PASSIVE SAMPLING of PBDEs in TURKEY's ATMOSPHERE: PRELIMINARY RESULTS

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Introduction

Persistent organic pollutants (POPs) are a group of compounds which are synthesized intentionally or unintentionally for industrial uses[1]. These compounds draw attention of the scientists across the world because of being persistent in the environment, toxic, bioaccumulative and biomagnification in food chain, and long range transportation ability[2]. POPs can be detected at the remote areas although there is not any production or usage of these chemicals. This can be explained by grasshopper effect that POPs evaporate into air from different sources on warmer periods and they reach to cold regions by short hops and deposited[3].

Polybrominated diphenyl ethers (PBDEs) whose certain commercial mixtures are classified as POPs are structurally similar to polychlorinated biphenyls (PCBs). Commercial mixtures of PBDEs are generally available at three different levels of bromination which are 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) and are used as flame retardants in textiles, plastic, automobile components, polyurethane foam and wire insulation industries[4]. They are known to be endocrine disruptors and neurotoxins, can lead to liver tumors, neurodevelopmental, and thyroid dysfunctions[5]. Among the listed PBDE groups, fully brominated deca-BDE is the most used one with the production rate of 54,800 metric tons per year worldwide[6]. Additionally, fully brominated deca-BDE is the least bioactive one among the PBDEs since they are poorly adsorbed and rapidly eliminated from the body. However, the other congeners with lower molecular weight are highly adsorbed and slowly eliminated from the body so they are known to be highly bioaccumulative[7].

Objectives of the current study are to measure ambient air concentrations of 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. Study is in progress and in this extended abstract we report the results from the first two sampling campaign. To the best knowledge of the authors, this is the most comprehensive study has been carried out in Turkey to represent profile of POP levels throughout the country. Additionally, a database consisted of a 1-year monitoring POPs monitoring activity will be created for residues in the atmosphere of Turkey.

Materials and methods

Sampling sites, extraction, and analysis

Sampling (Figure 1 and 2) was carried out in 16 cities of Turkey at urban and background sites (a total of 32 sampling sites) that were selected on east to west and north to south transects. 3-months sampling periods were between May-July 2014 (1st period) and August-October (2nd period) 2014. Average temperatures in the sampling periods were in the range of 10.6-24.2˚C and 12.9-25.6˚C, respectively. Air uptake rate of PUF discs were ranked from 5.6 to 12.7 m^3/day with the average value of 8.5 m^3/day. The target PBDEs were PBDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, and 209.

Sampling was done using bowl-type passive samplers and polyurethane foam discs (PUF). Solvent cleaned PUF discs were spiked with depuration chemicals (^{13}C PCB15, ^{13}C PCB32, PCB30, PCB107, PCB198 (200 ng of each), and d_6-ɣ-HCH (400 ng) before deployment. After a deployment period of 80 to 100 days depending on the sampling site, PUFs were brought back to the laboratory and kept in the refrigerator until analysis. Recovery efficiency test chemicals ($^{13}C_{12}$-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 PCB 209 (5 ng each)) were spiked on the PUFs before extraction and PUFs were extracted using approx. 200 mL of hexane:acetone (1:1) mixture for 18 hours. Following volume reduction on rotary evaporator and nitrogen blow down to an extract volume of 1 mL, clean up of extracts were carried out using 3 gr of 6% deactivated neutral alumina topped with 1 cm of granular sodium sulphate (both baked at 450 ºC overnight) on a 1 cm i.d. glass column. Elution of the column was carried out using 35 mL of 20% dichloromethane (DCM) in hexane. Final volume of extracts were 1 mL in iso-octane. 50 ng of $^{13}C_{12}$PCB 105 was used as internal standard

Analysis of PBDEs were carried out using an Agilent 7890B GC coupled with 5977A MSD which was operated negative chemical ionization (NCI) mode. 2 µL of split/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). 79 and 81 were the target and qualifier ions for all PBDEs congeners except PBDE-209 whose target and qualifier ions were set as 488.5 and 486.5, respectively.

Quality control

Recovery efficiencies of the target chemicals were estimated by spiking the PUF discs with surrogate chemicals prior to extraction. Average recovery efficiency was 86.7±3.6% (57.6-140%). The method detection limits for the chemicals of interest were 1.11, 1.40, 1.24, 2.83, 1.91, 1.49, 2.26, 3.36, 3.23, 1.54, 1.47, 1.67, 8.94, and 13.3 pg/m^3 with the order listed previously. Travel blanks, field blanks, and laboratory control samples were also analyzed with the same procedure applied to the PUF disks.

