

*Article*

## Seasonal Variations in Health Hazards from Polycyclic Aromatic Hydrocarbons Bound to Submicrometer Particles at Three Characteristic Sites in the Heavily Polluted Polish Region

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**Abstract:** Suspended particles with aerodynamic diameters not greater than 1  $\mu\text{m}$  ( $\text{PM}_{10}$ ) were sampled at the urban background; regional background; and urban traffic points in southern Poland. In total, 120 samples were collected between 2 August 2009 and 27 December 2010. Sixteen polycyclic aromatic hydrocarbons (PAHs) were determined in each sample. The samples were collected with a high volume sampler (Digitel). Afterwards, they were chemically analyzed with a gas chromatograph equipped with a flame ionization detector (Perkin Elmer Clarus 500). The mean concentration values of the PAH sum ( $\Sigma\text{PAH}$ ) and particular PAHs; the percentages of carcinogenic PAHs in total PAHs ( $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$ ); carcinogenic equivalent (CEQ); mutagenic equivalent (MEQ); and TCDD-toxic equivalent (TEQ) were much higher in the winter (heating) season than in the summer (non-heating) one. For both periods, the resulting average values obtained were significantly higher (a few; and sometimes a several dozen times higher) in the researched Polish region than the values observed in other areas of the world. Such results indicate the importance of health hazards resulting from  $\text{PM}_{10}$  and  $\text{PM}_{10}$ -bound PAHs in this Polish area.

**Keywords:** PAH; organic matter; PM<sub>1</sub>; health hazard; mutagenicity; carcinogenicity; TEF; municipal emission

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## 1. Introduction

The degree to which the ambient particulate matter-bound (PM-bound) polycyclic aromatic hydrocarbons (PAHs) are hazardous to health depends on: PAH concentrations both in the ambient air and in the PM mass; their mass distributions in respect to the particle size; and the physicochemical properties of PM.

Despite that fact that almost every PM-bound PAH, and PM itself, strongly affects human health, the ambient concentrations of only a few of them are limited. The following PAHs (16 congeners) are considered as a 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). According to the International Agency for Research on Cancer (IARC), 48 PAHs can be carcinogenic for humans or animals. The strength of their carcinogenicity grows with their molecular weight. However, it is still unknown if the carcinogenicity of PAHs (which always occur in the mixture form and never as a single compound in the air) may be ascribed to the individual hydrocarbons or if it is rather the concerted effect of some PAHs combined together.

BaP is a well-studied five-ring hydrocarbon. It is particularly important to the environmental toxicology as one of the most mutagenic and carcinogenic hydrocarbons [1–4]. It also constitutes a basis for defining the toxic (carcinogenic) equivalence factor (TEF) and the carcinogenic equivalent (CEQ) for other PAHs. Namely, a TEF for a PAH is defined as relative to the TEF of BaP (assumed to be 1). The CEQ of a PAH group is the linear combination of the TEF and the ambient concentrations of the PAHs from this group. TEF expresses absolute toxicity of a particular PAH, whereas CEQ specifies carcinogenicity of a PAH group in the air [5]. The so-called mutagenic equivalent (MEQ) or the TCDD-toxic equivalent (TEQ) can also be useful as indicators to assess the PAH mixture health effect [6].

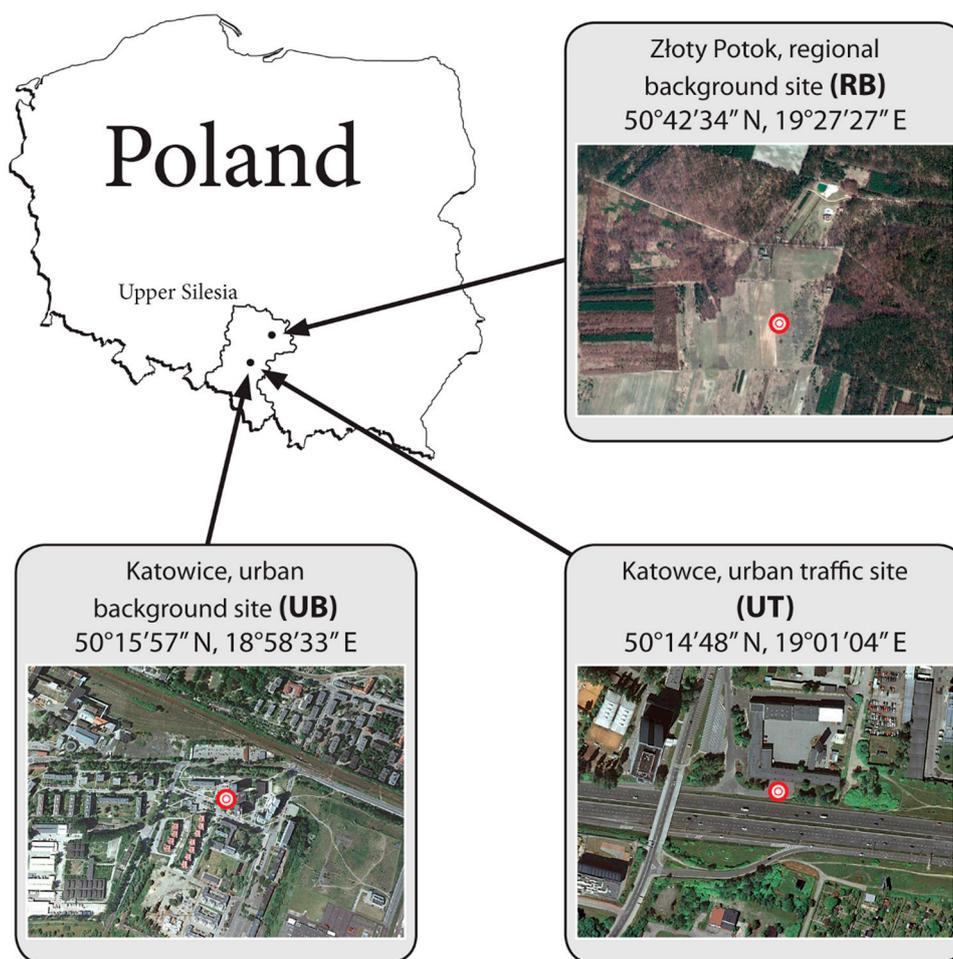
In Poland, and particularly in its southern part, PM comes mainly from energy production and municipal and industrial sources [7–10]. To some degree, Southern Poland is representative of those areas in East and Central Europe where power and heat are produced mainly from fossil fuels (coal), and the road traffic is still not so dense as in the western and northern parts of Europe, or even in the USA ten years ago. In other urbanized regions of Western Europe, air pollution with PM is mainly due to road traffic [11]. The PM<sub>1</sub>-bound PAHs, the concern of this paper, are well enough recognized both in Poland as well as in other European countries.

The following study presents the results of the research into the ambient concentrations of 16 PM<sub>1</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 (southern Poland). The measurement points were selected due to their specific emission conditions. Seasonal variations of 16 PM<sub>1</sub>-bound PAHs and their mutual correlations

in the seasons were discussed. Additionally, the seasonal variations in the exposure to the mixture of the PM<sub>1</sub>-bound PAHs were assessed with selected indicators ( $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$ , CEQ, MEQ and TEQ).

