



Persistent Organic Pollutants (POPs) on Fine and Coarse Atmospheric Particles Measured at Two (Urban and Industrial) Sites

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ABSTRACT

Particle size is an important parameter in terms of human health effects, fate and transport of pollutants associated with particulate matter (PM). Persistent organic pollutant (POP) (i.e., PAHs, PCBs, PBDEs, and OCPs) concentrations were measured on fine ($d_p < 2.5 \mu\text{m}$) and coarse ($2.5 \mu\text{m} < d_p < 10 \mu\text{m}$) aerosol samples collected at two (Urban and Industrial) sites in Izmir, Turkey. POP concentrations were ~ 2 times higher at the Industrial site due to the local sources (i.e., scrap processing iron-steel plants, ship-breaking activities, a petroleum refinery, and a petrochemical plant) that were recently shown to be hot spots emitting these pollutants. The size distribution of particle-phase POPs indicated that they were mostly ($> 50\%$) associated with fine PM. The larger contribution of all POP compounds to fine PM could be attributed to the higher sorption capacity of fine PM because of its relatively higher organic matter content compared to coarse PM. Fine PM fraction of POPs significantly increased with octanol-air partition coefficient (K_{OA}) ($p < 0.01$) since larger K_{OA} values favor the partitioning of POPs to PM. Relationships between fine PM percent and meteorological parameters (i.e., temperature and wind speed) were also investigated. Fine PM percent decreased with temperature and the correlations were significant for 51% of the compounds ($p < 0.01$), suggesting that the decrease in K_{OA} with increasing temperature results in less partitioning to PM. Fine PM fraction also decreased with wind speed ($p < 0.01$ for the 52% of the compounds) that could be attributed to increased resuspension of contaminated coarse particles with increasing wind speed. Using the experimental deposition velocities reported for several POPs in the study area it was shown that dry particle deposition velocity significantly decreases with increasing fine PM fraction ($p < 0.01$). This indicates that the increase in fine fraction of POPs with decreasing volatility may have important implications for their environmental fate and transport.

Keywords: POPs; Gas-particle partitioning; Particle size distribution.

INTRODUCTION

Atmospheric persistent organic pollutants (POPs) may be predominantly in the gas/particle-phase or distributed between two phases, depending on their physicochemical properties (i.e., supercooled liquid vapor pressure- P_L , octanol-air partition coefficient- K_{OA}) and temperature (Harner and Shoeib, 2002; Li *et al.*, 2008). Transfer of POPs between atmosphere and natural surfaces (soil, water, vegetation) occurs through gas absorption/volatilization, dry particle and wet deposition (Cetin and Odabasi, 2007a; Bozlaker *et al.*, 2008a).

Particle size is a significant parameter in terms of human health effects of particle-phase pollutants because of its

influence on inhalation exposure (Offenberg and Baker, 1999). Several POPs like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) are carcinogens/suspected carcinogens, mutagens, or endocrine disruptors (Bozlaker *et al.*, 2008a, b; Cetin and Odabasi, 2008). POPs pose significant health risks when associated with fine particles due to deposition in lungs. Particle size is also the controlling factor for the atmospheric residence time and removal mechanisms (i.e., dry and wet deposition) for the contaminants associated with particle-phase. It has been shown that dry and wet deposition processes significantly contribute to the loadings of POPs to surface waters and soils (Seinfeld and Pandis, 1998; Shannigrahi *et al.*, 2005; Cetin and Odabasi, 2007b; Bozlaker *et al.*, 2008b; Odabasi *et al.*, 2008; Castro-Jimenez *et al.*, 2012). Particle size distribution of PAHs has been studied extensively (Sheu *et al.*, 1997; Schnelle-Kreis *et al.*, 2001; Ji *et al.*, 2007; Park *et al.*, 2007; Saarnio *et al.*, 2008; Kawanaka *et al.*, 2009; Akyuz and Cabuk, 2009; Zhang *et*

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al., 2012a). However, there are only a few studies investigating the size distribution of atmospheric PCBs (Xu et al., 2005; Chrysikou et al., 2009; Han et al., 2010), OCPs (Wang et al., 2008; Chrysikou et al., 2009; Fu et al., 2009; Xu et al., 2011; Coscolla et al., 2014), and PBDEs (Deng et al., 2007; Mandalakis et al., 2009; Zhang et al., 2012b).

Most of these studies have reported that POPs were mostly associated with fine particles, non-volatile higher molecular weight compounds being in a greater extent. However, only a few of those studies attempted to investigate and explain the differences observed for the different organic compounds. Distribution of semivolatile organic compounds (SVOCs) between fine and coarse particles is a complex issue influenced by several mechanisms suggested previously: (i) compounds emitted mainly on fine PM can become associated with coarse particles by volatilization from fine particles followed by condensation onto coarse particles (redistribution) (Duan et al., 2007; Chrysikou and Samara, 2009; Luo et al., 2014), (ii) fine particles can grow by coagulation or vapor condensation and become coarse particles (Coscolla et al., 2014), (iii) wind induced resuspension of soil/road dust particles mainly contributes to large particles and shifts the size distribution either to coarse particles (contaminated soil/road dust) or to fine particles (non-contaminated soil/road dust) (Coscolla et al., 2014; Luo et al., 2014), (iv) preferential partitioning of SVOCs having different physicochemical properties (i.e., vapor pressure and K_{OA}) from gas-phase to fine particles due to their larger surface area (Luo et al., 2014), (v) large particles are removed from atmosphere more effectively during the transport, altering the size distribution in favor of fine PM (Coscolla et al., 2014; Luo et al., 2014). Among the different mechanisms affecting the size distribution of particulate POPs, only the effect of resuspension, dry deposition, and physicochemical properties (i.e., vapor pressure) were investigated by a few previous studies, probably due to the difficulties in proving the effect of mechanisms like redistribution and coagulation. To our knowledge, there have been no studies investigating the effect of meteorological parameters (i.e., temperature and wind speed) and K_{OA} on size distribution of particulate POPs.

The objectives of this study were (1) to determine the POP concentrations associated with particulate matter (PM) in an urban and industrial area and their distribution between fine ($d_p < 2.5 \mu\text{m}$) and coarse ($2.5 \mu\text{m} < d_p < 10 \mu\text{m}$) particles, (2) to investigate the effect of physicochemical properties (i.e., K_{OA}) and meteorological parameters (i.e., temperature and wind speed) on the size distribution of POPs in particle-phase.

