



Atmospheric concentration, spatial variations, and source identification of persistent organic pollutants in urban and semi-urban areas using passive air samplers in Bursa, Turkey

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Abstract

In this study, the concentration of ambient persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) were measured for 12 months in urban and semi-urban areas using a passive air sampler. During the sampling period, a total of 14 PAH ($\sum_{14}\text{PAH}$) concentrations measured in urban and semi-urban areas were found to be $54.4 \pm 22.6 \text{ ng/m}^3$ and $51.7 \pm 34.3 \text{ ng/m}^3$, respectively. Molecular diagnostic ratios (MDRs) were used to determine PAH sources. According to the MDR values, combustion sources were the most important PAH sources in both sampling areas. However, since the urban area is close to the industrial zone, the combustion sources occurred at high temperatures ($> 800 \text{ }^\circ\text{C}$), while the sources in the semi-urban area generally consisted of petrogenic fuel combustion. $\sum_{50}\text{PCB}$ concentrations measured in the urban and semi-urban areas were found to be $522.5 \pm 196.9 \text{ pg/m}^3$ and $439.5 \pm 166.6 \text{ pg/m}^3$, respectively. Homologous group distributions were used to determine the source of PCBs. According to the homologous group distributions, tri-, tetra-, and penta-chlorinated PCBs were dominant in both sampling areas. $\sum_{10}\text{OCP}$ concentrations measured in urban and semi-urban areas were found as $242.5 \pm 104.6 \text{ pg/m}^3$ and $275.9 \pm 130.9 \text{ pg/m}^3$, respectively. Also, $\alpha\text{-HCH}/\gamma\text{-HCH}$ and $\beta\text{-}/(\alpha + \gamma)\text{-HCH}$ ratios were used to determine the source of OCPs. Lindane was the predominant OCP in both sampling areas.

Keywords Passive air samplers · PAHs · PCBs · OCPs · Spatial variation

Introduction

Persistent organic pollutants (POPs) are chemicals that have biological accumulation, persistence, toxicities, carcinogenic effects, and a large number of natural and anthropogenic sources and have been widely used since the Second World War (Estellano et al. 2017; Ontiveros-Cuadras et al. 2019). These compounds can also be transported over long distances in the atmosphere (Wang et al. 2020b). The Stockholm Convention was signed in 2001 to reduce the environmental levels and emissions of POPs (Ruggeri et al. 2020).

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) are among the well-known POPs (Qu et al. 2019). PAHs are contaminants formed by combining two or more benzene rings that are clustered or angularly or linearly connected (Naing et al. 2020). PAHs have stable molecular structures since they come together with $\pi\text{-}\pi$ bonds (Zhang et al. 2020a). There are both anthropogenic and natural sources of PAHs. Anthropogenic sources are usually caused by the incomplete combustion of coal, wood, oil, or other organic matter (Naing et al. 2020). Natural sources of PAHs include volcanic eruptions and the open burning of fossil fuels (Gaurav et al. 2021). Although PCBs have historically been widely used in dielectric fluids and transformers, they were banned in the 1970s due to their high bioaccumulation and toxicity properties (Wang et al. 2011). OCPs were first used frequently as synthetic insecticides between the 1940s and 1960s. However, they were banned worldwide in the 1980s due to their negative characteristics for the environment and human health (Chen et al. 2020a).

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Molecular diagnostic ratios (MDRs) are used as a qualitative method to investigate the transport and fate of PAHs in a specific environment (Zhang et al. 2020b). This source identification method plays an essential role in determining emission sources. Volatile and semi-volatile PAH compounds vary widely at greater distances from the source region due to different reaction rates (Ji et al. 2019). Most MDRs consist of PAH pairs with the same molecular mass and physico-chemical properties (Amador-Muñoz et al. 2020). Homolog group distributions of PCBs are generally used to determine the distribution, transportation, and fate of PCB sources in the environment (Habibullah-Al-Mamun et al. 2019). Since the low-chlorinated PCBs have higher vapor pressures, they can be moved further away from a source (Hu et al. 2019). Therefore, the determination of homolog group distributions is critical in the source identification of PCBs. Diagnostic ratios are widely used to identify the sources of OCPs. α -HCH/ γ -HCH and β -/($\alpha + \gamma$)-HCH ratios are often used to identify possible sources (Kong et al. 2014; Sah et al. 2020).

The majority of researchers have focused on pollutant concentrations and their distribution between sampling points. In this study, the concentrations of different pollutants, their distribution between the sampling points and their sources, and their spatial changes were investigated. The specific objectives of the present study were to (i) measure the concentrations of PAHs, PCBs, and OCPs in the urban and semi-urban areas, (ii) identify the possible sources, and (iii) determine the regional changes of concentration values.

Material and Methods

Sampling areas, program, and preparation

Bursa is Turkey's fourth largest city in terms of population, with about 3 million inhabitants. Also, Bursa, according to the industry statistics inventory, is Turkey's largest industrial and automotive manufacturing center. Therefore, traffic, industry, and domestic heating are among the primary sources of air pollution in Bursa. Also, air pollution is felt more with the topographic structure of Bursa and the decrease of existing winds, especially in winter. In this study, ambient air samples were taken from urban and semi-urban areas in Bursa (Turkey) using a passive air sampler (PAS). The urban sampling area (40°17'11.16" N–29° 5'13.20" E) is approximately 1.5 km from the Bursa-Ankara highway, 3 km from the industrial zone, and 500 m from the nearest settlement. The semi-urban sampling area (40°10'8.30" N–29°10'26.82" E) is approximately 2 km from the nearest highway and 3 km from the nearest settlement.

