



The Role of Sources and Atmospheric Conditions in the Seasonal Variability of Particulate Phase PAHs at the Urban Site in Central Poland

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ABSTRACT

The 24-h records of polycyclic aromatic hydrocarbons (PAHs) concentrations in the particulate phase were obtained for the urban site (52.42°N, 16.88°E) in Poznań, one of the largest cities in central Poland, between January and December 2014. The main goal of this study was to identify major emission sources of PAHs congeners and factors controlling their seasonal variability. The most abundant in the particulate matter PAH compound was pyrene (mean concentration of $2.29 \pm 4.68 \text{ ng m}^{-3}$, maximum of 22.51 ng m^{-3}), followed by benzo(a)pyrene, dibenz(ah)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, phenanthrene, benzo(ghi)perylene, chrysene, benz(a)anthracene and fluoranthene. The results showed a sharp decrease in PAHs concentrations during summer measurements (photodecomposition, high precipitation frequency), and high levels of the quantified PAHs during cold study period (increase anthropogenic emission, low air temperature). During the cold season in 2014, predominant PAHs congeners were: pyrene (26.0%) and 5-ring PAH compounds such as benzo(a)pyrene (19.4%) > dibenz(ah)anthracene (13.7%) ≥ benzo(k)fluoranthene (13.3%) > benzo(b)fluoranthene (9.8%), mostly associated with mixed sources (i.e., combustion, wood burning, industrial emission, traffic emission), whereas during warm study period we observed a large contribution (> 20%) of pyrene, dibenz(ah)anthracene and benzo(a)pyrene in particulate matter. The summertime measurements showed that local emission from the traffic (i.e., diesel and gasoline exhausts) was the second important source of PAHs in aerosol. The coal combustion for residential heating and industrial usage were most pronounced PAHs sources during the entire study period. The multivariate statistical technique (Principal Component Analysis) combined with some diagnostic ratios were applied to provide detailed characteristics of sources and processes related to the polycyclic aromatic hydrocarbons in different seasons. The results from this study are in good agreement with most of the studies focused on seasonal variability of PAHs in the atmosphere.

Keywords: Polycyclic aromatic hydrocarbons; Low-molecular weight congener; High-molecular weight congener; Particulate matter; Principal Component Analysis; Diagnostic ratio.

INTRODUCTION

Most of the polycyclic aromatic hydrocarbons (PAHs) are mutagenic, teratogenic or carcinogenic and can adversely affect human health through inhalation, dermal contact and consumption (Ravindra *et al.*, 2001). In the atmosphere, PAH isomers can exist in the gaseous and particulate phase. PAHs are harmful pollutants of various molecular weight, which are released to the atmosphere mainly via high-temperature processes, including energy production from fossil fuels and incomplete combustion of coal, oil, metal smelting, municipal waste incineration, vehicular emission,

petroleum refining, coke production and low-temperature processes (Lammel *et al.*, 2015). The polycyclic aromatic hydrocarbons with molecular weight between 128 Da and 276 Da, such as naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), phenanthrene (Phe), fluorene (Flu), anthracene (Ant), benz(a)anthracene (BaA), chrysene (Chr), pyrene (Pyr), fluoranthene (Flt), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(123-cd)pyrene (IPy), benzo(ghi)perylene (BghiP) and dibenz(ah)anthracene (DahA), have been identified by the US Environmental Protection Agency as priority pollutants. According to the European recommendations, the concentration of benzo(a)pyrene (BaP) in the inhalable air should not exceed 1 ng m^{-3} (total content in PM_{10} fraction averaged over a calendar year). However, the values of BaP registered in the urbanized areas of the European Union are often higher than the previously mentioned reference level (Ravindra *et al.*, 2006). Apart from the 16

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priority PAHs indicated by the US EPA, there are also many other hazardous, condensed and low-volatile byproducts of PAHs reaction with hydroxyl-/nitro-radicals, ozone or other reactive species (Ren *et al.*, 2017).

The phase distribution of polycyclic aromatic hydrocarbons in the atmosphere is controlled by several factors, among which the most important are: volatility and lifetime of PAH congeners, thermal conditions and aerosol concentration (Wu *et al.*, 2014). Due to intensive coal and wood combustion and enhanced gas-to-particle partitioning of PAHs at low temperature, the increase in concentrations of these organic pollutants in aerosol phase can be more frequently observed during wintertime (Bourotte *et al.*, 2005, Shi *et al.*, 2009). Hence, colder study periods (fall and winter) may be considered as much more important with regard to air quality in the urban environment. Results from the ground-based observations at different worldwide locations have revealed a significant spatiotemporal variability of PAHs (Lee *et al.*, 2008, Yang *et al.*, 2010; Lee *et al.*, 2011; Hu *et al.*, 2012; Li *et al.*, 2017a; Ren *et al.*, 2017; Wang *et al.*, 2017) and influences of urban/industrial emission sources (Li *et al.*, 2014; Jin *et al.*, 2018; Li *et al.*, 2018). In the recent study, Hellén *et al.* (2017) have found that the local small-scale wood combustion was the main source of benzo(a)pyrene in the air over the Helsinki metropolitan area. The results from their study showed that residential wood combustion had much higher contribution to BaP concentration than local vehicular traffic, which was particularly visible during non-working days when traditional combustion devices (i.e., fireplaces and sauna stoves) were used.

In the recent decade, there has been an increasing number of studies focused on various PAH sources and their effects on human health in the urban environment (Allen *et al.*, 2008; Wang *et al.*, 2011; Wiriya *et al.*, 2016; Zhang *et al.*, 2018). However, such studies have been scarce in central Europe (Shahpoury *et al.*, 2015). In northern Poland, the preliminary studies were performed by Staniszevska *et al.* (2013), but they quantitatively determined only BaP concentrations in the ambient air. Also, the impact of meteorological conditions and regional-scale transport on PAHs distribution have not been well recognized.

The present study involves the results from a one-year field campaign during which 11 particle-bound PAHs were measured, i.e., Phe, Ant, Flt, Pyr, Chr, BaA, BbF, BkF, BaP, DahA, BghiP. The campaign was carried out at the urban site in Poznań Agglomeration - a densely populated area in Poland (central Europe). This was the first attempt to characterize PAHs concentrations in total particulate matter, in relation to different seasons, meteorological conditions and small-scale processes in this region. The chemical variables were subjected to the Principal Component Analysis (PCA) in order to identify potential sources of individual PAHs during cold and warm study periods. In addition, several diagnostic ratios of isomeric PAHs were used to examine differences in PAHs distribution over the study domain. Finally, the comparison with other studies was presented in the discussion section to estimate spatial differences in the global ΣPAHs distribution in the atmosphere.

MATERIALS AND METHODS

Measurement Site

The aerosol sampling was conducted at the urban research station located in the Botanic Garden of Adam Mickiewicz University in Poznań city, central Poland (lat. 52°42'N, long. 16°88'E). Poznań has a population of about 557 000 people and area of 261.9 km². The sampling site is surrounded by various emission sources, i.e., international airport Poznań-Ławica (about 4 km west), large coal-fired Karolin power plant (10 km northeast), semi-detached houses, 2-story buildings and busy local roads. Additionally, the study domain is directly exposed to air pollution from local domestic sewage, sewage treatment plants, industrial units producing metals and paints, smelters, waste incinerators, different manufactories, and agricultural activities.

Sampling Procedure

Aerosol samples were collected onto pre-combusted (5 h at 500°C) quartz-fiber filters (QMA, Whatman), in the period between January and December 2014, using a low-volume air sampler operated at a flow rate of 30 L min⁻¹. The aerosol sampler was placed on a mast at the rooftop of the monitoring station (5 m above ground level). The duration of each monthly field measurement campaign was 7 days. The samples were collected over 24-h, starting from 6 a.m. local time. Samples were collected under conditions that minimize the potential sources of contaminations (artifacts). After sampling, filters were sealed in separate polyethylene zipped bags and stored at -20°C until the main analysis. A total number of collected samples was 86 plus additional filters for QC/QA measures. The precision and accuracy of the sampling procedure were routinely controlled after each field campaign, i.e., blank filters were loaded for 3 min to the sampling system and the air was not pumped. The field blanks were transported to the laboratory, stored and quantitatively determined for PAHs in the same manner as the environmental samples. Results from this procedure showed no contamination during the sampling, i.e., mean PAH values in the field blanks were below 10% of the environmental samples. All filters were weighted before and after sampling to calculate the total particulate matter (TPM) mass concentration.