## 2. Materials and Methods

Twenty-four-hour samples of PM<sub>1</sub> were collected (with a high volume DIGITEL DHA-80 sampler (flow rate 30 m<sup>3</sup>·h<sup>-1</sup>) onto the quartz fiber filters (Whatman™ 1851-150 Grade QM-A, Piscataway, NJ, USA) at three sites in southern Poland (Figure 1); prior to sampling, the filters were baked at 600 °C for at least 6 h to remove any traces of organics.



**Figure 1.** Sampling sites.

The first point met the requirements for the so-called urban background site (UB); the second one represented the regional background site (RB); and the third one was the so-called urban traffic site (urban site directly affected by road traffic, UT). UB was located in a residential district in the western part of Katowice, approx. 3.2 km west of the city center. There were blocks of flats, commercial areas, and a railway line in its neighborhood. A post-mining terrain could be found at some distance off. UT was located near the A4 highway—Almost on its shoulder, approx. 1.5 km south of the city center. The volume of traffic was about 30,000 vehicles per day at this point. RB was located in Złoty Potok (commune of Janów), approx. 20 km south-east of Częstochowa and 25 km north of Zawiercie. It was

surrounded by meadows and agricultural lands. Several wood-heated chalets and a forester's house were approx. 150 m away.

The research took place between 2 August 2009 and 27 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. Six to fourteen (usually 10) 24-h samples of PM<sub>1</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: RB, UB and 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; Goettingen, Germany) according to the CSN EN 14907 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, filters were conditioned in a weighing room (min. 48 h; air temperature of  $20 \pm 1$  °C; and air relative humidity of  $50\% \pm 5\%$ ). After weighing, the filters were put into petri dishes wrapped light-tightly in aluminum foil and stored in a freezer at  $-18$  °C till the analysis.

The dust collected on a filter was extracted with  $3 \times 10$  cm<sup>3</sup> dichloromethane (DCM) for 30 min under ultrasonic agitation. The extract was percolated, washed and dried in helium atmosphere. The dry residue was dissolved in propanol-2 (CH<sub>3</sub>CH(OH)CH<sub>3</sub>), next distilled water was added to receive alcohol/water volume ratio 15/85. For selective purification, the obtained samples were solidified (SPE) via extraction in columns filled with octadecylsilane – C-18 (Supelclear™ ENVI-18 Tubes, Supelco, Bellefonte, PA, USA). Before the extraction, the columns were conditioned with methanol and next with a mixture of propanol-2/water (15/85). Subsequently, the sample was passed through the columns. After the extraction, the bed was dried under vacuum. The fraction of PAHs was eluted with two portions of 0.5 cm<sup>3</sup> of DCM. The extract of PAHs was thickened in helium to the volume of 0.1 cm<sup>3</sup>.

The SPE extracts were analyzed on a Clarus 500 Perkin Elmer gas chromatograph (PerkinElmer, Inc., Waltham, MA, USA) equipped with an auto-sampler. The compounds were separated on a capillary column (Restek RTX-5, 5% phenyl methyl siloxane, 30 m × 0.32 mm × 0.25 μm). The carrier gas (helium) flow in the column was maintained at the constant rate of 1.5 cm<sup>3</sup>·min<sup>-1</sup>. The 3 μL samples were introduced using splitless injection, the temperature of the injector was 240 °C. A flame ionization detector (FID) was used. For the PAHs analysis, the initial temperature of the oven, 60 °C, was held for 4 min, then the temperature grew at 10 °C·min<sup>-1</sup> to 280 °C and held for 14 min. The flow rates of hydrogen and air in the detector were 45 cm<sup>3</sup>·min<sup>-1</sup> and 450 cm<sup>3</sup>·min<sup>-1</sup>, respectively; the FID's temperature was 280 °C.

The calibration curves for the quantitative analysis were prepared for 16 standard PAHs. The linear correlation between the peak surface areas and PAH concentrations was checked within the range of 1–20 μg·mL<sup>-1</sup> (correlation coefficients: 0.99; PAH Mix PM-611 Ultra Scientific standard at the concentration of 100 μg·mL<sup>-1</sup> for each PAH in DCM).

The analysis of each campaign sample series was accompanied with the blank sample analysis. It consisted in the application of the whole analytical procedure to a clean quartz fiber filter. The blank result was used to adjust the PAH concentration, but only if the blank exceeded 10% of the PAH concentration. The limits of detection (LODs), obtained from the statistical development of the blank

results (10–11 blanks for each PAH; PN-EN 15549 standard), were between 0.01 and 0.03  $\text{ng}\cdot\text{m}^{-3}$  (average air flow rate = 700  $\text{m}^3/24\text{ h}$ ).

The method performance was verified through analyzing the NIST SRM 1649b reference material and comparing the results with the certified concentrations of the investigated PAHs. The standard recoveries were from 92% to 111%.

The cumulative health hazard from the PAH mixture was expressed quantitatively as the carcinogenic equivalent (CEQ) or mutagenic equivalent (MEQ) relative to the carcinogenicity or mutagenicity of BaP, respectively, or as the TCDD-toxic equivalent (TEQ) relative to the 2,3,7,8-tetrachlorodibenzo-p-dioxin toxicity. The indicators were computed for each site and, separately, for the heating and non-heating periods: CEQs as linear combinations of the concentrations of  $\text{PM}_{10}$ -related PAHs and their toxicity equivalence factors (TEF); MEQs as linear combinations of the concentrations and the PAH minimum mutagenic concentrations (MMC); TEQs as linear combinations of the concentrations of the  $\text{PM}_{10}$ -related PAHs and their TCDD-TEF. The values of TEF, MMC and TCDD-TEF for particular PAHs were taken from Nisbet and LaGoy [5], Durant *et al.* [2] and Willett *et al.* [12]. Additionally, the proportion of the concentration sum of seven carcinogenic PAHs (Ch, BaA, BbF, BkF, BaP, DBA and IP -  $\Sigma\text{PAH}_{\text{carc}}$  [13]) to the concentration sum of the 16 determined PAHs was calculated. The closer the value of  $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$  was to 1, the more hazardous  $\Sigma\text{PAH}$  was to humans.

### 3. Results and Discussion

In the heating season, the mean  $\text{PM}_{10}$  concentrations were 16.37  $\mu\text{g}\cdot\text{m}^{-3}$ , 40.70  $\mu\text{g}\cdot\text{m}^{-3}$ , 41.55  $\mu\text{g}\cdot\text{m}^{-3}$  at RB, UB and UT, respectively. They were 1.6–2.3 times higher than the mean  $\text{PM}_{10}$  concentrations in the non-heating season (Table 1). When compared to the European concentrations, the values were high. For example, winter concentrations of  $\text{PM}_{10}$  observed in Brno and Šlapanice (Czech Republic) in 2009 were 19.9  $\mu\text{g}\cdot\text{m}^{-3}$  and 19.2  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively [14]. Perrone *et al.* [15] measured even lower  $\text{PM}_{10}$  concentrations (13  $\mu\text{g}\cdot\text{m}^{-3}$ ) in southern Italy.

