Road Traffic Effects in Size-Segregated Ambient Particle-Bound PAHs

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) in 13 size fractions of ambient particulate matter (PM) were investigated at three sites in Katowice, Poland. PM was sampled with two of the same type 13-stage low-pressure impactors (DEKATI). One of them was used first at a motorway shoulder in the spring of 2012, and then, in the summer, at a busy crossroads. The second impactor was used in parallel with the first one at an urban background site in both the seasons. The PAH contents in PM were determined by means of gas chromatography (Perkin Elmer). The ambient concentrations of PAHs from particular PM fractions at the urban background site differed insignificantly from those at the two traffic sites. Although the concentrations of PAHs and total PAHs (PAH) for some PM size fractions were higher at the urban background site, the significant influence of traffic emissions on the mass size distributions and concentrations of PAHs in Katowice was proved. For example, the traffic effects can be seen in the shares of the PM_1-bound PAH and some PM_1-bound PAHs in the concentrations of PM-bound PAH and these PAHs, visibly higher at the motorway and crossroads. Also, the mass size distributions of some PM-bound PAHs reflect the traffic influence on the ambient PAH concentrations within the whole city in summer. As the traffic emissions cause high concentrations of PM-bound BaP and BaA, these two PAHs probably pose the main health risk related with ambient PAH inhalation in non-heating periods in Katowice.

Key words: Polycyclic aromatic hydrocarbons, Car exhaust, Benzo[a]pyrene, Health hazard, Diagnostic ratios

INTRODUCTION

The hazard from the ambient particulate matter-bound (PM-bound) polycyclic aromatic hydrocarbons (PAHs) depends on the PAH concentrations in the air and in PM, their distribution among PM size fractions, and on the physicochemical properties of PM.

PAHs are the first air pollutants identified as carcinogens. The strength of their carcinogenicity grows with their molecular weight. However, it has not been known so far how the carcinogenicity of ambient PAHs (in the air occurring always as a mixture, never singly) can be ascribed to the concerted effects of some number of PAHs and what role the individual hydrocarbons play. However, some individual PAHs, e.g. benzo[a]pyrene (BaP), are of special importance in environmental toxicology. BaP is one of the most mutagenic and carcinogenic hydrocarbons (Durant et al., 1996; Ravindra et al., 2008). In humans, BaP penetrates the whole body, accumulates in lungs, liver, spleen, kidneys, heart, muscles, and bodily fat (Elovaara et al., 2007). It is used to define the toxic

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(carcinogenic) equivalence factor (TEF) and the carcinogenic equivalent (CEQ), the former for individual PAHs in relation to the TEF of BaP (TEF of BaP is assumed to be 1), and the latter for a PAH group as the linear combination of the TEFs and the ambient concentrations of PAHs from this group. TEF expresses the absolute toxicity of a particular PAH; CEQ expresses the carcinogenicity of a group of PAHs (Nisbet and LaGoy, 1992). The mutagenic equivalent (MEQ) or the TCDD-toxic equivalent (TEQ), proposed in Rogula-Kozłowska et al., (2013) by the authors of this study, are also useful in assessing the PAH mixture influence on human health.

PAHs originate from pyrolysis or pyrosynthesis. In general, each process involving heating or (incomplete) combustion of organic compounds can yield PAHs. The chemical industry (production of coal and oil derivatives) and the combustion of materials containing carbon are the most important sources of PAHs within urbanized areas (Kozielska and Konieczy ski, 2008; Ravindra et al., 2008; Tobiszewski

and Namie nik, 2012). The combustion of coal, waste or biomass in household ovens, waste incineration, and combustion of gasoline and diesel fuel in car engines are the PAH sources within any populated area (e.g. Ravindra et al., 2006; Brown and Brown, 2012).

In recent years, road traffic has become one of the major air pollution sources in urbanized regions all over the world. The influence of traffic emissions on PM consists mainly in enriching fine PM in carbon compounds, such as PAHs, clearly visible in the fine PM chemical composition (Gianini et al., 2012; Sánchez-Jiménez et al., 2012; Daher et al., 2014; Rogula-Kozłowska, 2015a; Kozielska et al., 2015).

Nevertheless, the knowledge on the influence of traffic emissions on the chemical composition of particular PM size fractions is still insufficient, the traffic effects on the finest (i.e. submicron, PM_1 and ultrafine, $PM_{0.1}$) PM fractions being not recognized almost at all.

In the presented study, 16 PM-bound PAHs in 13 PM size fractions were investigated for their ambient concentrations at three sites in an urban area. Two sites were under road traffic effect, one was an urban background site. The 16 investigated PAHs were as follows: naphtalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Ch), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[ah]anthracene (DBA) and benzo[ghi]perylene (BghiP). The influence of traffic emissions on the toxicity factor values of these 16 PAHs (CEQ, MEQ and TEQ) was also assessed.

MATERIALS & METHOD

PM was sampled at three sites in Katowice, a large city in an industrialized region in Southern Poland, Upper Silesia (Fig. 1). One of the sites, an urban background (UB; 2008/50/EC Directive), was located in a living district surrounded by greenbelts, about 2,000 m from the Katowice center, beyond the direct influence of the industrial and traffic emissions (the nearest road, with the traffic density of less than 2,500 cars per 24h, was about 150 m away). The two other sampling sites were directly exposed to traffic emissions, one (HW) was situated at a highway shoulder, the other one (CR) at a busy crossroads. The meteorological conditions at the three sites were typical of the region.

