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Carcinogenic Polycyclic Aromatic Hydrocarbons in Urban Air Particulate Matter

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***Abstract*—**An assessment of the air quality of Győr (Hungary) was performed by determining the ambient concentrations of PM10-bound carcinogenic polycyclic aromatic hydrocarbons (cPAHs) in different seasons. A high volume sampler was used for the collection of ambient aerosol particles, and the associated cPAH compounds (benzo[a]pyrene (BaP), benzo[a]anthracene, benzofluoranthene isomers, indeno[123-cd]pyrene and dibenzo[ah]anthracene) were analyzed by a gas chromatographic method. Higher mean concentrations of total cPAHs were detected in samples collected in winter (9.62 ng/m^3) and autumn (2.69 ng/m^3) compared to spring (1.05 ng/m^3) and summer (0.21 ng/m^3). The calculated BaP toxic equivalent concentrations have also reflected that the local population appears to be exposed to significantly higher cancer risk in the heating seasons. Moreover, the concentration levels of cPAHs determined in this study were compared to other Hungarian urban sites.

***Keywords*—**Air, carcinogenic, PAH, PM10.

I. Introduction

POLYCYCLIC aromatic hydrocarbons (PAHs) are a class of organic compounds that consist of two or more fused aromatic rings without heteroatoms. The United States Environmental Protection Agency (US EPA) has selected 16 of these compounds (priority PAHs) for measurement in various environmental samples [1]-[3]. PAHs are generated by natural and anthropogenic sources [2]-[4]. Natural emissions come from forest fires, biosynthesis of some plants and volcanic eruptions. The incomplete burning of fossil fuels and organic materials, emissions of motor vehicles, power generation and industries are primarily responsible for the anthropogenic emissions of PAHs [2]-[4].

PAHs exist in the atmosphere in both vapor and particulate phase. The particle-associated PAHs are considered to be more harmful to human health because they are inhalable and ingestible and can deposit in the human respiratory system [5], [6]. The analysis of atmospheric particles with an aerodynamic diameter <10 µm (PM10) or less (e.g. PM2.5 and PM1) from urban regions has become important, considering the biological effects and potential health hazards they can impose. Particulate matter comprises several compounds including PAHs and their derivatives which display mutagenic and carcinogenic properties.

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In this study, the seasonal distributions of several US EPA probable or class B2 human carcinogen PAHs (benzo[a]pyrene (BaP), benzo[a]anthracene (BaA), benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, indeno[123-cd]pyrene (IND) and dibenzo[ah]anthracene (DahA)) associated with PM10 were assessed in Győr, Hungary. The levels of carcinogenic PAHs (cPAHs) determined in this study was compared to other Hungarian urban sites and a carcinogenic risk assessment model was also obtained for the concentration data.

II. Materials and Methods

A. Sampling

A total of 56 PM10 aerosol samples were collected at the monitoring station of Győr in the year of 2014. Győr is the most important city in northwest Hungary, and one of the seven main regional centers of the country [7], [8]. The location of the city is shown in Fig. 1. The number of 24-hour sampling days was 14 in every season. A Digitel High Volume sampler DHA-80 (Digitel Elektronik AG, Switzerland) was used for the sampling [9].

B. Analytical Procedure

The ultrasonic liquid-solid extraction of the filter sample (Advantec QR-100 quartz fibre) and the PAH analysis (BaP, BaA, IND, DahA and the sum of the three benzofluoranthene isomers (BF)) were conducted in accordance with the Hungarian standard method procedure [10]. The method of the analytical procedure and the gas chromatographic system were given in detail in our previous works [7], [8].

