International Journal of Earth, Energy and Environmental Sciences
ISSN: 2517-942X
Vol:9, No:8, 2015

Temporal Variation of PM10-Bound Benzo(a)pyrene Concentration in an Urban and a Rural Site of Northwestern Hungary

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***Abstract*—**The main objective of this study was to assess the annual concentration and seasonal variation of benzo(a)pyrene (BaP) associated with PM10 in an urban site of Győr and in a rural site of Sarród in the sampling period of 2008–2012. A total of 280 PM10 aerosol samples were collected in each sampling site and analyzed for BaP by gas chromatography method. The BaP concentrations ranged from undetected to 8 ng/m^3 with the mean value of 1.01 ng/m^3 in the sampling site of Győr, and from undetected to 4.07 ng/m^3 with the mean value of 0.52 ng/m^3 in the sampling site of Sarród, respectively. Relatively higher concentrations of BaP were detected in samples collected in both sampling sites in the heating seasons compared with non-heating periods. The annual mean BaP concentrations were comparable with the published data of different other Hungarian sites.

***Keywords*—**Air quality, benzo(a)pyrene, PAHs, polycyclic aromatic hydrocarbons.

I. Introduction

ATMOSPHERIC aerosols are very important ambient components in point of air quality. Monitoring the particulate matter with an aerodynamic diameter smaller than 10 μm (PM10) and PM10-bound polycyclic aromatic hydrocarbons (PAHs) could have important environmental significance due to the health risk associated with their exposure [1].

PAHs are a large group of complex organic chemicals, including carbon and hydrogen. They are composed of multiple fused ring structure containing at least two benzene rings [2]. These compounds are widely distributed in the atmosphere and most of the PAHs in the air are adsorbed on solid particles [3]. PAHs are mainly formed as pyrolysis by-products especially from the incomplete combustion of organic materials in industrial and other human activities [4]. Generally, the main possible way of human exposure to PAHs is from inhalation of ambient (outdoor) and indoor air, skin absorption and nutrition resulted of PAH formation during cooking at high temperatures or atmospheric deposition of PAHs onto fruits and vegetables [5]. The highest concentrations of atmospheric PAHs are usually found in urban areas due to the increasing vehicular traffic and industrial sources. The risk associated with human exposure to atmospheric PAHs is highest in the urban areas because of the density of population [6].

There are at least 10.000 different PAH compounds in the environment, which usually exist as mixtures rather than as individual chemicals, but in practice PAH analysis is restricted to the determination only some compounds. Benzo(a)pyrene (BaP) is the most well-known of them and it has been identified as the most relevant indicator PAH compound [7]. Chemical structure of BaP is shown in Fig. 1, this molecule contains five benzene rings. BaP is a by-product of incomplete combustion or burning of organic materials, as gasoline, diesel, wood, tobacco. BaP is commonly found with other PAHs in cigarette smoke, in grilled and broiled foods, and as a by-product of many industrial processes. BaP is also found in ambient air, indoor air, and in some water sources. Numerous epidemiologic studies have shown a correlation between exposure to PAHs containing BaP and increased risk of cancer in human epidemiologic studies [3], [8], [9].

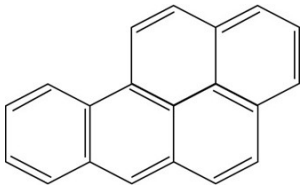

Fig. 1 Chemical structure of BaP

Considering all 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 [10]. However, the annual mean target value in the EU (also in Hungary) is 1 ng/m^3 [10], [11].

The aim of this work was to assess the concentration level of PM10-bound BaP in an urban site of Győr and in a rural site of Sarród in Hungary in the period of 2008–2012. The levels of BaP determined in our study were compared with published data of other sites in Hungary and in the world.

II. Materials and Methods

A. Study Area and PM10 Aerosol Sampling

Győr (47°41′02″N, 17°38′06″E) is the most important city in the northwest area of Hungary halfway between Wien,

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Bratislava and Budapest situated on one of the important roads of Central Europe. The city is the sixth largest in Hungary, and one of the seven main regional centres of the country. The number of inhabitants is about 130.000. Győr is a dynamically developing city due to its good geographic situation and as an emphasized centre in automotive industry. It has become one of the largest economic, industrial and traffic areas of Hungary. The monitoring site is located at one of the busiest junction of the city, where the main pollution source is the traffic.