Fine PM concentrations in Asian cities were similar to the Polish ones or even higher. In Tabriz (Iran), the  $\text{PM}_{10}$  concentrations measured in the urban and industrial-suburban sites were 28.4  $\mu\text{g}\cdot\text{m}^{-3}$  and 31.4  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively [16]. In Shanghai (China), the mean  $\text{PM}_{10}$  concentration was 78.9  $\mu\text{g}\cdot\text{m}^{-3}$  [17]. In Beijing (China), the  $\text{PM}_{2.5}$  concentration varied and depended on the measurement point location. Nonetheless, it was never lower than 100  $\mu\text{g}\cdot\text{m}^{-3}$  [18]. In Agra (India), the mean  $\text{PM}_{2.5}$  concentration differed at various locations and ranged between 91.2 and 308.3  $\mu\text{g}\cdot\text{m}^{-3}$  [19].

Similarly to  $\text{PM}_{10}$  concentrations, concentrations of the 16 PAH ( $\Sigma\text{PAH}$ ) sum and particular PAHs varied and depended on the season. The definitely higher 24-h  $\Sigma\text{PAH}$  concentrations were observed in the heating season, which was visible in the mean concentrations ranging between 23.1  $\text{ng}\cdot\text{m}^{-3}$  (RB) and 186.1  $\text{ng}\cdot\text{m}^{-3}$  (UT). In the non-heating season, the values ranged between 18.6  $\text{ng}\cdot\text{m}^{-3}$  (RB) and 56.0  $\text{ng}\cdot\text{m}^{-3}$  (UT) (Table 1). The biggest differences in the 24-h and mean seasonal concentrations of  $\Sigma\text{PAH}$  were found for UB, whereas the lowest values were observed at RB. The heating season  $\Sigma\text{PAH}$ /non-heating season  $\Sigma\text{PAH}$  ratios were 1.2, 4.6 and 3.3 at RB, UB and UT, respectively.

**Table 1.** The statistics of 24-h concentrations of PM<sub>1</sub> (μg·m<sup>-3</sup>) and PM<sub>1</sub>-bound PAHs (ng·m<sup>-3</sup>) at three locations in 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 = 20)			Non-Heating season (N = 20)		
	Min	Avrg ± SD	50% *	Min	Avrg ± SD	50%	Min	Avrg ± SD	50%	Min	Avrg ± SD	50%	Min	Avrg ± SD	50%	Min	Avrg ± SD	50%
	Max			Max			Max			Max			Max			Max		
PM <sub>1</sub>	3.49 71.41	16.37± 14.42	14.40	4.82 16.06	10.32± 3.51	10.17	17.33 73.59	40.70± 14.82	36.64	7.99 34.86	20.83± 8.50	24.24	20.50 88.34	41.55± 16.56	36.60	11.83 27.72	18.40± 4.48	17.17
16PAH	6.74 82.25	23.10± 17.82	17.49	3.48 45.32	18.57± 11.75	13.86	31.32 400.14	138.74± 87.07	116.28	16.18 58.59	30.26± 11.15	27.28	20.23 695.67	186.12± 162.63	132.4 2	8.23 179.89	56.02± 43.79	42.31
Na	0 0	0±0	0	0 0.48	0.02± 0.11	0	0 0	0±0	0	0 0	0±0	0	0 0	0±0	0	0 0	0±0	0
Acy	0 3.40	0.51± 0.81	0.11	0 1.74	0.35± 0.50	0	0 0.39	0.02± 0.09	0	0 4.52	0.62± 1.04	0.32	0 3.36	0.17± 0.75	0	0 0.42	0.02± 0.09	0
Ace	0 5.29	0.35± 1.18	0	0 1.16	0.12± 0.28	0	0 1.26	0.28± 0.38	0	0 16.32	2.64± 3.87	0.80	0 2.20	0.11± 0.49	0	0 1.45	0.14± 0.38	0
Flu	0.40 14.82	2.55± 3.28	1.61	0 7.97	2.81± 2.60	1.67	0.33 12.11	2.88± 3.37	1.10	0.40 1.44	0.82± 0.29	0.76	0 15.51	3.54± 4.16	2.16	0.77 25.06	6.11± 7.44	2.85
Ph	0 2.63	0.64± 0.92	0	0 2.19	0.93± 0.78	1.10	2.53 32.67	9.98± 8.29	6.64	0.53 16.97	3.62± 4.37	1.81	0 97.13	15.55± 23.31	7.54	0 18.16	1.69± 3.93	0.93
An	0 5.42	0.64± 1.34	0	0 6.61	0.75± 1.58	0	0 16.28	3.53± 4.73	1.73	0.28 12.91	2.16± 3.28	0.90	0 40.88	6.31± 9.85	2.63	0.35 17.24	4.84± 5.45	2.07
Fl	1.29 29.88	3.42± 6.25	1.96	1.33 6.37	2.65± 1.53	2.07	3.02 71.89	23.36± 17.22	18.76	1.23 6.01	2.01± 1.01	1.79	1.86 109.03	26.69± 28.30	15.20	0.55 8.91	3.62± 2.02	3.60
Py	0 4.73	1.86± 1.39	1.73	0 4.24	1.64± 1.14	1.49	3.53 60.49	20.30± 14.40	16.02	0.40 6.24	1.87± 1.47	1.17	1.67 90.12	21.51± 22.04	13.89	0.66 78.64	10.90± 19.18	2.98
BaA	0 13.16	2.05± 2.98	0.95	0 9.54	1.57± 2.63	0	3.78 51.28	17.67± 11.37	14.25	5.08 10.73	7.81± 1.83	7.75	1.72 76.14	19.02± 17.22	14.03	2.60 24.01	10.41± 4.46	9.44
Ch	0.62 8.60	3.26± 2.15	2.38	0.76 5.66	2.81± 1.78	2.71	5.19 37.56	17.30± 7.62	17.30	1.70 3.82	2.48± 0.50	2.34	2.24 59.95	19.85± 13.83	18.24	1.01 12.68	3.86± 2.34	3.23
BbF	0 6.61	1.55± 1.46	1.25	0 3.34	0.80± 1.13	0.42	3.17 24.64	9.95± 4.92	8.89	0 1.78	0.76± 0.67	0.62	1.29 35.88	14.23± 8.66	11.86	0 6.94	3.38± 2.46	3.83