C. BaP Equivalent Concentrations

The carcinogenic risk of PAHs mixture is often expressed by its BaP equivalent concentration (BaPE). The BaPE of atmospheric PAHs was calculated from (1) [7], [8], [11]:

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

D. Cancer Risk Estimates

According to US EPA [12], a human exposure depends on chronic daily intake (CDI) of every single contaminant inhaled by the receptor. CDI for carcinogenic substances is called life averaged daily dose (LADD) [13]. The LADD value (mg/kg·day) can be derived from (2) [12]–[15]:

$$LADD = CA \times IR \times ET \times EF \times ED \,/\, BW \times AT \quad (2)$$

where CA is a compound concentration (mg/m^3), IR (inhalation rate) is a breathing rate (m^3/h), EF (exposure frequency) is a number of exposures per year, ED (exposure duration) is a duration of exposure in years, ET (exposure time) is a number of hours per exposure, BW (body weight) is a default weight of the receptor body (kg), and AT (averaging time) is an average exposure extent over a lifetime (25,550 days, equal to 70 years for carcinogens) [13]–[15]. In this study, the CA was used for BaPE concentration.

Fig. 1 The location of Győr and some Hungarian monitoring stations

Appropriate default exposure parameters were obtained by an updated US EPA recommendation for resident adult (IR = 1 m^3/h, because inhalation rate is no longer used in (2), ET = 24 h/day, EF = 350 days/year, ED = 20 years, BW = 80 kg) [16].

Human health risk related to contaminated air depends on the extent exposure as well as the toxic effects on chemicals. The incremental lifetime cancer risk (ILCR) was calculated from (3) [12], [14], [15]:

$$ILCR = LADD \times SF \quad (3)$$

A slope factor (SF) is used to estimate an upper-bound probability of the individual developing a cancer as result of the lifetime exposure to certain level of potential carcinogen. SF for BaP (7.3 per mg/kg·day) was obtained from US EPA [17].

III. Results and Discussion

A. PM10 Concentration Level

The mean PM10 concentration was 23.04 μg/m^3 at the monitoring station of Győr, which is about two times less than the annual limit value of 40 μg/m^3 (Tables I and II). On average, a good air quality index was identified for PM10. Only 3.13% of the total samples exceeded the daily limit value of 50 μg/m^3.

B. Occurrence and Seasonal Distribution of PAHs

All PAHs examined in this study were identified in the aerosol samples. The mean concentrations were in order of BF > BaP > IND > BaA > DahA (Table II). The seasonal variation of individual PAHs and total cPAHs concentrations are shown in Figs. 2 and 3.

TABLE I
Air Quality Limit or Target Values and Quality Index Used in Hungary

Parameter	PM10		BaP	
	Daily (μg/m^3)	Annual (μg/m^3)	Daily (ng/m^3)	Annual (ng/m^3)
EU limit or target value [5]	50[a]	40	–	1
Hungarian limit value [18]	50[a]	40	1	0.12
WHO guideline value [6]	50[b]	20	–	0.12[c]
Quality index[d]				
1. Excellent	0–20	0–16	0–0.4	0–0.048
2. Good	20–40	16–32	0.4–0.8	0.048–0.096
3. Acceptable	40–50	32–40	0.8–1	0.096–0.12
4. Polluted	50–100	40–80	1–2	0.12–0.24
5. Heavily polluted	100≤	80≤	2≤	0.24≤

[a]Not to be exceeded on more than 35 days/year.
[b]99th percentile (3 days/year).
[c]As the WHO has not set AQG for BaP, the reference level in was estimated assuming WHO unit risk for lung cancer for PAH mixtures, and an acceptable risk of additional lifetime cancer risk of approximately $1 \cdot 10^{-5}$.
[d]Based on the Hungarian limit values (excellent: 0–40 %; good: 40–80 %; acceptable: 80–100 %; polluted: 100–200 %; heavily polluted: ≥ 200 %).

