n=1 for the other sites.

In all soil samples, BDE-209 was the most abundant congener and accounted for 79 to 99% of the total soil concentrations, followed by BDE-99 and -47 (Figure 4.7). Soil concentration of BDE-209 was 5 to 3615 times higher than concentrations of Σ_6PBDEs. 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 (ter Schure et al., 2004). 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 ∑$_7$PBDE concentration in soils around the electronic industry is probably due to the current use of deca-product during production (Figure 4.7).

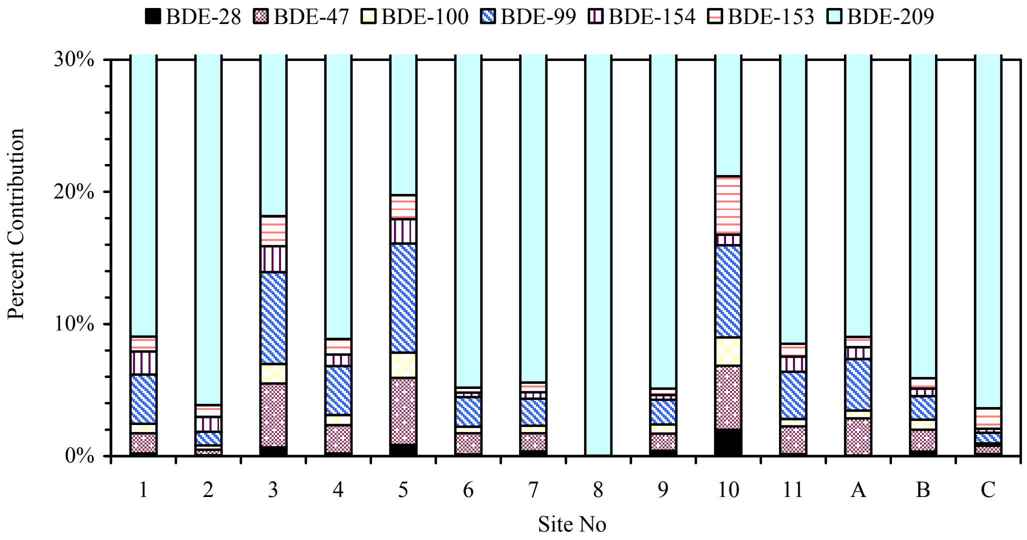

Figure 4.7 Percent contributions of individual congeners to ∑$_7$PBDE concentrations in soil (See Table 4.7 for site descriptions)

Generally, industrialized and urbanized regions had higher soil concentrations while Suburban soils have relatively low PBDE concentrations (∑$_7$PBDE concentrations were found as 560 ng kg^{-1} at the Suburban sampling site) (Table 4.7). This is consistent with a recent study reporting that in United Kingdom concentrations of PBDEs in soil decease with increasing distance from the city center (Harrad, & Hunter, 2006). In urban soil, it was found that ∑$_6$PBDE concentration (excluding BDE-209) was up to 110900 ng kg^{-1}, while in rural areas concentration decreased to 4545 ng kg^{-1} (Harrad, & Hunter, 2006). Soil concentrations observed in the present study were comparable to this range. Considering that BDE-209 was not measured in the UK study, it can be concluded that contamination of UK soils with penta-BDE mixture were significantly high compared soils in the Izmir area.

4.3.1 Soil-Air Exchange

Soil/air 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 (Meijer et al., 2001). The equilibrium partitioning of a chemical between air and soil is described by the dimensionless soil-air partition coefficient, K_{SA} as fallows:

$$K_{SA}=C_S\,\rho_s/C_A \tag{4.10}$$

where C_S is the soil concentration (ng g^{-1}, dry weight), ρ_s is the density of soil solids (g m^{-3}), and C_A is the gas-phase air concentration (ng m^{-3}). If the system is not at equilibrium the use of the term K_{SA} is incorrect and the values obtained from Equation (4.10) are defined as soil-air quotients (Q_{SA}) (Meijer, Shoeib, & Jantunen et al., 2003).

K_{SA} is dependent on temperature, humidity and the chemical and soil properties (Meijer, Shoeib, & Jantunen et al., 2003). Partitioning of persistent organic pollutants 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 (Harner et al., 2000). Hippelein & Mclachlan (1998) formulated a linear relationship that relates K_{SA} to K_{OA} and the organic carbon fraction of the soil as fallows:

$$K_{SA}=0.411\,\rho_s\,\phi_{OC}\,K_{OA} \tag{4.11}$$

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} (Hippelein & Mclachlan, 1998; Bidleman & Leone, 2004). Temperature dependent K_{OA} values can be measured directly for compounds of interest, while K_{SA} is soil-specific.

K_{SA} can also be expressed as a ratio of the fugacity capacity (Z value; mol m^{-3} Pa^{-1}) for soil and air:

$$K_{SA}=Z_{Soil}/Z_{Air} \tag{4.12}$$

The following equation can be used to calculate Z_{air} values:

$$Z_{Air}=1/(RT) \tag{4.13}$$

where R is the universal gas constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T is absolute temperature (K). Combining Equations (4.11), (4.12), and (4.13), Z_{soil} can be expressed as:

$$Z_{Soil}=0.411\rho_s\,\phi_{OC}\,K_{OA}/(RT) \tag{4.14}$$

Concentration of compounds (C_i, mol m^{-3}) can be converted fugacity (f_i, Pa) in medium *i* using the relationship:

$$f_i=C_i/Z_i \tag{4.15}$$

When performing this conversion for soil, we assume that the fugacity capacity of soil is due to entirely the organic matter fraction (Bidleman & Leone, 2004; Meijer et al., 2001).

Concurrent air and soil concentrations are ideally used to assess the fugacity gradients of individual PBDEs between the soil-air interfaces. The soil-air fugacity ratio (f_S/f_A) greater than 1 indicate that the soil is a source with net re-volatilization of compounds from soil; values less than 1 indicate that the soil is a sink and net gas-phase deposition occurs from air to soil.

The net soil/air gas exchange flux is driven by the fugacity difference between air and surface soil (Jaarsveld, Van Pul, & De Leeuw, 1997). The gas flux is a function of dimensionless soil-air partition coefficient, the concentration gradient and the overall mass transfer coefficient. The net flux (F_g, ng m^{-2} day^{-1}) is:

$$F_g = MTC\ (C_A - C_s\rho_s/K_{SA}) \tag{4.16}$$

where C_s is soil concentrations (ng g^{-1}, dry weight) and C_A is air concentrations (ng m^{-3}), MTC is overall mass transfer coefficient (cm s^{-1}), ρ_s is the density of the soil solids (kg L^{-1}) and K_{SA} is soil-air partition coefficient.

The overall mass transfer coefficients (MTC) of gaseous pollutants can be predicted by resistance model by analogy to electrical resistance. 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:

$$MTC = 1/(R_a + R_b + R_c) \tag{4.17}$$

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 can be represented by Hicks, Baldocchi, Meyers, Hosker, & Matt (1987). The atmosphere was assumed to be unstable over the sampling period, thus for unstable atmospheres:

$$R_a = 9/(u_{10}\sigma_\theta^2) \tag{4.18}$$

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.

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 & Hicks (1977) and is given as

$$R_b = (2/\kappa u^*)\ (Sc/Pr)^{2/3} \tag{4.19}$$

where Pr is Prandtl number of air (~0.72), Sc is the Schmidt number (ν/D_A); ν (cm^2 s^{-1}) is the kinematic viscosity, D_A (cm^2 s^{-1}) is the molecular diffusion coefficient of the contaminant in air, κ (~0.4) is the Karman's constant, 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.

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% (Meijer, Shoeib, Jantunnen et al., 2003, Harner, & Shoeib, 2002) and uncertainty in the overall MTC was 40%.

The average water and organic matter contents of soil samples were found as 5.2 and 7.4% (in dry sample), respectively. Organic matter fraction was assumed to be 1.5 times of the organic carbon fraction and the density of soil solids was taken 1.3 g cm^{-3} for all calculations. Temperature dependent K_{OA} values of the PBDE congeners used in Equation (4.11) were calculated as described in Section 4.1.4.

For a system in equilibrium, f_S/f_A value is approximately equal to 1 (Harner et al., 2000; Cousins & Jones, 1998). 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±0.21 (i.e., a range of 0.79-1.21). The fugacity ratios of all compounds fall outside this uncertainty range and we can be confident that for these compounds the soil and ambient air are not in equilibrium. Figure 4.8 shows the deposition tendency of congeners to the soil with fugacity ratios for all congeners <1.0. Figure 4.8 also shows the relationship between fugacities of soil and air (r^2=0.33-0.70). This close link between air-soil concentrations may suggest that atmosphere controls the surface soil PBDEs levels.

The calculated instantaneous soil-air gas exchange fluxes of PBDEs using Equation 4.16 were presented in Table 4.8. The average net $\sum_7$PBDE flux ranged from 12.34 (Urban) to 23.39 (Industrial) ng m^{-2} day^{-1} in summer, while in winter they ranged from 3.34 (Urban) to 11.56 (Suburban) ng m^{-2} day^{-1}. All congeners were deposited in both periods and all sites. Generally, summer fluxes were higher than winter fluxes except in 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.

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

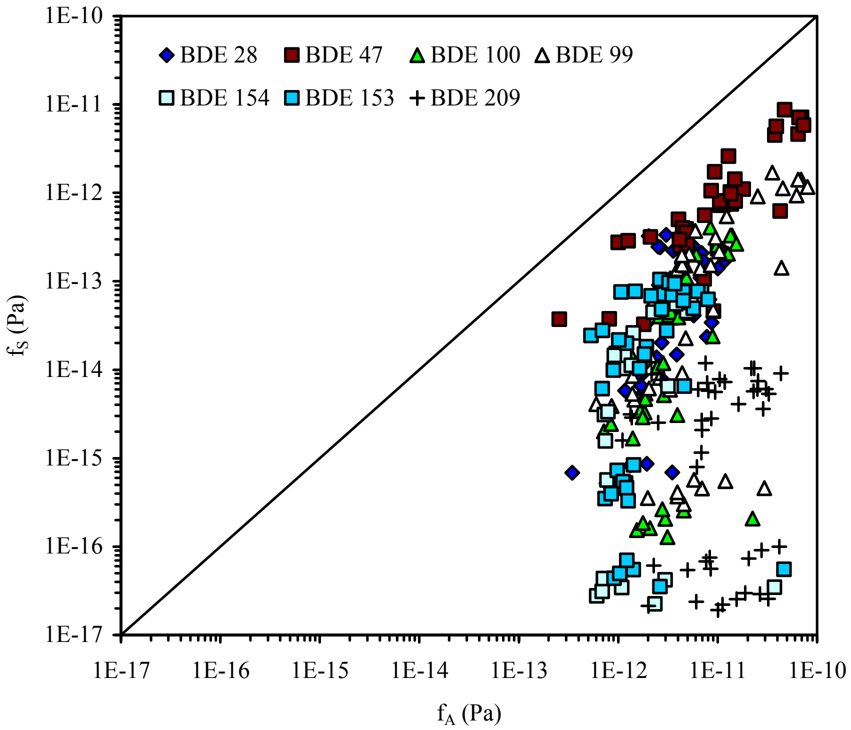

Figure 4.8 Relationship between the PBDE fugacities in soil and air for all congeners at all sites.The solid diagonal line represents a 1:1 relationship (equilibrium).

