

## Selected Organic Compounds in Fine Particulate Matter at the Regional Background, Urban Background and Urban Traffic Points in Silesia (Poland)

Kozielska, B.<sup>1\*</sup>, Rogula-Kozłowska, W.<sup>2</sup> and Klejnowski, K.<sup>2</sup>

<sup>1</sup>Department of Air Protection, Silesian University of Technology, 2 Akademicka St., 44-100 Gliwice, Poland

<sup>2</sup>Institute of Environmental Engineering, Polish Academy of Sciences, 34 M. Skłodowskiej-Curie St., 41-819 Zabrze, Poland

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**ABSTRACT:** Suspended particles with aerodynamic diameters not greater than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) were sampled at the urban background, regional background and urban traffic points in southern Poland. In total, 120 samples were collected between 2<sup>nd</sup> August 2009 and 27<sup>th</sup> December 2010. 16 polycyclic aromatic hydrocarbons (PAHs) and organic carbon (OC) were determined in each sample. The samples were collected with a high volume sampler (Digitel). Afterwards, they were chemically analysed with a gas chromatograph equipped with a flame ionization detector (Perkin Elmer Clarus 500) and thermo-optical carbon analyser (Sunset Laboratory Inc.). Over the whole measurement period, the mean concentrations of the sum of 16  $\text{PM}_{2.5}$ -bound PAHs and particular compounds within this group were very high at each measurement point. Particularly high values were observed for the heating season, in which the concentrations of the PAH sum and BaP exceeded 56 and 7  $\text{ng}/\text{m}^3$  (regional background), 343 and 25  $\text{ng}/\text{m}^3$  (urban background), and 166 and 14  $\text{ng}/\text{m}^3$  (urban traffic), respectively. It was showed that the emission related to heat production, particularly municipal emission (coal combustion in home furnaces in cities and coal and wood combustion in the countryside) were the main sources of the air pollution with PAHs in Silesia. Additionally, the traffic emission had probably a slight influence on the ambient concentrations of the  $\text{PM}_{2.5}$ -bound PAHs.

**Key words:** PAH, OC,  $\text{PM}_{2.5}$ , Diagnostic ratios, Municipal emission

### INTRODUCTION

Even though polycyclic aromatic hydrocarbons (PAHs) make a relatively small mass percentage in the ambient particulate matter (PM) and only a tiny fraction of the total organic matter content of PM, they are the most intensely investigated organic components of PM. The PAH content in PM partly characterizes the chemical composition of PM. It may also be useful to understand the PM origin. Above all, PAHs are investigated due to the adverse health effects they produce (e.g. Durant *et al.*, 1999; Massolo *et al.*, 2002; Kim *et al.*, 2013; Jyethi *et al.*, 2014; Chen *et al.*, 2014). PAHs are considered hazardous by the U.S. Environmental Agency (U.S. EPA) and the International Agency for Research on Cancer (IARC).

The degree to which the PM-bound PAHs are hazardous to humans depends on their ambient concentrations, mass distribution in respect to the particle size, and the physicochemical properties of PM. The health condition and habitat of the population may enhance or suppress the PM toxicity (Kameda *et al.*, 2005; Ji *et al.*, 2007; Badyda *et al.*, 2013). Despite

\*Corresponding author E-mail: barbara.kozielska@polsl.pl

the multi-factor correlation between the PM-bound PAHs and PM health effects, concentrations of only a few PM-bound PAHs are controlled in the atmosphere. The following PAHs (16 congeners) are considered as priority due to their health effects: naphthalene (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). In most countries, including Poland, the only limited concentration in the air is the ambient concentration of BaP bound to particles with aerodynamic diameters not greater than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ -bound BaP). As a result, the knowledge of the actual threat that the PM-bound PAHs pose to humans is very limited in countries such as Poland. This is also enhanced by the fact that the research into PM, particularly fine PM ( $\text{PM}_{2.5}$ , ambient particles with aerodynamic diameters not greater than 2.5  $\mu\text{m}$ ), has been conducted in Poland for a relatively

short time. Usually, the investigations are conducted only in the particularly critical areas and last for a very short time.

The PM concentrations, size distributions and chemical compositions are always observed within some limited area. The area is usually of a definite kind. The measurements consist in analysing PM samples collected at a single monitoring (sampling) point. The point is representative of the PM situation within the whole area. The areas are categorized by the law or are easy to define (rural site, urban background, suburban background, regional background, urban area, residential area, city centre, street canyon). The sampling point is representative of the PM situation in the area if the point and the area are in the relation defined by the regulations. The difficulties with the selection of such a point concern the sensitivity of the PM concentrations and chemical composition to even small shifts of the point location. The following study presents the results of the research into the ambient concentrations of 16 PM<sub>2.5</sub>-bound PAHs (Na, Acy, Ace, Flu, Ph, An, Fl, Py, BaA, Ch, BbF, BkF, BaP, IP, DBA and BghiP) at three locations in Silesia (Poland). The measurement points were selected due to their specific emission conditions. The following problems related to 16 PM<sub>2.5</sub>-bound PAHs were illustrated and discussed: seasonal variations of their ambient concentrations, their percentages in the PM mass and in the PM<sub>2.5</sub>-

bound organic carbon (OC) mass. Moreover, the possible origin of the discussed PAHs was indicated with the so-called diagnostic ratios.