MATERIALS AND METHODS

Sampling

Ambient air samples were collected at two sampling sites (urban and industrial) in Izmir, Turkey. Urban samples were collected at Yesildere located near a main street with heavy traffic and residential areas. The industrial site is located at Bozkoy village, at the Aliaga industrial region,

~5 km south of the Aliaga city center and ~45 km north of the metropolitan city of Izmir, Turkey. The area contains several pollutant sources including a large petroleum refinery and a petrochemicals complex, scrap processing iron-steel plants with electric arc furnaces (EAFs), scrap iron storage and classification sites, steel rolling mills, a natural gas-fired power plant, a very dense transportation activity of scrap iron trucks, a ship dismantling area, and busy ports with scrap iron dockyards (Fig. 1).

Daily ambient air samples ($n = 17$) were collected at the Industrial site between April 1 and 17, 2006 while samples ($n = 16$) were collected at the Urban site between April 19 and May 4, 2006. Meteorological data was obtained from meteorological stations located near the sampling sites. Wind speed ranged between 1.2–5.9 (average \pm SD, 3.2 ± 1.6) m s^{-1} and 0.8–8.5 (3.9 ± 2.4) m s^{-1} during the industrial and urban sampling programs, respectively. The average temperatures were $16.0 \pm 2.4^\circ\text{C}$ (range: 12.8–20.1) and $18.5 \pm 1.6^\circ\text{C}$ (15.6–21.8) at the Industrial and Urban sites, respectively. The prevailing wind directions in the area are WNW and NW. There were both northerly and southerly winds during the sampling programs. The location of the Industrial sampling site indicates that it is affected from the steel plant emissions when northerly winds prevail (Fig. 1).

Elevation of the sample inlet was 4 m from the ground level. POPs on fine ($< 2.5 \mu\text{m}$) and coarse ($2.5\text{--}10 \mu\text{m}$) particle fractions were collected on two 46.2 mm ($2 \mu\text{m}$ pore size) Teflon filters using a dichotomous sampler (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co., Inc., Albany, NY). The average sampling time was 24 h and the sampling volume was $24 \text{ m}^3 \text{ sample}^{-1}$ at a flow rate of $1 \text{ m}^3 \text{ h}^{-1}$.

Sample Preparation and Analysis

Prior to extraction, all samples were spiked with PCB (PCB-14, PCB-65, PCB-166), PAH (acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , perylene- d_{12}), OCP (PBDE-77), and PBDE (PBDE-77) surrogate standards to monitor the analytical recovery efficiencies. Samples were soaked in 40 mL of a 1:1 acetone:hexane mixture overnight. Then, they were ultrasonically extracted for 30 min. The extract volumes were transferred into hexane and reduced to 1 mL using a rotary evaporator and a high purity N_2 stream, and then they were spiked with 20 pg PBDE-128 (internal standard). Samples were then analyzed without any fractionation and cleanup since the sampling volume was substantially lower ($\sim 1/10$) compared to high volume sampling (Odabasi et al., 2008) and preliminary instrumental analysis did not indicate any matrix interferences.

Samples were analyzed for POPs with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). PAHs and PCBs were analyzed using electron impact ionization while negative chemical ionization (NCI) was used for PBDEs and OCPs. The capillary column used for PAHs, PCBs and OCPs was HP5-MS (30 m, 0.25 mm, 0.25 μm) while a DB5-MS column (15 m, 0.25 mm, 0.1 μm) was used for PBDEs. Helium was the carrier gas and high purity methane was the reagent gas for NCI. All POPs were analyzed in selected

