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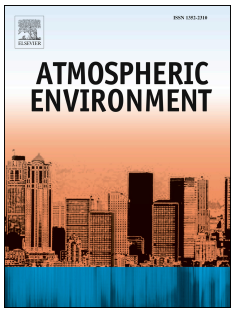

The first countrywide monitoring of selected POPs: Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and selected organochlorine pesticides (OCPs) in the atmosphere of Turkey

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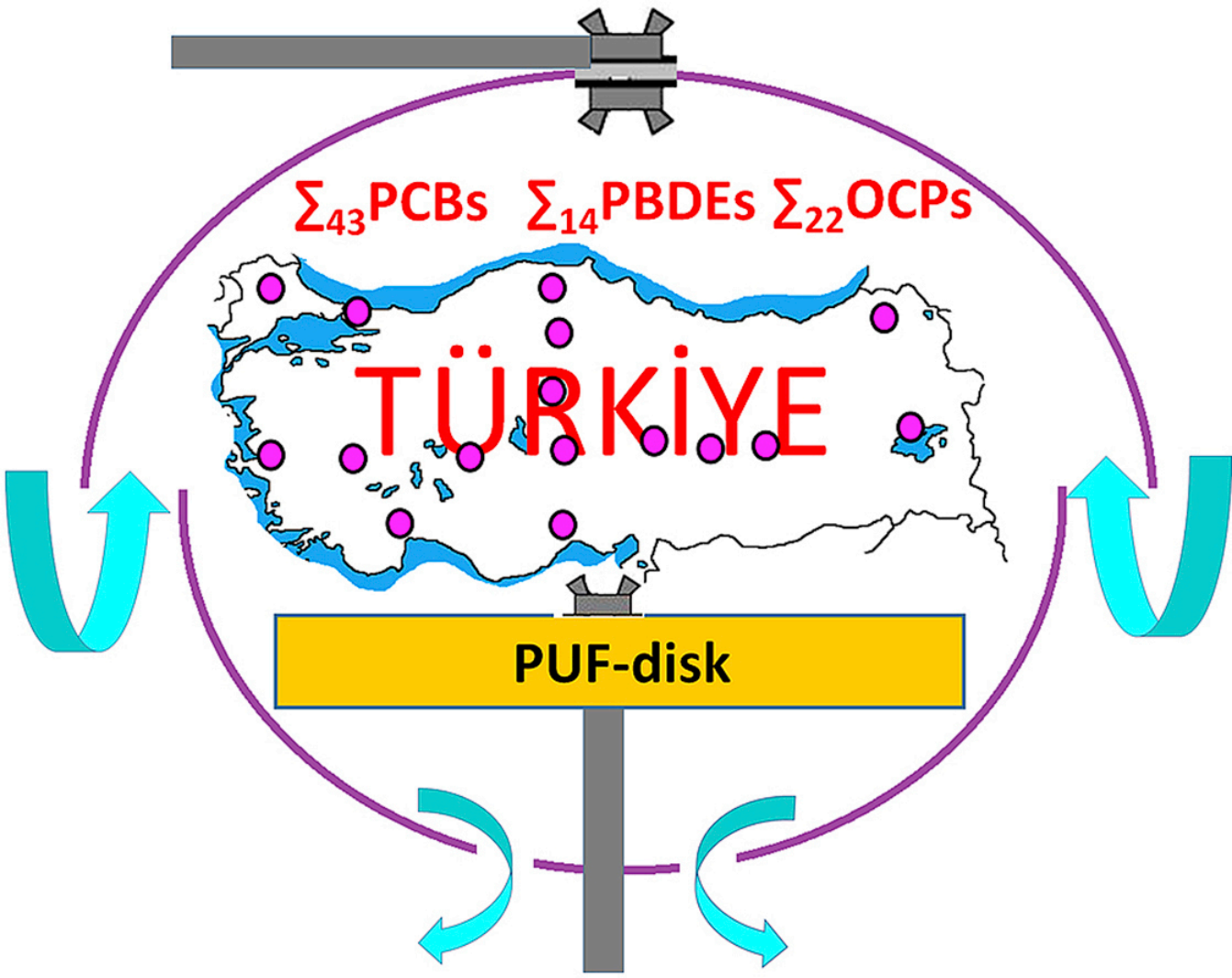
Σ_{43}PCBs Σ_{14}PBDEs Σ_{22}OCPs
TÜRKİYE
PUF-disk

The first countrywide monitoring of selected POPs: Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and selected organochlorine pesticides (OCPs) in the atmosphere of Turkey

Perihan Binnur Kurt-Karakus[1]*, Tugba Ugranli-Cicek[2], Sait C. Sofuoglu[2], Halil Celik[3], Elif Gungormus[2], Kadir Gedik[3], Aysun Sofuoglu[4], Hatice Eser Okten[2], Askın Birgul[1], Henry Alegria[5], Kevin C. Jones[6]

[1] Bursa Technical University, Faculty of Engineering, Department of Environmental Engineering, Mimar Sinan Mahallesi, Mimar Sinan Bulvari Eflak Caddesi No:177 16310 Yildirim, Bursa-TURKEY

[2] Izmir Institute of Technology, Department of Environmental Engineering, Gulbahce, Urla, 35430, İzmir-TURKEY

[3] Akdeniz University, Faculty of Engineering, Department of Environmental Engineering, Dumlupinar Bulvari 07058 Antalya-TURKEY

[4] Izmir Institute of Technology, Department of Chemical Engineering, Gulbahce, Urla, 35430, Izmir-TURKEY

[5]University of South Florida St Petersburg, Department of Environmental Science, Policy & Geography, 140 7th Avenue South, St Petersburg, FL 33701, U.S.A

[6]Lancaster Environment Center, Lancaster University, Lancaster, LA1 4YQ, UNITED KINGDOM

*Corresponding author, Bursa Technical University, Faculty of Engineering, Department of Environmental Engineering, Mimar Sinan Mahallesi Mimar Sinan Bulvari Eflak Caddesi No:177 16310 Yildırim, Bursa-TURKEY, Tel: +90 224 3003406; Fax: +90 224 3003419

Email: perihan.kurt@btu.edu.tr (P.B. Kurt Karakus)

Abstract

Atmospheric levels of 43 PCBs, 22 OCPs, and 14 PBDEs were determined in 16 cities at urban and rural sites by passive sampling to generate the first large-scale nationwide dataset of POP residues in Turkey's atmosphere. Sampling campaign was performed from May 2014 to April 2015 with three-month sampling periods at locations on east-west and north-south transects through the country to investigate seasonal and spatial variations, including long range atmospheric transport (LRAT). Factor analysis was conducted to infer on the potential sources. Overall average Σ_{43}PCBs concentration was 108±132 pg/m^3. PCB-118 (26.3±44.6 pg/m^3) was the top congener, and penta-CBs had the highest contribution with 54.3%. ΣDDTs had the highest annual mean concentration with 134±296 pg/m^3 among the OCP groups among which the highest concentration compound was *p'p*-DDE (97.6±236 pg/m^3). Overall average concentration of Σ_{14}PBDEs was 191±329 pg/m^3 with the highest contribution from BDE-190 (42%). Comparison of OCPs and PCBs concentrations detected at temperatures which were above and below annual average temperature indicated higher concentrations in the warmer periods, hence significance of secondary emissions for several OCPs and Σ_{43}PCBs, as well as inference as LRAT from secondary emissions. The first nationwide POPs database constructed in this study, point to current use, local secondary emissions, and LRAT for different individual compounds, and indicate the need for regular monitoring.

Keywords**:** PCBs; OCPs; PBDEs; passive sampling; urban and rural; Turkey

Capsule

The first country-wide passive sampling of selected POPs showed no unequivocal trends reflecting transitional location of Turkey

1. Introduction

It was decided by the Grand National Assembly in April 2009 that Turkey was to become a party to the Stockholm Convention (Official Gazette, 2009a). The decision was accepted by the Council of Ministers in July 2009 (Official Gazette, 2009b) whereas the legal procedure was completed in January 2010. As is the case for many Stockholm Convention ratifying countries, certain persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were never produced in Turkey. However, many products such as transformers, capacitors and flame retarded consumer products containing these chemicals were/are in use in the country. As a country with intensive agricultural practices, organochlorine pesticides (OCPs) were also widely used in Turkey until they were banned. Moreover, Turkey receives air masses from Europe, former Soviet countries, the Arabian Peninsula, and North Africa, which makes it an interesting country in terms of POPs due to its transitional location. PCBs, PBDEs, and OCPs are considered as POPs that are best known for their persistence to degradation in the environment. Therefore, they can undergo long range atmospheric transport (LRAT), and are subject to bioaccumulation in fatty tissues and in the food chain (Li et al., 2006). Most of the subject POPs (such as heptachlor, lindane, dieldrin, chlordane, etc.) were banned around the 1980s in Turkey.

One of the main obligatory tasks required under Stockholm Convention for ratifying countries is to monitor environmental levels of banned/phased out chemicals. In this manner, many of ratifying countries have conducted long-term systematic monitoring programs. Although the country is under the obligations of the Convention since 2010, Turkey is unfortunately lacking such long-term spatial and temporal monitoring activities of POPs. There exist studies to determine occurrence and seasonality of PCBs (Gedik and Imamoglu, 2010; Yenisoy Karakas et al., 2012; Kuzu et al., 2014; Kuzu, 2016; Kuzu et al., 2016; Kuzu and Saral, 2017; Dumanoglu et al., 2017), PBDEs (Cetin and Odabasi, 2007; Cetin and Odabasi, 2008; Odabasi et al., 2016) and OCPs (Yenisoy-Karakas et al., 2012; Kuzu, 2016) in the country. However, these studies are limited to several specific industrial and urban locations to measure seasonality of chemicals of interest.

