World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:10, No:10, 2016

Long-Term Monitoring and Seasonal Analysis of PM10-Bound Benzo(a)pyrene in the Ambient Air of Northwestern Hungary

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***Abstract*—**Atmospheric aerosols have several important environmental impacts and health effects in point of air quality. Monitoring the PM10-bound polycyclic aromatic hydrocarbons (PAHs) could have important environmental significance and health protection aspects. Benzo(a)pyrene (BaP) is the most relevant indicator of these PAH compounds. In Hungary, the Hungarian Air Quality Network provides air quality monitoring data for several air pollutants including BaP, but these data show only the annual mean concentrations and maximum values. Seasonal variation of BaP concentrations comparing the heating and non-heating periods could have important role and difference as well. For this reason, the main objective of this study was to assess the annual concentration and seasonal variation of BaP associated with PM10 in the ambient air of Northwestern Hungary seven different sampling sites (six urban and one rural) in the sampling period of 2008–2013. A total of 1475 PM10 aerosol samples were collected in the different sampling sites and analyzed for BaP by gas chromatography method. The BaP concentrations ranged from undetected to 8 ng/m^3 with the mean value range of 0.50-0.96 ng/m^3 referring to all sampling sites. Relatively higher concentrations of BaP were detected in samples collected in each sampling site in the heating seasons compared with non-heating periods. The annual mean BaP concentrations were comparable with the published data of the other Hungarian sites.

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

I. Introduction

PAHs associated with ambient particulate matter with an aerodynamic diameter smaller than 10 μm (PM10) could have important environmental significance and health protection aspects [1]-[3]. PAHs belong to organic contaminants that are composed of multiple fused ring structures containing at least two benzene rings. There are thousands of different PAH compounds in the environment, which usually exist as mixtures rather than as individual chemicals. PAHs are released into the environment from both natural and anthropogenic sources, but they are mainly formed by the incomplete combustion of organic materials [2]-[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 [4]-[6]. The highest atmospheric PAH concentrations can be usually observed 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 [7]. PAHs have significant mutagenic, carcinogenic, and toxic properties. Several experimental studies showed that different PAHs can produce cancer in experimental animals and humans as well [8]-[15].

The most well-known PAH compound is BaP [4]-[6]. BaP is a by-product of incomplete combustion or burning of organic materials, as gasoline, diesel, coal, and wood. Among the other PAHs, BaP is commonly found in several different sources as cigarette smoke, grilled foods, and as a by-product of industrial processes and it is also found in ambient air, indoor air, and in some water sources [4]. Numerous epidemiologic studies have shown a correlation between exposure to PAHs containing BaP and increased risk of cancer in human epidemiologic studies [6], [8], [13]-[15]. BaP is thought to probably cause lung and skin cancer. Moreover, embryotoxic effects of BaP have been described in experimental animals [16].

Considering all PAH compounds, only the BaP concentration level is regulated in Hungary and also in European Union (EU). The Hungarian daily and annual mean BaP limit values for health protection are 1 ng/m^3 and 0.12 ng/m^3, respectively [17]. However, the annual mean target value in the EU (also in Hungary) is 1 ng/m^3 [17], [18]. In Hungary, within the framework of the National PM10 Monitoring Program, the Meteorological Service has reported air quality monitoring data for several air pollutants including BaP, but these data present only the annual mean concentrations and maximum values [17]. Comparing the seasonal variation of BaP concentrations in the heating and non-heating periods can play an important role and can show difference [19].

The aim of this work was to assess the concentration level of PM10-bound BaP in different urban areas and in a rural monitoring site of Northwestern Hungary in the period of 2008–2013. The seasonal variation of BaP concentrations was also studied. The sampling sites were under the Government Office for Győr-Moson-Sopron County, Division of Environment and Nature, Environmental Protection Laboratory (Hungary), designated by the National PM10 Monitoring Program. Moreover, the levels of BaP determined

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in our study were compared with the published data of the other Hungarian sites.

II. Materials and Methods

A. Study Area and PM10 Aerosol Sampling

Atmospheric aerosol measurements were performed at the permanent urban sites of five cities located in the northwestern part of Hungary during the period of 2008–2013. Aerosol sampling from the rural site of Sarród was also carried out. The location of the sampling sites is shown in Fig 1.

Győr is the most important city in the northwestern area of Hungary situated on one of the important roads of Central Europe. The city is the sixth largest in Hungary, approximately with 130 000 inhabitants and it is a dynamically developing city owing to its good geographic situation and as an illustrious center in automotive industry. The monitoring site is located at one of the busiest junction of the city, where the main pollution source is the traffic [3].