HW, on the shoulder of the A4 highway, was a traffic site located about 1,500 m south of the city center and 1,200 m northwest of UB. The average traffic density at HW was 30,000 cars per 24h. North of HW,

there was a living quarter, south of HW-an open area of the A4 highway; further behind A4 (about 300 m away from the sampling site), there were some public utilities and detached houses of another living quarter.

CR was a traffic affected site as well, located in the city center, in the vicinity of two busy crossroads and the largest in Katowice roundabout. The distance between CR and UB was about 2,500 m.

PM was sampled in the spring of 2012 at HW and in the summer at CR. In both periods PM was also sampled at UB, exactly in the same time as at HW in the spring and at CR in the summer (Table 1). There were 4 sample-takings at HW, 5 at CR, and 9 at UB. A single sample-taking lasted for about 1 week (142-173 h in the spring; 123-145 h in the summer). The selection of a spring-summer period for PM sampling allowed to avoid the overshadowing effects of the emissions from fuel combustion for energy production on road traffic emissions. In a heating period, fossil fuel combustion for energy production is the strongest source of PM (and of PM-bound organic compounds, including PAHs) in entire Southern Poland (Rogula-Kozłowska et al., 2013; Kozielska et al., 2015).

Table 1. Dates of sample-takings of PM in Katowice

Spring (HW-UB)	Summer (CR-UB)
13.03.2012-19.03.2012	26.06.2012-02.07.2012
27.03.2012-02.04.2012	17.07.2012-23.07.2012
18.04.2012-24.04.2012	31.07.2012-06.08.2012
18.05.2012-25.05.2012	14.08.2012-20.08.2012
	28.08.2012-03.09.2012

PM was sampled with two identical 13-stage DLPI impactors (Dekati Ltd., Kangasala, Finland; air flow 30 dm^3/min), one being first used at HW (spring), then moved to CR (summer), the second being used at UB in the whole spring-summer period, in parallel with the first one (Table 1). The impactors collected samples of 13 PM size fractions, $PM_{0.03-0.06}$, $PM_{0.06-0.108}$, $PM_{0.108-0.17}$, $PM_{0.17-0.26}$, $PM_{0.26-0.4}$, $PM_{0.4-0.65}$, $PM_{0.65-1}$, $PM_{1-1.6}$, $PM_{1.6-2.5}$, $PM_{2.5-4.4}$, $PM_{4.4-6.8}$, $PM_{6.8-10}$, PM_{10-40} (subscript indexes are the intervals of the particle aerodynamic diameters in µm, not disjoint), onto Whatman quartz fiber filters (GE Healthcare Bio-Sciences Corp.; Piscataway, NJ, USA; QMA; ø25 mm; CAT No. 1851-025).

The filters and impactors were prepared for exposure in a laminar air-flow chamber. The exposed filters were put into Petri dishes that in lightproof aluminum foil wrappings were stored in a freezer at -18°C until the analysis.

The amounts of PAHs in a sample of a PM size fraction collected during one sample-taking onto a single filter were far below the detection limits of the

method for PAH determination used. Therefore, collective samples of each PM size fraction were prepared, for each season two. For the spring, one collective PM size fraction was prepared from the four samples of this PM fraction taken at HW, and the second from the four parallel samples taken at UB. Analogously, two collective samples of a PM fraction for the summer were prepared using the five samples of this fraction taken at CR and the five parallel samples from UB. A collective sample of a PM fraction was prepared by putting together 1.5-cm² fragments of all the filters containing this PM fraction samples collected at the same site and season. The fragments were cut out from the filters just before the analysis. This way, for each season and each sampling site, 13 collective PM size fraction samples were received (52 PM samples in total). The remaining parts of the exposed filters were used to determine the ambient concentrations of elemental and organic carbon; the results are presented in Rogula-Kozłowska (2014).

The cumulative PM fraction samples were analyzed for the 16 PAHs. The extraction method, the chromatography technique, and the validation parameters of the analyses are described in Rogula-Kozłowska et al. (2013) and Kozielska et al. (2015).

Three coefficients were computed that express the health hazard from the mixture of the 16 PAHs (PAH): carcinogenic equivalent (CEQ), mutagenic equivalent (MEQ), and TCDD-toxic equivalent (TEQ). The methods for their computing are given in Rogula-Kozłowska et al. (2013).

RESULTS & DISCUSSION

The analyses of the cumulative PM size fraction samples gave the average concentrations of the 16 PAHs from the 13 PM fractions in the spring and the summer of 2012 at HW, CR, and UB in Katowice (Table 2 and in Fig. 2-3).

The fractionated PAH concentrations in the spring were between about 0.15 and 3.6 ng/m³ at HW, and between about 0.2 and 3.6 ng/m³ at UB. At CR and UB in the summer they were much lower than at HW and UB in the spring, the PAH concentrations even two times. The reduction of the PAH ambient concentrations at the background site (UB) by half relative to the spring ones was a surprisingly strong effect of weakening of the road traffic in Katowice in the summer holiday.

