Selected Persistent Organic Pollutants in Ambient Air in Turkey: regional sources and controlling factors

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Abstract

As a result of its unique location, Turkey receives air masses from Europe, Russia, Middle East, and Africa, making it an important place in terms of long range atmospheric transport (LRT) of contaminants. Atmospheric levels of 22 organochlorine pesticides (OCPs), 45 polychlorinated biphenyls (PCBs), and 14 polybrominated diphenyl ethers (PBDEs) were measured in two metropolitan cities, Istanbul and Izmir, on a weekly basis from May 2014 to May 2015. Dichlorodiphenyltrichloroethane (DDT) and its derivatives were dominant OCP species, followed by isomers of hexachlorocyclohexane (HCH) at both sites. The annual mean concentration of ΣDDX (sum of *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDE, and *p,p′*-DDE) was 82 pg/m^3 for Istanbul and 89 pg/m^3 for Izmir, while these levels were about 46 pg/m^3 for ΣHCHs (sum of *α*-, *β*-, *γ*-, and *δ*-HCH) at both of the sites. At both stations, tri- and tetra-PCBs and tetra- and penta-PBDEs were dominant congeners. The temperature dependence indicates that both LRT and local contaminated areas contribute to the elevated levels. A Lagrangian particle dispersion model (FLEXPART) showed a few potential source regions in northern Africa and Middle East, southern-southwestern and eastern Europe including Russia, as well as from local domestic metropolitan areas.

Keywords: Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs), active sampling, particle dispersion modelling, Turkey

Synopsis:

Air masses from Europe, Russia, the Middle East and Africa carry POPs to Turkey which is a country located at an intersection of continents.

INTRODUCTION

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants (POPs) that are noticeable with properties of low water but high lipid solubility leading to bioaccumulation in environmental compartments. The atmosphere is the main pathway carrying the POPs to long distances due to their semi-volatile characteristics[1]. Hence, the presence of POPs even in the remote environments, where they have never been produced or used,[2, 3] is attributed to long-range atmospheric transport (LRT).

Among the three halogenated POP groups, the amounts of OCPs released to the environment were historically the highest with cumulative global usages (in metric tonnes) of 1500000, 550000, and 720000 for DDT, technical HCH, and lindane, respectively[4]. Volatilization from contaminated sites (from agricultural sites and forestry) and LRT are the main sources of OCPs[5, 6]. PCB congeners were used in many industrial processes such as electrical insulation, heat exchange fluids, plasticizers in paints, ink solvent/carriers in carbonless copy paper, adhesives, sealants, flame retardants, and plastics for their thermal stability, acid-, alkali-, and hydrolysis-resistance[7]. PBDEs, having similar structure as PCBs are brominated chemicals and were used as flame retardants in consumer products such as polymers, plastics, technological devices, textiles[8, 9]. The published studies agree on spatial and seasonal variations of the PCBs and PBDEs[10, 11].

Turkey was not a manufacturer of POPs including PCBs, PBDEs or most of the OCPs, but it became a party to the Stockholm Convention[12] as of 2010, resulting in the responsibility for prohibition/elimination/restriction of use of certain POPs, environmentally sound management of stockpiles/wastes, monitoring of POPs levels and preparation, and revision of a national implementation plan. Therefore, determination of POPs in the environmental media in Turkey has received increased attention, resulting in many studies reporting ambient air

77 concentrations of OCPs, PCBs, and PBDEs, some of which are cited here[13-18]. The detected
78 air concentrations were the results of contamination from past use, formation as a by-product,
79 and LRT from the countries where these compounds were produced and heavily used[14, 19].

80 Turkey receives air masses from Europe, Russia, the Middle East, and Africa, so the
81 goal of this study was to assess the levels of POPs and source regions for two major urban
82 centers with different characteristics. For this purpose, OCP, PCB, and PBDE concentrations
83 were measured for a year, and a Lagrangian particle dispersion-model, FLEXPART, was used
84 to investigate LRT of the target chemicals. Istanbul is the largest metropolis in Turkey with a
85 diverse industrial economy. Based on its location, LRT from different countries in Europe,
86 Asia, and the Mediterranean region could carry persistent contaminants to the city[20]. Izmir,
87 the third most populated metropolis in Turkey, is surrounded with agricultural areas as well as
88 chemical, steel scrap processing industries and two refineries. LRT from other countries is
89 believed to be an important contributor for ambient air POP levels in Izmir[21].

90 **MATERIALS AND METHODS**

91 **Chemicals and reagents**

92 All solvents were chromatography-grade and purchased from Merck (Merck EMD
93 Millipore, USA). Granular anhydrous Na_2SO_4 and alumina (90 active neutral, 0.063-0.2 mm
94 particulate size) were also from Merck. Details on analytical standards of recovery surrogate
95 ($^{13}C_{12}$- PCB-28, -52, -101, -138, -153, -180, and -209), and target chemicals are given in
96 Supporting Information (SI) Table S1.

97 **Study Area and Sample Collection**

98 Air samples were collected for a year between May 2014 and May 2015 at an suburban
99 site (41°9'6.06"N, 29°7'58.08"E, located in Beykoz,) in Istanbul, and at a rural site
100 (38°19'4.31"N, 26°38'17.71"E, located near the village of Gulbahce, which is about 60 km

away from city center) in Izmir (Figure 1, Table S2 and S3). Samples were numbered with respect to sample collection date. Istanbul is the largest city in Turkey with a population of 15,029,231[22] which has a transitional climate between the Continental and Mediterranean. The gross domestic product of Istanbul is significantly provided by the industry sector with a percentage of 30%, whereas the contribution of agriculture is only 1%[23]. Izmir is the third most populous city in Turkey with a population of 4,279,677[22], which has the Mediterranean climate. The sampling site in Istanbul is suburban while the site in Izmir is in a rural area. Istanbul sampling site is encircled by naturally vegetated fields and settlement whereas agricultural fields and naturally vegetated encircle Izmir site. However, depending on the wind direction both sites may be under the influence of the metropolitan areas in addition to effect of an industrial region that is about 60 km north of the sampling site in Izmir.