Fig. 1 Map of Hungary with the location of the studied monitoring sites (underlined). Some other Hungarian sites are also marked, which are included in this study

Esztergom is a port-town with automotive industrial activity, situated on the bank of River Danube. The number of inhabitants is about 30 000. The monitoring site is situated in the city center. Szombathely is the tenth largest city in Hungary and an important industrial center of western area of the country, located near the border with Austria. There are two monitoring sites in this city for PM10 aerosol sampling. Mosonmagyaróvár and Szentgotthárd are smaller cities with less inhabitants, approximately 30.000 and 9.000, respectively. Mosonmagyaróvár lies close to the Austrian and Slovakian border. Szentgotthárd is situated on the bank of River Rába near to the Austrian border and it is an important automotive industrial center of Western Hungary.

The monitoring site of Sarród is situated in the Fertő-Hanság National Park near to the border between Austria and Hungary. The sampling area located in a rural environment, without significant traffic and industrial activities, but influenced by human sources from agriculture and combustion [19].

A total of 1475 PM10 aerosol samples were collected in the northwestern part of Hungary in the period of 2008–2013 (see Table I for details). The number of 24-hour sampling days was 14 or 15 in every February, May, August and November (sampling periods I., II., III. and IV.). Collection of ambient aerosol particles was carried out by a Digitel High Volume sampler DHA-80 (Digitel Elektronik AG, Switzerland), they were chemically analyzed later [3]. This equipment is considered to be equivalent to the requirements of the European Standard for sampling PM10 matter [20]. Samples were taken onto high purity Advantec QR-100 quartz fiber filters (size: 150 mm diameter) for a period of 24 hours at a flow rate of 30 m^3/h.

TABLE I
Concentration Ranges, Mean Values and Standard Deviations of BaP in PM10 in Different Urban Areas as Well as in the Rural Site of Northwestern Hungary

Sampling site	Sampling period (n)	BaP (ng/m^3)
Esztergom (urban site)	2008–2013 (337)	ND–5.70 0.96±1.18
Győr (urban site)	2008–2013 (339)	ND–8.00 0.95±1.45
Szombathely[a] (2 urban sites)	2008–2013 (378)	ND–5.79 0.95±1.21
Mosonmagyaróvár[b] (urban site)	2013 (42)	ND–7.26 0.65±1.32
Szentgotthárd[b] (urban site)	2013 (42)	0.01–6.47 0.92±1.61
Sarród (rural site)	2008–2013 (337)	ND–4.07 0.50±0.77

ND=not detected, n=number of samples. [a]336 samples were collected at the Site-1 during the period of 2008–2013 and 42 samples were collected at the Site-2 in the sampling periods of II, III and IV of the year 2013; concentrations of BaP were calculated from the data of the two sites. [b]Aerosol samples were collected in the sampling periods of II, III and IV of the year 2013.

B. BaP Chemical Analysis

The ultrasonic liquid-solid extraction of the filter samples and the BaP analysis were carried out according to the relevant Hungarian standard method procedure [21]. For chemical analysis of the samples, a gas chromatography-mass selective detector (GC-MSD) system with an Agilent 6890 GC (Palo Alto, CA, USA), 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 were used. A description of the method was given in detail in our previous work [22].

III. Results and Discussion

A. BaP Concentration Levels

Table I presents the concentration levels of PM10-bound BaP at the monitoring sites of Northwestern Hungary in the period of 2008–2013. The BaP concentrations for the six-year sampling period ranged from undetected to 4.07 ng/m^3 with the mean value of 0.5 ng/m^3 at the rural site of Sarród. For the urban areas, the BaP concentrations ranged from undetected to 8 ng/m^3. The mean concentration values were varied between 0.65 and 0.96 ng/m^3 calculated for the whole sampling periods at the different urban sites.

The temporal variation of annual mean concentrations for each sampling sites during the study period are illustrated in Fig. 2. A significant difference can be observed between the annual mean BaP concentrations measured at urban sampling sites and the rural site of Sarród. The annual mean concentrations of BaP were in the range of 0.76–1.27 ng/m^3 in Esztergom, 0.51–1.54 ng/m^3 in Győr, 0.64–1.13 ng/m^3 in Szombathely and 0.34–0.81 ng/m^3 in Sarród in the period of 2008–2013 (Table II). Mean concentration values of 0.65 and 0.92 ng/m^3 were measured in Mosonmagyaróvár and Szentgotthárd in the year 2013, respectively. These results have indicated that the BaP concentration levels exceeded the Hungarian guideline 0.12 ng/m^3 in all years at the different sampling sites. Moreover, the annual mean concentrations of BaP in Esztergom, Győr and Szombathely often exceeded the EU and the equivalent Hungarian target value of 1 ng/m^3.