Results from several independent filter-based measurements indicated that some artifacts can be expected during sampling of semi-volatile organic compounds (Paolini *et al.*, 2016, Jin *et al.*, 2018). For instance, Paolini *et al.* (2016) reported that adsorption of gas-phase organic species onto filter matrix (positive artifact) and/or loss of semi-volatile compounds (negative artifact) by summertime volatilization can be observed. Some other researchers have found that on average 20% lower concentration of particulate PAHs can be obtained while using conventional samplers as compared with system equipped with denuder devices to remove reactive gaseous species, i.e., ozone, OH, NO₂ (Balducci *et al.*, 2017). However, it was also stated that when a denuder device is placed up-stream of the sampling filter to reduce the positive artifact, more negative artifact will be induced due to fact that removal of

gaseous compounds disturbs the gas-particle equilibrium and enhances the volatilization of the collected semi-volatile materials (Zhang and McMurry, 1991). In this study, we used filter-based system to collect airborne samples (without PUF plug dedicated to gaseous phase), therefore the gas/particulate partitioning modeling of semi-volatile compounds was not examined.

PAHs Analysis and QC/QA Procedure

Considering some previously published PAHs studies, we decided to apply the ultrasonic extraction as a relevant method for PAHs isolation from particulate matter samples (Hu *et al.*, 2012; Staniszewska *et al.*, 2013; Alam *et al.*, 2014; Mancilla *et al.*, 2016). Briefly, the extraction was performed with 4 mL of mixed acetonitrile-to-dichloromethane solvent of HPLC grade (3:1 v/v). The time and temperature programmed were as follows 20 min and 20°C. The extracts were then subsequently transferred to the cleanup 0.2 µm filter column according to aftertreatment procedure of Pereira *et al.* (2001). The concentrations of PAHs in 24-h particulate matter samples were quantitatively determined by high-performance liquid chromatography, using a Shimadzu HPLC system (LC-10AD VP Liquid Chromatograph, HPLC pump, low-pressure gradient flow controller, degassing unit, thermostat controller) coupled with UV diode array detection (SPD-M10Avp detector, $\lambda = 254$ nm). The chromatographic separation of PAHs was obtained through the use of a Kinetex C₁₈ column (250 mm × 4.6 mm i.d., particle size of 5 µm, Phenomenex) and acetonitrile-water as a mobile phase. The injection volume was 10 µL. The mobile phase flow was 1 mL min⁻¹. The method detection limit (MDL) for the measured PAHs, expressed as three times the blanks, was on average 0.02 ng m⁻³. The average recovery for the PAHs mix analysis was 75–90% (analytical standard of 16 PAHs for HPLC, Sigma-Aldrich). It should be noted that 2-ring PAHs, i.e., Naph, and 3-ring molecules such as Acy, Flu and Ace are present mainly in gaseous phase due to relatively high volatility, and therefore they were not considered in this study. In several other studies can be found similar approach (e.g., Lee *et al.*, 2011).

Meteorology and Statistical Analysis

The standard meteorological parameters were registered by automatic weather station at the Botanic Garden in Poznań and are shown in Table 1. During the sampling period, the coldest month was January (mean temperature of -2.6°C), and the warmest - June (mean temperature of 21.6°C), with relatively low precipitation depth of 35.2 mm. The relative humidity ranged between 62% (June) and 95% (January). In Poznań, the mean annual precipitation height in 2014 was 567.2 mm, with February as the typical driest month (< 1% of total precipitation depth).

The chemical data were checked for normality, extreme/outliers and the statistical analysis was carried out using Statistica ver. 12 software. The p-values of below 0.05 were considered as statistically significant. The parametric and non-parametric tests were applied to determine differences in PAHs concentrations in the following sampling seasons: spring (Mar–Apr–May), summer (Jun–Jul–Aug), fall (Sep–Oct–Nov) and winter (Dec and Jan–Feb).

In this study, we applied Principal Component Analysis (PCA) to quantify the principal factors representing major sources/processes associated with individual PAHs in the air samples. The PCA analysis was performed separately for winter and summer databases. Such an approach allowed to identify the predominant factor(s), i.e., emission sources, and chemical reaction onto atmospheric particles, controlling the seasonal variability of particulate PAHs. The PCA method has been previously applied to PAHs-related studies (Hu *et al.*, 2012). Here, prior to the PCA analysis, data were standardized, and then main calculations with Varimax rotation and Kaiser criterion (eigenvalues higher than 1) were computed. These aspects will be discussed in details in the next section.

RESULTS AND DISCUSSION

Concentrations of PAHs in Aerosol

Table 2 summarizes basic chemical information on the analyzed PAHs, together with the ranges and average ± SD values obtained for these compounds in aerosol samples

Table 1. Meteorological conditions and total PM concentration ($\mu\text{g m}^{-3}$) during the sampling campaign at the urban site in Poznań, central Poland.

Sampling month	T (°C)	Precipitation amount (mm)	Relative humidity (%)	Air pressure (hPa)	TPM ($\mu\text{g m}^{-3}$)
Jan	-2.9	47.9	95	1004.7	36.7
Feb	6.7	5.6	86	996.4	32.1
Mar	8.7	46.6	71	1018.1	52.3
Apr	9.9	62.7	84	1007.3	15.9
May	10.3	89.3	84	1000.3	10.7
Jun	21.6	35.2	62	1008.1	17.0
Jul	21.4	90.5	65	1000.6	18.5
Aug	15.0	50.7	75	1001.7	24.2
Sep	12.6	47.6	84	1002.1	27.0
Oct	8.3	38.7	89	1007.4	38.9
Nov	8.0	14.5	91	998.6	50.4
Dec	0.6	37.92	87	1008.0	61.3
Average*/TOTAL	10.0*	567.2	81.0*	1004.5*	32.1*

Table 2. 24-h average and maximum concentrations for 11 PAHs in particulate phase (ng m^{-3}) measured in Poznań, between January and December 2014. The n.d. is not determined

PAHs congener	Abbreviations	Molecular weight	Aromatic rings	Average \pm SD	MIN–MAX
Phenanthrene	Phe	178	3 (particulate)	0.43 ± 0.92	n.d.–4.47
Antracene	Ant	178	3 (particulate)	0.17 ± 0.35	n.d.–1.73
Fluoranthene	Flt	202	4 (particulate)	0.02 ± 0.16	n.d.–1.13
Pyrene	Pyr	202	4 (particulate)	2.29 ± 4.68	0.05–22.51
Chrysene	Chr	228	4 (particulate)	0.30 ± 0.59	0.04–2.69
Benzo(a)anthracene	BaA	228	4 (particulate)	0.25 ± 0.49	0.01–2.94
Benzo(b)fluoranthene	BbF	252	5 (particulate)	0.91 ± 1.67	0.03–10.43
Benzo(k)fluoranthene	BkF	252	5 (particulate)	1.12 ± 3.92	0.04–28.66
Benzo(a)pyrene	BaP	252	5 (particulate)	1.77 ± 3.62	0.14–20.46
Dibenz(a,h)anthracene	DahA	278	5 (particulate)	1.40 ± 2.08	0.24–8.72
Benzo(g,h,i)perylene	BghiP	276	6 (particulate)	0.41 ± 0.77	0.05–3.86

collected at the urban site in Poznań, between January and December 2014. The PAHs in TPM samples spanned a wide range of concentrations, from n.d. (for 3-ring congeners: Phe, Ant) to 28.66 ng m^{-3} (BkF). Relatively low average concentrations were found for 3-ring (Ant: 0.17 ng m^{-3}) and 4-ring PAHs (Chr and BaA: 0.30 and 0.25 ng m^{-3} , respectively). The average concentrations of 5-ring PAH compounds decreased in the following order: BaP (1.77 ng m^{-3}) > DahA (1.40 ng m^{-3}) > BkF (1.12 ng m^{-3}) > BbF (0.91 ng m^{-3}). Also, the mean concentrations observed for 5-ring PAHs, i.e., BkF, BaP and DahA, exceeded levels of 1 ng m^{-3} . The average concentration of BghiP in urban aerosol samples was $0.41 \pm 0.77 \text{ ng m}^{-3}$.

During the entire study period, the highest daily maximum levels (24-h) for 3-ring PAHs in Poznań were quite different, e.g., Ant - 1.73 and Phe - 4.47 ng m^{-3} (Table 2). The peak concentration among the 4-ring PAH congeners was found for Pyr (22.51 ng m^{-3}). This value was almost 20 times higher compared with Flt (Table 2). The peak concentrations of Chr and BaA in 24-h air samples were comparable (2.69 and 2.94 ng m^{-3} , respectively). In the present study, the 24-h maximum concentration of BkF in TPM was almost 1.5 times higher than the peak concentration of BaP (Table 2).

