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PASSIVE SAMPLING OF PCBS AND PBDES IN TURKEY'S ATMOSPHERE

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Introduction

Persistent organic pollutants (POPs) are synthetic organic chemicals which are synthesized either intentionally or unintentionally for industrial applications[1]. Their unique properties such as persistence in the environment, toxicity, bioaccumulation and biomagnification in fatty tissues of living organisms and potential for long range transportation increase environmental and health concerns related to these chemicals[2]. They can be transported from source areas to long distances via air and water currents and deposit to remote or pristine environments where they have never been produced or used previously.

Polychlorinated biphenyls (PCBs) are a group of POPs with 209 congeners. Commercial PCB mixtures have specific chlorine content such as Arochlor 1221, Kanechlor 300, and Clophen A60 with chlorine content of 21%, 41% and 60%, respectively[3]. They are mainly used as coolants in transformers, capacitors, and any other electrical instruments[4]. Exposure to PCBs can lead to irritation of nose and lungs, changes in the blood and liver, and gastrointestinal discomfort[4].

Polybrominated diphenyl ethers (PBDEs) are another groups of POPs that also have commercial mixtures. Commercial mixtures of PBDEs are mostly found at three different levels of bromination (penta- (consisted of mostly penta- and tetra-BDEs), octa- (consisted of mostly hepta- and octa-BDEs), and deca- (consisted of mostly nona- and octa-BDE)). PBDEs are utilized as flame retardants in plastics, textiles, automobile components, polyurethane foam and wire insulation industries[5]. They can have health effects on endocrine system, can cause to liver tumors, neurodevelopmental and thyroid dysfunctions[6].

Aims of this study are to measure atmospheric air concentrations of PCBs and PBDEs at urban and background sites in 16 cities in Turkey on a west to east and south to north transect and to investigate spatial and seasonal variations. This is the most comprehensive study that has ever been conducted in Turkey to reflect atmospheric profile of POPs levels throughout the country. Additionally, a database including of a one-year POPs monitoring activity was created for residues in the atmosphere of Turkey.

Materials and methods

Sampling sites, extraction, and analysis

Sampling (Figure 1 and 2) was performed in 16 cities of Turkey at urban and background sites (a total of 32 sampling sites). These sites were selected on east to west and north to south transects. Three-months sampling periods with totally 4 periods were between May-July 2014 (1st period), August-October (2nd period) 2014, November 2014-January 2015 (3rd period), and February-April 2015 (4th period). Average temperatures recorded in these periods were in the range of 10.6-24.2ºC (1st period), 12.9-25.6ºC (2nd period), -3.6-12.8ºC (3rd period), and 3.5-15.6ºC (4th period), respectively. Air uptake rate of PUF discs were in the range of 5.6 to 12.7 m^3/day (average value: 6.3 m^3/day). The target PCBs were PCB-18, -22, -28, -31, -41/64, -44, -49, -52, -54, -56, -60, -70, -74, -87, -90/101, -95, -99, 104, -105, -110, -114, -118, -123, -132, -138, -141, -149, -151, -153, -156, -157, -158, -167, -170, -174, -180, -183, -187, -188, -189, -194, -199, and -203. The target PBDEs were PBDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, and 209.

Bowl-type passive samplers and polyurethane foam discs (PUF) were used for passive air sampling (PAS). PUF discs previously cleaned by solvent were spiked with depuration chemicals ($^{13}C_{12}$PCB15, $^{13}C_{12}$PCB32, PCB30, PCB107, PCB198 (200 ng of each), and d_6-γ-HCH (400 ng) before deployment. Following an 80-100 days deployment period depending on the sampling site, PUFs were taken back to the laboratory and kept in the freezer until analysis. Surrogate chemicals for recovery efficiency test ($^{13}C_{12}$-PCB 28, $^{13}C_{12}$-PCB 52, $^{13}C_{12}$-PCB 101, $^{13}C_{12}$-PCB 138, $^{13}C_{12}$-PCB 153, $^{13}C_{12}$-PCB 180, and $^{13}C_{12}$-PCB 209 (5 ng each)) were spiked on the PUFs before extraction and PUFs were extracted using 200 mL of acetone:hexane (1:1) mixture for 18 hours. Then, volume reduction on rotary evaporator and nitrogen blow down to an extract volume of 1 mL was performed and clean-up of extracts were carried out using 3 gr of 6% deactivated neutral alumina topped with 1 cm of granular sodium sulfate (both baked at 450 ºC overnight) on a 1 cm i.d. glass column. Elution of the column was done using 35 mL of elution solution (20% dichloromethane in hexane). Final volume of extracts were reduced to 1 mL in iso-octane and 50 ng of $^{13}C_{12}$PCB 105 was used as internal standard.