## MATERIALS & METHODS

24-h samples of PM<sub>2.5</sub> were collected at three sites in southern Poland: urban background (UB) and traffic (UT, urban site directly affected by road traffic) points in Katowice, and a regional background point (RB) in Złoty Potok (Fig. 1). The samples were collected with a high volume sampler (Digitel DHA-80) onto the Whatman quartz fibre filters (QMA, Ø150 mm).

The research took place between 2<sup>nd</sup> August 2009 and 27<sup>th</sup> December 2010. There were two measurement campaigns at each sampling point held in each heating (January-March and October-December) and non-heating (April-September) season. 6-14 (usually 10) 24-h samples of PM<sub>2.5</sub> were collected in one campaign. Importantly, the campaigns were not consecutive at a given point. For example, in the heating season, the measurements were conducted in the following order: regional background point (RB), urban background (UB) and traffic points (UT). Afterwards, the sampling was conducted in the same way. Altogether, there were 40 24-h samples collected for each point (120 samples in total). The sampled dust mass was determined gravimetrically (Sartorius balance, resolution 0.01 g) according to the CSN EN 14907

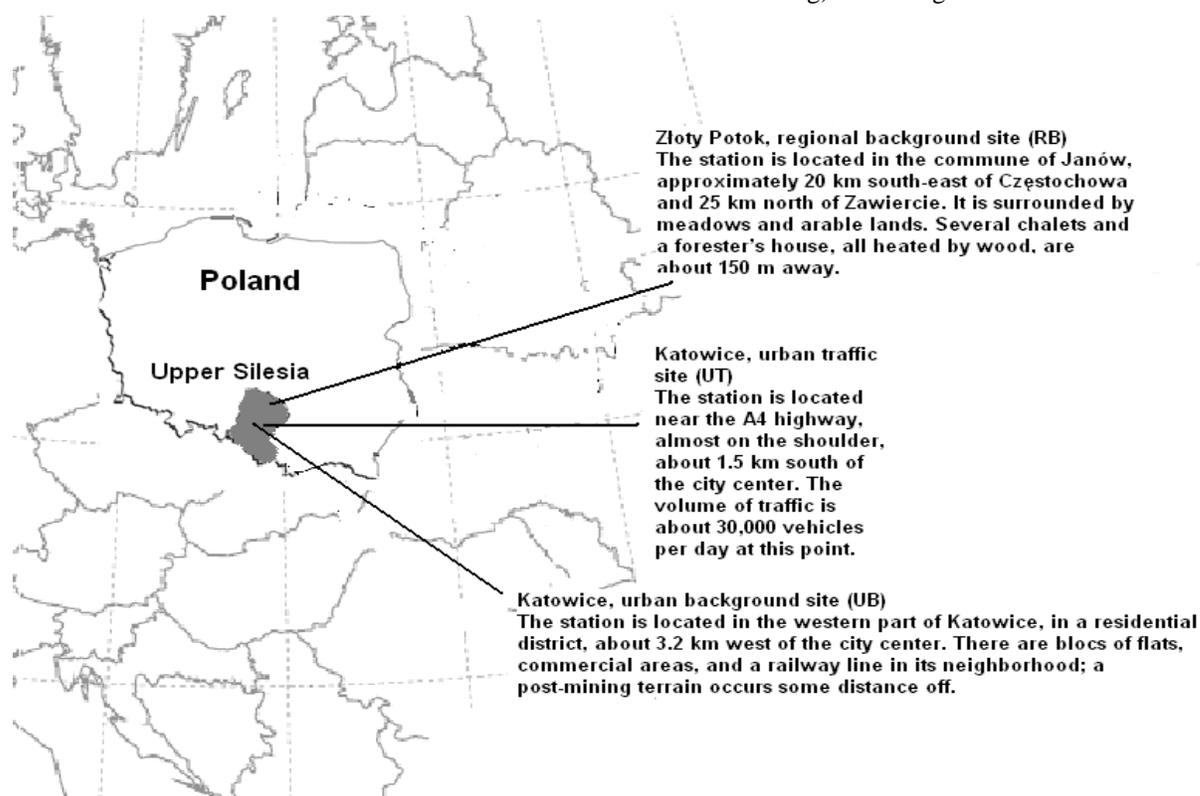


Fig. 1. Sampling sites

standard (Ambient air quality - Standard gravimetric measurement method for the determination of the PM<sub>2.5</sub> mass fraction of suspended particulate matter). Before each weighing, the filters were conditioned in a weighing room (min. 48 h; air temperature of 20 ± 1 °C; and air relative humidity of 50 ± 5%).

Two equal (Ø47 mm) circles were cut out from each exposed quartz filter just before the analysis. One filter with PM<sub>2.5</sub> was analysed for OC, whereas the other one was used to analyse 16 PAHs in PM<sub>2.5</sub>. PM samples were chemically analysed with a gas chromatograph equipped with a flame ionization detector (Perkin Elmer Clarus 500) and thermo-optical carbon analyser (Sunset Laboratory Inc.). The apparatus, details of PM extraction and the analysis parameters were described in the studies (Rogula-Kozłowska and Klejnowski, 2013, Kozielska *et al.*, 2013; Rogula-Kozłowska *et al.*, 2013).