Table 4.8 Soil/air gas exchange flux of PBDEs for summer and winter periods (ng m^{-2} day^{-1}).

Congener	Summer			Winter		
	Suburban	Urban	Industrial	Suburban	Urban	Industrial
BDE-28	0.51±0.19	0.78±0.68	0.81±0.36	0.30±0.13	0.45±0.23	0.79±0.44
BDE-47	1.08±0.86	2.73±2.31	6.97±2.37	1.06±0.69	0.72±0.43	1.89±0.95
BDE-100	0.54±0.27	0.66±0.35	1.73±0.59	1.05±0.57	0.41±0.28	0.64±0.31
BDE-99	0.78±0.61	1.18±0.67	8.32±3.48	2.18±1.68	0.63±0.42	2.00±1.32
BDE-154	0.39	0.36±0.16	0.72±0.25	0.62±0.56	0.16	0.28±0.11
BDE-153	0.46±0.21	0.73±0.50	1.00±0.40	0.55±0.32	0.15±0.05	0.45±0.24
BDE-209	9.23±9.53	6.14±5.95	3.84±3.98	7.64±6.10	1.15±1.08	5.02±4.60
Σ_7BDE	12.58±9.10	12.34±9.84	23.39±10.94	11.56±9.38	3.34±1.79	10.96±6.13

Table 4.9 shows the annual deposition fluxes of PBDEs in Suburban site including air/soil gas exchange, dry deposition and recently measured wet deposition (Cetin, 2006) fluxes. It was estimated that wet deposition also contributes

significantly to the total PBDE deposition to soil. Dry particle, wet, and gas deposition contributes 60, 32, and 8%, respectively to annual PBDE flux to the Suburban soil.

Table 4.9 Annual deposition fluxes of PBDEs in Suburban sampling site (ng m^{-2} $year^{-1}$)

	Wet flux	Dry flux	Gas flux
BDE-28	274	740	150
BDE-47	2080	4848	390
BDE-100	588	1878	290
BDE-99	3000	5635	524
BDE-154	223	1685	214
BDE-153	410	1619	180
BDE-209	12379	18614	3100
Σ_7BDE	18953	35019	4847
% Contribution	32	60	8

4.4 Window Organic Films

4.4.1 Comparison of Indoor and Outdoor Films

The summary of average concentrations of individual PBDEs are presented in Table 4.10. Average total PBDE ($\sum_7$PBDE) concentrations of organic films collected from residential sites ranged from 4.3 to 24.3 and 12.6 to 23.3 ng m^{-2} for indoor and outdoor film samples, respectively (Figure 4.9). Indoor/outdoor film concentration ratios ranged between 0.3-1.1 indicating that residential sites may be affected by both indoor and outdoor PBDE sources. The variations in indoor film concentrations may be due to different number and age of possible PBDE sources and/or different ventilation systems of buildings. However, the variations in outdoor film concentrations can be due to effect of outdoor sources.

Table 4.10 Average concentrations and range of individual PBDEs obtained from indoor and outdoor organic films for all regions (ng m^{-2})

Congener	Indoor			Outdoor		
	Min	Max	Avg±SD	Min	Max	Avg±SD
BDE-28	0.1	1.9	0.4±0.4	0.1	1.9	0.4±0.4
BDE-47	0.3	51.0	9.0±13.2	0.3	11.6	1.9±2.6
BDE-100	0.1	74.6	6.4±16.4	0.2	4.2	0.8±0.9
BDE-99	0.1	464.6	34.1±102.4	0.2	15.7	2.5±3.6
BDE-154	1.0	58.9	13.4±20.1	0.1	1.9	0.7±0.6
BDE-153	0.2	75.7	10.4±21.8	0.2	2.2	0.7±0.7
BDE-209	3.3	287.3	32.9±64.8	7.1	225.2	57.4±67.1
$\sum_7$PBDE	4.3	696.0	97.7±167.6	12.6	238.3	64.0±72.5

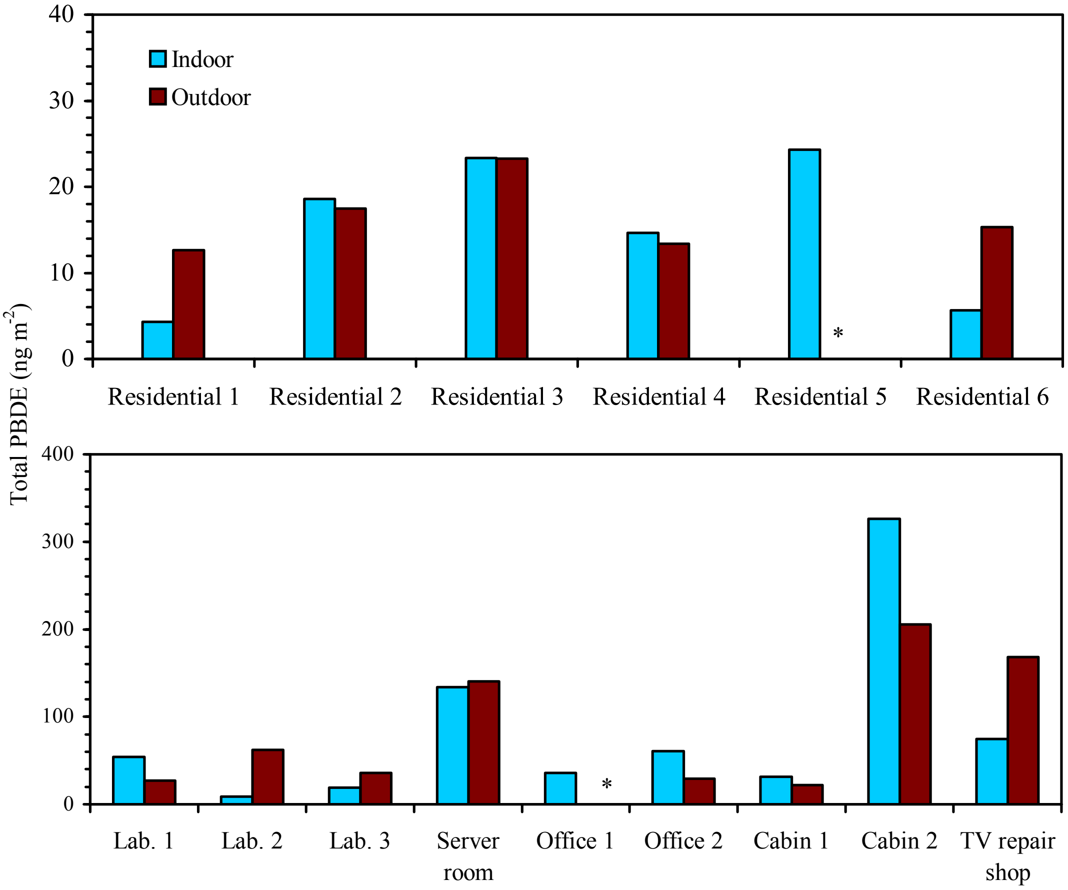

Figure 4.9 ∑7PBDE concentrations of both indoor and outdoor organic films collected from different sites with different characteristics. (*) not analyzed.

$\sum_7$PBDE concentrations obtained from the samples collected from Dokuz Eylul University Campus have variations in a site and indoor and outdoor basis. Considering indoor films, Lab. 1 (air pollution lab) and Server room have the highest concentrations with up to 134 ng m^{-2}, while the concentrations in Lab. 2 (computer lab with new computers produced in 2001) and Lab. 3 (GC lab) were relatively low (8.8 and 19.3 ng m^{-2}, respectively). The common issue in those sites with higher indoor concentrations was the usage of old computers (produced before 1998). To confirm the measured high concentrations, both indoor and outdoor sampling of 4 windows including Lab 1, Server room, Office 1 and ambient air sampling Cabin 1, were replicated (Figure 4.10).

At this point, their last cleaning time was known as ~19 months. The $\sum_7$PBDE concentrations increased about 2 times in the replicate samples except for Lab.1 (about 13 times increase was observed in that site). Thicker organic film on window surfaces was shown to increase the accumulation of particles and particle-associated chemicals (Liu, & Chen et al., 2003). Thus, the very long exposure time may cause this 2-fold increase. However, the serious increase in Lab. 1 ($\sum_7$PBDE concentrations of up to 696 ng m^{-2}) may also be the result of using an additional old computer in that site within this period confirming that old computers are likely to be the PBDE sources. Recently, Hazrati and Harrad (2006) have also related the high indoor air PBDE concentrations to the use of old computers. The outdoor concentrations of these four windows were also relatively high, ranging from 22 to 141 ng m^{-2}, suggesting that outdoor films were impacted from indoor sources during manual ventilation. Their replicates were about 2 times higher than those obtained in their first sampling parallel with indoor concentrations (except for Sampling Cabin 1 which its replicate concentrations were lower) supporting the time-integrated increasing pattern of pollutants on thicker films. It was clear that Cabin 1 was not cleaned for a long time (longer than 19 months) before its first sampling and thus, probably this resulted in its lower replicate concentrations (Figure 4.10).