Air was sampled once a week for a 24-hour period by using high-volume (High-Vol) samplers (Thermo-Andersen Model GPS-11 in Izmir, and Tisch Environmental TE-1000BLX in Istanbul), approx. 220 m^3 per sample in Izmir and approx. 287 m^3 per sample in Istanbul sampling site. Glass fiber filters (GFFs, 10.2 cm in diameter) and polyurethane foam plugs (PUF plug, 5.5 cm in diameter and 5 cm in length) were the sampling media. Two PUF plugs were placed in series to evaluate and eliminate breakthrough.

Sample Preparation and Chemical Analysis

All equipment and glassware was cleaned according to methods reported by USEPA[24] against contamination. The PUF plugs were cleaned up on Soxhlet apparatus using a series of solvent while GFF filters were baked at 450˚C for at least for 12 h before use. Target chemicals were extracted from PUF plugs using hexane (HEX):acetone (ACE) (1:1) mixture while GFFs were extracted using dichloromethane (DCM). $^{13}C_{12}$-PCB 28, 52, 101, 138, 153, 180, and 209 (50 ng each) was added to each sample to check the recovery rates. Extract volume was reduced to ~1 mL using rotary evaporator and under a gentle stream of N_2 gas.

126 Column chromatography cleanup was carried out using 3 g of 6% deactivated alumina and
127 column was eluted using 35 mL of 20% DCM in HEX. Final volume was 1 mL in isooctane,
128 and all samples were spiked with 50 ng of $^{13}C_{12}$-PCB 105 as internal standard. Further details
129 are given in Table S4.

130 Analysis of compounds of interest was performed on a GC (Agilent 7890B) coupled with
131 an MSD (Agilent 5977 MSD). Co-eluting congeners (PCB-41/64 and PCB-90/101) were
132 quantified together. Further details on capillary column, instrument operating conditions are
133 given in Table S5. Twenty-two OCP compounds, 45 PCB congeners, and 14 PBDE congeners
134 were selected as target pollutants (Table S1) in this study.

135 **Quality Assurance/ Quality Control (QA/QC)**

136 Laboratory and field blank samples were processed along with the samples and details
137 are given in Table S4. Method detection limit (MDL) values were calculated as average blank
138 concentration plus three standard deviations for the compounds that were observed in blank
139 samples. The instrumental detection limits (IDLs) are the analyte concentrations that would
140 generate a signal to noise ratio of at least 3:1. IDLs were used as MDL for non-detected
141 analytes in the blanks (MDL=IDL)[25]. MDL and IDL values of the targeted chemicals are
142 listed in Table S6.

143 Percent recovery efficiencies of recovery surrogate compounds from PUF plug
144 samples (n=129) ranged between 60.2% and 140% (87.5±15.1%) whereas the values ranged
145 59.6-139% (87.8±16.5) for GFFs (n=113). The target analytes were not corrected for
146 surrogate or procedural recoveries. Further details on recovery of individual surrogates are
147 given in Table S7. Although no surrogate compounds for PBDEs were included in the current
148 study but in a similar study conducted at the same time period as the current study in our
149 laboratory, average recovery efficiency of PBDE 77 was 92.9±13.3% (66.1% - 118) % (25 ng,

n=22). Further details on the procedural recovery and breakthrough test of target analytes are given in Table S4. A detection frequency of at least 25% was required for inclusion in the data analyses. Due to acceptable rates of breakthrough, gas phase concentrations were calculated as the sum of concentrations detected in top and bottom PUF plugs.

LRT Modeling

The Lagrangian particle dispersion model FLEXPART, version 8, was used for LRT modeling[26]. The model was run in backward mode, in order to identify the source regions of air pollutants at the sampling location[27]. For every sample, 1 particle per second (86400 per sample) were released, randomly between 0 and 200 m and their trajectories computed for five days back in time (Figure S1 and S2). FLEXPART model was driven with analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF) 3-hourly analyses with 1° × 1° resolution. The FLEXPART output resolution was set to hourly and the following vertical levels: 100, 200, 500, 1000, 2000, 5000, 10 000 and 15 000 m. The results are shown as plots of the residence time, which is a measure of the times particles resided in a grid cell. The prediction of source regions was made by using the Istanbul and Izmir samples with $\geq 95^{th}$ percentile values of ΣDDX (sum of *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDE, and *p,p′*-DDE), ΣHCHs (sum of *α*-, *β*-, *γ*-, and *δ*-HCH), Σ_{45}PCBs, and Σ_{14}PBDEs gas-phase concentrations (Figure S3-S5).

RESULTS AND DISCUSSION

In the current manuscript, unless otherwise stated, the concentrations reported are totals - the sum of gas and particle phase concentrations.

Ambient air POP concentrations

OCPs. The levels of selected OCP compounds in Istanbul and in Izmir are shown in Figure S6 while the monthly OCP levels are given in Figure S7 (for Istanbul) and Figure S8 (for Izmir). Compounds with detection frequencies <25 %, i.e. aldrin, HEPX (heptachlor epoxide), and endoSO_4 (endosulfan sulfate), are not reported. Annual average concentration of Σ_{22}OCPs in Istanbul and Izmir (Figure 1) were 264±158 pg/m^3 (nd-670 pg/m^3) and 323±348 pg/m^3 (nd-1350 pg/m^3), respectively. The dominant OCP compounds were determined as ΣDDX and ΣHCHs at both sampling stations. The most of detected OCP compounds have not been used in Turkey due to the restrictions and bans since 1970s-1980s[28]. A seasonal trend was not observed for any of the target OCP compounds, except for endrin in Istanbul. On the other hand, the ambient concentrations of most OCP compounds in Izmir station, such as DDTs, HCHs, HEPT (heptachlor), endrin, dieldrin, and β-endo (β-endosulfan), reached the maximum values in January - February 2015. A sharp rise in many targeted OCP compounds (*p,p′*-DDE, endrin, CC (cis-chlordane), TC (trans-chlordane), α-endo (α-endosulfan), β-endo, endoSO_4, and mirex) levels occurred on July 12, 2014 (Sample #10) in Izmir, which was an unexplained episodic situation (even when considering air mass analysis). These values, exceeding annual mean levels by more than a factor of 14 to 102, were not considered in the calculations.

