

A. CVETKOVIĆ<sup>1</sup>  
M. JOVAŠEVIC-STOJANOVIĆ<sup>2</sup>  
S. MATIĆ-BESARABIĆ<sup>1</sup>  
D.A. MARKOVIĆ<sup>3</sup>  
A.BARTOŇOVÁ<sup>4</sup>

<sup>1</sup>Public Health Institute of Belgrade, Belgrade, Serbia

<sup>2</sup>Vinča Institute of Nuclear Sciences, University of Belgrade Belgrade, Serbia

<sup>3</sup>Faculty for Applied Ecology "Futura", Belgrade, Serbia

<sup>4</sup>NILU Norwegian Institute for Air Research, Kjeller, Norway

#### SCIENTIFIC PAPER

UDC 503.2:504.5(497.11Belgrade)  
"2009/2012"

DOI 10.2298/CICEQ140305033C

## COMPARISON OF SOURCES OF URBAN AMBIENT PARTICLE BOUND PAHs BETWEEN NON-HEATING SEASONS 2009 AND 2012 IN BELGRADE, SERBIA

### Article Highlights

- Analysis of PM<sub>10</sub> and PM<sub>10</sub>-bound PAH was conducted in summer 2009 and 2012
- PAH concentration indicating an increasing strength of PAH sources relative to all PM<sub>10</sub> sources
- Major PAH sources are stationary sources, traffic (diesel and gasoline) and biomass burning
- Traffic was more intensive in 2012 while biomass burning was decreased in sampling periods

### Abstract

*Exposure to increased concentrations of polycyclic aromatic hydrocarbons (PAHs) is associated with adverse health problems and specifically with carcinogenic and mutagenic effects. The major PAH sources outdoors are: stationary sources from industry (power plants, incineration, local industry) and domestic sources as the residential heating, burning and pyrolysis of coal, oil, gas, garbage, wood, or other organic substances mobile emissions (diesel and petrol engines), biomass burning and agricultural activities (e.g., open burning of brushwood, straw, stubble). The aim of this study was to assess potential differences in particle-bound PAH levels and source contribution between summer 2009 and 2012 sampling campaigns done at the same location in Belgrade urban area. The sampling location is considered representative for a mix of residential, business and industrial areas of New Belgrade, an urban area that has been under rapid development. The average concentrations of PM<sub>10</sub> are slightly higher in summer 2012 than in 2009. PM-bound PAH follow the same trend as the PM indicating an increasing strength of PAH sources relative to all PM sources. Applying positive matrix factorization, three potential sources of PAHs in the atmosphere were distinguished: 1) stationary sources, 2) traffic (diesel and gasoline vehicle exhaust) and 3) local open burning sources (OBS). The analysis confirmed higher contribution of traffic and lower of OBS in summer 2012 than in 2009, reflecting higher traffic volumes and absence of or lower local OBS emissions due to burning wood, grass and domestic waste in 2012.*

*Keywords:* urban air pollution sources; monitoring; polycyclic aromatic hydrocarbons; positive matrix factorization.

In terms of potential harm to human health, PM<sub>10</sub> poses a high risk, as it penetrates into sensitive regions of the respiratory system and can lead to

health problems related to, e.g., respiratory, cardiovascular, immune and neural systems. About 33% of the EU urban population lives in areas where the EU air quality 24-h limit value for particulate matter (PM<sub>10</sub>) was exceeded in 2011. Extended to the EEA-32 countries, it was estimated that PM<sub>10</sub> daily limit values were exceeded in about 50% of urban areas. Current pollution levels, especially of PM and an important

Correspondence: A. Cvetković, Public Health Institute of Belgrade, Bul. Despota Stefana 54, 11000 Belgrade, Serbia.

E-mail: anka.filipovic@gmail.com

Paper received: 5 March, 2014

Paper revised: 29 August, 2014

Paper accepted: 10 September, 2014

PAH - benzo(*a*)pyrene (BaP) - clearly impact large urban populations [1].

PAHs in the atmosphere can be present in both gaseous and particle phases bonded on PM surfaces, depending on the size of the particulates and air temperature [2]. PAHs form during the process of pyrolysis of organic materials such as coal, oil, biomass, petrol and diesel fuel [3], fires in the forests and prairies, volcanic activity [4–6] as well as fires caused by human activity. The largest contributions originate from burning of fossil fuels. PAHs can also be synthesized by the activity of some bacteria [6] and plants [4,5]. The largest amount of PAHs in the environment comes from burning of coal [7], because fossil fuels contain significant quantities of aromatic hydrocarbons which have arisen during their formation by incubation of organic matter under specific conditions without the presence of oxygen. Anthropogenic PAHs arise mostly as products of various pyrolytic processes, especially incomplete combustion of organic matter during industrial activities, energy production (heat and electricity), combustion of waste, and as emissions from motor vehicles [8].

Bap has been used as an indicator of exposure to other harmful PAHs because it is known as a human carcinogen substance. Exposure of the European population to Bap concentrations above the target value (annual average higher than  $1 \text{ ng/m}^3$ ) is widespread, especially in central and eastern Europe. Between 22 and 31% of the urban population in EU was exposed to Bap concentrations above  $1 \text{ ng/m}^3$  in

the period 2009 to 2011 [1]. The increase in Bap emissions from domestic combustion for heating purposes in Europe over the last years is a matter of concern especially in urban areas [1].