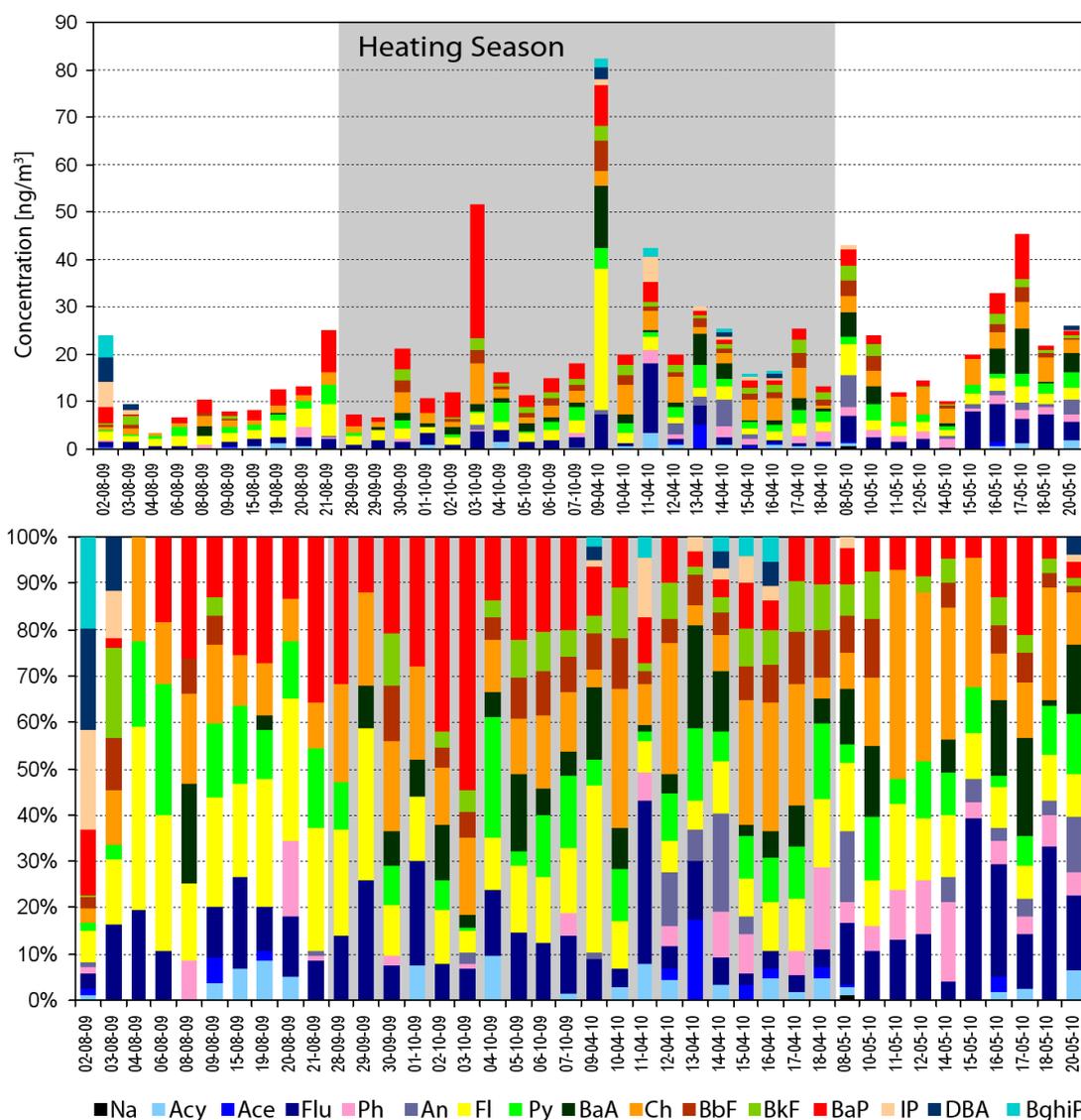
Table 1. Cont.

	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 = 20)			Non-Heating season (N = 20)		
	Min Max	Avrg ± SD	50% *	Min Max	Avrg ± SD	50%	Min Max	Avrg ± SD	50%	Min Max	Avrg ± SD	50%	Min Max	Avrg ± SD	50%	Min Max	Avrg ± SD	50%
BkF	0 3.09	1.24 ± 0.92	1.18	0 2.98	0.68 ± 0.96	0.22	3.22 26.09	10.74 ± 5.21	9.51	0 7.13	1.87 ± 1.58	1.56	1.79 34.51	13.80 ± 7.77	11.97	0 6.01	0.97 ± 1.38	0.68
BaP	0.80 28.23	4.03 ± 5.97	2.40	0 9.52	2.46 ± 2.61	1.51	4.52 32.28	12.48 ± 6.36	11.29	0.41 5.14	2.97 ± 1.39	3.15	1.48 46.70	14.27 ± 11.27	11.87	0 19.45	4.73 ± 3.92	4.13
IP	0 5.52	0.49 ± 1.25	0	0 5.15	0.38 ± 1.17	0	0.77 18.70	5.03 ± 4.18	3.95	0 1.07	0.35 ± 0.36	0.43	0 13.36	5.57 ± 3.83	5.89	0 6.59	0.51 ± 1.48	0
DBA	0 2.37	0.21 ± 0.58	0	0 5.25	0.37 ± 1.19	0	0 3.71	0.27 ± 0.85	0	0 0.94	0.24 ± 0.38	0	0 47.91	17.21 ± 12.92	11.59	0 57.64	4.77 ± 12.80	0.40
BghiP	0 1.82	0.30 ± 0.59	0	0 4.73	0.24 ± 1.06	0	0 17.17	4.95 ± 4.43	3.98	0 0.59	0.05 ± 0.16	0	0 23.00	8.29 ± 5.82	7.97	0 1.12	0.09 ± 0.28	0

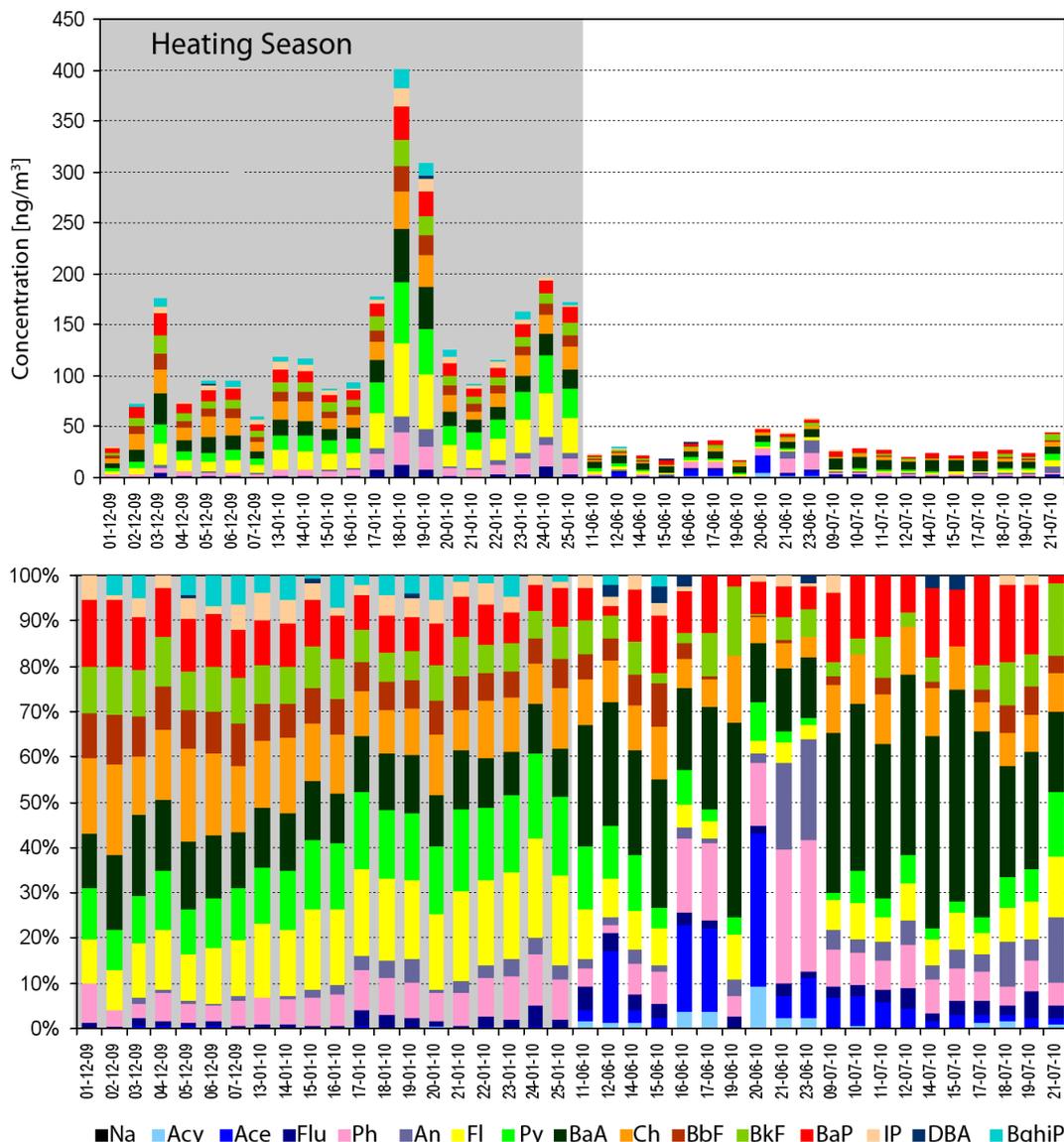
\* median.