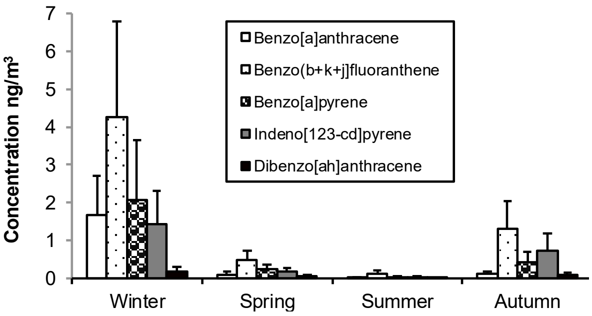

Fig. 2 Seasonal variation of individual PAHs at the monitoring station of Győr

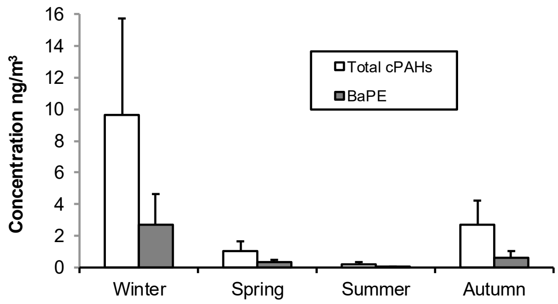

Fig. 3 Seasonal variation of total cPAHs and BaPE at the monitoring station of Győr

The total cPAHs mean concentrations were 1.05 ng/m^3 and 0.21 ng/m^3 in spring and summer, respectively. The elevated concentrations of particle-associated PAHs and total cPAHs in winter (9.62 ng/m^3) and autumn (2.69 ng/m^3) can be attributed to the increased emissions from heating sources, the transformation of gas/particle partitioning toward the particulate-phase induced by low temperature, the reduced photochemical degradation of some PAHs by solar radiation, and the lower dispersion due to meteorological conditions prevailing in winter [3], [15].

The seasonal profiles of particle-associated PAHs (percent contribution of each PAH compound to total cPAHs) are illustrated in Fig. 4. The sum of BF isomers accounted the highest percentage contribution in all seasons (45−61 %). The DahA was insignificant (1−5 %). The contribution of BaP and BaA to total cPAHs was higher in winter and spring than summer or autumn. However, the highest percentage of IND (27%) was measured in autumn.

TABLE II
PM10 AND PM10-BOUND PAH CONCENTRATION LEVELS FOR THE HUNGARIAN URBAN SITES IN 2014 AS WELL AS THE BACKGROUND SITE [16]

Sites	Maximum and mean concentrations						Percentage of samples exceeded the limit value (%)[a]		Mean percentage contribution of BaP to PM10 (%)
	PM10 (μg/m³)	PAH compounds (ng/m³)							
		BaA	BF	BaP	DahA	IND	PM10	BaP	
Győr	76.60 23.04	4.02 0.48	9.73 1.55	5.87 0.68	0.49 0.08	3.37 0.60	3.13	17.86	$2.95 \cdot 10^{-3}$
Miskolc	154.26 51.98	8.20 2.07	12.43 4.60	5.76 1.78	1.73 0.46	4.60 1.59	42.53	50.0	$3.42 \cdot 10^{-3}$
Nyíregyháza	99.70 37.46	10.76 1.45	28.96 4.94	13.56 1.99	2.23 0.32	15.96 2.46	23.21	48.21	$5.31 \cdot 10^{-3}$
Debrecen	74.0 27.81	17.63 2.66	31.22 6.41	20.01 3.19	3.57 0.46	21.53 3.18	12.73	49.09	$1.15 \cdot 10^{-2}$
Békéscsaba	76.50 26.18	8.97 1.24	24.04 4.14	14.58 1.74	1.40 0.26	10.29 1.44	8.93	44.64	$6.64 \cdot 10^{-3}$
Tapolca	64.5 22.25	1.0 0.18	3.90 0.92	1.60 0.35	0.30 0.07	1.20 0.35	3.57	8.93	$1.57 \cdot 10^{-3}$
Dunaújváros	125.6 30.62	11.50 0.88	42.40 3.50	14.20 1.22	4.70 0.34	1.20 0.35	14.29	27.78	$3.98 \cdot 10^{-3}$
Veszprém	82.80 28.07	3.70 0.93	10.40 2.66	4.40 1.14	0.80 0.19	13.10 1.13	16.07	42.86	$4.06 \cdot 10^{-3}$
Kecskemét	64.30 27.14	6.36 0.54	12.64 2.35	6.59 0.94	ND	7.7 0.94	12.50	33.93	$3.46 \cdot 10^{-3}$
Szombathely[b]	62.10 22.51	4.85 0.74	14.64 2.56	11.41 1.27	4.85 0.31	6.13 1.67	5.10	38.78	$5.64 \cdot 10^{-3}$
Mosonmagyaróvár	71.20 22.16	4.61 0.59	9.95 1.82	7.12 0.91	0.65 0.10	4.65 0.73	1.79	32.14	$4.11 \cdot 10^{-3}$
Szentgotthárd	64.06 18.34	6.66 0.99	13.60 2.76	8.03 1.36	0.97 0.18	6.69 1.39	3.57	33.93	$7.42 \cdot 10^{-3}$
Esztergom	64.80 22.31	5.76 0.54	13.53 1.83	7.72 0.86	0.85 0.11	5.76 0.77	5.36	23.21	$3.85 \cdot 10^{-3}$
Budapest[b]	99.10 33.91	–	–	9.44 1.22	–	–	16.22	44.14	$3.60 \cdot 10^{-3}$
Pécs	95.06 31.01	–	–	5.62 0.80	–	–	9.52	15.0	$2.58 \cdot 10^{-3}$
Százhalombatta	74.21 31.08	–	–	6.56 1.15	–	–	16.07	41.07	$3.70 \cdot 10^{-3}$
K-puszta (background)	54.0 18.89	2.45 0.48	7.10 1.97	3.30 0.80	0.64 0.12	4.22 1.02	3.64	36.36	$4.24 \cdot 10^{-3}$

