AMBIENT AIR PBDE CONCENTRATIONS ALONG AN EAST-WEST TRANSECT IN TURKEY

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Introduction

Persistent Organic Pollutants (POPs) are semi-volatile organic compounds that have become chemicals of concern over the recent decades due to their significant resistance to degradation, persistence in the environmental compartments, and their long-range atmospheric transport (LRAT) ability[1-2]. They have capacity to bioaccumulate through terrestrial and aquatic food chains to the levels that may cause adverse animal and human health effects such as immunotoxicity, neurotoxicity, developmental toxicity, cancer, mutagenicity, and endocrine disruption[2].

Polybrominated diphenyl ethers (PBDEs) are a group of aromatic brominated compounds which were used in abundance as additive flame-retardants. They have emerged as a significant class of environmental contaminants, being detected in a wide range of environmental and human biomonitoring, i.e., milk, blood plasma, and adipose tissue[3], as they were used in various consumer products including paints, plastics, foam furniture padding, textiles, rugs, curtains, televisions, building materials, aircrafts, and automobiles, accounting for 5% to 30% in some of these products by weight[4]. Global emissions of evaporative and fugitive PBDEs in 2016 were estimated to be 2.43–14.9 tons in which deca-BDE mixture accounted for 86.2–95.3 percent of total emissions. Landfills were reported to be the dominant source of evaporative and fugitive PBDE emissions (65.4 percent) while production ranked the second (32.2 percent). Combustion sources such as electric arc furnaces for steel making, secondary aluminum smelters, sintering, and power plants[5] are also significant contributors. Soils around the primary sources acting as a sink and accumulating POPs for long periods of time become important secondary sources[6].

Turkey receives air masses from Europe, Russia, the Middle East, and Africa. The literature indicates that areas in Europe and Russia are significant POP sources of LRAT[7]. The aim of this research was to measure ambient air PBDE concentrations along a South East – West transect that may help in elaboration on involving sources. Concentrations were measured using polyurethane foam – passive air samplers (PUF-PAS) in ten provinces that were divided into three groups as the South East, the Middle, and the West. Difference in concentrations between the three regions was assessed with hypothesis testing and Principal Components Analysis (PCA).

Materials and methods

Sampling sites and sample extraction

PUF-PAS were placed on a South East to West transect in ten provinces of Turkey: Adana, Gaziantep, Osmaniye, Karaman, and Malatya were clustered as the South-East group (G1), Denizli, Isparta, and Mugla were grouped as the middle group (G2), and Izmir and Bursa were grouped as the West (G3). Sampling sites are shown in Figure 1. The samplers were placed outside the urban areas. Samples were collected for seven months between December-2018 and July-2019. The mean temperature was 15.4 °C and the mean air uptake rate of PUF discs were 6.08 m^3/day during sampling period, which were determined by using depuration compounds (200 ng d_6-γHCH, 120 ng $^{13}C_{12}$ PCB-15, $^{13}C_{12}$ PCB-32, PCB-30, PCB-107, PCB-198). PUF disks were spiked with recovery surrogate chemicals (25 ng PBDE-77, PBDE-181) prior to extraction. PUFs were subjected to Soxhlet extraction for 24 h using 300 mL 1:1 acetone: hexane mixture. Extracts were concentrated to 1 mL and solvent exchanged to isooctane. Finally, all extracts were spiked with an internal standard (12 ng of $^{13}C_{12}$PCB105) and kept at -20 ºC until instrumental analysis.

Instrumental analysis

Analysis of PBDEs were carried out using an Agilent 7890B GC coupled with 5977A MSD which was operated on negative chemical ionization (NCI) mode. 2 µL of pulsed splitless-injected sample sent to the capillary column (DB-5-MS, 15 m, 0.25 mm i.d., 0.1 µm film thickness) by carrier gas, Helium (1.8 mL/min). The injector, ion source (70 eV), quadrupole and auxiliary were operated at 230 °C, 230 °C, 150 °C, and 320 °C, respectively. Temperature program was 1 min at 90°C, raised to 315°C, and 20 °C/min (wait 5 min). The target PBDEs were PBDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, and 209.

