

Monitoring of Long-Term Outdoor Concentrations of PAHs with Passive Air Samplers and Comparison with Meteorological Data

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Abstract The passive air sampler (PAS) is a common and useful tool for the sampling of semivolatile organic compounds in the ambient air. In a study performed in a semirural area of Bursa, sampling of polycyclic aromatic hydrocarbons (PAHs), was completed between February 4, 2013, and February 3, 2014, during 10-, 20-, 30-, 40- and 60 day periods for 1 year. To determine polycyclic aromatic compounds (PAH) concentrations, 3 PASs and 1 high-volume air sampler were run simultaneously, and sampling rates (R [m³/d]) were calculated seasonally and according to the ring numbers of the PAHs. R values varied from 0.66 to 22.41 m³/d. The relationship of these values with meteorological conditions was examined statistically, and the regressions performed were found to be consistent. This study identified 15 PAH compounds ($\sum_{15}\text{PAH}$). Concentration values of 10 day samples fluctuated from 6.4 to 1100 ng/m³. Seasonal averages of the concentrations of $\sum_{15}\text{PAHs}$ were detected to be 141 ± 72.5 ng/m³ for winter, 74 ± 59 ng/m³ for spring, 7 ± 0.6 ng/m³ for summer and 840 ± 170 ng/m³ for autumn. In this study, the toxicity equivalents of seasonal PAH concentrations obtained were determined to be 0.5, 0.3, 0.1, and 1.8 ng/m³ in winter, spring, summer and fall, respectively. The type posing a cancer risk has been identified as BaA.

Today, increasing air pollution, combined with intensive urbanization and industrialization, continues to affect both

human health and the environment. Among air pollutants, polycyclic aromatic hydrocarbons (PAHs) occur because they are not completely combusted through the burning of fossil fuels, wood and agricultural wastes (even during natural processes) (Cheng et al. 2013; Vardar et al. 2013). Temperature, vapor pressure, and the solubility of PAHs cause them to be in gas phase in the atmosphere and in particle phase on the surface of suspended solids (Wannaz et al. 2013; Baek et al. 1991). In addition, PAHs can be degraded by the effects of both solar radiation and temperature (depending on atmospheric conditions) (Chetwitayach et al. 2002), or they may be exposed to wet or dry deposition (Klanova et al. 2006; Brun et al. 2004). Some PAHs can be carcinogenic and genotoxic. They accumulate in the food chain and negatively affect the lives of organisms (Jaward et al. 2004; Wania et al. 2003).

Health-risk assessments associated with PAH uptake are often estimated on the basis of the benzo(a)pyrene (BaP) concentration in the air. Usually, in health-risk studies, BaP is used as a marker substance because it is the highest carcinogenic contributor in most studies (Halek et al. 2008; Karaca 2016). A toxicity-equivalency factor (TEF) for PAHs helps to characterize the carcinogenic properties of PAH mixtures exactly. TEFs are used to express the relative carcinogenic potentials of each PAH compared with BaP (Hu et al. 2007; Hanedar et al. 2014; Li et al. 2016).

Passive, especially sampler, techniques are particularly useful in the determination of air concentrations of PAHs and other semivolatile organic components. Of these sampler techniques, passive air samplers (PAS) are preferable today because they are inexpensive, easy to use, and do not require significant human intervention (Cupr et al. 2006; Fan et al. 2006). Moreover, PASs offer the advantage of being able to perform simultaneous

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measurements of pollutant concentrations (Zhang et al. 2008; Santiago and Cayetano 2007; Hazrati and Harrad 2007). A high-volume air sampler (HVAS), which requires energy and human intervention, is used to determine short-term concentration changes (Melymuk et al. 2011; Xie and Ebinghaus 2008; Gouin et al. 2005).

One of the passive sampler media used to determine concentrations of permanent and semivolatile organic compounds in the atmosphere is polyurethane foam disks (PFD) (Chaemfa et al. 2009; Harner et al. 2004). The operating principle of PASs is based on the absorption of semivolatile organic compounds in gas phase into polyurethane foam (PUF)-disk media in the sampler from the inner or outer atmosphere (Shoeib and Harner 2002). The relationship between the sampling rate and the concentration of semivolatile organic pollutants cannot be mathematically described (Klanova et al. 2006). Sampling rates of PASs are determined based on the loss of the depuration component (at a certain concentration) being added to the PUF (Santiago and Cayetano 2007; Shoeib and Harner 2002). Calibrating active and passive sampling data simultaneously makes it possible to determine sampling rates (Harner et al. 2013; Melymuk et al. 2011). This study was performed in a semirural area in Bursa, Turkey, between February 2013 and February 2014. The basic goals of this study were as follows:

- (i) the identification of sampling rates of PAHs according to seasons and ring numbers through the use of active and passive samplers simultaneously during 30 day periods;
- (ii) the calculation of PAH concentrations by passive sampling at different sampling times and periods during a 1 year period;
- (iii) the evaluation of the relationship between PAH concentrations and meteorological conditions; and
- (iv) the determination of the potential risk of human exposure to PAHs.

