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The Mass Distribution of Particle-Bound PAH Among Aerosol Fractions: A Case-Study of an Urban Area in Poland

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1. Introduction

Zabrze is one of the fourteen Silesian cities that form together the Silesian Agglomeration (Fig. 1-4). The Silesian Agglomeration lies in the center of the Silesia Province, occupies 1230 km^2, its population is about 2.1 million (1691 inhabitants per one square kilometer). It is one of the most urbanized and industrialized regions of Central Europe. Such a dense concentration of people on such a heavily urbanized and industrialized area is unique in Europe. About 50% of the Silesia Province gross product and 7% of the gross domestic product come from the Silesian Agglomeration. Six European capital cities, Berlin, Prague, Wien, Bratislava, Budapest and Warsaw, lie within 600 km from Katowice, the capital city of the Agglomeration. The main transport routes linking Poland with Western Europe run through it in all directions.

From the air protection point of view, the Silesian Agglomeration is one of the most interesting regions both in Poland and in Europe. Hard coal of better quality, mined in the western part of the Agglomeration since the 18th century, has been processed into coke and gas in five cities of the Agglomeration. Poorer quality coal, from the eastern part of the Agglomeration, is burnt in several great power stations, smaller power and heating plants, local heating plants and in domestic stoves. Almost all branches of industry, such as electrical, chemical, glass-making, textile, clothing, and ceramic industries, ferrous and non-ferrous metallurgy, machine-building, hard coal mining and coking very actively have been deteriorating the natural environment for about 200 years.

Nevertheless, three recent decades of economical changes forced in the Silesian Agglomeration the greatest in Poland drop of industrial air pollution (in Zabrze, yearly dust fall exceeded 2100 g m^{-2} in the 70s, oscillated between 700 and 800 g m^{-2} in the 80s, was less than 350 g m^{-2} after 1995). The concentration of the ambient particulate matter (PM) dropped significantly (Fig. 1). The greatest drop of the PM concentrations occurred between 1985 and 2000, when the total industrial emission of air pollutants drastically decreased in the effect of the transformation of the whole national industry and closing or restructuring of many great plants in the 80s. In 1990, the list of 80 Polish plants exerting the greatest impact on the

environment was announced. More than 20 of them were located in the Katowice Region whose the Silesian Agglomeration was a sub-region. The actions to lower the emission from these plants and limiting the output of heavy industry decreased the emission of dust and its gaseous precursors (Central Statistical Office of Poland [CSO], 1976-2001) and halved the ambient concentrations of dust at measuring points (at the beginning of the 80s, in Dąbrowa Górnicza the PM concentration was almost 0.5 mg m^{-3}). During the 90s, the PM concentrations continued to drop and since 2000 the yearly PM concentrations have remained constant at the approximate level between 65-110 µg m^{-3} depending on a measuring site. The industrial emission of PM and its precursors (SO_2, NO_x) has also remained almost stable (Central Statistical Office of Poland [CSO], 2001-2011).

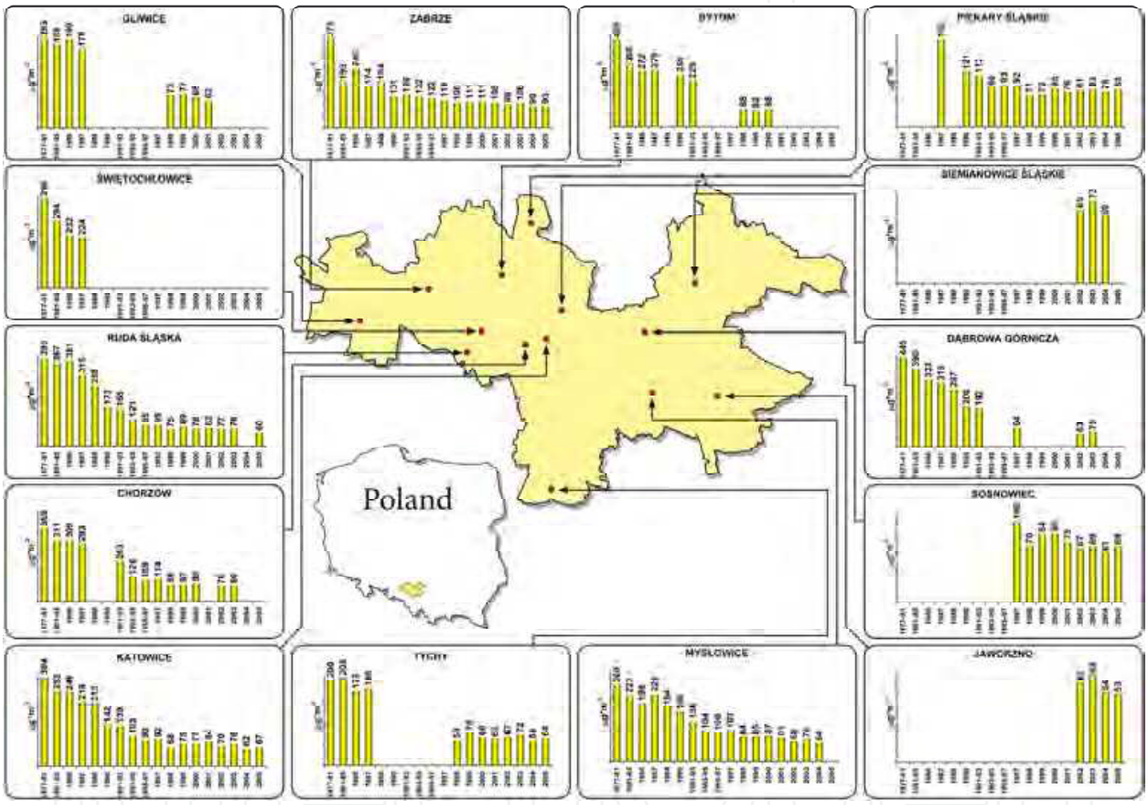


Fig. 1. The total PM concentrations (µg m^{-3}) in 14 cities of the Silesian Agglomeration in 1977-2005 (SSI, 1980-2006)

The concentrations of PM_{10}[1], although slightly lower than in the 90s, are still high in the Silesian Agglomeration and have also been stabilized in each of the cities since 2000 (Fig. 2).