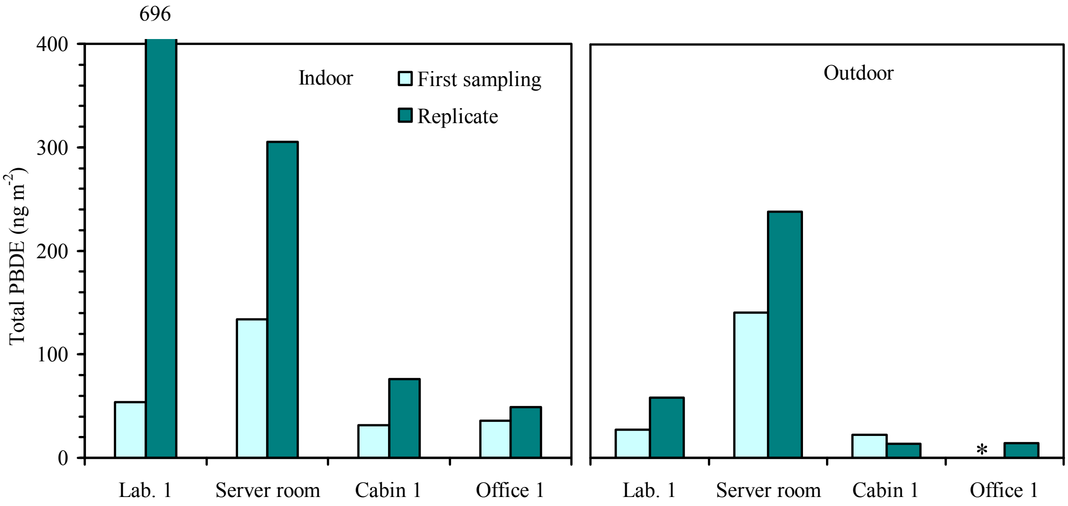

Figure 4.10 $\sum_7$PBDE concentrations of indoor and outdoor organic films collected from four sites in campus and their replicates. (*) not analyzed.

$\sum_7$PBDE concentration in outdoor film obtained from TV set repair shop was unexpectedly higher than indoor film concentration; 168.5 and 74.6 ng m^{-2}, respectively. Since PBDEs are used in electronic equipments of televisions, indoor concentrations were expected to be higher. Last cleaning time of outdoor window was known to be longer than indoor one in this sampling site. This may increase the organic film thickness and accumulation of pollutants. Also, the effect of indoor sources (TV parts) to outdoor window during ventilation may result in this higher outdoor concentration.

Both indoor and outdoor films collected from ambient air Sampling Cabin 2 near an industrial site (steel plants with electric arc furnaces) have relatively high $\sum_7$PBDE concentrations, 326 and 206 ng m^{-2}, respectively. High indoor concentrations may be due to the use of an old computer and various sampling and analytical equipment in a very small area. In Sampling Cabin 1, only one old computer used for meteorological data storage was present and this may be the reason of relatively lower indoor film concentrations in Cabin 1 than those obtained from Cabin 2. Steel plants are significant PBDE sources as recently was indicated by very high concentrations obtained from the nearby soil samples and a bag filter dust from an electric arc furnace. Therefore, the outdoor film concentrations collected near these plants were also high.

Recently, in Southern Ontario, Butt, Diamond, Truong, Ikonomou, et al. (2004) found that the total PBDE concentrations (sum of the concentrations o 41 congeners) were between 0.56-14.5 ng m^{-2} for outdoor window films and 19.4-75.9 ng m^{-2} for indoor films. Total PBDE concentrations at the Electronics Recycling Facility site were found to be 38.7 and 755 ng m^{-2} for outdoor and indoor films, respectively, confirming this industrial site as a PBDE source. They 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 (Butt, Diamond, Truong, Ikonomou, et al., 2004). In Manhattan, 6 weeks after the September 11th World Trade Center (WTC) attacks, $\sum_{41}$PBDE concentrations were found to range from 70 to 5910 ng m^{-2}, indicating the presence of great quantities of PBDE sources in WTC (Butt, Diamond, Truong, Ikonomou, Helm et al., 2004). Window film PBDE concentrations measured in the present study were within the ranges reported by these previous studies.

Indoor windshield film samples from 4 different vehicles including Nissan Micra, Alfa Romeo, Ford Fusion and Ford Focus (all 2004 or 2005 model cars) were also collected during winter and summer periods. The summary of results is presented in Table 4.11. In winter, Nissan Micra has the highest window film PBDE concentrations and the concentration for Ford Focus was the lowest. The indoor film PBDE concentrations were relatively low but comparable to concentrations observed at other indoor sites. Considering the comparably low time 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 very interesting that in summer, BDE-209, the most abundant congener of winter samples could not be detected in any vehicles. This can be explained by degradation of deca-BDE in sunlight (Söderström et al., 2004). Since automobiles can heat up to 90ºC, PBDEs may break down at much higher rates in solar-exposed cars then in other indoor environments. The concentrations of other congeners are very similar both in summer and winter periods. This is consistent with photolytic degradation property of deca-BDEs to lower congeners that were not included within target congeners in this study. Gearhalt & Pooselt (2006) have conducted a similar and 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 4.11). High sampling number, different model vehicles and/or different sampling condition may cause this wide range of concentrations.

Table 4.11 Average concentrations and range of individual PBDEs collected from indoor organic films of vehicles for summer and winter periods (ng m^{-2}).

	Winter (n=4)			Summer (n=4)			Literature[a]
	Min	Max	Avg±SD	Min	Max	Avg±SD	Avg.
BDE-28	0.2	0.26	0.22±0.03	0.12	0.24	0.17±0.06	3
BDE-47	1.33	2.48	1.91±0.47	0.29	1.06	0.82±0.36	65
BDE-100	0.35	0.7	0.53±0.15	0.23	0.31	0.27±0.03	53
BDE-99	1.42	3.29	2.34±0.77	0.42	1.12	0.93±0.34	158
BDE-154	0.12	0.24	0.18±0.06	0.11	0.23	0.18±0.06	32
BDE-153	0.15	0.31	0.22±0.08	0.14	0.4	0.28±0.11	41
BDE-209	2.82	92.78	25.72±44.71	ND	ND	ND	60
$\sum_7$PBDE	6.45	97.95	31.12±44.59	1.33	3.26	2.65±0.90	365[b]

[a] : Gearhart & Pooselt, (2006).

[b] : Sum of 11 congeners

4.4.2 Congener Patterns

In all outdoor film samples, BDE-209 was the most abundant congener with the average contribution of 87±11% to total PBDE concentrations. However, indoor films have variable congener patterns. Excluding 4 sites that have 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±8 % to total PBDE concentrations. In those 4 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±5% for other 3 cars in winter period, while in summer BDE-99 and -47 were the dominating congeners. Recently, Butt, Diamond, Truong, Ikonomou, et al. (2004) have found the same 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 (Butt, Diamond, Truong, Ikonomou, Helm et al., 2004).

To investigate the source profiles of measured PBDEs, they were fitted to a linear combination of the compositions of the technical products as applied for ambient air samples. The results of the fit are presented in Table 4.12, for indoor and outdoor film samples. Comparison of average and fitted congener profiles for all samples are also illustrated in Figure 4.11. The results of the fits show that samples collected from both outdoor and indoor films were dominated by penta and deca-mixtures; especially from indoor sites, up to 98% deca-BDEs were obtained. In Server room, indoor films also comprised of octa mixture suggesting presence of different sources of PBDEs in this site. Lab. 1, Office 1 and Cabin 1 samples were mostly composed of penta-mixtures in indoor film samples. The results of the fit of vehicle samples are also presented in Table 4.12. Except Nissan Micra, penta-mixture was dominant in all vehicles, while Micra consisted of deca technical product. All observed congeners except BDE-28 were fitted well to the commercial products ($p<0.01$) (Figure 4.11). r^2 values were 0.98 for indoor and 0.99 for outdoor samples and for both samples, slopes are 0.99 and intercepts are 0.21 and 0.09, respectively.

Table 4.12 Fractions of penta, octa and deca products in indoor and outdoor film samples

Sites	Indoor			Outdoor		
	f_P	f_O	f_D	f_P	f_O	f_D
Residential 1 (Suburban)	0.17	0.02	0.82	0.08	0.00	0.92
Residential 2 (Urban)	0.14	0.06	0.80	0.11	0.04	0.85
Residential 3 (Remote)	0.18	0.01	0.82	0.26	0.06	0.68
Residential 4 (Urban)	0.06	0.02	0.92	0.19	0.03	0.79
Residential 5 (Urban)	0.10	0.02	0.88			
Residential 6 (Urban)	0.15	0.09	0.76	0.06	0.03	0.91
Lab. 1-Air lab. (Suburban)	0.93	0.02	0.06	0.18	0.01	0.81
Lab. 2-Computer lab. (Suburban)	0.27	0.05	0.68	0.04	0.01	0.95
Lab. 3-GC lab. (Suburban)	0.06	0.01	0.93	0.03	0.01	0.96
Server Room (Suburban)	0.55	0.43	0.02	0.01	0.00	0.98
Office 1 (Suburban)	0.66	0.02	0.32	0.47	0.02	0.51
Office 2 (Suburban)	0.12	0.03	0.85	0.03	0.01	0.96
Sampling Cabin 1 (Suburban)	0.78	0.03	0.19	0.08	0.02	0.90
Sampling Cabin 2 (Industrial)	0.11	0.00	0.88	0.17	0.01	0.82
TV Repair Shop (Urban)	0.08	0.01	0.91	0.05	0.01	0.94
Vehicles						
Ford Fusion	0.65	0.01	0.34			
Ford Focus	0.53	0.02	0.45			
Nissan Micra	0.05	0.00	0.95			
Alfa Romeo	0.59	0.02	0.39			

However, this model tended to underestimate BDE-28. This may probably be due to higher volatilization tendency of low molecular weight congeners relative to higher ones and/or potential decomposition of higher congeners to lighters in the environment (Chen et al., 2006).