Compared to the western part of the world, number of studies on investigation of occurrence and fate of POPs including PCBs, OCP, and PBDEs in environmental compartments in Turkey is still limited, it is certainly of an increasing interest. Sources of PCB contamination was reported to be petrochemical plants, iron steel-plants, and ship

105 demolishing sites in the studies conducted in Aliaga (Kaya et al., 2012; Odabasi et al., 2015)
106 and waste landfill in Hamitler (Esen, 2013). Odabasi et al. (2016) reported average
107 concentration of Σ_{41}PCBs in background and industrial sites in Iskenderun (Turkey) as
108 180±140 pg/m^3 and 1600±900 pg/m^3, respectively. Summer concentrations of Σ_{41}PCBs in
109 Kutahya province were reported in the range of 31.6 pg/m^3 to 230.2 pg/m^3 (average value of
110 125.3±33.5 pg/m^3) while concentration range was 19.6 pg/m^3 to 675,1 pg/m^3 with an average
111 value of 187.9±132.9 pg/m^3 in winter (Dumanoglu et al., 2017). Average ambient gas-phase
112 $\sum_7$PBDE concentrations were between 189 ± 61 (summer) and 76 ± 65 pg/m^3 (winter) in
113 Izmir (Cetin and Odabasi, 2007a). Kurt-Karakus et al. (2017) reported Σ_{12}PBDEs
114 concentrations range between 110 and 620 pg/m^3 in Istanbul. Gas phase Σ_{23}OCPs average
115 concentration were in the range of 1.10 pg/m^3 and 42.5 pg/m^3 in Izmir (Ugranli et al. 2016).
116 Alpha-HCH showed the lowest concentration (2.10 pg/m^3) while endosulfan II showed the
117 highest concentration (73.01 pg/m^3) in samples collected from Bursa province in 2008-2009
118 (Cindoruk and Tasdemir, 2014). The congener pattern of PCBs was similar in air of Aegean
119 but PBDE levels were different between Greece and Turkey (Lammel et al., 2015).
120 Additionally, uniform concentration levels of long-lived chemicals were reported to be
121 dominated by LRAT or distribution within a region.

122 High volume active air sampling of POPs is a widely favored technique around the
123 world. However, after the awareness of the fact that remote areas might also been polluted by
124 POPs due to LRAT (Bowes and Jonkel, 1975), an alternative technique was required that
125 provides easy access, less operation cost and labor, and, above all, has no electricity
126 requirement. Development of passive air samplers (PAS) met these requirements, and they
127 have been widely used for measurement of relatively long term average gas phase
128 concentrations of POPs. Besides studies to determine ambient air POPs levels using active air
129 samplers in Turkey (Birgul and Tasdemir, 2012; Cindoruk and Tasdemir, 2014; Kuzu et al.,
130 2014; Odabasi and Cetin, 2012; Yolsal et al., 2014; Ugranli et al., 2016) there are limited
131 studies conducted in Turkey using polyurethane foam passive samplers (PUF-PAS) (Kaya et
132 al., 2012;Aydin et al., 2014; Odabasi et al., 2015; Odabasi et al., 2016; Kurt-Karakus et al.,
133 2017; Cetin et al., 2017). However, these studies were conducted in particular regions of the
134 country and there are no studies to investigate the levels of PCBs, PBDEs and OCPs
135 concurrently on a countrywide scale.

136 The aims of this study were (a) to measure atmospheric air concentrations of PCBs,
137 OCPs, and PBDEs at a total of 32 urban and rural places located in 16 provinces at an east-
138 west and a north-south transect in Turkey using PUF-PAS samplers, (b) to investigate spatial

and seasonal variations of target chemicals, and (c) to generate the first large-scale nationwide dataset of atmospheric PCB, PBDE, and OCP levels in Turkey.

2. Materials and Methods

2.1. Study Area and Sampling Program

Sixteen provinces with urban and rural sites in Turkey were selected on the centerline from East to West and North to South in addition to the three corner locations of Turkey (Figure 1,3, and 4; Supplementary Material Table S1). It was recommended that the rural sites should represent a diameter of a circular area of at least 100 km so the distance between the sampling locations was about 250-300 km (UNEP, 2007). Ease of transport, existence of contact people to take care of the samplers, and travel safety were the other criteria considered for sampling point selections. Urban sampling locations were representative of typical urbanized areas. Background sites were chosen to be remote from any potential sources such as populated/industrialized/agrochemical application areas, to ensure that they were representative of background levels.

Three-month sampling was performed in four periods; May-July 2014 (1^{st} period), August-October 2014 (2^{nd} period), November 2014-January 2015 (3^{rd} period), and February-April 2015 (4^{th} period). The sampling durations varied from 80 to 118 days depending on the availability and travel conditions on the field (Supplementary Material Table S1). Mean temperature ranges during the sampling periods were 12.9-25.6 ˚C (1^{st} period), 10.6-24.2˚C (2^{nd} period), -3.6-12.8˚C (3^{rd} period), and 3.5-15.6˚C (4^{th} period).

2.2. Chemicals and Reagents

All chromatography-grade solvents (acetone, hexane, dichloromethane, iso-octane), anhydrous sodium sulfate (granulated for trace organic analysis), and neutral alumina (90 active neutral, 0.063-0.2 mm particulate size) were purchased from Merck (Merck EMD Millipore, USA). Origins of recovery surrogate ($^{13}C_{12}$- PCB-28, -52, -101, -138, -153, -180 and -209), depuration compounds and target chemicals are given in Supplementary Material Table S2.

2.2. Sampler Preparation and Deployment

Polyurethane foam (PUF) disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g/cm^3; Tisch Environmental, Cleaves, Ohio, USA) were used as passive sampling medium. PUF disks were spiked with depuration compounds ($^{13}C_{12}$PCBs and native PCBs: 250 ng each, d_6-γ-HCH: 500 ng) prior to deployment since such compounds enable to measure sample volumes directly (Ockenden et al., 2001) whereas the rate of uptake of chemicals will be the same as the rate of loss of depuration compounds (Pozo et al., 2009; He and Balasubramanina, 2010). PUF disks were placed in stainless steel chambers at the sampling locations to prevent contamination by particle deposition, UV sunlight, and to minimize the effects of wind speed on the sampling rate (Tuduri et al., 2006). Further details on sampler preparation are given in Supplementary Material Table S3.

2.3. Extraction

PUF disks were spiked with recovery surrogate chemicals (50 ng each) prior to extraction and were subjected to Soxhlet extraction for 18 hours using 1:1 acetone:hexane mixture. After extraction, volume was reduced to 2 ml on a rotary evaporator, and was further concentrated to 0.5 ml in isooctane under a gentle N_2 stream. 6% deactivated alumina was used for clean-up of samples. Elution was done using 35 mL of 20% dichloromethane (DCM) in hexane. Final volume was 1 mL in isooctane and all extracts were spiked with internal standard (50 ng of $^{13}C_{12}$PCB-105) before instrumental analysis. Further details are given in Supplementary Material Table S3.

2.4. Instrumental Analysis

Analysis of PCB congeners was conducted on a GC (Agilent 7890B) coupled with an MSD (Agilent 5977 MSD) operated on EI (electron impact)-selective ion monitoring (SIM) mode. Separation of PCB congeners was performed on a capillary DB-5 column (60 m, 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) (co-eluting congeners (PCB-41/64 and PCB-90/101) were quantified together. Analysis of OCPs and PBDEs were conducted on the same instrument operated on NCI (negative chemical ionization)-selective ion monitoring (SIM) mode. Separation of OCPs and PBDEs were performed together on a capillary DB-5

column (15 m, 0.25 mm i.d., 0.1 µm film thickness). Details on instrument operating conditions and temperature program are given in Supplementary Material Table S4.

2.5. Quality Assurance (QA)/Quality Control (QC)

QA/QC measures included baking all glassware at 450 ºC and solvent-rinsing before use, running laboratory and field blanks, calculating method detection limit (MDL) and instrument detection limit (IDL), analysis of an NIST-SRM dust for PBDEs, and calculating percent recovery of ^{13}C-labelled surrogate compounds as well as calculating percent recovery of target chemicals via spiked samples. Method detection limit (MDL) and instrument detection limit (IDL) were calculated as follows: MDL=average concentration of target chemical in blank+3*std dev; IDL= lowest calibration level produced a signal that is distinguishable from a reagent blank at a 3:1 S/N ratio; and IDL=MDL (if analyte is not present in blank sample) (WDNRL, 1996). If any analyte was <MDL, then concentration of that analyte was taken as ½ of MDL of corresponding congener/chemical for statistical calculations. MDLs ranged from 1.83 – 8.85 pg/m^3 for individual PCBs, 1.01-4.84 pg/m^3 for individual PBDEs, and 2.32-5.40 pg/m^3 for OCPs. A full list of MDLs for target chemicals are given in Supplementary Material Table S5. The amounts of targeted POPs were negligible in the field blanks relative to the samples (<5%).