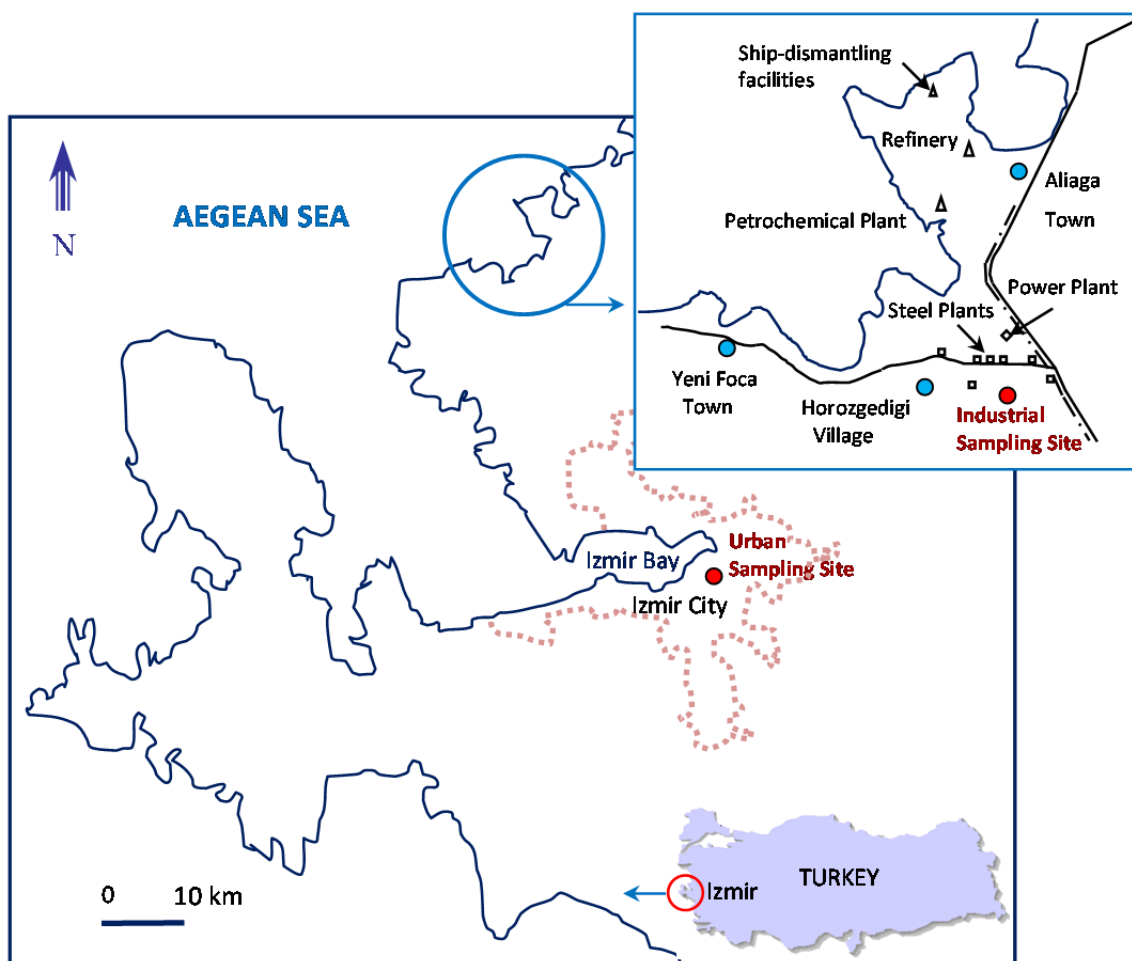


Fig. 1. Map of the study area. Border of densely populated areas is indicated by the dashed line.

ion monitoring mode (SIM). Compounds were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure. In all cases r^2 was > 0.99 . Further details for sample preparation and instrumental analysis could be found elsewhere (Cetin *et al.*, 2007; Bozlaker *et al.*, 2008a, b; Odabasi *et al.*, 2008; Odabasi *et al.*, 2009).

Average recoveries for the surrogate standards were $86 \pm 8\%$ (acenaphthene- d_{10}), $91 \pm 8\%$ (phenanthrene- d_{10}), $106 \pm 9\%$ (chrysene- d_{12}), $110 \pm 9\%$ (perylene- d_{12}), $102 \pm 4\%$ (PCB-14), $109 \pm 6\%$ (PCB-65), $108 \pm 5\%$ (PCB-166), and $68 \pm 7\%$ (PBDE-77). Instrumental detection limits (IDL) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. For $1 \mu\text{L}$ injection, the quantifiable amounts were 0.15, 0.10, 0.05–10.35, 0.02–0.35 μg for PAHs, PCBs, PBDEs, and OCPs, respectively. Field blanks (3 filters per site) were also analyzed to determine if there was contamination during sampling and sample preparation. The limit of detection of the method (MDL, ng) was defined as the mean blank mass plus three standard deviations ($\text{MDL} = \text{Mean blank value} + 3\text{SD}$). Instrumental detection limit was used for the compounds that were not detected in blanks. Average analyte amounts in blanks were generally $< 10\%$ of the amounts found in

samples. Sample quantities exceeding the MDL were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

RESULTS AND DISCUSSION

POP Concentrations in Atmospheric Particles

PCB, PBDE, PAH, and OCP concentrations measured in $\text{PM}_{2.5}$ and PM_{10} samples are presented in Table 1, along with total particulate matter (PM) concentrations (also see the Supplementary Material, Tables S1–S16). Slightly higher PM concentrations were measured at the industrial site (PM_{10} concentrations; 73 ± 53 and $60 \pm 28 \mu\text{g m}^{-3}$ for Industrial and Urban sites, respectively). Previous studies conducted in Turkey and around the world have reported that particle-phase $\Sigma_{16}\text{PAH}$ concentrations in air were dominated by medium to high molecular weight compounds (fluoranthene through benzo[*g,h,i*]perylene) (Bozlaker *et al.*, 2008a; Demircioglu, 2011a). $\Sigma_{16}\text{PAH}$ profiles in $\text{PM}_{2.5}$ and PM_{10} observed in the present study were similar to those reported previously. Unlike PAHs, there were no clearly dominating compounds for the particulate PCB samples collected in the present study. PBDE-209 was the most abundant compound in $\Sigma_7\text{PBDE}$ concentrations and it was followed by PBDE-99 and 47. A similar profile for atmospheric particle-phase

Table 1. Concentrations of POPs in PM_{2.5} and PM₁₀.