## RESULTS & DISCUSSION

Over the whole measurement period, the mean concentrations of the sum of 16 PM<sub>2.5</sub>-bound PAHs (PAH sum) at RB, UB and UT were 40.3 (24-h concentration range: 7.1-224.8) ng/m<sup>3</sup>, 196.8 (23.9-1658.5) ng/m<sup>3</sup>, 107.3 (18.6-645.4) ng/m<sup>3</sup>, respectively (Table 1). In the heating season, the mean concentrations at the same points were 56.8 ng/m<sup>3</sup>, 343.5 ng/m<sup>3</sup> and 166.4 ng/m<sup>3</sup>. In the non-heating season, the values were 23.8 ng/m<sup>3</sup>, 50.1 ng/m<sup>3</sup> and 51.1 ng/m<sup>3</sup>. The PM<sub>2.5</sub>-bound BaP is considered as an index of the air pollution with the whole PAH group (Chen *et al.*, 2014). Its mean concentration over the whole measurement period was 4.7, 14.1 and 9.8 ng/m<sup>3</sup> at RB, UB and UT, respectively. The values for the heating season were 7.0 (RB), 25.4 (UB) and 14.1 (UT) ng/m<sup>3</sup>, whereas the non-heating season concentrations were 2.4 (RB), 2.9 (UB) and 5.65 ng/m<sup>3</sup> (UT). The concentrations of the PAH sum and BaP demonstrated visible seasonal variations at all three points. Both mean values were higher for the heating season, in which the maximum 24-h concentrations of the PAH sum and BaP were also observed for each sampling point (Table 1). The mean (non-zero) concentrations of nearly all the compounds differed for each season at each measurement point. At UB, 16 PAHs appeared in the following order (from the highest to the lowest mean concentration):

-Fl>Py>BaA>Ph>Ch>BaP>BkF>BbF>An>Flu>IP>BghiP>DBA>Ace>Acy (heating season),

-An>BaA>Ch>Flu>Py>Ace>BkF>Ph>Fl>BbF>BaP>IP>Acy>DBA>BghiP (non-heating season).

Generally, the mean concentrations of the PAH sum and BaP were high in Silesia. The ambient concentrations of the PM<sub>2.5</sub>-bound PAHs and BaP were very high in the heating season. Martellini *et al.* (2012)

conducted a similar experiment in Tuscany (Italy). The results they obtained for the cold (heating) season for the suburban background, urban background and urban traffic points were 3.6 ng/m<sup>3</sup>, 6.7 ng/m<sup>3</sup>, 13.0 ng/m<sup>3</sup> (PAH sum) and 0.1 ng/m<sup>3</sup>, 0.47 ng/m<sup>3</sup>, 1.0 ng/m<sup>3</sup> (BaP), respectively. In the warm (non-heating) season, the observed values were 0.9 ng/m<sup>3</sup>, 1.7 ng/m<sup>3</sup> and 7.2 ng/m<sup>3</sup> (PAH sum) and 0.02 ng/m<sup>3</sup>, 0.049 ng/m<sup>3</sup> and 0.21 ng/m<sup>3</sup> (BaP). The research conducted at the roadside in Madrid (Spain) showed that the concentration of the PAH sum did not exceed 1 ng/m<sup>3</sup> in June 2009 and 4.5 ng/m<sup>3</sup> in February 2010. For the same location, the BaP concentration was 0.039 ng/m<sup>3</sup> and 0.256 ng/m<sup>3</sup> in June and February, respectively. For the urban background in Madrid, the concentrations of the PAH sum and BaP were even lower (Mirante *et al.*, 2013). Similarly, in the American cities (e.g. Atlanta), the concentrations of the sum of 16 and 28 PAHs were the highest at the motorway in winter months (October-December period); their maximum values were 3.1 ng/m<sup>3</sup> and 6.2 ng/m<sup>3</sup> for the sums of 16 and 28 PAHs, respectively (Li *et al.*, 2009).

Such high concentrations of PAHs as the ones measured in the presented experiment were previously observed in the Polish cities. In the urban background in Zabrze (a city 15 km away from Katowice), the mean concentration of the PM<sub>1</sub>-bound BaP was 16 ng/m<sup>3</sup> in winter 2007, whereas the concentration of the sum of 15 PM<sub>1</sub>-bound PAHs was 128 ng/m<sup>3</sup> (Rogula-Kozłowska *et al.*, 2012a). In summer, the values for the same point did not exceed 0.7 ng/m<sup>3</sup> (PM<sub>10</sub>-bound BaP) and 5.9 ng/m<sup>3</sup> (sum of 15 PM<sub>10</sub>-bound PAHs) (Rogula-Kozłowska *et al.*, 2012a). The PAH and BaP concentrations were relatively high in the non-heating season in Silesia. Nonetheless, they were much lower than the values observed in the heating season. They result from the PAH emissions from traffic and industry that have a significant influence on the air pollution in the region. In the heating season, large emissions of PM and PAHs from home furnaces and electric power plants (mainly hard and brown coal and biomass combustion) were also observed in the region (Rogula-Kozłowska *et al.*, 2012b; 2014; Rogula-Kozłowska and Klejnowski, 2013).