Air samples were collected monthly between May 2017 and April 2018 using PASs. The PASs were placed on a branch of a tree 1–2 m in height in the urban sampling area

and on a platform 2 m above the ground in the semi-urban sampling area. Sampling rates (R_s) values for individual POP compounds targeted in this study were calculated according to the model proposed by Herkert et al. (2016) (http://s-ihr41.ihr.uiowa.edu/pufpas_model). Since the R_s values were calculated for each POP compound and each sampling site, atmospheric POP concentrations were determined successfully. R_s values for PAHs ranged from 2.27 to 4.05 m³/day. Similarly, R_s values for OCPs ranged from 2.00 to 3.28 m³/day and ranged from 1.97 to 3.58 m³/day for PCBs. All R_s values are given in Table S1 (Supplementary material).

Sampling and instrumental analysis

The PUF disks were cleaned before being taken to the sampling area. First, the cleaning procedure was carried out with Soxhlet extraction using purified water, then acetone (ACE) (Merck, Darmstadt, Germany) (two times), and finally hexane (HEX) (Merck, Darmstadt, Germany). Each processing step lasted 24 h. After the cleaning process, the PUF disks were dried using a vacuum desiccator. Next, they were wrapped in aluminum foils until taken to the sampling area and kept in a deep freezer at –20 °C.

The PUF disks after sampling were extracted with the 300 mL ACE/HEX (v/v, 1/1) mixture for 24 h using the Soxhlet extraction method (Esen 2013; Sari et al. 2020a). In order to determine analytical efficiency, 1 mL of surrogate solution was added to samples before extraction. Extracted PUF disks were concentrated by rotary evaporator (Laborota 4001 Model, Heidolph, Germany). The rotary evaporator was operated at 30 rpm and 22–23 °C. Sample volumes were first reduced to 5 mL, then 10 mL of HEX was added, and finally reduced to 2 mL (Tasdemir et al. 2012; Sari et al. 2020a).

The samples exchanged to hexane were fractionated using a fractionating column consisting of glass fiber wool, 3 g of silicic acid hydrate (Sigma-Aldrich, 60,780), 2 g of aluminum oxide (Merck, Darmstadt, Germany), and 2 g of sodium sulfate (Na₂SO₄) (Merck, Darmstadt, Germany). The fractionating column was cleaned using 20 mL of dichloromethane (DCM) (Merck, Darmstadt, Germany) and 20 mL of petroleum ether (PE) (Merck, Darmstadt, Germany) to prevent possible contamination in the environment. Subsequently, 2 mL volumes of samples were passed through the column. Twenty-five milliliter PE was used for the elution of target PCBs (fraction 1), and 20 mL DCM was used for the elution of target PAHs and OCPs (fraction 2) (Cindoruk 2011; Esen 2013; Sari et al. 2020a). Finally, the sample volume was reduced again to 1 mL with the rotary evaporator. PCB samples were cleaned with high-purity sulfuric acid (H₂SO₄) (97–99%) for possible contamination (Günindi and Tasdemir 2010; Tasdemir et al. 2012).

Analysis of PCBs and OCPs was performed using the gas chromatograph (GC) device with the Agilent 7890A model micro-electron capture detector (μ ECD). Similarly, PAH analysis was performed using Agilent 7890A model GC and mass spectrometer (MS) with Agilent 5975C inert XL triaxial mass detector. The methods used with GC–MS and GC–ECD are described in detail in our other studies (Esen et al. 2010; Cindoruk 2011; Tasdemir et al. 2012; Esen 2013; Sari et al. 2020a, b). In this study, 14 PAHs (acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Py), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IcdP), dibenz(a,h)anthracene (DahA), and benzo(g,h,i)perylene (BghiP)); 50 PCBs (PCB#4/10, 6, 19, 12/13, 15/17, 31, 28, 22, 52, 44, 41/64/71, 74, 61/70, 66/95, 91, 56/60, 84, 99, 119, 81/87, 86, 135/144, 118, 123, 131, 153, 132/105, 138/163, 128, 174, 156/171/202, 172, 180, 199, 194, and 206); and 10 OCPs (α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor endo epoxide isomer A, endrin, endosulfan- β , endrin aldehyde, p,p'- DDT, and methoxychlor) were analyzed. Of these compounds, naphthalene and acenaphthylene were not included in the calculations due to their low recovery efficiency (<60%).

Quality assurance /quality control (QA/QC)

Blank samples were used to check and prevent any possible contamination during the transportation of the PUFs, the extraction, or the quantification procedures. All glassware used during the preparation of samples, sampling, and laboratory analyses was washed using tap water, distilled water, ACE, and PE, respectively. The surrogate standard was added to each sample before extraction for the determination of the analytical recovery efficiencies. Samples with recovery efficiency between 60 and 120% were included in the calculations. The surrogate standard consisted of naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12 (each 4000 ng) for PAHs and PCB#14, PCB#65, and PCB#166 (each 4 ng) for PCBs. External recovery standard was used for OCPs, which were not recovery-corrected since recovery efficiencies were generally higher than 70% (Cindoruk and Tasdemir 2014).

The GC–MS and GC– μ ECD instruments were calibrated before reading both blank and collected samples. Six level calibration standards were used for both instruments. Calibration standards used for PAHs were 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 μ g/mL and for PCBs and OCPs 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 ng/mL. The R^2 values of the calibration levels were higher than 0.99. The mid-level calibration standard was run to check the GC–MS and GC– μ ECD calibration requirements after every 100 samples. The limit of detection (LOD) and values were determined for individual POP

compounds. The LOD values were calculated as the sum of the average blank mass and three times the standard deviation (average + 3 std dev) (Sari et al. 2021). The instrument detection limits (IDLs) were calculated based on the lowest concentration of a calibration standard (signal:noise (S:N) ratio of 3:1). The IDL values for 1- μ L injection were 0.1 ng for PAHs, 0.15 pg for PCBs, and 0.04 pg for OCPs. The LOD values ranged from IDL to 30.48 ng for PAHs, from 0.26 to 9.18 pg for PCBs, and from 0.24 to 4.83 pg for OCPs. If the mass value of any POP compound was less than the LOD value, it was taken as half of that compound's IDL value for statistical analysis.