Materials and Methods

Sampling Program and Samplers

Outdoor air samples were collected from sampling points in the Bursa Uludağ University Campus (UUC) between the dates of February 4, 2013, and February 3, 2014, using HVASs and PASs. Samplers were placed at approximately 3 m height. The UUC sampling point that has been used by the researchers in recent years (Esen et al. 2010; Vardar et al. 2008) was approximately 20 km away from the

Bursa–Izmir highway. In this campus, which has >55,000 students, there were faculties and related administrative units, hospital, student hostels, and staff housing.

The ambient air samples were collected with an HVAS (GPS II Thermo Andersen). Average sampling volume was $322 \pm 141 \text{ m}^3$ and average sampling time was 53 ± 12 . A PAS consisted of a PUF disk placed in a shelter consisting of two hemispherical stainless steel containers, thus providing shelter from the elements but allowing air circulation. The diameter of the PUF disk placed in the sampler's diameter was 14 cm, thickness was 12 mm, surface area was 360.6 cm^2 , and density was 0.0168 g/cm^3 (Kaya et al. 2012; Hayward et al. 2010; Pozo et al. 2004). The dome structure minimizes the effects of air entering the sampler depending on the wind speed and the particle-phase inlet. Moreover, this dome prevented rainfall input and exposure to sunlight. Thus, degradation of PAHs and their exposure to desorption at increasing temperatures were prevented (Hazrati and Harrad 2007; Harner et al. 2004; Pozo et al. 2004). Throughout the sampling, meteorological parameters (temperature, humidity, wind speed, pressure) were collected at the sampling point's meteorological station (Vantage Pro 2 Model, Davis, USA). The average of meteorological data collected at the sampling point is listed in Table 1.

The sampling was performed for 1 year period in two ways. In the first one, active and passive samplings were performed simultaneously during four seasons for a 30 day period. In these periods, whereas samples were being collected in 2 day periods with a HVAS, parallel samples were collected with three pieces of PAS during 10, 20 and 30 days. In the second way, sampling continued with only three pieces of PAS.

Analysis of the Samples

Our analysis procedures are described in detail in previous studies (Tasdemir and Esen 2008; Cindoruk and Tasdemir 2007; Tasdemir and Esen 2007; Esen et al. 2006). In this section, some changes made in the analysis, which are emphasized and described briefly. All glassware used in both sampling and analysis were previously washed several times with hot tap water. Then the glassware was passed through pure water, methanol (MeOH), and dichloromethane (DCM) and allowed to dry for 1 night in an oven at $105 \text{ }^\circ\text{C}$. The glass-fiber filters (GFF) used in the HVAS were heated in a muffle furnace at $450 \text{ }^\circ\text{C}$ for 4 h to remove organic materials. Before the first use, PUFs were extracted for 24 h each in Soxhlet extraction with pure water, MeOH, DCM, and an acetone/hexane (ACE/HEX) (1:1) mixture. Then they were wrapped in aluminum foil, dried in an oven at $50 \text{ }^\circ\text{C}$, and stored in a freezer until use.

Table 1 Seasonal meteorological data

Seasons	Sampling dates	Temperature (°C)	Relative humidity (%)	Wind speed (km/h)	Pressure (bar)
Winter	04.02.2013–06.03.2013	8.03 ± 4.03	80.62 ± 13.70	0.68 ± 0.92	1020.07 ± 5.99
Spring	15.04.2013–04.05.2013	13.89 ± 5.93	76.21 ± 17.05	1.88 ± 4.04	806.71 ± 3.76
Summer	24.06.2013–18.07.2013	23.79 ± 4.30	69.01 ± 15.13	1.07 ± 1.15	1014.17 ± 1.05
Autumn	21.10.2013–22.11.2013	6.82 ± 5.76	78.64 ± 14.10	0.54 ± 0.86	1025.44 ± 7.59

Before extraction, PAH standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) were added to all samples to determine losses during the tests. PUFFs collected from the HVASs and PASs were extracted with the Soxhlet-extraction method. Samples were prepared at a ratio of 1:1 and subjected to extraction with the ACE/HEX mixture for 24 h. Samples taken from the extraction were subjected to volume reduction and conversion into HEX and then reduced to a volume of 2 mL under nitrogen gas. Sodium sulfate (Na₂SO₄ [Merck]) and aluminum oxide (Al₂O₃ [Merck]) to be used in the fraction process were activated by storing them in the muffle furnace at 450 °C for 4 h. Silicic acid ([H₄SiO₄] ≤ 100 mesh; Sigma Aldrich) was activated by storing it in the oven at 105 °C for 1 day. From the separation column, which was prepared with 3 g of silicic acid (3 % of water), 2 g of aluminum oxide (6 % of water), and 1 cm of sodium sulfate, 20 mL of DCM and PAH compounds were collected. By transforming the solvent into HEX with pure nitrogen, it was reduced to a volume of 1 mL and prepared for analysis by gas chromatography (GC)-mass spectrometry (MS).