Variability of PAHs in TPM in Different Seasons

During the sampling period of 2014, the mean annual total particulate matter (PM) concentration did not exceed $33 \mu\text{g m}^{-3}$. As shown in Table 1, the highest mean concentration of TPM was observed in December ($61.3 \mu\text{g m}^{-3}$), whereas the lowest value was found in May ($10.7 \mu\text{g m}^{-3}$). An average total PAHs mass concentration in samples collected at the urban site in Poznań during the one-year observations in 2014 was 9.07 ng m^{-3} , and on average corresponded to 0.02% of TMP mass. In general, TPM concentrations were found to reveal quite similar seasonal as PAHs congeners, with relatively higher levels in winter. This suggests that seasonal differences in aerosol composition, loading and origin could be one of the important factors to explain the variability of PAHs in the urban ambient air. As mentioned before, the main sources of PAHs in Poznań city include: industrial activities, vehicular traffic, re-suspension of road dust and contaminated soil, as well as the regional-scale/long-range transport of

pollutants. As pointed out by some other authors, the strong positive correlation between particulate matter and polycyclic aromatic hydrocarbons might suggest the same local anthropogenic sources or similar geographical origin of pollutants (Yang *et al.*, 2010). In this study, the wintertime correlation coefficient between total particulate matter and the measured Σ_{11} PAHs (the sum of 11 congeners) was relatively weak, suggesting more complex atmospheric processes and possibly other factors important for PAHs variability and distribution over this region.

It has been previously demonstrated that the concentration of particulate phase PAHs decreases through the photodegradation or heterogeneous chemical reactions with reactive gaseous pollutants, i.e., OH, NO_x , N_2O_5 , SO_2 , O_3 (Alam *et al.*, 2014). Considering different atmospheric conditions in both seasons, it can be seen that higher PAHs concentrations in TPM collected during winter were in part caused by low air temperature that enhanced the gas-particle partitioning, and by low intensity of solar radiation that mitigated the photochemical destruction of PAH compounds. As can be seen in Table 3, concentrations of almost all measured PAHs in wintertime samples exhibited significantly negative correlations with air temperature. In addition, wintertime concentrations of individual PAHs were positively correlated with SO_2 (0.776 – 0.998 , $p < 0.05$), suggesting that increased coal combustion was a significant source of organic pollutants during the cold study period. Compared to winter season, statistically significant negative correlations (> 0.500) were observed between some PAHs and relative humidity, indicating some influence of this parameter on chemical processes of PAHs (i.e., sorption) onto particles surface. Bandowe *et al.* (2014) have indicated direct role of ambient air temperature and pressure on the gas-particle partitioning of PAHs. They reported that low temperature and higher ambient pressure might lead to significant reduction in volatilization of semi-volatile organic compounds (from particle surfaces) and enhance their condensation onto particles, especially during winter measurements (Bandowe *et al.*, 2014).

The clear seasonal variability in particulate PAHs concentrations was found at the urban site in central Poland, with the maximum values in winter and the minimum in summer (Fig. 1(A)). During the cold study period, the highest

Table 3. Spearman correlation coefficients ($p < 0.05$) between individual PAHs and meteorological parameters in the air over Poznań during winter and summer study period in 2014.

	Pressure (hPa)		Temp (°C)		Rh (%)		Wind speed (m s ⁻¹)		Wind direction	
	winter	summer	winter	summer	winter	summer	winter	summer	winter	summer
Phe	0.489	0.296	-0.582	-0.182	-0.279	-0.551	-0.239	-0.040	-0.161	0.141
Ant	0.546	0.274	-0.633	-0.212	-0.230	-0.489	-0.283	0.026	-0.176	0.221
Flt	0.642	0.265	-0.675	-0.075	-0.162	-0.346	-0.337	-0.303	-0.172	-0.172
Pyr	0.513	0.244	-0.599	-0.195	-0.261	-0.437	-0.255	0.065	-0.164	0.225
Chr	0.437	0.299	-0.560	-0.180	-0.286	-0.535	-0.230	-0.028	-0.163	0.130
BaA	0.637	0.379	-0.659	-0.180	-0.175	-0.580	-0.303	-0.234	-0.147	-0.013
BbF	0.613	0.290	-0.640	-0.211	-0.200	-0.512	-0.285	0.031	-0.145	0.204
BkF	-0.304	0.340	0.092	-0.139	-0.304	-0.461	0.122	-0.279	-0.076	-0.080
BaP	0.557	0.318	-0.620	-0.193	-0.236	-0.532	-0.276	-0.024	-0.162	0.201
DahA	0.157	0.332	0.112	-0.272	-0.001	-0.419	0.318	-0.085	0.163	0.144
BghiP	0.515	0.337	-0.593	-0.245	-0.261	-0.543	-0.249	-0.020	-0.164	0.204

median concentration of Σ_{11} PAHs in urban aerosol (22.21 ng m⁻³, Fig. 1(A)) was observed in December 2014. Specifically, 4-ring PAHs together with 5-ring PAHs congeners showed on average 9 times higher median concentrations compared with 3-ring and 6-ring PAHs (Fig. 1(B)). These relationships reflect significant wintertime contribution to the PAHs budget, from local and regional sources mainly related to domestic heating (coal combustion, liquid fuel and wood burning in smaller heaters). For example, on 24th January 2014, when the air temperature dropped to -9°C, we observed high daily concentration of PM (60 µg m⁻³) that correlated with elevated levels of Pyr (21.62 ng m⁻³), BaP (16.92 ng m⁻³) and BkF (15.61 ng m⁻³). Additionally, as can be seen in Fig. 1(A), the peak concentrations of Σ_{11} PAHs (ca. 80 ng m⁻³) observed in January 2014, can be directly attributed to the specific synoptic conditions which were favorable to enhance the accumulation of local pollution plumes over the study domain (i.e., air temperature < 0°C, wind speed < 1 m s⁻¹, low mixing layer height, low precipitation depth and low photochemical activity). In a more recent study, Liu *et al.* (2017) quantified higher wintertime PAHs concentrations in PM_{2.5} form several sites in China as a result of calm winds, vertical temperature inversion, low temperature and atmospheric mixing height, and relatively low precipitation depth. In spring, the median concentration of Σ PAHs increased almost 4-times between March and April, but then, in May, it decreased rapidly to a minimum level of 0.2 ng m⁻³ (Fig. 1(A)). Moreover, summertime measurements showed the highest decline in PAH concentrations for 4-ring and 5-ring congeners, as compared to the spring observations (Fig. 1(B)). It should be noted that there were no statistically significant differences between spring and summer observed for concentrations of 3-ring and 6-ring PAHs (Fig. 1(B)), which can be explained by low contribution of organic compounds other than particulate PAH isomers related to combustion (i.e., wood burning in residential sector).

As shown in Fig. 1(A) and Table 1, the relatively low levels of PAHs in TPM observed during the summer months (June to August) were inversely related with the precipitation depth. For example, a large depth of a rainfall

that occurred in Poznań on July 2014 (90.5 mm, Table 1) was probably not a major factor affecting the TMP bound concentration levels of PAHs, however, it was significant for their wet deposition fluxes. Lower PAHs concentrations in summer were predominantly the effect of reduced anthropogenic emission of pollutants and higher solar radiation that enhanced photodecomposition of semi-volatile organic compounds such as BaA and BaP and their subsequent partitioning towards the gaseous phase (Fig. 1). It has been demonstrated that low concentrations of semivolatile compounds typically occur during warm study periods due to the fact that volatility of PAHs increases with temperature (Mancilla *et al.*, 2016). Mandalakis *et al.* (2002) examined total PAHs in the summertime aerosol and reported quite similar concentration ranges and relationships to those observed in the present study. Alam *et al.* (2014) have shown that respectively 51% and 33% of the total average concentration of BaA was related to the vapor phase during winter and summer season. They also highlighted that the rates of PAHs reactions in gaseous phase during the summer months were controlled by the abundance and concentration level of atmospheric oxidants such as OH, O₃ and NO₃ (Alam *et al.*, 2014). In this study, we did not measure PAHs concentrations in the vapor phase, so we cannot draw detailed conclusions in regard to the gaseous phase. However, as expected, significantly higher concentrations of particulate BaA and other 4-ring and 5-ring PAH compounds were obtained for the winter season (Fig. 1(B)). Moreover, the observed differences in PAHs concentrations for both study periods could be the result of a simple combination of (A) local, regional and long-range sources, (B) changes in atmospheric processes, and (C) different reactivity of PAH congeners. It is important to mention that unlike the winter emission, the summer one was not affected by such dominant source of PAHs as local coal combustion processes in residential sector. In some PAHs-related studies we can find a distinction between different coal combustion sources, e.g., domestic heating (at low temperature) and high-temperature industrial processes (i.e., coal-fired power plants, some processes in the industry sector, Liu *et al.*, 2017). As shown in Fig. 1(A), slightly higher values of PAHs were again observed in fall, but the