[a]Hungarian daily limit values (see Table II).
[b]Based on data of 2 monitoring sites.
– = No data

C. Carcinogenic Risk Assessment

BaPE concentrations calculated based on the individual PAH concentrations were frequently utilized to assess the potential health risk associated with exposure to PAHs. In this study, the mean value of BaPE for Győr was 0.91 ng/m³. However, it had shown similar patterns of seasonal distributions with total PAHs (Fig. 3). The BaPE in winter (2.69 ng/m³) was nearly 4 and 8 times higher than that in autumn (0.64 ng/m³) and spring (0.32 ng/m³), indicating that the heating increased the particle-associated PAHs exposure risk substantially. The BaPE concentration in summer was insignificant (0.04 ng/m³) due to the intensive sunlight for degradation [19].

The comparison of the BaPE concentrations observed for Győr with other cities is shown in Fig. 5. It was found that the highest BaPE levels were identified mainly in the eastern part of Hungary. Among the individual PAH compounds, it is evident that the concentration of BaP at the different sites presents certain risk. The mean and maximum BaP concentrations are summarized in Table II. The concentrations of BaP were often higher than the Hungarian daily limit value of 1 ng/m³ (Table I). Also, the annual mean BaP concentration levels were above the equal EU annual target value in most Hungarian cities. Heavily polluted annual air quality for BaP (> 2 ng/m³) was obtained for only one urban site located in the northern region of the country. For Győr, a good air quality of BaP was indicated based on the EU mean target value of 1 ng/m³. The mean percentage contributions of BaP to PM10 (%) are also shown in Table II. The range of BaP contributions of PM10 concentrations was about 0.006 and 0.01% at the different Hungarian sites.