Procedural recovery efficiencies for PCB-spiked samples (n=6) were in the range of 65% (PCB-153) to 100% (PCB-138) with the average of 80.5%. Average procedural recovery efficiency of spiked OCPs (n=6) and spiked PBDEs (n=6) were 78% (64%, *p,p'*-DDD - 103%, endrin) and 80% (69%, PBDE-28 - 94%, PBDE-138), respectively. Average recovery efficiencies (%) of the ^{13}C labelled surrogate compounds (n=209) was 83.4±16 (61.3-134.4), 89.3±18.3 (60.4-135), 86±13.6 (61-121.4), 86.8.4±11 (60.6-122), 91.5±11.8 (60.6-131.2), 89.7±17 (58.8-124) for $^{13}C_{12}$PCB-28,-52,-101,-138,-153,-180, and PCB-209, respectively. In the current study, only ^{13}C-labelled PCBs were used as recovery surrogate compounds. However, in a similar study conducted in our laboratory using the same analytical and instrumental method, samples (n=22) were spiked with 25 ng of PBDE-77 and recovery efficiency was ranged between 66.10% and 117.6% with a mean value of 92.9±13.3%. Moreover, in order to assess recovery efficiency of PBDEs replicate analysis of NIST SRM 2583 (n=5) (National Institute of Standards Technology, MD, USA) was conducted, and results showed that relative standard deviations of replicate analysis of individual PBDE congeners of interest ranged between 8.1% (BDE-47; 278 ng/g-330 ng/g) and 22.3% (BDE-

154; 61 ng/g-108 ng/g) with an average of 16.3%. Concentrations of PBDE congeners in SRM 2583 was reported by Stapleton et al. (2006). Percent recovery of PBDE congeners in the current study compared to concentrations reported by Stapleton et al. (2006) were 108%, 95%, 94%, 103%, 102%, 87%, 90%, 95%, 105%, 86%, 123%, and 115% for BDE-17, -28, -47, -66, -85, -99, -100, -138, -153, -154, -183, and -209, respectively. Relative standard deviations of detected concentrations of target PBDE congeners in SRM 2583 from concentrations reported by Stapleton et al., (2006) were ranged between 2.1 and 22.3% with an average deviation of 9.1%. Details on results of this analysis are given elsewhere (Kurt-Karakus et al., 2017). Field blanks were prepared by exposing a PUF disk to air for about 10 seconds at the selected sampling points (n=12) and subjecting to the same sample preparation procedure as samples.

2.6. Deriving Air Concentrations by Depuration Compounds

Concentrations of target congeners in gas phase in air were derived from the chemical amount accumulated in PUF disk (ng/sampler) divided by the effective air volume (V_{AIR}, m^3). Site-specific effective air volume (V_{AIR}) which is based on site specific linear phase sampling rates ($R_{sampling}$; m^3/day) was calculated using the equation proposed by Shoeib and Harner (2002). Air volume sampled by PUF-PAS was calculated using data on the loss of depuration compounds (Pozo et al., 2004; Gouin et al., 2005) and GAPS (Global Atmospheric Passive Sampling) template (Harner, 2016; Parnis et al., 2016). Average R value was 6.34 ± 2.74 m^3/day (Phase I: 2.04-5.53 m^3/day; Phase II: 5.61-12.15 m^3/day; Phase III: 1.18-7.91 m^3/day; Phase IV: 2.64-8.69 m^3/day) where the differences might have occurred based on meteorological conditions (Tuduri et al., 2006; Klánová et al., 2008).

2.7. Statistical Analysis

Concentration data of PCBs, PBDEs and OCPs showed non-normal distributions. Therefore, Mann-Whitney U test was used to compare the medians of two independent samples (median pollutant concentrations of urban and rural sites) and to investigate seasonal variation in pollutant concentrations through comparing the samples collected at higher (range: 14.4 – 25.6˚C) and lower (range: -3.6 – 14.1˚C) than average (14.2˚C) temperatures over the one-year sampling period. The test was performed by Minitab v16 software.

Comparison of data from the current study to results of other studies in Turkey and other regions of the world was based on average concentrations.

Factor analysis was used to analyze if variation in levels of 21 OCPs (except *o,p'*-DDD because it was not detected), 43 PCBs, and 14 PBDEs could be represented with a less number of components. It was expected that the factors would cover the compounds with similar variations originated from similar sources. Therefore, it could be used as a receptor oriented apportionment tool. The analysis was performed using SPSS software (v4). Varimax rotated principal component analysis was used. Eigen values of >1 and loadings of >0.5 were regarded as significant for interpretation of factors.

3. Results and Discussion

3.1. Ambient air concentrations of targeted POPs

3.1.1. PCBs

Annual average concentration of Σ_{43}PCBs was 108±132 pg/m^3. Kayseri (14.5±14.3 pg/m^3) and Izmir (403±428 pg/m^3) showed the lowest and the highest mean Σ_{43}PCBs concentration at urban sites. At rural sites, mean concentration in Aksaray (19.0±22.7 pg/m^3) was the lowest while Kastamonu (217±353 pg/m^3) showed the highest levels of Σ_{43}PCBs (Figure 1). In addition to the probable urban sources, the higher concentrations detected in Izmir may be related to emissions from the close-by Aliaga industrial area such as from ferrous scrap processing steel plants with electric arc furnaces (Odabasi et al., 2009; Odabasi et al., 2017). Actually, Σ_{43}PCB concentration detected 50 km West of Izmir at Urla was the second highest among the 41 sites around the globe (Pozo et al., 2006), and the second highest (Σ_7 indicator PCBs) after Thessaloniki, Greece among the 10 sites around the Aegean (Lammel et al., 2015). Pozo et al., (2012) measured concentrations of Σ_{43}PCBs at urban sites (16 pg/m^3) and rural sites (40 pg/m^3) in Chile from January to March 2007. Annual average concentration of Σ_{43}PCBs detected in this study was in the range of Σ_{41}PCBs reported in air in Kutahya (19.6-675.1 pg/m^3) (Dumanoglu et al., 2017).

In GAPS study, levels in urban sites were higher than those of suburban sites (Pozo et al., 2006). In a study in Chile, concentrations measured at urban sites were on average 1.2 times higher than those of rural sites, although not significantly different statistically ($p>0.05$), in agreement with the GAPS study.

307

308 The congener with the highest annual average among the targeted PCBs was PCB-118
309 with a value of 26.3±44.6 pg/m^3. PCB-54, PCB-156, and PCB-188 were not detected in the
310 samples. PCB-104, PCB-114, PCB-118, PCB-123, PCB-151, PCB-167, and PCB-203 had
311 higher mean concentrations at rural sites compared to urban sites. However, median
312 concentrations of the targeted PCBs at urban sites were not significantly different than those
313 measured at rural sites (p>0.05). Low to medium molecular weight congeners (PCB-18, -17, -
314 31, -28, -33, -52, -44, -70, and -101) were dominant in ambient air of Aliaga (Odabasi et al.,
315 2015). In this study PCB-101, -138 and -153 and -118 were higher at urban sites as opposed
316 to the case in Azerbaijan (Aliyeva et al., 2012) where only PCB118 was higher in urban sites.
317 Annual average contributions of homologue groups tri- to octa-CBs to the concentration are
318 shown in Figure 2a. The groups from the highest to lowest contributions were penta-CBs >
319 tetra-CBs > tri-CBs > hepta-CBs > octa-CBs > hexa-CBs. Dominance of lower Cl content
320 (≤% 5Cl) PCBs was observed in industrial, rural and urban (Zhang et al., 2008) areas. Birgul
321 et al. (2017) reported that PCB profile at all sampling sites was dominated by 4-Cl PCBs in a
322 study conducted in Bursa province in Turkey. In a study conducted by Kaya et al. (2012), low
323 molecular weight congeners (3- and 4-Cl) dominated the Σ_{41}PCB concentrations in Aliaga
324 industrial region in Turkey. Bozlaker et al. (2008) also reported dominance of 3-Cl to 5-Cl
325 PCBs in Aliaga industrial region of the country. Cindoruk et al. (2007) reported that PCBs
326 were often found as 3-Cl and 4-Cl (65.7% and 25.1%) for BOID (Bursa Organised Industrial
327 District) site of Bursa. Low molecular weight congeners (PCB- 17, 18, 28, 31, 33, 44, 49, and
328 52) dominated the Σ_{41}PCB concentrations reported in Kutahya ambient air by Dumanoglu et
329 al. (2017)

330 Composition of PCB mixtures, partitioning, vapor pressure, and water solubility are
331 the significant parameters effecting contribution of the groups (ATSDR, 2000). Besides, tri-
332 and tetra-CBs may travel long distances because they are lighter than other groups (penta-,
333 hexa-, hepta-, and octa-CBs) before depositing on the soil. Elevated penta-CB contribution
334 was consistent with the results of Du et al. (2009) performed in Philadelphia metropolitan
335 area. As a general view, the contribution of less chlorinated homologue groups (tri-, tetra, and
336 penta-CBs) were higher compared to those with higher number of chlorine atoms (hexa-,
337 hepta-, and octa-CBs) because increasing number of chlorine atom decreases vapor pressure
338 and water solubility. Therefore, PCB homologue groups ≤ penta-CBs tend to be in gas phase
339 and dissolve in water thereby increasing the possibility of detection in the atmosphere (Yeo et
340 al., 2003) but others tend to deposit on different surfaces. Low-molecular weight congeners

were mostly found to be higher at background sites, whereas those with high molecular weight were detected at suburban and urban sites (Du et al., 2009). In contrast, not only the urban sites but also rural sites were dominated by penta-CBs in this study, whereas the lighter groups (such as tri- and tetra-CBs) had lower percentages at the rural sites (Figure 2b), which may be associated with legacy uses of Aroclors in building materials and modern PCB containing paint and consumer products, light ballasts, sealants, and window caulking (Marek et al., 2017, and references therein).