The PAH concentrations observed in some Asian cities are as high as the concentrations in southern Poland. In Beijing (China), the concentrations of the sum of 16 PM<sub>2.5</sub>-bound PAHs were 46.15 ng/m<sup>3</sup>, 97.23 ng/m<sup>3</sup> and 106.68 ng/m<sup>3</sup> at the rural, roadside and urban points, respectively (Duan *et al.*, 2012). In Tiruchirappalli City (India), Mohanraj *et al.* (2011) observed that the mean concentrations of the sum of 9 PM<sub>2.5</sub>-bound PAHs ranged between 202.6 and 333.7 ng/m<sup>3</sup> in the years 2009-2010. What is important is the fact that high concentrations of PAHs in both cities were accompanied by high mean concentrations of PM<sub>2.5</sub> (e.g.

101.52-225.19 µg/m<sup>3</sup> in Beijing). In this study, the highest mean PM<sub>2.5</sub> concentration was observed at UB for the heating period. Its value did not exceed 75.5 µg/m<sup>3</sup> (Table 1). The above-mentioned data show that the mean permissible yearly concentration of the PM<sub>10</sub>-bound BaP (WHO 2000, EC 2004) could be possibly exceeded by a few or perhaps several times in the densely developed and populated areas. In the heating season in Silesia, the mean concentration of the PM<sub>2.5</sub>-bound BaP exceeded the indicated value by 25 times at the site located nearly in the city centre (UB), and by 14 times at the location exposed to traffic emission (UT). It is obvious that even higher concentrations can be expected for the PM<sub>10</sub>-bound BaP. The mean concentrations of the PM<sub>2.5</sub>-bound BaP were also higher than the permissible value for PM<sub>10</sub>-bound BaP (1 ng/m<sup>3</sup>) at the remaining location (RB). Such a situation is particularly dangerous for Silesian inhabitants. The mean percentage of organic carbon (OC) coming from 16 PAHs made only 0.49%, 0.81% and 0.72% (RB, UB and UT, respectively) of the carbon sum from all the organic compounds in PM (OC). A significant part of the remaining 99% of the OC mass also contained compounds that are dangerous for health (Min *et al.*, 2013; Gregoris *et al.*, 2014). Moreover, it is possible that a large part of PAHs (mainly the two- and three-ring ones) occurred in large concentrations in the gas phase (Ravindra *et al.*, 2006; Abdallah and Atia, 2014; Huang *et al.*, 2014) even though they were not found in the PM<sub>2.5</sub> observed in a given area (i.e. Na, Ace, Acy; Table 1). When it comes to the seasonal variations in PAH concentrations, the difference between the UT and UB points is characteristic. The values were significantly lower for UT, both for the PAH sum and BaP. For UT, the winter/summer concentration ratios of the PAH sum and BaP were 3.2 and 2.5, respectively. For UB, the values were 6.8 (16 PAHs) and 8.8 (BaP). At UT, the PAH concentrations were relatively high over the whole measurement period due to the stable traffic emissions.

On the other hand, the municipal emission had the biggest influence on the significant increase in the concentrations of PAHs and BaP in UB in the heating season. As UT was away from residential areas, the municipal emission effect was less powerful. Due to this correlation, it may also be concluded that traffic may have a less significant influence on the concentrations of organic compounds in the air in Katowice than it is intuitively assumed. When taking the mean BaP concentration in the non-heating season (2.9 ng/m<sup>3</sup>) as a certain background for Katowice, it is visible that traffic can cause the increase in the BaP level (2.7 ng/m<sup>3</sup>). The municipal emission can increase the BaP level to 8.4

(UT) and 22.5 (UB) ng/m<sup>3</sup>. Consequently, it is difficult to compare the concentrations of the PAH sum as some of the compounds are highly volatile and susceptible to transformations, particularly in the summer period (Kim *et al.*, 2009; Dvorská *et al.*, 2012). Nonetheless, it is clear that most of the discussed PAHs manifested the same correlations as BaP.

It is possible that the municipal emission was not the only factor responsible for high concentrations in the researched areas. The PAH concentrations were high at UB and RB in the heating and non-heating seasons, even though these areas are not well-developed and do not have significant sources of PAHs. The observed high concentrations of PAHs are stable and do not depend on the intensity of the local emission sources. Such a situation is probably caused by emissions from the energy industry, which depends on coal combustion in the discussed area.