PCBs (pg m ⁻³)	Industrial		Urban		PAHs ^a (ng m ⁻³)	Industrial		Urban	
	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀		PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀
PCB-18	9.3 ± 5.1	15 ± 7.5	12 ± 5.5	21 ± 8.6	ACY	0.06 ± 0.04	0.1 ± 0.05	0.05 ± 0.02	0.09 ± 0.04
PCB-17	3.2 ± 2.0	4.6 ± 2.5	4.7 ± 1.7	8.3 ± 2.8	ACT	0.04 ± 0.03	0.07 ± 0.03	0.05 ± 0.02	0.09 ± 0.04
PCB-31	13 ± 5.9	20 ± 7.7	10 ± 4.1	22 ± 12	FLN	0.1 ± 0.08	0.2 ± 0.09	0.1 ± 0.06	0.2 ± 0.1
PCB-28	14 ± 9.5	22 ± 13	9.0 ± 4.1	21 ± 13	PHE	0.5 ± 0.3	0.7 ± 0.3	0.5 ± 0.2	0.7 ± 0.3
PCB-33	6.1 ± 3.5	8.4 ± 5.8	4.7 ± 3.2	8.2 ± 10	ANT	0.09 ± 0.05	0.1 ± 0.06	0.05 ± 0.01	0.07 ± 0.03
PCB-52	9.2 ± 3.3	14 ± 5.2	6.7 ± 3.3	12 ± 4.0	CRB	0.03 ± 0.01	0.04 ± 0.03	0.01 ± 0.004	0.03 ± 0.04
PCB-49	6.4 ± 3.7	9.1 ± 4.5	4.8 ± 2.5	8.3 ± 3.7	FL	0.8 ± 0.5	1.0 ± 0.5	0.4 ± 0.1	0.5 ± 0.1
PCB-74	12 ± 3.6	15.4 ± 07	Nd	Nd	PY	0.9 ± 0.6	1.1 ± 0.6	0.4 ± 0.1	0.5 ± 0.1
PCB-70	14 ± 3.4	16 ± 8.4	Nd	Nd	BaA	1.3 ± 1.2	1.5 ± 1.3	0.4 ± 0.2	0.4 ± 0.2
PCB-95	4.4 ± 2.2	6.9 ± 3.5	2.5 ± 1.0	4.0 ± 1.4	CHR	2.9 ± 2.4	3.4 ± 2.8	1.1 ± 0.4	1.2 ± 0.4
PCB-101	8.4 ± 5.6	12 ± 8.8	5.1 ± 3.9	6.3 ± 2.7	BbF	2.2 ± 1.5	2.6 ± 1.7	1.1 ± 0.4	1.2 ± 0.4
PCB-99	4.5 ± 1.0	7.0 ± 2.6	4.8 ± 2.3	5.7 ± 3.0	BkF	2.1 ± 1.4	2.3 ± 1.6	0.9 ± 0.4	1.0 ± 0.4
PCB-87	6.2 ± 3.1	12 ± 7.0	3.5 ± 1.3	6.6 ± 1.7	BaP	1.6 ± 1.1	1.8 ± 1.2	0.8 ± 0.4	0.8 ± 0.4
PCB-110	14 ± 5.4	20 ± 11	7.7 ± 4.5	8.6 ± 6.9	IcdP	1.6 ± 0.9	1.8 ± 1.1	0.9 ± 0.4	1.0 ± 0.4
PCB-82	9.3 ± 5.6	13.8 ± 8.6	8.0 ± 2.9	8.0 ± 2.9	DahA	0.5 ± 0.3	0.6 ± 0.4	0.3 ± 0.1	0.3 ± 0.1
PCB-151	3.5 ± 0.7	4.2 ± 2.2	Nd	Nd	BghiP	1.8 ± 1.0	2.0 ± 1.2	1.3 ± 0.6	1.3 ± 0.6
PCB-149	7.8 ± 4.5	12 ± 8.3	5.7 ± 2.2	8.9 ± 3.7	Σ ₁₆ PAHs	16.5 ± 10.8	19.4 ± 12.5	8.3 ± 3.1	9.4 ± 3.1
PCB-118	16 ± 8.7	22 ± 12	11 ± 4.5	14 ± 5.6					
PCB-153	12 ± 10	16 ± 17	6.1 ± 2.3	7.2 ± 3.0	PBDEs (pg m ⁻³)				
PCB-132	9.8 ± 3.9	13 ± 6.7	5.6 ± 2.4	5.6 ± 2.4	PBDE 28	1.8 ± 0.9	2.9 ± 1.1	1.3 ± 0.5	2.3 ± 0.7
PCB-105	9.5 ± 7.9	14 ± 13	5.2 ± 1.9	5.2 ± 1.9	PBDE 47	11 ± 10	22 ± 15	4.5 ± 1.7	7.8 ± 2.4
PCB-138	22 ± 20	34 ± 33	13 ± 1.5	13.3 ± 1.5	PBDE 100	2.8 ± 2.8	4.5 ± 4.3	1.0 ± 0.3	1.6 ± 0.6
PCB-158	18 ± 18	23 ± 14	Nd	Nd	PBDE 99	13 ± 15	22 ± 21	4.1 ± 1.4	6.7 ± 2.1
PCB-187	7.4 ± 5.4	8.0 ± 6.7	Nd	Nd	PBDE 154	3.1 ± 3.4	5.0 ± 4.9	1.1 ± 0.3	1.7 ± 0.3
PCB-183	4.9 ± 2.1	5.6 ± 3.6	Nd	Nd	PBDE 153	4.6 ± 4.6	7.6 ± 6.8	2.2 ± 0.8	3.6 ± 1.1
PCB-180	14 ± 13	20 ± 19	5.0 ± 1.1	5.4 ± 0.9	PBDE 209	81 ± 66	142 ± 227	66 ± 63	108 ± 90
Σ ₂₆ PCBs	168 ± 121	272 ± 185	84 ± 36	153 ± 50	Σ ₇ PBDEs	116 ± 85	206 ± 246	80 ± 64	132 ± 92
OCPS ^b (pg m ⁻³)					PM (µg m ⁻³)	39 ± 25	73 ± 53	32 ± 23	60 ± 28
α-HCH	1.0 ± 0.2	1.4 ± 0.4	1.3 ± 0.6	2.2 ± 0.7					
γ-HCH	1.5 ± 0.5	2.3 ± 0.7	1.9 ± 0.8	3.3 ± 0.9					
CHLPYR	22 ± 16	31 ± 24	16.0 ± 9.0	35 ± 15					
HEPEPOX	1.7 ± 0.8	2.3 ± 1.3	1.4 ± 0.7	1.6 ± 0.9					
ESLF I	1.5 ± 0.8	2.1 ± 0.8	2.1 ± 0.9	3.5 ± 1.2					
p,p'-DDE	6.5 ± 4.7	9.5 ± 5.6	11 ± 5.3	16 ± 6.9					
ESLF II	1.2 ± 0.7	2.0 ± 1.0	1.1 ± 0.6	2.3 ± 0.8					
ESLF SUL	0.7 ± 0.3	1.1 ± 0.3	0.5 ± 0.2	1.3 ± 0.4					
p,p'-DDT	17 ± 12	21 ± 12	8.9 ± 4.5	25 ± 13					

^a acenaphthylene (ACY), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP);

^b α,γ-Hexachlorocyclohexane isomers (α,γ-HCH), chlorpyrifos (CHLPYR), heptachlor epoxide (HEP EPOX), endosulfan I (ESLF I), endosulfan II (ESLF II), endosulfan sulfate (ESULFATE), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE);
Nd: not detected.

PBDEs was recently reported by a study conducted in Izmir, Turkey (Cetin and Odabasi, 2007b). For OCPs, chlorpyrifos, p,p'-DDT and p,p'-DDE had the highest concentrations in PM (Table 1). Besides these, recently, endosulfans have also been found to be the dominating particle-phase OCPs in the same industrial area (Bozlaker et al., 2009).