The dominant OCP was found as ΣDDX with an annual mean level of 82.2±87.7 pg/m^3 and 89.2±121 pg/m^3 in Istanbul and Izmir, respectively. DDT has been banned in Turkey since 1985[28]. However, it might still be used in developing countries for agricultural and sanitary purposes due to its low price and effectiveness[29]. For the Istanbul station, April and March were resulted in higher monthly ΣDDX levels as 186±90 pg/m^3 and 155±108 pg/m^3, respectively. For the Izmir station, the monthly ΣDDX levels were as high as 237±69 pg/m^3 in March 2015, 200±164 pg/m^3 in January 2015, and 166±153 pg/m^3 in February 2015.

The use of dicofol is an emission source of DDT and its isomers, particularly *o,p′*-DDT[30, 31]. The *o,p′*-DDT/*p,p′*-DDT ratio for 14 different dicofol formulations used in Turkey was reported to range from 0.01 to 2.1[31]. In this study, the *o,p′*-DDT/*p,p′*-DDT ratio was 0.008 for Istanbul and 0.004 for Izmir, indicating minor influence of dicofol on air advected to these sites. The mean values for ratios of DDE/DDT and DDD/DDT were calculated as 0.34 and 0.08 for Istanbul, and 0.72 and 0.06 for Izmir, respectively. Therefore, DDT had been broken down and mostly converted to DDE over time. In Europe and elsewhere long after DDT ban, DDE now dominates DDX species in the abiotic environment[32].

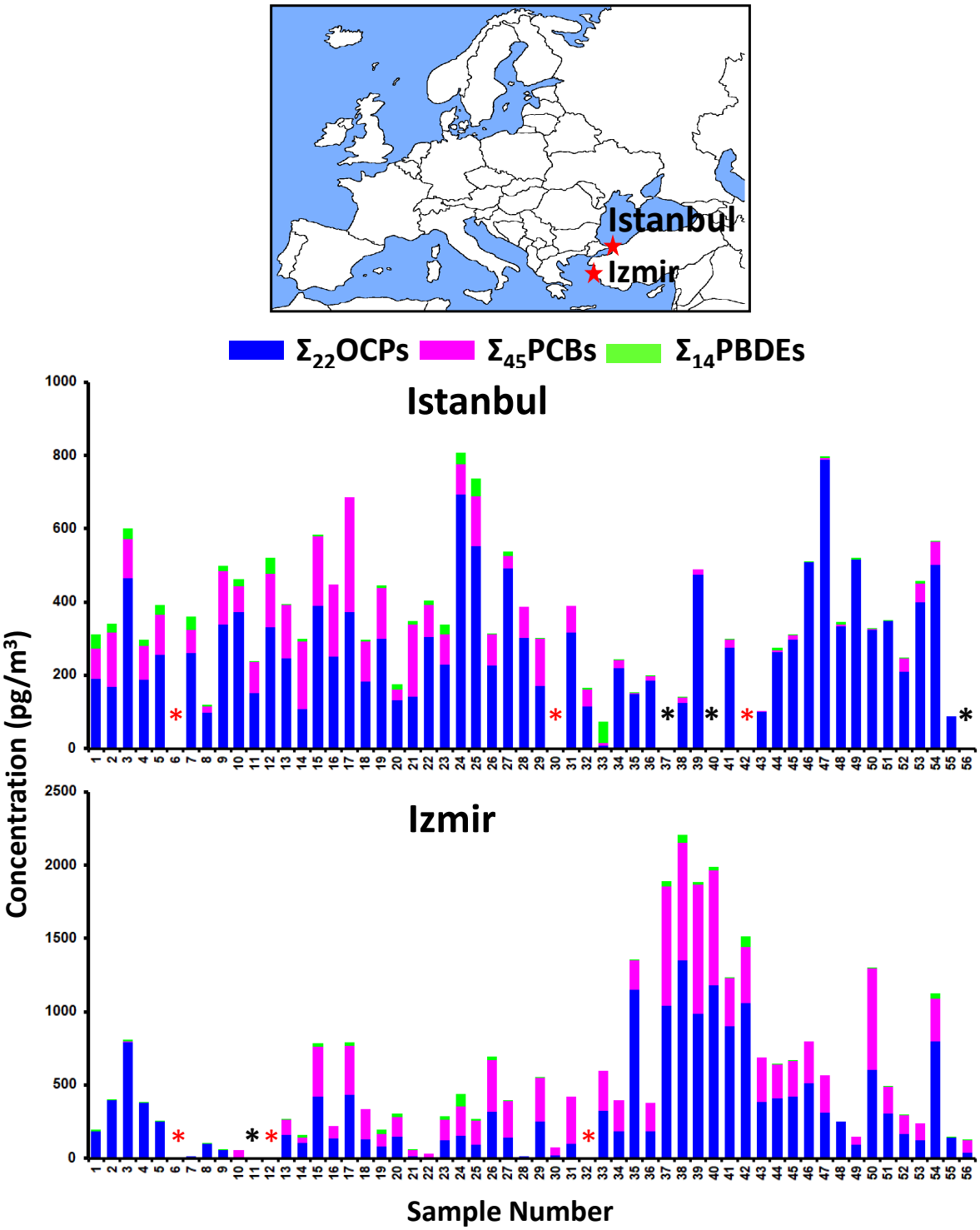


Figure 1. Total concentration of Σ_{22}OCPs, Σ_{45}PCBs and Σ_{14}PBDEs in (a) Izmir and (b) Istanbul (details of sampling are given in Table S2 and S3) (*no data due to instrument malfunction; *data <MDL)

HCHs were the second most dominant OCP group with annual mean concentrations of 45.2±37.6 pg/m^3 and 46.6±79.2 pg/m^3 in Istanbul and Izmir, respectively. The use of HCH