QA/QC

The mean recovery efficiency of PBDEs were 84±14 % and 84±13 % for PBDE-77 and PBDE-181, respectively. The method detection limit (MDL) for 13 PBDE congeners ranged between 0.06 pg/m^3 (PBDE-17) and 0.32 pg/m^3 (PBDE-209).

Figure 1. Sampling sites

Results and discussion

The average Σ_{14}PBDE concentration in G1 sampling points ranged between 203 pg/m^3 (Karaman) and 1178 (Osmaniye) pg/m^3. The highest average concentration congeners were PBDE-190 (101 pg/m^3) and PBDE-209 (933 pg/m^3) in Karaman and Osmaniye, respectively. The average Σ_{14}PBDE concentration in G2 sampling points ranged between 212 pg/m^3 and 283 pg/m^3. The dominant congener was PBDE-190 at all three G2 sampling points with an average value of 100 pg/m^3. The mean concentrations measured in Bursa and Izmir of G3 were 272 pg/m^3 and 173 pg/m^3. The highest congener concentration was measured in Bursa as 151 pg/m^3 for PBDE-190 which was the dominant congener at both of the G3 sampling points.

The mean Σ_{14}PBDE concentrations measured in this study are in order of G1 (517 pg/m^3) > G3 (395 pg/m^3) > G2 (247 pg/m^3). Concentrations and relative proportions according to the transect regions for each congener are illustrated in Figure 2 and Figure 3, respectively. While the lowest concentration value measured among all congeners was 0.28 pg/m^3 for PBDE-66, the highest mean concentration was measured as 325 pg/m^3 for PBDE-209. PBDE-17 (17.2 pg/m^3, 87%) PBDE-28 (28.4 pg/m^3, 79%), PBDE-47 (40.5 pg/m^3, 37%), PBDE-66 (0.51 pg/m^3, 46%), PBDE-85 (0.65 pg/m^3, 46%) concentration values were higher in G3, while PBDE-100 (36.5 pg/m^3, 37%) and PBDE-209 (325 pg/m^3, 70%) had the highest value in G2 and G1, respectively.

