

# WET DEPOSITION OF PERSISTENT ORGANIC POLLUTANTS (POPs) IN IZMIR, TURKEY

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## Introduction

Polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) are significant classes of persistent organic pollutants (POPs). There has been great interest on these semivolatile organic compounds (SOCs) in recent decades because of their high toxicity, persistence and carcinogenic/ mutagenic human health effects. POPs can be transported on local, regional and/or global scales depending on their physical and chemical properties. They can be removed from the atmosphere by dry particle deposition, gaseous deposition and wet deposition<sup>1,2</sup>. Wet deposition of POPs is an important process influencing their environmental fate and mobility. It plays an important role in scavenging both gaseous and particle-associated contaminants from the atmosphere during the periods of precipitation<sup>3</sup>. To date, several studies have investigated the levels of POPs in the atmosphere, dry deposition, surface water, and soil in Izmir<sup>1,2,4,5</sup>. However, there are no studies investigating wet deposition of POPs in this region and limited number of studies was reported all over the world<sup>6-10</sup>.

The objectives of this study were (1) to measure the concentrations of POPs such as PBDEs, PCBs, PAHs and OCPs in precipitation, (2) to determine the annual wet deposition fluxes of POPs, and to assess the relative importance of dry and wet deposition processes.

## Materials and methods

### Sample collection, preparation and analysis

Izmir is a highly industrialized metropolitan city (population: 4.11 million). Rainwater samples were collected (n=33) between September 2005 and July 2006 at a suburban site on a 4 m-high platform located on the Tinaztepe campus of the Dokuz Eylul University, 10 km southeast of Izmir's center. A metallic collector with a surface area of 0.024 m<sup>2</sup>, drained into an amber glass bottle was used for sampling. Rainwater sampling controlled manually. After sampling, rainwater was collected and its volume was determined. Samples were processed within 2 h of collection.

Rain samples were filtered through a glass fiber filter (47-mm diameter, 0.7 µm pore size) to collect particle-phase in series with a resin column (~ 10 g XAD-2) to collect dissolved-phase POPs. Prior to extraction, all samples were spiked with surrogate standards. Resin and filters were ultrasonically extracted for 60 min with a mixture of 1:1 acetone:hexane. Sodium sulfate was added to samples to remove residual water. The volume of extracts was reduced to 2 ml and transferred into hexane using a rotary evaporator and a high-purity N<sub>2</sub> stream. All samples were cleaned up and fractionated on an alumina-silicic acid column containing 3 g silicic acid (deactivated with 4.5% DI water) and 2 g alumina (deactivated with 6% DI water). The column was pre-washed with 20 mL dichloromethane (DCM) and 20 mL petroleum ether (PE). Then, the sample was added to the column and PCBs and PBDEs were eluted with 35 mL PE (Fraction 1) while PAHs and OCPs were eluted with 20 mL DCM (Fraction 2). The final extracts were solvent exchanged into hexane and were concentrated to 1 ml under a stream of N<sub>2</sub>.

All samples were analyzed for PAHs, PCBs, OCPs, and PBDEs in separate runs for each POP group with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). Fraction 1 was analyzed for PCBs and PBDEs. Then, equal volumes of Fraction 1 and 2 were combined and analyzed for PAHs and OCPs since lighter PAHs, p,p'-DDE, heptachlor, and aldrin are eluted partly with Fraction 1. 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 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.

Average recoveries for the surrogate standards were 74±12% (acenaphthene-d10), 78±13% (phenanthrene-d10), 79±17% (chrysene-d12), 76±19% (perylene-d12), 86±17% (PCB-14), 88±17% (PCB-65), 89±19% (PCB-166), and 61±9% (PBDE-77). For 1 µl injection, instrumental detection limits (IDL) were 0.15, 0.10, 0.05-0.35, 0.02-0.35 pg for PAHs, PCBs, PBDEs, and OCPs, respectively. Blank filters and resin columns (n=3 for each) were also analyzed. The limit of detection of the method (MDL, ng) was defined as the mean blank mass plus three standard deviations. IDL was used for the compounds that were not detected in blanks. Average analyte amounts in blanks were generally <5% 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