Σ₁₆PAH, Σ₂₆PCB, and Σ₇PBDE concentrations in both PM_{2.5} and PM₁₀ were ~2 times higher at the Industrial site while comparable levels of OCPs were found at both sites. Recently, using Positive Matrix Factorization, five PAH sources were identified in Aliaga area as biomass and coal combustion, iron-steel production, unburned crude oil and

petroleum products, and diesel and gasoline exhaust emissions with contributions of 40, 27, 27, 3, and 3%, respectively (Aydin *et al.*, 2014). PCB sources were iron-steel production and ship breaking activities, coal and wood combustion, and evaporative emissions from technical PCB mixtures with contributions of 57, 31, and 12%, respectively (Aydin *et al.*, 2014). Sources of particle-phase PAHs were investigated using diagnostic plots and diagnostic ratios in Izmir urban area and it was indicated that traffic emissions (petroleum combustion) and residential heating were the dominant PAH sources (Demircioglu *et al.*, 2011a). Other previous studies in Aliaga have also indicated that iron-steel plants, ship-breaking activities, petroleum refinery and petrochemical plant are significant POP emitters in the region (Cetin and Odabasi, 2007b; Odabasi *et al.*, 2009; Odabasi *et al.*, 2015). Therefore, higher PAH, PCB, and PBDE concentrations observed in the industrial site of the present study could be attributed to emissions from the industries located in the vicinity of the sampling site. On the other hand, similar OCP levels observed in industrial and urban sites could be due to lack of any specific nearby sources at both sites. Bozlaker *et al.* (2009) have shown that variations of atmospheric OCP levels in the Aliaga region are driven by dry/wet deposition and air-surface exchange (i.e., absorption in winter, volatilization in summer), and seasonal local/regional applications of current-use pesticides (i.e., endosulfans and chlorpyrifos).

Comparisons have indicated that the PAH concentrations in PM₁₀ (19.4 ± 12.5 and 9.4 ± 3.1 ng m⁻³) were within the ranges reported in the literature (Wu *et al.*, 2006; Chrysikou and Samara, 2009; Li *et al.*, 2011). PM₁₀ PBDE concentrations measured in the present study (206 ± 246 and 132 ± 92 pg m⁻³) were about an order of magnitude higher than those found in Greece in particulate air samples (Mandalakis *et al.*, 2009) (excluding BDE-209) and at a UK site (Wilford *et al.*, 2008). However, Deng *et al.* (2007) have measured considerably high Σ_6 PBDE concentrations (excluding BDE-209) in air particles around an electronic waste recycling site in South China. OCP concentrations found in this study were ~2 fold higher than ones measured by Xu *et al.* (2011) in China (45 ± 13 pg m⁻³ for Σ_{18} OCPs in PM₁₀) and distinctly lower than those reported by Chrysikou and Samara (2009) (sum of DDTs and HCHs concentrations in PM ~210 pg m⁻³). In the present study, particulate PCB concentrations (272 ± 185 and 153 ± 50 pg m⁻³) were higher than those reported by Cindoruk *et al.* (2007) at another industrial site (Bursa) in Turkey (particle-phase concentration, 48 pg m⁻³ for Σ_{41} PCBs), while lower than those reported by Chrysikou and Samara (2009) for Σ_5 PCBs including PCB-28, -101, -118, -153, and -180 in the urban areas (PM concentrations of 224 and 185 pg m⁻³ for two different sites).

The Size Distributions of POPs

The presence of POPs in fine PM is important in terms of human health since they have the ability to penetrate through the respiratory track and deposit into lungs. The distribution of particle-phase POPs between fine ($d_p < 2.5$ μm) and coarse ($2.5 \mu\text{m} < d_p < 10 \mu\text{m}$) fractions indicated that POPs were mostly associated with fine particles (Fig.

2). More than 85% of total PAHs were associated with fine particles. The fine fraction of PAHs generally increased with their molecular weights (Fig. 2). For example, fine fraction of FLN was 50% for both sites while the fine fractions of BghiP were 90 and 97% for Industrial and Urban sites, respectively. Similar results were reported in the literature (Offenberg and Baker, 1999; Kaupp and McLachlan, 2000; Chrysikou and Samara, 2009; Lammel *et al.*, 2010). The percent distributions of PCBs and PBDEs in fine PM were ~60 and it was up to 80 for OCPs (Fig. 2).

Similar to the results of the present study, majority of the previous studies have reported that SVOCs were mostly associated with fine particles (Duan *et al.*, 2007; Chrysikou and Samara, 2009; Luo *et al.*, 2014). A few previous studies have reported that the mass fractions of contaminants in fine particles increased with decreasing vapor pressures (Offenberg and Baker, 1999; Zhang *et al.*, 2012b; Luo *et al.*, 2014). Octanol-air partition coefficient (K_{OA}) has been commonly used to investigate and to model the gas-particle partitioning of organic compounds assuming that octanol is a good surrogate for organic matter in particles (Harner and Shoeib, 2002; Odabasi *et al.*, 2006a, b; Cetin and Odabasi, 2008; Li *et al.*, 2008). The correlation between fine particle percent and K_{OA} (adjusted for air temperature measured over the sampling periods) for the whole data set (all PAHs, PCBs, OCPs, and PBDEs) was statistically significant ($R^2 = 0.21$, $p < 0.01$) (Fig. 3). Compounds with high octanol-air partition coefficients (K_{OA}) were associated in a greater extent with fine particles. Among all compound groups, PBDEs (especially PBDE 209) behaved differently. Although fine PM fractions for PBDEs increased with K_{OA} , they presented a relatively gradual increase with K_{OA} . Using a dynamic uptake model, Cetin and Odabasi (2008) have shown that several weeks/months are required for PBDEs having high K_{OA} values to reach equilibrium between the gas and particle-phase. Therefore, the different behavior of PBDEs could be attributed to non-equilibrium conditions. When PBDEs are excluded from correlation, K_{OA} explains the 50% of the variability in fine PM fractions ($R^2 = 0.50$, $p < 0.01$). Another important parameter for the gas-particle partitioning of POPs is the organic matter (OM) content of particles (Harner and Shoeib, 2002; Odabasi *et al.*, 2006a, b; Cetin and Odabasi, 2008; Li *et al.*, 2008) which has been overlooked in the previous studies investigating the factors affecting the particle size distributions of POPs. Several recent studies have reported that the elemental and organic carbon content of fine atmospheric PM is substantially higher than those for coarse particles (Offenberg and Baker, 2000; Viidanoja *et al.*, 2002; Harrison *et al.*, 2004; Chow *et al.*, 2008; Jaafar *et al.*, 2014; Rogula-Kozłowska, 2014). Thus, the larger contribution (> 50%) of all POP compounds could be attributed to higher sorption capacity of fine PM because of its higher OM content, and association of non-volatile compounds primarily with fine PM is due to their large K_{OA} values.