Results and discussion

PAH concentrations and possible sources

The average concentrations of a total of 14 PAHs (\sum_{14} PAH) in the atmosphere were found to be 54.4 ± 22.6 ng/m³ (ranging from 24.4 to 91.3 ng/m³) and 51.7 ± 34.3 ng/m³ (ranging from 13.9 to 107.4 ng/m³) for the urban and semi-urban areas, respectively (Fig. 1a). The highest PAH concentrations were determined in December and January, while the lowest PAH concentrations were determined in July and August in both sampling areas. In general, high PAH levels were measured in the winter months, which are associated with increased domestic heating. The low efficiency of fossil combustion reportedly increases PAH concentrations in the winter months (Albuquerque et al. 2016). The PAH concentrations measured in December, January, and February in the semi-urban area were higher than in the urban area. Similar PAH concentrations were measured in both sampling areas in March and November (Fig. 1a). The semi-urban area is located on the mountainside, and for this reason, the weather is colder than the urban area. Therefore, fossil fuel is used earlier for domestic heating in semi-urban areas than in urban areas. In addition, there are more settlements in the semi-urban area than in the urban area. For these reasons, more fossil fuels are used in the months when the temperature drops. The PAH concentrations measured from April to October in the urban area were higher than in the semi-urban area. The high PAH concentrations measured in the urban area are explained by the fact that the region represents an area where industry and traffic are dense.

In this study, the seasonal PAH concentrations obtained for both sampling areas are shown in Fig. 1b. The seasonal distribution of \sum_{14} PAH concentrations ranged from 34.2 to 78.4 ng/m³ for the urban area and from 18.2 to 98.0 ng/m³ for the semi-urban area. The highest PAH levels in both sampling areas were measured in the winter and autumn seasons, while the lowest PAH levels were measured in the spring and summer seasons. High atmospheric PAH concentrations

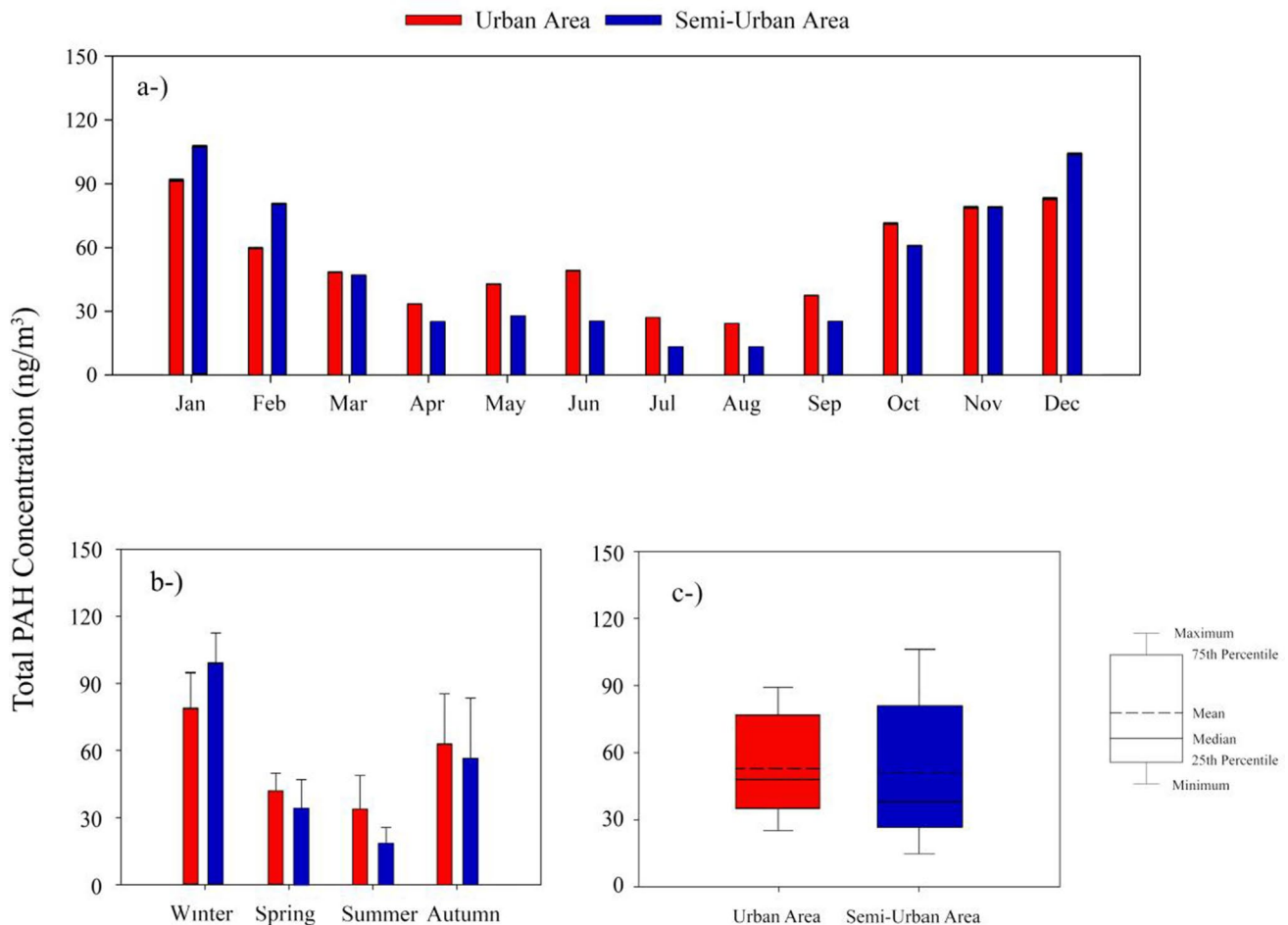


Fig. 1 Monthly (a), seasonal (b), and annual (c) PAH distributions for the sampling areas