## EXPERIMENTAL

### Air sampling

The sampling site, a background urban monitoring station, Omladinskih Brigada Street ( $44^\circ 49'7''$  N,  $20^\circ 28'5''$  E, 116 A), is located in a mixed business and residential area of New Belgrade (Figure 1). In the radius of 5 km of this monitoring site, there are the following pollution sources: Belgrade district heating plants; business trade centers, mega markets; high traffic density arterial road (140,000 cars per day pass a bridge over the Sava river); kindergartens, schools; residential area central heating facilities using gas and oil; agricultural activities.

During the campaign in 2009, the sampling equipment was placed on the roof of the Medical Institute at a height of about 15 m. Average values of  $\text{PM}_{10}$  from the automatic station located at ground level along the same building, were lower than average  $\text{PM}_{10}$  concentrations collected during campaigns in the period 2007/2008 [9]. Three years later, in 2012, the monitoring was performed at the site located at ground level, next to the automatic monitoring station.

The sampling campaigns were performed in the framework of the WeBIPATR project in non-heating



Figure 1. Sampling site location.

season covering spring and summer, May 25<sup>th</sup> - July 20<sup>th</sup> 2009. Follow-up campaigns were conducted during a non-heating season of 2012, as an additional analysis to monitoring done in the framework of regular monitoring program of the Institute of Public Health of Belgrade.

Aerosol sampling was conducted using European reference low-volume samplers (Sven/Leckel LVS3) with inlet for PM<sub>10</sub> fraction, with flow rates 2.3 m<sup>3</sup> h<sup>-1</sup>. Particles were collected onto 47 mm Whatman QM-A quartz fiber filters. The PM was sampled on a daily basis (24 h, beginning at 7 a.m.) with one "field blank" per week, in compliance with the EU Directive (EEC, 1999).

### Chemical analysis

Gravimetric measurement and determination of PM<sub>10</sub> fraction of particulate matter were prepared according to EN 12341 [10]. Collected samples were prepared according to Compendium Method TO-13A [11]. The exposed area of quartz fiber filters was approximately 12 cm<sup>2</sup>. The filter portion of 6 cm<sup>2</sup> was used for solvent extraction. PAHs were extracted in microwave with mixture of solvents hexane: acetone (12.5 ml *n*-hexane:12.5 ml acetone) according to EPA 3546. After the extraction, the solvent volume was reduced by rotary evaporation under a reduced pressure (55.6 kPa and with 0.2 ml isoctane as a keeper) to 1 ml. After that, *n*-hexane solution was reduced under nitrogen stream at room temperature to 0.5 ml and analyzed.

All samples were analyzed by GC Agilent 6890 N with mass selective detector Agilent 156 5973 MSD. Capillary column DB-5 MS (30 m×0.25 mm×25 µm) was used. The GC conditions were: 1 ml/min helium flow, oven temperature program started at 70 °C (held 4 min), ramp 8 °C/min to 310 °C (hold 5 min), solvent delay was 5 min and time of run 46 min. The injector temperature was set to 300 °C, the transfer line to 280–310 °C. The identification and quantification of PAH was done according to retention times and the internal standard method. Calibration curves were prepared with PAH concentrations between 5–200 ng/ml in *n*-hexane. Concentration of the recovery standard was from the middle of calibration curve and recovery efficiencies were between 80–110%.

As external standard for calibration curve we used Ultra Scientific PAH Mixture PM-831, which consists of 16 compounds, each of 500.8±2.5 µg/ml concentration. As internal standard, we used Ultra Scientific Semi-Volatiles Internal Standard Mixture ISM-560 with deuterated compounds: Acenaphthene-d10; chrysene-d10; 1,4-dichlorobenzene; naphthalene-d8;

perylene-d12; phenanthrene-d10. Prior to analysis, calibration curves for the 16 PAHs were obtained by spiking known quantities of substances, all with an *R*<sup>2</sup> of the calibration curve above 0.995. Method detection limit (MDL) was calculated as three times signal/noise, and method quantification limit (MQL) as 3.3 times MDL. MQL for all PAHs was 0.02 ng/m<sup>3</sup>.

The accuracy of the method was calculated by analyzing the European reference material ERM-CZ100 FINE DUST (PM10-LIKE) from the IRM (Institute for Reference Materials and Measurements of the EC JRC). We obtained errors below 15 % and recoveries from 85 to 110%.

Repeatability test was performed by seven analyses of a standard PAH solution. Reproducibility was evaluated by analysis of the same standard on five different days. In both cases, relative standard deviations (*RSD*) of the relative response factors were below 15% for all PAHs.

Field and laboratory blank, also as a duplicate sample, were prepared and analyzed, and all concentrations were corrected with reference to blank and recovery.