224 was banned in 1985 in Turkey[28]. The highest monthly ΣHCHs level was measured as
225 77.9±78.7 pg/m^3 in July 2014 and 75.8±53.6 pg/m^3 in March 2015 in Istanbul. A clear
226 seasonality was not observed in HCH levels in Istanbul, similar to that of many targeted OCP
227 compounds, which suggests that secondary sources (re-volatilization from soils which earlier
228 received contaminated depositions) were not dominant[33], but advection was. Contrary to the
229 highest ΣHCHs level measured in Istanbul in July 2014, ΣHCHs level in this month was
230 comparably low (3.3±8.2 pg/m^3) in Izmir. The highest monthly concentrations of HCHs were
231 measured as 179±104 pg/m^3 in January 2015, and 160±164 pg/m^3 in February 2015 in Izmir.
232 So, HCHs were detected at higher levels in the coldest months at Izmir station, on the
233 contrary to the notion that higher concentrations occur with increase in temperature due to
234 increasing volatilization from contaminated terrestrial surfaces to the atmosphere[34]. Yao et.
235 al.[35] investigated lindane concentrations for one year after the Canadian ban on lindane for
236 agricultural use. In contrast with decrease of, γ–HCH air concentrations over the Great Lakes
237 region, during the sampling period a γ–HCH air pollution episode resulted in an increase of
238 the concentration by 2 orders of magnitude suggesting a localized emission in the city from an
239 unknown and episodic source.

240 Two targeted HCHs, *β*- and *δ*-HCH, were rarely encountered in the samples collected
241 at both stations, while *α*- and *γ*-HCH were quantified in most samples in accordance with
242 other studies. The contribution of *γ*-HCH level to the annual mean ΣHCHs concentration was
243 found to be 52% and 66% in Istanbul and Izmir, respectively. The reported levels of *α*-HCH in
244 Turkey ranged from 17.3±10.7 pg/m^3 (in 2005[19]) to 111±125 pg/m^3 (in 2003[36]). The levels of
245 *α*-HCH measured in this study were lower at both sampling sites even compared to the
246 minimum concentrations reported in previous studies.

247 **PCBs.** The mean concentration of Σ_{45}PCBs at each sampling event in Istanbul and
248 Izmir (Figure 1) were 69.7±69.6 pg/m^3 (nd-317 pg/m^3, 83% in gas phase (Figure S4)) and

207±225 pg/m^3 (nd-880 pg/m^3, 93% in gas phase (Figure S4)), respectively. The most dominant congeners detected in ambient air were PCB 44 and PCB 18 at Istanbul station, while they were PCB 28, 18, and 22 at Izmir station (Figure S9). Tetra- followed by tri-CBs dominated the homologue pattern at both sites. The contribution of $\Sigma_4$tri-CBs and $\Sigma_9$tetra-CBs to the Σ_{45}PCBs levels were found to be 28% and 46% in Istanbul; 30% and 33% in Izmir, respectively. Once deposited (or directly emitted) to soil, the higher chlorinated congeners (PCB 138, 149, 157, 158, etc.) remain close to the point of source[37]. In this study, penta-CBs to octa-CBs were observed at noteworthy levels during the sampling period, with 26% and 36% percent of the mean Σ_{45}PCBs levels at Istanbul and Izmir stations, respectively. The use of PCBs in Turkey has been banned since 1996. However, it may still be produced unintentionally as by-products of thermal processes or industrial processes or it may outgas from old electric installations and buildings. Steel production from scrap with arc furnaces has been shown to emit PCBs[38] while the contaminated soils act as an important secondary source in summer[39].

Monthly mean concentrations of the targeted PCB homologues are shown in Figure S10. A rise in PCB concentrations may be anticipated in warmer sampling months at both stations. Compatibly, the highest atmospheric PCB concentrations for most of the homologues were observed in August 2014 in Istanbul. However, the levels of PCBs in Izmir were higher in January and February 2015. The winter time concentration increase in Izmir could be attributed to the shallow mixing height, as well as southerly winds compared to the dominating northerly winds (Table S3). The monthly mean concentration of $\Sigma_9$tetra-CBs was measured as 89±59 pg/m^3 in August 2014 in Istanbul, approximately 2.8 times higher than its annual mean. The ratio for $\Sigma_4$tri-, Σ_{10}penta-, Σ_{10}hexa-, and $\Sigma_7$hepta-CBs ranged between 3.0 and 7.1. In Izmir, the highest monthly levels were found to be 136±70 and 149±26 pg/m^3 in January and February 2015, for $\Sigma_4$tri-CBs with approximately 2.5 times higher than the

annual mean concentration of $\Sigma_4$tri-CBs. The ratio for the rest of the PCB homologue groups ranged between 2.0 and 4.4.

PBDEs. The mean Σ_{14}PBDEs level (Figure 1) was 10.8±16.3 pg/m^3 (nd-73 pg/m^3, 62% residing in gas phase (Figure S5)) in Istanbul, and was 10.8±16.6 pg/m^3 (nd-70.4 pg/m^3, 70% residing in gas phase (Figure S5)) in Izmir. There is no significant difference between the annual means of Σ_{14}PBDEs of the two sampling sites. A previous study conducted at the same sampling site as in this study in Izmir in July 2012[21] reported mean concentration of Σ_3PBDEs (-47, -99, and -100) as 8.5 pg/m^3. In spite of the prohibitions on tetra- and penta-BDEs, which are more toxic and bioaccumulative than the other congeners with large number of bromine atoms, their ($\Sigma_3$tetra-BDEs and $\Sigma_3$penta-BDEs) contributions were found to be the highest with 37% and 25% percent in Istanbul; 60% and 15% percent in Izmir, respectively, followed by $\Sigma_2$tri-BDEs having 13% percent at both sites. In most published studies and also studies in the Izmir area[40], PBDE-209 was the dominating congener. However, although it was detected in samples in the current study, it was not the dominant congener in the samples. As shown in Figure S11, the annual mean concentrations of the most dominant congeners which are tetra-BDEs (BDE-66, -47, and -71) were measured around 1 pg/m^3 in Istanbul, and 1.5-2.5 pg/m^3 in Izmir. The commercial penta-BDE was mainly used as a flame retardant in polyurethane foams for mattresses and cushioning in upholstered products[41]. Prior to the restrictions and bans, the commercial mixture of octa-BDE were usually used in electronics and plastic industries[41]. Over time, in goods but also in the atmosphere, they could degrade through debromination and convert to lower BDEs[42]. The targeted hexa- and hepta-BDEs (BDE-138, -153, -154, and -183) were hardly detected during the whole sampling period, except BDE-190. The annual mean concentration of deca-BDE (BDE-209) in Istanbul and Izmir was found as 1.44±6.85 and 0.77±3.95 pg/m^3, respectively. There was an interpretable seasonal variation in PBDE homolog concentrations for Istanbul station, whereas those measured in

Izmir station were not (Figure S12). The release of PBDE congeners to the atmosphere depends on human activities (e.g. manufacturing processes, recycling wastes, emitting from waste disposal sites), as well as volatilization from contaminated sites, rendering the monthly time series without a trend.

