

Characterization of Polycyclic Aromatic Hydrocarbons in Ambient Air PM_{2.5} in an Urban Site of Győr, Hungary

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

Abstract—In Hungary, the measurement of ambient PM₁₀-bound polycyclic aromatic hydrocarbon (PAH) concentrations is great importance for a number of reasons related to human health, the environment and compliance with European Union legislation. However, the monitoring of PAHs associated with PM_{2.5} aerosol fraction is still incomplete. Therefore, the main aim of this study was to investigate the concentration levels of PAHs in PM_{2.5} urban aerosol fraction. PM_{2.5} and associated PAHs were monitored in November 2014 in an urban site of Győr (Northwest Hungary). The aerosol samples were collected every day for 24-hours over two weeks with a high volume air sampler provided with a PM_{2.5} cut-off inlet. The levels of 19 PAH compounds associated with PM_{2.5} aerosol fraction were quantified by a gas chromatographic method. Polluted air quality for PM_{2.5} ($>25 \mu\text{g}/\text{m}^3$) was indicated in 50% of the collected samples. The total PAHs concentrations ranged from 2.1 to 37.3 ng/m^3 with the mean value of 12.4 ng/m^3 . Indeno(123-cd)pyrene (IND) and sum of three benzo(a)fluoranthene isomers were the most dominant PAH species followed by benzo(ghi)perylene and benzo(a)pyrene (BaP). Using BaP-equivalent approach on the concentration data of carcinogenic PAH species, BaP, and IND contributed the highest carcinogenic exposure equivalent (1.50 and 0.24 ng/m^3 on average). A selected number of concentration ratios of specific PAH compounds were calculated to evaluate the possible sources of PAH contamination. The ratios reflected that the major source of PAH compounds in the PM_{2.5} aerosol fraction of Győr during the study period was fossil fuel combustion from automobiles.

Keywords—Air, PM_{2.5}, benzo(a)pyrene, polycyclic aromatic hydrocarbon.

I. INTRODUCTION

PARTICULATE matter (PM) is the term used to describe condensed phase (solid or liquid) particles suspended in the atmosphere. PM has been related to a wide range of health effect [1]-[3]. Epidemiological studies have established linkage between the concentration/composition of the inhalable (particle size $<10 \mu\text{m}$) and respirable (particle size $<2.5 \mu\text{m}$) fractions and adverse respiratory health effects. Because of the particular interest, these fractions are designated as PM₁₀ and PM_{2.5}, respectively. PM_{2.5}, often called fine PM, also comprises ultrafine particles having a

diameter of less than $0.1 \mu\text{m}$. In most locations in Europe, PM_{2.5} constitutes 50–70% of PM₁₀ [2].

PM comprises several compounds including PAHs and their derivatives which display mutagenic and carcinogenic properties [4]-[6]. PAHs are formed during the incomplete combustion of fossil fuels, biomass or other organic substances like tobacco or food. In urban areas, a large amount of PAHs are derived from incomplete combustion in motor vehicle engines, especially heavy-duty trucks and diesel engines. PAHs exist in the atmosphere in both vapor and particulate-phase.

There are more than 100 different PAHs, among which 16 have been categorized by the United States Environmental Protection Agency (US EPA) as priority pollutants. The most well-known PAH compound is BaP [7]-[10]. Numerous epidemiologic studies have shown a correlation between exposure to PAHs containing BaP and increased risk of cancer in human [8]-[10]. A summary report on air quality in Europe [3] has presented that many monitoring stations are approaching and exceeding the target value of 1 ng/m^3 for BaP for rural, urban, traffic, and other (including industrial) station types. 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.

Győr is the most important city in northwestern Hungary, and one of the seven main regional centers of the country. It is located halfway between Wien, Bratislava, and Budapest in Central Europe. The carcinogenic PAHs (BaP, benzo(a)anthracene (BaA), sum of three benzo(a)fluoranthene isomers (Bb(k)F), IND and dibenz(ah)anthracene (DahA)) associated with PM₁₀ aerosol fraction are monitored at the permanent monitoring site of Győr under the Hungarian Air Quality Monitoring Network from the year 2008 [11], [12]. However, the concentrations of PM_{2.5}-bound PAHs are not measured. Therefore, the main aim of this work was to investigate the concentration levels of PM_{2.5} as well as associated PAHs in an urban site of Győr. The sampling was carried out in November 2014. The source of PAHs was estimated using the characteristic ratios of PAHs.

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II. MATERIALS AND METHODS

A. Collection of Aerosol Samples

The monitoring station of Győr 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 Digitel High Volume sampler DHA-80 (Digitel Elektronik AG, Switzerland) was used for the collection of ambient PM_{2.5} aerosol particles at the monitoring station of Győr in November 2014. Samples were taken onto high purity quartz fiber filters (Whatman QMA, size: 150 mm diameter) for a period of 24 hours over 2 weeks at a flow rate of 30 m³/h. The sampler was loaded with 14 filters, which were changed automatically every 24 hours. About 720 m³ of air was pumped through a filter from midnight to midnight.