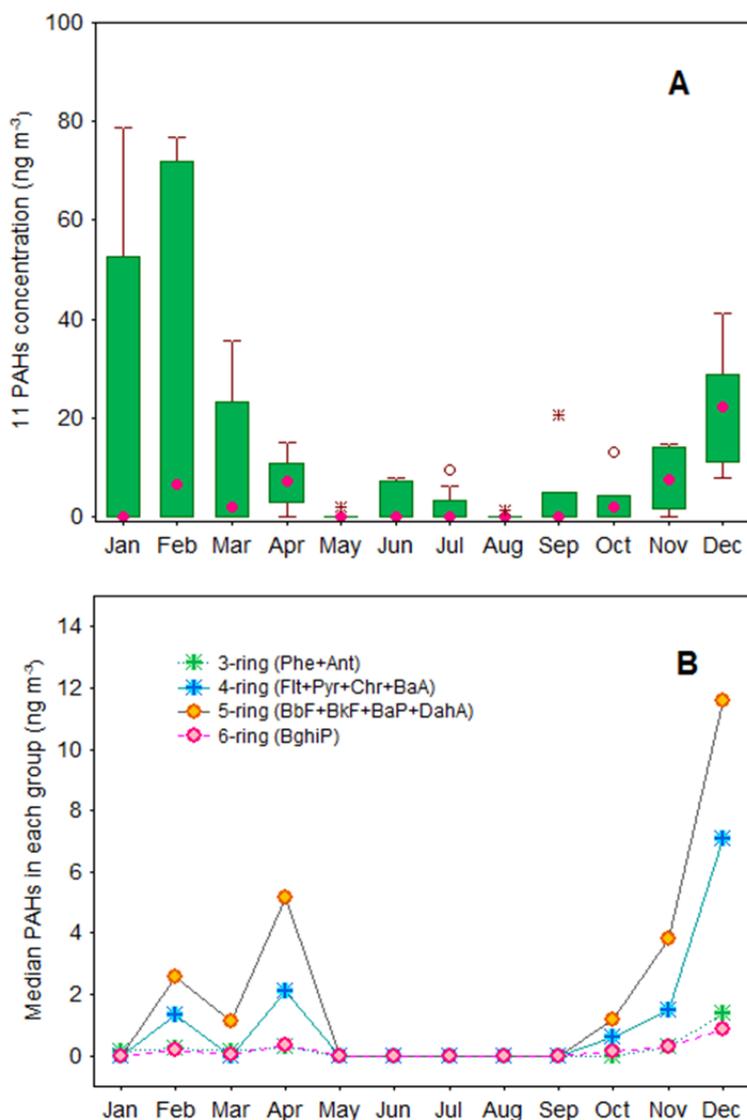


Fig. 1. The month-to-month variability in (A) median of the total TPM-bound PAHs concentration, and (B) median TPM-bound concentrations of PAHs grouped according to the number of aromatic rings. The upper and lower box bounds on Fig. 1(A) represent the upper/lower 25 % values, the upper and lower whiskers represent the maximum/minimum values and red dot in the middle of the boxes represents the median value. The Kruskal-Wallis test was used to find differences between seasons (spring: March to May, summer: June to August, autumn: September to November, winter: December to February). The differences were statistically significant at 5% confidence level

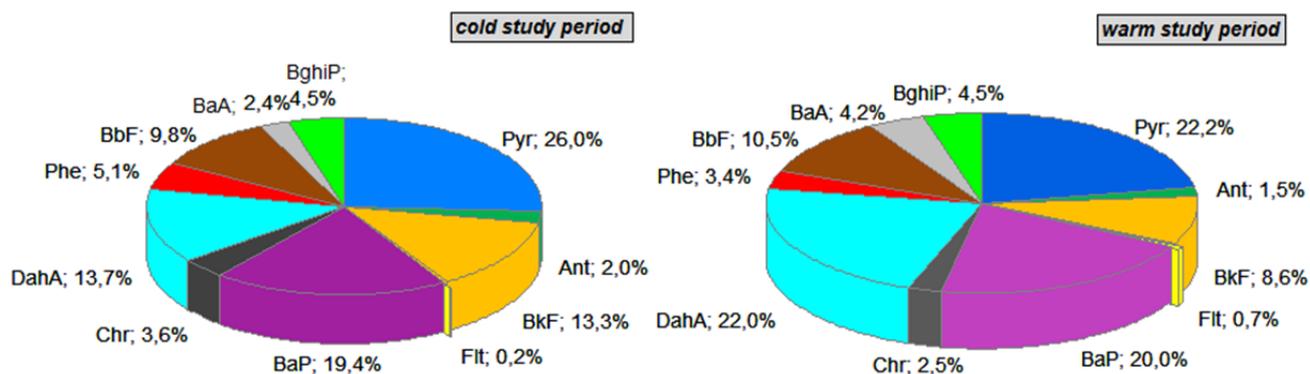


Fig. 2. Distribution of PAHs in TPM in relation to the study season (cold and warm) at the urban site in central Poland, 2014.

maximum concentration of Σ_{11} PAHs did not exceed 18 ng m^{-3} . The seasonal trend in PAHs concentrations, presented in this work, was consistent with other studies (Lee *et al.*, 2011).

Particulate Matter Bound PAHs Concentration – A Brief Review of Similar Studies

The mean concentration of the measured PAHs ($\Sigma\text{PAHs} = 11$) in Poznań was $9.07 \pm 16.56 \text{ ng m}^{-3}$, with the maximum of 78.93 ng m^{-3} . As can be seen in Table 4, the sum of PAHs concentrations in urban aerosol samples collected in this study were quite different from previous measurements in Flanders, Belgium (Ravindra *et al.*, 2006) and Alpine sites in France (Marchand *et al.*, 2004). Concentrations of Σ_{11} PAHs in air samples over Poznań were almost 2-times higher in comparison with values reported in Athens (Mandalakis *et al.*, 2002). More recent studies by Yang *et al.* (2010), Hu *et al.* (2012), Ren *et al.* (2017) and Saha *et al.* (2017) showed high PAHs concentrations in urban particulate matter over the polluted Asian megacities (Table 4). For example, the mean concentrations of Σ_{14} PAHs congeners in wintertime total suspended particles from Xi'an (China) were on average 6 times higher than those reported in our study, indicating strong influence of coal combustion, local basin-like topography and relatively low precipitation depth (Ren *et al.*, 2017). Measurements carried out at 3 different sites (traffic/urban/residential) in Changsha city, China, also showed high average Σ_{16} PAHs during summer (24.736 ng m^{-3}) and winter (19.337 ng m^{-3}), with dependence on local vehicle exhausts, cooking activities and construction dust (Yang *et al.*, 2010). In another study, the Σ_{19} PAHs concentration was 105.3 ng m^{-3} , indicating significant risk for public health (Li *et al.*, 2017b). Lai *et al.* (2017) also showed high PAHs concentration in samples collected at the industrial site in Kaohsiung, Taiwan (Table 4). Previous studies by Hu *et al.* (2012) have shown concentration ranges of 14 PAHs in total suspended particles to be similar to those from the present study. A detailed analysis of main reasons for the temporal similarities between concentration levels of PAHs in this study and other urban sites reflected local and regional impact of various urban emission sources and atmospheric processes during long-range transport.

Also, the concentrations of PAHs congeners measured in the air samples from Poznań revealed significantly lower levels than those registered in the urban aerosol collected in the Upper Silesian Industrial Region, southern Poland (Błaszczuk *et al.*, 2017). Furthermore, as compared with other European field studies presented in Table 4, high median concentration of PAHs was also found at the urban background site in Zabrze, southern Poland (Rogula-Kozłowska *et al.*, 2013), suggesting the strong effect of vehicular and industrial emission.

In a mid-scale city in central China, Wang *et al.* (2009) reported remarkably high levels of the total PAHs ($n = 17$) in urban aerosol samples, i.e., 536 ng m^{-3} and 161 ng m^{-3} in winter and spring, respectively, indicating the intensive domestic coal burning and petroleum combustion as major sources of PAHs. Also, they found an average Σ_{17} PAHs concentration of 0.65 ng m^{-3} at the marine site in Okinawa

Island, which was 80 times lower than values determined at Mt. Tai in summer period (Wang *et al.*, 2009). In this study, the sum of the quantified PAHs was significantly lower than the values observed in Seoul, South Korea (Lee *et al.*, 2011) or Lumbini, Nepal (Chen *et al.*, 20217). However, in contrast to the aforementioned study, relatively low mean values of Σ_{12} PAHs were observed at the regional background site in Jeju Island, South Korea (Lee *et al.*, 2008).

Factors Affecting PAHs Variability in Two Seasons

Fig. 2 shows the distribution of PAHs in TPM in relation to the following study seasons, i.e., cold (September to February) and warm (March to August). Briefly, no clear differences in PAHs distribution were observed among the 2 selected seasons in this study, presumably because of more complex effect of environmental parameters and local emission on PAHs levels. It should be pointed out that even if the distribution of PAHs in selected seasons showed no clear variation, the differences in proportions of individual PAHs were observed.