Historical Variation

To our best knowledge, current study is the first study on OCPs related ambient air monitoring in Istanbul. Therefore, it is not possible to investigate historical variation of OCP levels in ambient air of Istanbul. Previously, PCB levels were investigated in ambient air of Istanbul between May 2012 and May, 2013[43, 44]. The mean level of Σ_{84}PCBs in summer-autumn and winter-spring was reported to be 420 pg/m^3 (88% in gas phase) and 360 pg/m^3 (86% in gas phase), respectively. In the current study, these levels were found to be 117 pg/m^3 (85% in gas phase) in summer-autumn and 15.5 pg/m^3 (74% in gas phase) in winter-spring. However, it should be noted that number of the studied PCB congeners being different hinders the comparison. In contrast to the current study, the mean ambient air concentrations of Σ_{12}PBDEs were high (260±60 pg/m^3) in samples collected in February-March 2012 at an urban site (Besiktas) in Istanbul[18].

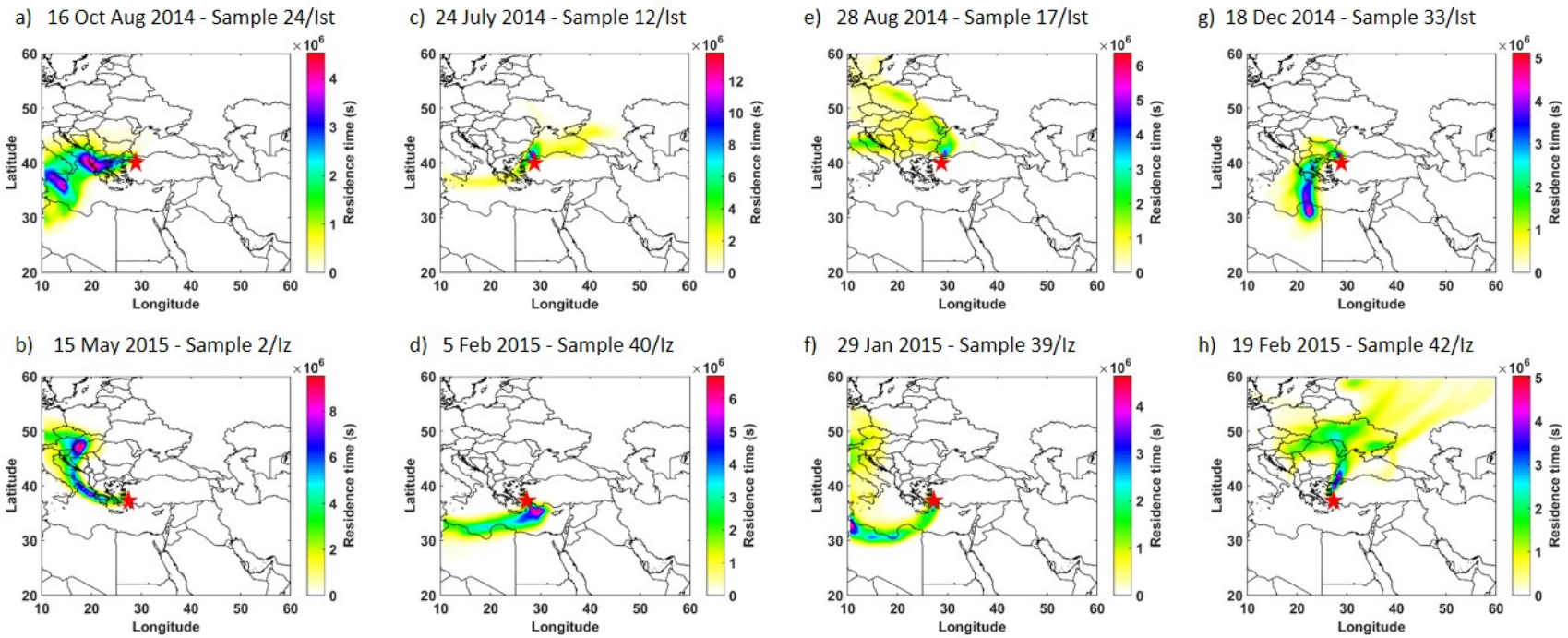
Izmir sampling site was among those of rural sites of the Global Atmospheric Passive Sampling (GAPS) study that collected samples over four seasons in 2005, using PUF disks[45]. In 2005, the average ΣHCHs (sum of α- and γ-HCH), ΣDDTs (sum of DDT and DDE isomers), and Σ_7PCBs (PCB-28, -52, -101, -118, -138, -153, and -180) levels were reported as 29 pg/m^3, 51 pg/m^3, and 644 pg/m^3 in winter; 48 pg/m^3, 60 pg/m^3, and 287 pg/m^3 in summer, respectively. Moreover, in 2005, the concentration of Σ_5PBDEs (PBDE-28, -47, -66, -100, and -99) for winter was not reported, while the average Σ_5PBDEs level in summer was found to be below detection limit (BDL). The MDLs of PBDE 47 and PBDE 100 for the Izmir sampling site were in the range of 0 to 1 ng/PUF in the GAPS study[45]. Also, IDLs for PBDEs were