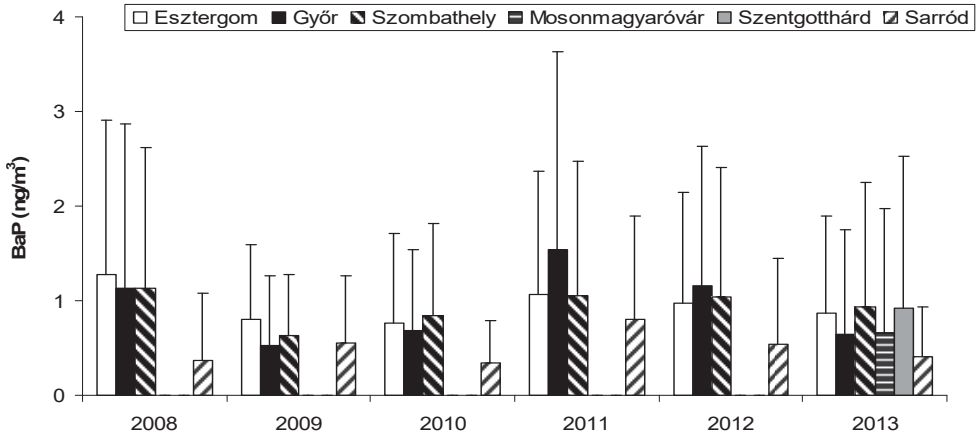

Fig. 2 Annual mean concentrations of BaP in the urban areas and a rural site of Northwestern Hungary in the period of 2008–2013 (error bars represent one standard deviation)

B. Seasonal Variation of BaP Concentrations

The seasonally distribution of BaP concentrations at the urban sampling sites and the rural site of Sarród are illustrated in Fig. 3.

Significantly 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 annual mean BaP concentration data for the heating and non-heating periods for each sampling site shows the same tendency (Fig. 4). Approximately, 20-30 times higher mean concentrations were detected in the heating seasons compared to the non-heating seasons.

Considering the individual samples, the BaP concentration measured in only the sampling periods of I. and IV. exceeded the Hungarian daily limit value of 1 ng/m^3 in some cases. In Esztergom the 37%, in Győr 29%, in Szombathely 38%, in Mosonmagyaróvár 21% and in Szentgotthárd 33% of the total samples showed higher values than the limit value. Similar concentration trend was observed in Sarród where the BaP concentrations in 18% of the total samples were higher than the daily limit value.

C. Comparison of BaP Concentration with Other Cities

The comparison of the annual mean BaP concentrations observed for the urban and the rural sites of the northwestern region of Hungary with other Hungarian cities and the background site of K-Puszta is summarized in Table II. The measured BaP concentrations are comparable with the published data of the other Hungarian sites based on the Hungarian PM10 Monitoring Program [17] in the period of 2008–2013.

The annual mean concentrations of BaP for the Hungarian cites were in the range of 0.3–4.72 ng/m^3. The data show that the levels of carcinogenic BaP in samples from Eszetrgom,

Győr, Szombathely, Mosonmagyaróvár, Szentgotthárd, and Sarród were similar and almost the same or lower than measured in other Hungarian sites excluding K-puszta. This latter sampling site is a background station without any significant human pollution source. Relatively higher concentrations were measured in some northeastern and eastern cities as Debrecen, Nyíregyháza, and Miskolc. The annual mean concentrations of BaP almost in all Hungarian cities often exceeded the EU target value of 1 ng/m^3. However, the annual mean BaP concentrations observed for the rural sites of Sarród and K-puszta were below the target value in the examined years.

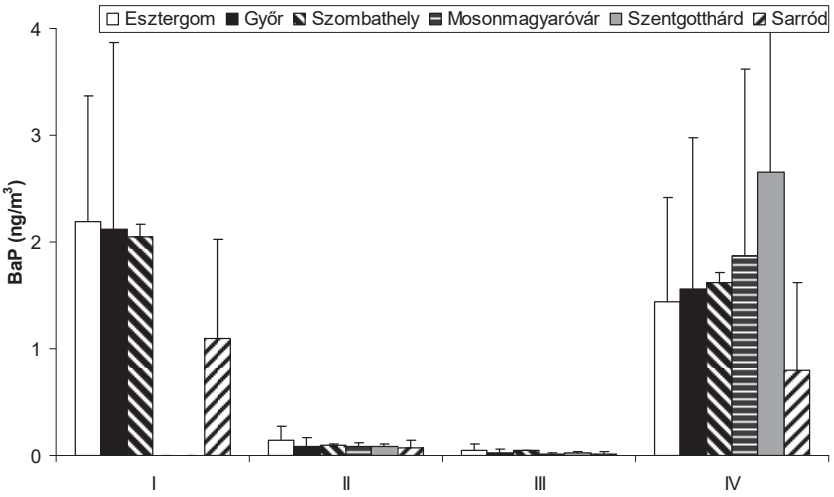

Fig. 3 Seasonally distribution of BaP concentrations at the sampling sites of Northwestern Hungary in the period of 2008–2013 (error bars represent one standard deviation)