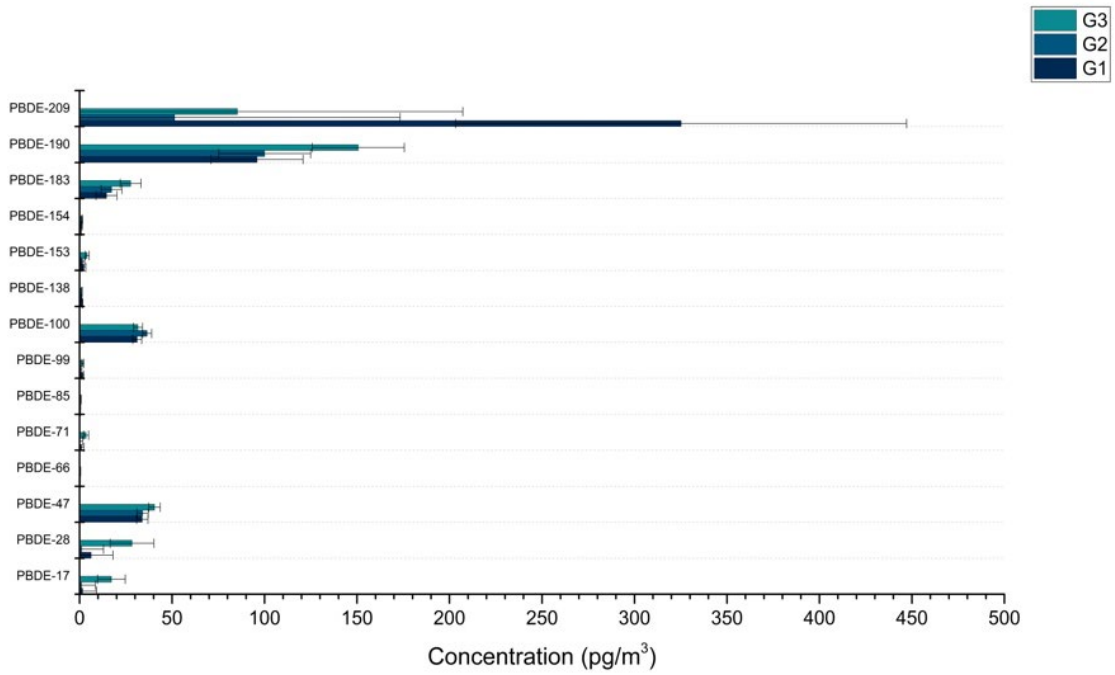

Figure 2. The mean PBDE congener concentrations of the three regions along the transect.

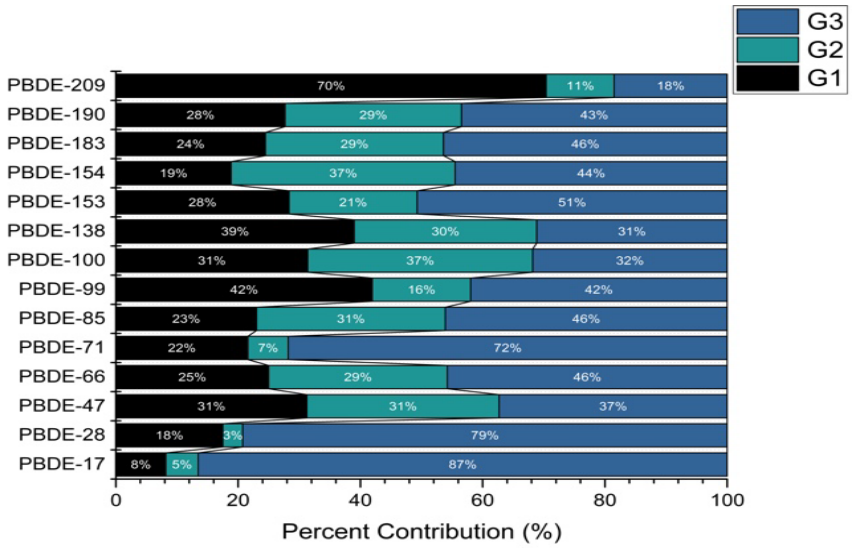

Figure 3. The relative group proportions for PBDE congeners.

Whether the data was distributed normally within the groups was evaluated using the Shapiro Wilk test[8]. The assumption of normality could not be made for none of the congeners. Therefore, Kruskal Wallis test was used for testing if there is a significant difference between the three groups. There was a difference in the medians at a significance level $\alpha = 0.05$ for five PBDE congeners that were PBDE-28 ($p=0.008$), PBDE-99 ($p=0.016$), PBDE-85 ($p=0.046$), PBDE-154 ($p=0.010$) and PBDE-190 ($p=0.021$). Results of PCA are shown in Figure 4. Fig. 4a shows that the measured PBDE congeners in G1 were compiled into three groups roughly by molecular weight (1) PBDE-47 and PBDE-28, (2) PBDE-99, PBDE-100 and PBDE-138, and (3) PBDE-85, PBDE-154 and PBDE-183. In G2 (Fig. 4b), PBDE-99 and PBDE-138 were individually separated while PBDE-47, -183, and -190 formed a third compilation. In G3 (Fig. 4c), however, nine congeners were all separated showing no groupings. The differences in PCA results indicate that the three regions along the studied transect may be under the effect of different and/or varying sources.