Association of POPs with fine PM was further explored using the relationships between fine PM percent and meteorological parameters (i.e., temperature and wind speed). Fig. 4 illustrates the relationships between fine PM

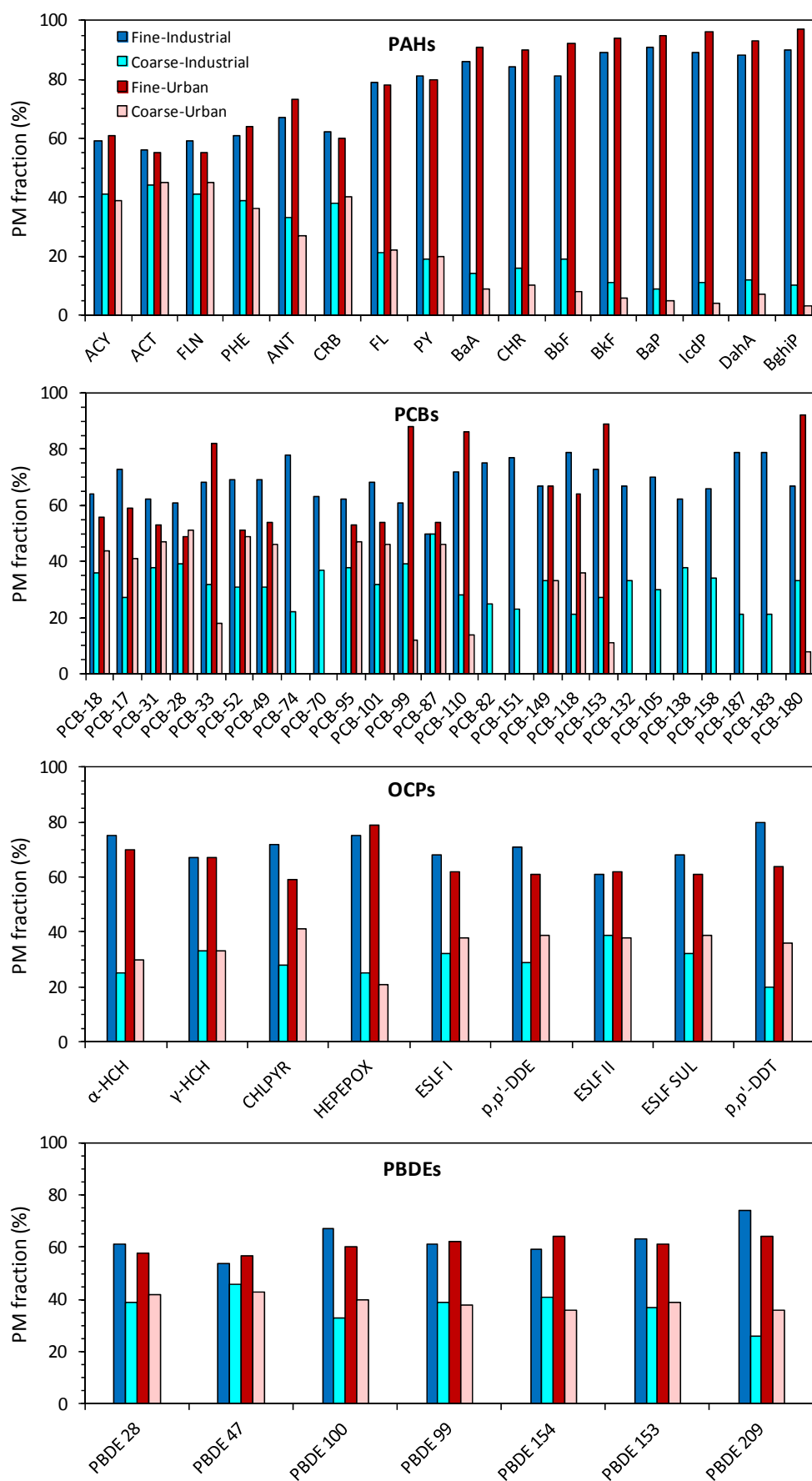


Fig. 2. Percent distributions of POPs in fine and coarse PM.

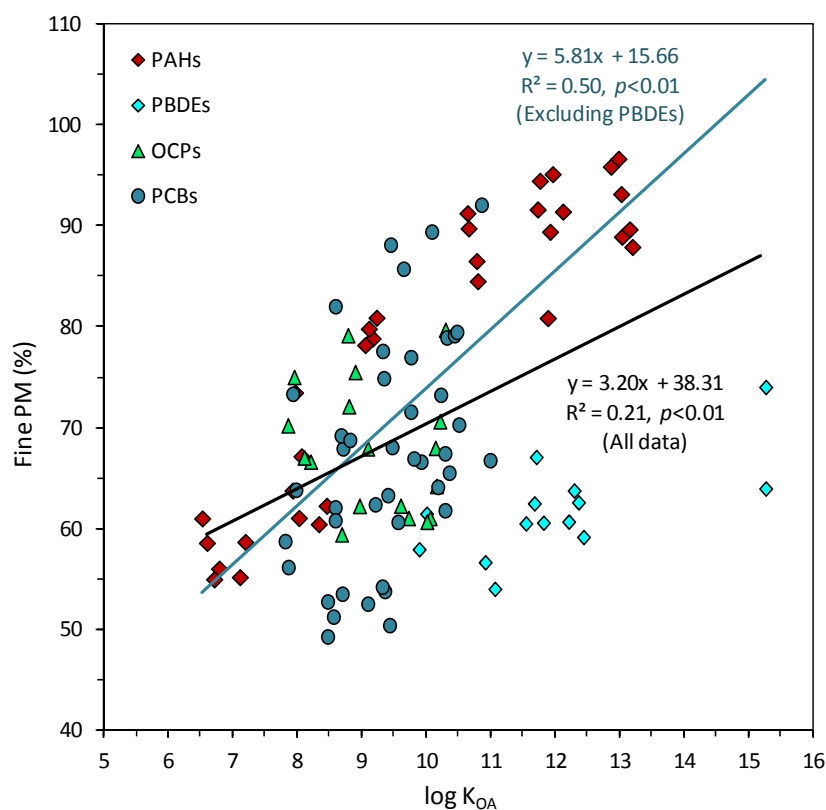


Fig. 3. Variation of fine fractions of POPs with octanol-air partition coefficients (taken from Harner and Bidleman, 1996; Zhang *et al.*, 1999; Chen *et al.*, 2002; Harner and Shoeib, 2002; Brackevelt *et al.*, 2003; Cetin and Odabasi, 2005; Odabasi *et al.*, 2006a, b).

percent and meteorological parameters for the selected compounds from each POP group. Fine PM percent decreased with temperature and temperature explained 1 to 57% of the variation in fine PM percent ($R^2 = 0.01\text{--}0.57$). Overall, the correlations were significant for the 51% of the compounds ($p < 0.01$), suggesting that temperature may be an important parameter altering the size distribution of particulate POPs. K_{OA} decreases with increasing temperature (Odabasi *et al.*, 2006b) favoring partitioning to gas-phase. Therefore, increasing temperature decreases fine PM percent by decreasing K_{OA} which is also consistent with the relationship shown in Fig. 3.