The analysis of samples and witnesses was performed using MS. We used an Agilent 7890A GC, with an Agilent 5975C inert XL three-axis mass detector attached to it, located in the Air Pollution Laboratory of Uludağ University, Engineering Department. In GC–MS, a capillary column (HP5-MS, 30 m × 0.32 mm × 0.25 μm) was used. The injector, ion source, and quadrupole temperatures were 295, 300, and 180 °C. The oven temperature program was maintained to an initial temperature of 50 °C for 1 min, increased to 200 °C at a rate of 25 °C/min, increased from 200 to 300 °C at a rate of 8 °C/min, and maintained at 300 °C for 5.5 min. As the carrier gas, we used helium gas at 1.4 mL/min constant flow and with high purity. MS was performed in ion- monitoring mode, which was selected for high precision. PAH compounds were detected according to the target and qualifying ions and retention times of PAH compounds. Determination of PAH types was performed based on the retention time and target ion peaks. In the analysis of samples, 15 PAH compounds were targeted as follows: naphthalene (NAP), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FL), pyrene (PYR),

benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), BaP, indeno(1,2,3-c,d) pyrene (IcdP), dibenz(a,h)anthracene (DahA), and benzo(g,h,i)perylene (BghiP).

Quality Assurance/Quality Control

Samples with recovery efficiencies of 30–120 % were taken into account. Efficiency averages according to types of yield averages are as follows: For HVAS, they were naphthalene-d8 77 ± 25 %; acenaphthene-d10: 69 ± 26 %; phenanthrene-d10 72 ± 26 %; chrysene-d12 77 ± 21 %; and perylene-d12 74 ± 23 %; and for the PAS, they were naphthalene-d8 74 ± 26 %; acenaphthene-d10 72 ± 23 %; phenanthrene-d10 67 ± 23 %; chrysene-d12 74 ± 27 %; and perylene-d12 74 ± 19 %.

To detect potential contamination during sampling, witness samples were collected from PUF disks and cartridge samples. The limit of detection (LOD) was calculated by adding the SDs to the average of the PAH amounts (nanograms) measured in the witnesses for each PAH type after multiplying it by 3. LOD values determined for PAH types varied between 0.4 ng (BghiP) and 1051.6 ng (NAP) for the HVAS and between 0.8 ng (IcdP) to 641.5 ng (NAP) for the PAS. In cases where the PAH amount was smaller than the LOD value, the calculated value was not used in the calculations.

Results and Discussion

Determination of Sampling Rate

In passive air sampling, the increasing accumulation of pollutants in the PUF-disk media (PDM) is explained by accumulation resistance and mass transfer in the PDM-air cross-section. Mass accumulation in the PDM (M , ng) is calculated as follows (Santiago and Cayetano 2007; Pozo et al. 2004; Shoeib and Harner 2002):

$$M = k_A A_{PDM} C_A \Delta t = b \Delta t \quad (1)$$

Here, k_A is the mass-transfer coefficient in ambient air (m/day); A_{PDM} is the passive disk exposure area (m²); C_A is the air concentration (ng/m³); and Δt is the sampling time

(days). Against the sampling time, the slope obtained from the graph of passive sampling mass made during these periods is b , the mass sampling rate (ng/d). The value of b is equal to the multiplication product of $k_A A_{PDM} C_A$ (m^3/d) and $k_A A_{PDM}$ (m^3/d) and represents the passive sampling rate. Thus, the passive sampling rate R (m^3/d) is calculated as follows:

$$R = b/C_A \quad (2)$$

To observe seasonal changes, active and passive samplers were run simultaneously for 30 days in each of the four seasons. The mass accumulations of passive air samples for all seasons during the 10-, 20- and 30 time periods were calculated for those with 2- to 3-ring, 4-ring, and 5- to 6-ring PAH compounds as described in Eq. 2 (Fig. 1). The seasonal and annual b values were found to be statistically appropriate, and R^2 values varied between 0.687 and 0.983.

The convection of PAHs in the atmosphere varies depending on volatility, evaporation, dissolution, dry/wet deposition, and gas adsorption processes. Therefore, the behaviors of PAHs in the atmosphere are closely associated with molecular weights (Mastral et al. 2003; Pankow and Bidleman 1992). In this study, the sampling rates of PAHs (R) were calculated; they were evaluated by taking into account molecular weights and the number of rings. The $\Sigma_{15}PAH$ compound molecular weight is classified as low molecular weight (128–178 g/mol) with 2–3 rings, medium molecular weight (202–228 g/mol) with 4 rings, and high molecular weight with 5–6 rings (252–278 g/mol) (Tao et al. 2009; Melymuk et al. 2011).