Ch, BaP, Fl, Py and BaA had the largest mean percentage in the PAH sum in RB. Altogether, their values were 71.6% and 66.6% for the heating and non-heating seasons, respectively (Table 1). For UB and UT, the percentage of particular compounds in the mass of 16 PAHs depended on the season. The heating season in UB was dominated by Fl, Py, BaA, Ch and BaP (total percentage - 63.1%). On the other hand, An, BkF and BaA had the largest percentage in the non-heating season (18.3%, 8% and 15.8%, respectively). In UT, which was exposed to the traffic emission, DBA, BaA, Ch, Fl and Py made 58.8% in the heating season. In the non-heating season, BaA, Py, BaP and Ch had altogether 53.5% percentage in the PAH sum. The share of 9 PAHs (with 4-6 rings) in the sum of 15 PAHs – the 9PAH/15PAH ratio (Table 2) – indicates combustion as the main emission source in RB. The Fl/(Fl+Py) ratio ~0.5 points to the highly probable dominance of the emission from wood combustion in the formation of the PAH concentrations in RB (De La Torre-Roche *et al.*, 2009). Similarly, the IP/(IP+BghiP) ratio >0.5 (heating season) indicates biomass combustion as the emission source (Yunker *et al.*, 2002). The BbF/BkF ratio >0.5 may point to the presence of diesel fumes (Pandey *et al.*, 1999; Park *et al.*, 2002), which is possible in rural areas due to the common use of agricultural equipment fuelled with diesel petrol. The BaA/BaP ratio for PM<sub>2.5</sub> was 1.04 in the heating season. According to the literature data, such a value may suggest wood combustion as the source of PAHs and dust to which PAHs are bound (Li and Kamens, 1993). The ratio value was much higher in the non-heating season, which may confirm the thesis on the dominant influence of the biomass combustion on the contents of carbon substances in PM at this location.

**Table 1. The statistics concerning the concentrations of PM<sub>2.5</sub>, PM<sub>2.5</sub>-bound PAHs and OC at three locations and for two measurement periods**

	Regional background (RB)						Urban background (UB)						Traffic point (UT)					
	heating season (N=20)			non-heating season (N=20)			heating season (N=20)			non-heating season (N=20)			heating season (N=19)			non-heating season (N=20)		
	avg±std	min	max	avg±std	min	max	avg±std	min	max	avg±std	min	max	avg±std	min	max	avg±std	min	max
PM <sub>2.5</sub> ; µg/m <sup>3</sup>	31.12±19.18	5.80	78.84	19.83±6.65	8.28	35.44	75.39±51.91	18.50	255.08	23.80±7.04	14.56	40.17	50.56±28.51	20.02	120.46	27.97±11.78	11.80	51.78
OC; µg/m <sup>3</sup>	928±478	2.22	1782	528±2.04	2.05	1047	31.56±21.31	828	99.14	6.99±1.57	423	10.34	19.55±13.04	6.56	52.98	9.16±5.31	3.76	20.28
1OPAH; ng/m <sup>3</sup>	56.84±46.54	1285	224.83	23.77±37.34	7.06	17531	34.46±378.53	52.12	1668.52	30.13±16.05	23.85	83.41	166.38±167.27	18.55	645.37	51.10±25.05	20.88	102.45
Na; ng/m <sup>3</sup>	0±0	0	0	0±0	0	0	0±0	0	0	0±0	0	0	0±0	0	0	0.02±0.11	0	0.47
Acx; ng/m <sup>3</sup>	0.29±0.39	0	0.98	0.92±2.94	0	12.77	0.40±0.99	0	3.59	1.02±1.45	0	6.33	0±0	0	0	0.41±0.94	0	4.06
Acx; ng/m <sup>3</sup>	0.40±0.48	0	1.72	0.56±1.60	0	7.23	0.52±1.03	0	3.41	3.48±4.77	0	16.35	0±0	0	0	1.26±3.24	0	13.88
Flu; ng/m <sup>3</sup>	1.94±2.36	0	9.95	3.21±11.81	0	53.38	13.45±16.49	0	67.54	3.65±4.65	0.50	21.11	3.73±3.74	0	17.38	1.73±1.40	0	5.42
Ph; ng/m <sup>3</sup>	1.50±1.85	0	6.36	1.15±4.60	0	20.63	34.87±69.49	0	315.66	3.28±3.96	0	16.53	10.07±15.42	0	50.85	1.10±1.10	0	3.86
An; ng/m <sup>3</sup>	0.20±0.33	0	1.05	0.44±1.99	0	8.89	15.23±29.50	0	132.64	9.06±5.48	0.42	17.48	4.50±6.21	0	16.72	3.76±4.41	0	17.64
Fl; ng/m <sup>3</sup>	7.28±6.48	2.30	29.14	2.69±3.21	0.61	15.41	59.94±73.82	5.83	305.99	3.28±1.01	1.83	5.84	22.42±27.30	2.42	80.17	3.79±1.65	0	7.15
Py; ng/m <sup>3</sup>	7.85±8.12	1.13	36.22	2.75±4.36	0	20.40	51.77±61.40	5.08	260.95	3.52±1.99	0.51	7.13	19.96±22.71	2.05	79.56	8.43±15.77	1.03	69.61
BaA; ng/m <sup>3</sup>	6.57±6.93	1.92	33.12	2.03±1.97	0	9.47	42.39±38.58	6.49	156.67	7.42±3.04	2.78	15.97	19.76±20.30	2.89	87.51	7.20±4.02	1.02	14.49
Ch; ng/m <sup>3</sup>	8.80±6.64	1.81	192	4.13±2.87	0.53	14.73	32.65±25.87	7.22	103.15	3.90±2.88	1.88	14.61	18.18±17.53	3.00	71.07	5.51±6.42	1.63	31.29
BbF; ng/m <sup>3</sup>	5.23±4.79	0.39	181	1.90±4.11	0	18.86	20.23±15.51	4.91	62.89	3.10±1.46	0	7.02	12.43±10.64	0	45.83	3.97±4.28	0	15.59
BkF; ng/m <sup>3</sup>	5.39±5.29	0	24.59	1.27±2.59	0	11.79	21.74±16.17	5.63	71.72	3.40±1.75	0	7.43	11.50±10.23	0	42.89	3.12±3.80	0	11.00
BaP; ng/m <sup>3</sup>	7.02±5.70	1.17	23.30	2.43±2.04	0.40	8.32	25.40±19.43	6.06	81.45	2.89±1.90	0	8.09	14.05±14.40	1.73	61.39	5.65±2.43	1.72	9.12
IP; ng/m <sup>3</sup>	2.01±1.95	0	6.73	0.11±0.49	0	2.18	12.70±13.22	0.45	56.08	1.66±2.34	0	9.43	3.71±5.93	0	21.09	1.37±2.61	0	10.30
DBA; ng/m <sup>3</sup>	0.84±1.95	0	6.48	0.18±0.80	0	3.38	2.03±4.22	0	15.23	0.47±1.20	0	4.95	18.88±18.12	0	78.35	2.34±3.28	0	9.82
BghiP; ng/m <sup>3</sup>	1.54±1.40	0	4.39	0±0	0	0	10.15±8.64	0	26.94	0±0	0	0	7.18±7.84	0	32.40	1.42±2.55	0	8.02
BaP/1OPAH; [%]	13.21±7.44	5.59	42.09	14.39±8.46	1.97	29.31	9.46±3.72	4.88	19.54	5.77±2.90	0	11.36	9.17±3.03	3.08	16.62	12.57±7.15	4.54	34.31
1OPAH/OC; [%]	0.57±0.24	0.26	1.33	0.42±0.46	0.13	1.82	0.92±0.52	0.32	2.51	0.70±0.25	0.33	1.24	0.77±0.47	0.12	1.49	0.66±0.48	0.19	1.86
1OPAH/PM <sub>2.5</sub> [%]	0.20±0.11	0.09	0.56	0.11±0.12	0.03	0.49	0.40±0.22	0.16	1.03	0.23±0.10	0.11	0.45	0.31±0.20	0.06	0.62	0.21±0.14	0.08	0.55