### Emission source identification using diagnostic ratio and positive matrix factorization

Two methods are used for source identification, diagnostic ratios and receptor modeling. The ratios of some PAHs, PAH diagnostic ratios, are suggested to be characteristic of certain sources [12,13]. In recent years serious attention was given to PAH levels in ambient urban areas all over the world and PAH diagnostic ratio is the tool that has been widely applied for determination of the potential emission sources of PAHs in ambient air [4,12–18]. Application of this tool enables distinguishing between diesel and gasoline combustion emissions as well as characterizing major stationary sources.

Alongside with diagnostic ratio it is recommended to apply receptor modeling, provided that enough experimental data is available. Receptor models include a range of multivariate analyses using results of chemical analysis of samples of certain types of aerosols to determine the type, location and contribution of pollution sources [19,20]. Receptor models focus on the pollutants in the very point of testing; this is the opposite of dispersion models, which use information on pollutant emissions from the sources (assuming that the emissions are known) and predict concentrations of pollutants taking into account atmospheric dispersion, chemical transformations and other physical-chemical processes.

Positive matrix factorization (PMF) analysis [21,22] is a powerful tool for receptor modeling which utilizes uncertainty estimates associated with the concentrations.. PMF allows the user to utilize the detection limit of each method and the uncertainty in the chemical analysis along with the concentrations. Missing data can be replaced prior to the analysis *e.g.*, using a median value of the species [23]. PMF model reduces the effect of very large values by treating them as outliers [21]. Interpretation consisting of identification of factors and their allocation to source (or source combinations) is subjective, based on knowledge of PAH markers for individual emission sources [24-27].

Major sources of PAHs, especially in large urban areas, are gasoline and diesel vehicles [15-17,25,27,28]. Other significant sources are coal and oil combustion as well as biomass combustion [15,25,27-30].

Phe, Pyr and Fla are emitted by coal burning [31,25,27,28] while Bap and Fla are emitted by wood burning [31,25,27,28]. Pyr, Fla and Bbf are present in exhaust gasses from the cars without catalyst [25,27,28,32-34]. Compounds Pyr, Fla, Bbf and Bpe are released by fossil fuels combustion [25,27,28,33]. Phe, Baa and Bap also come from emissions from motor vehicles [25,27-29]. Baa is formed during combustion of diesel fuel and natural gas, while Bap comes from automobile emissions with and without catalyst [4]. Phe, Chr, Baa i Pyr are released by traffic [35] as well as Bpe, Dba, Bap, Bbf, Bkf and Inp [25,27,28,31]. Typical markers for diesel combustion are Phe, Pyr, Fla and Chr [25,27,28,36]. Bpe and Inp also originate from traffic [25,27,28,30].

PAH's typical for stationary sources (industry, cement production and power plants) are Bap, Baa and Bep [31], and also Ant [37]. Ane, Phe, Fla, Fle and Pyr are also markers for municipal solid waste [38].

## RESULTS AND DISCUSSION

### PM and PAH concentration

The results for mean daily  $\text{PM}_{10}$  mass concentrations are given in Table 1. The concentrations are slightly higher in summer 2012 than in 2009. The average concentrations of  $\text{PM}_{10}$  were  $23.1 \mu\text{g}/\text{m}^3$  in 2009 and  $29.8 \mu\text{g}/\text{m}^3$  in 2012. Figure 2 shows that PM-bound PAH follow the same trend as the PM. Table 2 presents mean daily concentration, standard deviation, median, minimum and maximum value of each of 16 priority PAHs in the two campaigns.

The average concentrations for sum of 16 priority PAHs in  $\text{PM}_{10}$  fractions were  $2.55 \text{ ng}/\text{m}^3$  in summer 2009 and  $3.83 \text{ ng}/\text{m}^3$  in summer 2012. No significant difference ( $P < 0.05$ ) was observed for variance or for mean values of total PAH, Nap, Ane, Any, Fle, Phe, Baa, Chr and Inp concentrations between campaigns in summer 2009 and 2012. Ant, Pyr and Daa mean values were significantly higher and Bba and Bap significantly lower in summer 2009.

Table 1. Statistical parameters of PM concentrations ( $\text{PM}_{10}, \mu\text{g}/\text{m}^3$ ); Number of samples: 53

Data type	Sampling time	
	Summer 2009	Summer 2012
Average	23.1	29.8
Standard deviation	9.9	12.0
Median	21.5	28.8
Maximum	54.9	69.6
Minimum	6.8	9.2
98-Percentile	50.4	58.9
95-Percentile	43.9	50.9

### Emission sources

Diagnostic ratios indicated that the main observed sources were gasoline and diesel vehicles but

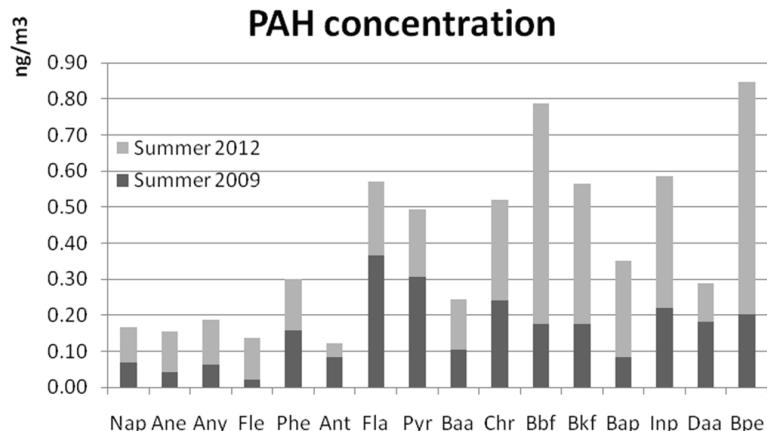


Figure 2. PAH concentrations in summer 2009 and 2012.