Using the mean of 13 samples collected in all seasons by HVAS, the air concentration of that season (C_A) was calculated. The b values obtained were divided by this air concentration, and the annular sampling rates for each

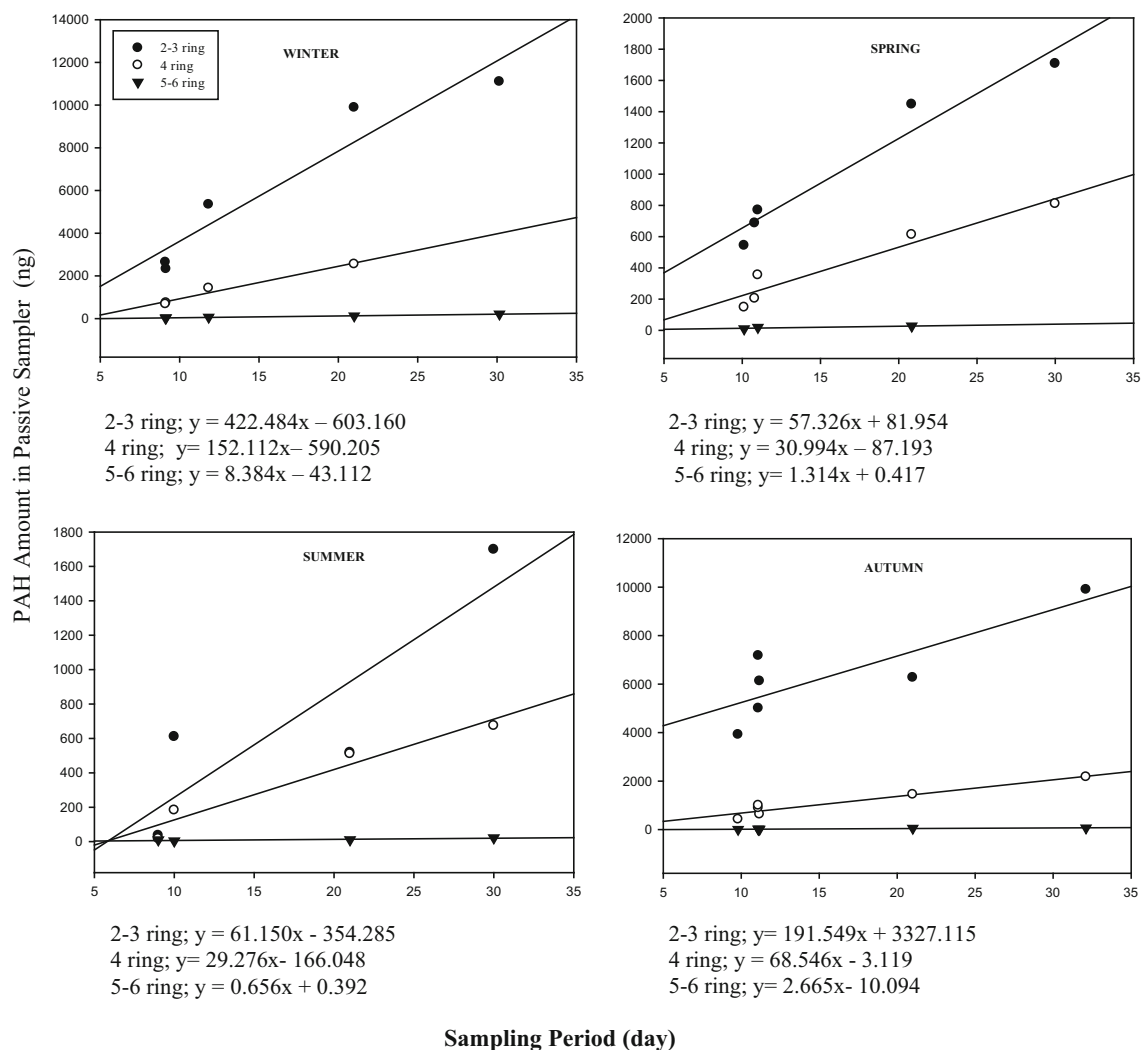


Fig. 1 PAH accumulation due to season and ring number

season (m^3/day) were calculated. These values varied from 0.66 to $22.41 \text{ m}^3/\text{d}$ (Table 2).

In their 2011 study, Melymuk et al. performed passive sampling of persistent organic pollutants (POPs) and calculated the R values. They performed active and passive sampling in parallel, and R values varied from 0.66 to $24 \text{ m}^3/\text{d}$. Using a similar sampling approach, a study performed by Bartkow et al. in (2004) showed that whereas the sampling rates of PAHs varied from 0.6 to $6.1 \text{ m}^3/\text{d}$, sampling rates detected using depuration compounds were measured at approximately $3 \text{ m}^3/\text{d}$ (Table 3).

The concentrations of high molecular-weight PAHs in the atmosphere are higher in winter and autumn months (Harner et al. 2013; Vardar et al. 2008; Tasdemir and Esen 2007; Odabasi et al. 2006). Although these types are attached to the filter in the HVAS, some amount of transition may occur to the PUF disk in passive sampling (Kennedy et al. 2010; Motelay-Massei et al. 2005). The correlation of R values obtained in a study performed in the external environment with meteorological conditions was analyzed statistically. The regression performed was found to be consistent for PAHs with 2–3 and 4 rings except for wind speed and pressure. In those with 5–6 rings, R^2 values were found to be lower, and thus there was no significant relationship. PAHs in the outside air may be associated depending not only on meteorological conditions but also on particle diameters and atmospheric physics (Eisler 2000). Sampling rates were analyzed with the meteorological conditions to determine the effects of meteorological conditions on the PFD. Two-, 3-, 4- and 5-ring PAHs were correlated with temperature, relative humidity, and wind speed by employing Pearson product moment correlation, yet a strong correlation was not found among them ($p > 0.05$).