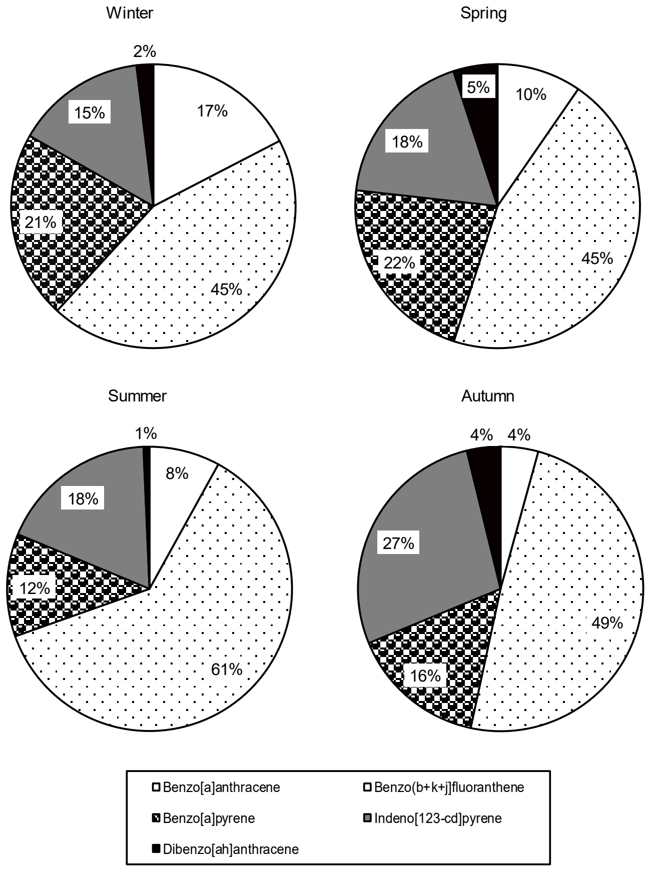

Fig. 4 Composition pattern (%) of PAHs at the monitoring station of Győr

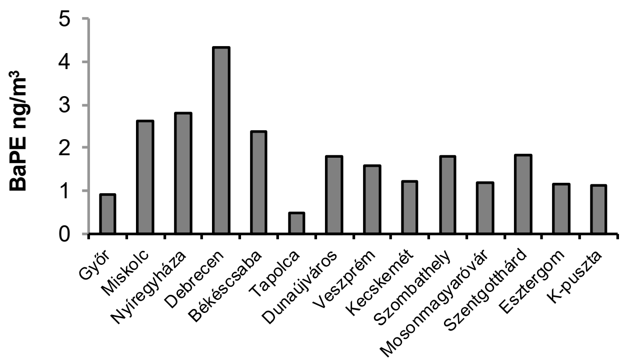

Fig. 5 Mean BaPE concentration levels for the Hungarian urban sites and the background site of K-puszta

The calculated values of LADD of the examined Hungarian sites, and the associated ILCR values are presented in Table III. LADD values of carcinogenic PAHs by way of inhalation of PM10 were between 4.07×10^{-8} mg/kg·day and 3.56×10^{-7} mg/kg·day. On the basis of LADD values, the total ILCR was calculated to be between 2.97×10^{-7} and 2.60×10^{-6}. These values are close to the acceptable limit of 10^{-6}–10^{-4} as acknowledged by regulatory agencies or not exceeded the value of 10^{-6} [12]. The calculated ILCR value for Győr was 5.52×10^{-7}. Among the Hungarian sites, Győr was on the second tier in terms of ILCR values for PAHs.

TABLE III
LADD AND ILCR VALUES FOR PAHS OF THE HUNGARIAN URBAN SITES AND THE BACKGROUND SITE OF K-PUSZTA

Sites	LADD (mg/kg·day)	ILCR
Győr	7.56×10^{-08}	5.52×10^{-07}
Miskolc	2.16×10^{-07}	1.58×10^{-06}
Nyíregyháza	2.31×10^{-07}	1.69×10^{-06}
Debrecen	3.56×10^{-07}	2.60×10^{-06}
Békéscsaba	1.95×10^{-07}	1.43×10^{-06}
Tapolca	4.07×10^{-08}	2.97×10^{-07}
Dunaújváros	1.49×10^{-07}	1.09×10^{-06}
Veszprém	1.29×10^{-07}	9.42×10^{-07}
Kecskemét	9.96×10^{-08}	7.27×10^{-07}
Szombathely	1.49×10^{-07}	1.09×10^{-06}
Mosonmagyaróvár	9.79×10^{-08}	7.15×10^{-07}
Szentgotthárd	1.51×10^{-07}	1.10×10^{-06}
Esztergom	9.44×10^{-08}	6.89×10^{-07}
K-puszta	9.21×10^{-08}	6.72×10^{-07}

IV. CONCLUSION

A study on atmospheric concentration of cPAHs bound to PM10 was carried out for Győr during the year 2014. A significant seasonally distribution of individual PAHs and total cPAHs was identified. On the basis of the mean ILCR values and the comparison of the data with other Hungarian urban sites or the background site, it is evident that the risk resulting from the exposure to air contaminated by PAHs is acceptable for Győr. However, the seasonally distributions of PAHs and the calculated BaPE concentrations have indicated that the local population appears to be exposed to significantly higher cancer risk in the heating seasons.

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