Table 2. Mean daily concentration ( $\text{ng}/\text{m}^3$ ) of PAH in  $\text{PM}_{10}$  in 2009 and 2012

PAH	Year	Data type				
		Mean	SD	Medain	Min	Max
Nap	2009	0.07	0.06	0.06	0.02	0.28
Naphthalene	2012	0.06	0.15	0.02	0.03	1.14
Ane	2009	0.05	0.06	0.02	0.02	0.30
Acenaphthalene	2012	0.07	0.27	0.02	0.02	1.97
Any	2009	0.07	0.07	0.03	0.02	0.26
Acenaphthene	2012	0.06	0.22	0.02	0.02	1.67
Fle	2009	0.03	0.03	0.02	0.02	0.10
Fluorene	2012	0.06	0.21	0.02	0.02	1.55
Phe	2009	0.16	0.10	0.19	0.03	0.31
Phenanthrene	2012	0.12	0.16	0.08	0.03	1.03
Ant	2009	0.08	0.06	0.11	0.03	0.22
Anthracene	2012	0.03	0.07	0.02	0.02	0.55
Fla	2009	0.37	0.90	0.13	0.02	6.43
Fluoranthene	2012	0.19	0.14	0.16	0.02	0.55
Pyr	2009	0.31	0.32	0.13	0.02	1.68
Pyrene	2012	0.18	0.13	0.17	0.02	0.54
Baa	2009	0.11	0.13	0.05	0.03	0.79
Benz(a)anthracene	2012	0.14	0.11	0.11	0.03	0.45
Chr	2009	0.24	0.23	0.18	0.02	1.48
Chrysene	2012	0.28	0.18	0.24	0.04	0.80
Bbf	2009	0.18	0.12	0.16	0.02	0.47
Benzo(b)fluoranthene	2012	0.61	1.42	0.36	0.07	10.80
Bbk	2009	0.18	0.13	0.16	0.02	0.58
Benzo(k)fluoranthene	2012	0.39	0.50	0.25	0.05	3.43
Bap	2009	0.09	0.07	0.06	0.02	0.32
Benzo(a)pyrene	2012	0.27	0.22	0.21	0.04	1.11
Inp	2009	0.22	0.26	0.15	0.02	1.38
Indeno(1,2,3-cd) pyrene	2012	0.36	0.57	0.23	0.02	4.04
Daa	2009	0.19	0.18	0.15	0.02	0.68
Dibenz(a,hl)anthracene	2012	0.09	0.16	0.06	0.02	1.16
Bpe	2009	0.21	0.16	0.19	0.02	0.68
Benzo(ghi)pyrene	2012	0.64	1.64	0.37	0.03	12.38
$\Sigma\text{PAH}$	2009	2.55	1.61	2.05	0.33	9.83
$\Sigma\text{PAH}$	2012	3.48	4.52	2.36	0.48	32.84

also some mixed open burning sources, *e.g.*, grass/coal/wood as well as other combustion sources. Table 3 shows the observed ratios of selected PAH, calculated for PAH bound on  $\text{PM}_{10}$ . Traffic as a dominant source of emissions is expected at an urban station in an area with high traffic density. The ratios of  $\text{Inp}/(\text{Bpe}+\text{Inp})$  were between 0.35–0.70, indicating that the potential sources of  $\text{PM}_{10}$  in the atmosphere are diesel (4,15) and other fuel combustion, and grass, coal and wood burning [39]. The ratios of  $\text{Baa}/\text{Chr}$  (0.28–1.2) and  $\text{Bap}/\text{Bpe}$  (0.3–0.78) indicate as well that one of the emission sources is the traffic – gasoline vehicles exhaust [15–17]. It is the similar in

observed period, 2009 and 2012. The value for  $\text{Fla}/(\text{Fla}+\text{Pyr})$  confirmed that gasoline [7,29,30,39] but also pyrogenic and grass/coal/wood combustion are important emission sources of  $\text{PM}_{10}$  in the atmosphere in summer.