Sarród is situated in the northwestern part of Hungary near to the border between Austria and Hungary, in the Fertő-Hanság National Park. The sampling area located in a rural environment, without significant traffic and industrial activities, but influenced by human sources from agriculture and combustion.

The two sampling sites are under the North Transdanubian Regional Environmental Protection and Nature Conservation Inspectorate Laboratory (Hungary), designated by the National PM10 Monitoring Program. A total of 280 PM10 aerosol samples were collected at each monitoring station in the period of 2008–2012. The number of 24-hour sampling days was 14 in every February, May, August and November (sampling periods I., II., III. and IV.).

A Digitel High Volume Sampler DHA-80 (Digitel 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 [12]. 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 m^3/h.

B. Chemical Analysis of BaP

The ultrasonic liquid-solid extraction of the filter sample and the BaP 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 [14].

III. Results and Discussion

A. Concentration of BaP

Table I presents the concentration levels of PM10-bound BaP in the urban atmosphere of Győr and in the rural site of Sarród in the period of 2008–2012. The BaP concentrations for the five-year sampling period ranged from undetected to 8 ng/m3 with the mean value of 1.01 ng/m^3 in the sampling site of Győr, and from undetected to 4.07 ng/m^3 with the mean value of 0.52 ng/m^3 in the sampling site of Sarród, respectively.

The data show the diversity of the type, location, and environmental influence of the two sampling sites. There is a significant difference between the annual mean BaP concentrations measured in Győr and Sarród, respectively. Relatively higher annual mean levels of BaP were detected at the urban site of Győr compared to the rural site of Sarród. The annual average concentrations of BaP were in the range of 0.53–1.54 ng/m^3 in Győr. This indicates that BaP concentration exceeded the Hungarian annual limit value in all the five years. However, the annual average concentrations of BaP for years 2009 and 2010 were below the EU and the equivalent Hungarian target value of 1 ng/m^3. The annual average BaP concentrations observed for Sarród were below the target value in every year.

TABLE I
Concentration Ranges, Mean Values and Standard Deviations of BaP in PM10 at the Urban Site of Győr and Rural Site of Sarród, Hungary (ng/m^3)

Sampling site	Year	BaP
Győr	2008	ND–8.00 1.13±1.73
	2009	ND–3.54 0.53±0.73
	2010	ND–3.63 0.68±0.85
	2011	0.02–6.92 1.54±2.08
	2012	0.02–5.22 1.16±1.47
Sarród	2008	ND–3.30 0.36±0.71
	2009	ND–2.90 0.55±0.72
	2010	ND–1.93 0.34±0.45
	2011	ND–3.92 0.81±1.09
	2012	ND–4.07 0.54±0.91

ND = not detected

B. Seasonal Variation of BaP Concentration

The temporal distribution of BaP concentrations in Győr and Sarród are illustrated in Figs. 2 and 3. Relatively higher BaP concentrations were detected in samples collected in sampling periods I. and IV. (February and November) compared with sampling periods II. and III. (May and August). The reason of this difference in each sampling year could be explained by the periodicity of heating and non-heating seasons.

The comparison of the BaP concentration data for the heating and non-heating periods for both sampling site shows the same tendency. These results are summarized in Table II.

The BaP concentration measured in Győr exceeded the Hungarian daily limit value of 1 ng/m^3 in 31 % of the samples collected in periods I. and IV. Concentrations in all samples collected in other seasons were under this limit value. Similar concentration trend was observed in Sarród where BaP concentrations in 18 % of the samples were higher than the daily limit value.

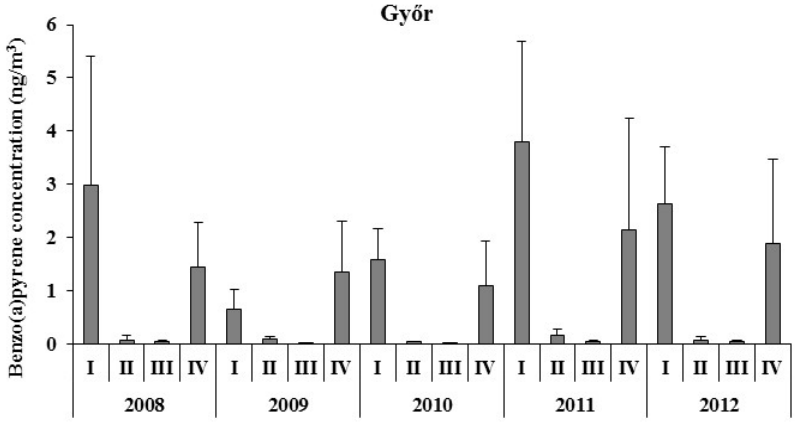

Fig. 2 Temporal variation of BaP concentrations in Győr, Hungary (error bars represent one standard deviation)