During the warm and cold study periods, the contribution of 3-ring (Ant, Phe) and 6-ring (BghiP) compounds to the total sum of PAHs was substantially low compared to the contribution of 5-ring (BbF, BkF, BaP, DahA) and 4-ring PAHs such as Pyr (Fig. 2). The dominant PAH congener in aerosol samples collected during the cold season was Pyr (26.0%), followed by BaP (19.4%), DahA (13.7%) and BkF (13.3%). The remaining compounds accounted for ca. 28% of the total PAHs. During the cold season, 5-ring PAHs represented up to 56% of the total sum of PAHs, and were followed by 4-ring PAHs, which contributed 32% to the ΣPAHs . During the warm study period, less than 5% of the quantified PAHs in TPM was represented by 3-ring compounds, while the contribution of 4-ring PAHs was 29.6%. In Poznań city, significantly lower percentage of Phe and Ant (low-MW) in the measured PAHs was found in warm compared to cold season, which could be explained by PAHs partitioning into the gaseous phase at higher temperatures. It is well known that the degree of gas-particle conversion of semivolatile organic compounds such as PAHs is temperature-dependent (Dachs *et al.*, 2002). Hence, high PM loading and relatively low air temperature are very important factors that favor the efficient transfer of more volatile PAH compounds to the particulate phase, whereas high air temperatures may be more preferential for gaseous PAHs formation.

The observed enhancement in the concentration of high molecular weight (high-MW) PAHs during wintertime measurements was in agreement with the previous study by Staniszewska *et al.* (2013), and confirmed highly influential role of low temperature in PAHs partitioning towards the particulate phase. As mentioned above, air temperature affects both the low- and high-MW PAHs congeners. Fig. 3 presents the relationships between concentrations of 8 individual PAH congeners and the ambient air temperature for January 2014. As can be seen, in the temperature range of $-10^\circ\text{C} < T < 0^\circ\text{C}$, the increase in concentrations of particulate phase Pyr, BaP and BkF was evident as the temperature decreases (Fig. 3). This result clearly indicates

Table 4. The average and ranges of PAHs concentration (ng m^{-3}) measured in total suspended particles in different studies.

Site/country	Σ PAHs	Type	Average	Range	References
Poznań/Poland	11	urban	9.07	0.13–78.93	This study
Dąbrowa Górnicza/Poland	15	urban/industrial	52.9	18.0–117.7	Błaszczak <i>et al.</i> (2017)
Zabrze/Poland	15	urban background	-	153.9	Rogula-Kozłowska <i>et al.</i> (2013)
Alpine sites/France	11	mountain	-	3.5–47.6 (winter)	Marchand <i>et al.</i> (2004)
Sites in Flanders/Belgium	17	urban	-	0.84–14.1	Ravindra <i>et al.</i> (2006)
Athens/Greece	13	urban	4.94	-	Mandalakis <i>et al.</i> (2002)
Xi'an/China	14	urban	57 (winter)	-	Ren <i>et al.</i> (2017)
Guiyang/China	14	urban	-	1.1–80.2	Hu <i>et al.</i> (2012)
Ho Chi Minh/Vietnam	10	urban	-	52.5–72.3	Hien <i>et al.</i> (2007)
Mt. Halla, Jeju Island/ South Korea	12	coastal	0.223	-	Lee <i>et al.</i> (2008)
Seoul/South Korea	12	regional background	25.0	-	Lee <i>et al.</i> (2011)
3 sites in Changsha/ China	16	traffic/urban/residential	24.736 (summer), 19.337 (fall)	-	Yang <i>et al.</i> (2010)
Baoji/central China	17	urban	536 (spring), 161 (winter)	-	Wang <i>et al.</i> (2009)
Mt. Tai/China		mountain	52 (summer), 9.2 (spring)	-	
Okinawa Island/Japan		Marine	0.65	-	
Jinan/China	19	urban	105.3	-	Li <i>et al.</i> (2017b)
Kaohsiung/Taiwan	16	industrial	158	-	Lai <i>et al.</i> (2017)
Beijing/China	12	downtown	63.49	12.56–228.86	Saha <i>et al.</i> (2017)
Kolkata/India	12	downtown	142.79	15.38–496.72	
Lumbini/Nepal	15	rural	91.6	-	Chen <i>et al.</i> (2017)
Nyalam/Nepal	15	semi-urban	5.57	-	

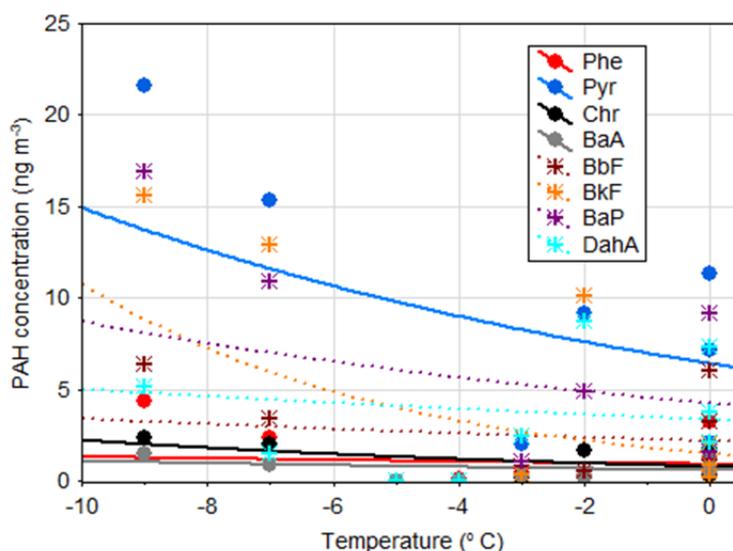


Fig. 3. Exponential correlations between PAH concentrations and air temperature obtained in January 2014 at the urban site in Poznań city. Phe: $r = -0.15$; $p = 0.51$, Pyr: $r = -0.20$; $p = 0.37$, Chr: $r = -0.25$; $p = 0.26$, BaA: $r = -0.08$; $p = 0.72$, BbF: $r = -0.07$; $p = 0.75$, BkF: $r = -0.22$; $p = 0.33$, BaP: $r = -0.16$; $p = 0.48$, DahA: $r = -0.20$; $p = 0.37$, BghiP: $r = -0.17$; $p = 0.46$. Flt and BghiP were not presented.

that the relative reactivity of various PAHs in the urban atmosphere was significantly variable. Similar dependencies have been previously recognized by several authors (Lee *et al.*, 2011, Ren *et al.*, 2017, Wang *et al.*, 2017). Alam *et al.* (2014) have found that the loss of 3- and 4-ring PAHs was well correlated with their reactivity towards hydroxyl radical in gas phase. They also observed greater depletion of low-MW compounds transported with aged air masses as compared with high-MW (Alam *et al.*, 2014). These findings might also help explain higher concentrations of low-MW PAHs (i.e., 2, 3-ring) during the cold season in the present study. Furthermore, it has been previously highlighted by some authors that meteorological factors such as lower mixing layer height and atmospheric turbulence might significantly influence the short-term variability of gaseous and particulate PAHs in the urban atmosphere (Dachs *et al.*, 2002).

As illustrated in Fig. 2, among the 5-ring PAHs in aerosol samples collected during the warm season of 2014, DahA exhibited the highest contribution (22.0%), followed by BaP (20.0%), BbF (10.5%) and BkF (8.6%). It is important to point out that contribution of BaP was relatively high in both seasons (Fig. 2). This suggests that mixed local anthropogenic sources, mostly related to local industrial processes, coal combustion, vehicle emission and chemical reactions were the most dominant factors influencing BaP levels in the atmosphere over the study site. Our previous study have shown that the coal combustion for residential heating in winter study period was relatively higher compared with summer season (Siudek, 2016). However, in this study, the effect of domestic heating was probably not the most important factor controlling PAHs levels during the cold study period. Some other emission sources and environmental parameters (i.e., meteorological factors) are expected to be responsible for seasonal variations of PAHs distribution.

The seasonal distribution trend of PAHs measured in this study and relatively higher input of less volatile 4-ring congeners to the total sum of PAHs in cold than in warm season, are consistent with the recent studies by Ren *et al.* (2017) and Wang *et al.* (2017). This can be explained by several factors, i.e., less intensive photochemical oxidation, lower mixing layer height, higher emission from industrial and residential combustion associated mainly with domestic heating. Also, higher contribution of 5-ring PAHs during the warm season in this study is consistent with results presented by Ren *et al.* (2017). Recent studies by Marr *et al.* (2006) showed that the 6-ring particle-bound PAH - BghiP is mainly associated with gasoline-fueled vehicle exhausts. In Poznań city, the contribution of BghiP congener to the total PAHs sum was similar (4.5%) during the cold and warm study periods, reflecting the constant impact of local traffic emission on the atmospheric burden of aerosols during the entire study campaign.