Analysis of PCBs and PBDEs were carried out by an Agilent 7890B GC coupled with 5977A MSD. It was operated in electron impact (EI) – selective ion monitoring (SIM) mode for PCBs. 2 µL sample was splitless injected to the column (DB-5, 30 m, 0.25 mm i.d., 0.1 µm film thickness) by carrier gas, Helium (1.1 mL/min). Injector, ion source (70 eV), quadrupole, and auxiliary were operated at 200°C, 230°C, 150°C, and 310°C, respectively. Temperature programme was 1 min at 90°C, 15°C/min to 160°C, 3°C/min to 210°C, and 10°C/min to 310°C (wait 10 min) for PCBs. However, PBDEs were analyzed in negative chemical ionization (NCI) mode. 2 µL of splitless injected sample sent to the capillary column (DB-5, 15 m, 0.25 mm i.d., 0.1 um film thickness) by carrier gas, Helium (1.1 mL/min). The injector, ion source (70 eV), quadrupole, and auxiliary were operated at 200 °C, 150 °C, 150 °C, and 310 °C, respectively. Temperature programme was 2 min at 80°C, 10°C/min to 285°C (wait 5 min), and 25 °C/min to 315°C (wait 5 min).

Quality control

Mean recovery efficiency of PCBs and PBDEs were 80.5% (64.7-100%) and 80±3.6% (69-94%), respectively. Travel blanks, field blanks, and laboratory control samples were also analyzed with the procedure applied to the PUF disks. The method detection limits (MDL) of PCB homologue groups were in the range of 3.26-5.37 pg/m^3 for tri-CBs, 2.84-8.85 pg/m^3 for tetra-CBs, 2.98-4.25 pg/m^3 for penta-CBs, 2.11-5.46 pg/m^3 for hexa-CBs, 1.83-4.58 pg/m^3 for hepta-CBs, and 3.17-3.26 pg/m^3 for octa-CBs. MDL of the targeted PBDEs are given in Table 1.

Results and Discussion

One-year mean level of Σ_{43}PCBs was found as 108±132 pg/m^3. The lowest and highest mean levels were 14.5±14.3 pg/m^3 (Kayseri) and 403±428 pg/m^3 (Izmir) at urban sites, respectively while these values were 19.0±22.7 pg/m^3 (Aksaray) and 217±353 pg/m^3 (Kastamonu), respectively at rural sites (Figure 1). PCB 118 was the highest average level congener among the others (26.3±44.6 pg/m^3). Additionally, the homologue groups with the highest and lowest contributions were penta-CBs (54.3%) and hexa-CBs (3.22%), respectively.

One-year average concentration of Σ_{14}PBDEs was 191±329 pg/m^3. The lowest and highest mean levels for urban sites were in the range of 31.7 pg/m^3 (Antalya) - 442 pg/m^3 (Kirklareli) whereas the range for rural sites were 6.86 pg/m^3 (Van) - 641 pg/m^3 (Antalya), respectively. Spatial distribution of Σ_{14}PBDE concentrations is shown in Figure 2. Among the congeners, BDE-190 (42%), -99 (24.4%), and -47 (20.6%) had the highest annual mean concentration.

Average levels of Σ_{43}PCBs and Σ_{14}PBDEs were found to be higher in the 3rd sampling period (November 2014 - January 2015) (Table 2). In general, median levels recorded at urban sites were similar to those measured at rural sites ($p>0.05$). When the mid-point of the temperature range (14.2ºC) is chosen to group samples as low (range: -3.6-14.1 ºC) and high (range: 14.4-25.6 ºC) temperature, the difference in the median concentrations of Σ_{43}PCBs and Σ_{14}PBDEs was not significant for urban sites ($p>0.05$). The difference in the median concentrations with temperature was significant for Σ_{43}PCBs ($p=0.047$) but it was not significant for Σ_{14}PBDEs for rural sites.

Average levels of Σ_{43}PCBs were measured in urban and rural sites of Chile as 160 and 40 pg/m^3 between January-March 2007[8]. Esen et al. also recorded mean concentration of Σ_{29}PCBs at urban sites in Bursa, Turkey as 311 pg/m^3 from June 2008 to 2009[9]. Urban and rural sites averages measured in this study were 117 and 100 pg/m^3, respectively. The mean concentrations of Σ_7PBDEs measured at urban and rural sites in China, Japan, and South Korea in the periods of March-May and August-October 2008 were 15.4, 2.47, and 7.05 pg/m^3, respectively[7]. Mean levels of Σ_{10}PBDEs were < detection limit (BDL) for urban site and 9 pg/m^3 for rural site of Tuscany Region, Italy from April to July 2008[10]. Melymuk et al. recorded lower levels of Σ_{27}PBDEs at 19 sites in Toronto with a range of 0.47 - 110 pg/m^3, urban sites having higher concentrations than rural sites[11].

In conclusion, generally urban sites had higher concentrations of Σ_{43}PCBs and Σ_{14}PBDEs than those of rural sites. Detected concentrations in this study were either higher in some cases compared to concentrations reported from other locations of the globe or comparable in most cases with the reported values of other studies. This was the first large scale nationwide database investigating spatial and temporal POPs monitoring in Turkey. Since use of PCBs and PBDEs was forbidden in Turkey, results of the study are important to indicate that these compounds are present in Turkish environmental compartments and they should be monitored regularly.

