Bull Environ Contam Toxicol (2012) 88:438–442
DOI 10.1007/s00128-011-0516-4

Polycyclic Aromatic Hydrocarbons at Different Crossroads in Zagreb, Croatia

Anica Šišović · Gordana Pehnec · Ivana Jakovljević · Martina Šilović Hujić · Vladimira Vađić · Ivan Bešlić

Received: 31 August 2011 / Accepted: 28 December 2011 / Published online: 5 January 2012

Abstract Polycyclic aromatic hydrocarbons (PAHs) were measured in the PM_{10} particle fraction collected at two different measuring sites in Zagreb, Croatia. In summer, concentrations of all PAHs at both sites were low. In winter, mass concentrations of all PAHs measured at southern site were much higher than those at north. Contents of all PAHs in the PM_{10} particle fraction were much lower in summer than that in the winter period. For example, average content of BaP in PM_{10} in summer was 2.26 ng/mg at site A and 4.17 ng/mg at site B, while in winter it was 34.72 and 46.69 ng/mg, respectively.

Keywords Air pollution · Benzo(a)pyrene · PM_{10} particle fraction · Urban

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion of fossil fuels and other organic materials. PAHs originate from a large variety of natural and industrial processes. In cities without industry, the main sources of PAHs are motor vehicles and residential heating (Srogi 2007). Contribution of PAH sources to the atmosphere will depend on a number of factors, including the emission rate of sources, geography and local weather conditions (Ravindra et al. 2008). Some studies have found that PAHs with two or three benzene rings exist in the vapour phase, while PAHs with more than five rings are primarily in the particulate phase; the latter then move into the soil, water, sediments and vegetation through dry or wet deposition (Possanzini et al. 2004; Srogi 2007). It is generally accepted that PAHs are preferentially bound to small particles (Srogi 2007; Ravindra et al. 2008). Some PAHs are mutagenic while some are carcinogenic and they should not be present in the air, or their concentrations should be the lowest possible (WHO 2000). More than 500 PAHs have been identified in the air but routine measurements include only up to 20 PAHs. Benzo(a)pyrene (BaP) is the most commonly measured PAH and it is used as an indicator of carcinogenic hazard in polluted environments.

This paper presents PAH mass concentrations measured in PM_{10} particles (particles with aerodynamic diameter less than 10 µm), at two different measuring sites in Zagreb, Croatia. Samples were collected on working days in summer and winter periods. The aim of the study was to find out in which part of the city and in which part of the year residents of Zagreb are exposed to higher concentrations of PAHs. Contents of PAHs in PM_{10} particle fraction and ratios of some PAHs were calculated in order to determine main pollution sources at both measuring sites.

Materials and Methods

Samples were collected at two measuring sites, located in different parts of Zagreb. Measuring site A was located in the northern low-rise residential part of Zagreb with a low population density, and modest traffic. House heating around site A is mostly on gas, but some households still use oil, wood or coal for heating and cooking. Site B was located in the southern part of the city near a busy crossroads, parking lot, and entrance to the underground garage. It is very populated area with buildings connected to district heating system. At both sites, twenty-four hour samples of PM_{10} particles were collected on quartz filters with

---

A. Šišović · G. Pehnec (✉) · I. Jakovljević · M. Šilović Hujić · V. Vađić · I. Bešlić
Institute for Medical Research and Occupational Health, Zagreb, Croatia
e-mail: gpehnec@imi.hr

a low volume PM_{10} Sven Leckel sampler from about 50 m^3 of air. The samplers were set at about 1.5–2 m above the ground, and about 10–20 m away from the road. Samples were taken only on working days in summer (July and August) and winter (November and December) of 2008. After collection, samples were wrapped in aluminium foil and kept in a deep freezer at −18°C until analysed. Concentrations of the PM_{10} fraction were determined gravimetrically by weighing on Mettler Toledo MX-5 microbalance, before placing the samples in deep freeze.