Ratio of  $\text{Bap}/\text{Bpe}$  confirmed that beside traffic there was also a non-traffic source present near the sampling site during both sampling period (39). Diagnostic ratio of  $\text{Ant}/(\text{Ant}+\text{Phe})$  is above 0.1 especially for summer 2009, which is the value for wood combustion as a potential source emission of  $\text{PM}_{10}$  in air [30,32]. It is unusual for urban site where the traffic is expected as major emission source. These results

Table 3. Comparison of the ratios of selected particle-bound PAHs in the four campaigns

Ratio	Source and value	Ratios determined	
Inp/(Bpe+Inp)	Diesel: 0.35-0.70 [4,15] Pyrogenic: >0.2 [39] Petrogenic: <0.2 [39]	Summer 2009 0.52	Summer 2012 0.36
	Grass,coal,wood combustion: >0.5 [39] Fuel combustion: 0.2-0.5 [39]		
Baa/Chr	Gasoline: 0.28-1.2 [15-17]	0.43	0.51
Bap/Bpe	Coal: 0.9-6.6 [16] Vehicles: 0.3-0.78 [16]	0.42	0.41
Fla/(Fla+Pyr)	Coal: 0.53 [7] and >0.5 [29,30] Gasoline: 0.40-0.5 [30] Pyrogenic: >0.4 [39] Petrogenic: <0.4 [39]	0.54	0.52
	Grass,coal,wood combustion: >0.5 [39] Fuel combustion: 0.4-0.5 [39]		
Bpe/Inp	Diesel: 1.1 [29]	0.92	1.77
Bkf/Inp	Diesel: 0.5 [39]	0.80	1.07
Ant/(Ant+Phe)	Wood combustion: >0.1 [30,32] Pyrogenic: >0.1 [39] Petrogenic: <0.1 [39]	0.34	0.21
Baa/(Baa+Chr)	Pyrogenic: >0.35 [39] Petrogenic: <0.2 [39]	0.30	0.33
Bap/Bpe	Non traffic: <0.6 [39] Traffic: >0.6 [39]	0.42	0.41

could be indicating some local emission source near the sampling site. It is confirmed by PMF.

The results obtained using diagnostic ratios are in agreement with the results of the PMF [40] analysis. As input data to PMF we used 16 species of PAHs determined in 53 PM<sub>10</sub> samples in 2009 and in 55 samples in 2012 (both taken in non-heating season). Each PMF factor profile was compared with several source profiles reported in literature.

Between three and five factors were considered and optimal solutions of the PMF procedure. Three factors were extracted at the sampling site in both periods: 1) stationary sources (combustion of oil, coal, residential heating, thermal power plant, local industry), 2) traffic (diesel and gasoline vehicle exhaust) and 3) OBS-opening burning sources (mix of wood, and biomass burning, solid waste and grass burning). PMF factors contributions for a 3-factor solution in summer are shown in Figure 3.

**Factor 1.** Represents stationary sources such there are local industry and power generation and accounts for 38.8% (0.9 ng/m<sup>3</sup>) in 2009 and 38.7 % (1.3 ng/m<sup>3</sup>) of total PAHs in summer 2012. Main congeners are Fla, Baa, Ant, Pyr and Chr. Percentage contribution of this factor was almost the same for

summer 2009 and 2012. The influence of stationary sources was unchanged during observed periods.

**Factor 2.** The percentage contribution of this factor was 30.7% (0.7 ng/m<sup>3</sup>) in 2009 and 49.1% (1.6 ng/m<sup>3</sup>) in 2012. PAHs in Factor 2 are tracers for diesel and gasoline vehicle exhaust emissions. BbF and BkF are the highest loaded PAHs on this factor but Ane, Phe, Bbf, Bkf, Bap, Inp and Bpe are also present. Tracers that represent diesel exhaust emission are Nap, Flu, Phe, Ant, Flt, Pyr and Chr. Bbf and Bpe represent petrol exhaust emission. During the reporting period, a bridge across the Sava river (Ada Bridge) was built in this area [43]. The bridge crosses over the tip of Ada Ciganlija island and connects the municipalities of Čukarica and New Belgrade. Construction began in 2008, and the bridge was opened on January 1<sup>st</sup>, 2012. Traffic over the new bridge contributed to a higher traffic density in the vicinity of the sampling site. This is confirmed by higher percentage contribution of traffic source to PAH total in 2012 (Figure 4).

**Factor 3.** Represents mix of burning and combustion of grass/coal/wood as well as garbage and domestic waste. The percentage contribution of this factor to total PAH levels was 31.3% (0.7 ng/m<sup>3</sup>) in 2009 and 12.2% (0.4 ng/m<sup>3</sup>) in 2012 is coming from