Table 2 Passive sampling rates

Seasons	Ring classification	Sampling rate (m^3/d)
Winter	2–3	5.09
	4	3.60
	5–6	22.41
Spring	2–3	1.51
	4	2.35
	5–6	5.07
Summer	2–3	12.53
	4	7.19
	5–6	5.70
Autumn	2–3	0.66
	4	0.79
	5–6	3.79

PAH Concentration

In this study, we aimed to detect changes in seasonal concentrations of PAHs using passive samplers. Sampling periods in winter (December–February), spring (March–May), summer (June–August), and autumn (September–November) were classified according to the country's climatic conditions. Concentrations were calculated (ng/m^3) by dividing passive sampling mass (ng) by the passive sampling rate (m^3/d) of the season and the sampling period of the sample being analyzed.

Ten-Day Total PAH Concentrations and Evaluation with Meteorological Conditions

Passive samplers are preferred in the long-term sampling of semivolatile organic compounds because they are easy to operate (Klanova et al. 2006). In this study, which was performed from February 2013 to February 2014, samples were usually collected every 10 days. During this period, the concentration values of $\sum_{15}\text{PAH}$ varied from 6.4 to $1100 \text{ ng}/\text{m}^3$ (Fig. 2). The average concentrations for $\sum_{15}\text{PAH}$ were found to be 141 ± 73 , 74 ± 59 , 7 ± 0.6 , and $840 \pm 170 \text{ ng}/\text{m}^3$ in winter, spring, summer, and autumn, respectively.

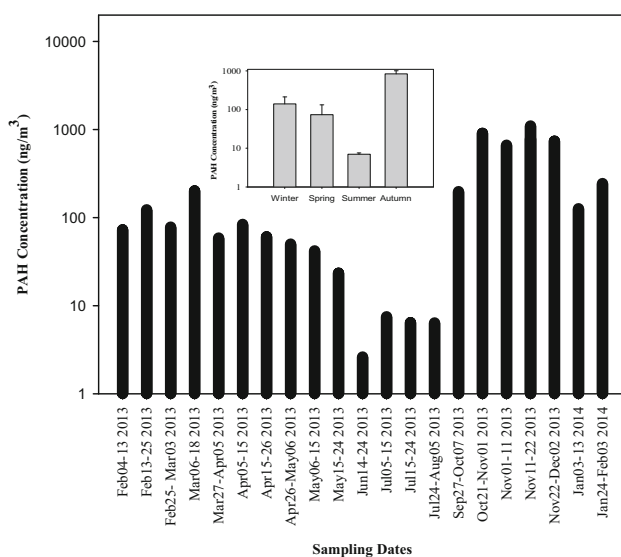
Seasonal concentration values in the HVAS for $\sum_{15}\text{PAH}$ were reported to be $343 \pm 239 \text{ ng}/\text{m}^3$ in winter, $16 \pm 12 \text{ ng}/\text{m}^3$ in spring, $9 \pm 5 \text{ ng}/\text{m}^3$ in summer, and $152 \pm 253 \text{ ng}/\text{m}^3$ in autumn from July 2004 to June 2005 (Esen 2006). Low temperatures were determined by comparison with seasonal averages in the late fall months. Therefore, differences may be expected because the sampling was performed 9 years later and used different samplers. In addition, the settlements around the sampling areas, as well as their populations, change over time, and there may be shifts between seasons.

In a study performed in Izmir (one of Turkey's industrial cities), PAS and the ambient air quality of PAHs in all four seasons from 2009 to 2010 were investigated. $\sum_{16}\text{PAH}$ concentrations in 40 different regions (including industrial, urban, and rural areas) varied from 1.6 to $838 \text{ ng}/\text{m}^3$. High PAH concentrations were found in areas containing steel plants, oil refineries, petrochemical complexes, and ship-dismantling activities. In addition, due to the combustion of coal and wood in urban areas during winter months, warmth-induced high PAH emissions were observed (Aydin et al. 2014; Kaya et al. 2012).