Since the decision related to the ban of PCB utilization in 1996 was published in 1993 in the official gazette in Turkey (Official Gazette, 1993), long range transport from places with considerable point sources and volatilization from deposited surfaces can be the potential origin of PCBs (Cleverly et al., 2007; Wania et al., 2003). On the other hand, Gedik and Imamoglu (2010) reported imported amounts of PCBs from producer (Germany, France, Italy and Spain) and non-producer (Belgium-Luxembourg, Ireland and Austria) countries to Turkey between 1996 and 2003 (which corresponds to a period after the ban on PCBs utilization) and total imported PCBs amounted to be about 95000 kg. A partially successful inventory study revealed the presence of a total of 6 capacitors and 189 transformers containing PCBs were present in the country in 2006 (Acara, 2006), while the updated National Implementation Plan (NIP) of the country reported that identification of a total of 290 transformers and 1972 capacitors containing PCBs were identified (Acara, 2008). As mentioned by Gedik and Imamoglu (2010), part of this equipment was still in use while others were stored for disposal in the future. Erickson and Kaley (2011) states that one of the most important sources can be electronic wastes because PCBs were extensively used in transformers, capacitors, and heat transfer fluid in the past. Therefore, places where e-wastes were processed, PCB-contaminated equipment storage areas and/or landfills might be significant sources of contamination.

3.1.2. OCPs

OCPs investigated in this study were used in the past to prevent, control or destroy insects and diseases causing harmful effects on plants and animals. Volatilization from agricultural soils contaminated by OCPs in the past are the main sources to air (Aliyeva et al., 2012; Cindoruk, 2011; Odabasi and Cetin, 2012; Pozo et al., 2011). The mean concentrations ranked as ΣDDT (*p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD) (134 pg/m^3) > ΣHCH (α + β + γ + δ- isomers) (64.4 pg/m^3) > HCB (45.1 pg/m^3) > Σendrin+dieldrin (30.4

pg/m^3) > Σendosulfan (*α*-, *β*-, -SO_4) (27.2 pg/m^3) > Σheptachlor+heptachlorepoxide (24.1 pg/m^3) > Mirex (13.4 pg/m^3) > Σchlordane (*cis*- + *trans*-chlordane) (2.14 pg/m^3). *o,p'*-DDD was not detected in the samples but ΣDDT was the pollutant group with the highest average concentration. ΣHCH, HCB, ΣDDT, and Σendosulfan were the groups that are generally found to be higher at urban sites than rural sites among the listed groups.

HCHs have different mixtures such that technical HCH is a mixture rich in *α*-isomer (*α*: 55-80%, *β*: 5-14%, *γ*: 8-15%, *δ*: 2-16% *Ɛ*: 3-5%) whereas *γ*-isomer (> 90%) dominates lindane (Vijgen et al., 2006). Lindane was one of the compounds forbidden in 1979 in Turkey (Ahioglu, 2008). The annual average ΣHCH concentration (64.5±288 pg/m^3) comprised 19.1% of the total OCP level, with a range of <MDL (Van) to 867 pg/m^3 (Kirklareli) at the urban sites, and of 4.45 pg/m^3 (Çankırı) to 134 pg/m^3 (İstanbul) at the rural sites (Figure 3a). The annual average at the urban sites (93.6±397 pg/m^3) were 2.5 times higher than those of rural sites (35.1±73.1 pg/m^3) but the difference was not significant statistically (p>0.05). The dominating HCH isomers were *α*- (22.0±92.8 pg/m^3) and *β*- (21.8±96.1 pg/m^3). The average concentrations of *γ*- and *δ*- isomers were 7.34±45.7 pg/m^3 and 13.4±86.8 pg/m^3, respectively (Supplementary Material, Figure S1a). *β*-HCH was also dominating HCH isomer in Bursa (Esen, 2013; Cindoruk and Tasdemir, 2014) whereas *α*-HCH was also the dominating isomer in the studies of Aliyeva et al. (2012) and Devi et al. (2011). The mean *α*-HCH/*γ*-HCH ratios for urban and rural sites were 2.26 and 7.68, respectively. The ratios between 4 and 7 might show that atmospheric concentrations were affected from usage of technical-HCH, while <4 might indicate that levels were under the mixed influence of lindane and technical-HCH utilization (Su et al., 2006). The ratio for the rural sites was >7 probably because *γ*-HCH has a lower residence time in the atmosphere due to high reaction rate of hydroxyl radicals with *γ*-isomer and lower Henry's Law constant than *α*- isomer (Brubaker and Hites, 1998).

Production and sale of DDT was prohibited in 1978 and 1985 in Turkey, respectively (Ahioglu, 2008). ΣDDT concentrations varied from 12.5±15.6 to 686±754 pg/m^3 at the urban sites and from 11.7±8.62 to 484±789 pg/m^3 at the rural sites. The spatial variation of ΣDDTs is shown in Figure 3b. Érseková et al. (2014) indicated that the highest levels of ΣDDTs was detected from March to August 2006 at urban sites of Serbia (986 pg/m^3) and Romania (448 pg/m^3), and rural site of Romania (330 pg/m^3) with the mean of 295 pg/m^3 that was 2.1 folds higher than the mean calculated in this study (134±296 pg/m^3). *p,p'*-DDE had the highest mean level among the listed isomers for all sampling periods similar to measured values in the Czech Republic (Klánová et al., 2006) whereas o,*p'*-DDD was not detected as in the GAPS study (Pozo et al., 2006) (Supplementary Material, Figure S1b). Since *p,p'*-DDT is converted

to *p,p'*-DDE by UV radiation during atmospheric transport, concentration of *p,p'*-DDE could be elevated due to this (Atlas and Giam, 1988). Furthermore, volatilization of DDD and DDE formed from decomposition of DDT in the soil by microorganisms may be another source (ATSDR, 2002). *p,p'*-DDT contributed 16% of ΣDDT in this study compared to 12% in the study conducted at urban, rural, and wetland areas of India (Zhang et al., 2008). Contribution of *p,p'*-DDT to ΣDDT was 54% in the non-heating period and 38% in the heating period in Izmir (Ugranli et al., 2016). The mean concentrations of all isomers were found to be higher at urban sites. Mean *p,p'*-DDE/*p,p'*-DDT ratios were greater than 1 at urban (5.21) and rural sites (3.80) implying aged usage of DDT in Turkey similar to that in Azerbaijan (Aliyeva et al., 2012). This ratio was found as 0.73 in the non-heating period and 1.51 in the heating period in a suburban area in Izmir (Ugranli et al., 2016).

The mean concentration of Σendosulfan at the urban sites (35.0±83.2 pg/m^3) was higher than that of the rural sites (19.4±39.2 pg/m^3). Endo-SO_4 was the least detected isomer (only 2 times out of 128 samples) with the average of 0.57±4.74 pg/m^3. The mean *β*-endosulfan (15.2±59.8 pg/m^3) level was higher than *α*-endosulfan (11.5±12.5 pg/m^3). In spite of the fact that the urban sites were dominated by *β-e*ndosulfan (*α*-endosulfan: 12.4±13.8 pg/m^3, *β-e*ndosulfan: 22.8±79.2 pg/m^3), their levels were similar at the rural sites (*α*-endosulfan: 10.6±10.9 pg/m^3, *β-e*ndosulfan: 7.75±28.2 pg/m^3). *α*-endosulfan/*β-e*ndosulfan ratio for urban sites was 0.55 but it was 1.38 for rural sites. *α*-endosulfan is mostly found in elevated levels at agricultural sites in the literature (such as olives, sunflower, and vineyards) (Estellano et al., 2012). Therefore, it is reasonable that rural sites had higher *α*-endosulfan from local application. Global concentrations (Weber et al. 2010 and references therein) along with those measured in Turkey (such as by Odabasi et al. (2008) and Ugranli et al. (2016)) reflect endosulfan levels during it was in use. However, the profile since its ban may be in the process of shifting from α- to β-isomer due to differences in the degradation rates in soil, which depend on type of soil in terms of biological activity (Bussian et al., 2015). Furthermore, the turnover may also occur during LRAT as the travel distances increase from application sites where it is still in use (Carrera et al., 2002; Weber et al., 2010). In fact, there are reports of α/β<1 (Schrlau et al., 2011; Wang et al., 2014) including from Turkey, urban Bursa where it was 0.61 and 0.86 at two sites (Cindoruk, 2011 and personal communication). Nevertheless, the observation of α/β<1 in this study is based on the whole dataset which contains high β-isomer concentrations at Malatya (127 pg/m^3) and Mersin (139 pg/m^3) in Period-I, and very high concentrations at Istanbul (221 pg/m^3) and Kars (609 pg/m3) in

Period-II. If these four data points are not considered, α/β ratio retreats to a value (1.64) in line with the majority of the literature.

