

Seasonal Variation of Polycyclic Aromatic Hydrocarbons Associated with PM₁₀ in Győr, Hungary

A. Szabó Nagy, J. Szabó, Zs. Csanádi, J. Erdős

Abstract—The main objective of this study was to assess the seasonal variation of atmospheric polycyclic aromatic hydrocarbon (PAH) concentrations associated with PM₁₀ in an urban site of Győr, Hungary. A total of 112 PM₁₀ aerosol samples were collected in the years of 2012 and 2013 and analyzed for PAHs by gas chromatography method. The total PAH concentrations (sum of the concentrations of 19 individual PAH compounds) ranged from 0.19 to 70.16 ng/m³ with the mean value of 12.29 ng/m³. Higher concentrations of both total PAHs and benzo[*a*]pyrene (BaP) were detected in samples collected in the heating seasons. Using BaP-equivalent potency index on the carcinogenic PAH concentration data, the local population appears to be exposed to significantly higher cancer risk in the heating seasons. However, the comparison of the BaP and total PAH concentrations observed for Győr with other cities it was found that the PAH levels in Győr generally corresponded to the EU average.

Keywords—Air quality, benzo[*a*]pyrene, PAHs, polycyclic aromatic hydrocarbons.

I. INTRODUCTION

POLYCYCLIC aromatic hydrocarbons (PAHs) are an important class of the organic pollutants containing two or more fused aromatic rings of carbon and hydrogen atoms, which have received considerable attention because of their toxic and carcinogenic properties and their relatively long lifetime in the environment [1], [2]. The US Environmental Protection Agency (EPA) has identified 16 unsubstituted PAHs as priority pollutants for measurement in environmental samples. Combination of their physicochemical properties, such as low aqueous solubility, moderate vapor pressure, high octanol–water partition coefficient and persistence in environment, make them capable of long-range transport [2].

The risk associated with human exposure to atmospheric PAHs is highest in cities, considering the density of population, increasing vehicular traffic, and scarce dispersion of the atmospheric pollutants [3]. Sources of PAHs in urban atmosphere include automobiles, re-suspended soils, refineries and power plants. Additional contributions to ambient air levels arise from tobacco smoking, heating sources and road dust. Natural sources such as forest fires and volcanic eruptions are less important. Most of the probable human carcinogenic PAHs are found to be associated with particulate

matter (PM), especially in fine mode particles in ambient air [4]. For this reason, humans are exposed to PAHs mainly through respiratory tract.

The aim of this work was to assess the concentration level and distribution of PM₁₀-bound PAHs in an urban site of Győr (Hungary) in the years of 2012 and 2013. Győr is the most important city in northwest Hungary, and one of the seven main regional centers of the country. The monitoring station is under the North Transdanubian Regional Environmental Protection and Nature Conservation Inspectorate Laboratory, designated by the National PM₁₀ Monitoring Program. Also, the levels of PAHs determined in our study were compared with published data of other urban sites.

II. MATERIALS AND METHODS

A. Study Area and PM₁₀ Aerosol Sampling

Győr is located halfway between Wien, Bratislava and Budapest in Central Europe. The geographical location of city is 47°41'02"N, 17°38'06"E and has an urban population of 130 thousand. The climate of Győr is continental characterized by 10.23°C annual average temperature, and 595 mm annual total precipitation. Győr is a dynamically developing city due to its good geographic location and as an emphasized center in automotive industry. It has become one of the largest economic, industrial and traffic areas of Hungary. The monitoring station is located at the junction of Tihanyi Street and Ifjúság Boulevard, approximately 3 km south of the city center. It can be classified as an urban traffic station.

A total of 112 PM₁₀ aerosol samples were collected at the monitoring station of Győr in the years of 2012 and 2013. The number of 24-hour sampling days was 14 in every February, May, August and November. A Digital High Volume sampler DHA-80 (Digital Elektronik AG, Switzerland) was used for the collection of ambient aerosol particles, which were chemically analyzed later. This equipment is considered to be equivalent to the requirements of the European Standard for sampling PM₁₀ matter [5]. Samples were taken onto high purity Advantec QR-100 quartz fibre filters (size: 150 mm diameter) for a period of 24 hours at a flow rate of 30 m³/h.