Fine PM percent also decreased with wind speed and wind speed explained 1 to 61% of the variation in fine PM percentages ($R^2 = 0.01\text{--}0.61$). Overall, the correlations were significant for the 52% of the compounds ($p < 0.01$), suggesting that wind speed may be an effective parameter altering the observed size distribution of POPs in particles. A recent study conducted in the Aliaga region has indicated that resuspension from fugitive sources (i.e., paved and unpaved roads, scrap, slag, electric arc furnace filter-dust, and coal piles) contribute substantially to the atmospheric PM in the area and the resuspended material is highly contaminated (Kara *et al.*, 2015). Odabasi *et al.* (2009) have also suggested that there are fugitive PM sources for POPs in the study area. Therefore, the observed decrease in fine PM fraction with wind speed in the present study could be attributed to increased resuspension of contaminated

coarse particles with increasing wind speed.

Implications for Atmospheric Fate and Transport

Particle size is a controlling factor for the atmospheric residence time and removal mechanisms (i.e., dry and wet deposition) for the contaminants associated with particle-phase. Consistent with the results of the present study it was found that the dry deposition velocity of PAHs generally decreased with increasing molecular weight (Odabasi *et al.*, 1999; Vardar *et al.*, 2002; Shannigrahi *et al.*, 2005; Bozlaker *et al.*, 2008a). Similarly the fine fraction is related to properties of compounds (i.e., MW and K_{OA}). Thus, dry deposition velocity could also be related to fine fraction. Dry deposition velocity was not measured in the present study. However, dry deposition velocities of several POPs were recently determined in the study area based on concurrent particle-phase air concentrations and deposition fluxes measured with dry deposition plates (Cetin and Odabasi, 2007b; Bozlaker *et al.*, 2008a, b; Bozlaker *et al.*, 2009; Demircioglu, 2011b). Using these experimentally measured deposition velocities for several POPs in the study area and fine fractions measured in the present study it was shown that dry particle deposition velocity significantly decreases with increasing fine PM fraction ($R^2 = 0.48$, $p < 0.01$, Fig. 5). This indicates that the increase of fine PM fraction with decreasing volatility may have important implications for the environmental fate and transport of POPs. As fine particles have smaller deposition velocities,

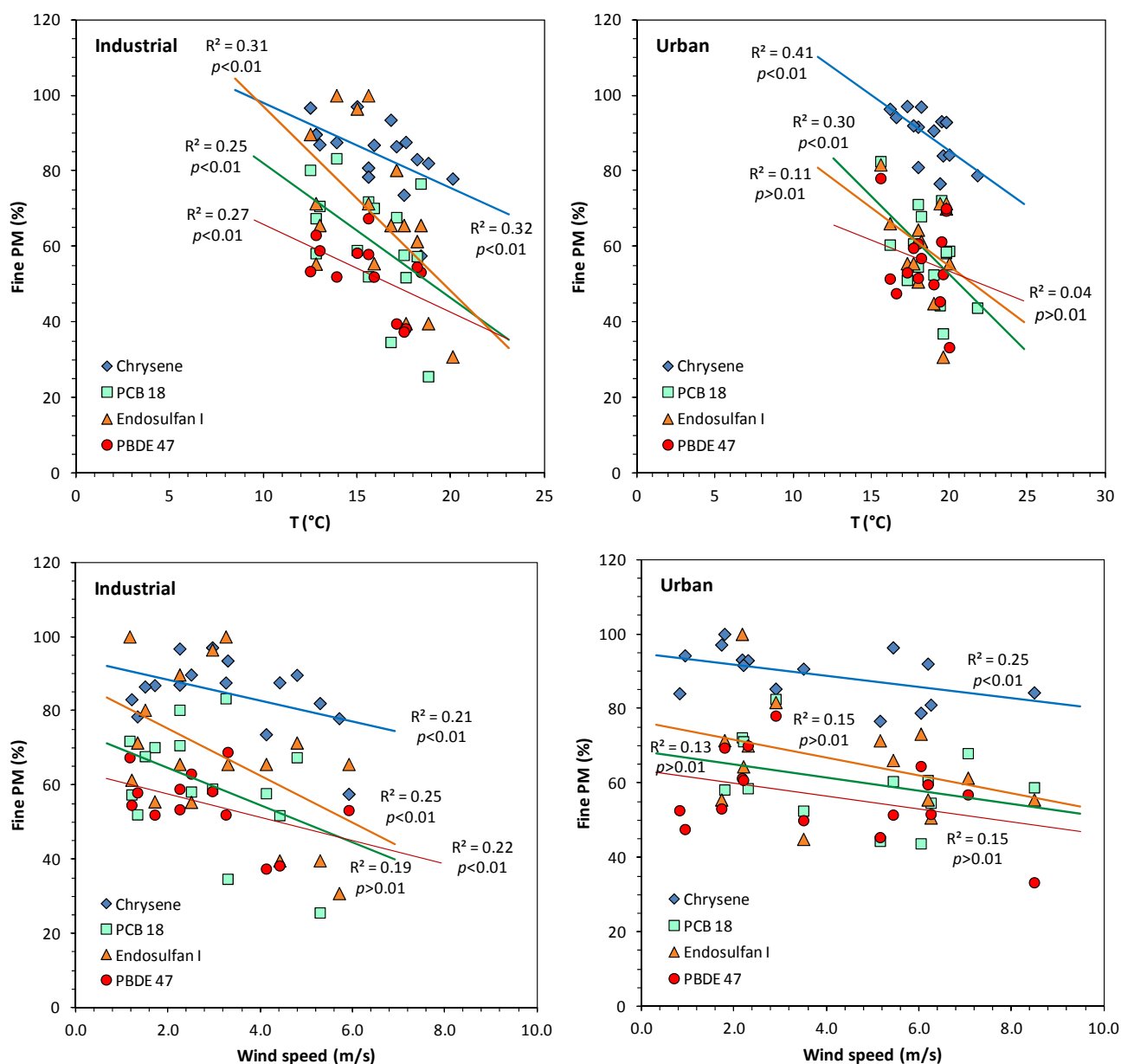


Fig. 4. Relationships between fine PM percent and temperature and wind speed.