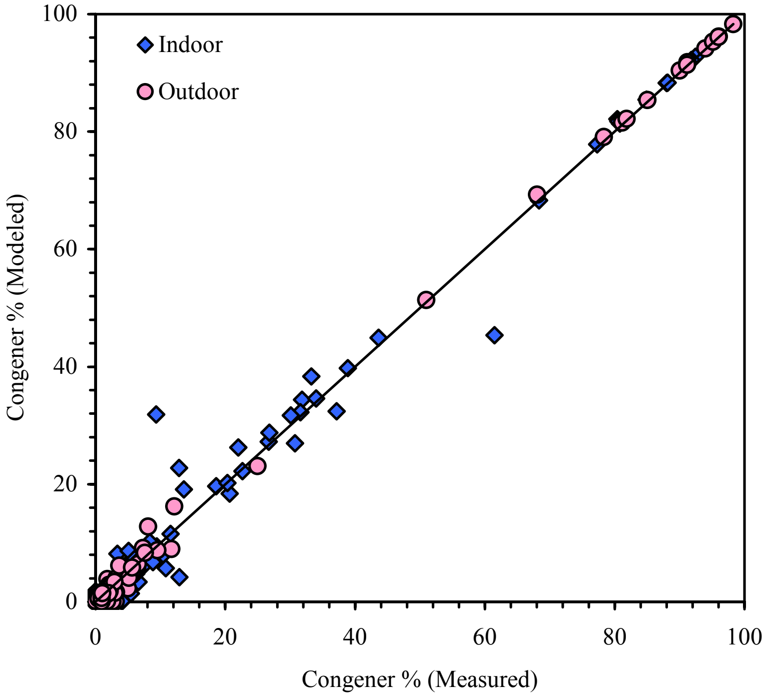

Figure 4.11 Comparison of congener profiles for all window organic film samples and fitted congener profiles for indoor and outdoor films.

4.4.3 Estimation of Gas-phase Ambient Air Concentrations

Gas phase compounds are capable of partitioning into the surface film, dependent on the relative fugacity between the air and the film. It is possible to determine ambient air concentrations with the knowledge of film-air partition coefficient (K_{FA}) and sampling rate (Shoeib and Harner, 2002). It was suggested that window organic films can be used as convenient passive samplers for ambient air and gas-phase air concentrations can be calculated with the assumption of gas-phase in air and compounds in film are at equilibrium (Butt, Diamond, Truong, Ikonomou, et al., 2004). Gas-phase air concentrations can be quantified using K_{OA} (Harner & Shoeib, 2002) and f_{oc} values:

$$K_{FA} = f_{oc}\, K_{OA} \tag{4.20}$$

where f_{oc} is the fraction of organic carbon in the film.

Recently, organic carbon fraction of films on impervious surfaces was assumed to be 7.65% (Liu, Diamond et al., 2003), 10% (Butt, Diamond, Truong, Ikonomou, et al., 2004; Kwamena et al., 2006), 5% (Lam et al., 2005). Gingrich et al. (2001) assumed the organic content of bulk surface films (organic phase plus particles) as 20% in their calculations. In ambient air of Izmir, average organic matter content of total suspended particles (TSP) was found as 57%. In Toronto, the range of mass percentage of $PM_{2.5}$ composed of organic carbon was found from 30 to 40% (Lee, Brook, Dabek-Zlotorynska, & Mabury, 2003). These differences in composition of surface films and typical particulate matter was hypothesized to be either due to the preferential deposition of larger diameter particles and/or greater losses via reaction of organic compounds in the films (Lam et al., 2005). The observation of low abundances of reactive PAHs compared to the unreactive ones in film samples collected from Toronto was suggested to be the evidence of losses of organic compounds via reactions (Gingrich et al., 2001).

In this study, organic carbon fraction was assumed to be 10%, which was the average of all other assumptions. 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 1µm (Beyer, Wania, Gouin, Mackay, & Matthies, 2002; Gill, Gradel, & Weschler, 1983; Gingrich et al., 2001). In model studies, to assess the reactions in surface films, film thickness was assumed to be 0.5 µm (Kwanema et al., 2006). This value was taken in this study. The ambient air temperature was higher than 30°C during the sampling of window organic films. Thus, the K_{OA} value at this temperature was calculated were calculated as described in Section 4.1.4.

Average calculated gas-phase concentrations of individual PBDEs are presented in Table 4.13 along with the recently measured concentrations in ambient air representative for Suburban, Industrial, and Urban sites. Calculated $\sum_7$PBDE gas phase concentrations ranged between 1.6-32.6 (average 6.2) pg m^{-3} for outdoor window films, while they were between 1.4-167.4 (22.2) pg m^{-3} for indoor films, consistent with the predominance of indoor sources of PBDEs. Calculated and measured values were similar for BDE-47 and -100. For these congeners, the gas-phase in air and compounds in film may be at equilibrium. However, calculated gas-phase concentrations were underestimated for BDE-99, -153, -154 and -209 and overestimated for BDE-28. Recently, it was reported that Equation 4.20 is suitable for compounds whose log K_{OA}<11 (Butt, Diamond, Truong, Ikonomou, et al., 2004). The log K_{OA} values of these four congeners are very high (>11) and their underestimated results agreed with this hypothesis. Butt, Diamond, Truong, Ikonomou, et al. (2004) have also calculated gas-phase air concentrations of PBDEs with the film-air partition coefficient and found the same trend that lower molecular weight PBDEs were overestimated and higher ones were underestimated. Therefore, organic films can give tentative results on gas-phase ambient air concentrations.

Table 4.13 Average outdoor calculated (using K_{FA}) and measured ambient air gas-phase concentrations of individual PBDEs (pg m^{-3}) and their log K_{OA} valus at 30°C.

Congener	log K_{OA} (at 30°C)	Calculated concentrations			Ambient air concentrations[c]		
		Campus (Suburban)	Residential (Urban)	Industrial	Suburban[d]	Urban	Industrial[d]
BDE-28	9.4[a]	1.654	3.770	15.572	0.31	0.72	1.18
BDE-47	10.3[a]	1.088	1.692	12.872	0.75	2.47	11.26
BDE-100	10.8[a]	0.091	0.208	1.219	0.35	0.65	2.62
BDE-99	11.1[a]	0.183	0.234	2.729	0.48	1.19	12.54
BDE-154	11.7[a]	0.005	0.031	0.084	0.20	0.29	1.10
BDE-153	11.5[a]	0.011	0.045	0.123	0.29	0.70	1.42
BDE-209	15.1[b]	0.000	0.001	0.006	5.96	6.41	6.20

[a] : Harner & Shoeib, 2002.

[b] : Calculated as described in Section 4.1.4.

[c] : Measured in present study at Campus, Yesildere and Horozgedigi regions.

[d] : Ambient air data obtained in these sites situated at locations near the correspondig outdoor sampling sites.

The results of this study showed that impervious surfaces such as window glasses are important media in urban areas that can act as both sources and sinks. Organic films should be used as a simple tool to evaluate atmospheric concentrations of PBDEs and they give information about sources of these pollutants. Considering people spend most of their time indoors, the film also provides a route of human exposure to PBDEs or other SOCs with similar characteristics such as PCBs, PAHs and/or pesticides.

4.5 Air-Water Exchange of PBDEs

4.5.1 Henry's Law Constants

The Henry's law constant (H) is an important parameter that plays a fundamental role in predicting the transport, behavior and fate of POPs in the environment and it is required to model the chemical transfer between air and water.

The Henry's Law constant is often expressed as (Bamford et al., 1999):

$$H = P_g/C_w \tag{4.21}$$

where P_g is the gas-phase partial pressure (Pa) and C_w is the dissolved concentration (mol m^{-3}). Using the ideal gas law [$p = (nRT)/V$] to convert partial pressure to moles per cubic meter (mol m^{-3}) of air, dimensionless Henry's law constant (H') can be obtained as:

$$H' = H/RT \tag{4.22}$$

The temperature dependence of H' can be depicted as:

$$-RT \ln H' = \Delta H_H - T\Delta S_H \tag{4.23}$$

where ΔH_H (J mol^{-1}) and ΔS_H (J mol^{-1} K^{-1}) are the enthalpy and entropy of the phase change from the dissolved phase to the gas phase, respectively. Solving Equation (4.23) for $\ln H'$ gives the following (Bamford et al., 1999):

$$\ln H' = -\Delta H_H/RT + \Delta S_H/R \tag{4.24}$$

After directly measuring H' at different temperatures, ln H' versus 1/T can be plotted and ΔH_H and ΔS_H can be obtained from the slope and the intercept, respectively.

Experimental H′ was calculated as follows:

$$H' = C_g/[(C_{w(n)} + C_{w(n+1)})/2] \tag{4.25}$$

where C_g (ng L^{-1}) is the time-integrated gas-phase BDE concentration and $C_{w(n)}$ and $C_{w(n+1)}$ are the dissolved BDE concentrations (ng L^{-1}) measured at the beginning and end of air sampling period, respectively.

Measurement and evaluation of air-water exchange of PBDEs were within the objectives of this study. Thus, H′ experiments were conducted at five different environmental temperatures including 5, 15, 25, 30 and 40°C. Duration of each experiment was 3 days (3x24 h). For each individual experiment, three H′ values (n=3) were calculated using the concentrations of PBDEs determined in aqueous (n=4) and gas-phase samples (n=3) that were collected over the experimental duration. However, since the aqueous BDE concentrations were below the detection limit at the end of the sampling period, it was not possible to determine H′ values for few experiments. These replications provide a measure of the precision of the experimental method. For most BDEs, the relative standard deviations associated with the mean H′ value were less than 30%, and no systematic differences, within experimental variability, were observed among the different temperatures. The Henry's law is valid for dilute concentrations. For compounds that are slightly or even moderately soluble in water, with a reasonable accuracy H can be approximated by the ratio of the compound's vapor pressure and its aqueous solubility (Schwarzenbach et al., 1993). In the present study, the initial BDE concentrations in water were dilute (<4% of their solubility) (except BDE 209). The aqueous concentrations were generally decreased over the experimental durations (3 days) by a factor of greater than 2.0 (31% of the samples) and this resulted in H′ measurements at different concentrations. No systematic changes in measured H′

values were observed for different aqueous concentrations. These results were consistent with the previous studies reviewed by Schwarzenbach et al. (1993) reporting that there were no significant effects of solute concentration on measured H values.

The measured Henry's law constant values of PBDE congeners at five different temperatures are presented in Table 4.14. The H values for PBDEs were not experimentally measured previously as a function of temperature, but they were estimated at 25°C (Tittlemier et al., 2002, Wania & Dugani, 2003). Tittlemier et al. (2002) estimated the Henry`s law constants at 25°C as the ratio of subcooled liquid vapor pressures (P_L) and aqueous solubilities (S_w). P_L values were determined using the gas chromatographic-retention time (GC-RT) technique and S_w values were measured with the generator column technique. Wania & Dugani (2003) have also reported H values for PBDEs at 25°C based on their compilation and evaluation of literature data (Table 4.14). The agreement between the H values measured at 25°C in this study and those reported by previous studies was very good (Table 4.14).