In the spring, Na, Fl, Py, BaA, Ch and BaP were detected in all the PM fractions at both HW and UB; Flu was found in neither one at UB. The mass shares of the 16 PAHs bound to PM_1 in their total masses in PM were between 35 (Pyr) and 100% (Ace) at HW and between 30 (BaP) and 87% (DBA) at UB. The shares of PM_1-bound PAH in PM-bound PAH were 53 and 45% at HW and UB, respectively. The highest ambient fraction-bound PAH concentrations were those of PAH bound to $PM_{0.4–0.65}$, $PM_{0.65–1.0}$, and $PM_{1.0–1.6}$, at both HW and UB (Fig. 2).

Fl, Py, BaA, Ch and BaP were found in all the 13 PM fractions at both CR and UB in the summer; Ace and An were found in neither fraction at neither of the
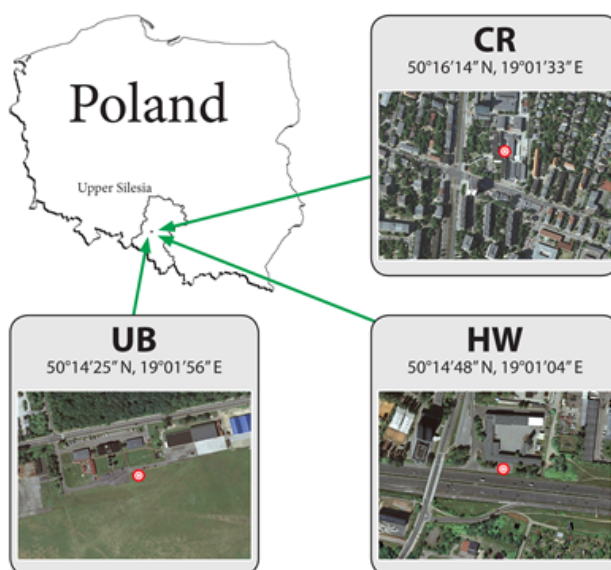

Fig.1. Location of the sampling sites in Katowice

Table 2. Mean ambient concentrations of 13 PM fractions-related PAH at HW and UB (13 March - 19 June 2012) and at CR and UB (20 June - 3 September 2012)

Fraction (µm)	Site	PAH, ng/m³ 13 Mar -19 Jun 2012	PAH, ng/m³ 20 Jun - 3 Sep 2012
0.03-0.06	HW/CR	0.253	0.221
	UB	0.300	0.278
0.06-0.108	HW/CR	0.384	0.147
	UB	0.203	0.302
0.108-0.17	HW/CR	0.167	0.318
	UB	0.273	0.297
0.17-0.26	HW/CR	0.350	0.274
	UB	0.333	0.492
0.26-0.40	HW/CR	0.615	0.683
	UB	0.514	0.660
0.40-0.65	HW/CR	2.363	1.772
	UB	2.892	1.554
0.65-1.0	HW/CR	3.575	2.218
	UB	2.411	2.030
1.0-1.6	HW/CR	2.223	0.474
	UB	3.641	0.577
1.6-2.5	HW/CR	1.568	0.357
	UB	0.945	0.301
2.5-4.4	HW/CR	1.670	0.286
	UB	2.461	0.286
4.4-6.8	HW/CR	0.883	0.225
	UB	0.696	0.545
6.8-10.0	HW/CR	0.154	0.070
	UB	0.281	0.179
> 10.0	HW/CR	0.380	0.082
	UB	0.289	0.120
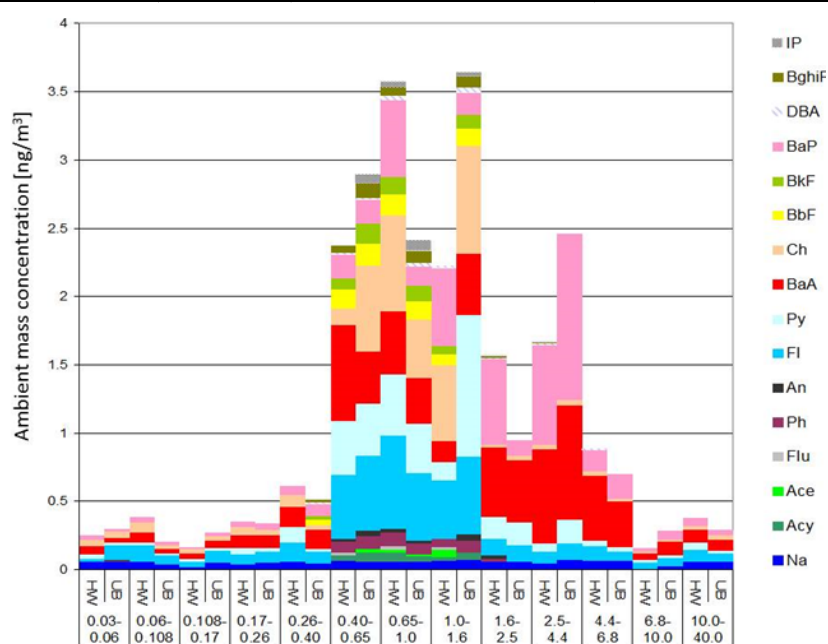
Fig. 2. Mean ambient concentrations of 16 PAHs bound to 13 PM fractions at HW and UB (13 March - 19 June 2012)