The mean concentrations of nearly all the compounds differed in each season at each measurement point. For example, for UT, the mean concentrations of 16 PAHs in the heating season were in the decreasing order Fl > Py > Ch > BaA > DBA > Ph > BaP > BbF > BkF > BghiP > An > IP > Flu > Acy > Ace (0.1–26.7 ng·m<sup>-3</sup>); whereas, the order was Py > BaA > Flu > An > DBA > BaP > Ch > Fl > BbF > Ph > BkF > IP > Ace > BghiP > Acy (0.02–10.9 ng·m<sup>-3</sup>) in the non-heating season.

The profile of 16 PM<sub>1</sub>-bound PAHs is illustrated in Figures 2–4. In RB, Ch, Fl, BaP, Flu, Py had the biggest total percentages in ΣPAH (67.9% and 72.8% of the ΣPAH mass in the heating and non-heating seasons, respectively). In the heating season in UB, BaA, Fl, Ch, BaP and Py constituted 66.1% of the ΣPAH mass. BaA, BaP, Ph and Ch were dominant in the non-heating season (total value = 58.0%). The PAH profile in UT was slightly different - BaA, Py, Fl, Ch, DBA, BaP and BbF made 74.4% of the ΣPAH mass. In the heating season, Fl, DBA, Ch, Py, BaA, BkF, BbF and BaP were responsible for 82.6% of the ΣPAH mass. In the non-heating season, BaA, Py, BaP, Flu and An constituted 65.9% of the ΣPAH mass (BaA made 22.8%).



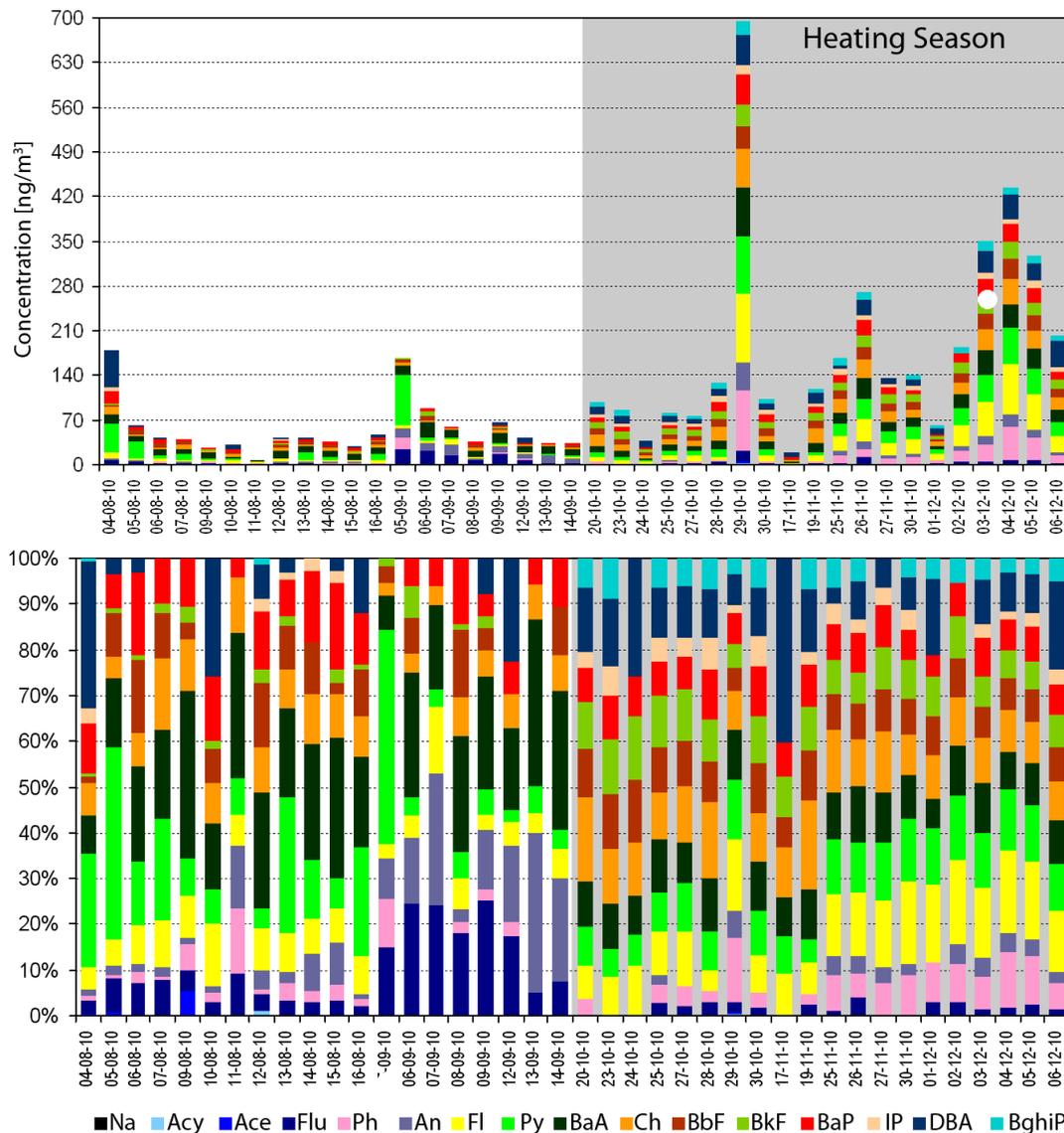
**Figure 2.** Twenty-four-hour concentrations of 16 PAHs contained in PM<sub>1</sub> and percentages of specific PAHs in the PAH sum at the regional background point (RB).



**Figure 3.** Twenty-four-hour concentrations of 16 PAHs contained in PM<sub>1</sub> and percentages of specific PAHs in the PAH sum at the urban background point (UB).