reported as <0.01 ng for PBDE-28, -47, -66 and <0.02 ng for PBDE-99 and -100. In a study conducted in July 2012[21], the average concentrations of ΣHCHs (sum of α- and γ-HCH) and ΣDDTs (sum of DDT and DDE isomers), Σ_7PCBs (PCB-28, -52, -101, -118, -138, -153, and -180) and Σ_5PBDEs (PBDE-28, -47, -66, -100, and -99) were measured as 13.8 pg/m^3, 12.9 pg/m^3, 55.3 pg/m^3, and 8.50 pg/m^3, respectively. Comparison of the results of the current study to the average ΣHCHs levels measured in the summer of 2005 and 2012 in the two above-cited studies showed that ΣHCHs ranged 14-41 pg/m^3, while the average ΣDDTs levels ranged 13-60 pg/m^3 in the 10-year time frame. Only one of the two previous studies reported wintertime concentrations but based on passive sampling[45]. The average wintertime concentrations of ΣHCHs (133±110 pg/m^3) and ΣDDTs (150±142 pg/m^3) measured in this study in the winter of 2015 are 4.6 and 2.9 times higher than those measured in 2005. The mean Σ_7PCBs level of 14±17 pg/m^3 in summer 2015 is much lower than those of 2005 (287 pg/m^3) and 2012 (55 pg/m^3), while the difference in winter averages between 2005 (644 pg/m^3) and 2015 (100 pg/m^3) is less pronounced. The mean Σ_5PBDEs level in winter was found to be 11.3±13.7 pg/m^3 in the current study, however, a corresponding value was not available from the GAPS study. The average summer Σ_5PBDEs concentrations measured in 2015 (5.6±6.7 pg/m^3) and 2012 (8.5 pg/m^3) are similar, but it was BDL in 2005. Overall, the above comparisons among 2005, 2012, and 2015 at the same sampling site show that fairly similar levels with some fluctuations for OCPs and PBDEs, and for PCBs when the extreme levels measured in 2005 in the GAPS study are left out. The variability in concentrations, therefore, may indicate that different sources or source areas dominate at different times. A comparison of PCB levels measured at a suburban Izmir location in 2003[17] with those measured in 2012 at this site also rendered a conclusion of similar concentrations.

LRT Modeling

It is reported that chemical properties, meteorological conditions and relative magnitudes of the pollutants' concentrations in near-ground and advected air effect the transport of chemicals.[6] The highest LRT potential was reported for HCB (hexachlorobenzene) with 110000 km, while for most of the banned pesticides it ranged from 5200 (α-HCH) to 100 km (aldrin) as characteristic travel distances in air.[46] The distance was calculated as 4200-580 km in air from tetra to deca-CBs[46]. Therefore, it can be concluded that most of the compounds measured in this study have LRT potential.

FLEXPART modeling showed that origin of air masses to Istanbul and Izmir were from eastern and northern Europe, western Russia, the Mediterranean and Aegean Sea areas as well as local (Table S1 and S2). Local air masses arrived from possible contaminated areas such as the metropolitan areas of Istanbul, Kocaeli, and Izmir, while regional air masses mostly arrived from northern Africa, eastern Europe, and Russia. While in the latter cases, the residence time of air masses during the last days before arrival at the sites was often very short, the influence of local sources during advection shortly before arrival of air at the site cannot be excluded. Some of the samples (#2, 9, 25, 27, 39, and 43) collected in Istanbul (Figure S1) were potentially influenced by the Izmir area, while some of the samples (#3, 8, 15, 19, 20, 37, 41, 42, 46, 49, and 53) collected in Izmir (Figure S2) were potentially influenced by the Istanbul metropolitan area. Source regions predicted using backward simulations are presented for episodes with high levels of ΣDDX, ΣHCH, Σ_{45}PCBs, and Σ_{14}PBDEs (Figure 2) in the following sections.



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373 Figure 2. Residence times of air masses received at Istanbul and Izmir stations for the samples with >95th percentile (a-b) ΣDDX, (c-d) ΣHCH,

374 (e-f) Σ_{45}PCBs, and (g-h) Σ_{14}PBDEs gas-phase concentrations (Red stars indicate the sampling locations)

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379 **OCPs.** Regions in northern Africa, eastern Europe, and Russia were indicated as
380 potential source regions for ΣDDX for the Istanbul site, based on samples #10/Ist, 17/Ist,
381 24/Ist, 25/Ist and 27/Ist (Figure S1), with ≥95th percentile gas-phase ΣDDX concentrations.
382 However, in particular for advection via the Marmara Sea (e.g., #24/Ist, 25/Ist, 27Ist) sources
383 within western Turkey may have been influential. Sources within W Turkey were indicated to
384 have the highest potential sources of ΣHCHs in many cases (see samples , 12/Ist, 24/Ist and
385 47/Ist in Figure S1). Regional sources were also pointed by the samples measured in July
386 2014 (samples #9/Ist to 12/Ist in Figure S1) and by the samples measured in March 2015
387 (samples #44/Ist to 47/Ist in Figure S1) (had the highest particle phase ΣHCHs concentration).
388 An α-HCH/γ-HCH ratio of <1 points to the effects of regional sources, while >1 indicates the
389 LRT[36]. This ratio was found to be <1 for all months at Istanbul station (Figure S14), except
390 May 2015 (2.54), in agreement with the residence time distribution graphs (samples #53/Ist to
391 56/Ist in Figure S1). Samples collected from different areas around the Aegean Sea have
392 shown that OCP levels in some part of Greece were higher than those of Izmir and Bursa,
393 Turkey in our previous study[21]. Pribylova et al. [47] as well as Kirchner et al. [48] reported
394 elevated atmospheric pentachlorobenzene, HCB, pentachloroanisole and ocachlorostyrene
395 concentrations in central and eastern Europe including Ukraine and Russian Federation, in
396 agreement with our study. The butter samples collected from Ukraine had higher levels of
397 HCH and DDT species, compared to other European countries, except Romania[49].
398 Atmospheric OCP levels in Libya have not been reported, however ΣDDX and ΣHCHs levels
399 in human breast milk were detected to be higher than the maximum residue limit[50].