PCA for PAHs Variability vs. Winter and Summer Study Periods

A multivariate statistical *Principal Component Analysis* (PCA) have been applied in numerous studies to evaluate the impact of various types of anthropogenic emissions on PAHs concentrations and their distribution in different seasons (Yang *et al.*, 2010, Hu *et al.*, 2012). In this study, results from the PCA (Table 5) were coupled with the diagnostic ratios (Table 4) that have been widely adopted for tentative discrimination of PAHs sources in the urban atmosphere by different authors, e.g., Bourotte *et al.* (2005), Allen *et al.* (2008), Wang *et al.* (2009), Yang *et al.* (2010), Wang *et al.* (2017).

The total variance of the quantified PAHs ($n = 10$, Flt was excluded from this PCA analysis) accounted for 89% and 94% of the winter and summer data, respectively (Table 5).

Table 5. The Principal Component Analysis for 10 PAHs in urban aerosol samples collected in Poznań during the winter and summer of 2014. The Varimax normalized rotation and Kaiser criterion (eigenvalues > 1) were used to extract the principal components. All data were standardized. Data in bold font represent correlation of variables greater than 0.700.

PAHs	PC1-winter	PC2-winter	PC1-summer	PC2-summer
Phe	0.913	0.339	0.855	0.386
Ant	0.888	0.434	0.913	0.368
Pyr	0.928	0.363	0.989	0.084
Chr	0.917	0.278	0.939	0.271
BaA	0.437	0.867	0.543	0.810
BbF	0.596	0.777	0.946	0.224
BkF	0.911	−0.314	0.063	0.978
BaP	0.887	0.431	0.973	0.173
DahA	0.000	0.569	0.278	0.865
BghiP	0.931	0.353	0.911	0.375
% Variance	76	13	77	17
Eigenvalue	7.64	1.31	7.74	1.68
Suggested sources	Multiple sources	Traffic emission	Multiple sources	Traffic emission

Specifically, the PC1 explained comparable percentage of the total variance in both seasons (for winter and summer: 76% and 77%, respectively), whereas contribution of the PC2 to the overall variance of Σ_{10} PAHs ranged between 13% (winter) and 17% (summer).

The PC1-winter showed the highest load for 7 PAHs, i.e., BghiP (0.931), Pyr (0.928), Chr (0.917), Phe (0.913), BkF (0.911), and slightly lower for Ant and BaP (0.888 and 0.878, respectively). This principal component reflected mixed sources of PAHs in the atmosphere during the winter study period, which were associated mainly with the intensive coal and wood combustion for residential heating (Ant, BaA, Pyr), coal combustion in energy sector (Pyr, Chr), traffic emission (BkF, BaP), gasoline emission (BghiP), diesel emission (Pyr) and biomass burning (BaP). In this study, PC1-winter was considered to describe PAHs compounds that originate from multiple sources, with significant contribution from coal combustion (Chr, Pyr, BghiP). The PC2-winter was strongly correlated with two PAH congeners with high loadings, i.e. BaA and BbF (0.867 and 0.777), which can be emitted from vehicles, suggesting the predominance of traffic sources. The high loadings of these PAHs were in agreement with previous measurements by Hu *et al.* (2012), who identified both congeners as typical indicators of diesel vehicles and gasoline emission.

In summer, number of PAHs with high loadings (> 0.800) associated with PC1-summer (77% of the total variance) was similar to PC1-winter. The PC1-summer showed high loadings of Pyr, BaP, Chr, Ant, BghiP, BbF and Phe, whereas the PC2-summer was dominated by BaA, BkF and DahA, which correlations were more significant than for the PC2-winter. The high load of Pyr (0.989) and BaP (0.973) in PC1-summer indicated that the vehicular emission was an important source of PAHs during the warm study period in Poznań. The combination of PAHs in PC2-summer also revealed a significant impact of gasoline-fueled vehicle emission (DahA) plus diesel truck emission (BkF), with relatively high contribution of local industrial processes (BaA). Moreover, key findings from the study by Yang *et al.* (2010) provided the evidence for industrial

emission associated with high content of 4- and 5-ring PAHs (BaA, BaP), and strong influence of heavy-duty diesel vehicles on BbF concentration in TPM during summer and fall sampling periods. In addition, Wang *et al.* (2017) identified four distinct sources of PAHs in PM_{2.5} and PM₁₀, i.e., pollution from industry (BghiP, BbF, BkF, DahA, Chr, Ace), coal combustion (Flu, Phe, Ant, Flt, Pyr, BaA, Chr), traffic emission (BkF, BbF, BaA, Chr, BghiP) and biomass burning (Nap, Acy, Ace, Flu, BaA, DahA).

Several previous studies have reported the particulate-phase PAHs content in particulate matter (Fang *et al.*, 2004, Fon *et al.*, 2007, Machado *et al.*, 2009, Šišović *et al.*, 2012, Shi *et al.*, 2015). Šišović *et al.* (2012) found that the difference in average content of BaP in PM₁₀ was more pronounced in winter (34.72 ng mg^{−1}) than in summer (2.26 ng mg^{−1}). In the present study, we reported higher TPM-bound Σ_{11} PAHs during the wintertime measurements (mean 18.3 $\mu\text{g g}^{-1}$) compared to warm study period (mean 12.4 $\mu\text{g g}^{-1}$). The mean content of PAHs in aerosol in other studies were relatively higher than in Poznań, i.e., 831 $\mu\text{g g}^{-1}$ (Fang *et al.*, 2004), 219.2 $\mu\text{g g}^{-1}$ (Shi *et al.*, 2015) and 63.4 $\mu\text{g g}^{-1}$ (Fon *et al.*, 2007), while in studies of Mochado *et al.* (2009) the Σ_{11} PAHs content in total suspended particles was 17.8 $\mu\text{g g}^{-1}$.

It should be highlighted that the above results were also dependent on changes in the meteorological situation (local circulation, long-range atmospheric transport) and emission strength, resulting in large seasonal variation in PAHs distribution in aerosols at the urban site.

Diagnostic Ratios for PAHs in TPM – Comparison with Other Studies

The diagnostic ratios of PAHs (referred to as mass concentration ratios of selected congeners) have been previously used as indicators of various anthropogenic sources of organic pollutants, e.g., petrogenic, pyrogenic, vehicle emission (Ravindra *et al.*, 2006; Allen *et al.*, 2008; Wang *et al.*, 2010; Yang *et al.*, 2010; Wang *et al.*, 2011; Hu *et al.*, 2012; Tobiszewski and Namieśnik, 2012; Błaszczczyk *et al.*, 2017).

In the present study, the potential sources of PAHs in the urban atmosphere were examined based on 5 diagnostic ratios (DRs), and compared with the recently recommended values for different sources (Table 6).

The wide range of DRs for $BaA/(BaA + Chr)$ might indicate that the particle-bound PAHs are derived from different sources, including traffic emission and fossil fuel/coal/wood combustion. Yunker *et al.* (2002) have pointed out that the value of $BaA/(BaA + Chr)$ ratio above 0.35 can be a good marker of pyrolytic sources and coal/wood combustion. As can be seen in Table 6, $BaA/(BaA + Chr)$ ratio of 0.41–0.55 (Yang *et al.*, 2010) can be the evidence for large impact of gasoline emission and diesel engines on 4-ring PAH levels in submicron particles. The values of $BaA/(BaA + Chr)$ ratio reported by Wang *et al.* (2011) for urban surface dust of Guangzhou, China, are in good agreement with our measurements, suggesting that vehicular traffic emission was one of the significant sources of particulate PAHs in Poznań. Hu *et al.* (2012) obtained higher ratios of $BaA/(BaA + Chr)$ (0.52–0.73) than values in our study, which can suggest the high-temperature processes such as oil/coal burning, industrial emission and traffic emission as predominant sources of PAHs in Guiyang, China.

Relatively high values of the BbF/BkF ratio (1.88) and $Phe/(Phe + Ant)$ ratio (0.37) obtained in this study may additionally support the abovementioned findings (local diesel emission was one of the most influential factors for PAHs distribution during the entire sampling period). The value of the BbF/BkF ratio was consistent with those reported in the past studies by Ravindra *et al.* (2006) and Błaszczuk *et al.* (2017), whereas the $Phe/(Phe + Ant)$ ratio was lower than that obtained by Wang *et al.* (2009) and Hu *et al.* (2012). In addition, based on the BaA/Chr ratio of 0.65 and $BaP/BghiP$ ratio of 2.19 obtained in this study, we again identified vehicle exhausts as important source of PAHs.