Results and discussion

Concentrations of Σ_{14}PBDEs for urban sites were in the range of 3.79 (Van) - 191 (Malatya) pg/m^3 with an average value of 37.9 pg/m^3, whereas the range for rural sites were 1.49 (Aksaray) - 328 (Malatya) pg/m^3 with an average value of 33.9 pg/m^3, respectively for the 1st period. The levels varied from 12.2 (Kayseri) to 292 (Kırklareli) pg/m^3 with an average value of 59.4 pg/m^3, and 5.75 (Van) to 129 (Antalya) pg/m^3 with an average value of 31.3 pg/m^3, for urban and rural sites, respectively in the 2nd period. Spatial distribution of Σ_{14}PBDE concentrations in the 1st and 2nd sampling periods are shown in Figure 1 and Figure 2, respectively. Since the PUF sampler located in the rural site of Kırklareli at the 1st sampling period was lost, it is not shown in Figure 1. Urban sites had higher Σ_{14}PBDEs concentrations in 12 out of 15 cities (Kırklareli excluded) in the 1st period (Figure 1), whereas this ratio decreased to 10 out of 16 in the 2nd period (Figure 2). In general, average concentrations at urban sites were significantly higher than those measured at rural sites (p=0.04). When the mid-point of the temperature range (18˚C) is chosen to group samples as low (n=12, range: 10.6-17.7 ˚C) and high (n=20, range: 19.0-25-6 ˚C) temperature, the difference in the mean concentrations was significant for urban sites (p=0.10) but not for rural sites (p=0.25).

Among the homologue groups of PBDEs, tetra-BDEs were generally the most dominant one in the 1st (n=21/31) and 2nd (n=24/32) periods. Among the congeners, deca-BDE (PBDE 209) was detected only once in the whole sampling period, whereas BDE-47, -66, -99, -190 were the most frequently detected congeners found in all samples. Similarly, BDE-47 and - 99 were mostly detected ones in the study of Li et al.[8]. BDE-209 was the most dominant congener in the active-sampling study conducted in urban, suburban, and industrial sites of Izmir[9], while it was not detected in Izmir in this study.

The concentrations of PBDEs were measured at urban and rural sites in China, Japan, and South Korea in the periods of March-May and August-October 2008[8]. The average levels of Σ_7PBDEs were 15.4, 2.47, and 7.05 pg/m^3, respectively. Average concentrations of Σ_{10}PBDEs were below detection limit (BDL) for urban site and 9 pg/m^3 for rural site of Tuscany Region, Italy for the sampling period of April-July 2008[10]. The mean concentration of Σ_{14}PBDEs was found as 1.52 pg/m^3 in King George Island, Antarctica (pristine area) between 2009-2010[11]. Levels of Σ_8PBDEs measured throughout Asia were in the range of <0.13-340 pg/m^3, and similar to concentrations measured in the current study (1.49-328 pg/m^3)[12]. Melymuk et al. measured lower levels of Σ_{27}PBDEs at 19 locations in Toronto with a range from 0.47 to 110 pg/m^3, urban sites having higher concentrations than rural sites[13]. Average concentration of Σ_7PBDEs measured at two urban sites (57 pg/m^3) in Izmir was 1.7 times higher than the average level in this study (32 pg/m^3), but the level measured in suburban site (24 pg/m^3) was similar to mean concentration at rural site (21.6 pg/m^3)[9].