[1]For a number $d>0$, PM_d is the fraction of the particles that have the aerodynamic diameter not greater than d. For $0<c<d$, PM_{c-d} denotes the fraction of particles with the diameters between c and d. We have:
$PM_{2.5}$–particles with the aerodynamic diameter not greater than 2.5 µm (fine particles)
$PM_{2.5-10}$–particles with the aerodynamic diameter between 2.5 and 10 µm (coarse particles)
PM_{10}–particles with the aerodynamic diameter not greater than 10 µm ($PM_{2.5}$ and $PM_{2.5-10}$ together)

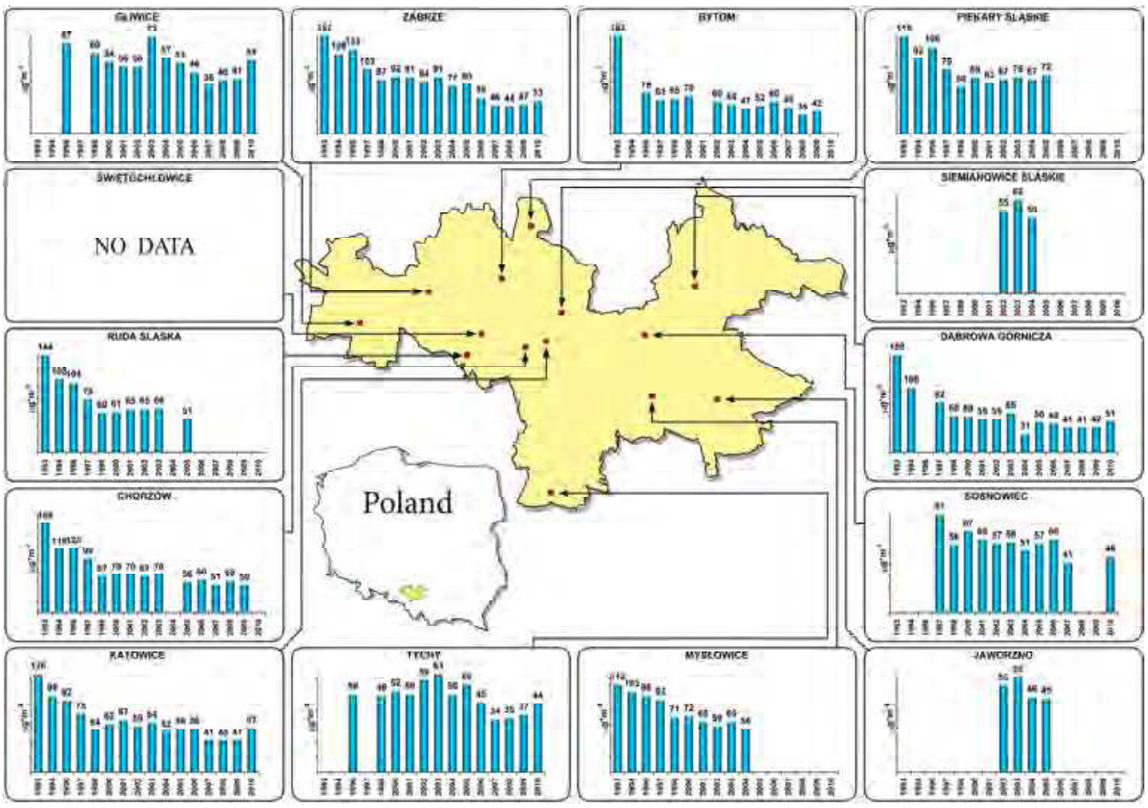


Fig. 2. The PM_{10} concentrations (μg m^{-3}) in 14 cities of the Silesian Agglomeration in 1993-2010 (SSI, 1980-2006; The Provincial Inspector for Environmental Protection in Katowice [PIEP], 2002-2011)

There are hundreds of organic compounds to be found in PM, among them more than one hundred polycyclic aromatic hydrocarbons (PAH). Since PAH tend to have low vapor pressures, they are usually adsorbed onto PM in the atmosphere. The vapor pressure of a PAH is inversely proportional to the number of rings it contains. As a result, the larger molecular weight PAH (≥ 4) are mostly adsorbed onto PM in atmospheric samples, while the lower molecular weight PAH can be found both free in the atmosphere and bound to particles. In some conditions, from 72% to even > 98% of four-, six-, and seven-ring ambient PAH are bound onto particles of PM_3 and PM_7 (Sheu et al., 1997). Seventeen PAH: acenaphtene (Acy), acenaphthylene (Ace), anthracene (An), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), benzo(g,h,i)perylene (BghiP), chrysene (Ch), dibenzo(a,h)anthracene (DBA), fluoranthene (Fl), fluorene (F), phenanthrene (Ph), pyrene (Py) and indeno(1,2,3-cd)pyrene (IP) are most often investigated. The most hazardous property of air pollutants is their carcinogenicity. Seven PAH: BaA, BaP, BbF, BkF, Ch, DBA and IP the USEPA classified as probable human carcinogens (http://www.epa.gov/).

The most important natural sources of PAH are forest fires and eruptions of volcanoes. However, amounts of the natural ambient PAH are small compared to the amounts of the anthropogenic PAH. The majority of anthropogenic PAH come from incomplete combustion of fossil fuels or organic matter (Sienra et al., 2005; Zou et al., 2003). In urban air this

includes PAH combustion in car engines and residential heating (Harrison et al., 1996; Manoli et al., 2004; Kristensson et al., 2004).

Since 1977, in all cities of the Silesian Agglomeration, the State Sanitary Inspection (SSI, Department in Katowice) has measured ambient concentrations of PM-bound BaP continuously and 8 other PAH periodically (Fl, BaA, Ch, BbF, BkF, DBA, BghiP, IP; several years in each city). The total ambient concentration of these nine PAH drastically decreased in the period 1977—2005 (Fig. 3). The concentrations of PM-bound BaP dropped rapidly in all cities of the Agglomeration in 1980—1990 (Fig. 4). In each city the vast yearly concentrations of BaP from 1977—1981, reaching 500 ng m^{-3} in Ruda Śląska, decreased several times during this decade. During the 90s, the concentrations of BaP dropped to less than 20 ng m^{-3} in each city of the Agglomeration. These concentrations have been still very high and hazardous to humans and the concentrations of PM_{10}-bound BaP, measured since 2001, were high (Fig. 4), like the concentrations of PM-bound one.

In general, the ambient particles with the aerodynamic diameter greater than 10 μm are not inhalable. Therefore, from the sanitary point of view, the concentrations of PM_{10} should be the measure of the hazard from ambient particles. In all cities of the Agglomeration, the yearly average concentrations of PM_{10} and PM_{10}-bound BaP exceed their permissible levels (40 μg m^{-3} and 1 ng m^{-3}, respectively, Fig. 2). The limit of 40 μg m^{-3} on the yearly average concentration of PM_{10} has been in effect in majority of the European countries for about 20 years (in Poland since 1998). Although the air quality has been improving for the latest thirty years, there is no city in the Silesian Agglomeration where this standard was not yearly exceeded in the period 1993-2010 (Fig. 2). Even the yearly average $PM_{2.5}$ concentrations, measured continuously since 2001 in Zabrze, exceed 25 μg m^{-3}, the standard for the $PM_{2.5}$ concentrations, every year (Rogula-Kozłowska et al., 2010; Klejnowski et al., 2007a, 2007b, 2009; PIEP, 2002-2011). Although the spectacular reduction of the industrial emissions, especially of coarse dust, caused significant drop of the concentrations of PM and PM-bound BaP the PM_{10} concentrations decreased only a little (Fig. 2).