POPs associated with these particles may be transported for long distances and can be detected in remote areas.

Recent studies conducted in the study area of the present study have shown that dry and wet atmospheric deposition significantly contribute to the loadings of PAHs, PCBs, OCPs, and PBDEs to surface waters and soils (Cetin and Odabasi, 2007b; Cetin and Odabasi, 2007a; Bozlaker et al., 2008a, b; Odabasi et al., 2008). However, most of the recent studies did not consider the variability in dry deposition velocities by assuming equal values for all compounds (Gotz et al., 2008; Zhang et al., 2009; Yue et al., 2011; Castro-Jiménez et al., 2012). Deposition velocity is affected by the meteorological parameters, physical properties of the particle (i.e., size, shape, and density), and the type and roughness characteristics of the receptor surface (Vardar et al., 2002; Seinfeld and Pandis, 1998). It was reported that

coarse particles have up to 100 times higher dry deposition velocities than fine particles (Seinfeld and Pandis, 1998). Thus, selection of an appropriate deposition velocity is crucial since the assumption of a constant value may introduce large uncertainties.

Recently, dry deposition velocities of POPs in suburban sites were found to be higher than those measured for Urban and/or Industrial sites (Cetin and Odabasi, 2007b; Demircioglu et al., 2011b). This spatial difference in deposition velocities may be due to different size distributions of urban/industrial and suburban particles. Since large particles dominate the atmospheric dry deposition, higher deposition velocities were attributed to larger particles from resuspension of polluted soil, dust particles from paved/unpaved roads, and non-vegetated areas at the suburban site. Relatively smaller dry deposition velocities that were

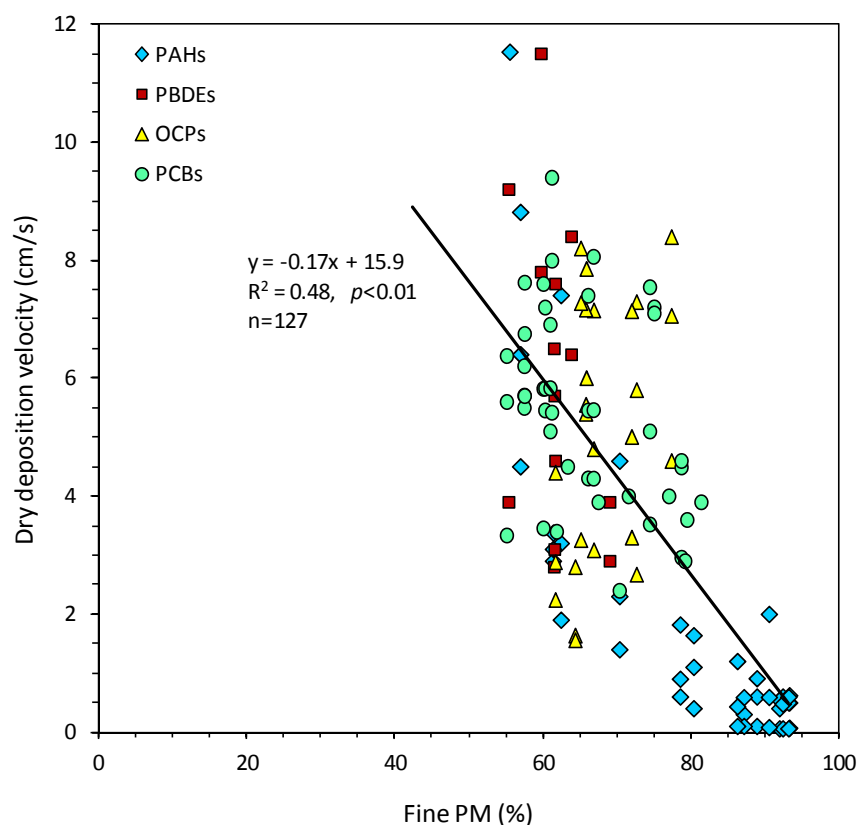


Fig. 5. Variation of dry deposition velocities of POPs measured recently in the study area (Cetin and Odabasi, 2007b; Bozlaker et al., 2008a, b; Bozlaker et al., 2009; Demircioglu, 2011b) with fine PM fractions determined in the present study.

measured in urban and/or industrial sites are consistent with the association of PAHs primarily with fine PM.

CONCLUSIONS

Persistent organic pollutant concentrations were measured on fine and coarse aerosol samples collected at two (Urban and Industrial) sites in Izmir, Turkey. POP concentrations were ~2 times higher at the Industrial site due to the local sources like scrap processing iron-steel plants, ship-breaking activities, a petroleum refinery, and a petrochemical plant that were shown to be emitting these pollutants.

The size distribution of particulate POPs indicated that they were mostly associated with fine PM (> 50%). This was attributed to the higher sorption capacity of fine PM because of its higher organic matter content compared to coarse PM.

Fine PM fraction of POPs significantly increased with octanol-air partition coefficient (K_{OA}) ($p < 0.01$) since larger K_{OA} values favor the partitioning of POPs to PM. Relationships between fine PM percent and meteorological parameters (i.e., temperature and wind speed) were also investigated. Fine PM percent decreased with temperature and the correlations were significant for 51% of the compounds ($p < 0.01$), suggesting that the decrease in K_{OA} with increasing temperature results in less partitioning to PM. Fine PM fraction also decreased with wind speed ($p < 0.01$ for the 52% of the compounds). This was attributed to

increased resuspension of contaminated coarse particles with increasing wind speed.

Using the experimental deposition velocities reported for several POPs in the study area it was shown that dry particle deposition velocity significantly decreases with increasing fine PM fraction ($p < 0.01$). This indicates that the increase in fine fraction with decreasing volatility may have important implications for environmental fate and transport of POPs.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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