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two sites. The PM_1-bound PAH made 79% and 74% of the PM-bound PAH mass at CR and UB, respectively. For all the 16 PAHs, the masses of their PM_1-bound parts were from 0 (BbF and BkF) to 100% (Acy, Flu, Ph, DBA and BghiP) of their total masses in PM at CR, and from 55% (BbF) to 100% (Flu, DBA and BghiP) at UB. At both CR and UB, the highest ambient concentrations of fraction bound PAH and most PAHs were the $PM_{0.4–0.65}$-, and $PM_{0.65–1.0}$-bound ones (Fig. 3).

The ambient PM-bound PAH concentrations were higher at UB than at both HW and CR (spring-summer). However, the main source of traffic emissions, car exhaust, releases mainly fine and ultra-fine particles (Kittelson, 1998; Maricq, 2007), and the road traffic related PAHs at the road traffic affected sites occur as the compounds adsorbed to these particles (Zhu et al., 2008, Ringuet et al., 2012b). So, not surprisingly, the clear effects of traffic appeared at HW and CR in the PM_1-bound PAH ambient concentrations and the ratios of the PM_1-bound PAH mass to the masses of PM-bound BaA and BaP (traffic emission markers; Hu et al., 2012; Callén et al., 2011), much higher than at UB. Therefore, regardless of its ambient concentrations, the PM-bound PAHs at traffic sites, such as HW and CR, can pose greater health hazard than those at the sites similar to UB, beyond road traffic influence, because at traffic sites PAHs are bound to very fine particles that are capable of penetrating into deep regions of the human respiratory system. This health hazard can be still greater during rush hours. In Silesian cities, during rush hours, the $PM_{2.5}$-bound PAH concentrations exceed 100 ng/m³ (Kozielska et al., 2013).

Coarser particles, PM_{1-10}, contained more PAHs at UB than at HW in the spring and at CR in the summer. At UB, the mass share of PM_{1-10} in PM is probably higher than at both HW and CR, where traffic is the major pollution source. It is also possible that at UB, located within a residential area, great parts of PM and PM-bound PAHs come from municipal sources even in summer (combustion of wood, coal and waste in household ovens; biomass combustion in gardens and garden lots; Rogula-Kozłowska, 2014; 2015a). Such emissions contain large particles (soot/salt agglomerates) that adsorb all types of pollutants, particularly organic (Rogge et al., 1993; Pöschl, 2005). At UB, Py and Ch (Fig. 2 and 3), coal and biomass combustion markers (Harrison et al., 1996; Ravindra et al., 2008), had high mass shares in PM_{1-10}-bound PAH; these shares were higher than at HW and CR. Also $PM_{0.17-0.26}$-, $PM_{0.4-0.65}$-, and $PM_{0.65-1}$-bound Py and Ch had higher ambient concentrations at UB than at HW and CR. However, the simple PAH source identification by computing molecular diagnostic ratios points to traffic emissions shaping the ambient PAH concentrations not only at HW and CR, but also at UB (Table 3), and most probably these emissions came from gasoline car engines.

In the spring, the mass size distributions of the PAHs at HW differed significantly from those at UB. At HW, most of the PAH mass size distributions were
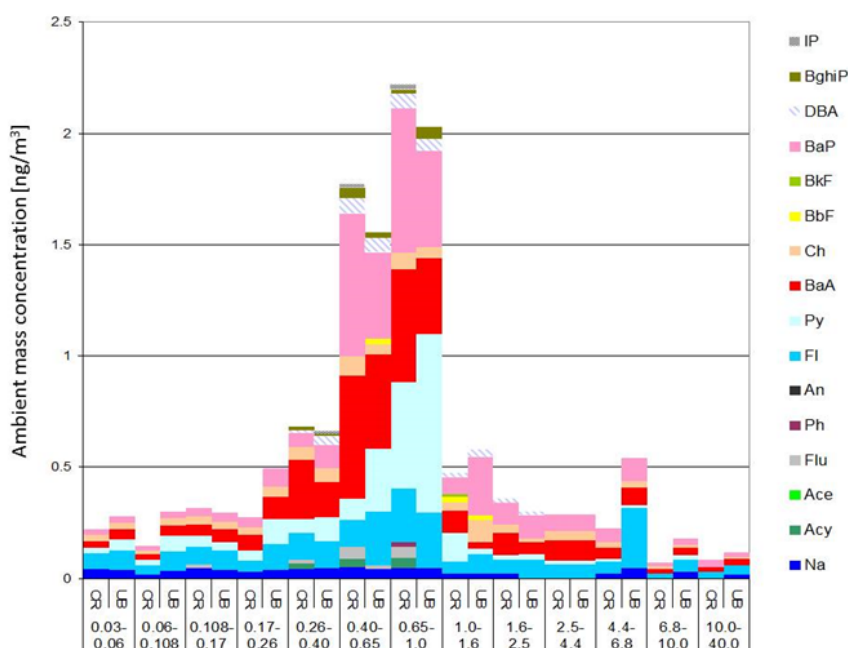

**Fig. 3. Mean ambient concentrations of 16 PAHs bound to 13 PM fractions at CR and UB
(20 June - 3 September 2012)**

bi- or trimodal, two modes usually being ultrafine or fine. The absolute maxima of the distribution density functions occurred in the interval of the particle diameters smaller than 1 µm. The maxima within greater particle diameters were much lower. Most of the PAHs had also a local maximum in the interval of diameters smaller than 0.1 µm (Fig. 4).