B. Gravimetric Analysis

Before and after sampling, the filters were conditioned for 48h at 20±1 °C and 50±5% relative humidity. The particle total mass was determined by weighing of the sampling filters before and after sampling using a micro-analytical balance (precision of 0.01 mg) and the PM_{2.5} concentration was calculated from the weighed mass on the filter and the sampling volume. After the sampling, the filters were wrapped in aluminum foil separately and stored in a refrigerator at 4 °C until chemical analysis.

C. Chemical Analysis of PAHs

The 16 PAHs identified by the US EPA as priority pollutants (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene (FLT), pyrene (PYR), BaA, chrysene (CHR), benzo(b)fluoranthene, benzo(k)fluoranthene, BaP, DahA, IND, benzo(ghi)perylene (BghiP)), 2-methylnaphthalene, benzo(j)fluoranthene and benzo(e)pyrene 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 [13]. A gas chromatography-mass selective detector (GC-MSD) system 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 [12]. The limit of detection was about 0.02 ng/m³. 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. PM_{2.5} Concentration

The PM_{2.5} mass concentrations during the sampling period are demonstrated in Fig. 1. The PM_{2.5} concentrations ranged from 12.44 to 36.92 µg/m³ with the mean value of 23.90 µg/m³ in the Győr aerosol samples. The pollution exceeded the 24-hour World Health Organization (WHO) Air Quality Guideline (AQG) value of 25 µg/m³ in 50% of the collected

samples due to increased emissions from combustion in the cold season.

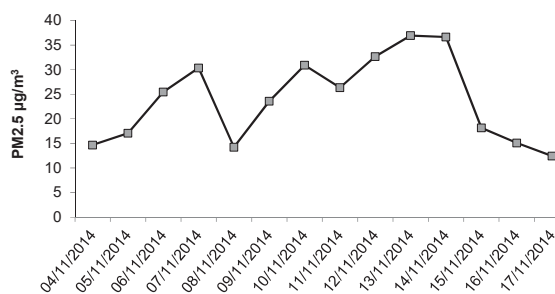


Fig. 1 PM_{2.5} concentrations

B. Concentrations of Total PAHs and Compositional Pattern

The total PAH concentrations were in the range of 2.14–37.27 ng/m³ with the mean value of 12.40 ng/m³. The distribution of total PAH concentrations is illustrated in Fig. 2.

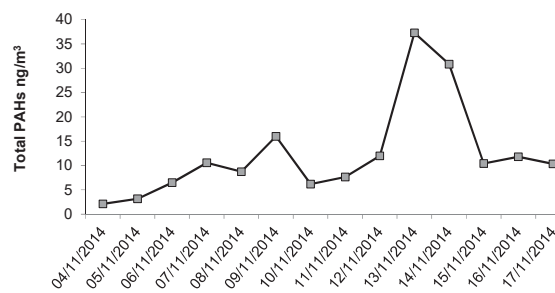


Fig. 2 Concentrations of total PAHs

The compositional pattern of PAHs by aromatic rings in the urban site of Győr is shown in Fig. 3. The high molecular weight (HMW) PAHs with 5 and 6 aromatic rings (mainly IND > Bb(k)F > benzo(ghi)perylene (BghiP) > BaP) were the most abundant PAHs in PM_{2.5} samples, which averaged 83% of total PAHs. The middle molecular weight (MMW) PAHs (4-ring) contributed 16% of the mass of the total PAHs. Only a relatively insignificant amount of low molecular weight (LMW) PAHs (2 and 3 rings) was found in the PM_{2.5} samples.

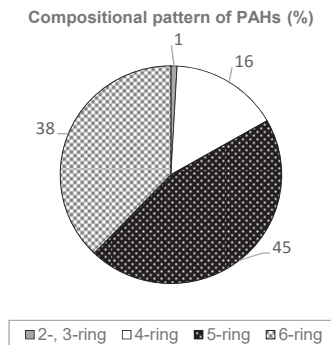


Fig. 3 Compositional pattern of PAHs by total aromatic rings

C. Levels of Carcinogenic PAHs

The mean concentrations of the carcinogenic PAH species are illustrated in Fig. 4. The concentrations of the BaP which is regarded the most toxic PAH compound ranged from 0.19 to 5.26 ng/m³ with the mean value of 1.50 ng/m³. The BaP concentration exceeded the value of 1 ng/m³ in 64% of the collected samples. The comparison the mean BaP concentration determined in our study with some published data of other urban sites presents in Table I. It was found that the relatively high BaP level may be explained by the sampling period of heating season.