In a study performed by Wang et al. (2011) in 2007–2008, $\sum_{15}\text{PAH}$ concentration was examined in 40 rural and urban regions. Winter, spring, summer, and autumn PAH concentrations were detected at 521, 252, 145, and $377 \text{ ng}/\text{m}^3$, respectively. Santiago and Cayetano examined $\sum_{13}\text{PAH}$ types during 4 periods of 42 or 53 days

Table 3 Passive sampling rates for other studies (m³/d)

R (m ³ /d)	Types of pollutants	Sampling method	Calculate method of sampling rate	References
2.0–8.3	PCB	PUF disk	Depuration compound	Shoeib and Harner (2002)
3.0–4.0	PAH and PCN	PUF disk	Depuration compound	Jaward et al. (2004)
1.5–5.7	OCP and PCB and PBDE	PUF disk	Depuration compound	Gouin et al. (2005)
2.40–3.95	PAH	PUF disk	Depuration compound	Santiago and Cayetano (2007)
1.3–10	PAH	PUF disk	Depuration compound	Bohlin et al. (2010)
4.21–4.93	PAH	PUF disk	Depuration compound	Kaya et al. (2012)
2.2–7.8	PAH	PUF disk	Depuration compound	Cheng et al. (2013)
5.0 ± 3.6	PAC	PUF disk	Depuration compound	Harner et al. (2013)
0.6–6.1	PAH	SPMD	Concurrent sampling	Bartkow et al. (2004)
0.57–1.95	PCB and PBDE	PUF disk	Concurrent sampling	Hazrati and Harrad (2007)
7.0	PAH and PCB and OCP	PUF disk	Concurrent sampling	Klanova et al. (2008)
2.1–7.2	OCP and PCB	PUF disk	Concurrent sampling	Chaemfa et al. (2009)
0.66–24	PAH and PCB and PBDE	PUF disk	Concurrent sampling	Melymuk et al. (2011)
0.66–22.41	PAH	PUF disk	Concurrent sampling	This study

**Fig. 2** Total PAH concentrations of 10 day samples

each from May 24 to December 6, 2005. In this study, which used three rural and three urban areas, total PAH concentrations varied from 41 to 135 and 41 to 170 ng/m³, respective to grouping (Santiago and Cayetano 2007).

Total PAH concentrations we examined in the literature were assessed according to the four seasons and the dry/wet seasons. Of those studies examining PAH concentrations in ambient air, the values submitted by the researchers in İzmir are similar to those found in our study. Although other studies do not report equally similar values,

the relationships they show between temperature and PAH concentrations are similar.

Multiple linear regression was applied to determine the relationship between the PAH concentrations and meteorological parameters. A strong relationship was found between PAH concentrations and temperature ($p = 0.001$) and between PAH concentrations and relative humidity ($p = 0.038$). However, a weak relationship was determined between PAH concentrations and wind speeds ($p = 0.290$). Concentrations are much lower in summer than in the other three seasons. Because PAHs are subject to photochemical degradation and evaporation at high temperatures in summer, lower concentrations have been observed in the atmosphere (Wannaz et al. 2013; Wang et al. 2011). The sampling area is located in a semirural area; it is within the university campus, and the majority of the population consists of students from the surrounding neighborhood. The decline in the population of this area in the summer due to the university's summer break and the lack of heating use in the summer leads to total PAH concentrations being lower during this period than the other seasons. Emission sources of PAHs are known to be proportional to population density (Motelay-Massei et al. 2005; Garban et al. 2002). In the winter and fall seasons, total PAH concentrations are higher than in spring and summer because domestic heating-induced PAH emissions increase during the cold winter and autumn months (Vardar et al. 2008; Liu et al. 2007; Tasdemir and Esen 2007). When particle phase (high molecular-weight) PAHs cling to precipitation and gas phase (low molecular-weight) PAHs dissolve in precipitation, they are deposited to the earth's

surface (Birgül et al. 2011; Gaga et al. 2009). For this reason, although combustion-induced PAH emissions are high in winter and autumn, the increase in winter snowfall explains the lower total PAH concentrations in this period compared with autumn (Wannaz et al. 2013; Motelay-Massei et al. 2005).

Concentrations of PAHs Sampled During Different Periods and Evaluation by Species

In this study examining \sum_{15} PAHs, total PAH concentrations of 20-, 30-, 40-, and 60 day samples taken on different dates during the sampling time ranged from 0.3 to 544, 1.6 to 557, 6.5 to 179, and 1.6 to 211 ng/m³, respectively. Similar to other studies in the literature, PHE type was observed as dominant followed by FLN and FL types (Cheng et al. 2013; Choi et al. 2012; Motelay-Massei et al. 2005). Moreover, NAP and ACE species, which were not evaluated due to their low level of efficiency, are among the dominant types in many samples. The samples taken during these periods were evaluated according to their species in each season (Table 4). As shown in this study performed with PASSs, the dominant PAHs are low and medium molecular weight types (NAP ACE, FLN, PHE, ANT, FL and PY). High molecular-weight PAH types (BaA, CHR, BbF, BkF, BaP, IcdP, DahA ve BghiP) are less dominant (Choi et al. 2012; Kennedy et al. 2010; Santiago and Cayetano 2007; Motelay-Massei et al. 2005). These differences in concentration result from the increased use of heating in winter and autumn. PAHs in

particle phase mainly spread from local sources, whereas those in gas phase can be transported over long distances (Choi et al. 2012; Ravindra et al. 2008). This explains the concentrations of highway traffic-induced PAH types in the west such as FLN, FL, and PY types found in the neighborhoods around the semirural sampling area (Wannaz et al. 2013; Larsen and Baker 2003; Harrison et al. 1996).