measured in winter compared to summer are explained by local emission sources and increased long-range atmospheric transport. For example, using more fuel for heating during the winter months causes PAH concentrations to increase. In addition, meteorological factors are among the effective mechanisms on the temporal distribution of PAHs. Changes in ambient temperature play an important role in the absorption mechanisms and degradation of PAHs. Thus, higher PAH concentrations are measured in winter than in summer (Hong et al. 2020). Relatively higher PAH concentrations measured in winter and autumn have been attributed to lower temperatures, low solar radiation, low photodegradation, and lower mixing height (Thang et al. 2020). Also, fossil fuels for domestic heating in winter and autumn increase PAH concentrations (Albuquerque et al. 2016). In this study, the concentrations obtained and both monthly and seasonal distributions were similar to those reported in other studies (Qin et al. 2013; Chen et al. 2014; Li et al. 2014, 2019; Albuquerque et al. 2016). The annual distributions of PAHs measured in the urban and semi-urban areas are shown in Fig. 1c. According to the annual distribution

of PAH concentrations, there was a significant difference between the minimum and maximum concentrations in the semi-urban area compared to the urban area ($p < 0.05$). This may be due to the fact that PAH sources in the urban area did not change much throughout the year.

Molecular diagnostic ratios (MDRs) are the commonly used method for determining the sources of PAHs (Motelay-Massei et al. 2007). Many studies in the literature have used MDRs to determine the sources of PAHs in various environments (Katsoyiannis et al. 2007; Motelay-Massei et al. 2007). Among these ratios, $\text{Ant}/(\text{Ant} + \text{Phe})$, $\text{Fl}/(\text{Fl} + \text{Py})$, $\text{BaA}/(\text{BaA} + \text{Chr})$, and $\text{IcdP}/(\text{IcdP} + \text{BghiP})$ ratios are mostly used to determine the sources of PAHs in the literature (Katsoyiannis et al. 2007; Motelay-Massei et al. 2007; Tobiszewski and Namieśnik 2012; Sari et al. 2020b). $\text{Ant}/(\text{Ant} + \text{Phe})$ ratios are often used to distinguish combustion or petroleum emissions. If the $\text{Ant}/(\text{Ant} + \text{Phe})$ ratio is higher than 0.1, it means that high temperatures (> 800 °C) are effective in the formation of PAH, while if this ratio is less than 0.1, PAHs are usually produced by chemical reactions both slowly and at low temperatures (Chen et al. 2020b). $\text{Fl}/$

(Fl + Py), BaA/(BaA + Chr), and IcdP/(IcdP + BghiP) ratios are used to distinguish petroleum and combustion emissions. If the Fl/(Fl + Py) ratio is less than 0.4, it refers to petroleum sources, and if it is greater than 0.5, it refers to combustion sources. This ratio shows that mixed sources (liquid fossil fuel combustion) are effective between 0.4 and 0.5 (He et al. 2014; Sari et al. 2020b; Wang et al. 2020a). Similarly, if the BaA/(BaA + Chr) ratio is less than 0.2, PAHs are generally produced by petrogenic emissions, and if this ratio is greater than 0.35, it refers to combustion sources. Similar situations apply for IcdP/(IcdP + BghiP) ratios. “The combustion-derived PAHs (COMPAHs) are defined as a combination including Fl, Py, BaA, Chr, BbF, BkF, BaP, IcdP, and BghiP” (Li et al. 2016). The positive correlation between COMPAH and total PAH concentrations means that combustion is the dominant source (He et al. 2014). The MDR values and the correlation results between COMPAH and total PAH obtained in this study are shown in Fig. 2.

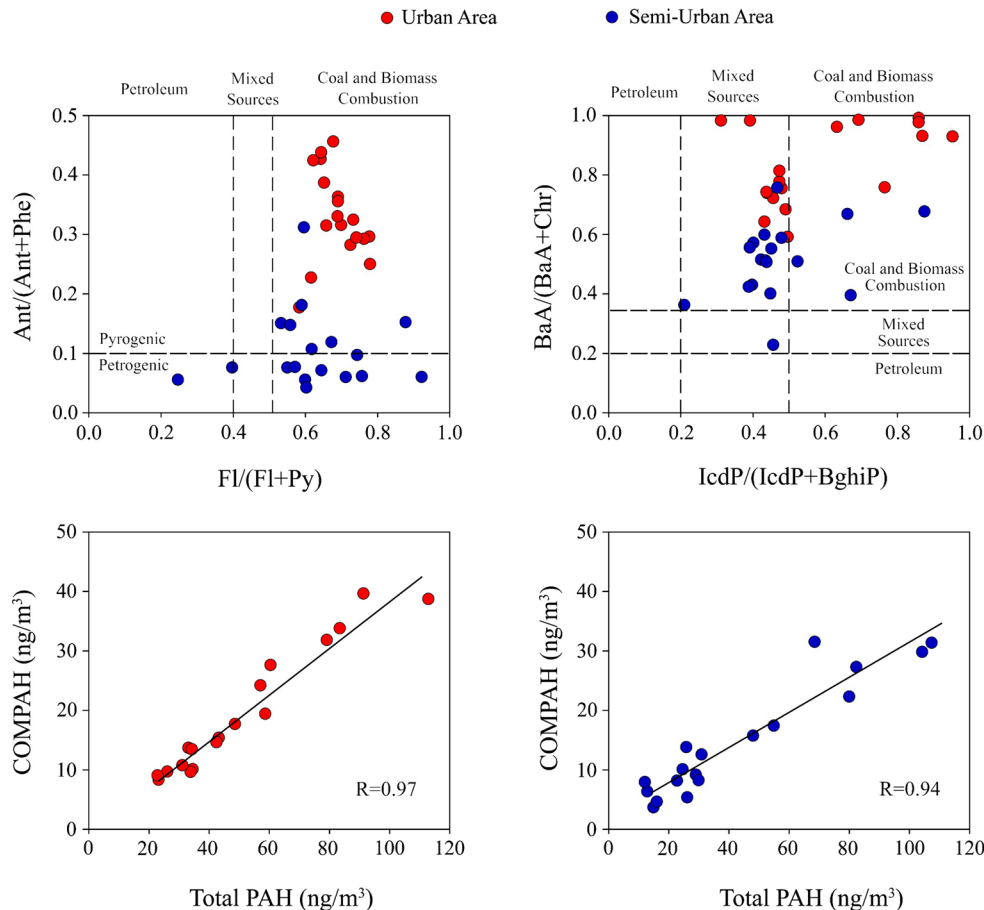
The Ant/(Ant + Phe) ratios in the urban area were calculated as higher than 0.1. This means that PAHs in this area were formed at high temperatures. In this case, it is consistent with the fact that this area represents a region where the industry is dense. In general, coal and biomass combustion emissions were dominant in both areas according to both