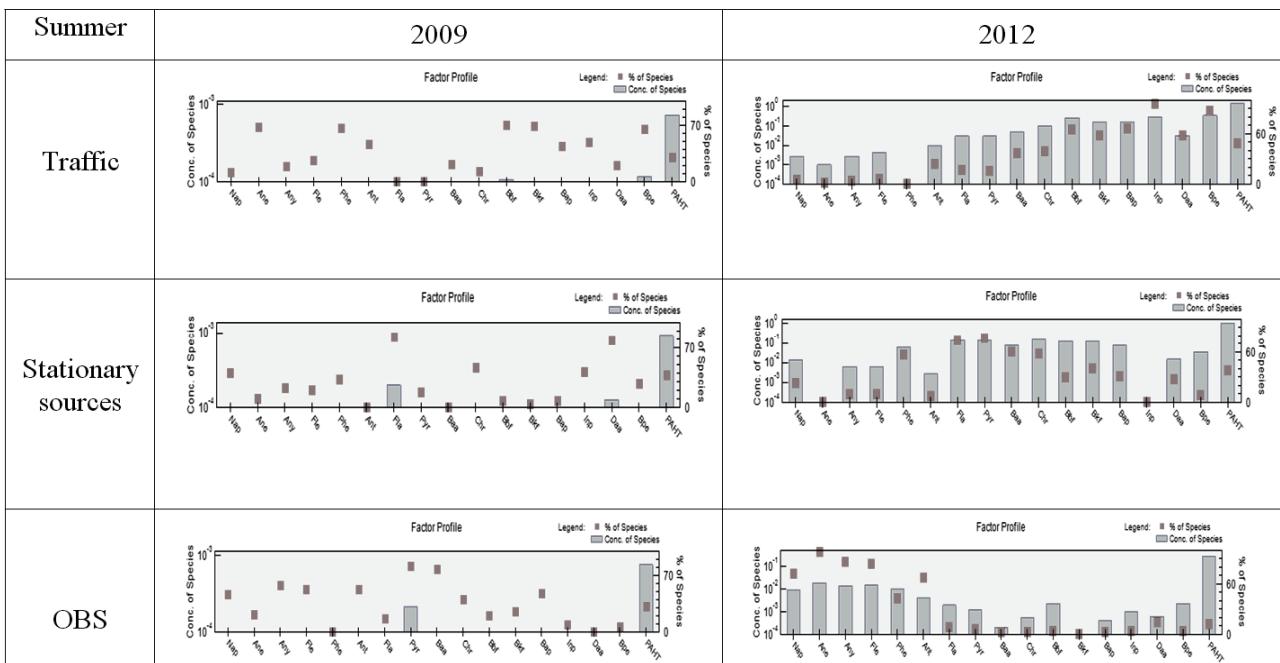


Figure 3. PMF factor contributions for a 3-factor solution, summer 2009 compared to summer 2012.



Figure 4. Percentage contribution of identified emission sources to the total PAHs.

this source. The main markers are as usual Nap, Ane, Any, Fle, Phe and Ant. High contribution of this factor is unexpected for the type of the sampling site and for the sampling period urban area in summer. The explanation could be a presence of the so-called "cardboard city", an informal settlement, or locally classified as unhygienic settlement, serving as an informal asylum in the capital of Serbia [44]. It was located in Belgrade's municipality of New Belgrade, less than 1 km from the sampling site. The inhabitants are supplied with electricity illicitly from a nearby public lighting (electricity in the resort was only at night when the city lights work). An overload of this illicit power connection causes occasional fires. The settlement was completely evicted and cleared in 2009 in connection with the erection of a nearby University Village Belville, home to all athletes participating at the 2009 Summer Universiade games. The Belville complex, completed in May 2009, consists of a

120,000 m<sup>2</sup> residential area, 34,800 m<sup>2</sup> commercial and business facilities comprising and 6,100 m<sup>2</sup> educational facilities. The complex also includes 22,000 m<sup>2</sup> of office space. In preparation for the Universiade, the complex caused displacement of part of the Roma population living in the nearby unhygienic settlements [45]. That is the likely reason for the decreasing contribution of Factor 3 and the same time increasing Factor 1 to total PAH levels in 2012. The ratio of Ant/(Ant+Phe) is much higher in the first period (0.40) than in the second (0.27), which indicates higher contribution of wood burning to total PAH prior to the removal of the settlement.

Relative contribution of the different factors is shown in Figure 4.

## CONCLUSION

The average concentrations of PM<sub>10</sub> are slightly higher in summer 2012 (29.8 µg/m<sup>3</sup>) than in 2009

( $23.1 \mu\text{g}/\text{m}^3$ ). PM-bound PAH follow the same trend as the PM indicating an increasing strength of PAH sources relative to all PM sources. The average concentrations for sum of 16 priority PAHs in  $\text{PM}_{10}$  fractions were  $2.55 \text{ ng}/\text{m}^3$  in summer 2009 and  $3.83 \text{ ng}/\text{m}^3$  in summer 2012.  $\text{PM}_{10}$  mean concentrations were slightly higher in 2012. Total PAHs mean concentrations were not significantly different ( $P < 0.05$ ), although Ant, Pyr and Daa mean values were significantly higher and Bba and BaP significantly lower in summer 2009 than three years later. Total PAHs in 2009 were 0.011% of  $\text{PM}_{10}$  but 0.013% in 2012. It was useful to estimate PAH emission profiles using diagnostic ratios to determine potential sources of PAH emissions to ambient air in the so-called New Belgrade. An analysis of the database by source apportionment technique using molecular markers confirmed the results. We identified three emission sources: 1) stationary sources, 2) traffic (diesel and gasoline vehicle exhaust) and 3) OBS-opening burning sources. Traffic was more intensive in 2012 than three years earlier while OBS was decreased between the two sampling periods. Although the influence of OBS factor decreased in 2012 in comparison with 2009 it may be underlined that the factor that represents opening burning sources (mix of wood, grass and domestic waste burning) persists over time and still contributes about 10% to total PAH bonded on  $\text{PM}_{10}$  in ambient air.

### Acknowledgements

This work was supported by the following projects and sponsors: WeBIOPATR (2006-2009) funded by the Research Council of Norway; III41028, INGEMAS (2011-2014) funded by the Ministry of Education, Science and Technological Development of Serbia (2011-2014) and Municipality of Belgrade, Secretary of Environmental Protection.