The analysis was performed using a Varian Pro Star high performance liquid chromatograph (HPLC) with a fluorescence detector and programmed changes in excitation and emission wavelength to optimize selectivity and sensitivity for individual PAH species (Šišovic and Fugaš 1991; Eiguren-Fernandez and Miguel 2003). PAHs were separated on a Varian stainless steel Pursuit 3 PAH column (100 × 4.6 mm). The mobile phase was a mixture of acetonitrile and water, and the flow rate was 0.5 mL/min. To prepare calibration curves, a commercial PAH standard was used (Supelco EPA 610 PAHs Mix). Standard working solutions were obtained by diluting the certified ones with Merck HPLC-grade acetonitrile. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo(a)antrazene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(ghi)perylene (BghiP), and indeno (1,2,3-cd) pyrene (Ind). The detection limit, which equalled the triple standard deviation of the lowest concentration included in the calibration curve, varied from 0.005 ng/μL for BaP to 0.008 ng/μL for BghiP. For every set of samples we performed two blank tests and no PAHs were detected. Quantification limit for PAHs in 500 μL of acetonitrile and 50 m^3 of air varied from 0.05 ng/m^3 for BaP to 0.08 ng/m^3 for BghiP. Recoveries of PAHs were determined by adding a standard amount of a known PAH to a blank filter. The average recoveries of all analyzed PAHs varied from 94.5% to 98%. The detailed procedure for the preparation of samples was described earlier (Šišovic and Fugaš 1991).

Results and Discussion

Table 1 shows average mass concentrations and other statistically important parameters of PAHs and PM_{10} particle fractions measured in two different parts of the city.

Table 1 Average mass concentrations and other statistically important parameters of PAHs (ng/m^3) and PM_{10} particle fractions (μg/m^3) measured in two different parts of the city

Measuring period	Site		PAH									PM_{10}
			Flu	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	Ind	
Summer	A (N = 34)	$C_{min.}$	0.002	0.001	0.002	0.013	0.004	0.008	0.014	0.019	0.012	8.5
		$C_{max.}$	0.041	0.030	0.064	0.116	0.169	0.099	0.115	0.098	0.108	54.9
		C	0.011	0.008	0.011	0.041	0.051	0.025	0.041	0.051	0.040	21.4
		STD	0.009	0.007	0.012	0.027	0.033	0.018	0.024	0.023	0.023	9.70
		SE	0.0015	0.0012	0.0020	0.0045	0.0056	0.0030	0.0042	0.0039	0.0040	1.689
	B (N = 34)	$C_{min.}$	0.003	0.001	0.001	0.019	0.024	0.010	0.012	0.019	0.012	1.9
		$C_{max.}$	0.053	0.041	0.087	0.178	0.674	0.166	0.441	0.623	0.377	67.3
		C	0.019	0.011	0.018	0.079	0.104	0.040	0.073	0.094	0.057	23.8
		STD	0.013	0.0009	0.0164	0.033	0.107	0.026	0.071	0.098	0.060	12.87
		SE	0.0022	0.0016	0.0028	0.0057	0.0183	0.0045	0.0122	0.0168	0.0103	2.207
	t		2.987	1.387	1.991	5.227	2.772	2.806	2.457	2.520	1.563	0.853
Winter	A (N = 34)	$C_{min.}$	0.018	0.014	0.110	0.180	0.173	0.083	0.158	0.101	0.162	19.2
		$C_{max.}$	2.324	1.990	3.658	4.278	3.337	1.847	4.028	3.777	3.789	65.1
		C	0.505	0.410	0.808	1.143	1.150	0.595	1.147	0.797	0.894	36.8
		STD	0.511	0.437	0.728	0.877	0.702	0.381	0.799	0.755	0.763	12.116
		SE	0.088	0.075	0.125	0.150	0.120	0.065	0.137	0.129	0.131	2.109
	B (N = 33)	$C_{min.}$	0.062	0.025	0.062	0.187	0.315	0.151	0.274	0.219	0.150	13.1
		$C_{max.}$	8.314	9.256	11.892	12.882	9.263	4.575	11.404	11.773	9.381	104.9
		C	1.336	1.252	2.250	2.873	2.462	1.208	2.762	2.395	2.279	55.6
		STD	2.062	2.225	2.746	2.924	1.961	0.993	2.557	2.439	2.100	24.831
		SE	0.359	0.387	0.478	0.509	0.341	0.173	0.445	0.425	0.365	4.323
	t		2.251	2.134	2.919	3.260	3.623	3.317	3.469	3.600	3.566	3.905

N number of samples, C_{min} minimum value, C_{max} maximum value, *C* arithmetic mean, *STD* standard deviations, *SE* standard error