At UB, the PAH distribution density functions had their maxima in the interval of the particle diameters smaller than 2.5 µm; most of them and PAH had also the maxima between 2.5 and 10 µm. Like the distributions at HW, they were bi- or trimodal. However, the bimodal distributions at UB not always had maxima within the smallest diameters.

In the summer, on the contrary, the mass size distributions of particular PAHs at UB were very similar to those at CR. The maxima of the distribution density functions between 2.5 and 10 µm, occurring in the spring for most PAHs at HW and UB, occurred for all PAHs and PAH at both CR and UB, but the summer ones were much lower (Fig. 5). Also, the differences between these maxima at CR and at UB for particular PAHs and PAH (the summer) were lower than those between the maxima at HW and at UB (the spring). The maxima of the density functions in the interval of diameters smaller than 0.1 µm, occurring for PAH and some PAHs at CR and lacking at UB, are the only essential difference between the PAH mass size distributions at CR and UB. This similarity of the PAH distributions at such different sites in the summer may be attributed to the unfavorability of the ambient conditions to diversification of the sizes of the particles on which PAHs condense (Dvorská et al., 2011). Also, the summer lowering of municipal PAH emissions may

have allowed for prevalence of more evenly distributed ambient traffic PAHs.

The differences in the PAH concentrations between the sites were very small, slightly higher PAH concentrations were observed at UB in both of the seasons. On the other hand, the density functions of the mass size distributions of some PAHs at HW and CR had maxima in the interval of particle diameters smaller than 0.1 µm, what did not occur at UB and can be attributed to ultrafine particles of soot containing PAHs and freshly emitted by car engines (Cadle et al., 1999; Maricq, 2007). They can stay in their primary form for very short time, especially in urban areas. They quickly form large soot agglomerates (Fujita and Ito, 2002) or increase their size by adsorbing various compounds to their developed surfaces (Mikhailov et al., 2006; Levitt et al., 2007). They cannot reach UB as such from distant sources, they must be local. Such small primary particles from distant sources reached UB as secondary big particles, enriching the coarser PM fractions with PAHs. Ambient gaseous PAHs (2-, 3- and some 4-ring) at UB, particularly in the summer, were most probably adsorbed to the coarse particles, both directly at UB or earlier on the way to UB. In the spring, the individual residential heating still continued and biomass burning in gardens already started. Such a combustion releases large amounts of unburnt carbon and particles of salts and minerals into the air (Rogula-Kozłowska et al., 2013; Rogula-Kozłowska, 2014).

The ambient PM-bound BaP concentrations in Katowice at UB (not effected directly by traffic), HW and CR (both directly affected by traffic), are higher than elsewhere in the world except for some Asian sites (Rogula-Kozłowska, 2015b). However, the ambient PM-

Table 3. PAH diagnostic ratios for various emission sources and at HW, CR, and UB in Katowice