The poor air quality conditions in the cities of the Agglomeration are due to bad spatial arrangement of industrial and urban infrastructure. The industrial objects are interspersed with living quarters. The differences in the level of industrialization, urbanization and land use cause spatial non-homogeneity of the air pollution from industrial, municipal or vehicular sources even over small areas. The area of the Agglomeration is also affected by periodically occurring episodes of very high concentrations of air pollutants (especially of PM_{10} in winter in city centers), which inflate the yearly PM concentrations.

The inventory of the Silesian air pollution sources from 2006 contains 107 business entities emitting PM_{10} and BaP within the Silesian Agglomeration (Air protection program [APP], 2010). In 2006, they emitted 4.9 Gg of PM_{10} and 1.3 Mg of benzo(a)pyrene into the air. In average, this industrial emission was 44% and 28% of, respectively, the total PM_{10} and BaP emissions in the Agglomeration. The municipal and household emission[2], mainly from local heating plants and domestic stoves, have even greater share in the PM_{10} and the BaP total

[2]Heating plants and furnaces fed with solid fuel (mainly coal) are main sources of PM_{10} and BaP. They include small (local) heating plants and domestic stoves. In the Silesian Agglomeration, the estimated average of the household heat demands covered by solid fuel combustion in domestic stoves is still greater than 34%. The emissions of PM_{10} and PM_{10}-bound BaP from the solid fuel furnaces are more than 94% of their totals in the surface emission. It is due to bad technical condition and age of the heating plants and stoves and also to the poor quality of the combusted coal.

concentrations. In 2006, it was 5.3 Gg and 3.2 Mg, what made 47% and 71% of the total PM_{10} and BaP emissions. This contribution is even greater in a heating season—in winter.

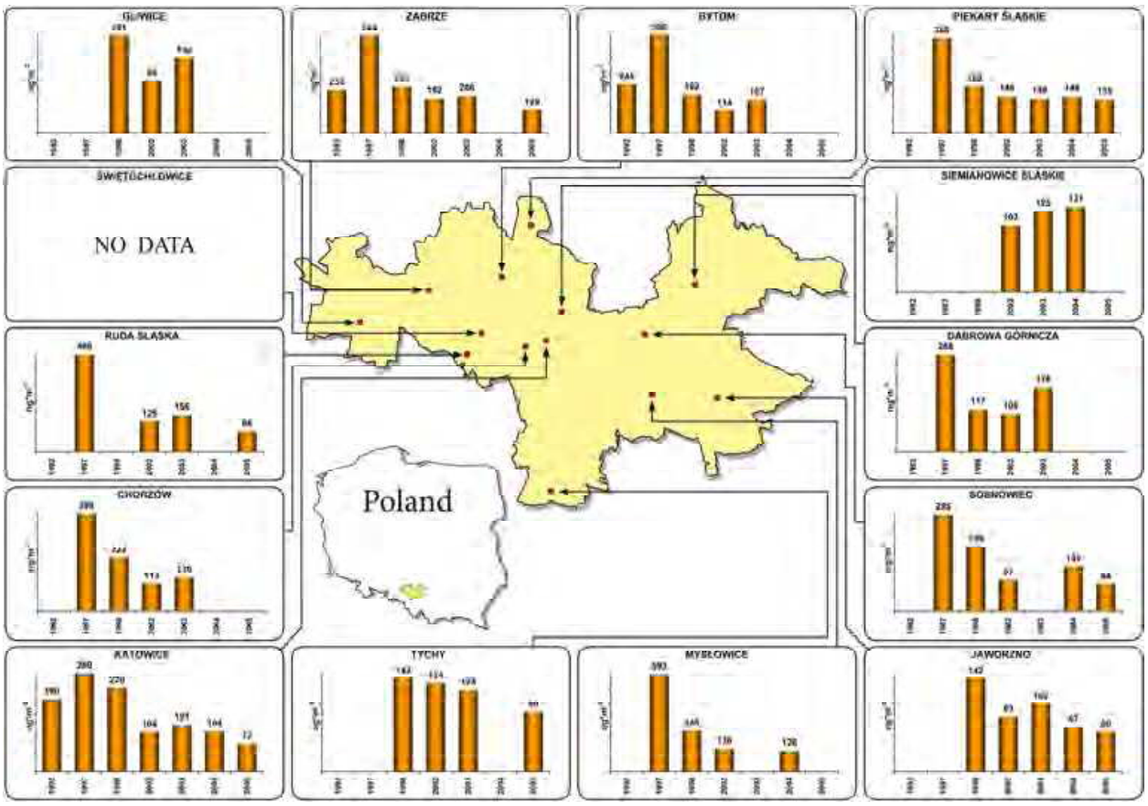


Fig. 3. The concentrations of the sum of 9 PM-bound PAH (Fl, BaA, Ch, BbF, BkF, BaP, DBA, BghiP, IP) in 14 cities of the Silesian Agglomeration in 1992-2005 (SSI, 1993-2006)

The elevated autumn and winter PAH concentrations in the Agglomeration my be linked with the emission from municipal sources. The seasonal dependence of the PM-bound PAH concentrations was observed in three Silesian cities: Katowice, Sosnowiec and Zawiercie in 2008. The seasonal PAH concentrations were 5.1-18.6 ng m^{-3} in spring, 5.4-7.6 ng m^{-3} in summer, 6.8-24.0 ng m^{-3} in autumn and 26.2-61.3 ng m^{-3} in winter (Zaciera et al., 2010).

Although the reduction of the industrial emission improved the air quality in the Silesian Agglomeration the hazard from PM_{10} (especially from the smallest particles) might grew owing to growth of vehicular emission. For the last two decades, the Poles have imported more than 920000 second-hand cars yearly. Majority of the cars were older than 10 years, they did not meet the emission standards and had high fuel-consumption.