The linearity of total PAH concentrations during different sampling periods was examined. During the spring-interim periods (March 6, 2013, to April 15, 2013 [period 1] and May 15, 2013, to June 24, 2013 [period 2]), samples from the 20- and 40 day periods were evaluated together. \sum_{15} PAH concentrations of the 20- and 40 day samples were 148.8 and 178.7 ng/m³ in the period 1 and 5.3 and 6.5 ng/m³ during period 2 period, respectively, and were linear. In the summer-interim period (July 27, 2013, to October 7, 2013) and winter-interim period (November 22, 2013, to February 3, 2014), 2 PSs and 2 60 day samples were collected. Although these samples overlap by 50 days, there were differences between the total PAH concentrations of the two samples. The reason for this difference during the summer-interim period is the absence of some species. The winter-interim period begins with autumn and ends with winter. As mentioned previously, average total PAH concentrations were 840.0 ± 170.0 ng/m³ in autumn and 141.4 ± 72.5 ng/m³ in winter. This seasonal concentration difference is observed in the 60 day samples including two seasons during the winter-interim period. Specifically, the 60 day sample concentration, which begins in autumn and ends in winter, was 211.0 ng/

Table 4 Seasonal PAH-compound concentrations

	Winter			Spring		Summer				Autumn		
	20 d	30 d	60 d	20 d	40 d	20 d	30 d	40 d	60 d	20 d	30 d	40 d
NAP	25.23	37.67	UDL	31.18	21.03	1.91	0.90	UDL	UDL	9.75	37.67	5.09
ACE	5.28	23.63	1.70	1.60	1.48	UDL	0.96	UDL	UDL	53.52	38.68	1.84
FLN	22.20	54.73	28.45	25.18	20.02	0.81	0.97	1.05	2.02	36.94	95.23	24.55
PHE	37.44	53.74	46.49	63.87	84.97	182	1.24	2.34	1.11	114.91	65.70	25.53
ANT	2.32	6.65	3.58	5.35	5.93	0.15	0.13	0.16	0.10	15.47	5.58	1.59
FL	21.43	37.12	41.64	12.97	27.00	155	1.69	1.70	0.90	40.28	37.12	29.07
PYR	9.33	15.79	22.45	6.57	12.72	1.04	1.10	0.88	0.43	21.25	20.84	12.59
BaA	1.53	2.10	2.59	0.74	1.94	0.17	0.22	0.12	0.13	2.85	2.10	1.82
CHR	1.49	1.54	1.73	0.70	2.04	0.17	0.11	0.13	0.08	2.20	1.45	1.08
BbF	0.11	0.12	0.15	0.09	0.36	0.07	0.02	0.02	0.05	0.25	0.10	0.06
BkF	0.06	0.06	0.06	0.08	0.49	0.02	0.03	0.01	0.02	0.08	0.04	0.02
BaP	0.03	0.03	0.06	0.03	0.17	0.02	0.01	0.01	UDL	0.07	0.03	0.03
IcdP	0.03	0.04	0.05	0.03	0.25	0.01	0.02	0.01	UDL	0.20	0.04	0.03
DahA	UDL	UDL	0.01	0.01	UDL	UDL	UDL	UDL	UDL	0.02	UDL	UDL
BghiP	0.03	0.04	0.05	0.06	0.25	0.03	0.03	0.02	0.02	0.10	0.03	0.03
4 ring	33.78	56.54	68.40	20.97	43.70	2.93	3.12	2.84	1.54	66.58	61.51	44.55

UDL Under detection limit

m^3 , whereas the 60 day sample concentration taken in winter was 87.0 ng/m^3 . In addition, in the 10 day (738.2 , 126.4 , and 243.8 ng/m^3), 30 (304.6 ng/m^3), and 40 day (103.3 ng/m^3) samples, a descending trend was observed after 30 days. In the study performed by Motelay Massei et al. (2005), the linear sampling period was observed to be approximately 120 days, and ACE, ACY, FLN, ANT and PHE types were observed after 50, 100, 125, and 100 days, respectively, in the study performed by Melymuk et al. (2011). For statistical data analysis purposes, PAH concentration variations depending on the sampling periods are regressed. A linear increase is observed, which indicates that when sampling periods increase, the mass collected also increases. This fits the theory well, and its r value is approximately 0.49.

In the literature, low PAH levels were reported in summer, whereas higher PAH levels were given in winter. For statistical data analysis purposes, we also did a regression between mass collected on PUF versus ambient air temperatures. We did it for each sampling period (i.e., 10-, 20-, 30-, 40-, and 60 day periods). We saw that when temperature increases, collected mass decreases. This is a reasonable finding because the literature indicated that PAH concentrations in the ambient air decrease with the increase in temperature. The R values vary between 0.74 and 0.99.