### Rainwater POP concentrations

Total (dissolved+particle) volume weighted mean (VWM) concentrations for  $\Sigma_{16}$ PAHs,  $\Sigma_{18}$ PCBs,  $\Sigma_{17}$ OCPs and  $\Sigma_7$ PBDEs were 785, 19.2, 50.5 and 29.6 ng l<sup>-1</sup>, respectively (Table 1). Low molecular weight (LMW) compounds (phenanthrene, acenaphthylene, and fluorene) dominated the  $\Sigma_{16}$ PAH concentrations. No previous measurement of POPs in wet deposition in this area was available for comparison. However, this compound profile is similar to ambient air PAH profile measured recently in the same site<sup>1,11</sup>. BDE-209 was the dominant compound for  $\Sigma_7$ PBDEs and it was followed by BDE-99 and 47. Recently, a similar ambient air PBDE profile was reported in this area<sup>4</sup>. Low chlorinated congeners (PCB-18, 31, and 28) dominated the  $\Sigma_{18}$ PCB concentrations. Chlorpyrifos, a current use pesticide, was the dominant compound for OCPs; similar to the ambient air trends obtained from an urban site (Guzelyali)<sup>5</sup> and an industrial site (Aliaga)<sup>2</sup> in Izmir, Turkey.

Table 1. Volume weighted mean POP concentrations (dissolved+particle-phase) in wet deposition samples

PBDEs	C (ng L <sup>-1</sup> )	Dissolved (%)	PCBs	C (ng L <sup>-1</sup> )	Dissolved (%)	OCPs <sup>b</sup>	C (ng L <sup>-1</sup> )	Dissolved (%)
PBDE-28	0.44	78	PCB-18	4.33	77	α-HCH	0.60	91
PBDE-47	3.33	77	PCB-17	1.73	76	γ-HCH	0.85	84
PBDE-100	0.94	82	PCB-31	3.17	80	HEP	2.95	100
PBDE-99	4.79	79	PCB-28	2.78	81	ALD	1.72	100
PBDE-154	0.36	73	PCB-33	1.14	85	CHLPYR	31.9	74
PBDE-153	0.65	77	PCB-52	1.14	78	HEPEPOX	4.81	89
PBDE-209	19.1	61	PCB-49	1.22	77	γ-CHL	0.74	97
$\Sigma_7$ PBDEs	29.6	67	PCB-44	0.17	75	ESLF I	1.42	89
			PCB-70	0.33	100	α-CHL	0.58	100
PAHs <sup>a</sup>			PCB-95	0.43	81	t-NONA	0.54	100
ACY	95.3	86	PCB-101	0.49	88	p-p'-DDE	1.29	76
ACT	23.6	73	PCB-99	0.15	100	END	0.28	98
FLN	90.8	81	PCB-87	0.96	55	ESLF II	1.02	95
PHE	329	85	PCB-110	0.41	91	p-p'-DDD	0.40	97
ANT	21.3	89	PCB-151	0.09	94	c-NONA	0.15	99
CRB	11.2	88	PCB-149	0.47	90	ESULFATE	0.57	94
FL	69.8	85	PCB-153	0.13	98	p-p'-DDT	0.79	97
PY	58.1	85	PCB-187	0.04	100	$\Sigma_{17}$ OCPs	50.5	82
BaA	8.19	73	$\Sigma_{18}$ PCBs	19.2	78			
CHR	18.3	70						
BbF	19.1	56						
BkF	9.49	52						
BaP	5.92	60						
IcdP	10.5	56						
DahA	4.56	38						
BghiP	9.04	45						
$\Sigma_{16}$ PAHs	785	82						

<sup>a</sup> 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)

<sup>b</sup> α,γ-Hexachlorocyclohexane isomers (α,γ-HCH), heptachlor (HEP), aldrin (ALD), chlorpyrifos (CHLPYR), heptachlor epoxide (HEP EPOX), endosulfan I (ESLF I), endosulfan II (ESLF II), endosulfan sulfate (ESULFATE), α-chlordane (α-CHL), γ-chlordane (γ-CHL), trans-nonachlor (t-NONA), cis-nonachlor (c-NONA), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), tetrachlorodiphenylethane (p,p'-DDD), dichlorodiphenyl dichloroethane (p,p'-DDE).