\*the sample was destroyed when the PAH content was being determined

**Table 2. Diagnostic ratios for PAHs at selected urban, suburban and rural sites (literature data) and in the researched areas**

Location	Sampling period	Fraction PM	Diagnostic ratios										References
			Ph(Th+An)	H(Bl+Py)	BaP/BghiP	IP/BghiP	IP/(IP+BghiP)	BaA/BaP	BaA/(BaA+Ch)	BbF/BkF	9PAH/15PAH		
Złoty Potok (Poland), rural background	2009/2010, heating season	PM <sub>2.5</sub>	0.89	0.51	4.49	1.60	0.56	1.04	0.41	1.00	0.90		
	2009/2010, non-heating season	PM <sub>2.5</sub>	-	0.55	-	-	-	1.66	0.32	1.35	0.89		
Katowice (Poland), urban background	2009/2010, heating season	PM <sub>2.5</sub>	0.68	0.52	3.16	1.45	0.59	1.62	0.55	0.98	0.86	This study	
	2009/2010, non-heating season	PM <sub>2.5</sub>	0.27	0.52	-	-	1.00	3.07	0.66	1.05	0.60		
Katowice (Poland), traffic point	2010, heating season	PM <sub>2.5</sub>	0.59	0.51	1.71	0.36	0.22	1.58	0.51	1.10	0.77	Rogula-Kozłowska et al., 2012a	
	2010, non-heating season	PM <sub>2.5</sub>	0.31	0.46	-	-	0.67	1.72	0.58	1.60	0.78		
Zabrze (Poland), urban background	summer 2007	PM <sub>1.0</sub>	0.75	0.42	-	-	-	0.23	0.10	1.29	0.54	Eh-Mu barak et al., 2014	
		PM <sub>2.5</sub>	0.76	0.43	-	-	-	0.16	0.11	1.25	0.57		
	PM <sub>1.0</sub>	0.77	0.44	-	-	-	0.08	0.08	1.26	0.60			
	PM <sub>1.0</sub>	0.82	0.47	-	-	-	1.11	0.51	0.93	0.82			
	PM <sub>2.5</sub>	0.81	0.46	-	-	-	1.11	0.51	0.92	0.82			
winter 2007	PM <sub>1.0</sub>	0.80	0.46	-	-	-	1.11	0.50	0.92	0.81			
Riyadh (Saudi Arabia), metropolitan area	Dex 2010	PM <sub>1.0</sub>	0.76	0.50	0.30	-	0.37	-	-	1.18	0.87	Hanedar et al., 2014	
	Istanbul (Turkey) urban area I	-	0.48	1.04	1.28	0.31	-	-	-	2.9	-		
Istanbul (Turkey) urban area II	Oct 2006-Dec 2007	TSP	-	0.60	1.15	1.61	0.36	-	-	4.5	-	Ladji et al., 2014	
		PM <sub>1.0</sub>	-	0.29	1.35	0.85	0.28	-	-	5.8	0.49		
Algiers (Algeria), urban area, vehicle traffic	Oct 2007	PM <sub>1.0</sub>	0.83	0.52	-	-	0.33	-	-	-	-	Duan et al., 2012	
Beijing (China), rural	Feb 2006	PM <sub>1.0</sub>	-	0.54	-	0.47	-	-	0.33	-	-		
Beijing (China), roadside	Jan 2006	PM <sub>1.0</sub>	-	0.52	-	0.45	-	-	0.44	-	-		
Beijing (China), urban	Jan 2006	PM <sub>1.0</sub>	-	0.51	-	0.51	-	-	0.44	-	-		