It has also to be noted that the carcinogenic risk of atmospheric PAHs mixture is often expressed by the carcinogenic potency index (BaPE). BaPE has been introduced, as in (1) [12], [14]:

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

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

In our present study, the BaPE concentrations ranged from 0.27 to 7.48 ng/m³. The carcinogenic exposure equivalent concentrations were found in order of BaP (1.50 ng/m³) > IND (0.24 ng/m³) > Bb[*k*]F (0.21 ng/m³) > DahA (0.20 ng/m³) > BaA (0.03 ng/m³).

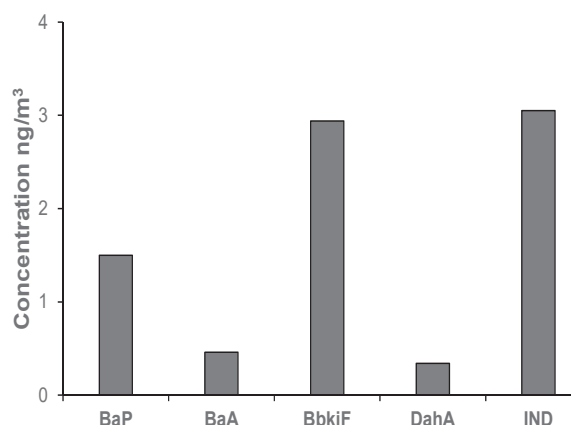


Fig. 4 Mean concentrations of the carcinogenic PAH species

D. PAH Sources

According to the formation mechanisms, PAHs can be classified as pyrogenic or petrogenic PAHs. Normally, petrogenic sources (unburned crude oil and petroleum products such as gasoline, kerosene, diesel, lubricating oil and asphalt) are characterized by the dominance of LMW PAHs, whereas pyrogenic sources (incomplete combustion of diesel/shale/crude oil/coal leads) are characterized with greater contents of MMW and HMW PAHs. The ratios between LMW and sum of MMW and HMW PAHs are often used to identify different sources of PAHs [20], [21]. The pyrolytic source is characterized by a ratio <1, whereas petrogenic sources show a greater ratio. The high fraction of MMW and HMW PAHs and the values of LMW/(MMW+HMW) ratio indicate pyrogenic sources in all of the PM_{2.5} samples of Győr.

Also, some diagnostic ratios of the selected PAHs were calculated for this study [20], [21]. The FLT/(FLT+PYR) ratio values are between 0.4–0.5 and indicate fossil fuel combustion of PAHs. All the values of IND/(IND+BghiP) ratio are >0.5 and also show pyrogenic origins. However, the ratio values of BaA/(BaA+CHR) are between 0.2–0.5 and show mixed sources of pyrogenic combustion and petrogenic sources. The BaP/BghiP ratio obtained in this study indicate traffic source in the samples (values are >0.6). Vehicular emissions can be derived from both gasoline and diesel engines based on ratios of PYR/BaP, BaP/(BaP+CHR), FLT/(FLT+PYR) and IND/(IND+BghiP) [6], [12].

TABLE I
COMPARISON OF PM-BOUND BaP MEAN CONCENTRATIONS WITH PREVIOUS STUDIES

Location	Particle size	BaP (ng/m ³)	Reference
Győr, Hungary	PM _{2.5}	1.50 (autumn)	This study
	PM ₁₀	0.91 (annual)	[11]
Budapest, Hungary	PM ₁₀	0.19	[14]
Zabrze, Poland	PM _{2.5}	19.19 (winter)	[15]
Cantabria, Spain	PM _{2.5}	0.02	[16]
Cantabria, Spain	PM ₁₀	0.04–0.13 (3 sites)	[16]
Madrid, Spain	PM ₁₀	0.2	[16]
Zaragoza, Spain	PM ₁₀	0.5	[16]
Seville, Spain	PM ₁₀	0.56	[17]
Italy, Rome	PM ₁₀	1.1	[16]
London, UK	PM ₁₀	1.4	[16]
Zagreb, Croatia	PM ₁₀	1.2	[16]
Kosetice, Czech Republic	PM ₁₀	0.42	[18]
Gdynia, Poland	PM ₁₀	1.29	[19]

Although molecular ratios are often used for characterizing possible pollution sources, these ratios are only semi-quantitative. Furthermore, these ratios can be altered due to the reactivity of some PAH species with the other atmospheric species, such as ozone and/or oxides of nitrogen. In addition to the atmospheric reactivity, degradation that may occur during the sampling process can also modify the atmospheric PAH levels and thus the ratios between PAHs [6].

IV. CONCLUSION

Study on atmospheric concentration of 19 PAHs bound to PM_{2.5} was carried out during a 2-week sampling period in November 2014. The high fraction of MMW and HMW PAHs in total PAHs were detected and it was indicated pyrogenic PAH sources. The carcinogenic BaP was observed in relatively high concentrations in the aerosol samples. Comparison the mean BaP concentration determined in our study with some monitoring data of other European urban sites it was found that the relatively high BaP level may be explained by the sampling period of heating season. Results from this study revealed that the monitoring of PAHs associated with PM_{2.5} in the urban area of Győr would be required.

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