B. Chemical Analysis of PAHs

The 16 PAHs identified by the US EPA as priority pollutants (listed in Table I), 2-methylnaphthalene (mNAP), benzo[*j*]fluoranthene (BjF) and benzo[*e*]pyrene (BeP) were monitored. The ultrasonic liquid-solid extraction of the filter sample and the PAH analysis were conducted in accordance with the Hungarian standard method procedure [6]. A gas chromatography-mass selective detector (GC-MSD) system

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consisting of an Agilent 6890 GC (Palo Alto, CA, USA) with an Rtx-5MS Integra GC column (30 m long, 0.25 mm internal diameter, 0.25 μm coating, 5% diphenyl – 95% dimethyl polysiloxane; Restek Bellefonte, PA, USA) and an Agilent 5973 MSD was used in the study. The method was described in detail in our previous work [7]. The limit of detection was about 0.02 ng/m^3 . The total PAH concentration was calculated as the sum of the concentrations of 19 PAH species for each collected sample.

III. RESULTS AND DISCUSSION

A. Concentration of Total PAHs

Table I presents the concentration levels of PM_{10} -bound PAHs in the urban atmosphere of Győr in the years of 2012 and 2013. All of the priority 16 US EPA PAH compounds, mNAP, B₁F and BeP were identified in the Győr PM_{10} samples. The total PAH concentrations for the two-year sampling period were in the range of 0.19–70.16 ng/m^3 with the mean value of 12.29 ng/m^3 . The temporal distribution of total PAH concentrations is illustrated in Fig. 1 (a). Relatively higher PAH concentrations were detected in samples collected in November and February compared with May and August. This trend may be caused by fewer car journeys made in cities in summer, and decreased residential and power station fuel combustion for heating and energy in the spring and summer months. In a previous study [8], 13 PAHs could be evaluated quantitatively in PM_{10} aerosol samples of Budapest in the period of 2004–2007. Similar to the results of Győr determined in our study, relatively higher concentrations of PAHs were detected in aerosol samples of Budapest during winter compared with other seasons.

A lot of previous studies [8]–[22] have been reported about PM_{10} -bound PAH levels measured in other urban areas of the world, although a direct comparison of literature data is difficult due to the analytical methods used, and the compounds considered in each study. However, comparison of the total PAH concentrations observed for Győr with other cities was attempted (Table II). The total PAH concentrations in the atmosphere of Győr are relatively higher than found in Budapest (Hungary) and Santiago de Chile (Chile). However, the levels of total PAHs in Győr are relatively similar to the most European urban sites listed in Table II. The lower mean concentrations measured in Baltimore (USA) may be explained by the sampling period without heating. The levels of total PAHs in Győr and other European or African and American sites are considerably lower than that reported in most cities of Asia.

B. Concentration of Benzo[a]pyrene

One of the best characterized and most toxic PAH compound is benzo[a]pyrene (BaP), which is generally used as the indicator PAH [23]. Among the PAH compounds, only the BaP concentration is regulated in Hungary and also in EU. The Hungarian daily and annual average limit values for health protection are 1 ng/m^3 and 0.12 ng/m^3 , respectively

[24]. However, the annual mean target value in the EU (also in Hungary) is 1 ng/m^3 [23], [24].

TABLE I
CONCENTRATION RANGES, MEAN VALUES AND STANDARD DEVIATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN PM_{10} AT THE URBAN SITE OF GYŐR, HUNGARY (ng/m^3)