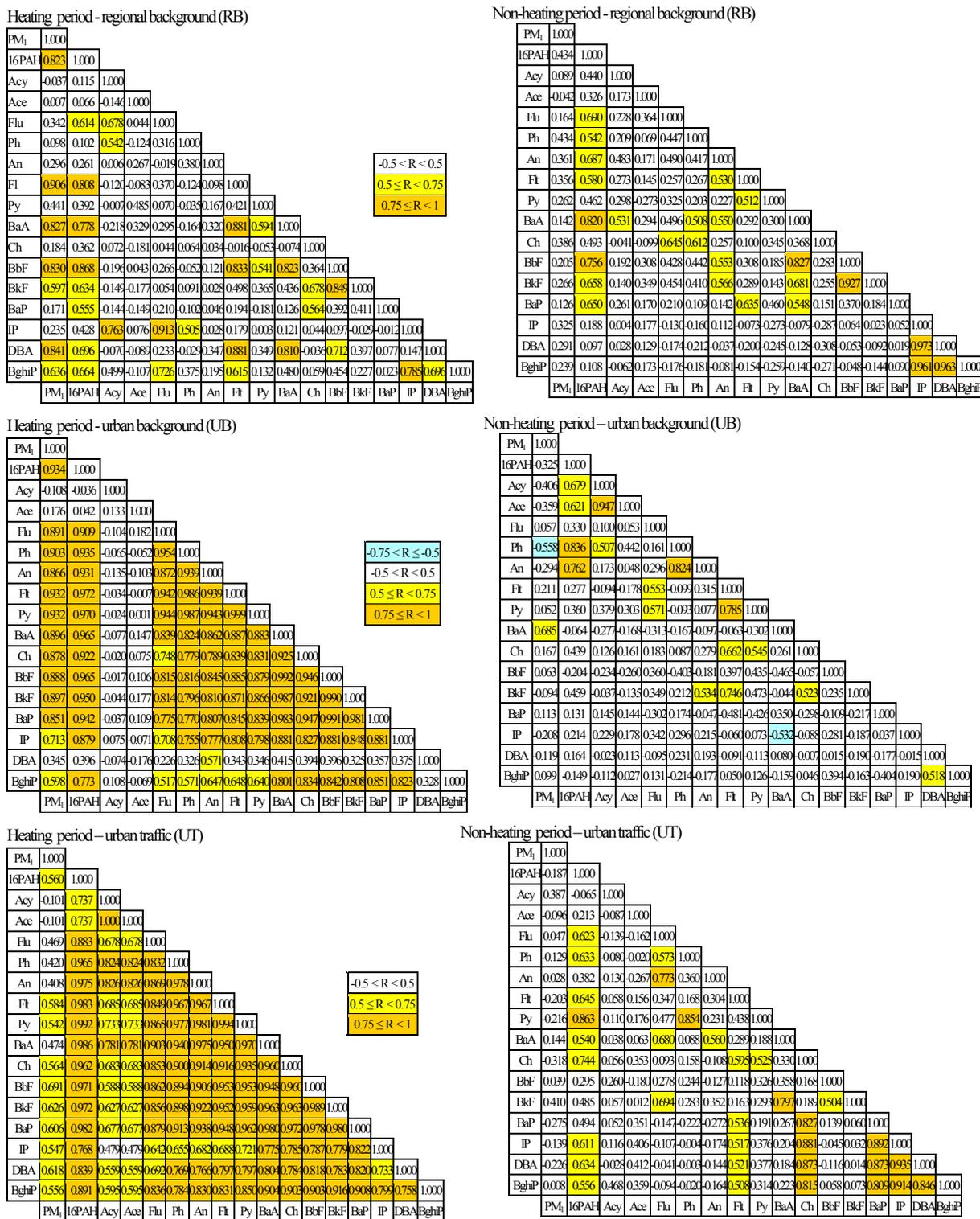
On several winter days (03.10.2009 and 9.04.2010 at RB, 17–19.01.2010 at UB, 29.10.2010 at UT), some PAHs had unusually high mass contributions to  $\sum$ PAH and ambient concentrations and caused very high  $\sum$ PAH ambient concentrations. At each point they were BaA, Py, Fl, Ch, BaP, and BbF, markers of the emissions from coal combustion and incineration [4]. Such high ambient concentrations of these compounds in the high pollution episode days may be accounted for by intensified fuel combustion (heating season) and also by the meteorological conditions favoring accumulation of the pollutants in the near-ground layer of the atmosphere.

The differences in the PAH profiles, both between the points and within the surroundings of each measurement point between the seasons, reflected the differences in the PAH origin at the points and in seasons. The finding was corroborated by the differences in the linear correlation coefficients calculated between the concentrations of specific PAHs, the PAH sum and PM<sub>1</sub> for the points and seasons (Figure 5).



**Figure 4.** Twenty-four-hour concentrations of 16 PAHs contained in PM<sub>1</sub> and percentages of specific PAHs in the PAH sum at the traffic point (UT).

In the non-heating season in UT, RB and UB, there were high values of correlations between the concentrations of heavier PAHs (*i.e.*, BghiP or DBA), which confirmed the dominant influence of the PAH emission from traffic sources [10,18,20,21]. It seems that due to the lack or to the significant reduction of emissions from other sources, traffic and industry (including energy production) were dominant sources of PAHs in the air of southern Poland. In the heating period (particularly in UB and UT), concentrations of most examined compounds were highly correlated. It is possible that the activity of numerous PAH sources was responsible for such a situation. In UB, these were mainly low emissions (coal and biomass combustion in home furnaces) and more intensive (than in summer) energy production (mainly based on the hard and brown coal combustion). In UT, the same sources were active; additionally, there was a strong influence of the traffic emission. In RB, mainly local and dispersed sources and the inflow of pollutants from other, more polluted regions, affected the air pollution with PAHs in both seasons [10,22,23].



**Figure 5.** Correlation matrices for 24-h concentrations of PM<sub>1</sub>, sum of 16 PAHs and particular PAHs in two averaging periods for three locations in Silesia (Poland).

It is worth taking into account the high BaP percentage in the concentration of 16 PAHs. For the examined areas and over the whole measurement period, it was 9%–13%. The ambient concentration of the PM<sub>10</sub>-bound BaP (BaP bound to particles not greater than 10 μm) has the limit that should not be exceeded; the yearly permissible ambient concentration of PM<sub>10</sub>-bound BaP is 1 ng·m<sup>-3</sup> [24,25].

Consequently, the mean PM<sub>1</sub>-bound BaP concentrations in RB, UB and UT were very high. The values were 3.24 ng·m<sup>-3</sup> (4.03 ng·m<sup>-3</sup>—Heating season; 2.46 ng·m<sup>-3</sup>—Non-heating season), 7.72 ng·m<sup>-3</sup> (12.48 ng·m<sup>-3</sup>—Heating season; 2.97 ng·m<sup>-3</sup>—Non-heating season) and 9.5 ng·m<sup>-3</sup> (14.27 ng·m<sup>-3</sup>—Heating season; 4.73 ng·m<sup>-3</sup>—Non-heating season) in RB, UB and UT, respectively. Such a finding shows that even though RB was located far away from the anthropogenic emission sources, the BaP and PM<sub>1</sub>-bound BaP concentrations exceeded the permissible level more than three times there. In UB in the densely developed and populated area, the permissible BaP value was exceeded nearly eight times, whereas the value was almost 10 times higher in UT. High BaP concentrations were observed both in the heating season and the remaining part of the year. Such a situation was not observed in other European regions even though the permissible mean yearly values were also exceeded in the Czech cities. Nonetheless, the PM<sub>1</sub>-bound BaP concentrations did not exceed 0.39 ng·m<sup>-3</sup> [14]. The research conducted at the roadside and urban background in Madrid (Spain) showed that the BaP concentration in winter was 0.24 ng·m<sup>-3</sup> and 0.054 ng·m<sup>-3</sup>, respectively. In summer, the BaP concentrations observed in Madrid (Spain) were even lower [26]. On the other hand, the BaP concentrations as high as those observed in RB, UB and UT are typical for cities in southern Poland and are observed every year. For example, 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 [27].