The annual average concentration of Σheptachlor was measured as 24.3±159 pg/m^3. An extremely large value was detected at the urban site of Kirklareli (1758 pg/m^3) so the mean level of this site is much greater than the other locations. The annual mean level of Σheptachlor at the urban sites varied from <MDL to 458±867 pg/m^3 (mean: 35.2±218 pg/m^3), whereas average concentrations were in the range of <MDL to 103±191 pg/m^3 (mean: 13.2±50.0 pg/m^3) at the rural sites. One-year average concentrations at urban sites (except Kirklareli) and rural sites (except İstanbul) were <30 pg/m^3. Mean heptachlor epoxide concentrations for both urban (29.3±2188 pg/m^3) and rural sites (8.50±48.9 pg/m^3) were greater than heptachlor levels measured at urban (5.89±14.9 pg/m^3) and rural sites (4.74±13.7 pg/m^3). Annual average concentration of chlordane (TC+CC) was very low (average: 2.15±13.3 pg/m^3) and found only 9 out of 128 samples. Average level of chlordane was 3.44±17.8 pg/m^3 (maximum: 137 pg/m^3) at urban sites and 0.85±5.76 pg/m^3 (maximum: 44.2 pg/m^3) at rural sites. Mean level of CC and TC were 2.11±10.9 pg/m^3 and 1.32±7.26 pg/m^3 at urban sites and 0.46±2.56 pg/m^3 and 0.39±3.09 pg/m^3 at rural sites, respectively. Urban sites were enriched by TC with 61.4% of TC+CC average. The detection frequency of aldrin was only 2 out of 128 samples. Annual average level of Σendrin+aldrin+dieldrin was 30.4±121 pg/m^3. The average concentrations at urban and rural sites were between <MDL and 105±182 pg/m^3, and between <MDL and 366±617 pg/m^3, respectively. Mean concentrations at urban and rural sites were 24.4±54.0 pg/m^{3}and 36.5±163 pg/m^3, respectively. Dieldrin was found to be the dominant isomer for both urban and rural sites whereas the levels of aldrin were almost zero (Supplementary Material, Figure S1c). Annual mean (urban+rural) of Mirex was found as 13.4±66.6 pg/m^3 and the detection rate was 19 out of 128 samples. The range of means was from <MDL to 23.0±46.1 pg/m^3 (average: 5.62±17.7 pg/m^3) at urban sites and from <MDL to 176±352 pg/m^3 (average: 21.4±92.2 pg/m^3) at rural sites. Since Mirex binds to soil particles or sediment in water, it does not volatilize to air easily (ATSDR, 1995), so this might be the reason for the low detection rate. Turgut et al. (2012) and Voigt et al. (2013) reported presence of Mirex in soil and all human milk samples collected from villages located on 0m, 121m, 408m, 981m, 1881m altitudes of Taurus Mountains in southern Turkey. However, the main reason is most probably minimal LRAT (Turgut et al., 2012; Voigt et al., 2013) because it was not registered/used (Acara, 2008; Turgut et al., 2012; Voigt et al., 2013) in Turkey. Annual mean level of HCB was 45.3±197 pg/m^3. The sampling locations with the lowest and highest mean levels were Çankırı and Kars among urban sites, and Antalya and İstanbul

among rural sites. The annual mean levels measured at urban and rural sites were 57.7±230 pg/m^3 and 32.8±157 pg/m^3, respectively. Spatial variation graphs of OCPs are given in Supplementary Material (Figure S2-S8).

Overall, extreme or high annual average concentrations of OCP groups were found in Kirklareli, Istanbul, and Kars, for which LRAT may be a possible explanation, because these locations are three of the four the most northern sites in this study, i.e., the area where air masses from the northerly direction arrive to the country. Dominant wind directions during the one-year sampling period were NNE for Istanbul and NE for Kars (Supplementary Material, Figure S9). NNE is also the dominant wind direction in Kirklareli (Vardar, 2003). Hence, the results of this study may indicate that long range transport from the northerly directions are possible sources of OCP contamination.

3.1.3. PBDEs

PBDEs especially penta-, octa-, and deca- formulations have been widely used as flame retardants in computers, plastic products, textiles, and electronic equipment (Baek et al., 2008). PBDEs (penta-, octa-, and deca-BDEs) have recently been banned (Stockholm Convention, 2017). The overall annual average Σ_{14}PBDE concentration was found as 191±329 pg/m^3. It was 183±260 pg/m^3 and 200±387 pg/m^3 for the urban and rural sites, respectively (Figure 4). In the literature, PBDE congeners were reported to be <MDL in all sampling sites in Brazil and Chile (Pozo et al., 2004; Meire et al., 2012; Pozo et al., 2012). The highest annual mean levels were measured at Kirklareli among the urban sites and at Antalya among the rural sites in this study. Annual mean levels of BDE-17, -28, -100, -153, and -154 were <0.5 pg/m^3. BDE-190 (42%), -99 (24.4%), and -47 (20.6%) had the three highest contributions to Σ_{14}PBDEs. While other studies have indicated BDE-209 as the predominant congener, our results are not without precedent. Wang et al., (2010) reported that BDE-47 and -99 had the highest contributions with the range of 22-72% and 14-47%, respectively in the Tibetan Plateau. Jaward et al. (2004) also found these compounds as the dominant contributors, contributing 75% to total BDEs. There is also a study from Turkey reporting a lower gas phase BDE-209 concentration (6.8 pg/m3) compared to BDE-100 (9 pg/m3) and BDE-47 (8.2 pg/m3) (Cetin and Odabasi, 2007). BDE-47 and -99 are the main components of the commercial product, Bromkal 70-5DE with around 70-80% of the mixture (Sundström and Hutzinger, 1976; Sjödin et al., 1998). Atmospheric travel distance of BDE-47 is greater than BDE-99 (Wania and Dugani, 2003). Since contribution of BDE-99 was slightly

higher than BDE-47, not only LRAT but also volatilization from sinks or formerly contaminated sites may be possible sources of these congeners. BDE-183, which is a major component of commercial octa-BDE (Stockholm Convention, 2008), was not detected in the samples and this suggests that the usage of octa-BDEs in Turkey and the affecting regions may be negligible.

3.2. Seasonal Variation

The concentrations detected in four sampling periods at urban and rural sites are listed in Table 1. Because there are differences between calendar and observed seasons among different regions of Turkey, the seasonality was evaluated for two temperature regimes: samples collected at higher (range: 14.4 – 25.6˚C) and lower (range: -3.6 – 14.1˚C) than average (14.2˚C) temperatures over the one-year sampling period. Comparison of the groups would indicate temperature dependence in relation to seasonal variation. It is found that most of the target chemicals were at higher average levels in the Period II (August – October 2014), except Mirex, Σ_{43}PCBs, and Σ_{14}PBDEs, which were at higher concentrations in Period III (November 2014 - January 2015). Therefore, it may be speculated that the warmer the sampling period, the higher the average pollutant concentration probably due to volatilization from sinks or contaminated sites. Zhang et al. (2013) also reported the highest average concentration of six indicator PCBs in winter as 44.4 pg/m^3 compared to summer (21.6 pg/m^3), while Baek et al. (2010) measured higher mean concentration of Σ_8PCBs in spring-summer period (77.7 pg/m^3) compared to fall-winter period (31.7 pg/m^3). Vilavert et al. (2014) also reported higher average Σ_7PCB (indicators) levels with 27.7 pg/m^3 in spring in Spain. ΣHCHs, TC+CC, ΣDDT, and ΣDDE levels were higher in autumn (38.5 pg/m^3, 331 pg/m^3, 215 pg/m^3, 178 pg/m^3, respectively) in China (Zhang et al., 2013).

The difference in the median concentrations of the two temperature groups were significant at urban sites for HCB (p<0.0001), *p,p'*-DDT (p=0.039), dieldrin (p=0.023), and *β*-endosulfan (p=0.001). Endo-SO_4 was not found at urban sites, and the median levels of the remaining OCPs, Σ_{43}PCBs and Σ_{14}PBDEs were not significantly different at urban sites. The difference in the median levels with temperature was significant at rural sites for HCB (p<0.0001), dieldrin (p=0.002), endrin (p=0.007), heptachlor (p=0.002), *p,p'*-DDE (p=0.010), Mirex (p=0.044), *β*-endosulfan (p=0.012), and Σ_{43}PCBs (p=0.047), while the median concentrations of the other OCPs and Σ_{14}PBDEs were not significantly different at rural sites. In general, HCB, DDTs, and endosulfan had higher concentrations in the warmer periods both

at urban and rural sites, which points out the significance of the secondary emissions. PCBs also had similar behavior at urban sites depending on the significance level (p=0.047).

3.3. Factor Analysis

Scree and loading plots (Figures S10-S15), and final statistics and factor loadings (Tables S6-S17) of the analyses presented in this section can be found in the Supplementary Material. The analysis of OCPs resulted in 6 factors for both urban and rural sites, explaining 79% and 81% of the variation, respectively. For rural sites, Factor-1 contributed with 41%, with high loadings of β-endosulfan, Endo-SO_4, chlordane (TC and CC), heptachlor epoxide, dieldrin, endrin, α-HCH, and *p,p'*-DDE, which contain both some parent and some degradation products. Factor-2, contributing with 14%, is loaded by HCH isomers (β-, γ-, and δ-) and aldrin. The remaining factors are comprised of *p,p'*-DDT and heptachlor (Factor-3), *o,p'*-DDT and *o,p'*-DDE (Factor-4), Mirex (Factor-5), and HCB (Factor-6). Similar to rural sites, Factor-1, -2 and -3 (explaining 33%, 16%, and 14% of the variation, respectively) are a mix of chlordane (CC and TC), endosulfan (α-, β-, and -SO_4), *p,p'*- and *o,p'*-DDT, *p,p'*-DDE, HCH isomers (α-, β-, γ-, and δ-), and dieldrin and endrin for urban sites containing both some parent and degradation compounds. The remaining factors are mainly formed of parent compounds: β-endosulfan and heptachlor (Factor-4), aldrin, Mirex (Factor-5), and *p,p'*-DDT (Factor-6). In summary, the measured OCP concentrations were mainly contributed both by primary sources of HCHs and chlordane and by secondary sources with degradation products such as Endo-SO_4 and heptachlor epoxide, whereas DDT, HCB, and Mirex contribute much less.