In Gliwice, from April to June 2003, in a trafficked street canyon (1400 vehicles per hour), the average PM_{10} concentration was 94.0 μg m^{-3} and was higher by 40.0 μg m^{-3} than the one measured 100 m apart. The average concentration of total PAH, equal to 191.56 ng m^{-3}, was 1.5 times greater than the background concentration (Grynkiewicz-Bylina et al., 2005). In Zabrze, in summer 2005, the average concentration of the total PM_{10}- and the total $PM_{2.5}$-bound PAH at crossroads were 65.6 ng m^{-3} and 44.4 ng m^{-3}, and were 1.9 and 3.4 times greater than the background concentrations, respectively (Ćwiklak et al., 2009). In Bytom, on

the turn of February and March 2007, the average concentrations of the total vehicular $PM_{2.5}$- and the total vehicular PM_{10}-bound PAH were between 56.2 and 73.4 ng m^{-3} and 75.1 and 91.0 ng m^{-3}, respectively. The significant in this city influence of the industrial emission and the emission from low sources was excluded by proper location of the measuring points (Kozielska et al., 2009).

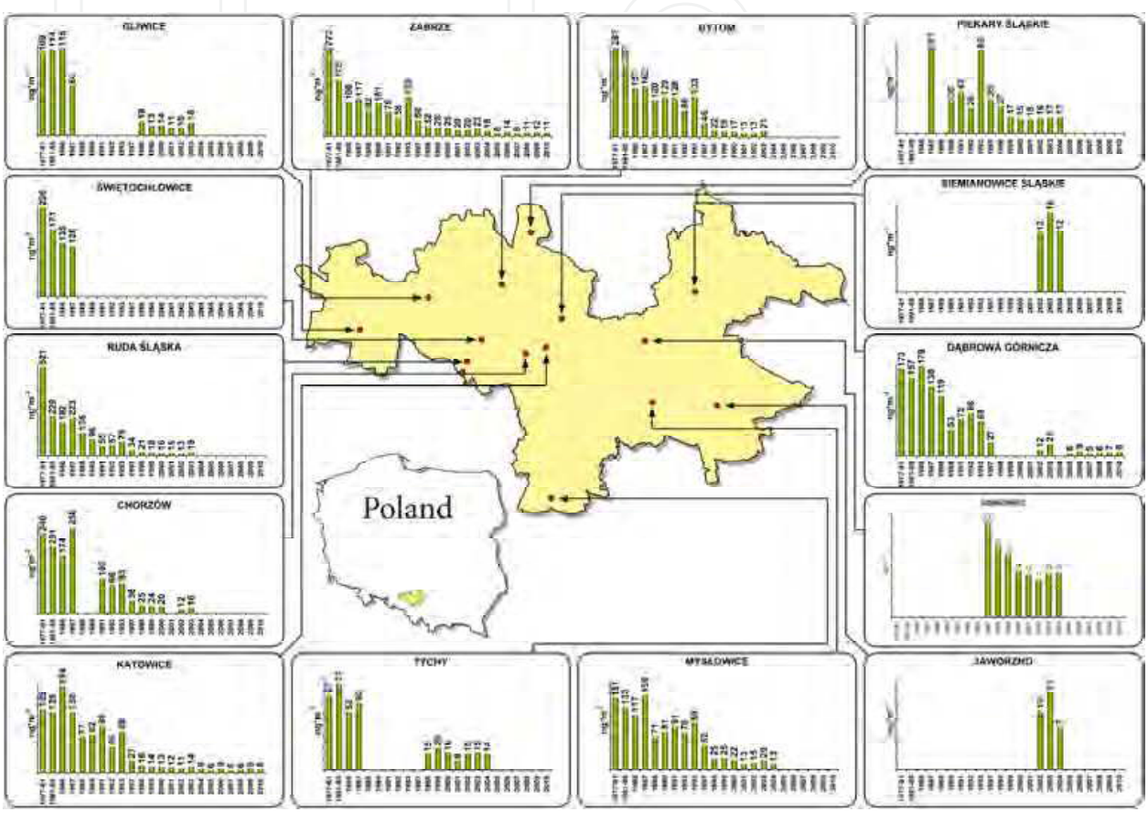


Fig. 4. The concentrations of PM-bound BaP in 1977-2001 and PM_{10}-bound BaP in 2002-2010 in 14 cities of the Silesian Agglomeration (SSI, 1982-2006; PIEP, 2005-2011)

The hazard from the air pollution in the neighborhood of trafficked roads is also elevated by the elevated toxicity of traffic PM_{10} containing allergens and carcinogens, also PAH (Kinney et al., 2000; Pakkanen et al., 2003; Vogt et al., 2003).

Now, in the Silesian Agglomeration, when the number of industrial and of the vast fugitive emission sources of PM (mine heaps, dumps) decreased, main PM and PAH sources are domestic furnaces, heat and power plants and road traffic. In the Agglomeration, the industrial and the municipal sources contribute to the air pollution much more than such sources in the Western Europe countries (EMEP, 2009), and the role of vehicular emission grows. As a result, the proportion of fine particles in PM increases. Ambient fine particles have relatively great surface to adsorb PAH (Ravindra et al., 2001; Sheu et al., 1997), so the fine dust is richer in PAH than the coarse one. Therefore, investigation of the particle size distribution of PM and the PAH content of PM fractions is crucial to abate the adverse effects of PM.

The work presents the method and the results of the investigations of the mass distribution of some PM-bound PAH among the PM fractions in the Silesian Agglomeration. The investigated PAH, three-ring: Acy, Ace, F, Ph, An, four-ring: FI, Py, BaA, Ch, five-ring: BbF, BkF, BaP, DBA and six-ring: BghiP, and IP, are on the USEPA CWA list of the priority pollutants.

2. Methods

The site in Zabrze, selected for the experiment, is representative of the air pollution conditions typical in the Silesian Agglomeration – by the Directive 2008/50/EC definition, it is an urban background measuring point (Directive, 2008). The effects of the industrial and the municipal emissions on living quarters of the Agglomeration are represented and may be observed here very well.

Ambient dust was sampled with the use of a thirteen stage DEKATI low pressure impactor (DLPI), which collects thirteen PM fractions onto thirteen separate substrate filters (Table 1). The principle of DLPI operating may be found in (Klejnowski et al., 2010).

There were two periods of sampling: from 7 May to 2 August (summer) and from 26 October to 27 December (winter) 2007. One sample-taking lasted about one week. Seven such sample-takings were done in winter and nine in summer, the measurements covered the sampling periods in 98 and 92%, respectively, and whole summer (2nd and 3rd quarter of 2007) and winter (1st and 4th quarter of 2007) in 27% and 45%.

The mass of the dust collected on aluminum substrates was determined by weighing the substrates before and after exposure on a Mettler Toledo micro-balance. Before weighing, the substrates were kept in the weighing room for 48 hours (temperature 20±2^{0}C, relative air humidity 48±5%). The concentrations of the fractions of PM were computed from the volume of air passed through the impactor and the masses of the dust collected on its stages. All the samples (substrates), till analyzing, were kept in a refrigerator in tight and lightproof containers.