Table 4.14 Henry`s Law Constants (Pa m^3 mol^{-1}) at different temperatures between 5 and 40 °C

Congener	5°C	15°C	25°C	30°C	40°C	literature, 25°C
BDE-28	1.01±0.20	2.34±0.55	4.83±0.67	7.92±2.66	29.38[a]±14.16	5.10[b], 1.92[c], 0.68[d]
BDE-47	0.18±0.01	0.56±0.12	0.85±0.35	1.78±0.21	3.78[a]±0.18	1.50[b], 1.12[c], 0.47[d]
BDE-100	0.06±0.003	0.09±0.01	0.24[a]±0.06	0.53±0.15	0.92[a]±0.27	0.07[b], 0.38[c], 0.32[d]
BDE-99	0.10±0.004	0.17±0.02	0.60±0.11	0.96±0.58	3.35±0.47	0.23[b], 0.53[c], 0.25[d]
BDE-154	0.03±0.01	0.07±0.02	0.08[a]±0.04	0.29±0.11	0.45±0.16	0.24[c], 0.20[d]
BDE-153	0.06±0.01	0.08±0.02	0.26±0.08	0.44±0.16	1.12±0.21	0.07[b], 0.29[c], 0.30[d]
BDE-209	0.01±0.001	0.02±0.004	0.04[a]±0.01	0.11±0.04	0.19±0.03	0.02[c]

[a] : n=2

[b] : Tittlemier et al. (2002)

[c] : Wania & Dugani (2003)

[d] : Calculated as the ratio of K_{OW}/K_{OA}. K_{OW} from Braekevelt et al. (2003), K_{OA} from Harner & Shoeib (2002)

There is a strong correlation between the experimental H′ values of PBDEs and temperature (Figure 4.12). For all PBDE congeners H increases with temperature more than 15 times (15.3 times for BDE 100 and 34.1 times for BDE 99) over the studied temperature range. The variation in H′ with temperature was expressed using the van't Hoff equation (Equation 4.24, Figure 4.12). Assuming enthalpy and entropy are independent of temperature over the experimental temperature range, the slope and intercept of the line were obtained from the plot of (ln H′) vs. (1/T) yields the enthalpy (ΔH_H, kJ mol^{-1}) and entropy (ΔS_H, kJ mol^{-1}.K^{-1}) of phase change, respectively. The r^2 values for the plots of (ln H′) vs. (1/T) ranged between 0.92 and 0.99 (Table 4.15) indicating the assumption that ΔH_H and ΔS_H are constant over the experimental temperature range and that the temperature dependence of H can be accurately modeled by van't Hoff equation is valid. The slopes (B) and the intercepts (A) for the Equation (4.24) [$\ln H' = A + B/T(K)$] were tabulated in Table 4.15. ln H′ values can be calculated at any temperature using A and B values with a relative standard error of <13% except for BDE 154 (range, 6% for BDE 28 -17% for BDE 154) (Table 4.15).

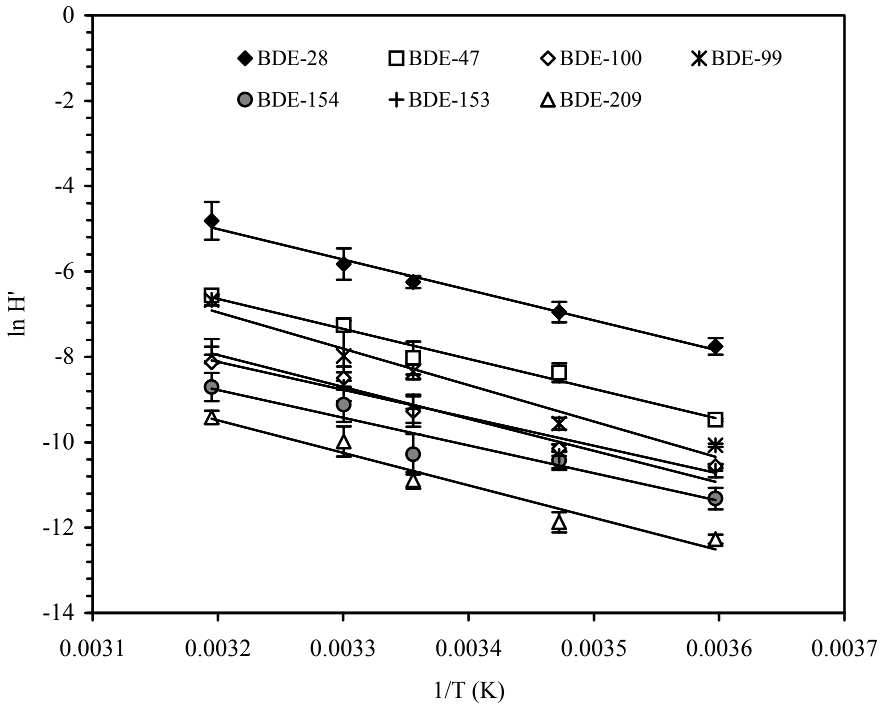

Figure 4.12 Measured H′ values for seven PBDE congeners over the temperature range 5 to 40°C. Error bars are 1 SD.

Table 4.15 The regression parameters (±standard errors) for the equation ln H′=A+B/T(K)

Congener	r^2	A	B
BDE-28	0.99	17.8±1.5	-7125±455
BDE-47	0.97	15.9±2.3	-7029±667
BDE-100	0.95	12.7±2.9	-6515±842
BDE-99	0.97	20.3±3.1	-8513±930
BDE-154	0.92	12.0±3.8	-6501±1108
BDE-153	0.96	16.0±2.9	-7475±850
BDE-209	0.95	14.8±3.3	-7601±980

Calculated enthalpies and entropies of phase change in this study are presented in Table 4.16 along with the literature values for the enthalpy of vaporization (ΔH_{vap}) and the enthalpy of phase transfer between octanol and air (ΔH_{OA}). There are no reported ΔH_H values for PBDEs in the literature. ΔH_H values range between 54.1-70.8 kJ mol^{-1} and they are lower than ΔH_{vap} values. This is consistent with thermodynamic principles that suggests the effect of temperature on H (ΔH_H) should be lower than (ΔH_{vap}) by an amount close or equal to enthalpy of solvation (ΔH_{SOL}) (Schwarzenbach et al., 2003; Bamford et al., 2000). Previously reported ΔH_H ranges for other POPs are 14.5-167 kJ mol^{-1} for PCBs (Bamford et al., 2000) and 35.4-100 kJ mol^{-1} for PAHs (Bamford et al., 1999). ΔH_H values for PBDEs determined in this study were within these ranges.

Table 4.16 Measured enthalpy (ΔH_H) and entropy (ΔS_H) of H in this study, the previously reported enthalpies of vaporization (ΔH_{vap}) and the enthalpies of phase transfer between octanol and air (ΔH_{OA})

Congener	ΔH_H (kJ mol^{-1})	ΔS_H (kJ mol^{-1} K^{-1})	ΔH_{vap} (kJ mol^{-1})	ΔH_{OA} (kJ mol^{-1})
BDE-28	59.2	0.15	79.7[a]	74.5[c]
BDE-47	58.4	0.13	94.6[a], 92[b]	97[c]
BDE-100	54.3	0.11	102[a]	105[c]
BDE-99	70.8	0.17	108[a], 100.3[b]	91.1[c]
BDE-154	54.1	0.10	113[a]	94.4[c]
BDE-153	62.1	0.13	110[a], 107.6[b]	98.2[c]
BDE-209	63.2	0.12		

[a] : Tittlemier et al. (2002)

[b] : Wong et al. (2001)

[c] : Harner & Shoeib (2002)

Figure 4.13 shows the relationship between the logarithm of Henry's law constant at 25°C and the molar volume (cm^3 mol^{-1}) of seven PBDEs. H values decrease with the increasing molar volume ($r^2 = 0.74$). However, molar volume can not account for all the variation in H values for different congeners. Henry's law constants for congeners having the same molar volumes (BDE 99 and 100, BDE 153 and 154) differ 2.5-3.4 times. In a recent study conducted by Bamford et al. (2000), it was observed that there was a significant variation in H with the number of ortho-halogen substitutions within the same molecular weight class for PCBs. As the number of ortho-chlorine substitutions increase, the H values increase. Wong et al. (2001) have also observed the same dependence for vapor pressures of PBDEs that within a same homologue group. The vapor pressure increases with the number of bromine substitutions in the ortho-position to the ether link. Ortho position refers to the four positions (2,2′, 6,6′) adjacent to the ether link. However, a larger data set is required in order to assess the same relationship. For H values of the seven congeners (only two congeners within the same molecular weight) included in the present study, it is not possible to evaluate their variations in H with the number of ortho-bromine substitutions.

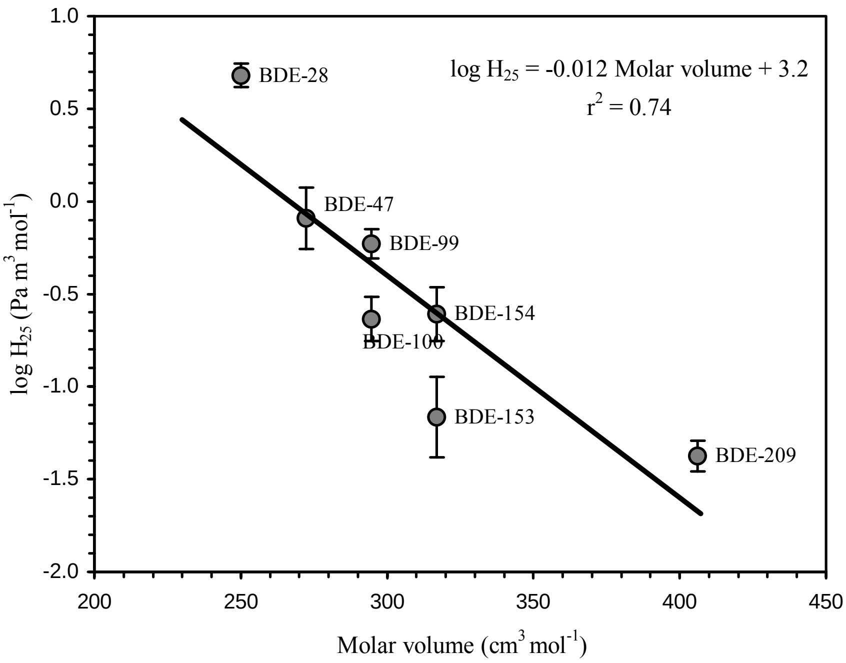

Figure 4.13 Relationship between the logarithm of Henry`s Law constant at 25°C and the molar volume of PBDEs. Error bars are 1 SD.