Lower molecular weight PAHs were mainly found in dissolved phase but this phase distribution decreased with increasing molecular weight. For example, by average, 89% of ANT was found in dissolved phase while this distribution decreased to 38% for DahA. Similar trend was observed for PBDEs; the contribution of dissolved fraction was 82% for BDE-100 while it was 61% for BDE-209. However, PCBs and OCPs were mostly in dissolved phase contributing an average of 78 and 82%, respectively.

Temporal variations of rainwater POP concentrations are shown in Figure 1. Throughout the sampling period, rainwater PCB, OCP and PBDE concentrations followed decreasing trends from fall to the winter and increasing trends from winter to spring/summer (Figure 1). Atmospheric PCBs, OCPs and PBDEs measured in the study area indicated that summer concentrations were higher compared to those measured in winter<sup>2,4,5,11</sup>. Fugacity and flux calculations also indicated that higher summertime concentrations are due to increased volatilization of POPs from soil or water as a result of higher temperatures during summer<sup>2,4,5,11,12</sup>. Therefore, the temporal variations of rainwater PCB, OCP and PBDE concentrations (i.e., lower concentrations in winter and higher concentrations in fall, spring and summer) could be explained by the combined effect of atmospheric concentrations and precipitation amounts (e.g., lower air concentrations and higher precipitation amounts in winter). Temporal variations of rainwater PAH concentrations were similar to that other POPs, however the decrease in winter was less pronounced. Atmospheric PAHs measured in the study area indicated that concentrations in winter were higher compared to those measured in summer. This was attributed to increase in PAH emissions due to residential heating during winter<sup>1</sup>. Thus, relatively small decrease in PAH rainwater concentrations could be due to the higher air concentrations in winter.

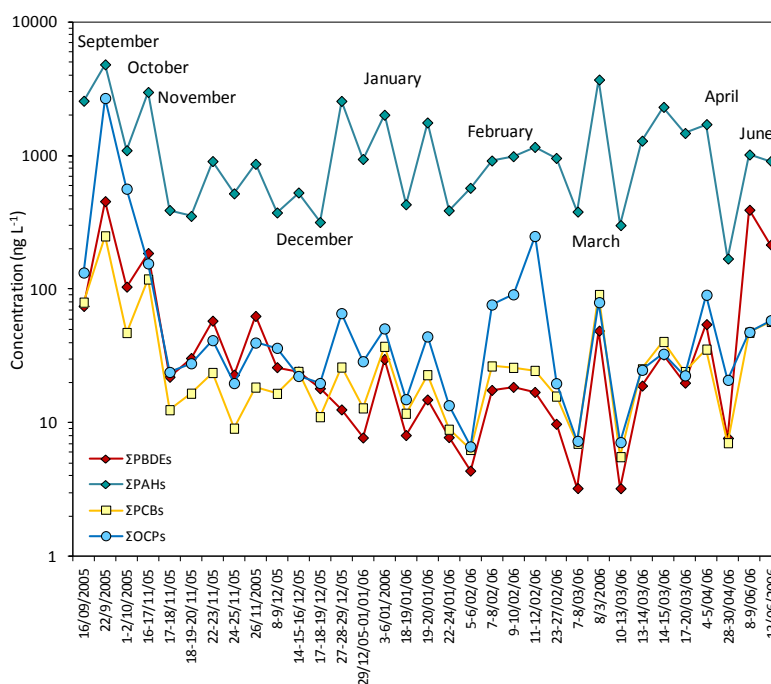


Figure 1. Temporal variation of rainwater POP concentrations (dissolved+particle).

### Wet deposition fluxes

Annual flux for  $\Sigma_7$ PBDEs was  $18.74 \mu\text{g m}^{-2} \text{year}^{-1}$  (Table 2). PBDE fluxes were mainly in dissolved phase for all congeners except BDE-209 which had comparable proportions in both phases. Annual flux for  $\Sigma_{16}$ PAHs was  $497.4 \mu\text{g m}^{-2} \text{year}^{-1}$ ; higher MW PAH fluxes had comparable amounts in both phases while lower MW ones were mostly in dissolved phase. Wet deposition fluxes for  $\Sigma_{18}$ PCBs and  $\Sigma_{17}$ OCPs were  $9.40$  and  $31.94 \mu\text{g m}^{-2} \text{year}^{-1}$ , respectively, and they were predominantly in dissolved phase.