The winter and summer samples were developed separately. For each of the thirteen PM fractions, all its samples (7 in winter and 9 in summer samples per fraction) were extracted together in an ultrasonic bath in dichloromethane (CH_2Cl_2). The extract was percolated, washed and dried by evaporating in the helium atmosphere. The dry residue was diluted in propane-2 ($CH_3CH(OH)CH_3$) and distilled water was added to receive the proportion 15/85 (v/v) of propanol-2 to water. For selective purification, the resulting samples were solidified (SPE) by extracting in columns filled with octadecylsilane (C_{18}, Supelco). PAH were eluted with the use of dichloromethane (CH_2Cl_2). The extract of a PAH fraction was condensed in the helium atmosphere to the volume of 0.5 cm^3. The samples were analysed on a Perkin Elmer Clarus 500 gas chromatograph with a Flame Ionization Detector (FID). An RTX-5 Restek capillary 30 m x 0.32 mm x 0.25 µm column was used to separate the sample components. The flow of the carrier gas, helium, was 1.5 cm^3 min^{-1}. Calibration curves for 15 PAH standards were used in quantitative determinations. The linear correlation of the surfaces of the peaks with the PAH concentrations was checked in the concentration range 1 – 4 ng µl^{-1}. The correlation coefficient ranged from 0.90 to 0.97. The time of the whole analysis was 40 min. FID was provided with hydrogen (45 cm^3 min^{-1}) and air (450 cm^3 min^{-1}). The recoveries of PAH were determined using a standard containing the 15 PAH. They ranged from 85% to 93%.

3. Discussion of the results

3.1 Concentrations of PM- and PM-bound PAH. Origin of PAH in Zabrze

The winter PM_{10} concentrations exceeded 46 μg m^{-3}, the summer ones reached almost 19 μg m^{-3} (Table 1). Such a difference is due to very high emission of PM from combustion of fossil fuels in winter, specific of the Silesian Agglomeration (Rogula-Kozłowska et al., 2008; Pastuszka et al., 2010). The average concentrations of PM_{10} and PM in the experimental period (33.5 μg m^{-3} and 32.5 μg m^{-3}) were lower than the yearly concentrations of PM_{10} in 2007 and PM in 2005 (Fig. 1 and 2). The explanation may by that the former were sampled with DLPI at about 5 m above the ground level during about 16 weeks, missing a part of winter when in Zabrze the highest PM concentrations occur (Klejnowski et al., 2007a, 2009), the latter were measured by SSI at the height 2.5 m during the whole year.

Fraction, μm		PM, μg m^{-3}	PAH, ng m^{-3}															
			Acy	Ace	F	Ph	An	Fl	Py	BaA	Ch	BbF	BkF	BaP	DBA	BghiP	IP	∑PAH
0.03-0.06	W	0.4	nd	nd	0.14	0.14	nd	0.03	0.04	nd	0.08	0.07	0.08	0.05	nd	nd	nd	0.62
	S	0.09	0.01	0.02	0.02	0.05	nd	0.04	0.02	nd	0.11	0.14	0.14	0.04	0.01	0.05	0.06	0.7
0.06-0.108	W	0.59	nd	nd	0.11	0.1	nd	0.04	0.06	nd	nd	0.07	0.11	nd	nd	nd	nd	0.49
	S	0.3	0.02	0.03	0.08	0.14	0.09	0.02	0.02	nd	0.05	0.1	0.07	0.04	nd	nd	nd	0.66
0.108-0.17	W	1.54	nd	nd	0.16	0.16	0.05	0.07	0.07	0.04	0.09	0.22	0.18	0.15	nd	nd	nd	1.19
	S	0.64	0.01	0.03	0.14	0.17	0.03	0.03	0.09	nd	0.06	0.15	0.06	0.03	0.01	0.01	0.01	0.84
0.17-0.26	W	6.57	0	0.05	0.12	0.25	0.03	1.29	1.4	1.62	1.83	1.16	1.25	1.37	0.06	0.21	0.25	10.88
	S	1.25	0.01	0.01	0.09	0.16	0.1	0.02	0.04	0.01	0.01	0.04	0.02	0.01	nd	0.01	nd	0.52
0.26-0.40	W	8.19	nd	0.1	0.28	0.99	0.33	5.08	6.75	5.79	5.51	4.17	4.35	5.39	0.24	0.03	1.96	40.97
	S	2.08	nd	nd	0.04	0.1	0.01	0.02	0.02	0.01	0.03	0.02	0.04	0.02	nd	nd	nd	0.3
0.40-0.65	W	8.77	0.09	0.1	0.27	1.1	0.16	4.64	5.03	5.29	5.06	3.79	4.2	4.86	0.23	1.67	2.14	38.65
	S	3.09	nd	nd	0.03	0.1	0.02	0.02	0.02	0.01	0.04	0.01	0.02	0.02	nd	nd	nd	0.31
0.65-1.0	W	7.59	0.1	0.08	0.28	1.33	0.31	4.65	4.68	5.04	4.54	3.36	3.59	4.27	0.2	1.1	1.77	35.3
	S	2.2	nd	nd	0.01	0.02	nd	0.02	0.01	nd	0.05	0.01	0.03	0.01	nd	nd	nd	0.14
1.0-1.6	W	5	0.1	0.05	0.13	0.86	0.06	3.23	4.24	3.31	3.48	1.88	2.13	2.79	0.09	0.34	0.78	23.47
	S	1.67	0.01	nd	nd	0.02	nd	0.02	0.01	0.01	0.03	0.05	0.06	0.01	nd	nd	0.01	0.24
1.6-2.5	W	2.66	nd	nd	0.04	0.09	0.22	0.26	0.26	0.26	0.3	0.21	0.28	0.32	nd	0.02	0.08	2.34
	S	1.5	0.02	0.03	0.15	0.16	0.04	0.03	0.04	nd	nd	0.1	0.07	0.13	nd	nd	nd	0.77
2.5-4.4	W	2.19	nd	nd	0.1	0.17	0.12	0.04	0.05	0.05	nd	0.05	0.04	nd	nd	nd	nd	0.63
	S	2.15	nd	0.01	0.02	0.04	0.01	0.02	0.01	nd	0.09	0.04	0.02	0.11	nd	nd	nd	0.37
4.4-6.8	W	1.55	nd	nd	0.14	0.21	0.09	0.02	0.04	nd	0.08	0.11	0.11	0.08	nd	nd	nd	0.88
	S	1.99	0.02	0.04	0.09	0.06	0.02	0.03	0.03	nd	0.07	0.07	0.05	0.17	nd	nd	nd	0.62
6.8-10.0	W	1.24	nd	nd	0.14	0.13	0.04	0.02	0.03	nd	0.08	0.08	0.12	0.05	nd	nd	nd	0.69
	S	1.94	nd	0.01	0.02	0.02	0.01	0.02	0.06	nd	0.04	0.07	0.07	0.06	nd	nd	nd	0.39
> 10.0	W	2.28	nd	nd	0.15	0.19	0.09	0.04	0.04	nd	0.04	0.1	0.11	0.08	nd	nd	nd	0.85
	S	2.9	0.01	0.02	0.05	0.06	0.01	0.02	0.05	nd	0.08	0.02	0.03	0.13	nd	nd	nd	0.48

nd – not detected

Table 1. The concentrations of 13 PM fractions and the fraction-related PAH in Zabrze in winter (W) and summer (S) 2007