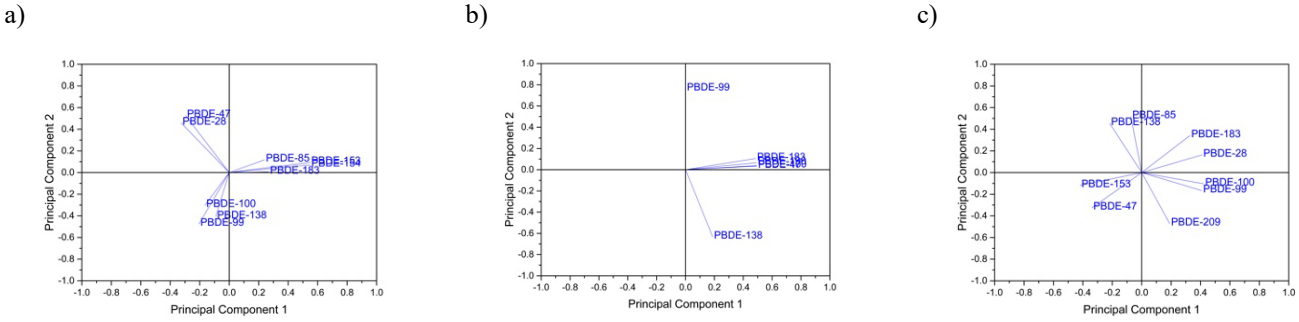

Figure 4. PCA loading plots for each transect group a) G1 b) G2 c) G3.

Lammel et al.[9], collected passive samples in Bursa and Izmir in 2012. The average Σ_5PBDE concentration measured in Izmir (8.5 pg/m^3) was much higher than that for Bursa (0.7 pg/m^3) while the highest congener concentration was reported as 7.5 pg/m^3 for PBDE 28. In this study the mean PBDE-28 concentration of Izmir and Bursa (G3) was measured as 28.4 pg/m^3. Cetin et al.[10] conducted studies in different regions of Izmir, Turkey, during winter and summer seasons. The highest Σ_7PBDE concentration was reported in industrial region in both seasons. The mean concentrations reported for winter season were 21±17 pg/m^3, 40± 16 pg/m^3, 43±9 pg/m^3, 53±18 pg/m^3 for suburban, urban1, urban2, and industrial region, respectively. Those concentrations were higher in summer season except urban1. Concentrations were reported as 24±10 pg/m^3, 32±17 pg/m^3, 82±28 pg/m^3, 117±23 pg/m^3 in order of suburban, urban1, urban2, and industrial. PBDE-209 was the dominant congener at all sites, followed by PBDE-99 and PBDE-47. Besis et al.[11] collected 22 active daily samples in 2012 at the same site as in this study. Except for PBDE-209, the average Σ_8PBDE concentration was 10.8 pg/m^3 for the gas phase, 3.57 pg/m^3 for the particulate phase, and 14.37 pg/m^3 for the total concentration. However, the average gas phase

PBDE-209 concentration was 90 pg/m^3, the particulate phase 93 pg/m^3, and the total 183 pg/m^3 was higher than the sum of other congeners. Kurt Karakus et al.[12] collected passive samples in urban and rural areas of Turkey in 2014-15. The reported mean Σ_{14}PBDE concentrations varied between 99.3 pg/m^3 and 566 pg/m^3 in urban, and between 5.29 pg/m^3 to 709 pg/m^3 in rural areas. The mean concentration values of $\sum_{14}$ PBDE measured in this study are between those reported by Kurt Karakus et al.[12] In this study, like Cetin et al.[10] reported, PBDE-209 was the dominant congener and lowest mean value was found in G2 as 51.42 pg/m^3. Tlili et al.[13] reported $\sum_8$PBDE concentration between 2.84 pg/m^3 and 185 pg/m^3 at the center of Paris, France. Jaward et al.[14] reported $\sum_8$PBDEs concentration for four Asian countries. The highest concentration was reported for China where the range was between 0.13 pg/m^3 and 340 pg/m^3. For the other three countries, levels (in order of highest concentration measured) were Japan (71 pg/m^3), Singapore (29 pg/m^3), and South Korea (27 pg/m^3), respectively. Harrad et al.[15] measured $\sum_8$PBDE congeners in 10 locations of West Midland, UK. Concentration ranged from 2.84-8.47 among sampling locations which were urban, suburban, and rural. The values measured in this study were relatively higher than the values measured in different countries.

In conclusion, PBDE concentrations and relative group proportions for each congener varied between three groups of locations along a South East – West transect in Turkey. There were significant differences in the mean concentrations of some congeners. Congeners were compiled differently with PCA in the three groups along the transect. The results of this study indicate that sources that determine the concentrations in different regions of the country are probably different.

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