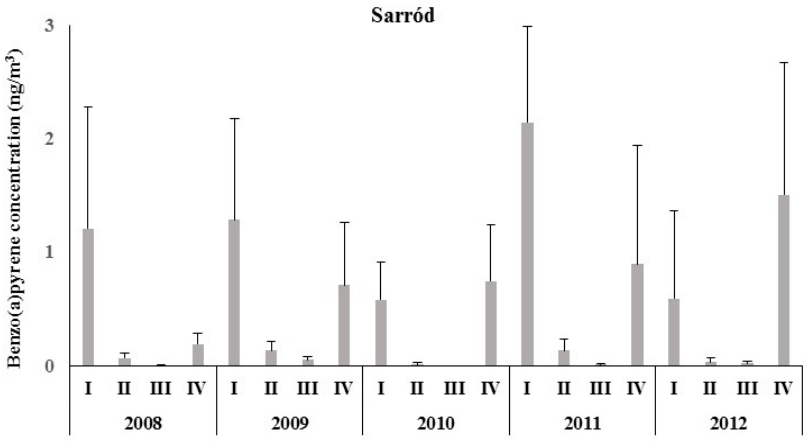

Fig. 3 Temporal variation of BaP concentrations in Sarród, Hungary (error bars represent one standard deviation)

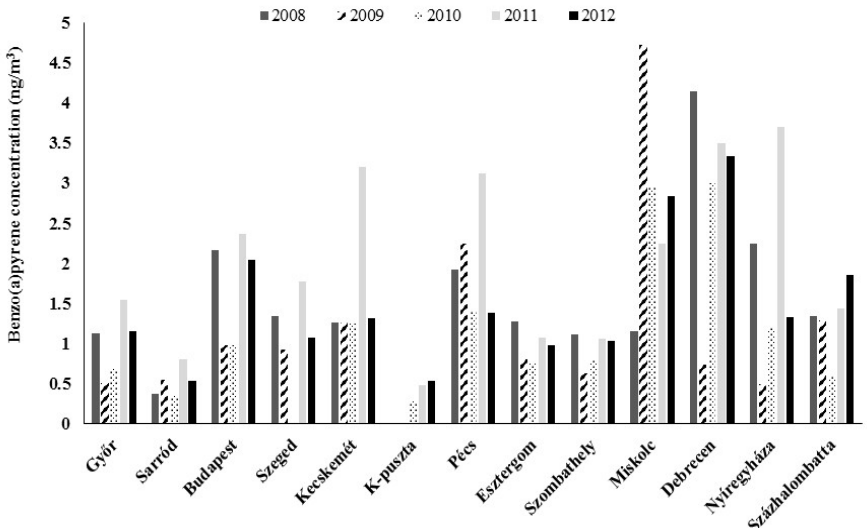

Fig. 4 The annual BaP concentrations in different Hungarian cities and the rural sites of Sarród and K-puszta in the period of 2008–2012

TABLE II
CONCENTRATION RANGES, MEAN VALUES AND STANDARD DEVIATIONS OF BAP IN PM10 IN HEATING AND NON-HEATING SEASONS AT THE URBAN SITE OF GYŐR AND RURAL SITE OF SARRÓD, HUNGARY (ng/m^3)

Sampling site	Year	Heating season	Non-heating season
Győr	2008	0.50–8.00	ND–0.44
		2.18±1.92	0.05±0.08
	2009	ND–3.54	0.02–0.16
		0.99±0.80	0.06±0.04
	2010	0.43–3.63	ND–0.07
		1.32±0.77	0.02±0.02
	2011	0.41–6.92	0.02–0.43
		2.94±2.14	0.10±0.11
	2012	0.37–5.22	0.02–0.33
		2.26±1.37	0.05±0.06
Sarród	2008	0.02–3.30	ND–0.17
		0.68±0.89	0.04±0.04
	2009	0.18–2.90	ND–0.29
		1.00±0.78	0.09±0.07
	2010	0.19–1.93	ND–0.04
		0.67±0.43	0.01±0.01
	2011	0.13–3.92	ND–0.34
		1.52±1.13	0.07±0.10
	2012	0.05–4.07	ND–0.11
		1.05±1.08	0.03±0.03