The winter concentration of total PAH (ΣPAH) in Zabrze in 2007 were only a little higher than the average concentration of the sum of 9 PAH (Σ9PAH) observed by SSI in 2005 (Table 2, Fig. 3). The summer concentrations of ΣPAH in Zabrze in 2007 were lower than 7 ng m^{-3}. The average concentrations of BaP, in 2007 (about 10 ng m^{-3} in the whole measuring period, 1 ng m^{-3} and 20 ng m^{-3} in summer and winter) very well agree with the BaP concentrations measured by SSI in the recent years (Fig. 4).

The winter concentrations of ΣPAH bound onto particular PM fractions in Zabrze in 2007 were from 0.5 to almost 41.0 ng m^{-3}. ΣPAH bound onto $PM_{0.26-0.40}$, $PM_{0.40-0.65}$, $PM_{0.65-1.0}$ had the greatest concentrations (Table 1) because of the high concentrations of Fl, Py, BaA, Ch, BbF, BkF, BaP.

The summer concentrations of ΣPAH bound onto PM fractions in Zabrze in 2007 were from 0.15 to 0.85 ng m^{-3}. ΣPAH bound onto $PM_{0.03-0.06}$, $PM_{0.06-0.108}$, $PM_{0.108-0.17}$, $PM_{0.17-0.26}$, $PM_{1.6-2.5}$ and $PM_{4.4-6.8}$ had higher concentrations than ΣPAH bound to other fractions.

In winter, the PM concentrations and the concentrations of majority the PM fractions were two or three times higher than in summer. For $PM_{0.03-0.06}$ it was 4.5, for $PM_{0.17-0.26}$ more than 5 and for $PM_{0.26-0.40}$ almost 4 times (Table 1). The $PM_{2.5-10}$ concentrations in summer were close to or higher than the $PM_{2.5-10}$ winter concentrations.

The masses of $PM_{2.5}$ and PM_1 were 89 and 72% in winter and 68 and 51% in summer of the mass of PM_{10}, respectively (Fig. 5). The concentrations of ΣPAH behaved similarly. In winter, the concentrations of $PM_{2.5}$ and PM_1-bound ΣPAH were 99 and 82% of the PM_{10}-bound ΣPAH concentrations; in summer it was 77 and 69%, respectively. Despite the disparities between the concentrations of PM_{1-}, $PM_{1-2.5}$ and $PM_{2.5-10}$-bound ΣPAH in both seasons (Fig. 5), the mass contributions of ΣPAH to PM_1, $PM_{1-2.5}$, and $PM_{2.5-10}$ was 0.02—0.04% in summer and 0.38, 0.34 and 0.04% in winter, respectively. In each season, PM_1 and $PM_{1-2.5}$ had almost equal PAH contents. It means that in each season, PM_1 and $PM_{1-2.5}$ as well as PM_1- and $PM_{1-2.5}$-bound PAH came from the same sources.

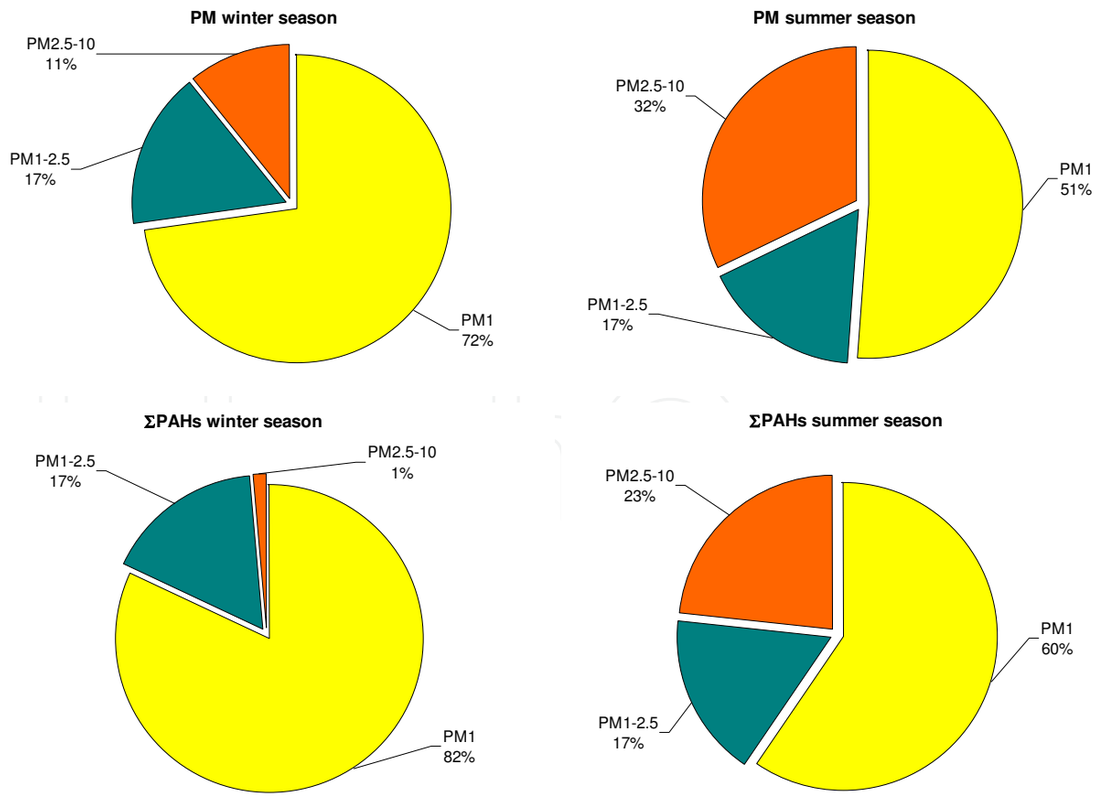


Fig. 5. Contribution of PM_1, $PM_{1-2.5}$ and $PM_{2.5-10}$ to PM_{10} and PM_1-, $PM_{1-2.5}$- and $PM_{2.5-10}$-bound ΣPAH to PM_{10}-bound ΣPAH in Zabrze in winter and summer 2007

The differences between the summer and the winter concentrations of the fraction-bound ΣPAH are greater than the differences between the concentrations of the PM fractions. The concentrations of ΣPAH bound onto $PM_{0.17-0.26}$, $PM_{0.26-0.40}$, $PM_{0.40-0.65}$, $PM_{0.65-1.0}$, $PM_{1.0-1.6}$ are greater from 21 to 251 times in winter than in summer. Noticeably, these fractions are usually formed by primary particles originating from combustion (Chow, 1995; Zhao et al., 2008; Wingfors et al., 2011).