Fl/(Fl + Py) and BaA/(BaA + Chr) ratios. Similarly, IcdP/(IcdP + BghiP) ratios were often higher than 0.4 for urban and semi-urban areas. Also, high correlation levels between COMPAH and total PAH concentrations meant that combustion sources were dominant (He et al. 2014). The correlation between COMPAH and total PAH was strong, with a correlation coefficient of $R=0.97$ in the urban area and $R=0.94$ in the semi-urban area. According to both MDR and correlation results between COMPAH and total PAH, combustion sources dominated in both areas. Combustion sources in the urban area occurred at high temperatures ($> 800\text{ }^{\circ}\text{C}$) originating from industry ($\text{Ant}/(\text{Ant} + \text{Phe}) > 0.1$), while in the semi-urban area, they were usually caused by the combustion of petrogenic-derived fuels.

PCB concentrations and possible sources

The mean monthly concentrations of a total of 50 PCBs ($\sum_{50}\text{PCBs}$) in the atmosphere were found to be $522.5 \pm 196.9\text{ }\mu\text{g}/\text{m}^3$ (ranging from 271.4 to 826.6 $\mu\text{g}/\text{m}^3$) and $439.5 \pm 166.6\text{ }\mu\text{g}/\text{m}^3$ (ranging from 243.2 to 727.2 $\mu\text{g}/\text{m}^3$) for the urban and semi-urban areas, respectively (Fig. 3a). Several studies have recently reported the PCB concentrations in ambient air in Bursa (Günindi and

Fig. 2 The MDR values and the correlation results between COMPAH and total PAH



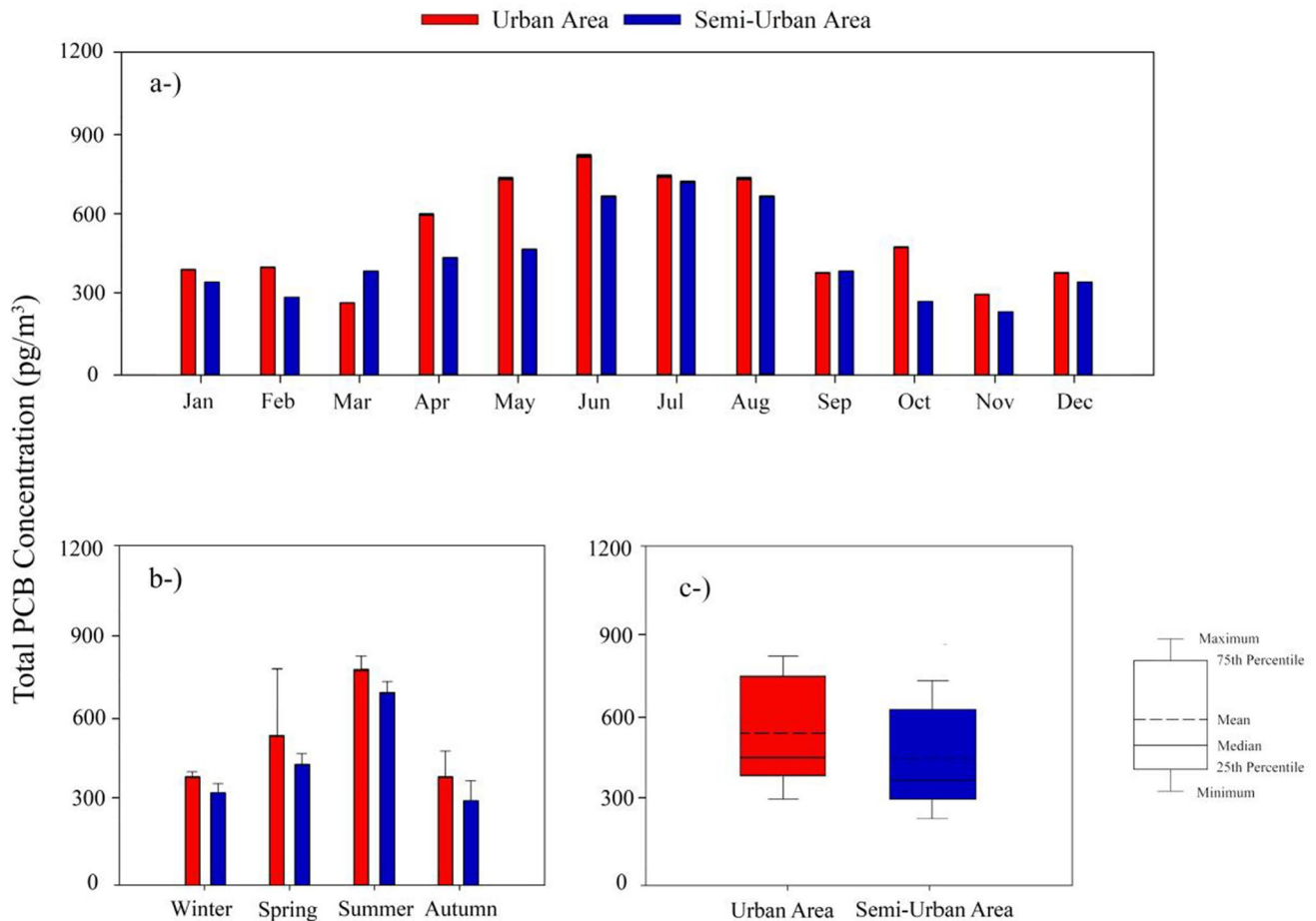


Fig. 3 Monthly (a), seasonal (b), and annual (c) PCB distributions for the sampling areas

Tasdemir 2010; Tasdemir et al. 2012; Birgül et al. 2017; Sari et al. 2020a). The concentrations obtained in this study are similar to those reported in the literature (Günindi and Tasdemir 2010; Tasdemir et al. 2012; Aydın et al. 2014; Birgül et al. 2017; Sari et al. 2020a).