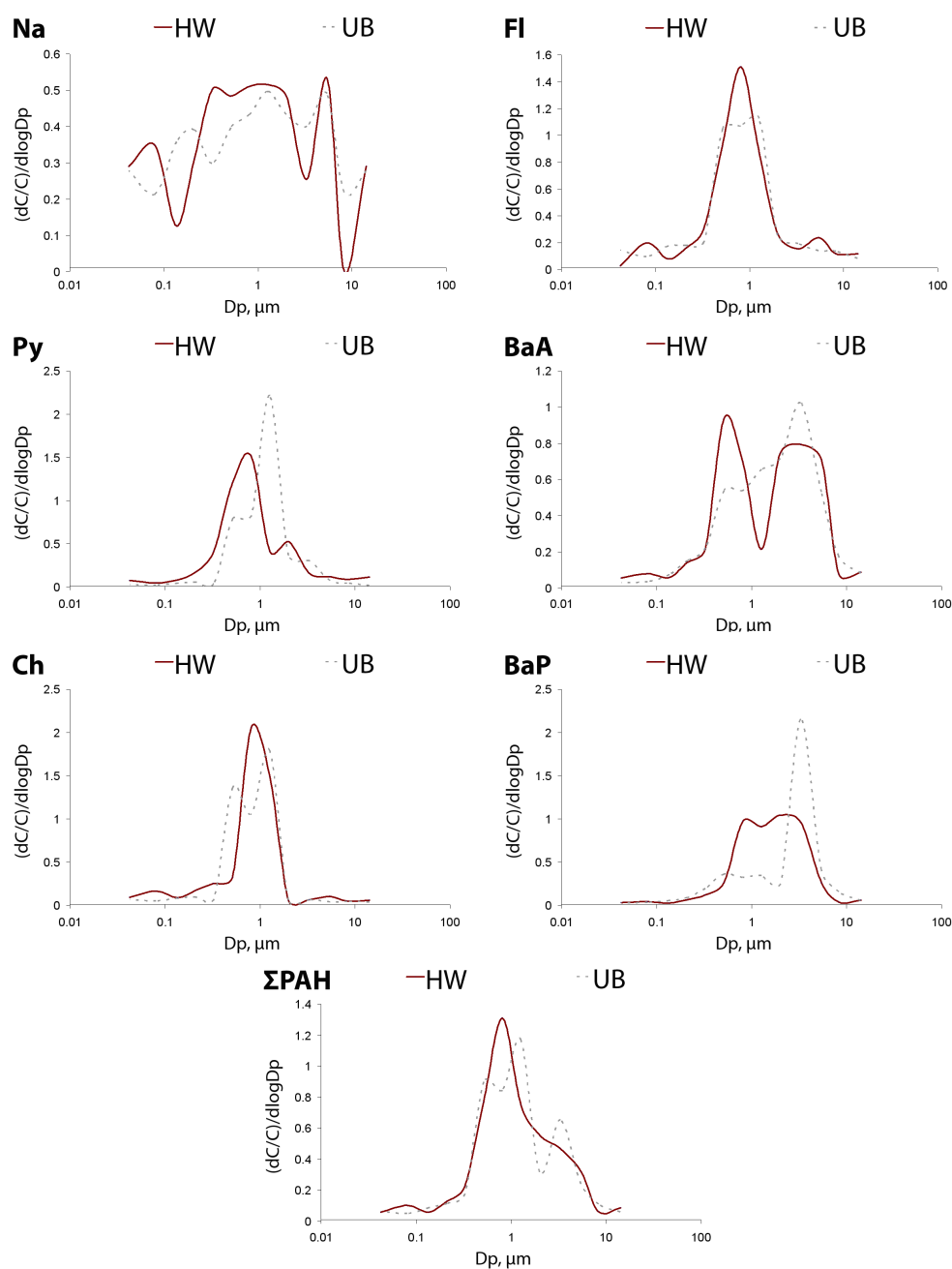| Ratio	HW/UB	CR/UB	Range	Source Type	Reference
Flu/(Flu+Py)	0.05/–	0.12/0.01	< 0.5	Petrol emissions	Tobiszewski and
			> 0.5	Diesel emissions	Namie nik (2012) and
Fl/(Fl+Py)	0.61/0.52	0.52/0.51	0.4-0.5	Liquid fossil fuels	references therein
BaP/BghiP	22.68/7.69	22.59/22.61	< 0.6	Non-traffic emissions	
			> 0.6	Traffic emissions	
IP/(IP+BghiP)	0.27/0.37	0.31/0.15	0.2-0.5	Petroleum combustion	
BaA/(BaA+Ch)	0.66/0.60	0.79/0.75	> 0.35	Vehicular emissions	
BaP/(BaP+Ch)	0.63/0.51	0.79/0.77	0.5	Diesel	Khalili et al., 1995
			0.73	Gasoline	
BaA/BaP	1.15/1.45	1.03/0.88	0.5	Gasoline	Li and Kamens, 1993
			1	Diesel	
IP/BghiP	0.36/0.58	0.45/0.17	< 0.4	Gasoline	Caricchia et al., 1999
			~ 1	Diesel	

Fig. 4. Mass size distributions of the PM-bound PAHs at HW and UB (13 March -19 June 2012)

bound PAH concentrations at HW and CR are close to or even lower than at other traffic affected locations (Rogula-Kozłowska, 2015b). The high ambient BaP concentrations in Southern Poland cities, including Katowice, are due to high municipal emissions and to much higher than elsewhere in Europe emissions from industry and power production from hard and brown coal. The PM-bound PAH concentrations in Southern Poland cities are very high only in a heating season, the BaP ones the whole year (Kozielska et al., 2015; Rogula-Kozłowska, 2015b), and even such a strong traffic emission source as the motorway in Katowice

cannot elevate PM-bound PAH concentrations to levels much higher than elsewhere. However, road traffic adds significantly to the ambient concentrations of some PAHs, including BaP, but first of all it increases the PM_1-bound BaP share in total PM-bound BaP, making the hazard from PM at traffic affected sites, such as HW or CR, greater than at sites such as UB, beyond the direct traffic impact.