### REFERENCES

- [1] EEA, Air quality in Europe - 2013 report (2013), <http://www.eea.europa.eu/publications/air-quality-in-europe-2013> (last accessed February 2014)
- [2] Y. Tasdemir, F. Esen, Atm. Research **84** (2007) 1-12
- [3] EC Working Group on Polycyclic Aromatic Hydrocarbons, Ambient air pollution by polycyclic aromatic hydrocarbons (PAH), Position paper, EC/DG Environment, 2001
- [4] W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, B.R.T. Simoneit, Sci. Technol. **27** (1993) 636-651
- [5] W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, B.R.T. Simoneit, Sci. Technol. **27** (1993) 2700-2711
- [6] W. Wilcke, J. Grown, J. Plant Nutr. Soil Sci. **163** (2000) 229-248
- [7] E.J. Kim, J. Oh, Y.S. Chang, Sci. Total Environ. **311** (2003) 177-189
- [8] S.R. Wild, K.C. Jones, Environ. Pollut. **88** (1995) 91-108
- [9] J. Joksić, M. Radenković, A. Cvetković, S. Matić-Besarić, M. Jovašević-Stojanović, A. Bartonova, K.E. Yttri, Chem. Ind. Chem. Eng. Q. **16** (2010) 251-258
- [10] CEN, EN12341. Air Quality. Determination of  $\text{PM}_{10}$  Fraction of Suspended Particulate Matter. Reference Method and Field Test Particulate to Demonstrate Reference Equivalence of Measurement Methods, Brussels, 1998
- [11] EPA/625/R-96/010b, Compendium Method TO-13A, Center for Environmental Research Information Office of Research and Development, U.S. EPA, Cincinnati, OH, 1999, <http://www.epa.gov/ttnamti1/files/ambient/airtox/to-13arr.pdf> (last accessed February 2014)
- [12] M. Tobiszewski, J. Namieśnik, Environ. Pollut. **162** (2012) 110-119
- [13] M.S. Callen, J.M. Lopez, A. Iturmendi, A.M. Mastral, Environ. Pollut. **30** (2012) 1-9
- [14] J. Mantis, A. Chaloulakou, C. Samara, , Chemosphere **59** (2005) 593-604
- [15] N.R. Khalili, P.A. Scheff, T.M. Holsen, Atmos. Environ. **29** (1995) 533-542
- [16] M.F. Simcik, S.J. Eisenreich, P.J. Lioy, Atmos. Environ. **33** (1999) 5071-5079
- [17] N. Tang, T. Hattori, R. Taga, K. Igarashi, X. Yang, K. Tamura, H. Kakimoto, V.F. Mishukov, A. Toriba, R. Kizu, K. Hayakawa, Atmos. Environ. **39** (2005) 5817-5826
- [18] S.-U. Park, J.-G. Kim, M.-J. Jeong., B.-J. Song, Archives Environ. Contam. Toxicol. **60** (2010) 676-589
- [19] P.K. Hopke, K. Ito, T. Mar, W.F. Christensen, D.J. Eatough, R.C. Henry, E. Kim, F. Laden, R. Lall, T.V. Larson, H. Liu, L. Neas, J. Pinto, M. Stolzel, H. Suh, P. Paatero, G.D. Thurston, J. Exposure Anal. Environ. Epidemiol. **16** (2006) 275-286
- [20] J.G. Watson, J. Crow, J. Plant Nutr. Soil Sci. **163** (2004) 229-248
- [21] P. Hopke, A guide to Positive Matrix Factorization, 2001, [www.epa.gov/ttn/amtic/files/ambient/pm25/workshop/layer-men.pdf](http://www.epa.gov/ttn/amtic/files/ambient/pm25/workshop/layer-men.pdf) (last accessed February 2014)
- [22] Y. Bruinen de Bruin, K. Koistinen, Yli-Tuomi, S. Kephalopoulos, M. Jantunen, Report of European Commission, Bruxelles, 2006
- [23] P. Paatero, J. Comp. Graph. Stat. **8** (1999) 854-888
- [24] B. Srimuruganandam, S.M. Shiva Nagendra, Chemosphere **88** (2012) 120-130
- [25] U.M. Sofowote, H. Hung, A.K. Rastogi, J.N. Westgate, P.F. Deluca, Y. Su, B.E. McCarry, Atm. Environ. **45** (2011) 967-976
- [26] J.M. Lim, J.H. Lee, J.H. Moon, Y.S. Chung, K.H. Kim, Atmos. Res. **95** (2010) 88-100
- [27] J. Hu, C.Q. Liu, G.P. Zhang, Y.L. Zhang, Atmos. Res. **118** (2012) 271-279
- [28] M. Vestenius, S. Leppnen, P. Anttila, K. Kyllonen, J. Hatakka, H. Hellen, A.P. Hyvarinen, H. Hakola, Atmos. Environ. **45** (2011), 3391-3399