4.5.2 Water Concentrations in Guzelyali Port

Total dissolved-phase PBDE concentrations ($\sum_7$PBDEs) were 212±65 and 87±57 pg L^{-1} (average±SD) for summer and winter seasons, respectively and they were 271±60 and 479±340 pg L^{-1} for particle-phase (Table 4.17). For six BDE congeners, including BDE-28, 47, 99, 100, 153 and 154, dissolved and particle-phase concentrations were similar during the sampling periods. However, for BDE-209, particle-phase concentrations were ~8 times higher than dissolved-phase concentrations in winter. BDE-209 was the dominating congener in both phases and periods, followed by BDE-99 and 47. In summer, BDE-209 contributed 42 and 52% to total dissolved and particle-phase concentrations, respectively. In winter, its contribution to total dissolved and particle-phase concentrations was 63 and 92%, respectively.

Table 4.17 Water concentrations of individual PBDEs in pg L^{-1} (average±SD).

	Dissolved phase		Particle phase	
	Summer	Winter	Summer	Winter
Congener	(n=8)	(n=7)	(n=8)	(n=7)
BDE-28	2.7±1.4	1.4±0.9	3.1±1.0	1.5±0.9
BDE-47	40±9	9.5±3.0	34±7	11±5
BDE-100	11±3	3.4±1.2	11±2	3.8±1.5
BDE-99	57±15	14±5	53±10	16±7
BDE-154	5.4±1.3	1.6±0.9	5.7±0.8	1.8±0.6
BDE-153	8.2±2.1	2.5±1.1	8.3±1.1	2.7±1.5
BDE-209	89±52	54±46	157±47	443±329
$\sum_7$PBDE	212±65	87±57	271±60	479±340

Due to the abundance of BDE-209, the data set was divided into two subsets as BDE-209 and $\sum_6$BDEs (Figure 4.14). Particle-phase water BDE-209 concentrations were significantly higher especially in winter periods (Figure 4.14). The distribution of PBDEs between dissolved and particulate fractions were similar in winter and summer periods, except BDE-209. Particulate fractions of six BDE congeners were 50 and 53% for summer and winter periods, respectively (Figure 4.14). However, particulate fractions for BDE-209 were 64% and 89% for summer and winter periods, respectively indicating its predominant partition into particulate matter. Recently, Oros et al. (2005) reported that the ∑PBDEs were mostly partitioned into the suspended particulate matter fraction with the relative abundances between 78-93% of total PBDE concentrations. In the present study, only the partition of BDE-209 was similar to this observation.

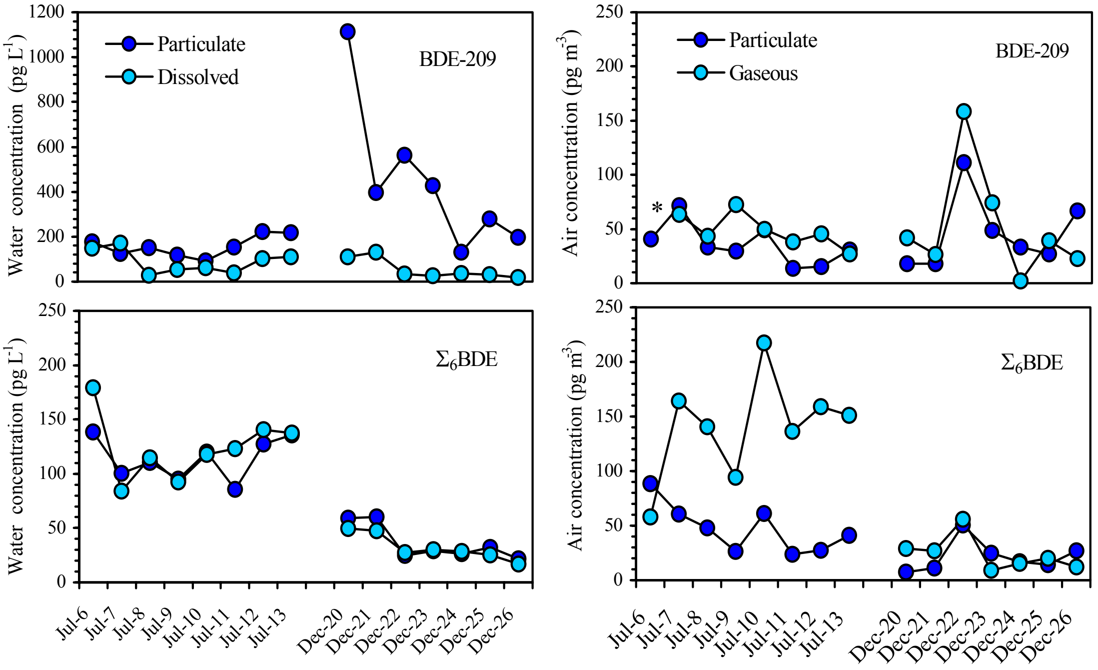

Figure 4.14 Water (particle and dissolved) and ambient air (particle and gas-phase) concentrations of BDE-209 and $\sum_6$BDE for summer and winter 2005 sampling periods. (*) Not analyzed.

There is limited information on PBDEs in environmental waters. The sum of dissolved and particle-phase individual PBDE concentrations ranged between 0.2-191 pg L^{-1} and BDE-47, 99 and 209 were the dominating congeners in the San Francisco Estuary (Oros et al., 2005). BDE 28, 47, 100 and 183 were the dominating congeners while BDE-209 was detected only in trace amounts at five sampling locations in Hong Kong (Wurl et al., 2006). However, in most locations PBDE concentrations were low or below detection limit. The mean dissolved and particle-phase seawater concentrations for eight congeners were 71 and 28 pg L^{-1}, respectively, and they were 149 and 38 pg L^{-1} for sea-surface microlayer (Wurl et al., 2006).

4.5.3 Air-Water Exchange

According to the two-film model, mass transfer is limited by the rate of molecular diffusion through thin films of air and water on either side of the surface (Schwarzenbach et al., 2003).The gas flux across a water surface is a function of Henry's law constant, the concentration gradient and the overall mass transfer coefficient (Hoff et al., 1996; Schwarzenbach et al., 2003). The net flux (F_g, ng m^{-2} day^{-1}) is driven by the fugacity difference between air and surface water:

$$F_g = K_g (C_g - C_w H/RT) \qquad (4.26)$$

where C_w and C_g are the water and air concentrations (ng m^{-3}), H is the Henry's law constant (Pa m^{-3} mol^{-1}), R is the universal gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), and T is temperature at the air-water interface (K). The gas phase overall mass transfer coefficient (K_g) is related to individual mass transfer coefficients for the liquid and gas films, k_w and k_a, as follows:

$$1/K_g = (1/k_a) + (H/RTk_w) \qquad (4.27)$$

Mass transfer coefficients of water vapor, oxygen (O_2) and carbon dioxide (CO_2) have been related to wind speed by many researchers The following equations can be used to estimate k_a and k_w for organic compounds (Nightingale, Liss, & Schlosser, 2000; Schwarzenbach et al., 2003):

$$k_{a(compound)}\ (\mathrm{cm\ s^{-1}}) = (0.2\ U_{10} + 0.3)\,[D_{a(compound)}/D_{a(H2O)}]^{0.6} \qquad (4.28)$$

$$k_{w(compound)}(\mathrm{cm\ s^{-1}}) = [(0.24\ U_{10}^{2} + 0.061\ U_{10})/3600]\,[D_{w(compound)}/D_{w(CO2)}]^{0.5} \qquad (4.29)$$

where D_a and D_w (cm^2 s^{-1}) are the diffusivities in air and water, respectively, and U_{10} is the wind speed 10 m above the water surface (m s^{-1}).

Concurrent air and water concentrations are ideally used to assess the state of equilibrium for individual POPs between the air-water interfaces. The water-air fugacity ratio ($f_W/f_A=H'C_w/C_g$) >1.0 indicate net volatilization of compounds from water, values <1.0 indicate net gas-phase deposition from air. For a system in equilibrium, f_W/f_A value is ~1.0.

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_w, H and K_g values are taken into account. The uncertainties of C_a and C_w were determined as 10% from the relative standard deviations of sample surrogate recoveries (Bamford et al., 2002). Uncertainty in H values was found to be<13% in present study (Cetin & Odabasi, 2005), however propagating the additional uncertainty for salting-out correction increases this value to 16%. Unlike k_a, k_w is not linearly related to wind speed. Averaging wind speeds for long periods may underestimate k_w and K_g. The relationship of Henry's law constant (H) with temperature is also non-linear. To determine the nonlinear influences of meteorological parameters on K_g, a sensitivity analysis was conducted using data averaged over 1 min intervals. The change in K_g ranged from -2% (BDE 28) to 0.1% (BDE 209) relative to the estimates based on long term averages of wind speed and temperature. The overall uncertainty of K_g value was assumed to be 40%, based on the results of sensitivity analysis, previous evaluations, and the uncertainties in the air and water-side mass transfer coefficients (k_a and k_w), (Bamford et al., 2002; Hoff et al., 1996; Nelson et al., 1998; Nightingale et al., 2000).

A propagation of the errors that are associated with the calculation indicated that the equilibrium is represented by an f_W/f_A of 1.0±0.21 (i.e., a range of 0.79-1.21). The fugacity ratios of all compounds (except the ratios for BDE-47 for three samples) fall outside this uncertainty range and we can be confident that for these compounds the water and ambient air are not in equilibrium (Figure 4.15). Fugacity ratios for BDE-28 were generally >1.0 indicating net volatilization while the ratios for other congeners (<1.0) indicated deposition to the surface water (except for two samples) (Figure 4.15).