For each of $PM_{0.06-0.108}$, $PM_{0.108-0.17}$, $PM_{0.17-0.26}$, $PM_{0.26-0.40}$, $PM_{0.40-0.65}$ and $PM_{1.6-2.5}$, among the fifteen PAH bound onto each of these fractions, Ph, one of the markers of emission from car engines (Harrison et al., 1996), had the highest summer concentrations. The summer concentrations of F, Py, An and Ch bound onto these fractions were also high. These PAH are also attributed to combustion of gasoline and oil in car engines (Chang et al., 2006; Miguel et al., 1998). In winter, Py, BaA, Ch, BbF and BkF had the greatest concentrations among the 15 PAH in each of these fractions. They belong to CPAH (Prahl & Carpenter, 1983), the nine so called combustion PAH (Fl, Py, BaA, BbF, BkF, BaP, BeP, IP and BghiP; Rogge et al., 1993a, 1993b; Kavouras et al., 1999; Bi et al., 2002; Manoli et al., 2002, 2004; Sienra et al., 2005). In winter, about 80% of the mass of these PAH was in PM_1. In summer, almost 100% of DBA and BghiP and about 80% of IP were in PM_1. Each of the remaining PAH was contained in particles greather than 1 μm at least in several dozen percent (Fig. 6).

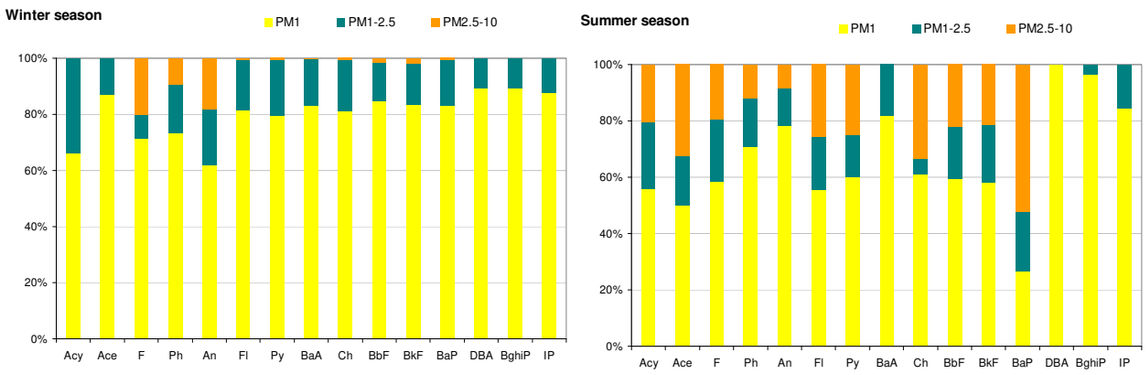


Fig. 6. Contribution of PM_1-, $PM_{1-2.5}$- and $PM_{2.5-10}$-bound PAH to PM_{10}-bound PAH in Zabrze in winter and summer 2007

In summer, the concentration of PM_1-bound BaP was a little more than 20% of the concentration of PM_{10}-bound BaP. The concentrations of BaP were greatest among the concentrations of $PM_{1-2.5}$- and $PM_{4.4-6.8}$-bound PAH.

The winter and the summer profiles of PM-bound PAH differ. In winter, five- and four-ring PAH were 87% of PM-bound ΣPAH. In summer, five- and four-ring PAH were only 58.5% of PM-bound ΣPAH. Three-ring PAH were 39.1% of PM-bound ΣPAH in summer, six-ring PAH were 6.6% and 2.4% of PM-bound ΣPAH in winter and summer, respectively (Table 1).

In winter, $PM_{0.26-0.40}$, $PM_{0.40-0.65}$, $PM_{0.65-1.0}$, $PM_{1.0-1.6}$ were richest in PAH (Fig. 7). $PM_{0.26-1.6}$ contained more than 88% of each: ΣPAH, six-, five- and four-ring PAH; for three-ring PAH it was over 67%. In summer, the PM fractions of PAH between the fractions was uniform except for six-ring PAH, whose contribution to $PM_{0.03-0.06}$ was over 73%.

The mass size distribution of PM is multimodal. Usually, PM is represented by three subdistributions (modes). They are called the nucleation, accumulation and coarse modes. The nucleation mode covers the mass distribution of the population of particles with diameters up

to approximately 0.1 µm, the accumulation mode – the mass distribution of the particles with diameters in the interval 0.1-2 µm, and the coarse mode is for the particles with diameters greater than 2 µm (Willeke & Whitby 1975; Sverdrup & Whitby, 1977; Hinds, 1998). In practice, the particles in the nucleation mode weigh very little and the mass distribution density may have only two maxima, representing the accumulation and the coarse modes.

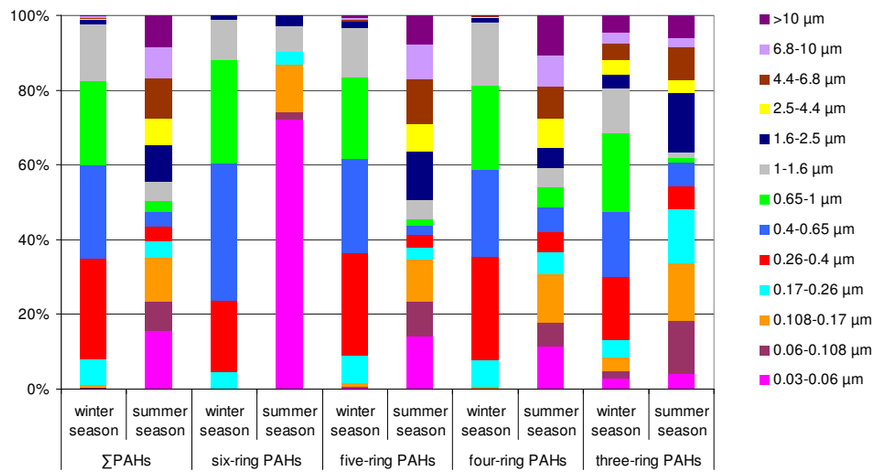


Fig. 7. Distributions of ΣPAH, six-ring PAH, five-ring PAH, four-ring-PAH and three-ring PAH among 13 PM fractions in Zabrze in winter and summer 2007

In Zabrze, in summer 2007, the PM mass distribution with respect to the particle aerodynamic diameter was bimodal. The probability density function had two maxima, one in the interval of particle diameters 0.4-0.65 µm (accumulation mode), and the second between 6.8 and 10 µm (coarse mode, Fig. 8). In winter, the mass distribution was unimodal, the density function had its only maximum between 0.26-0.4 µm.