The analysis of PCBs resulted in 9 and 7 factors for rural and urban sites, explaining 85% and 83% of the variation, respectively. However, Factor-1 explained >40%, and three more contributed with >5% for both rural and urban sites. For rural sites, Factor-1 accounting for a variation of 43%, is highly loaded by PCBs -180, -141, -167, -87, -151, -153, -132, -149, -158, and -110. Factor-2 is highly loaded by PCBs -194 and -157 while Factor-3 is moderately loaded by -95 and -203, explain 8.7% and 7.4% of the variation, respectively. These factors, with a total variation of 59% explained, contain congeners of Aroclors 1254 and 1260, therefore, can be ascribed to technical PCB mixtures (Aydin et al., 2014; Cetin 2016; Odabasi et al., 2016; and references therein). Factor-4 (PCB-123 and -118) and Factor-5 (PCB-52, -170, -114) may be ascribed to combustion (Aydin et al., 2014), Factor-6 (PCB-31, -28, and -18) and Factor-9 (PCB-22) may be indicating LRAT (Gregoris et al., 2014; Stafilov et al.,

2011; and references therein), while Factor-6 (PCB-187 and -183) can also be considered as technical mixtures (Kanechlor-600, Aydin et al., 2014; Cetin 2016; Odabasi et al., 2016; and references therein). Differently for urban sites, Factor-1 accounting for 44% of the variation, is highly loaded by PCBs -110, -18, 153, -31, -138, -28, and moderately loaded by 16 CBs, which contain tri-, penta-, and hexa-CBs, indicating short and long range atmospheric transport (Stafilov et al., 2011 and references therein; Gregoris et al., 2014). Factor-2 has high loadings of PCBs -189, -104, -174, -194, and -157, explains 14% of the variation with highly chlorinated congeners and can be ascribed to Araclor 1260. Factor-3, explaining 8.7% and loaded by PCBs -141, -203, and -99 can also be ascribed to short range atmospheric transport (Stafilov et al., 2011 and references therein; Gregoris et al., 2014). Factor-4, explaining 6.3% and loaded by PCBs -118 and -123, could indicate combustion, however, the moderate negative loading by PCB-170 does not allow for this interpretation. In summary, the urban concentrations were contributed mainly by the technical mixtures and their constituents' transport from short and long distances.

The analysis was also conducted with the overall dataset that was formed by adding PBDEs to OCPs and PCBs. The analysis of the rural-sites dataset revealed 17 factors. However, only four factors contributed with >5%, explaining a total of 52% of the variation. Factor-1, explaining 24.8%, has high loadings of PCB congeners (-87, -180, -141, -151, -167, -153, -149,-132, -158, -110) and PBDE-85. Factor-2, explaining 13.3%, is highly loaded by OCPSs: α-HCH, chlordane (CC and TC), β-endosulfan, dieldrin and endrin, and degradation products including Endo-SO_4, heptachlor epoxide, and *p,p'*-DDE. Factors -3 and -5, explaining 7.9% and 4.6%, respectively, have high loadings of PBDEs (-47, -99, -190 and -138, -28, respectively), while Factor-4, explaining 6%, of PCBs (-194, and -157) and Factor-6, explaining 4.4%, of aldrin, along with moderate loadings of δ-, β-, γ-HCHs). In addition, although with small percentages of variation explained, other parent OCPs (HCB, α-endosulfan, Mirex, *p,p'*-DDT as Factors -17, -16, -15, -10, respectively) and DDTs (*o,p'*-DDE and *o,p'*-DDT as Factors -12 and -13, respectively) also appear as sources. In addition to *p,p'*-DDT, Factor-10 includes PCB-31, -28, and -18, indicating that *p,p'*-DDT is associated with LRAT. The analysis of the urban-sites dataset revealed 16 factors. However, only four factors contributed with >5%, explaining a total of 57% of the variation. Factor-1, explaining 27.1%, has high loadings of PCBs (-31, -105, -167, -151, -110, -18, and -28). OCPs (heptachlor epoxide, CC, γ-HCH, β-HCH, TC, α-HCH) and PBDEs (-85, -154, and -66) are high loadings to Factor-2, explaining 14.3%. PCBs (-174, -189, -104, -194, and -189) are high loadings to

Factor-3, explaining 8.4%. PBDEs (-47, -190, and -99) and PCBs (-118 and -123) load Factor-4 with 7.0% variation explained. Factors -5 and -6, with respective contributions of 4.9% and 4.7% to the explained variation, are loaded by *p,p'*-DDD, endosulfans (*β*- and -SO_4), and PCBs -203, -141, -99, respectively. In addition, endrin-dieldrin (Factor-7), *o,p'*-DDT (Factor-10), aldrin and Mirex (Factor-14), PBDE-209 (Factor-11) appear as separate sources. Identification of PCBs, OCPs, and PBDEs having separate variations at rural sites (Factors -1 to -5, explaining 56% of the variation) and appearance of parent OCPs as separate sources (HCB, *α*-endosulfan, Mirex, *p,p'*-DDT) along with attributions made within PCBs and OCPs datasets indicate local sources/short range transport and LRAT contribute to the measured concentrations. A similar elucidation can also be made for urban sites except that some OCPs and PBDEs appear to show similar variation (Factor-2) indicating a common urban source, which may be co-contaminated soils, OCP-applied buildings and/or building materials (Melymuk et al., 2013).

4. Conclusions

The aims of this study were to measure ambient air concentrations of 43 PCBs, 22 OCPs, and 14 PBDEs in urban and rural sites of 16 cities by PUF-PAS, to examine spatial and seasonal variations on an east to west and south to north transect, and to generate the first large-scale nationwide data set for atmospheric POPs in Turkey. Results of the study have built up a valuable data focused on a geographical area poorly described until now. A broad range of air concentrations were observed for compounds of interest in addition to a fairly consistent pattern of relative abundance for each group of contaminants across seasons and locations. Levels determined in this study were in consonance with levels of target chemicals reported in other studies conducted in Turkey and with levels found for European sites, with some exceptions. Penta-CBs had the highest portion in the total concentration with 54.3%; the contribution decreased as the molecular weight of homologue groups increased. The five OCPs with highest levels were listed as *p,p'*-DDE, HCB, *α*-HCH, *β*-HCH, and *p,p'*-DDT. One-year overall mean concentration of Σ_{14}PBDEs for urban and rural sites were 183±260 pg/m^3 and 200±387 pg/m^3, respectively. The difference in concentrations of urban and rural sites was not significant, whereas some compounds were at significantly higher levels in the warmer periods indicating the secondary emissions, which was also pointed to LRAT from secondary emission areas by the factor analysis for the whole dataset.

Usage of chemicals of interest of this study has been forbidden in Turkey in different times in a time span from 1979 to 2001. Therefore, the reason for detection of varying levels which can be considered as higher concentrations in some cases in comparison to the values reported in literature around the world may be due to local volatilization from secondary sources and/or waste sites as well as LRAT from surrounding areas. Particularly, levels and presences of target chemicals in Kars, Van and Kirklareli provinces that lack any known sources of PCBs and OCPs may be an important indicator of LRAT of these chemicals. A clear conclusion of the current study is the lack of unequivocal temporal and spatial trends of target POPs in Turkish ambient air. This, in turn, makes it impossible to carry out an assessment, in any degree, of effectiveness of any measurements implemented by the Stockholm Convention in the country. Therefore, formation, implementation and maintenance of a long-term and regular Turkish air monitoring program in a more wider spatial coverage and in much longer time periods is a must for the exact assessment of POPs time trends, distribution and fate in the environment.

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Figure captions

Figure 1. Spatial variation in concentrations of Σ_{43}PCBs

Figure 2. Percent contribution of PCB homologue groups to the total concentration (a) one-year average, (b) urban and rural sites

Figure 3. Spatial variation in concentrations of (a) ΣHCHs and (b) ΣDDTs

Figure 4. Spatial variation of Σ_{14}PBDEs

Table captions

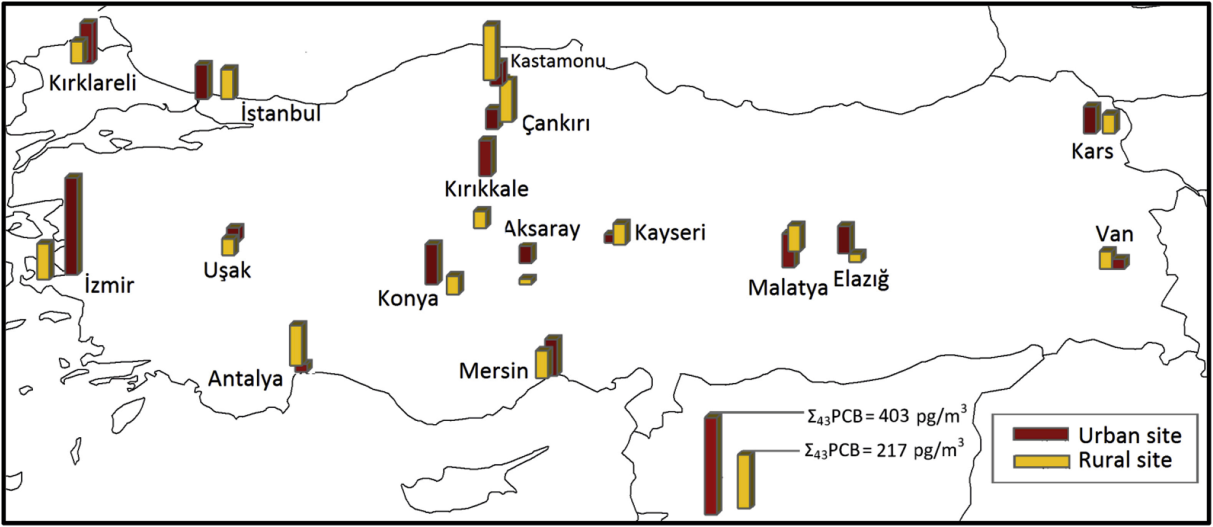
Table 1. Seasonal variation of targeted POPs at urban and rural sites (pg/m^3)