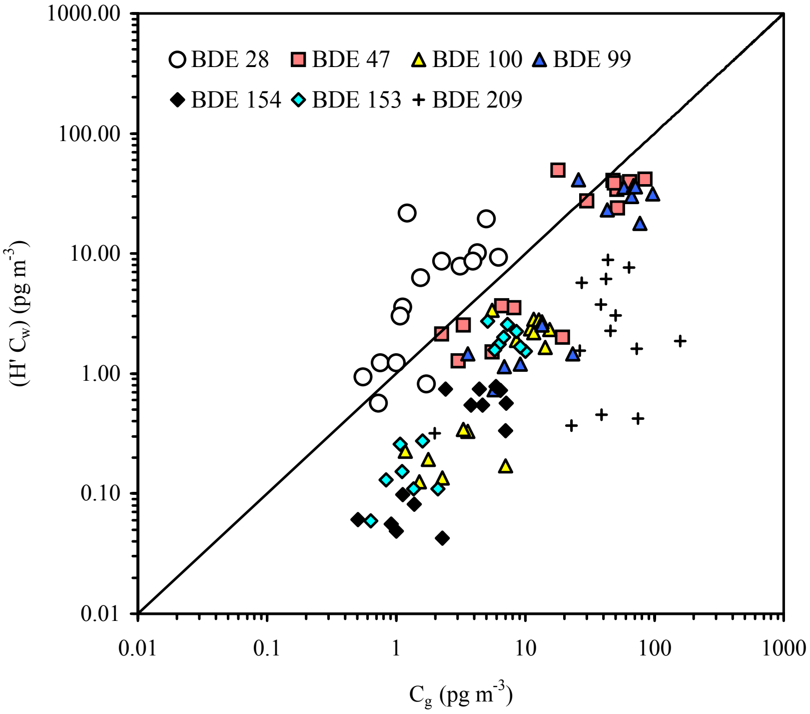

Figure 4.15 Relationship between the PBDE fugacities in water and air. The solid diagonal line represents a 1:1 relationship (equilibrium).

Recently, Jaward et al. (2004) have found evidence for a close linking between air-water concentrations and they have suggested that water column processes are controlling the atmospheric occurrence of POPs. Similar observations have been reported for polycyclic aromatic hydrocarbons (PAHs) in the New York-New Jersey, Harbor Estuary (Gigliotti et al., 2002). In the present study, the gas and dissolved-phase concentrations for individual BDEs were significantly correlated (r^2=0.33-0.55, p<0.05, except for BDE-209, r^2=0.05, p>0.05). Similar correlations were also observed between air and water fugacities (Figure 4.15) indicating that even in a coastal environment, the atmosphere controls the surface water PBDE levels. This suggests that sediment may not contribute significantly to surface water concentrations. The lack of correlation between the air-water concentrations for BDE 209 may be due to the slow exchange for this less volatile congener that does not allow for air-water coupling. It was suggested that the close coupling of air-water concentrations has important implications for future rates of POP removal from the global "recyclable pool" (Jaward et al., 2004).

The parameters used for calculation of air-water exchange and dry deposition fluxes were presented in Table 4.18. Net fluxes of PBDEs were calculated using 15 paired atmospheric gas and dissolved-phase water samples collected at the sampling site (Table 4.3 and 4.17) and above equations:

Table 4.18 Parameters Used for Calculation of Air-water Exchange and Dry Deposition Fluxes.

	H^a (25°C)	Regression parameters[a] [ln H′=A + B/T(K)]		k_s[b]	V_p[c]	D_a (25°C)[d]	D_w (25°C)[e]
Congener	(Pa m^3 mol^{-1})	A	B	(Lmol^{-1})	(cm s^{-1})	(cm^2 s^{-1})	(cm^2 s^{-1})
BDE 28	4.83±0.67	17.8±1.5	-7125±455	0.35	7.8±3.5	0.0505	$5.90x10^{-6}$
BDE 47	0.85±0.35	15.9±2.3	-7029±667	0.39	3.9±1.7	0.0483	$5.58x10^{-6}$
BDE 100	0.24±0.06	12.7±2.9	-6515±842	0.40	6.4±2.5	0.0463	$5.32x10^{-6}$
BDE 99	0.60±0.11	20.3±3.1	-8513±930	0.41	3.1±1.6	0.0463	$5.32x10^{-6}$
BDE 154	0.08±0.04	12.0±3.8	-6501±1108	0.43	2.8±1.4	0.0446	$5.10x10^{-6}$
BDE 153	0.26±0.08	16.0±2.9	-7475±850	0.43	4.6±1.6	0.0446	$5.10x10^{-6}$
BDE 209	0.04±0.01	14.8±3.3	-7601±980	0.53	2.9±1.8	0.0393	$4.40x10^{-6}$

[a]: (average±SD) for H, (average±SE) for A and B. H′ is the dimensionless Henry's law constant (H′=H/RT) (Cetin & Odabasi, 2005).

[b]: k_s is the salting-out constant (L mol^{-1}) calculated using the method by Ni & Yalkowski (2003). H^*, the Henry's law constant in saline water was calculated using [log (H^*/H)=k_s C_s] where C_s is the molar concentration of salt solution (measured as 0.51 and 0.62 M for winter and summer samples, respectively).

[c]: V_p (overall particle dry deposition velocity, cm s^{-1}) (average±SD) obtained from Suburban and Urban 1 sampling sites in present study.

[d]: Calculated using the Fuller method (Schwarzenbach et al., 2003)

[e]: Calculated using the Hayduk and Laudie method (Schwarzenbach et al., 2003).

The net BDE flux ranged from -8.6 (volatilization, BDE-47) to 28.0 (deposition, BDE-209) ng m^{-2} day^{-1} (Figure 4.16). The BDE-28 fluxes were mainly volatilization while other congeners generally deposited to water during the sampling periods. BDE-47 and 99 had had their single negative values in the first sampling day due to comparably high dissolved and low gas-phase concentrations. Except BDE-209, all congeners have seasonal variations in flux with less depositional trend in winter (Figure 4.16). Since the ambient gas-phase BDE concentrations were higher in summer (except BDE-209), higher depositional fluxes were observed during this period. BDE-209 fluxes also fluctuated due to variable concentrations, however a seasonal trend was not observed. On the average, dissolved-phase concentrations of BDE-28 were two times lower in winter than those measured in summer. H value also increases with temperature. Therefore, volatilization was higher in summer while it decreased in winter and in a single day BDE-28 was deposited (Figure 4.16).

The estimated uncertainty in the fluxes by error propagation ranged between 41 (BDE-209)-59% (BDE-28) for individual congeners (overall, ±47%). However, relatively higher uncertainty values for BDE-28 and 47 were calculated for five sampling days (71-114%). The fluxes for these samples were comparably lower than the other days and their high uncertainty values were probably due to the proximity to equilibrium.

The atmospheric stability may affect the air-water exchange fluxes. When the water surface is colder than the atmosphere, a strong temperature inversion develops as air travels from land over the water, reducing vertical mixing. In contrast, when the water surface is warmer than the overlying air, vertical mixing is enhanced (Honrath, Sweet, & Plouff, 1997; Angevine et al., 2004). Based on meteorological conditions on Lake Superior and literature data, Honrath et al. (1997) suggested that the air-water exchange fluxes may be reduced by ~50% during periods of stable-over lake conditions. In the present study, the average air-water temperature differences ($\Delta T=T_{water}-T_{air}$) were -4.8 and 6.7°C in winter and summer sampling periods, respectively, suggesting that the atmospheric stability over the water may have been affected. However, the magnitude of this effect could not be determined since the influence of stability is not taken into account by the model used for flux estimation.

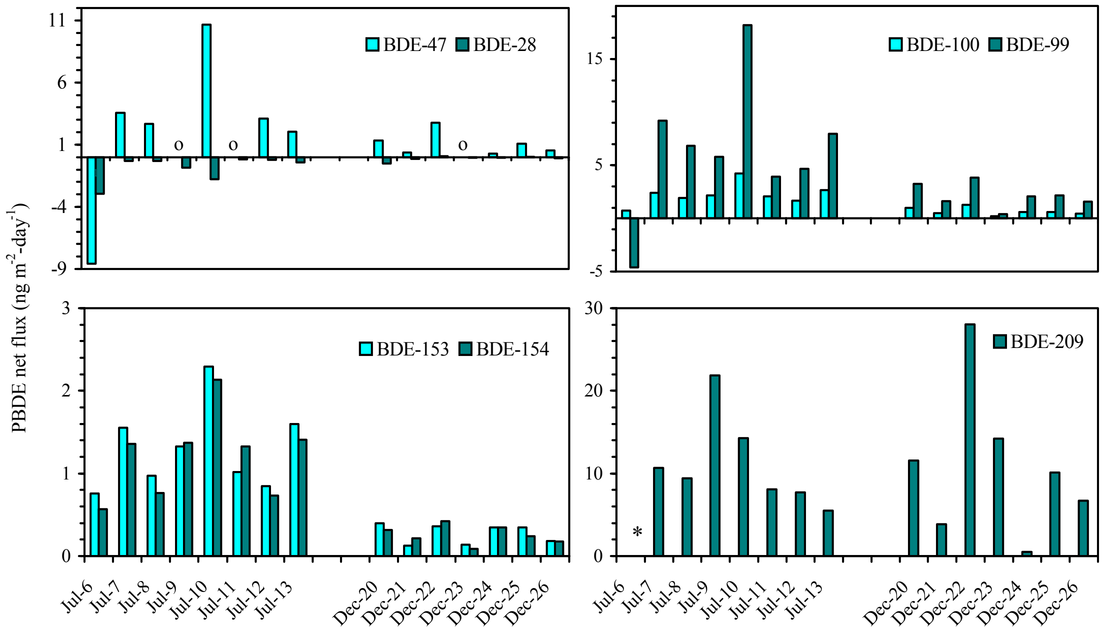

Figure 4.16 Net gas exchange fluxes of individual BDEs (ng m^{-2} day^{-1}) for summer and winter 2005 sampling periods. (*) not analyzed, (o) not calculated (near equilibrium). Negative values indicate volatilization from water.

4.5.4 Comparison of Gas and Particulate Dry Deposition Fluxes in Guzelyali Port.

The dry deposition fluxes of organics associated with particles can be estimated using an overall dry deposition velocity (V_p) and particle-phase air concentrations (C_p) (Equation 2.1).