In addition to wet deposition, dry particle deposition is an important process for POPs. Previously measured annual dry deposition fluxes for POPs in same sampling area<sup>1,12,13</sup> were compared with wet deposition fluxes to

determine the relative importance of atmospheric dry and wet deposition mechanisms (Table 2). Dry deposition was the major removal mechanism for most of the PAHs and PCBs and wet deposition contributed <20% to total (wet+dry) deposition. However, both processes were comparable for PBDEs. Wet deposition was predominant process for some OCPs such as  $\alpha$ -CHL,  $\gamma$ -CHL and t-NONA and both processes were comparable for CHLPHYR and HEPEPOX. While dry deposition was the key process for PAHs, contribution of wet deposition was higher for low MW PAHs.

Table 2. Annual wet deposition fluxes measured in this study and dry deposition fluxes of POPs ( $\mu\text{g m}^{-2}\text{year}^{-1}$ ) reported previously

PBDEs	DD	WD	WD (%)	PCBs	DD	WD	WD (%)	OCPs	DD	WD	WD (%)
PBDE-28	0.67	0.28	29	PCB-18	21.84	2.06	9	$\alpha$ -HCH	12.34	0.38	3
PBDE-47	2.22	2.11	49	PCB-17	12.68	0.81	6	$\gamma$ -HCH	11.63	0.53	4
PBDE-100	1.10	0.60	35	PCB-31	9.18	1.60	15	HEP	9.01	1.88	17
PBDE-99	1.80	3.04	63	PCB-28	11.46	1.44	11	ALD	NA	1.09	
PBDE-154	0.97	0.23	19	PCB-33	10.29	0.51	5	CHLPHYR	38.72	20.20	34
PBDE-153	1.07	0.41	28	PCB-52	11.47	0.56	5	HEPEPOX	6.96	3.05	30
PBDE-209	18.03	12.07	40	PCB-49	11.22	0.60	5	$\gamma$ -CHL	0.26	0.47	64
$\Sigma_7$ PBDE	24.68	18.74	43	PCB-44	NA	0.10		ESLF I	21.80	0.89	4
				PCB-70	NA	0.21		$\alpha$ -CHL	0.32	0.37	53
PAHs				PCB-95	4.48	0.21	5	t-NONA	0.16	0.34	69
ACY	NA	60.53		PCB-101	4.65	0.26	5	p-p'-DDE	8.79	0.80	8
ACT	NA	14.96		PCB-99	2.79	0.07	2	END	NA	0.18	
FLN	488.4	57.56	11	PCB-87	5.23	0.33	6	ESLF II	3.84	0.59	13
PHE	1148	208.9	15	PCB-110	4.25	0.23	5	p-p'-DDD	5.79	0.25	4
ANT	62.96	13.49	18	PCB-151	NA	0.05		c-NONA	0.28	0.09	25
CRB	62.20	7.08	10	PCB-149	4.81	0.26	5	ESULFATE	1.42	0.33	19
FL	224.4	44.27	16	PCB-153	NA	0.08		p-p'-DDT	80.05	0.50	1
PY	297.6	36.86	11	PCB-187	NA	0.03		$\Sigma_{17}$ OCPs	201.3	31.94	14
BaA	48.33	5.19	10	$\Sigma_{18}$ PCBs	114.4	9.40	8				
CHR	86.40	11.58	12								
BbF	161.0	11.99	7								
BkF	62.08	5.99	9								
BaP	56.13	3.75	6								
IcdP	114.2	6.62	5								
DahA	143.5	2.89	2								
BghiP	88.21	5.73	6								
$\Sigma_{16}$ PAHs	3043	497.4	14								

DD: Dry deposition (Cetin and Odabasi<sup>11</sup>; Demircioglu et al.<sup>1</sup>; Odabasi<sup>13</sup>), WD: Wet deposition, NA: not available

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