Human Exposure

The results of this study, which examined PASs and long-term atmospheric PAH concentrations, were compared with those from past studies performed in the same area. The comparison shows that PAH sources have increased with the growth in population and that the effects of PAHs on human health have become important. The United States Environmental Protection Agency (USEPA) has examined the effects of human exposure to PAHs and identified two PAH groups: carcinogenic and noncarcinogenic (USEPA 1984). The health-risk assessment of PAHs is performed using toxic-equivalent factor (TEF) values. The TEF values of Nisbet and LaGoy (1992), which are widely used in the literature, were used in this study. By multiplying these values by seasonal PAH concentrations, BaP equivalent concentrations were calculated according to the seasons (Cheng et al. 2013; Petry et al. 1996).

$$\sum \text{BaP}_{eq} = \sum (C_n * \text{TEF}_n) \quad (3)$$

$\sum \text{BaP}_{eq}$: Total toxicity equivalent concentration (ng / m^3)

C_n : Concentration of each of the PAH species in the sample (ng/m^3)

TEF_n : Toxicity-equivalency factors for each PAH species in the sample (dimensionless)

$\sum \text{BaP}_{eq}$ values were calculated to be 0.5, 0.3, 0.1, and 1.8 ng/m^3 for 15 species of PAH ($\sum_{15} \text{BaP}_{eq}$) in winter, spring, summer and autumn, respectively, and to be 0.3, 0.2, 0.1, and 0.6 ng/m^3 for seven species of PAH (BaA, CHR, BbF, BkF, BaP, IcdP ve DahA) ($\sum_7 \text{BaP}_{eq}$) that are carcinogenic (Fig. 3). $\sum_{15} \text{BaP}_{eq}$ and carcinogenic $\sum_7 \text{BaP}_{eq}$ values are proportional to each other in all seasons. Although the $\sum_{15} \text{BaP}_{eq}$ value and $\sum_7 \text{BaP}_{eq}$ are very close in summer, they were found to be relatively low compared with the other seasons. The reason for this may be the use of fossil fuels for residential heating in winter, spring, and autumn (Xia et al. 2013; Liu et al. 2008). In the literature, Petry et al. (1996) reported atmospheric PAH $\sum_{16} \text{BaP}_{eq}$ values to be 0.96 ng/m^3 , and Fang et al. (2004) reported them to be 12.6 ng/m^3 . In addition, in the study performed by Kennedy et al. (2010) in eight different regions for winter and summer, $\sum_{20} \text{BaP}_{eq}$ values ranged from 0.036 to 0.33 ng/m^3 and from 0.042 to 0.93 ng/m^3 . In this study, BaA had the highest toxicity-equivalence concentration for each season.

Conclusions

This study was performed at UUC where the researchers had already examined the atmospheric concentrations of POPs in the past. Given the scope of this study, PASs were preferred because of their low cost and ease of use for long-term air sampling of PAHs. Seasonal sampling rates were determined using the data obtained as a result of the

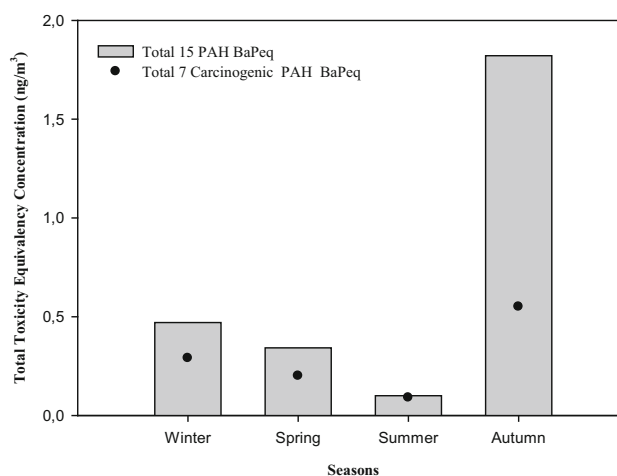


Fig. 3 Seasonal variation of $\sum_{15} \text{PAH BaP}_{eq}$ and carcinogenic $\sum_7 \text{PAH BaP}_{eq}$ concentrations

parallel sampling with HVAS and PASs. *R* values ranged from 0.66 to 22.41 m³/d depending on season and ring number. We found a statistically significant correlation between the sampling rates (similar to those in the literature) of PAH compounds with 2 to 3 and 4 rings and meteorological conditions (temperature, humidity) ($R^2 = 0.61\text{--}0.75$). In the monitoring studies of ambient air quality using PASs, it must be considered that differences in sampling rates can be seasonal and even spatial. Total PAH concentration values obtained at different periods varied from 6.4 to 1100 ng/m³. This concentration difference is associated with seasonal emission sources, short-term population changes in the region, and photosynthetic decays. Passive samplings are parallel with each other for the 10-, 20-, 30-, 40- and 60 day processes. When these data were observed, the PAH compounds with low and medium molecular weights were dominant. Moreover, the linearity of total PAH concentrations of the 30-, 40-, and 60 day samples were investigated in different sampling periods. Although the samples were linear in the spring- and summer-interim periods, no linearity was observed in the winter-interim period due to seasonal concentration differences, sources, and meteorological conditions. The affects of PAHs on human exposure were detected to be 0.5, 0.3, 0.1, and 1.8 ng/m³ for $\sum_{15}\text{BaP}_{eq}$ values in winter, spring, summer, and autumn, respectively. The obtained values are consistent with those reported in the literature.

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