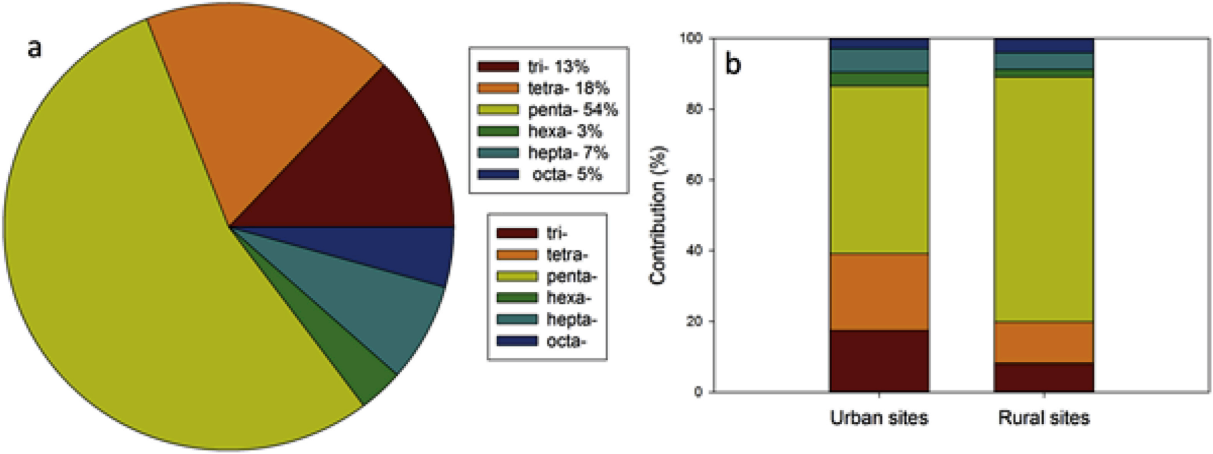
Table 1. Seasonal variation of targeted POPs at urban and rural sites (pg/m^3)

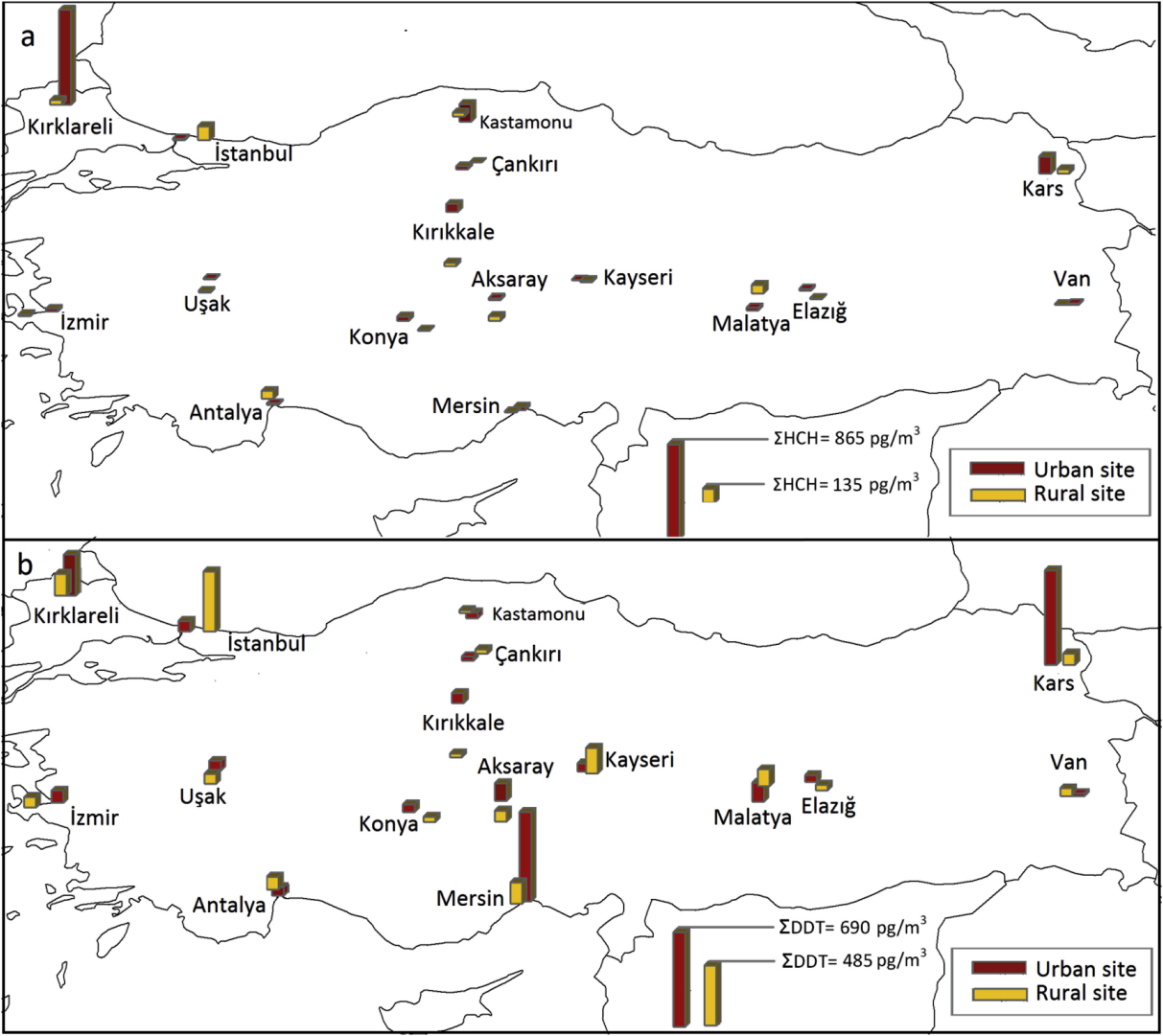
		R (m^3/day)	T (^{0}C)	ΣHCHs	HCB	ΣDDTs	ΣENDO	ΣHEP	TC+CC	ΣENDs	Σ_{22}OCPs	Σ_{43}PCBs	Σ_7iPCB	Σ_{14}PBDEs
								URBAN						
1ST PERIOD	n*,[a]			8	11	7	9	2	2	9	12	12	8	12
	Mean	7.75	20.19	101	19.9	187	64.2	27.7	19.1	60.4	295.70	118.53	22.8	99.3
	SD	1.44	3.80	211	10.2	278	57.4	5.88	16.7	44.0	291.96	80.89	15.0	103
	Min. (**)	5.34	10.6	<MDL (5.38)	<MDL (9.80)	<MDL (13.9)	<MDL (6.82)	<MDL (23.5)	<MDL (7.29)	<MDL (14.6)	<MDL 32.84)	<MDL (5.36)	<MDL (6.72)	<MDL (28.4)
	Max.	9.87	24.7	612	41.8	801	174	31.8	30.9	129	1053.45	242.34	48.5	399
	Median	7.82	19.8	12.7	15.5	123	56.1	27.7	19.1	47.5	219.54	117.54	20.7	69.9
	GM	7.62	19.8	24.2	17.8	80.1	42.6	27.4	15.0	46.2	191.05	81.21	18.4	70.6
								RURAL						
	n*			8	11	8	9	2	0	7	11	10	7	11
	Mean	8.47	20.2	22.9	13.2	124	28.5	29.4	<MDL	82.2	201	64.3	20.3	103
	SD	1.92	3.92	16.2	4.64	79.0	21.2	29.5	<MDL	75.7	167	34.1	9.41	219
	Min. (**)	5.77	10.6	<MDL (6.76)	<MDL (4.61)	<MDL (25.2)	<MDL (4.53)	<MDL (8.55)	<MDL	<MDL (7.44)	<MDL (15.9)	<MDL (20.7)	<MDL (5.39)	<MDL (7.50)
	Max.	12.7	24.7	46.4	20.5	279	73.8	50.3	<MDL	174	514	111	34.2	758
	Median	8.30	19.2	17.8	13.5	125	24.3	29.4	<MDL	36.3	150	68.3	20.3	35.6
	GM	8.28	19.8	17.6	12.4	97.9	21.9	20.7	<MDL	47.4	128	54.4	17.8	39.7
								URBAN						
2ND PERIOD	n*			15	16	15	15	5	3	4	16	16	11	16
	Mean	9.08	18.8	289	208	363	78.8	378	58.5	37.8	1070	117	25.7	162
	SD	1.85	3.52	795	440	647	157	772	69.7	45.3	1892	87.9	20.9	212
	Min. (**)	5.83	12.9	<MDL (5.21)	18.6	<MDL (32.2)	<MDL (5.34)	<MDL (13.6)	<MDL (2.86)	<MDL (7.15)	53.0	6.25	<MDL (4.01)	36.2
	Max.	11.9	25.6	3112	1375	2153	637	1758	137	104	6508	281	70.0	878
	Median	9.49	17.7	39.3	35.4	125	29.2	28.6	36.1	19.9	255	106	17.0	70.5
	GM	8.89	18.5	47.4	61.3	144	35.3	60.7	24.1	21.8	374	72.7	19.7	101
								RURAL						
	n*			13	16	16	14	7	1	8	16	15	13	16
	Mean	8.79	18.8	74.4	111	198	46.5	66.5	44.2	54.5	551	98.2	20.9	91.9
	SD	1.54	3.52	130	307	397	74.8	142	0.00	121	1324	83.5	10.9	91.0
	Min. (**)	5.61	12.9	<MDL (5.86)	19.1	18.2	12.3	7.22	44.2	6.35	76.8	11.5	5.55	19.5
	Max.	12.2	25.6	482	1261	1666	303	389	44.2	354	5502	369	46.5	408
	Median	9.04	17.7	11.6	31.4	96.6	25.3	14.0	44.2	11.0	218	85.5	19.0	72.7
	GM	8.66	18.5	26.6	41.5	96.7	28.8	19.3	44.2	17.0	243	73.2	18.3	69.1
								URBAN						
3RD PERIOD	n*			9	9	14	11	6	1	4	16	15	15	14
	Mean	3.12	4.80	53.8	40.3	112	23.7	37.0	4.11	35.1	199	164	63.4	566
	SD	0.88	4.34	99.9	20.2	156	25.2	36.0	na	19.6	281	234	63.9	225
	Min. (**)	1.61	-3.64	<MDL (7.14)	<MDL (10.0)	<MDL (7.63)	<MDL (3.86)	<MDL (5.92)	na	<MDL (14.1)	33.8	14.1	7.18	197
	Max.	4.55	12.83	319	70.7	603	76.5	96.0	na	61.4	1174	969	269	1099
	Median	3.22	3.31	24.3	47.5	48.8	10.2	22.1	4.11	32.5	87.8	98.7	50.5	562