Average mass concentrations of the PM$_{10}$ particle fraction in the summer at both sites were low and similar. At site A, the average concentration was 21.4 µg/m^3 and varied from 8.5 to 54.9 µg/m^3. At site B, the average concentration was 23.8 µg/m^3 and varied from 1.9 to 67.3 µg/m^3. Average concentrations of all measured PAHs were also low at both sites. They were all higher at site B, but it was not statistically significant for Pyr, BaA and Ind (Student *t* test, $p < 0.05$). The difference in PAH levels between sites was most pronounced for Flu, Chr and BkF ($p < 0.01$). Average mass concentration of BaP at site B was 0.073 ng/m^3 while at site A the average BaP concentration was 0.041 ng/m^3. Concentrations of BaP measured at the same sampling site ten years ago (Šišović et al. 2002) were very similar, the average concentration being 0.05 ng/m^3. Those BaP levels are comparable with levels measured in Spain (Callén et al. 2008). For example, average BaP mass concentrations in Zaragoza was 0.089 ng/m^3 during warm season, which is similar as in Zagreb on site B. Low concentrations of all PAHs in summer were caused by many factors, such as photochemical, thermal and chemical degradation of PAHs at higher temperatures (Ravindra et al. 2008). Higher concentrations of all PAHs at site B in summer may be a consequence of the sampling location (near a busy crossroads, parking lot, and entrance to the underground garage).

In winter, average mass concentrations of PM$_{10}$ particles at both sites were much higher than those in summer (Table 1). Average concentration of PM$_{10}$ at site A was 36.8 µg/m^3 (ranging from 19.2 to 65.1 µg/m^3), and was significantly lower than those at site B, where it was 55.6 µg/m^3 (ranging from 13.1 to 104.9 µg/m^3). Mass concentrations of all PAHs from both sites were much higher in winter than those in summer. Concentrations of all PAHs (except Flu and Pyr) were statistically significantly higher at site B ($p < 0.01$). Average mass concentration of BaP at site A was 1.147 ng/m^3 and ranged from 0.101 to 4.028 ng/m^3. Average concentration of BaP at site B was 2.762 ng/m^3, and ranged from 0.274 to 11.404 ng/m^3. Chr had the highest average concentration at site B, 2.873 ng/m^3. Concentrations of Chr, BbF and BaP at site A were the highest and very similar (about 1.145 ng/m^3). Comparing with the study of Callén et al. (2008), BaP concentrations in winter in Zaragoza were much lower (0.500 ng/m^3) than in Zagreb. In downtown Rome Possanzini et al. (2004) found that concentration of BaP in particulate phase was