The risk indicators (carcinogenic equivalent (CEQ), mutagenic equivalent (MEQ), and TCDD-toxic equivalent (TEQ)) computed for the Polish traffic sites
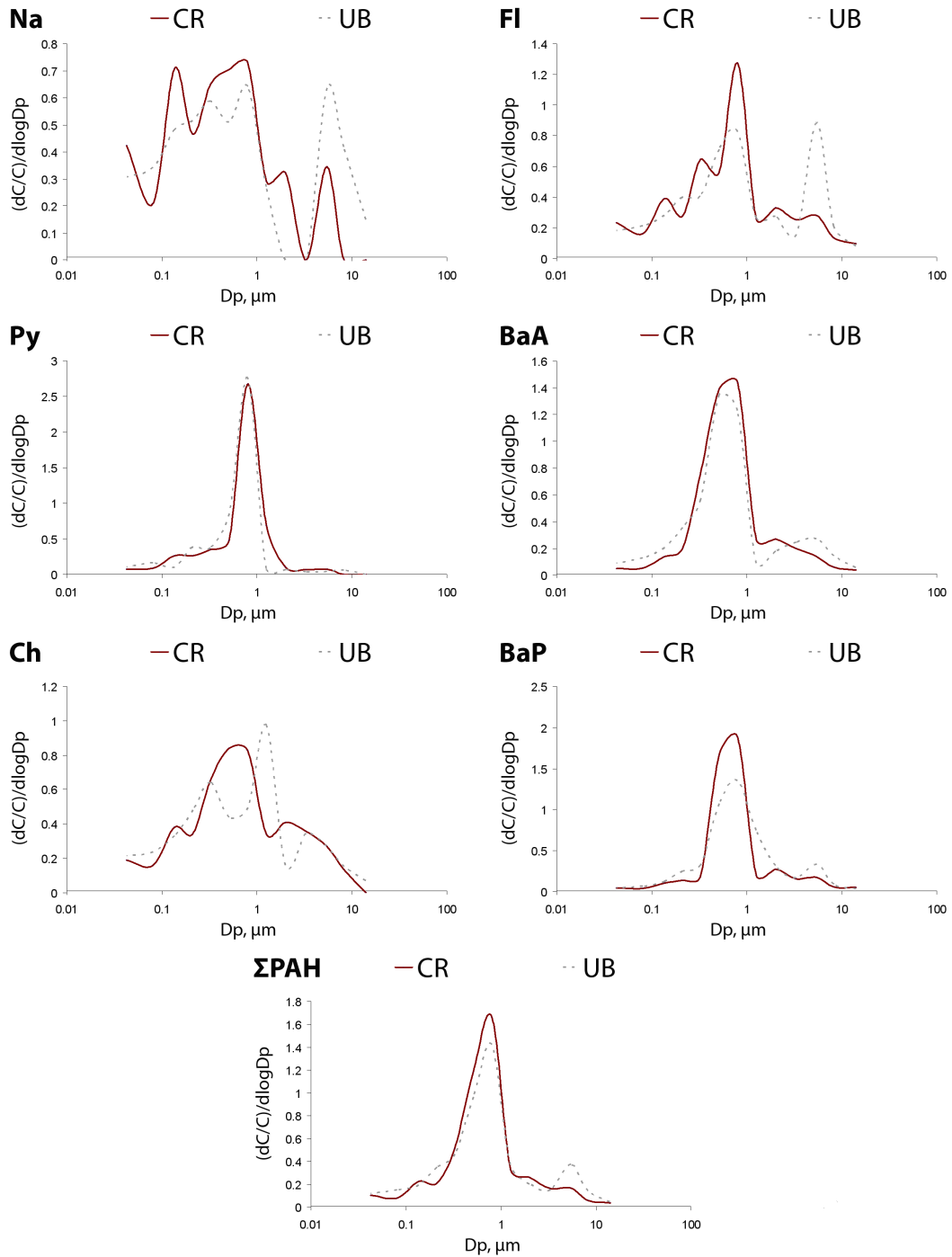
Fig. 5. Mass size distributions of the PM-bound PAHs at CR and UB (20 June - 3 September 2012)

are higher than almost all the other indicators (except for Delhi in India and Oporto in Portugal; Table 4), regardless of the PAH concentrations. The health hazard from ambient PM-bound PAH at the Polish traffic sites is great. Moreover, it has not changed for quite a long time because the risk indicators for HW and CR in 2012 are similar to the indicators calculated for Zabrze and Ruda l ska based on data from 2005 (Kozielska et al., 2013).

PM-bound PAHs pose a great health hazard in Polish cities independently of a season in the year. However, really big risk indicators are computed using data coming (at least partially) from a heating period (Katowice, urban traffic 2009-2010). In non-heating periods, the indicators are still high, but much lower and mostly due to traffic emissions. The ambient BaP background concentrations are high all over Poland, mainly because of combustion of solid fossil fuels for

Table 4. Mean ambient concentrations of PM_1- and PM_{10}-bound PAH and mean values of the three risk indicators (CEQ, MEQ and TEQ) at HW, CR, UB and in some other regions under the strong traffic emission influence