Reported overall particle dry deposition velocities (V_p) for various POPs range between 0.4 and 6.7 cm s^{-1} (Odabasi, Sofuoglu et al., 1999). In present study V_p values for PBDEs determined using particle dry deposition and ambient air samples collected at an urban site in Izmir, Turkey ranged between 2.9 (BDE-209)-7.8 cm s^{-1} (BDE-28) (Table 4.18). Dry deposition fluxes (F_p) for PBDEs in Guzelyali Port were estimated using these deposition velocities and particle-phase air concentrations (Table 4.19). In summer, particle fluxes were between 6.4±2.6 (BDE-154) and 89±47 (BDE-209) ng m^{-2} day^{-1} (average±SD), while they were 2.7±1.9 (BDE-154) and 116±84 (BDE-209) ng m^{-2} day^{-1} in winter. Same seasonal trend as air-water exchange fluxes was observed. Except BDE-209, summer fluxes were higher than winter particle fluxes. On the average, summer fluxes were higher than winter particle fluxes. On the average, estimated particle fluxes were approximately an order of magnitude higher than gas-exchange fluxes. These relatively large particle fluxes suggest that the dry deposition may also be a significant input to surface waters.

The V_p values for PBDEs determined at a suburban site were higher than those obtained at the Urban 1 site by a factor of 1.3-2.4 (average±SD, 1.8±0.4) (Table 4.6). Based on these observations, it was estimated that the uncertainty in V_p values used in calculation of particle-phase fluxes in the present study was a factor of 2.

Table 4.19 Calculated Overall Mass Transfer Coefficients, Air-water Exchange Fluxes[a], and Particle Dry Deposition Fluxes (average±SD).

Congener	Summer			Winter		
	K_g	Net gas flux	Particle flux	K_g	Net gas flux	Particle flux
	(m day^{-1})	(ng m^{-2} day^{-1})	(ng m^{-2} day^{-1})	(m day^{-1})	(ng m^{-2} day^{-1})	(ng m^{-2} day^{-1})
BDE 28	89±36	-0.9±1.0	7.2±4.4	167±81	-0.1±0.2	5.9±3.3
BDE 47	194±57	2.2±6.9	42±22	241±86	1.1±0.9	23±16
BDE 100	260±57	2.2±1.0	25±11	263±79	0.7±0.4	15±10
BDE 99	220±58	6.5±6.8	62±30	254±81	2.1±1.1	26±16
BDE 154	268±55	1.2±0.5	6.4±2.6	262±76	0.3±0.1	2.7±1.9
BDE 153	249±56	1.3±0.5	13±6	257±77	0.3±0.1	5.7±2.8
BDE 209	255±50	11.1±5.4	89±47	244±69	10.7±8.9	116±84

[a] Negative values indicate volatilization of PBDEs from water

In addition to gas-exchange and particle deposition, other PBDE inputs into the Bay (i.e., wet deposition, run-off, and industrial discharges) contribute to the water column total PBDE inventory, however it is not possible to estimate their magnitude and relative importance. However, the observed close air-water coupling indicates that air-water exchange is an important PBDE input to Izmir Bay. The importance of deposition as an input or volatilization as a removal process relative to advection of PBDEs out of the water column of Izmir Bay was further assessed by comparing the residence times of dissolved-phase PBDEs in the water column reflecting only air-water fluxes versus the residence time of water in the inner Bay. The hydraulic residence time for the inner Bay water is 85 days (Sayin, 2003). The residence time of PBDEs in the water column (τ_{AW}), considering only dissolved-phase PBDEs that are subject to air-water exchange, is given by (Gigliotti et al., 2002):

$$\tau_{AW} = \text{Inventory/Net flux} = (C_{dissolved}\, H_w)/F_g \tag{4.30}$$

The residence times of PBDEs were calculated using the estimated net fluxes (F_g, ng m^{-2} day^{-1}), measured dissolved-phase concentrations ($C_{dissolved}$, ng m^{-3}), and the average water depth for the inner Bay (H_w, 10 m). τ_{AW} values of PBDEs ranged from 70 to 142 days and the hydraulic to gas-exchange residence time ratios were between 0.73 and 2.81. These results suggest that PBDE gas-exchange is at least as or a more important mechanism than advection and the observed dynamic air-water coupling is feasible. (Table 4.20).

Table 4.20 The summary of the ratio of dissolved PBDE inventory to net flux in the water column.

	Residence time of PBDEs			Ratio: Hydraulic/ Gas exchange		
Congener	AVG±SD	Summer	Winter	AVG±SD	Summer	Winter
BDE-28	95±65	54	143	1.55±1.32	2.28	0.73
BDE-47	142±117	111	173	1.05±0.79	1.03	1.06
BDE-100	70±60	69	72	1.82±1.01	1.86	1.79
BDE-99	96±74	96	97	1.34±0.80	1.27	1.42
BDE-154	70±49	55	90	1.79±1.12	2.12	1.36
BDE-153	94±71	75	115	1.29±0.72	1.49	1.05
BDE-209	130±181	91	170	2.23±2.06	1.66	2.81

CHAPTER FIVE
CONCLUSIONS

5.1 Conclusions

Seven PBDE congeners including BDE-28, -47, -99, -100, -153, -154 and -209 were investigated in ambient air, soil, organic films and water samples in Izmir, and generally all of the target copmpounds were found in all samples investigated indicating that Izmir is seriously contaminated with PBDEs.

Ambient air studies were carried out at four sampling sites including Suburban, Urban 1, Urban 2 and Industrial sites and their spatial and seasonal variations were investigated. Highest $\sum_7$PBDE concentrations were obtained from Industrial site with the average summer concentrations of 117.46±22.71 pg m^{-3}, indicating that this industry (Steel plant) is very likely to be the PBDE source. PBDE concentrations obtained in this study were within the range of previously measured values around the world. BDE-209 was the most abundant congener at all sites, followed by BDE-99 or -47. Measured PBDEs were fitted to a linear combination of the compositions of the technical products and found that samples collected from four different regions were dominated by penta and deca mixtures.

Gas-particle partitioning of PBDEs were also examined using Junge-Pankow and K_{OA}-based models and found that both models tend to overestimate the sorption of six congeners excluding BDE-28. A good agreement was obtained between the measured and predicted ø values for BDE-28 in K_{OA}-based model while Junge-Pankow model underestimated this congener. Gas-particle partitioning models estimate that higher brominated congeners like BDE-209 are expected to be particle bound >99%. However, the average proportion of BDE-209 in this study was 70±22% at four different sites in Izmir and lies between the extreme values (0-100% particle-phase) reported previously.

Dry deposition samples were collected in Suburban and Urban 1 sampling sites concurrently with ambient air samples. Average particle phase $\sum_7$PBDE fluxes measured with dry deposition plates were 67.63 and 136.59 ng m^{-2} day^{-1}, for Suburban and Urban 1, respectively. Particulate fluxes were dominated by BDE-209 and the average flux of BDE-209 was ~2 times higher at Urban 1 than those obtained from Suburban site. As particle scavenging is the main route of PBDE dry deposition, this result is consistent with higher amounts of particles at Urban 1. Particle dry deposition velocities ranged from 11.5 (BDE-28) to 3.9 cm s^{-1} (BDE-209) for Suburban site and 7.8 (BDE-28) to 2.8 cm s^{-1} (BDE-154) for Urban 1 site with an overall average velocity of 5.8±3.7 cm s^{-1} for both sites. The particle dry deposition velocities of PBDEs were within the range of previously reported values for other POPs around the world.

Indoor and outdoor organic films in window glasses were investigated at different sites in Izmir. Average total PBDE ($\sum_7$PBDE) concentrations of organic films for all sites were 97.7±167.6 and 64.0±72.5 ng m^{-2}, for indoor and outdoor samples, respectively, and they were dominated by technical penta and deca-BDE mixtures. Relatively high indoor film PBDE concentrations were observed in offices running old computers. Use of an additional old computer within the sampling period resulted in seriously higher $\sum_7$PBDE concentrations as shown by a replicate sample taken from same site (Lab 1). Outdoor film concentrations have variations related to the proximity to possible PBDE sources. For example, relatively higher $\sum_7$PBDE concentrations were found in the outdoor film near a steel plant using metal scrap. Windshield film samples from vehicles were also analyzed and average $\sum_7$PBDE concentrations in winter was 31.12±44.59 ng m^{-2}. However, their concentrations were significantly decreased in summer probably be due to degradation of BDEs (especially BDE-209) at very high temperatures and strong solar radiation. Gas-phase ambient air concentrations of PBDEs were calculated using film-air partition coefficient and $\sum_7$PBDE concentrations of 6.2 and 22.2 pg m^{-3} were obtained for outdoor and indoor films, respectively. The estimated outdoor concentrations were compared to ones measured recently in the area. Only concentrations of BDE-47 and

-100 were comparable, however relatively more volatile PBDEs were overestimated while nonvolatile ones were underestimated.

The air-water exchange of PBDEs was also investigated using paired air-water samples (n=15) collected from Guzelyali Port in Izmir Bay. Average dissolved-phase $\sum_7$PBDEs concentrations were 212±65 and 87±57 pg L^{-1} in summer and winter, respectively. BDE-209 was the most abundant congener in all samples, followed by BDE-99 and -47. Average ambient gas-phase $\sum_7$PBDE concentrations were between 189±61 (summer) and 76±65 pg m^{-3} (winter). Net air-water exchange fluxes ranged from -0.9±1.0 (BDE-28) (volatilization) to 11.1±5.4 (BDE-209) ng m^{-2} day^{-1} (deposition). The BDE-28 fluxes were mainly volatilization while the other congeners were deposited. Gas and dissolved-phase concentrations were significantly correlated (r^2=0.33-0.55, p<0.05, except for BDE-209, r^2=0.05, p>0.05) indicating that the atmosphere controls the surface water PBDE levels in this coastal environment. Estimated particulate dry deposition fluxes ranged between 2.7±1.9 (BDE-154)-116±84 ng m^{-2} day^{-1} (BDE-209) indicating that dry deposition is also a significant input to surface waters in the study area.

5.1 Suggestions

Possible artifacts associated with the high volume air sampling including the adsorption of gas-phase chemical to the filter and the breakthrough of the gas-phase compounds through the PUF should be further investigated and quantified for BDE-209.

Air water exchange studies should be expanded to be representative for whole Izmir bay. The observed impact of seasonal (summer-winter) variations on the fluxes suggests that additional studies should be carried out in spring and fall.

The study on PBDEs should be focused on the Industrial region that has relatively high PBDE concentrations especially for steel plant. Dry and wet deposition and more soil sampling should be performed in this region.

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