400

401 The contributions of the regions in northern Africa and southern Europe on ΣDDX
402 levels are considerable for Izmir station (see samples #2/Iz, 4/Iz, 38/Iz, 39/Iz, and 54/Iz with
403 ≥95th percentile gas-phase ΣDDX concentrations in Figure S2). The samples #40/Iz to 47/Iz

(Figure S2) with dominant particle phase concentrations was influenced by the Marmara Sea area (particularly samples #41/Iz, 42/Iz, and 46/Iz) and also the Aegean Region (West Turkey) (sample 44/Iz and 45/Iz). Air masses passed over northern Africa and eastern Ukraine/southern Russia in January and February 2015 might have influenced the highest levels of ΣHCHs measured at the Izmir site (samples #37-41/Iz in Figure S2). Again, the sampling events in November, December and July 2014 and in March, April and May 2015 (ratios of α-HCH/γ-HCH ranged from 1.09-4.64, Figure S14) indicated that LRT could be the main source of HCHs in majority of the year in Izmir, in aggrement with residence time distributions (Figure S2).

PCBs. The highly possible sources of Σ_{45}PCBs for Istanbul sampling point were found to be in regions around the Black Sea as indicated by samples #14-17/Ist (Figure S1) containing the highest gas-phase Σ_{45}PCBs levels. The Black Sea was indicated to be the main potential source region which might be under the influence of sources on its shorelines. Apart from secondary sources from soils, also re-volatilisation following inversion of diffusive air-sea exchange of PCBs from polluted coastal waters are possible, as found elsewhere in the Eastern Mediterranean.[51] PCB production was ended in Russia in 1993[52] but PCBs are still in use as the total amount of PCBs in PCB-containing equipment is approximately 27,000-35,000 tons[53]. Russia has been reported to be one of the main emission regions of PCBs due to extensive use of PCBs in the past[54]. The contribution of the Mediterranean and some adjacent countries (including Bulgaria) to the total European PCB emissions was reported to be about 25%[55]. Coincidence of advection from N-NE i.e., across the Black Sea, with high levels in Istanbul are supported by few measurements in air from Eastern Europe (relevant for maxima found in samples #14-17/Ist): PCBs were elevated in Leova, Moldova (ca. 150 km W of Odessa), ≈10 pg m^{-3} for $\sum_7$PCBs at least until the year 2013, and at Moussala, Bulgaria (mountain site, ca. 450 km WNW of Istanbul), ≈10 pg m^{-3} for $\sum_7$PCBs in the year 2014.[56]

Ukraine, having an intensive steel production industry and yet a significant source of PCBs release also was reported as a potential source to Istanbul for PCBs[44]. Athens, a metropolitan city of the Eastern Mediterranean Basin, was also reported to be a source for atmospheric pollutants[57]. A wide spreading area over Athens to Izmir, then to Istanbul was also remarkable with a high residence time for sample #2/Ist with a higher Σ_{45}PCBs concentration. The Aliağa industrial region in the Izmir area, with iron-steel plants and ship dismantling facilities which are major PCB emitters[39], was shown to have a high contribution to atmospheric PCBs in Istanbul[58]. Electric arc furnaces that process ferrous-scrap were determined as hot spots for POPs[38], and were reported to impact the Izmir metropolitan area[59, 60]. However, the concentrations of the other samples collected on dates indicating regional sources under the influence of southern winds (passing Aliağa, i.e. samples #9/Ist, 27/Ist, 39/Ist, and 43/Ist) were found as about 1.5 times lower than the annual mean gas form Σ_{45}PCBs concentration in Istanbul. There are also unintentional current sources. Mainly PCB-11, along with PCB-52 and -209 were identified as signature congeners for pigments in modern paints.[61, 62] Silicone-based adhesives were identified to be sources of mainly monochlorinated CBs, dominated by PCB -2 and -3, followed by dichlorinated CBs, in particular PCB-6, -11, and -13.[63] Polymer resins in kitchen cabinetry were identified as a major source of PCB-47, PCB-51, and PCB-68[64]. Target analytes of this study, however, included only PCB-52, not permitting elaboration on the current indirect sources.

Local sources in the metropolitan area itself were indicated to be dominant in Izmir (Figure S2). Potential LRT sources for PCBs to Izmir appeared to be in northern Africa, indicated by samples #38-40/Iz (Figure S2) having the highest gas-phase Σ_{45}PCBs levels. Oil, petrochemical, aluminum, iron and steel production might be important sources of PCBs[65] and yet the petrochemical industry is the backbone of the Libyan economy. No measurements are available to compare with from Libya, though. The PCB levels could be affected by the air

flows from eastern Europe with respect to samples #37/Iz and 50/Iz (Figure S2). In addition, the mean concentration of samples #10/Iz, 15/Iz, 17/Iz, 26/Iz, and 29/Iz (Figure S2), of which residence times indicated local sources under the influence of northern winds (passing Aliaga), was about 2 times higher than the annual mean Σ_{45}PCBs concentration at the Izmir site.

PBDEs. FLEXPART modeling showed that the highest Σ_{14}PBDEs concentrations (samples #33/Ist and 25/Ist in Figure S1) may be associated with air masses originated from northern Africa, where there are no restrictive measures on PBDEs in Libya[66], and no information available on their atmospheric levels. Based on the quantity of industrial waste (34×10^4 tons/year) and composition (47% steel, metallurgical, mechanical, and electrical industries, followed by 3% wood, paper, and printing industries, and 2% textile, hosiery, and confection industries)[59] in Libya, northern Africa could be a source of PBDEs. The region encompassing Albania, Greece, and northwestern Turkey is indicated as a potential source for Σ_{14}PBDEs based on the samples #24/Ist, 3/Ist, and 1/Ist (Figure S1). Besis, Lammel, Kukučka, Samara, Sofuoglu, Dumanoglu, Eleftheriadis, Kouvarakis, Sofuoglu, Vassilatou and Voutsa [40] measured total concentration of indicator PBDEs as 18.8 pg/m^3 in central Greece, and as 10.8 pg/m^3 in Izmir. Dilovası, a district of the Kocaeli metropolitan city in northwestern Turkey, is a heavily industrialized region with many companies in various sectors mainly including iron–steel, aluminum, chemicals, paint[60, 67] which may be sources of PBDE emissions. However, Σ_{14}PBDEs concentration were not found to be elevated, that ranged from <LOD to 4.62 pg/m^3, for the samples collected on dates indicating regional sources under the influence of Kocaeli (samples #13/Ist, 16/Ist, 18/Ist, 19/Ist, 44/Ist and 47/Ist in Figure S1).