- [29] Z. Zencak, J. Klanova, I. Holoubek, Ö. Gustafsson, Environ. Sci. Technol. **41** (2007) 3850-3855
- [30] M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre, Org. Geochem **33** (2002) 489-515
- [31] A. Papageorgopoulou, E. Manoli, E. Touloumi, C. Samara, Chemosphere **39** (1999) 2183-2199
- [32] C.A. Pio, C.A Alves, A.C. Duarte, Atmos. Environ. **35** (2001) 1365-1375
- [33] I.G. Kavouras, P. Koutrakis, M. Tsapakis, E. Lagoudari, E.G. Stephanou, D.V. Baer, P. Oyola, Environ. Sci. Technol. **35** (2001) 2288-2294
- [34] I.G. Kavouras, J. Lawrence, P. Koutrakis, E.G. Stephanou, P. Oyola, Atmos. Environ. **33** (1999) 4977-4986
- [35] H. Budzenski, I. Jones, J. Bellocq, C. Pierad, P. Garriques, Mar. Chem. **58** (1997) 85-97
- [36] D.J.T. Smith, R.M. Harrison, Atmos. Environ. **30** (1996) 2513-2525
- [37] M. Akyüz, H. Çabuk, Sci. Total Environ. **405** (2008) 62-70
- [38] Y.K. Park, W. Kim, Y.M. Jo, Aerosol Air Qual. Res. **13** (2013) 1365-1372
- [39] R. Brandli, T.D. Bucheli, T. Kupper, J. Majer, F.X. Stadelmann, J. Taradellas, Environ. Pollut. **148** (2007) 520-528
- [40] C.K. Li, R.M. Kamens, Atmos. Environ. **27A** (1993) 523-532
- [41] <http://www.beoelektrane.rs/?p=208#more-208>
- [42] <http://www.imt.co.rs/>
- [43] [http://en.wikipedia.org/wiki/Ada\\_Bridge](http://en.wikipedia.org/wiki/Ada_Bridge)
- [44] Belgrade Municipality, <http://www.beograd.rs/cms/view.php?id=1453417> (last accessed February 2014)
- [45] [http://en.wikipedia.org/wiki/2009\\_Summer\\_Universiade](http://en.wikipedia.org/wiki/2009_Summer_Universiade) (last accessed February 2014).

A. CVETKOVIĆ<sup>1</sup>  
M. JOVAŠEVIĆ-STOJANOVIĆ<sup>2</sup>  
S. MATIĆ-BESARABIĆ<sup>1</sup>  
D.A. MARKOVIĆ<sup>3</sup>  
A.BARTOŇOVÁ<sup>4</sup>

<sup>1</sup>Gradski zavod za javno zdravlje,  
Beograd, Srbija

<sup>2</sup>Institut za nuklearne nauke Vinča,  
Univerzitet u Beogradu, Beograd,  
Srbija

<sup>3</sup>Fakultet za primenjenu ekologiju  
Futura, Beograd, Srbija

<sup>4</sup>NILU Norwegian Institute for Air  
Research, Kjeller, Norway

#### NAUČNI RAD

## POREĐENJE IZVORA EMISIJE POLICKLIČNIH AROMATIČNIH UGLJOVODONIKA (PAH) ADSORBOVANIH NA ČESTICE U TOKU NEGREJNE SEZONE 2009 I 2012 GODINE U BEOGRADU, SRBIJA

Izloženost povećanoj koncentraciji policikličnih aromatičnih ugljovodonika povezana je sa zdravstvenim problemima posebno sa kancerogenim i mutagenim efektima. Glavni izvori PAH u spoljašnjoj sredini su: stacionarni izvori od industrije (termoelektrane, spaljivanje otpada i lokalne industrije) i izvori iz domaćinstva, kao što su centralno grejanje, sagorevanje i piroliza uglja, ulja, gase, smeća, drveta ili organskih supstanci (dizel i naftni motori), sagorevanje biomase i poljoprivredne aktivnosti (otvoreno sagorevanje slame, pruća i strnjike). Cilj ove studije je bio da procene potencijalne razlike u nivou koncentracije PAH prisutnih u respirabilnim česticama ( $PM_{10}$ ), kao i njihove izvore emisije u periodu između kampanja u toku leta 2009 i 2012 na istom mernom mestu u urbanoj zoni Beograda. Merno mesto je reprezentativno kao mešovita stambena, poslovna i industrijska zona na Novom Beogradu, urbana zona koja se ubrzano razvija. Srednja koncentracija  $PM_{10}$  je blago povećana u 2012. u odnosu na 2009. PAH-ovi adsorbovani na respirabilnim česticama su pratili trend  $PM_{10}$  pokazujući povećano učešće u svim izvorima emisije čestica. Primenom receptorskog modelovanja, metode faktorske analize (PMF), identifikovana su tri izvora emisije: 1) stacionarni izvori, 2) saobraćaj (dizel i benzin iz izduvnih gasova vozila) i 3) lokalni otvoreni izvori sagorevanja (OBS). Analiza je potvrdila veći uticaj saobraćaja i manji OBS u leto 2012. u odnosu na 2009, zbog povećanog saobraćaja i odsustva lokalnog izvora emisije OBS (sagorevanje drveta, trave i otpada iz domaćinstva) u 2012. godini.

Ključne reči: izvori emisije zagadenja u urbanim regijama, monitoring, policiklični aromatični ugljovodonici, PMF.