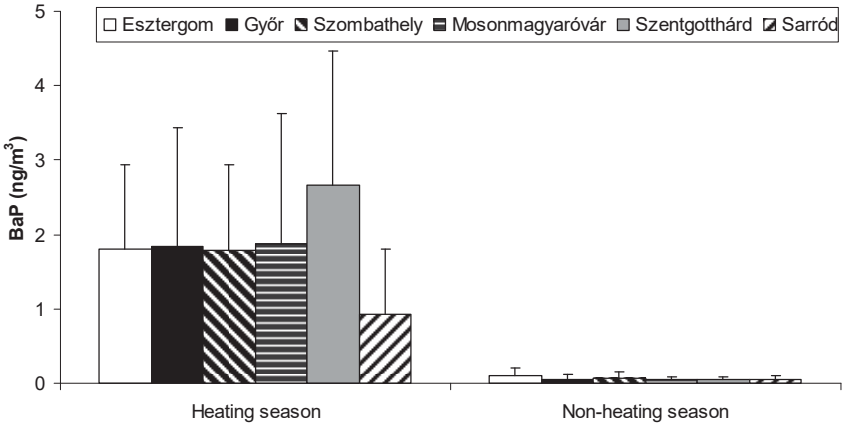

Fig. 4 BaP concentrations in heating and non-heating seasons at the sampling sites of Northwestern Hungary in the period of 2008–2013 (error bars represent one standard deviation)

It should also be noted that a summary report on air quality in Europe [18] has presented that many stations are approaching and exceeding the target value for BaP for rural, urban, traffic, and other (including industrial) station types. The BaP emissions and concentrations in Europe over the past years are characteristically increasing and it is affecting the exposure of the European population to BaP, especially in urban areas. The main emission sources are the household and industrial fuel combustion sectors. They are responsible for 84% of the total emissions of BaP in the EU. It was found that the BaP levels in Hungary generally corresponded to the EU average [22].

IV. Conclusion

The concentrations of PM10-bound BaP were monitored at the urban and rural sites of Northwestern Hungary during a six-year sampling period. The concentration levels and seasonal distribution were assessed. The concentration levels determined at some urban sites often exceeded the annual mean EU target value of 1 ng/m^3. However, 20-30 times higher mean concentrations were detected in the heating seasons compared to the non-heating seasons at all sampling sites. Thus, the local population appears to be exposed to significantly higher cancer risk in the heating seasons. Moreover, our results have highlighted that the future Hungarian air quality studies should be focused on source apportionment of BaP as well as carcinogenic risk assessment

especially in the northeastern and eastern part of the country.

TABLE II
COMPARISON OF ANNUAL MEAN BAP CONCENTRATIONS (RANGES AND MEAN VALUES FOR THE EXAMINED YEARS) MEASURED IN SOME HUNGARIAN URBAN AREAS AS WELL AS IN RURAL SITES IN THE PERIOD OF 2008–2013 [17]

Sampling site	Sampling period (n)	Ranges and Mean (ng/m^3)
Budapest	2008–2013 (335)	0.51–1.54 1.80
Debrecen	2008–2013 (337)	0.74–4.15 2.91
Esztergom	2008–2013 (337)	0.76–1.27 0.96
Győr	2008–2013 (339)	0.51–1.54 0.95
Kecskemét	2008–2013 (334)	0.99–3.20 1.55
K-puszta (rural background)	2010–2013 (204)	0.30–0.63 0.49
Miskolc	2008–2013 (335)	1.16–4.72 2.62
Mosonmagyaróvár	2013 (42)	- 0.65
Nyíregyháza	2008–2013 (337)	0.5–3.70 1.62
Pécs	2008–2013 (284)	1.4–3.12 2.02
Sarród (rural)	2008–2013 (337)	0.35–0.81 0.50
Százhalombatta	2008–2013 (336)	0.60–1.85 1.29
Szeged	2008–2009, 2011–2012 (224)	0.92–1.77 1.28
Szentgotthárd	2013 (42)	- 0.92
Szombathely	2008–2013 (378)	0.64–1.12 0.96

n=number of samples

ACKNOWLEDGMENT

This work was funded by the Széchenyi István University, Hungary. We are indebted to István Vass, Bálint Kauker, Zsuzsanna Károly Némethné, Ibolya Vadász Reményiné, Tünde Takács Kovácsné, Lajosné Bakódy, and Péter Lautner (Government Office for Győr-Moson-Sopron County, Division of Environment and Nature, Environmental Protection Laboratory, Hungary) for chemical analyzes, data and site information.

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