The highest PCB concentrations were determined in June, while the lowest PCB concentrations were determined in March in the urban area. In the semi-urban area, the highest concentration of PCBs occurred in July, while the lowest concentrations were determined in November. Due to the evaporation of PCBs at high temperatures, atmospheric levels also increase in the summer months (Ozcan and Aydın 2009). Therefore, evaporation may have been effective at high PCB levels measured in the summer months in both sampling areas. Considering the seasonal distribution of PCBs, the highest concentrations were measured in summer, while the lowest concentration levels were measured in autumn and winter at both sampling areas (Fig. 3b). The atmospheric input of PCBs reaches maximum levels in the summer due to the evaporation of congeners from hot ambient conditions (Hogarh et al. 2013). Similar

results were obtained in most studies on PCBs in the literature (Ozcan and Aydın 2009; Hogarh et al. 2013; Aydın et al. 2014; Birgül et al. 2017). The annual distributions of PCBs measured in the urban and semi-urban areas are shown in Fig. 3c. Considering the annual distribution of PCBs, higher concentrations were observed in the urban area. Some of the factors that have been reported in the literature as having contributed to contemporary levels of PCBs in the environment include improper storage of PCB-containing waste, incineration of municipal or industrial wastes, evaporation from contaminated surfaces, accidental disposal of PCB-containing waste, and using old electronic equipment (Aydın et al. 2014). As the urban area was close to industry, annual PCBs were found to be higher than in the semi-urban area.

Homolog groups of PCBs in air samples generally provide information about transport, possible sources, and fate (Habibullah-Al-Mamun et al. 2019). For example, if high homolog group PCBs are dominant in one area, uses of technical PCB mixtures may prevail locally. On the other hand, if low homolog group PCBs are dominant in an

area, long-range transport and secondary emission source factors may be dominant (Birgöl et al. 2017). Moreover, the differences between homologous groups are due to physicochemical differences between PCB congeners with different chlorine numbers (Hu et al. 2019). In this study, seasonally calculated homolog group distributions for the urban and semi-urban areas are shown in Fig. 4.

Penta (ranging from 21.1 to 28.6%)- and tri (ranging from 18.3 to 22.2%)-chlorinated PCBs formed dominant homologs groups in the urban area. Similarly, penta (ranging from 25.2 to 29.1%)-chlorinated PCBs were predominant in all seasons in the semi-urban area. Also, tetra (ranging from 16.9% to 19.8%)-chlorinated PCBs were predominant in the spring, summer, and autumn seasons in the semi-urban area (Fig. 4). High-chlorinated PCBs (hepta-, octa-, and nona-CBs) were not dominant in both sampling areas. This situation could be explained by collecting the gas phase chemicals by diffusion with the PUF-disk sampler (Birgöl et al. 2017). A study conducted by Sari et al. (2020a) reported that penta (37%)- and tetra (22%)-chlorinated PCBs were the dominant homolog groups for Bursa in 2014. Another study conducted by Birgöl et al. (2017) reported that tetra (31.5–81.6%)-chlorinated PCBs were the dominant homolog group for Bursa in 2014. Cindoruk and Tasdemir (2007) also reported that tri (64.6%)- and tetra (22.9%)-chlorinated PCBs were the dominant homolog groups for Bursa in 2005.

Especially in the summer months, PCBs evaporated with the increase in temperature and this increased their concentration in ambient air (Hogarh et al. 2013). Also, due to the low saturated vapor pressure of low-chlorine PCBs, they can be transported further from a source compared to high-chlorine PCBs (Hu et al. 2019). In addition to the increase in temperature, the predominance of di-chlorinated PCBs in both sampling areas during the summer months (Fig. 4), as

well as the PCB concentrations in these months, was thought to be affected by the atmospheric transport.

OCP concentrations and possible sources

The mean monthly concentrations of a total of 10 OCPs ($\sum_{10}\text{OCPs}$) were found to be $242.5 \pm 104.6 \text{ pg/m}^3$ (ranging from 105.3 to 448.6 pg/m^3) and $275.9 \pm 130.9 \text{ pg/m}^3$ (ranging from 104.8 to 546.4 pg/m^3) for the urban and semi-urban areas, respectively. The concentrations obtained in this study were consistent with reported studies in the literature (Batterman et al. 2008; Yang et al. 2008; Syed et al. 2013; Zhang et al. 2013; Gevao et al. 2018). The highest concentrations were observed in June, while the lowest concentrations were observed in April in both sampling areas (Fig. 5a). Regarding the seasonal distribution of OCPs, the highest concentrations were observed in the summer season, while the lowest levels were observed in the spring season (Fig. 5b). High OCP concentrations seen in the summer season can be explained by increasing agricultural activities in this season (Qu et al. 2015). According to the annual distribution of OCP concentrations, higher levels were determined in the semi-urban area compared to the urban area (Fig. 5c). This situation is consistent with the fact that agricultural activities are more common in a semi-urban area.