Summary and Remarks

The concentrations of polycyclic aromatic hydrocarbons

(PAHs) in TPM were determined during the one-year measurement campaign carried out at the urban site in Poznań city (central Poland). We identified major sources of PAHs and examined their seasonal differences. The Σ PAHs concentrations were on average 14.35 ng m^{-3} in winter and 3.80 ng m^{-3} in summer. The lower summertime PAHs concentrations compared to wintertime measurements, were attributed to photodegradation of semi-volatile compounds, significant differences in anthropogenic emission, precipitation regime and atmospheric conditions. The most abundant PAH compounds were high-molecular-weight congeners such as Pyr, BaP, DahA, BkF, BbF and BghiP. However, no significant difference in PAHs distribution among cold and warm study period was observed. In particular, during the cold study period we observed high contribution of 4-ring Pyr (26%), followed by BaP (19.4%), DahA (13.7%) \geq BkF (13.3%), while in summer and spring the highest contribution was found for Pyr (22.2%) and DahA (22.0%), followed by BaP (20.0%) and BbF (10.5%). This was because of similar urban/industrial activities and the role of various meteorological parameters, and heterogeneous atmospheric processes both in gaseous and particulate phase. Results from the PCA and diagnostic ratios indicated that PAHs over Poznań were mostly of the mixed origin (petrogenic, pyrogenic), with significant contribution from vehicular emission. It was found that incomplete combustion processes and domestic soot emission from residential sector can significantly contribute to the PAHs loading in particulate matter, especially in the period from late October to early April (heating season), due to intensified combustion of coal and wood in older systems. We suggest that this specific period should be further considered due to the fact that residential heating is one of the main sources of air pollution and contributes to elevated PAHs concentrations, especially in the case of very cold winter.

This study indicates the need to continue comprehensive studies on PAHs distribution and transformation, not only in TPM but also in PM_{10} , $PM_{2.5}$ and PM_{10} , to estimate urban aerosol impact on climate, environment and human health.

Table 6. Diagnostic ratios for PAHs in particulate matter at the urban site in central Poland, between January and December 2014, and other locations.

Diagnostic ratio	Recommended Value	Suggested source	Reference
$BaA/(BaA + Chr)$	0.26	Traffic emission	<i>This study</i>
	0.20–0.35	Petroleum combustion	Yunker <i>et al.</i> (2002)
	0.17–0.40	Traffic emission	Wang <i>et al.</i> (2011)
	0.41–0.55	Traffic emission	Yang <i>et al.</i> (2010)
	0.52–0.73	Coal combustion	Hu <i>et al.</i> (2012)
BbF/BkF	1.88	Diesel	<i>This study</i>
	> 0.5	Diesel	Ravindra <i>et al.</i> (2006); Błaszczuk <i>et al.</i> (2017)
$Phe/(Phe + Ant)$	0.37	Traffic emission	<i>This study</i>
	0.70–0.98	Coal combustion	Wang <i>et al.</i> (2010); Hu <i>et al.</i> (2012)
BaA/Chr	0.65	Traffic emission	<i>This study</i>
	1.58	Coal combustion	Allen <i>et al.</i> (2008)
$BaP/BghiP$	2.19	Traffic emission	<i>This study</i>
	0.82	Petroleum refining	Allen <i>et al.</i> (2008)
	> 0.6	Traffic combustion	Liu <i>et al.</i> (2017)
	< 0.6	Non-traffic	Liu <i>et al.</i> (2017)

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REFERENCES

- Alam, M.S., Delgado-Saborit, J.M., Stark, C. and Harrison, R.M. (2014). Investigating PAH relative reactivity using congener profiles, quinone measurements and back trajectories. *Atmos. Chem. Phys.* 14: 2467–2477.
- Allen, A.G., de Rocha, G.O., Cardoso, A.A., Paterlini, W.C., Machado, C.M.D. and de Andrade, J.B. (2008). Atmospheric particulate polycyclic aromatic hydrocarbons from road transport in southeast Brazil. *Transport Res Part D* 13: 483–490.
- Balducci, C., Cecinato, A., Paolini, V., Guerriero, E., Perilli, M., Romagnoli, P., Tortorella, C., Nacci, R.M., Giove, A. and Febo, A. (2017). Volatilization and oxidative artifacts of PM bound PAHs at low volume sampling (2): Evaluation and comparison of mitigation strategies effects. *Chemosphere* 189: 330–339.
- Bandowe, B.A.M., Musel, H., Huang, R.J., Ho, K., Cao, J., Hoffmann, T. and Wilcke, W. (2014). PM_{2.5}-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and cancer risk assessment. *Sci. Total Environ.* 473–474: 77–87.
- Błaszczak, E., Rogula-Kozłowska, W., Klejnowski, K., Fulara, I. and Mielżyńska-Śvach, D. (2017). Polycyclic aromatic hydrocarbons bound to outdoor and indoor airborne particles (PM_{2.5}) and their mutagenicity and carcinogenicity in Sielsian kindergartens, Poland. *Air Qual. Atmos. Health* 10: 389–400.
- Bourotte, C., Forti, M.C., Taniguchi, S., Bicego, M.C. and Lotufo, P.A. (2005). A winter time study of PAHs in fine and coarse aerosols in São Paulo city, Brazil. *Atmos. Environ.* 39: 3799–3811.
- Chen, P., Li, C., Kang, S., Rupakheti, M., Panday, A.K., Yan, F., Li, Q., Zhang, Q., Guo, J., Ji, Z., Rupakheti, D. and Luo, W. (2016). Characteristics of particulate-phase polycyclic aromatic hydrocarbons (PAHs) in the atmosphere over the central Himalayas. *Aerosol Air Qual. Res.* 17: 2942–2954.
- Dachs, J., Glenn, T.R., Gigliotti, C.L., Brunciak, P., Totten, L.A., Nelson, E.D., Franz, T.P. and Eisenreich, S.J. (2002). Process driving the short-term variability of polycyclic aromatic hydrocarbons in the Baltimore and northern Chesapeake Bay atmosphere, USA. *Atmos. Environ.* 36: 2281–2295.
- Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.P.C., Yang, I.L. and Chen, M.H. (2004). Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. *Sci. Total Environ.* 327: 135–146.
- Fon, T.Y.W., Noriatsu, O. and Hiroshi, S. (2007). Polycyclic aromatic hydrocarbons (PAHs) in the aerosol of Hihashi Hiroshima, Japan: Pollution scenario and source identification. *Water Air Soil Pollut.* 182: 235–243.
- Hellén, H., Kangas, L., Kousa, A., Vestenius, M., Teinilä, K., Karppinen, A., Kukkonen, J. and Niemi, J. (2017). Evaluation of the impact of wood combustion on benzo[*a*]pyrene (BaP) concentrations; ambient measurements and dispersion modeling in Helsinki, Finland. *Atmos. Chem. Phys.* 17: 3475–3487.
- Hien, T.T., Thanh, L.T., Kameda, T., Takenaka, N. and Bandow, H. (2007). Distribution characteristic of polycyclic aromatic hydrocarbons with particle size in urban aerosol at the roadside in Ho Chi Minh city, Vietnam. *Atmos. Environ.* 41: 1575–1586.
- Hu, J., Liu, C.Q., Zhang, G.P. and Zhang, Y.L. (2012). Seasonal variation and source apportionment of PAHs in TSP in the atmosphere of Guiyang, Southwest China. *Atmos. Res.* 118: 271–279.
- Jin, T., Han, M., Han, K., Fu, X. and Xu, X. (2018). Health risk of ambient PM₁₀-bound PAHs at bus stops in spring and autumn in Tianjin, China. *Aerosol Air Qual. Res.*, in Press.
- Lai, Y.C., Tsai, C.H., Chen, Y.L. and Chang-Chien, G.P. (2017). Distribution and sources of atmospheric polycyclic aromatic hydrocarbons at an industrial region in Kaohsiung, Taiwan. *Aerosol Air Qual. Res.* 17: 776–787.
- Lammel, G., Dvorská, A., Klánová, J., Kohoutek, J., Kukučka, P., Prokeš, R. and Sehill, A.M. (2015). Long-range atmospheric transport of polycyclic aromatic hydrocarbons is worldwide problem — Results from measurements at remote sites and modelling. *Acta Chim. Slov.* 62: 729–735.
- Lee, J.Y., Kim, Y.P. and Kang, C.H. (2011). Characteristics of the ambient particulate PAHs at Seoul, a mega city of Northeast Asia in comparison with the characteristic of the background site. *Atmos. Res.* 99: 50–56.
- Lee, J.Y., Kim, Y.P., Kaneyasu, N., Kumata, H. and Kang, C.H. (2008). Particulate PAHs levels at Mt. Halla site in Jeju Island, Korea: Regional background levels in northeast Asia. *Atmos. Res.* 90: 91–98.
- Li, H., Liu, G. and Cao, Y. (2014). Content and distribution of trace elements and polycyclic aromatic hydrocarbons in fly ash from a coal-fired CHP plant. *Aerosol Air Qual. Res.* 14: 1179–1188.
- Li, Q., Kang, S., Wang, N., Li, Y., Li, X., Dong, Z. and Chen, P. (2017a). Composition and sources of polycyclic aromatic hydrocarbons in cryoconites of the Tibetan Plateau glaciers. *Sci. Total Environ.* 574: 991–999.
- Li, Y., Yang, L., Chen, X., Gao, Y., Jiang, P., Zhang, J., Yu, H. and Wang, W. (2017b). PM_{2.5}-bound PAHs in