PAH compound (total rings)	2012	2013
Naphthalene (2)	0.02–0.54	ND–0.22
	0.15±0.13	0.06±0.08
2-Methylnaphthalene (2)	0.02–0.55	ND–0.25
	0.13±0.12	0.08±0.09
Acenaphthylene (3)	ND–0.38	ND–0.19
	0.06±0.11	0.02±0.04
Acenaphthene (3)	ND–0.04	ND–0.03
	<ND	<ND
Fluorene (3)	ND–0.89	ND–0.18
	0.13±0.21	0.03±0.04
Phenanthrene (3)	0.03–8.65	ND–2.22
	1.47±2.55	0.27±0.45
Anthracene (3)	ND–0.85	ND–0.28
	0.13±0.24	0.03±0.05
Fluoranthene (4)	0.03–13.09	ND–4.83
	2.67±4.49	0.74±1.08
Pyrene (4)	0.02–10.22	ND–4.14
	2.13±3.42	0.66±0.94
Benz[a]anthracene (4)	ND–5.52	ND–4.08
	1.31±1.82	0.60±0.89
Chrysene (4)	ND–5.04	ND–4.25
	1.36±1.75	0.89±1.16
Benzo[b+k+j]fluoranthene (5)	0.07–10.54	0.03–10.84
	3.02±3.45	1.29±1.85
Benzo[e]pyrene (5)	0.02–2.91	0.02–3.63
	0.84±0.95	0.52±0.66
Benzo[a]pyrene (5)	0.02–5.22	ND–6.68
	1.16±1.47	0.65±1.10
Dibenzo[ah]anthracene (5)	ND–0.70	ND–0.68
	0.17±0.22	0.09±0.13
Indeno[123-cd]pyrene (6)	0.02–6.63	ND–5.63
	1.64±2.04	0.69±0.95
Benzo[ghi]perylene (6)	0.03–4.19	0.02–4.25
	1.04±1.21	0.55±0.71
Total PAHs	0.31–70.16	0.19–43.65
	17.40±22.59	7.17±9.07
Benzo[a]pyrene-equivalent (BaPE)	0.03–7.13	ND–8.54
	1.68±2.10	0.89±1.41

ND = not detected

The concentrations of BaP ranged from undetected to 6.68 ng/m^3 with the mean value of 0.91 ng/m^3 in the Győr PM_{10} samples (Table I). Similar to the concentration trends of total PAHs, relatively higher BaP levels were detected in samples collected in November and February (Fig. 1b). The BaP concentration exceeded the Hungarian daily limit value of 1 ng/m^3 in 63 % of the samples collected in heating seasons. The annual average concentration of BaP for year 2013 was below the EU and the equivalent Hungarian target value. A summary report [24] on the Hungarian PM_{10} sampling program in 2012 has highlighted that the annual average concentrations of BaP almost in all Hungarian cities exceeded the EU target value and the exposure value excess was due to the traffic and domestic heating, collectively. The annual average concentrations of BaP for the Hungarian cities were in the range of 0.53–3.34 ng/m^3 . The two highest concentration levels were detected in the northeastern region of Hungary.

However, BaP concentration data for seasonally distribution were not reported.