Hexachlorocyclohexanes (HCHs) were among the most common pesticides produced for agricultural use worldwide between the 1950s and 1980s (Balázs et al. 2018). Technical HCHs are compounds containing about α -HCH (60–70%), β -HCH (5–12%), γ -HCH (10–15%), δ -isomer (6–10%) and very low amounts of other isomers (Garmouma and Poissant 2004; Sun et al. 2016). These isomers have different physical and chemical properties. For example, while α -HCH can be transported over long distances in the atmosphere, β -HCH is more resistant to environmental degradation and hydrolysis

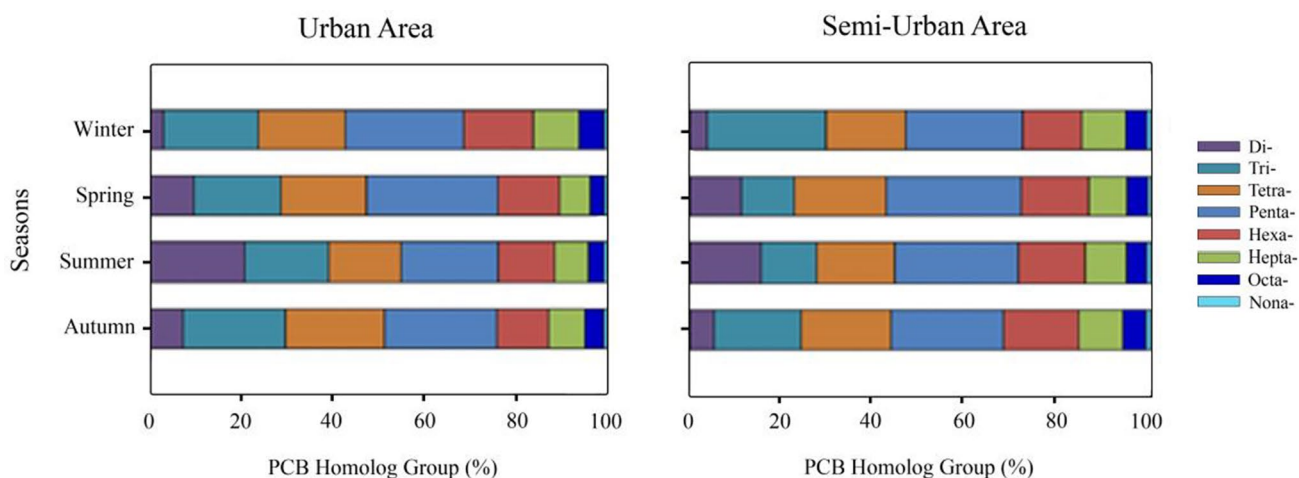


Fig. 4 Seasonal homologous group distributions for urban and semi-urban areas

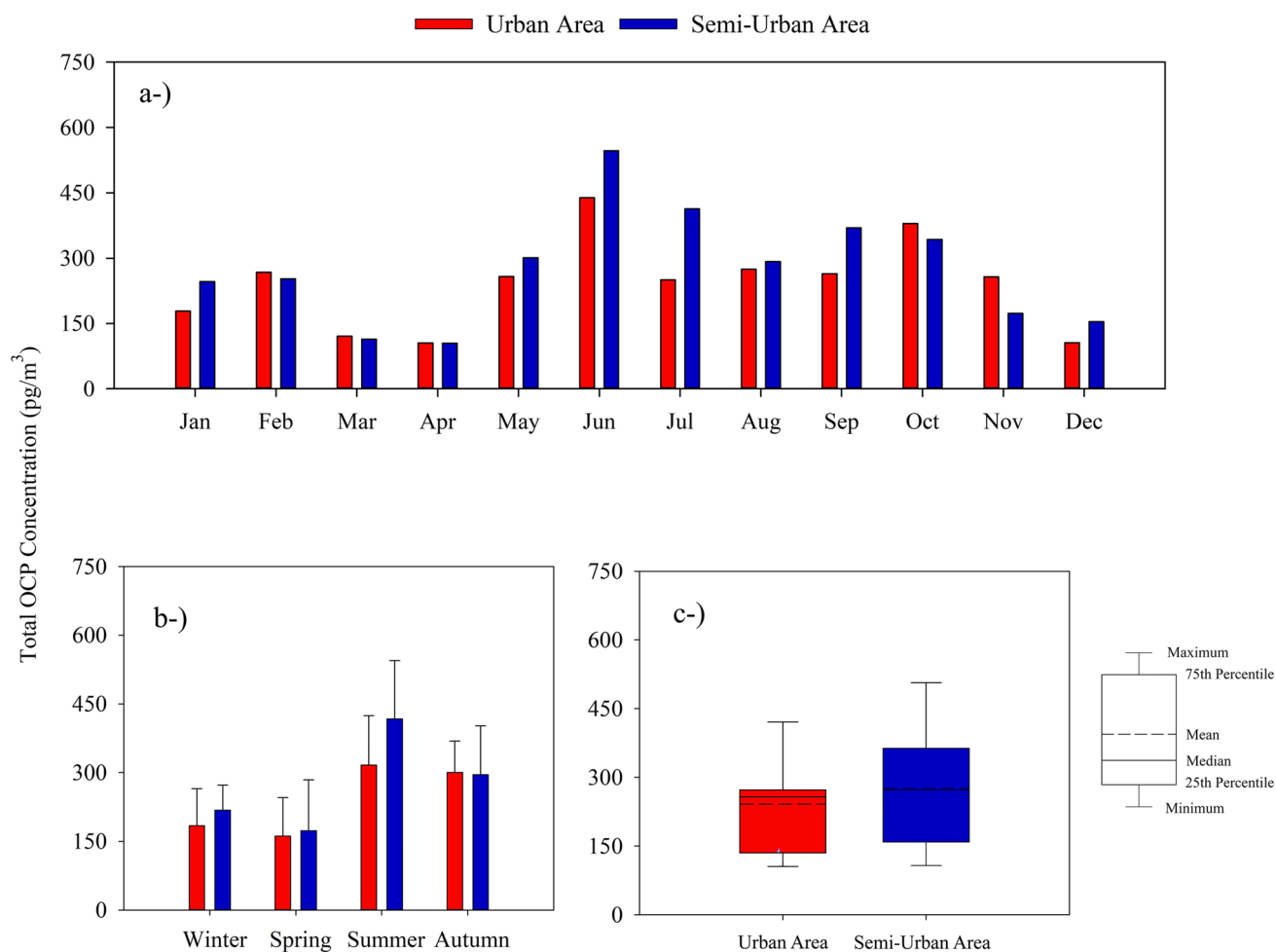


Fig. 5 Monthly (a), seasonal (b), and annual (c) OCP distributions for the sampling areas