- indoor and outdoor of hotels in urban and suburban of Jinan, China: Concentrations, sources, and health risk impacts. *Aerosol Air Qual. Res.* 17: 2463–2473.
- Li, Z., Fan, L., Wang, L., Ma, H., Hu, Y., Jiang, Y., An, C., Liu, A., Han, J. and Jin, H. (2018). PAH profiles of emitted ashes from indoor biomass burning across the Beijing-Tianjin-Hebei region and implications on source identification. *Aerosol Air Qual. Res.* 18: 749–761.
- Liu, D., Lin, T., Syed, J.H., Cheng, Z., Xu, Y., Li, K., Zhang, G. and Li, J. (2017). Concentration, source identification and exposure risk assessment of PM_{2.5}-bound parent PAHs and nitro-PAHs in atmosphere from typical Chinese cities. *Sci. Rep.* 7: 10398.
- Machado, M.C.S., Loyola, J., Quiterio, S.L., da Rocha, G.O., de Andrade, J.B. and Arbilla, G. (2009). Particulate-associated polycyclic aromatic hydrocarbons and their dry deposition fluxes from a bus-station in the Rio de Janeiro Metropolitan Area, Brazil. *J. Braz. Chem. Soc.* 20: 1565–1573.
- Mancilla, Y., Mendoza, A., Fraser, M.P. and Herckes, P. (2016). Organic composition and source apportionment of fine aerosol at Monterrey, Mexico, based on organic markers. *Atmos. Chem. Phys.* 16: 953–970.
- Mandalakis, M., Tsapakis, M., Tsoga, A. and Stephanou, E.G. (2002). Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). *Atmos. Environ.* 36: 4023–4035.
- Marchand, N., Besombes, J.L., Chevron, N., Masclat, P., Aymoz, G. and Jaffrezou, J.L. (2004). Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: Sources and temporal patterns. *Atmos. Chem. Phys.* 4: 1167–1181.
- Marr, L.C., Dzepina, K., Jimenez, J.L., Reisen, F., Bethel, H.L., Arey, J., Gaffney, J.S., Marley, N.A., Molina, L.T. and Molina, M.J. (2006). Sources and transformations of particle-bound polycyclic aromatic hydrocarbons in Mexico city. *Atmos. Chem. Phys.* 6: 1733–1745.
- Paolini, V., Guerriero, E., Bacaloni, A., Rotatori, M., Benedetti, P. and Mosca, S. (2016). Simultaneous sampling of vapor and particle-phase carcinogenic polycyclic aromatic hydrocarbons on functionalized glass fiber filters. *Aerosol Air Qual. Res.* 16: 175–183.
- Pereira, P.A., Andrade, J.B. and Miguel, A.H. (2001). Determination of 16 priority polycyclic aromatic hydrocarbons in particulate matter by HRGC-MS after extraction by sonication. *Anal. Sci.* 17: 1229–1231.
- Ravindra, K., Mittal, A.K. and Van Grieken, R. (2001). Health risk assessment of urban suspended particulate matter with special reference to polycyclic aromatic hydrocarbons: A review. *Rev. Environ. Health* 16: 169–189.
- Ravindra, K., Bencs, L., Wauters, E., de Hoog, J., Roekens, E., Bleux, N., Berghmans, P. and Van Grieken, R. (2006). Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. *Atmos. Environ.* 40: 771–785.
- Ren, Y., Zhou, B., Tao, J., Zhang, Z., Wu, C., Wang, J., Li, J., Zhang, L., Han, Y., Liu, L., Cao, C. and Wang, G. (2017). Composition and size distribution of airborne particulate PAHs and oxygenated PAHs in two Chinese megacities. *Atmos. Res.* 183: 322–330.
- Rogula-Kozłowska, W., Kozielska, B., Klejnowski, K. and Szopa, S. (2013). Hazardous compounds in urban PM in the central part of Upper Silesia (Poland) in winter. *Archiv. Environ. Prot.* 39: 53–65.
- Saha, M., Maharana, D., Kurumisawa, R., Takada, H., Yeo, B.G., Rodrigues, A.C., Bhattacharya, B., Kumata, H., Okuda, T., He, K., Ma, Y., Nakajima, F., Zakaria, M.P., Giang, D.H. and Viet, P.H. (2017). Seasonal trends of atmospheric PAHs in five Asian megacities and source detection using suitable biomarkers. *Aerosol Air Qual. Res.* 17: 2247–2262.
- Shahpoury, P., Lammel, G., Holubová Šmejkalová, A., Klánová, J., Příbylová, P. and Váňa, M. (2015). Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides in background air in central Europe – investigating parameters affecting wet scavenging of polycyclic aromatic hydrocarbons. *Atmos. Chem. Phys.* 15: 1795–1805.
- Shi, G.L., Feng, Y.C., Wu, J.H., Wang, Y.Q., Xue, Y.H. and Zhu, T. (2009). Source identification of polycyclic aromatic hydrocarbons in urban particulate matter of Tangshan, China. *Aerosol Air Qual. Res.* 9: 309–315.
- Shi, G.L., Zhou, X.Y., Jiang, S.Y., Tian, Y.Z., Liu, G.R., Feng, Y.C., Chen, G. and Liang, Y.K.X. (2015). Further insights into composition, source and toxicity of PAHs in size-resolved particulate matter in a megacity in China. *Environ. Chem.* 34: 480–487.
- Šišović, A., Pehnec, G., Jakovljević, I., Šilović Hujčić, M., Vadić, V. and Bešlić, I. (2012). Polycyclic aromatic hydrocarbons at different crossroads in Zagreb, Croatia. *Bull. Environ. Contam. Toxicol.* 88: 438–442.
- Siudek, P. (2016). Distribution and variability of total mercury in snow cover – A case study from a semi-urban site in Poznań, Poland. *Environ. Sci. Pollut. Res. Int.* 23: 24316–24326.
- Staniszewska, M., Graca, B., Beldowska, M. and Saniewska, D. (2013). Factors controlling benzo(a)pyrene concentration in aerosols in the urbanized coastal zone. A case study: Gdynia, Poland (Southern Baltic Sea). *Environ. Sci. Pollut. Res.* 20: 4154–4163.
- Tobiszewski, M. and Namieśnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162: 110–119.
- Wang, G., Kawamura, K., Xie, M., Hu, S., Gao, S., Cao, J., An, Z. and Wang, Z. (2009). Size-distribution of *n*-alkanes, PAHs and hopanes and their sources in the urban, mountain, and marine atmospheres over East Asia. *Atmos. Chem. Phys.* 9: 8869–8882.
- Wang, Q., Jaing, N., Yin, S., Li, X., Yu, F., Guo, Y. and Zhang, R. (2017). Carbonaceous species in PM_{2.5} and PM₁₀ in urban area of Zhengzhou in China: Seasonal variations and source apportionment. *Atmos. Res.* 191: 1–11.
- Wang, W., Huang, M.J., Kang, Y., Wang, H.S., Leung, A.O.W., Cheung, K.C. and Wong, M.H. (2011). Polycyclic

- aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: Status, sources and human health risk assessment. *Sci. Total Environ.* 409: 4519–4527.
- Wiriyaa, W., Chantara, S., Sillapapiromsuk, S. and Lin, N.H. (2016). Emission profiles of PM₁₀-bound polycyclic aromatic hydrocarbons from biomass burning determined in chamber for assessment of air pollutants from open Burning. *Aerosol Air Qual. Res.* 16: 2716–2727.
- Wu, S.P., Yang, B.Y., Wang, X.H., Yuan, C.S. and Hong, H.S. (2014). Polycyclic aromatic hydrocarbons in the atmosphere of two subtropical cities in southeast China: Seasonal variation and gas/particle partitioning. *Aerosol Air Qual. Res.* 14: 1232–1246.
- Yang, F., Zhai, Y.B., Chen, L., Li, C.T., Zeng, G.M., He, Y.D., Fu, Z.M. and Peng, W.F. (2010). The seasonal changes and spatial trends of particulate-associated polycyclic aromatic hydrocarbons in the summer and autumn in Changsha city. *Atmos. Res.* 96: 122–130.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D. and Sylvestre, S. (2002). PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAHs source and composition. *Org. Geochem.* 33: 489–515.
- Zhang, N., Cao, J., Li, L., Ho, S.S.H., Wang, Q., Zhu, C. and Wang, L. (2018). Characteristics and source identification of polycyclic aromatic hydrocarbons and *n*-alkanes in PM_{2.5} in Xiamen. *Aerosol Air Qual. Res.*, in Press.
- Zhang, X.Q. and McMurry, P.H. (1991). Theoretical analysis of evaporative losses of adsorbed or absorbed species during atmospheric aerosol sampling. *Environ. Sci. Technol.* 25: 456–459.

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