Location	Period		Fraction	PAH	[a]CEQ ng/m³	[b]MEQ	[c]TEQ pg/m³	References
Atlanta, USA	Jan-Mar 2004		PM$_{2.5}$	1.94	0.48	0.53	2.19	Li et al. (2009)
	Oct-Dec 2004			3.33	0.90	0.97	3.52	
Delhi, India	Winter 2007		PM$_{10}$	81.50	59.75	20.07	106.42	Singh et al. (2011)
	Summer 2007/2008		PM$_{10}$	33.10	23.09	7.87	42.82	
Oporto, Portugal	Winter 2008		PM$_{10}$	13.48	22.58	3.31	16.74	Slezakova et al. (2010)
Oporto, Portugal	2008		PM$_{10}$	20.79	12.34	4.98	23.85	Slezakova et al. (2011)
Paris, France	Day	IX	PM$_{10}$	6.71	0.28	0.31	1.22	Ringuet et al. (2012a)
	Night	2010		7.05	0.36	0.43	1.68	
Florence, Italy	Cold	2009 -	PM$_{2.5}$	10.15	5.43	2.17	11.79	Martellini et al. (2012)
	Warm	2010		4.99	1.54	0.54	3.47	
Madrid, Spain	Summer 2009		PM$_1$	0.70	0.12	0.09	0.43	Mirante et al. (2013)
	Winter 2009			4.1	0.51	0.51	2.55	
Zagreb, Croatia	Summer 2007		PM$_{10}$	0.49	0.10	0.14	0.56	Šišovi et al. (2012)
	Winter 2008			18.82	3.64	4.91	16.12	
Zabrze, Poland	Jun-Aug 2006		PM$_{2.5}$	12.3	1.48	1.9	10.29	Kozielska et al. (2013)
Ruda 1 ska, Poland				17.6	1.57	0.87	6.62	
Katowice, Poland	H	Mar-Jun 2012	PM$_1$	7.71	1.75	1.23	264.18	This study
	W		PM$_{10}$	14.20	4.16	3.54	413.93	
	UB		PM$_1$	6.93	1.80	0.85	318.59	
			PM$_{10}$	14.95	4.22	2.87	503.85	
	CR	Jun-Sep 2012	PM$_1$	5.63	2.06	1.69	96.06	
			PM$_{10}$	7.05	2.43	2.06	127.98	
	UB		PM$_1$	5.61	1.63	1.29	87.38	
			PM$_{10}$	7.49	2.24	1.91	122.81	

[a]carcinogenic equivalent

power production (Rogula-Kozłowska et al., 2013; Rogula-Kozłowska, 2014); in non-heating periods road traffic maintains PM-bound BaP ambient concentrations in Polish cities high (Fig. 2 and 3).

CEQ=0.001×[Na]+[Acln]+[Acn]+[Flu]+ [Phen]+[Flt]+[Pyr])+0.01×([An]+[Ch]+[BghiP]) +0.1×([BaA]+[BbF]+ [BkF]+[IP])+1×[BaP]+5× [DahA]; values 0.001, 0.01, 0.1 and 1 are the toxic equivalence factors (TEF) for specific PAHs, taken from Nisbet and LaGoy (1992); [b]mutagenic equivalent MEQ=0.00056×[Acnl]+0.082×[BaA]+ 0.017×[Ch]+0.25×[BbF]+0.11×[BkF]+1×[BaP]+0.31×[IP] +0.29×[DahA]+0.19×[BghiP]; values 0.00056, 0.082, 0.017, 0.25, 0.11, 1, 0.31, 0.29, 0.19 and 0.01 are the minimum mutagenic concentrations (MMC) for specific PAHs, taken from Durant et al. (1996); [c]TCDD-toxic equivalent TEQ=0.000025×[BaA]+0.00020×[Ch]+ 0.000354×[BaP]+0.00110×[IP]+0.00203×[DahA]

+0.00253×[BbF]+0.00487×[BkF]; values 0.000025, 0.00020, 0.000354, 0.00110, 0.00203 and 0.00487 are TCDD-TEF, i.e., toxic equivalency factor related to 2,3,7,8-tetrachlorodibenzo-p-dioxin TCDD (for TCDD, TEF = 1.0) for specific PAHs, taken from Willet et al. (1997); [x] denotes the ambient concentration of the substance x (in proper units)

CONCLUSIONS

In the spring 2012, in Katowice, Poland, the ambient concentrations of PAH bound to 13 PM size fractions were relatively low, they did not exceed 15 μg/m³ at the big highway and were no more than a half of this at the crossroads in the summer 2012 (holiday time). In general, they did not differ from those measured in these periods at the urban background site, although the PM$_1$-bound PAH concentrations were slightly higher at the two traffic sites.

The mass size distributions for selected PM-bound PAHs point to the traffic emissions as the main PAH source at the crossroads in Katowice in summer. There are no significant traffic-generated differences in the mass size distribution of the PM-bound PAHs between the urban background site and the crossroads. In the spring 2012, the differences in the mass size distributions of PAH and of some PAHs between the highway and the urban background site were big. The car exhaust was the main source of the ambient PM-bound PAHs only at the highway, at the urban background site most of the PAHs were adsorbed to big PM particles coming probably from combustion of solid fossil fuels. A part of the ambient PAHs could also originate from this combustion.

The health hazard from the ambient PAH at the traffic sites in Katowice was high, higher than at similar sites worldwide. Despite high background BaP concentrations, due to high municipal and industrial emissions (compared to other European cities, very clearly observed in heating periods), the high health hazardousness of PAHs in Katowice was evidently due to traffic, which maintains high ambient PM-bound BaP concentrations in Polish cities also in non-heating periods. In Katowice, the health risk indicators computed for PM-bound PAH at the highway in the spring and at the crossroads in the summer did not significantly differ from those at the urban background site in both seasons. In the non-heating period, these indicators depended mainly on traffic emissions, what means elevated health hazard from traffic emissions to traffic participants in rush hours.

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