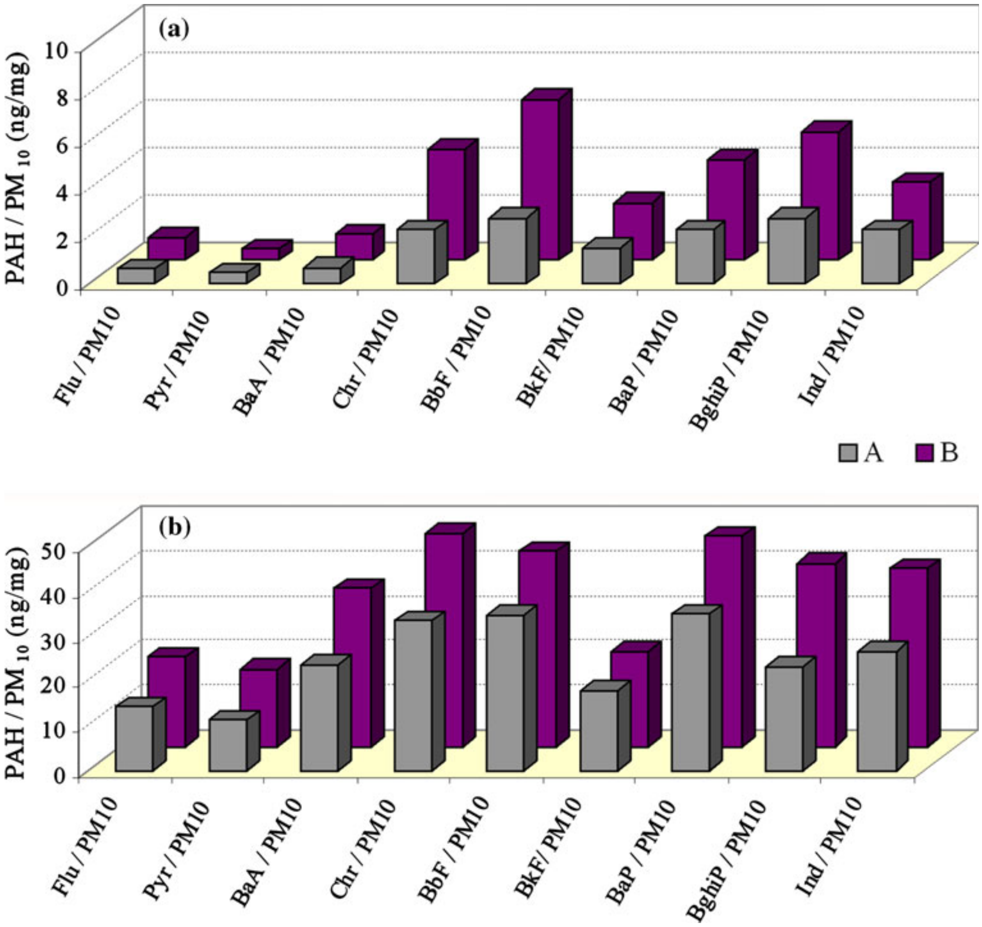

Fig. 1 Average PAH content in the PM$_{10}$ particle fraction (ng/mg) in summer (**a**) and winter (**b**) period

Table 2 Diagnostic ratios between some PAHs in PM_{10} (average ± standard deviation)

	Site	Flu/(Flu + Pyr)	BaP/BghiP	Ind/BghiP	Ind/(Ind + BghiP)	BaA/Chr	BaP/(BaP + Chr)
Summer	A	0.58 ± 0.18	0.79 ± 0.17	0.78 ± 0.19	0.43 ± 0.06	0.26 ± 0.10	0.51 ± 0.07
	B	0.65 ± 0.16	0.77 ± 0.15	0.64 ± 0.19	0.38 ± 0.07	0.21 ± 0.11	0.44 ± 0.09
Winter	A	0.53 ± 0.11	1.68 ± 0.15	1.22 ± 0.19	0.54 ± 0.07	0.67 ± 0.11	0.51 ± 0.09
	B	0.59 ± 0.09	1.25 ± 0.39	0.97 ± 0.18	0.49 ± 0.04	0.66 ± 0.17	0.51 ± 0.06

2.4 ng/m^3 in cold season, which is comparable with site B in Zagreb. Chr in downtown Rome was higher than in Zagreb at site B and it was 3.9 ng/m^3. Higher concentrations of PM_{10} and all PAHs at both sites in winter depended on the strength of the source (house heating, higher traffic intensity), and on weather conditions.

PAH contents in the PM_{10} particle fraction (ng/mg) were calculated for summer and winter period (Fig. 1). Average PAH contents in summer were low at both sites. They were higher at site B, but the difference was statistically significant only for Chr, BbF and BghiP ($p < 0.05$). Content of BbF was the highest at both sites; it was 2.74 ng/mg at site A, and 6.69 ng/mg at site B. Content of Pyr was the lowest at both sites; it was about 0.45 ng/mg. Average BaP content was 2.26 ng/mg at site A, and 4.17 ng/mg at site B. In winter, average PAH contents of all PAHs measured at both sites were much higher than those measured in summer. Contents of all PAHs were higher at site B, but only contents of Chr, BghiP and Ind were statistically significant at $p < 0.05$. Content of BbF and BaP was highest at site A, about 34.66 ng/mg. At site B, content of Chr was the highest, 47.46 ng/mg. Average BaP content at site A was 34.72 ng/mg. Average BaP content at site B was higher and was 46.69 ng/mg.