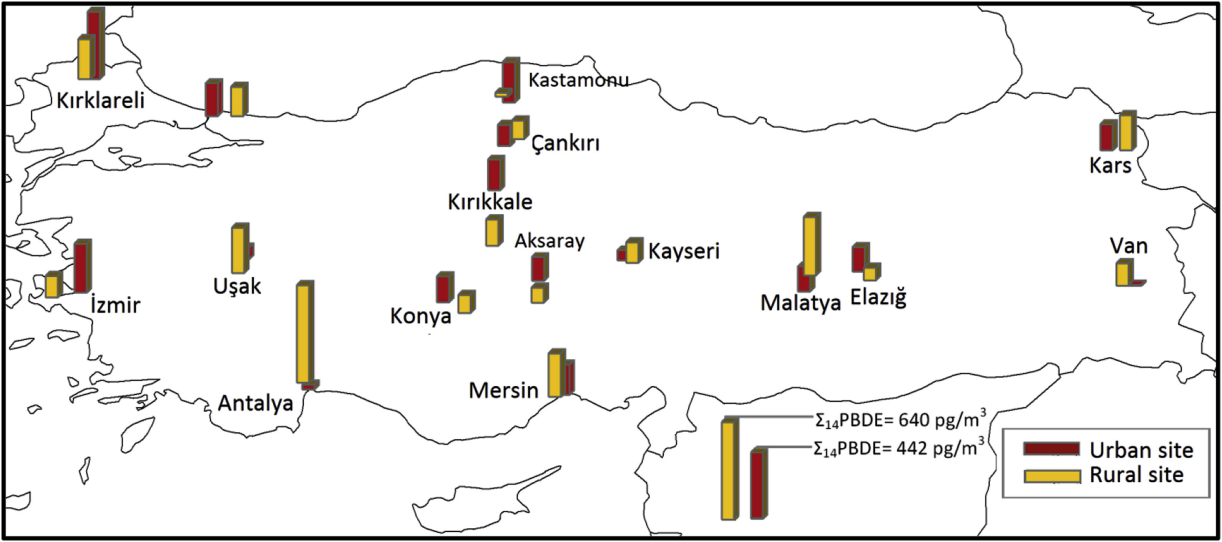
	GM	2.99	4.23	25.2	34.4	57.0	14.0	23.8	4.11	30.9	116	98.5	45.3	520
								RURAL						
	n*			11	13	13	11	12	0	3	15	15	15	14
	Mean	3.85	4.80	41.2	63.9	133	13.9	23.9	<MDL	16.8	307	187	85.2	709
	SD	1.86	4.34	43.0	35.1	182	13.3	24.0	<MDL	13.2	309	197	103	559
	Min. (**)	1.18	-3.64	<MDL (6.54)	<MDL (17.4)	<MDL (10.7)	<MDL (4.61)	<MDL (6.17)	<MDL	<MDL (7.03)	28.3	31.9	16.3	278
	Max.	7.91	12.83	150	120	695	50.4	93.4	<MDL	31.8	1114	747	383	2422
	Median	3.80	3.31	21.4	63.0	69.9	8.24	18.5	<MDL	11.7	196	107	45.5	496
	GM	3.43	4.23	25.9	54.1	73.6	10.5	17.5	<MDL	13.8	213	128	55.2	585
								URBAN						
	n*			14	8	14	14	5	1	6	16	14	14	3
	Mean	4.39	9.68	25.8	18.9	139	15.8	16.8	2.11	22.3	193	100	43.4	5.29
	SD	0.81	3.63	22.1	7.74	138	16.3	9.33	na	17.7	148	28.9	9.63	1.71
	Min. (**)	3.01	3.51	<MDL (5.81)	<MDL (12.6)	<MDL (30.4)	<MDL (5.48)	<MDL (8.27)	2.11	<MDL (6.17)	40.6	<MDL (60.5)	<MDL (30.6)	<MDL (3.41)
	Max.	6.13	15.60	76.5	36.7	515	65.2	27.2	2.11	56.3	565	145	65.7	6.76
	Median	4.26	8.89	18.1	17.0	79.5	9.32	13.8	2.11	18.8	139	93.8	41.7	5.69
	GM	4.32	9.01	18.9	17.9	93.9	11.9	14.7	2.11	17.8	148	96.2	42.4	5.08
4TH PERIOD								**RURAL**						
	n*			15	8	15	16	2	2	2	16	15	15	3
	Mean	5.45	9.68	40.3	18.3	56.1	10.2	11.3	4.69	7.35	123	93.1	38.1	19.7
	SD	1.82	3.63	71.9	5.98	40.8	8.10	0.20	1.53	2.00	92.6	76.9	17.7	15.3
	Min. (**)	2.64	3.51	<MDL (4.73)	<MDL (8.89)	<MDL (10.3)	4.04	<MDL (11.2)	<MDL (3.61)	<MDL (5.94)	12.2	<MDL (38.7)	<MDL (19.8)	<MDL (2.95)
	Max.	8.69	15.60	298	29.3	135	38.9	11.4	5.78	8.77	369	338	87.6	32.8
	Median	5.73	8.89	21.5	18.1	44.2	7.99	11.3	4.69	7.35	94.9	71.4	36.6	23.4
	GM	5.14	9.01	23.3	17.4	42.0	8.70	11.3	4.57	7.22	94.6	76.5	35.2	13.1

(*) number of samples with concentration value >MDL; [a] passive sampler in rural site in Kirklareli province was lost; (**) Values in parenthesis represents minimum value of >MDL concentration; ΣHCHs: sum of α-.β-.γ-.δ-HCH ; ΣDDTs: sum of (o.p'-DDT.-DDD.-DDE) and (p.p'-DDT.-DDD.-DDE); ΣENDO: α-endulsulfan+β-endosulfan+endosulfan sulphate; ΣHEP: Heptachlor+heptachlor epoxide; ΣENDs=aldrin+endrin+dieldrin; Σ_6iPCB: Indicator PCBs (congeners -28, -52, -101, 118, 138, 153, 180); not calculated; SD: standard deviation; Min. Minimum value; Max. Maximum value; GM: Geometric mean


Kırklareli
İstanbul
Kastamonu
Çankırı
Kırıkkale
Aksaray
Kayseri
Kars
Van
İzmir
Uşak
Konya
Malatya
Elazığ
Antalya
Mersin
Σ_{43}PCB = 403 pg/m^3
Σ_{43}PCB = 217 pg/m^3
Urban site
Rural site


a
tri- 13%
tetra- 18%
penta- 54%
hexa- 3%
hepta- 7%
octa- 5%
tri-
tetra-
penta-
hexa-
hepta-
octa-
b
Contribution (%)
0
20
40
60
80
100
Urban sites
Rural sites


a
Kırklareli
İstanbul
Kastamonu
Çankırı
Kırıkkale
Aksaray
Kayseri
Kars
Van
Uşak
İzmir
Konya
Malatya
Elazığ
Antalya
Mersin
ΣHCH= 865 pg/m3
ΣHCH= 135 pg/m3
Urban site
Rural site
b
Kırklareli
İstanbul
Kastamonu
Çankırı
Kırıkkale
Aksaray
Kayseri
Kars
Van
Uşak
İzmir
Konya
Malatya
Elazığ
Antalya
Mersin
ΣDDT= 690 pg/m3
ΣDDT= 485 pg/m3
Urban site
Rural site


Kırklareli
Kastamonu
Çankırı
Kırıkkale
Aksaray
Kayseri
Kars
Van
İzmir
Uşak
Konya
Malatya
Elazığ
Antalya
Mersin
Σ14PBDE= 640 pg/m3
Σ14PBDE= 442 pg/m3
Urban site
Rural site

Highlights

- First complete analysis of PCBs, PBDEs and OCPs in Turkish air on a country-wide scale
- Spatio-temporal variations at a total of 32 urban and rural sites using PUF disk passive samplers
- Urban sites generally present higher POP levels than rural areas, but no statistical differences
- Higher concentrations in the warmer periods pointing significance of secondary emissions
- Need for a longer term, wider coverage and regular monitoring program of POPs in Turkey