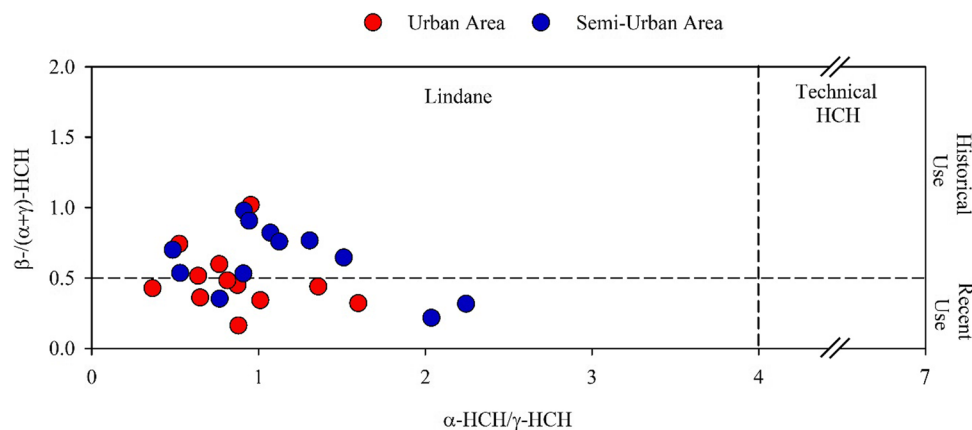
(Da et al. 2014). Among the HCH isomers, γ -HCHs, also known as lindane, form the most active group and are often used as insecticides (Yang et al. 2018). During the sampling period, total HCH (sum of α , β , γ , and δ) concentrations were found to be 141.5 ± 65.0 pg/m³ for the urban area and 189.8 ± 111.1 pg/m³ for the semi-urban area. Thus, β -HCH was the dominant HCH isomer in both sampling areas. In previous studies in Bursa, β -HCH was reported to be the dominant HCH isomer (Cindoruk 2011; Esen 2013), possibly due to atmospheric transport from contaminated areas and evaporation from vegetation (Cindoruk 2011).

The ratios of α -HCH/ γ -HCH and β -/($\alpha + \gamma$)-HCH are often used in source identification of HCHs (Kong et al. 2014). For example, if the α -HCH/ γ -HCH ratio is less than 4, lindane is dominant, whereas if the α -HCH/ γ -HCH ratio is between 4 and 7, technical HCHs are dominant (Da et al. 2014). Similarly, if the β -/($\alpha + \gamma$)-HCH ratio is higher than 0.5, it means that the pesticide has been used in the past, and if the ratio is less than 0.5, then the pesticide has been used recently

(Liu et al. 2012). In this study, α -HCH/ γ -HCH and β -/($\alpha + \gamma$)-HCH ratios calculated for urban and semi-urban areas are shown in Fig. 6.

The mean α -HCH/ γ -HCH ratios were found to be 0.87 for the urban area and 1.15 for the semi-urban area. According to the α -HCH/ γ -HCH ratios, lindane was predominant in both sampling areas. A study conducted by Cindoruk (2011) in Bursa stated that α -HCH/ γ -HCH ratios were generally higher than 1.0. In another study conducted in Bursa, α -HCH/ γ -HCH ratios were reported to vary between 0.27 and 0.55 (Esen 2013). A study conducted by Kurt-Karakus et al. (2018) across Turkey reported the average α -HCH/ γ -HCH ratios as 2.26 for urban areas. Although these compounds have long been banned, it is thought that high concentrations of γ -HCHs are reintroduced into the atmosphere through illicit use, pure lindane use, and evaporation from formerly contaminated areas (Cindoruk 2011). According to β -/($\alpha + \gamma$)-HCH ratios, most of the pesticides have been used recently. In a study by Wu et al. (2020), they stated that until 2019, lindane

Fig. 6 The ratio of $\beta/(\alpha + \gamma)$ -HCH versus α -HCH/ γ -HCH for the urban and semi-urban areas



was used to control termites in China, while in Japan, it was still used for wood preservatives.

Conclusions

In this study, concentration, spatial variations, and possible sources of POPs, namely, PAHs, PCBs, and OCPs, were determined using a passive air sampler in urban and semi-urban areas for 12 months. The average annual PAH and PCB concentrations were higher in the urban area, while OCP concentrations were higher in the semi-urban area. Industrial and traffic activities were contributory source factors in the urban area, while agricultural activities were generally implicated in the semi-urban area. Combustion was the primary source of PAHs in both sampling areas. Combustion sources in the urban area occurred at high temperatures (> 800 °C) originating from industry ($\text{Ant}/(\text{Ant} + \text{Phe}) > 0.1$), while in the semi-urban area, they were usually caused by the combustion of petrogenic-derived fuels. With local emission sources and increased long-range atmospheric transport, PAH concentrations were higher in winter seasons than in summer seasons. In addition, meteorological factors such as low mixing height, solar radiation, and photo-degradation in winter seasons caused higher PAH concentrations in these seasons. Low-chlorinated PCBs (tri-, tetra-, and penta-chlorinated PCBs) were dominant in both sampling areas. This situation was explained by the collecting of the gas phase chemicals by diffusion with the PUF-disk sampler. Due to the evaporation of PCBs at high temperatures, higher concentration was measured especially in summer seasons compared to winter seasons. Isomer distributions of HCHs were used to determine the sources of OCPs. According to the α -HCH/ γ -HCH ratios, lindane was determined to be relatively elevated in both sampling areas. Also, $\beta/(\alpha + \gamma)$ -HCH ratios were greater in urban areas than in semi-urban areas. According to this result, most of the pesticides were used recently in the semi-urban area. In

addition, higher OCP concentrations were measured in summer than in winter, due to increased agricultural activities and evaporation of OCPs in summer.

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Fatma Esen: methodology, data curation, writing (original draft), writing (review and editing), visualization, supervision.

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Availability of data and materials The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

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