Ratios of some PAHs were calculated in order to determine the main pollution sources (Table 2). The ratio Flu/(Flu + Pyr) did not differ significantly between seasons and between locations ($p < 0.01$). According to the previous studies, the ratio Flu/(Flu + Pyr) between 0.2 and 0.5 is characteristic for exhaust gases, 0.4–0.5 for liquid fossil fuel (vehicle or crude oil) combustion, while >0.5 suggest coal, grass or wood combustion (Yunker et al. 2002; Zhang et al. 2004). Values about 0.60 found in this study are comparable with values from the study of Zhang et al. (2004) and Fu et al. (2010), and higher than those found by Kishida et al. (2008) in Hanoi. Ratio Flu/(Flu + Pyr) obtained in this study suggest that PAHs in particles in Zagreb originate not only from vehicle exhaust gases but also from coal and wood combustion. Ratio BaP/BghiP is used to distinguish traffic exhaust from coal combustion sources. Ratio between 0.3 and 0.4 indicates auto exhausts, 0.46–0.81 diesel combustion and 0.9–6.6 coal combustion, and it is usually higher in winter than in summer (Simcik et al. 1999; Fu et al. 2010). In Zagreb, ratio BaP/BghiP was about 0.77 in summer (traffic and diesel combustion) and it was much higher in winter (1.25–1.67) suggesting contribution from coal and wood combustion due to winter heating. Ratios Ind/BghiP and Ind/(Ind + BghiP) were higher in winter, and during both seasons they were higher at site A. The InP:BghiP ratio in gasoline exhaust is 0.4, whereas this ratio for diesel exhaust is approximately 1.0 (Moon et al. 2006). In Zagreb both sources contribute to PAH levels and diesel is more represented at site A. According to the study of Yunker et al. (2002) ratio Ind/(Ind + BghiP) <0.5 indicate petroleum combustion and <0.7 combustion of wood. Similar results were obtained for urban influenced samples Fraser River and Strait of Georgia (Yunker et al. 2002). Ratios BaA/Chr in Zagreb were three times higher in winter, and no difference between sites was found. Winter ratios correspond to vehicle and coke oven, and summer values to diesel and gasoline (Simcik et al. 1999). Finally, BaP/(BaP + Chr) was about 0.51 except for site B in summer (0.44). Values less than 0.33 indicates vehicle with catalyst, 0.49 gasoline, 0.73 diesel (Ravindra et al. 2008). At site B in summer gasoline is the main source, while at site A, and during the winter at both site there is higher contribution from diesel. During the winter wood and coal combustion contribute to PAH levels in the air at both sites.

PM_{10} particle fraction and PAH mass concentrations measured in the PM_{10} particle fraction in Zagreb, at both measuring sites show seasonal variations with higher concentrations in the winter. PAH concentrations at site B were about two times higher. Higher concentrations at site B may be due to the busy crossroads, parking lots and entrance to the garage. PAH content in PM_{10} particles was also higher in winter. Ratios of some PAHs indicate that PAHs originate mostly from traffic and diesel combustion, but also from wood and coal combustion, especially at residential part of the city.

References

Callén MS, de la Cruz MT, López JM, Murillo R, Navarro MV, Mastral AM (2008) Some inferences on the mechanism of atmospheric gas/particle partitioning of polycyclic aromatic hydrocarbons (PAH) at Zaragoza (Spain). Chemosphere 73: 1357–1365

Eiguren-Fernandez A, Miguel AH (2003) Determination of semivolatile and particulate polycyclic aromatic hydrocarbons in SRM 1649a and PM 2.5 samples by HPLC-fluorescence. Polycycl Aromat Compd 23:193–205

Fu S, Yang Z–Z, Li K, Xu X-B (2010) Spatial characteristics and major sources of polycyclic aromatic hydrocarbons from soil and respirable particulate matter in a mega-city, China. Bull Environ Contam Toxicol 85:15–21

Kishida M, Imamura K, Takenaka N, Maeda Y, Viet PH, Bandow H (2008) Concentrations of atmospheric polycyclic aromatic hydrocarbons in particulate matter and the gaseous phase at roadside sites in Hanoi, Vietnam. Bull Environ Contam Toxicol 81:174–179

Moon H-B, Kannan K, Lee S-J, Ok G (2006) Atmospheric deposition of polycyclic aromatic hydrocarbons in an urban and a suburban area of Korea from 2002 to 2004. Arch Environ Contam Toxicol 51:494–502

Possanzini M, Di Palo V, Gigliucci P, Scianò MCT, Cecinato A (2004) Determination of phase-distributed PAH in Rome ambient air by denunder/GC-MS method. Atmos Environ 38: 1727–1734

Ravindra K, Sokhia R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation: a review. Atmos Environ 42:2895–2921

Simcik FM, Eisenreich SJ, Lioy PJ (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos Environ 33:5071–5079

Srogi K (2007) Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ Chem Lett 5:169–195

Šišović A, Fugaš M (1991) Comparative evaluation of procedures for the determination of PAH in low-volume samples. Environ Monit Assess 18:235–241

Šišović A, Škrbec A, Vadjić V, Kalinić N, Hršak J (2002) PAH levels and profiles in the suspended particulate matter in Zagreb through four seasons. Environ Monit Assess 74:217–224

WHO Regional Office for Europe (2000) Air quality guidelines, 2nd edn. WHO, Copenhagen, Denmark

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33:489–515

Zhang Z, Huang J, Yu G, Hong H (2004) Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ Pollut 130:249–261