The samples with high concentrations (#42/Iz, 54/Iz, 40/Iz, and 38/Iz, Figure S2) implicated regions in northern Africa, southern and eastern Europe as potential source areas for Izmir .

To the best knowledge of the authors, there are no reports of atmospheric PBDE levels in Ukraine, Libya, and Romania. Atmospheric PBDE levels in Florence, Italy[68] were found to be comparable to levels of samples collected from different countries but PBDE 209 levels in Florence was among the highest in Europe. Regional sources also have high contribution to Σ_{14}PBDEs detected in Izmir station (sample #19/Iz in Figure S2). Aliaga area was reported to be a source of atmospheric PBDEs[65]. The mean concentrations of the other samples under the influence of northern winds (passing Aliağa, for samples #5/Iz, 10/Iz, 15/Iz, 17/Iz, 26/Iz, 29/Iz, and 48/Iz in Figure S2) were 16 pg/m^3, about 1.6 times higher than the annual mean Σ_{14}PBDEs concentration.

Consistent monitoring of air concentrations of POPs in the environment is the key activity to assess the effectiveness of international efforts to minimize the release of the chemicals to the environment. POPs monitoring under the Global Monitoring Plan of the Stockholm Convention is including few stations in eastern Europe (run by the EMEP and MONET programs).[69]

Temperature Dependence

The temperature dependence of POP concentrations in air can be used to infer on LRT. Thermodynamically, the gas-phase behavior of semi-volatile organic compounds can be described with Clausius–Clapeyron (C-C) equation ($\ln P=(\Delta H_v/R)(1/T)+b$), where P is partial pressure (atm), T is temperature (K), ΔH_v is the heat of vaporization (kJ mol^{-1}) that is referred as the enthalpy of surface-air exchange (ΔH_{SA}), and R is the universal gas constant. The regression of lnP versus 1/T being linear ($lnP=m(1/T) + b$), negative-steep slopes indicate the effect of local emissions while shallow or positive slopes point to the effect of LRT. Hoff et al.[33] investigated nonlinearity of C-C plot for chlordane and concluded that a linear C-C plot

503 with a high R^2 value implies dominance of only one exchange process, while a positive
504 curvature, especially at low ambient temperatures, indicates the effect of LRT. However, it
505 should be noted that C-C analysis could indicate local re-emission but not unintentional
506 primary sources in urban and industrial areas.

507 There was only one significant correlation with very steep slope (for HEPT) in
508 Istanbul suggesting its volatilization from a past contaminated area for southerly trajectories.
509 For Izmir, on the other hand, the analysis indicated ΣDDX mainly originated from local
510 sources based on southerly trajectories, whereas significant positive slopes for ΣDDX, HEPT,
511 α-endo, mirex, and ΣPCBs for northerly trajectories indicated the effect of LRT. The analysis
512 for individual PCB congeners resulted in positive slopes in Izmir. The slopes were significant
513 ($p<0.1$) for PCB-18, 22, 28, 44, 52, 56, 70, 74, 90, 99, 138, 141, 149, and 153 while the rest of
514 the congeners had positive shallow slopes with no significance. In general, coffecient of
515 determination levels were>0.3. In contrast to Izmir, a few congeners (PCB-44, 95, 110, and
516 149) resulted in negative significant slopes ($p<0.05$) in Istanbul while they were not
517 significant for the rest of the congeners. Temperature dependency for Σ_{45}PCB and Σ_{14}PBDE
518 was reflective of the individual congeners, therefore, only the two are reported here. Table S8
519 presents results of Clausius−Clapeyron analysis for advection from northerly (315°-45°) and
520 southerly (135°-225°) sectors. Inclusion of wind speed and direction as independent variables
521 in addition to 1/T, and conducting multiple linear regression analysis yielded that individual
522 congeners seldomly had significant relation with wind variables in agreement with previous
523 research[70], therefore not presented here.

524 The FLEXPART analysis has generally shown southerly air flows in the higher
525 concentrations days in January and February 2015 in Izmir. It is also reported that in winter
526 times western Turkey is under the influence of mainly easterly, southeasterly, southerly, and
527 anticyclonic weather pattern, which increase PM_{10} concentrations to above average levels.[71]

In addition, there is information that episodes of dust transport from North Africa occurred during our sampling campaign, significantly affecting PM_{10} concentrations in Turkey.[72, 73] Consequently, there is evidence that LRT may have a significant effect on POP levels in Izmir on top of local surface exchange and unintentional sources, i.e. Aliaga Industrial Area and Izmir metropolitan area , which may even reach episodic levels that can mask the local sources.

Temperature dependency analysis was retested separately for northerly and southerly trajectory days since high concentrations occurred mainly with southerly advection. In general, the opposite to the characteristic pattern of temperature dependence of congeners was observed. Mandalakis and Stephanou investigated lack of seasonality in atmospheric PCB concentrations at a coastal area in the Mediterranean Sea.[74] Some of the congeners were correlated positively but not significantly with temperature. They concluded that LRT, as a considerable source, along with the long sampling duration (24 hour masking day-night time changes) and relatively narrow range of average wind speed could hide the seasonality of local emissions.

Overall, despite the widespread occurrence of monitoring studies on OCPs, PCBs and PBDEs in other regions of the world, this study provided a year-long dataset for Turkey, where POPs studies are not as widespread as in other regions and yet no continuous monitoring of POPs is available. The data obtained in this study do not follow the trend of commonly reported results of the past studies, therefore, such interesting results could be useful, particularly for future research, and provides interesting insights into the atmospheric behavior/transport of these compounds on a regional level. This result raised a few questions and is somewhat unexpected and warrants further analysis. Moreover, the attempt to assess emission sources of the target analytes measured in this study was not very successful due to lack of POPs data from potential source areas identified in the current study. Therefore, for a better regional/continental emissions evaluation of POPs as well as assessment

of complement with Stockholm Convention, there is certainly a need for long-term and continuous monitoring of these chemicals in the region.

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Notes

The authors declare no competing financial interest.

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