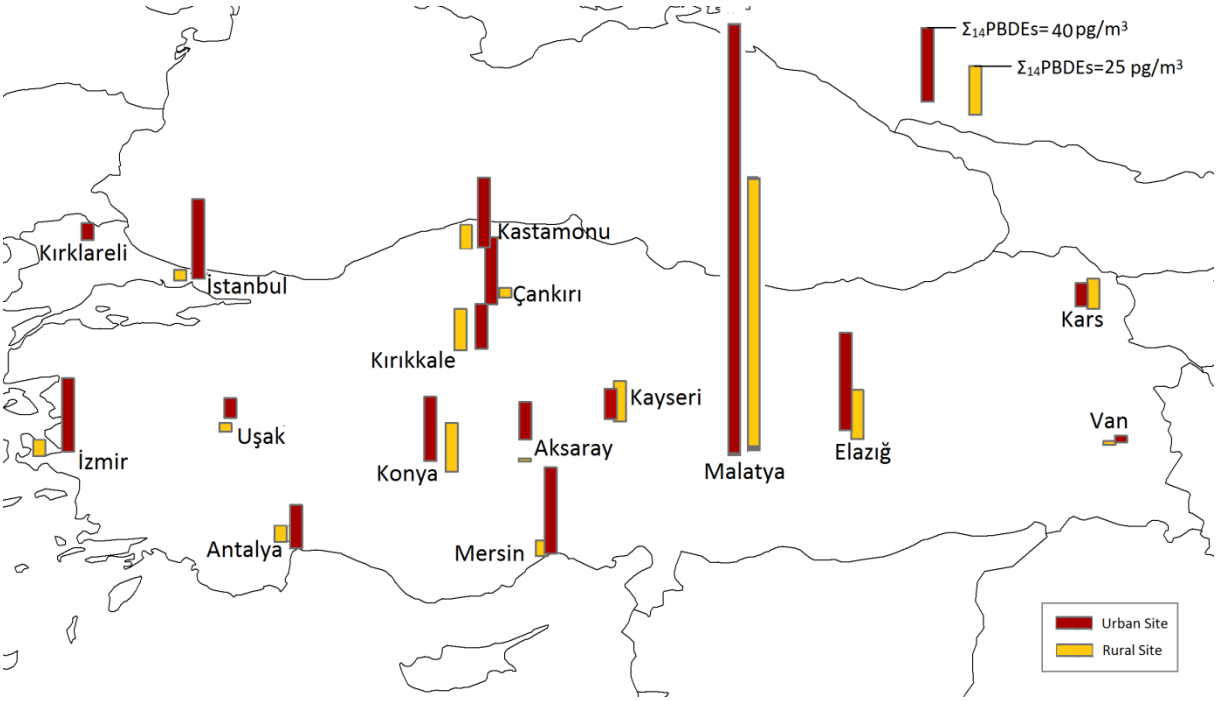

Figure 1. Concentration profile of Σ_{14}PBDEs throughout Turkey for 1st period (pg/m^3), largest bar: 328 pg/m^3

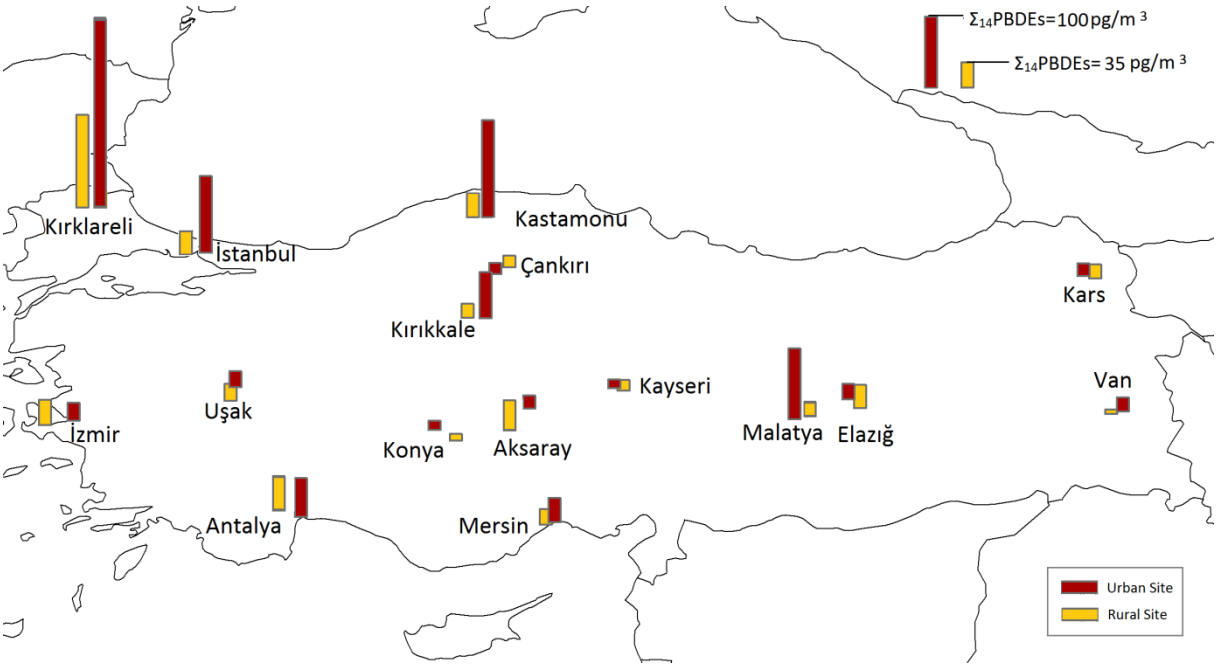

Figure 2. Concentration profile of Σ_{14}PBDEs throughout Turkey for 2nd period (pg/m^3), largest bar: 292 pg/m^3

As a conclusion, generally urban sites showed higher concentrations of Σ_{14}PBDEs compared to rural sites. Concentrations were higher in some cases compared to concentrations reported from other locations of the globe, however, in most cases detected concentrations were within the reported values of other researches. Current study is the first large scale spatial and temporal POPs monitoring study in Turkey and study is still under process. Results showed that PBDEs were at detectable levels in ambient air in Turkey. Since PBDEs were not manufactured in Turkey, results of the study is important to show that these chemicals are present in Turkish environmental compartments and they should be monitored regularly.

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