Table 2 presents BaP concentrations and the following indicators of the exposure to the PAH mixture: carcinogenic equivalent (CEQ), mutagenic equivalent (MEQ), TCDD-toxic equivalent (TEQ), and percentages of seven PAHs determined in this study, whose carcinogenic influence was confirmed in the sum of the determined PAHs ( $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$ ). The way in which each indicator was calculated is given under the table. The values in the table were calculated with the results obtained in this study and additionally, results from other world regions taken from the publications quoted in Table 2 [6,10,14,26,28–33].

In the heating season, the mean CEQs for the whole monitoring period were 5.85 ng·m<sup>-3</sup> (range: 0.01–30.33 ng·m<sup>-3</sup>)—RB; 18.46 ng·m<sup>-3</sup> (range: 5.78–51.93 ng·m<sup>-3</sup>)—UB; and 106 ng·m<sup>-3</sup> (range: 19.36–303.78 ng·m<sup>-3</sup>)—UT. They were unquestionably higher than the non-heating season values. It was particularly visible for UT, where CEQ was approx. seven times higher in the heating season than its mean value in the non-heating season.

In the European cities, the CEQ values were lower at the urban and background locations than in Złoty Potok or Katowice (Poland). The values obtained for Asian cities (e.g., Urumqi in China, and Chennai City and Delhi in India) were as high as or higher than those observed in Poland. The values observed for Urumqi and Chennai City in the urban area in winter were 43.18 ng·m<sup>-3</sup> and 20.72 ng·m<sup>-3</sup>, respectively. The value for Chennai City was even higher in summer (44.29 ng·m<sup>-3</sup>) with the BaP concentration of 25.6 ng·m<sup>-3</sup>. On the other hand, the CEQ value did not exceed 1 ng·m<sup>-3</sup> in Madrid (Spain), Atlanta (USA), or Bumardas and Chréa (Algeria).

**Table 2.** Concentration values of BaP, CEQ, MEQ, TEQ and  $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$  for PM-bound PAHs in various world regions.

City, Country	Sampling Point	Sampling Period	BaP	CEQ	MEQ	TEQ	$\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$	Reference
			ng·m <sup>-3</sup>		pg·m <sup>-3</sup>			
Złoty Potok, Poland <sup>1</sup>	regional background		4.03	5.85	4.87	7.36	0.52	
Katowice, Poland <sup>1</sup>	urban background	heating season 2009/2010	12.48	18.46	20.47	91.95	0.56	This study
	traffic point		14.27	106.00	29.54	147.79	0.63	
Złoty Potok, Poland <sup>1</sup>	regional background		2.46	4.50	4.29	13.80	0.50	
Katowice, Poland <sup>1</sup>	urban background	non-heating season 2009/2010	2.97	5.29	4.23	13.71	0.59	
	traffic point		4.73	15.46	6.45	20.42	0.55	
Zabrze, Poland <sup>1</sup>	urban background	Winter 2007/2008	16.09	25.04	25.24	116.03	0.66	[6]
Zabrze, Poland <sup>2</sup>	crossroads	June–August 2006	1.1	1.48	1.90	10.29	0.48	[10]
Ruda Śląska <sup>2</sup>	roadside		0.3	1.57	0.87	6.62	0.84	
Brno, Czech Republic <sup>1</sup>	large city	Winter 2009	1.39	5.35	3.19	9.65	0.55	[14]
		Winter 2010	2.82	8.71	5.85	15.81	0.57	
		Summer 2009	0.35	3.17	0.84	2.74	0.58	
		Summer 2010	0.15	0.45	0.29	0.83	0.54	
Šlapanice, Czech Republic <sup>1</sup>	small town	Winter 2009	1.65	5.94	3.72	10.63	0.67	[14]
		Winter 2010	2.84	9.24	5.98	16.56	0.58	
		Summer 2009	0.39	3.08	0.93	2.93	0.58	
		Summer 2010	0.15	0.35	0.27	0.79	0.57	
Madrid, Spain <sup>1</sup>	roadside	Winter 2009	0.24	0.51	0.51	2.55	0.47	[26]
	urban background		0.054	0.12	0.11	0.62	0.56	
	roadside	Summer 2009	0.034	0.12	0.09	0.43	0.47	
	urban background		0.022	0.10	0.05	0.26	0.57	

Table 2. Cont.

City, Country	Sampling Point	Sampling Period	BaP	CEQ ng·m <sup>-3</sup>	MEQ	TEQ pg·m <sup>-3</sup>	$\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$	Reference
Bumardas, Algeria <sup>1</sup>	urban		0.111	0.43	0.26	0.37	0.44	
Rouiba-Réghaia, Algeria <sup>1</sup>	industrial district	October 2006	0.296	1.48	0.70	1.33	0.62	[28]
Chr�a, Algeria <sup>1</sup>	forested mountains		0.018	0.11	0.04	0.08	0.39	
Florence, Italy <sup>2</sup>	urban background	Cold 2009–2010	0.47	2.72	0.99	5.39	0.78	
	urban traffic		1.0	5.43	2.17	11.79	0.74	
Livorno, Italy <sup>2</sup>	suburban background		0.20	0.83	0.44	2.10	0.63	[29]
Florence, Italy <sup>2</sup>	urban background	Warm 2009–2010	0.049	0.41	0.14	1.01	0.61	
	urban traffic		0.21	1.54	0.54	3.47	0.60	
Livorno, Italy <sup>2</sup>	suburban background		0.02	0.09	0.07	0.37	0.46	
Urumqi, China <sup>2</sup>	urban	Winter 2010/2011	2.21	43.18	13.39	63.40	0.77	[30]
		Autumn 2010	0.53	10.09	2.56	12.77	0.93	
Chennai City, India <sup>2</sup>	commercial region	Winter 2009/2010	6.5	13.44	25.77	111.22	0.31	[31]
	urban region		8.1	20.72	37.42	136.13	0.28	
	residential region		16.2	19.68	24.28	37.32	0.13	
	industrial region		24.4	39.78	58.52	242.65	0.21	
Chennai City, India <sup>2</sup>	commercial region	Summer 2009	10.3	16.88	25.96	79.58	0.29	
	urban region		25.6	44.29	77.37	246.68	0.47	
	residential region		6.2	13.85	26.64	94.19	0.39	
	industrial region		8.5	38.37	91.24	516.48	0.33	

Table 2. Cont.