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Table 1. MDL of targeted chemicals

Analyte	PAS (pg/m^3)	Analyte	PAS (pg/m^3)
pbde17	1.01	pbde 85	3.66
pbde 28	1.16	pbde154	3.48
pbde 71	1.30	pbde153	1.41
pbde 47	1.86	pbde138	1.76
pbde 66	3.94	pbde183	1.78
pbde100	2.18	pbde190	4.23
pbde 99	1.85	pbde209	4.84

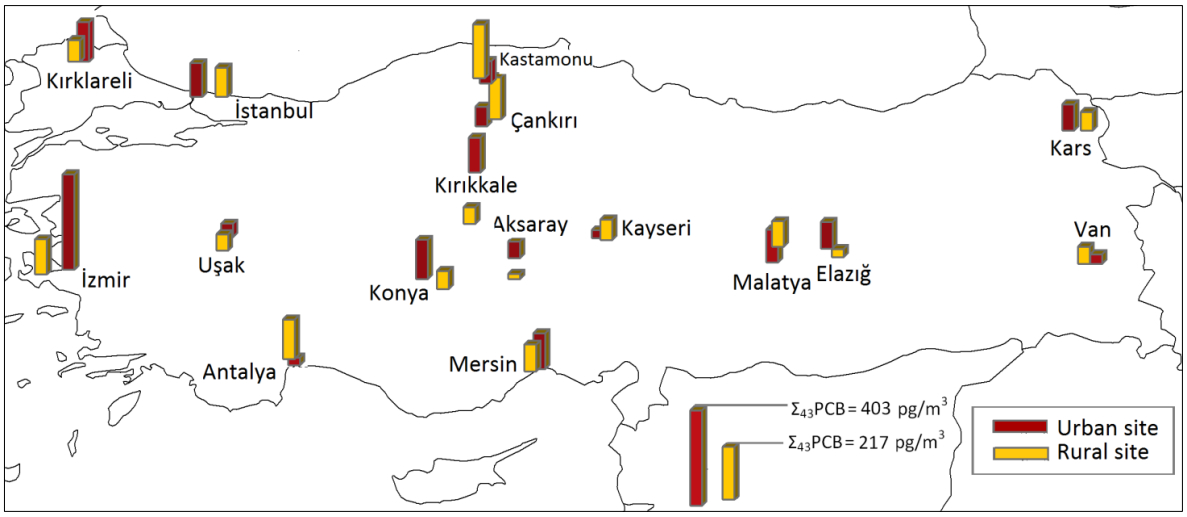

Figure 1. Mean concentration profile of Σ_{43}PCBs throughout Turkey

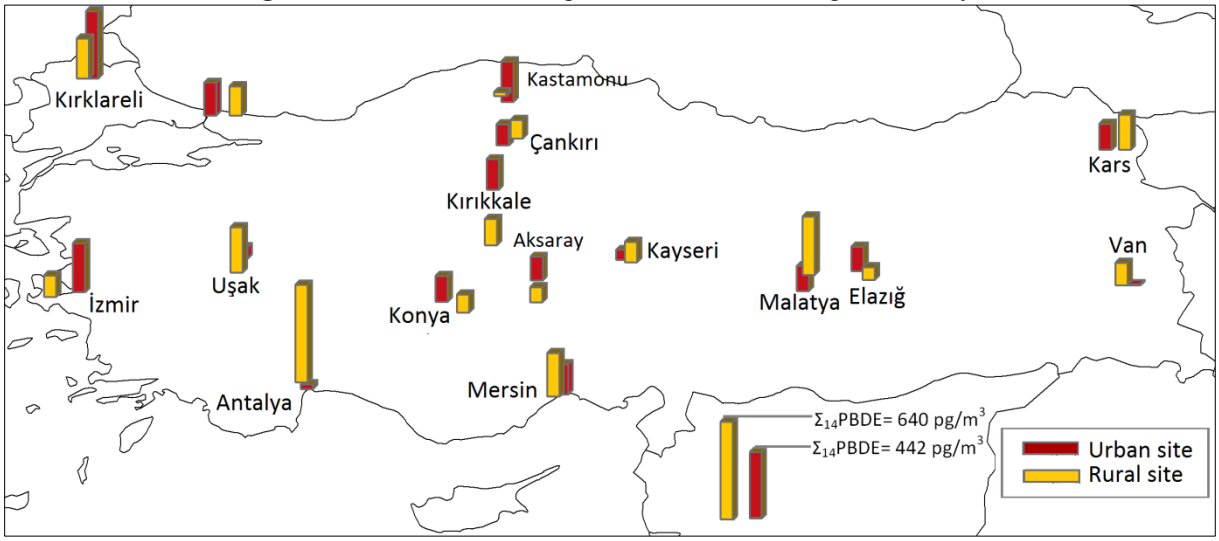

Figure 2. Mean concentration profile of Σ_{14}PBDEs throughout Turkey

Table 2. Seasonal variation of PCBs and PBDEs at urban and rural sites (pg/m^3)

	1st period		2nd period		3rd period		4th period	
	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural
Σ_{43}PCBs	83.7	42.9	110	89.2	166	174	83.4	96.2
Σ_{14}PBDEs	74.5	70.6	162	91.9	495	620	0.99	3.70