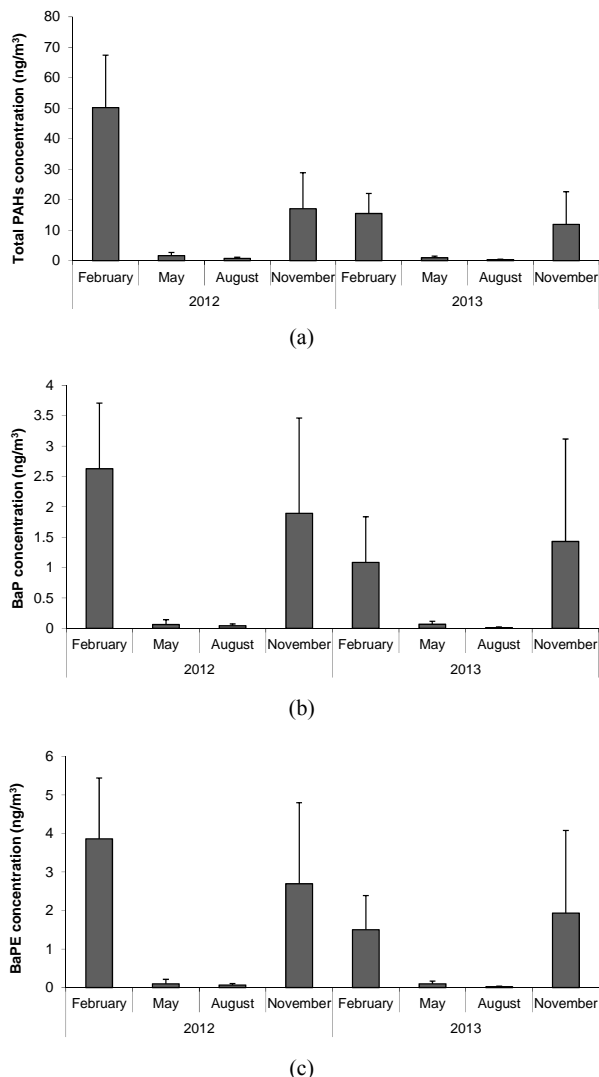


Fig. 1 Temporal variation of total PAHs, BaP and BaPE concentrations in PM₁₀ in Győr, Hungary

The comparison of the BaP concentrations observed for Győr with other cities listed in Table II has shown similar results as the total PAHs. It should also be noted that a summary report on air quality in Europe [23] has presented that many stations are approaching and exceeding the target value for BaP for rural, urban, traffic and other (including industrial) station types in 2012. The increase in BaP emissions and concentrations in Europe over the past years is therefore a matter of concern, as it is aggravating the exposure of the European population to BaP, especially in urban areas. The main emission sector is the commercial, institutional and household fuel combustion sector, responsible for 84 % of the total emissions of BaP in the EU.

C. PAHs with Different Numbers of Rings

The compositional pattern of PAHs by aromatic rings in the urban site of Győr is shown in Fig. 2. The four-ring PAHs were the most abundant PAHs in PM₁₀ samples in February, which averaged 50.3 % of total PAHs. However, the five ring PAHs were the most dominant PAHs in May, August and November (averaged 32.5 %, 36.5 % and 47.9 % of total PAHs, respectively). On average, the sum of the three benzofluoranthene isomers (BbkjF) and fluoranthene were the most dominant species followed by pyrene and indeno[123-cd]pyrene (IND). The carcinogenic species (BaP, benz[a]anthracene (BaA), BbkjF, IND and dibenzo[ah]anthracene (DahA)) together contributed 43.2 % of the mass of the total PAHs on average.

TABLE II
COMPARISON OF TOTAL PAHs AND BaP CONCENTRATIONS (RANGE AND MEAN) MEASURED IN GYŐR WITH RESULTS OBTAINED IN OTHER CITIES AROUND THE WORLD

Sampling site / sampling year	N	Total PAHs (ng/m ³)	BaP (ng/m ³)	Reference
<i>Europe</i>				
Győr, Hungary / 2012–2013	19	0.19–70.16	ND–6.68	Present study
Budapest, Hungary / 2006–2007	13	0.2–14.9	0.01–1.16	[8]
Kosetice, Czech Republic / 2005	16	1.3–101.3	0.003–2.69	[9]
Naples, Italy / 1996–1997	16	2–130	0.03–12	[10]
Oporto, Portugal / Nov–Dec 2008	18	16.8–149	0.14–4.78	[11]
Seville, Spain / 2000–2001	16	2.1–14.6	0.11–0.98	[12]
Zaragoza, Spain / 2003–2004	13	3.8–54	0.05–1.9	[13]
<i>Asia</i>				
Amritsar, India / Nov 2011	16	37–274	0.61–2.7	[14]
Delhi, India / Dec 2008–Nov 2009	16	22–258	0.95–23.6	[15]
Guangzhou, China / 2002–2003	14	8.11–106.3	0.45–11.04	[16]
Hong Kong, China / 2005	23	0.2–22	-	[17]
Banwol, South Korea / Jan 2002–Feb 2003	16	8.07–177	-	[18]
<i>America</i>				
Baltimore, USA / July 1997	23	0.352–8.26	0.029–0.64	[19]
Fairbanks, Alaska / 2009	20	-	-	[20]
Santiago de Chile, Chile / July 2000	17	2.97–11.58	0.32–1.47	[21]
<i>Africa</i>				
Bizerte, Tunisia / 2009–2010	14	9.38–44.81	0.63–3.87	[22]