City, Country	Sampling Point	Sampling Period	BaP	CEQ ng·m <sup>-3</sup>	MEQ	TEQ pg·m <sup>-3</sup>	∑PAH <sub>carc</sub> /∑PAH	Reference
Delhi, India <sup>2</sup>	traffic point	Winter 2007	9.9	28.92	24.27	125.43	0.67	[32]
		Summer 2007/2008	5.1	17.64	10.60	57.76	0.62	
Atlanta, USA <sup>2</sup>	urban	April–June 2004	0.04	0.10	0.12	0.48	0.47	[33]
	suburban-highway		0.066	0.15	0.18	0.66	0.51	
	rural		0.015	0.05	0.05	0.23	0.44	
	urban	October–December 2004	0.265	0.53	0.59	2.27	0.64	
	suburban-highway		0.492	0.90	0.97	3.52	0.68	
rural	0.199	0.48	0.46	2.12	0.70			

<sup>1</sup> PM<sub>1</sub> <sup>2</sup> PM<sub>2.5</sub>; CEQ = 0.001 × ([Na] + [Acy] + [Ace] + [Flu] + [Ph] + [Fl] + [Py]) + 0.01 × ([An] + [Ch] + [BghiP]) + 0.1 × ([BaA] + [BbF] + [BkF] + [IP]) + 1 × [BaP] + 5 × [DBA]; values of 0.001, 0.01, 0.1 and 1 are the so-called toxic equivalence factors (TEF) for specific PAHs, taken from the study [5]; MEQ = 0.00056 × [Acy] + 0.082 × [BaA] + 0.017 × [Ch] + 0.25 × [BbF] + 0.11 × [BkF] + 1 × [BaP] + 0.31 × [IP] + 0.29 × [DBA] + 0.19 × [BghiP]; values of 0.00056, 0.082, 0.017, 0.25, 0.11, 1, 0.31, 0.29, 0.19 and 0.01 are the so-called minimum mutagenic concentrations (MMC) for specific PAHs, taken from the study [2]; TEQ = 0.000025 × [BaA] + 0.00020 × [Ch] + 0.000354 × [BaP] + 0.00110 × [IP] + 0.00203 × [DBA] + 0.00253 × [BbF] + 0.00487 × [BkF]; values of 0.000025, 0.00020, 0.000354, 0.00110, 0.00203, 0.00253 and 0.00487 are the so-called TCDD-TEF, *i.e.*, toxic equivalency factor relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin TCDD (for TCDD, TEF = 1.0) for specific PAHs, taken from the study [12]; ∑PAH<sub>carc</sub>/∑PAH = ([BaA] + [BaP] + [BbF] + [BkF] + [Ch] + [DBA] + [IP])/([Acy] + [Ace] + [Flu] + [Ph] + [An] + [Fl] + [Py] + [BaA] + [Ch] + [BbF] + [BkF] + [BaP] + [DBA] + [BghiP] + [IP]).

In winter, the MEQ values in UB and UT were also high, *i.e.*, 20.27  $\text{ng}\cdot\text{m}^{-3}$  (range: 6.61–55.21  $\text{ng}\cdot\text{m}^{-3}$ ) and 29.54  $\text{ng}\cdot\text{m}^{-3}$  (range: 4.55–89.13  $\text{ng}\cdot\text{m}^{-3}$ ), respectively. Similar values were obtained in Zabrze (Poland), Chennai City (India) and Delhi (India). The calculated values were much lower in other locations, particularly in the European ones. For Polish locations, the MEQ values were always higher in the heating season. On the other hand, the MEQ values calculated in summer for Chennai City (India) in the urban and industrial regions were much higher than in winter, *i.e.* 77.37  $\text{ng}\cdot\text{m}^{-3}$  and 91.24  $\text{ng}\cdot\text{m}^{-3}$ , respectively.

In the heating season, the CEQ and MEQ at UB were three to four times higher than the values observed at RB. The TEQ values were 12.5 times higher (UB—91.9  $\text{pg}\cdot\text{m}^{-3}$ ; RB—7.4  $\text{pg}\cdot\text{m}^{-3}$ ). At UT (heating season), TEQ was also high (147.8  $\text{pg}\cdot\text{m}^{-3}$ ). A similar situation was observed in Chennai City (India), where TEQ values exceeded 200  $\text{pg}\cdot\text{m}^{-3}$  and reached 516.5  $\text{pg}\cdot\text{m}^{-3}$  in the industrial region. In the non-heating season in UB and UT, the mean TEQ values were definitely lower than in the heating season (RB was an exception). In general, the values were still higher than in the European locations.

The mean concentrations of seven carcinogenic PAHs [13] in the heating season were 4.2–4.5 times higher in UT and UB than in the non-heating season. For  $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$ , no significant visible seasonal change was observed at three Polish locations. In the heating season, only in UT was the indicator value slightly higher than in the non-heating season. For the remaining measurement points, the values were similar and ranged between 0.52 and 0.59. For most measurement points for which CEQ, MEQ and TEQ were calculated, the  $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$  ratio was 0.45–0.60 (Table 2). In the extreme cases, the observed values were 0.84 (roadside; Ruda Śląska, Poland), 0.77 and 0.93 (urban area; Urumqi, China), and 0.78 (urban background; Florence, Italy).

Extremely low values were seen in the research conducted by [31]. The  $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$  ratios differed from the remaining ones and were 0.13–0.47. The remaining indicators of the exposure to the PAH sum (CEQ, MEQ, TEQ and BaP concentration) were high in comparison to other locations.

#### 4. Conclusions

The detailed analyses helped to reach the following conclusions:

- 1 over the whole measurement period, mean concentrations of the  $\text{PM}_{10}$ -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;
- 2 concentrations of the sum of 16  $\text{PM}_{10}$ -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 previously;
- 3 the highest concentrations of most PAHs were observed at UT point, both in the heating and in the non-heating seasons;
- 4 in the typical urban background area, mainly municipal emissions (burning coal, biomass, waste and rubbish in home furnaces) and energy production (mainly based on hard and brown coal combustion) influence PAH concentrations in the air; in the urban site located near highway, the same sources were active as in the urban background area; additionally, there was a strong influence of the traffic emission. In RB, mainly local and dispersed sources and

- the inflow of pollutants from other, more polluted regions, affected the air pollution with PAHs in both seasons;
- 5 high percentage of BaP in the PAH sum (9%–13%) and very high ambient concentrations of the PM<sub>1</sub>-bound BaP, particularly in the heating season (4–14 ng·m<sup>-3</sup>), may pose a serious threat to the Silesia inhabitants; 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);
  - 6 in the heating season, the mean CEQs for the whole monitoring period were 5.85 ng·m<sup>-3</sup> in RB, 18.46 ng·m<sup>-3</sup> in UB, and 106 ng·m<sup>-3</sup> in UT; they were unquestionably higher than the non-heating season values and definitely higher than the values obtained in other European regions;
  - 7 MEQ, TEQ and  $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$ , proposed by the authors as other indicators of the exposure to the PAH mixture, were very high in the Upper Silesian urban area when compared to other regions; the highest indicator values were observed in the heating season;
  - 8 it may be suspected that in Central, Central-East and East Europe traffic is not the primary PAH source; the PM-bound PAHs come mainly from the fossil fuel combustion for heat and power production.

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### Author Contributions

The study was completed with cooperation between all authors.

### Conflicts of Interest

The authors declare no conflict of interest.

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