Table 2. Diagnostic ratios for PAHs at selected urban, suburban and rural sites (literature data) and in the researched areas

Location	Sampling period	Fraction PM	Pb/(Pb+Am)	Fl(Fl+Py)	Bap/BghiP	Ip/BghiP	Ip/(Ip+BghiP)	Diagnostic ratios			References
								BaA/BaP	BaA/(BaA+Ch)	BbF/BkF	
Coimbatore (India), suburban residential area	Mar 2009-Feb 2010 (once a month)	PM <sub>2.5</sub>	-	-	0.58	1.15	0.48	-	0.13	3.85	-
Coimbatore (India), mixed commercial and residential area	Mar 2009-Feb 2010 (once a month)	PM <sub>2.5</sub>	-	-	0.74	1.12	0.44	-	0.34	5.49	Mohanraj et al., 2012
Coimbatore (India), urban commercial area	Mar 2009-Feb 2010 (once a month)	PM <sub>2.5</sub>	-	-	1.60	1.99	0.66	-	0.24	1.67	-
Coimbatore (India), urban highway area	Mar 2009-Feb 2010 (once a month)	PM <sub>2.5</sub>	-	-	0.53	0.73	0.36	-	0.12	0.89	Evangelopoulos et al., 2010
Kozani (Greece), urban area surrounded by opencast coal mining	warm season, 2005-2006	PM <sub>2.5</sub>	-	0.43	-	-	0.31	-	0.64	-	0.90
Shanghai (China), urban area	cold season, 2005-2006	PM <sub>2.5</sub>	-	0.50	-	-	0.37	-	0.64	-	0.93
Duisburg (Germany), urban background	2006/2008 autumn, Oct - Nov 2002	PM <sub>2.5</sub>	-	0.52	-	-	0.45	-	0.27	-	-
Prague (Czech Republic) urban background	winter, Nov 2002 - Jan 2003	PM <sub>10</sub>	-	0.55	2.56	-	0.66	-	-	-	-
Amsterdam (The Netherlands), urban background	winter, Jan - Mar 2003	PM <sub>2.5</sub>	-	0.58	1.64	-	0.61	-	-	-	Saarnio et al., 2008
Helsinki (Finland), urban background	spring, Mar - May 2003	PM <sub>10</sub>	-	0.56	1.64	-	0.61	-	-	-	-
Barcelona (Spain), urban background	spring, Mar - May 2003	PM <sub>2.5</sub>	-	0.51	1.36	-	0.57	-	-	-	-
Athens (Greece), urban background	summer, Jun-Jul 2003	PM <sub>10</sub>	-	0.51	1.38	-	0.58	-	-	-	-
		PM <sub>2.5</sub>	-	0.56	1.18	-	0.48	-	-	-	-
		PM <sub>10</sub>	-	0.55	1.19	-	0.47	-	-	-	-
		PM <sub>2.5</sub>	-	0.40	0.43	-	0.41	-	-	-	-
		PM <sub>10</sub>	-	0.41	0.42	-	0.40	-	-	-	Quiterio et al., 2007
Rio de Janeiro (Brazil), suburban area with industrial and vehicular emissions	Mar 2005-Aug 2005	PM <sub>10</sub>	-	0.37	-	-	-	0.84	0.23	-	0.62

Symbols: 9PAHs = Fl+Py+BaA+Ch+BbF+BkF+BaP+IP+BghiP; 15PAH = Acy+Ace+Flu+Ph+An+Fl+Py+BaA+Ch+BbF+BkF+BaP+DBA+IP+BghiP

Comments: \*) Due to the index construction, the ratios for RB, UB and UT are presented only when it was possible to calculate them for at least 50% of cases in a given averaging period.