N = number of PAH compounds

ND = not detected

- = no data

PAHs can be classified according to their molecular weight, i.e., low molecular weight (LMW) PAHs with fewer than four aromatic rings and high molecular weight (HMW) PAHs with four or more aromatic rings, which are released to the environment from different sources. For example, petrogenic

sources are characterized by the dominance of LMW PAHs, whereas pyrogenic sources are characterized with greater contents of HMW PAHs [14]. It has also been reported that LMW PAHs can be tracers for wood, grass, and industrial oil combustion. In contrast, HMW PAHs are usually associated with coal combustion and vehicular emissions. Therefore, ratios between LMW and HMW PAHs are used to identify different sources of PAHs. The pyrolytic source are characterized by a ratio <1 , whereas petrogenic sources show a greater ratio (>1). Comparatively, the high fraction of HMW PAHs in total PAHs and the ratios between LMW and HMW PAHs indicate mainly pyrogenic sources in the PM_{10} samples of Győr. Petrogenic sources were identified only in the non-heating seasons.

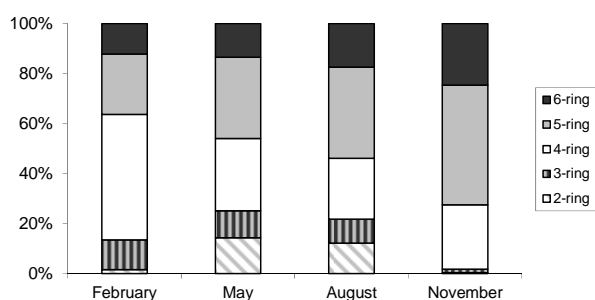


Fig. 2 Compositional pattern of PAHs by total aromatic rings in PM_{10} in Győr, Hungary

D. Carcinogenic Risk Assessment

It is well known that BaP is easily degraded in the presence of sunlight and oxidants. Due to degradation, BaP concentration alone does not give a good indication of the hazard posed by all the PAHs. The carcinogenic potential of PAHs could be underestimated if this compound alone is taken as the representative of carcinogenicity. For better quantification of aerosol carcinogenicity related to whole PAH fraction, BaP-equivalent carcinogenic potency index (BaPE) has been introduced, as in (1) [8]:

$$BaPE = BaA \times 0.06 + BF \times 0.07 + BaP + DahA \times 0.6 + IND \times 0.08 \quad (1)$$

wherein BF includes all the isomers of benzo[fluoranthene].

The BaPE index tries to parameterize the health risk for human health related to ambient PAH exposure, and is calculated by multiplying the concentrations of each carcinogenic congener with its carcinogenic factor obtained in laboratory studies. In this study, the BaPE concentrations ranged from undetected to 8.54 ng/m^3 (Table I). BaPE had shown similar patterns of seasonal distributions with total PAHs and BaP (Fig. 1). The mean BaPE values were 2.50 and 0.07 ng/m^3 in the samples collected in heating and non-heating seasons, respectively. Thus, the local population appears to be exposed to significantly higher cancer risk in the heating seasons.

IV. CONCLUSION

The concentrations of PM_{10} -bound PAHs (16 US EPA PAHs, mNAP, BbF and BeP) were determined in an urban site of Győr during a two-year sampling period. Also, the levels of PAHs determined in our study were compared with published data of other urban sites. Relatively higher concentrations of PAHs were detected in the Győr PM_{10} samples collected in the heating seasons compared with spring and summer. The average concentration of BaPE was 36 times higher in the heating seasons than in non-heating seasons. Concentration ratios between LMW and HMW PAHs reflected a pattern of pyrogenic input as a major source of PAHs. Moreover, the comparison of the BaP and total PAH concentrations observed for Győr with other cities it was found that the PAH levels in Győr generally corresponded to the EU average. However, the annual average BaP concentrations at the individual urban sites around Hungary often exceeded the EU target value. It is important to reduce BaP pollution to concentration lower than it specified in current legislation.

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