ND: not detected

C. Comparison of BaP Concentration with Other Cities

Fig. 4 illustrates that the annual mean concentration of BaP observed for Győr and Sarród is comparable with published data of other Hungarian cities from the Hungarian PM10 sampling program [10] in the same period between 2008 and 2012. The annual average concentrations of BaP for the Hungarian cites were in the range of 0.3–4.72 ng/m^3. The data illustrated in Fig. 4 show that the levels of carcinogenic BaP in Győr and Sarród samples were almost the same or lower than measured in several other Hungarian sites excluding K-puszta, which is a background station without any significant human pollution source. Relatively high concentration levels were detected in some northeastern and eastern cities (Miskolc, Debrecen and Nyíregyháza), probably due to the industrial activity.

The annual average concentrations of BaP in the examined years almost in all Hungarian cities exceeded the EU target value. However, the annual average concentrations of BaP observed for the rural site of Sarród and K-puszta were below the limit value.

Comparison of the BaP concentrations observed for Győr with other cities in the world is shown in Table III. The BaP concentrations in the atmosphere of Győr are relatively similar to the most European urban sites listed in Table III. The levels of BaP in Győr and other European, African and American sites are significant lower than that reported in most cities of Asia. The BaP concentrations measured in the rural Sarród are almost twice higher than the rural Virolahti (Finland) sampling site. The reason may be found in the different meteorological environment and lower combustion activities.

IV. CONCLUSION

The concentrations of PM10-bound BaP were determined in an urban site of Győr and a rural site of Sarród during a five-year sampling period of 2008–2012. The levels of BaP determined in our study were compared with published data of other Hungarian and worldwide urban and rural sites. Relatively higher concentrations of BaP were detected in samples collected in both sampling sites in the heating seasons compared with non-heating periods. Moreover, our results has highlighted that the future Hungarian air quality studies should focus on source apportionment of BaP.

TABLE III
COMPARISON OF BAP CONCENTRATIONS (RANGE AND MEAN) MEASURED IN GYŐR AND SARRÓD WITH RESULTS OBTAINED IN OTHER CITIES AROUND THE WORLD

Sampling Site/Sampling Year	BaP (ng/m^3)
Europe	
Győr, Hungary (urban) /2008–2012(Present Study)	ND–8.00 1.01
Sarród, Hungary (rural) /2008-2012(Present Study)	ND–4.07 0.52
Kosetice, Czech Republic (urban) /2005[15]	0.003–2.69 0.42
Naples, Italy (urban) / 1996–1997[6]	0.03–12 2.21
Oporto, Portugal (urban) /Nov–Dec 2008[16]	0.14–4.78 2.02
Seville, Spain (urban) /2000–2001[17]	0.11–0.98 0.56
Virolahti, Finland (rural) /2007-2008[18]	0.03–1.67 0.23
Zaragoza, Spain (urban) /2003–2004[19]	0.05–1.9 0.29
Asia	
Amritsar, India (urban) /Nov 2011[20]	0.61–2.7 1.20
Delhi, India (urban) /Dec 2008–Nov 2009[21]	0.95–23.6 5.90
Guangzhou, China (urban) / 2002–2003[22]	0.45–11.04 3.71
Hong Kong, China (urban) / 2005[23]	ND
Banwol, South Korea (urban) / Jan 2002–Feb 2003[24]	ND
America	
Baltimore, USA (urban) / July 1997[25]	0.029-0.641 0.124
Fairbanks, Alaska (urban) / 2009	ND
Santiago de Chile, Chile (urban) / July 2000	0.32–1.47 0.9
Africa	
Bizerte, Tunisia / 2009–2010	0.63–3.87 2.04

ND = no data

ACKNOWLEDGMENT

This work was funded by the Széchenyi István University, Hungary. We are indebted to István Vass, Bálint Kauker, Zsuzsanna Károly Némethné, Tünde Takács Kovácsné, Lajosné Bakódy, and Péter Lautner (North Transdanubian Regional Environmental Protection and Nature Conservation Inspectorate Laboratory, Hungary) for chemical analyzes data and site information.

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