At UB, the share of 9 PAHs (with 4-6 rings) in the sum of 15 PAHs – the 9PAH/15PAH ratio (Table 2) – was high (0.86). This suggests combustion as the main source of PAHs (Gogou *et al.*, 1996; Mantis *et al.*, 2005; Ravindra *et al.*, 2006; 2008). Both in the heating and in the non-heating seasons, the Fl/(Fl+Py) ratio was >0.5 for both PM fractions, which indicates the dominance of the emissions from wood and biomass combustion (De La Torre-Roche *et al.*, 2009). The Fl/(Fl+Py) ratio >0.52 may also point to the coal combustion as the emission source (Yunker *et al.*, 2002; Saarnio *et al.*, 2008; De La Torre-Roche *et al.*, 2009). The BaA/(BaA+Ch) ratio was 0.55 in the heating season, which confirms coal combustion as a significant emission source (Tang *et al.* 2005; Kong *et al.*, 2010). Similarly, the IP/(IP+BghiP) > 0.5 for both seasons denotes coal, wood and biomass combustion as the emission sources (Yunker *et al.*, 2002; Manoli *et al.*, 2004; Ravindra *et al.*, 2008; Kong *et al.*, 2010). The BbF/BkF ratio >0.5 may point to the presence of diesel fumes (Pandey *et al.*, 1999; Park *et al.*, 2002), which is rather possible in the industrial agglomeration with high petroleum consumption for transport. For UT, the share of 9 PAHs (with 4-6 rings) in the sum of 15 PAHs – the 9PAH/15PAH ratio (Table 2) – was the lowest for all locations (~0.77). Nevertheless, the value still suggests combustion as the main source of PAHs (Gogou *et al.*, 1996; Mantis *et al.*, 2005; Ravindra *et al.*, 2006, 2008). The combustion character is different from other locations as the percentage of compounds with high number of benzene rings was the lowest. The percentage of the 3-ring PAHs was higher, which is characteristic for fuel combustion in diesel engines (Table 1). Therefore, the BbF/BkF ratio > 0.5 may indicate the presence of diesel fumes in the researched area (Pandey *et al.*, 1999; Park *et al.*, 2002), which can be intuitively assumed for such a site. At the same time, the Ph/(Ph+An) ratio (0.59 and 0.31 for the heating and non-heating periods, respectively) suggests the emission from petrol engines as the main emission source (Alves *et al.*, 2001). The BaA/(BaA+Ch) (0.51 and 0.58 for the heating and non-heating seasons, respectively) and IP/(IP+BghiP) (0.22 and 0.67 for the heating and non-heating seasons, respectively) ratios also designate vehicles as the main emission source in this area (Neilson 1998; Kavouras 2001; Yunker *et al.*, 2002). It is possible that fossil fuel combustion dominates at this point in the heating season (Fl/(Fl+Py) ranging between 0.4 and 0.5 (De La Torre-Roche *et al.*, 2009). The calculated diagnostic ratios can be seen as specific for the discussed area types. The ratios obtained for RB in Zloty Potok in the heating season are representative for areas with dispersed emission sources and the dominance of biomass burnt to obtain energy (Table 2). The ratios for UB in Katowice can

characterize an urban background with the dominant coal combustion emission. For example, the diagnostic values are similar to the ratios obtained for the urban background point in Zabrze (15 km away from Katowice; Table 2).

## CONCLUSIONS

The following conclusions were reached after careful analyses were carried out:

- over the whole measurement period, the mean concentrations of the PM<sub>2.5</sub>-bound PAH sum and particular compounds within this group were high at each of the three selected points in Silesia; particularly high values were observed for the heating season;
- the highest concentrations of most PAHs were observed at the UB point in the heating season; for the non-heating season, the area under the direct influence of the traffic emission (UT) demonstrated the highest values;
- the concentrations of the sum of 16 PM<sub>2.5</sub>-related PAHs and BaP in the air in Silesia were higher than most values observed in other regions of the world; nonetheless, they did not differ from the concentrations measured in this area earlier;
- in Silesia, regardless of the seasonal and spatial variations in the PM<sub>2.5</sub>-bound BaP ambient concentrations, its percentage in the sum of 16 PAHs was 6-14%; the mass of the PAH sum made not more than 1% of the total PM<sub>2.5</sub>-bound OC mass;
- the high percentage of BaP in the PAH sum and the very high concentrations of the PM<sub>2.5</sub>-bound BaP, particularly in the heating season, may pose a serious threat to the inhabitants of the Silesia regions; the risk does not only concern the residents of large cities and regions located close to important traffic emission sources, it also involves people who dwell in the “clean” areas far away from large urban agglomerations (regional/rural background);
- the seasonal variations in the PAH sum and BaP in the air and the characteristic ratios of those concentrations for the selected locations showed that the emission related to the heat production, particularly municipal emission, was the main source of the air pollution with PAHs in Silesia; the traffic emission might have a slight influence on the PM<sub>2.5</sub>-bound PAH concentrations;
- the analysis of the diagnostic ratios indicates fuel combustion as the main source of PAHs at the three selected points; at the RB point, wood and fossil fuel combustion in the heating season and the petroleum combustion (probably in the agricultural equipment engines) in the non-heating season influenced the PM<sub>2.5</sub>-bound PAH concentrations; at the UB point, coal and petroleum combustion had the biggest impact on the PAH emission; at the UT point, petrol and petroleum combustion affected PAH emissions; nonetheless, the

solid fuel combustion emission also had a visible impact on the PM<sub>2.5</sub>-bound PAH concentrations at this point.

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