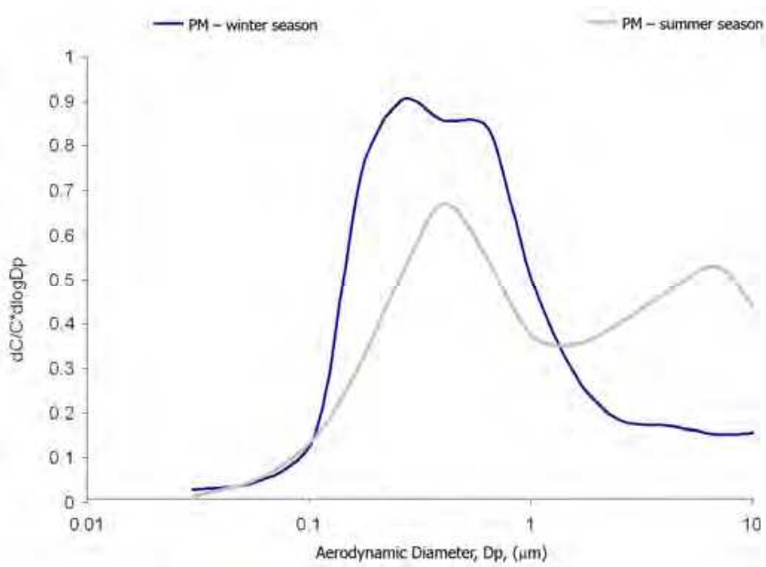


Fig. 8. Mass size distribution of PM relative to the aerodynamic diameter in Zabrze in winter and summer 2007

In winter, the PAH and ΣPAH mass distributions with respect to particle aerodynamic diameter of the particles they were adsorbed onto, except for the three-ring PAH, were bi- or trimodal, with one mode, like for PM, between 0.26 and 0.4 μm (Fig. 9 and 10). The second maximum occurred usually between 0.65 and 1.0 μm (except for BbF, BkF, BaP) and the third one between 4.4 and 6.8 μm or 6.8 and 10 μm (except for BaA, IP, DBA and BghiP). Three-ring PAH, in winter and in summer, were not detectable in some PM fractions (Table 1) because the lighter than Ph ambient species occur in the gaseous form (Guo et al., 2003; Fang et al., 2006; Akyüz & Çabuk, 2008). In summer, ΣPAH and, in general, four-, five-, and six-ring PAH (Fl, Py, Ch, BbF, BkF, BaP) had tri- or bimodal distributions. The distributions of IP and BghiP were bimodal, and of DBA—unimodal.

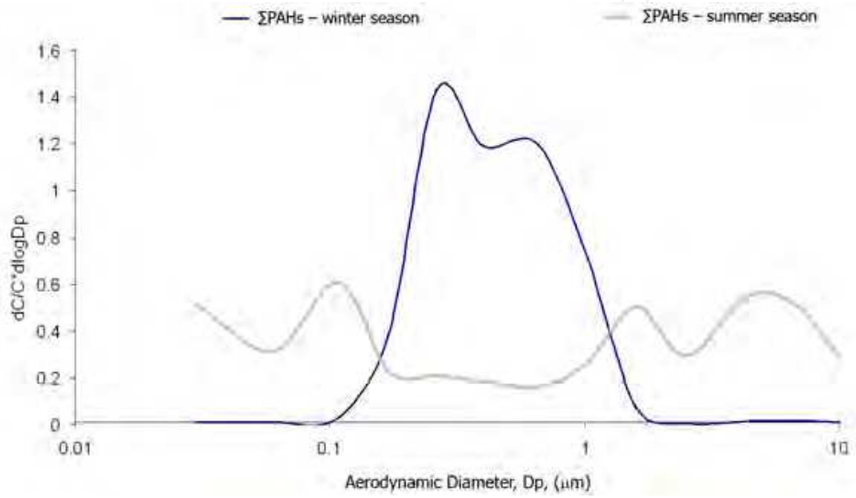


Fig. 9. Mass size distribution of PM-bound ∑PAH relative to the aerodynamic diameter of the particles PAH are adsorbed on in Zabrze in winter and summer 2007

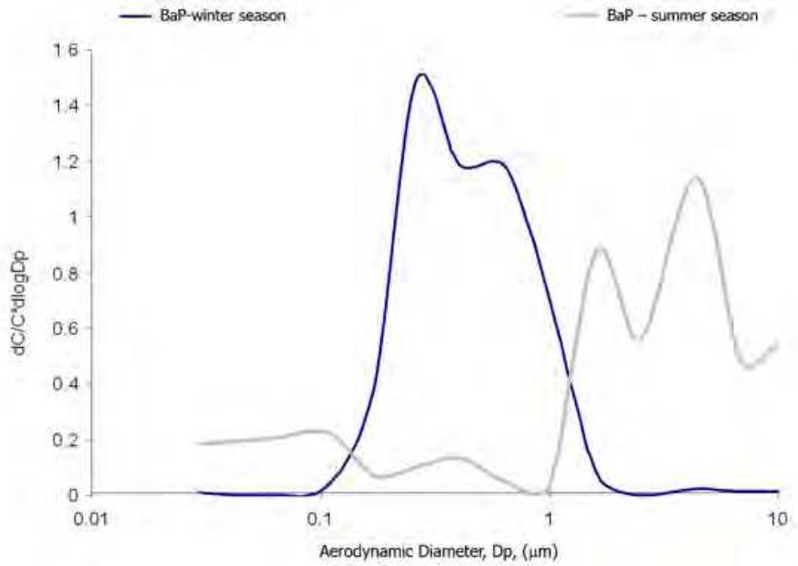


Fig. 10. Mass size distribution of PM-bound BaP relative to the aerodynamic diameter of the particles BaP is adsorbed on in Zabrze in winter and summer 2007

Like in winter, in summer too, majority of the probability functions of PAH and the function of ΣPAH had one maximum between 1.0 and 1.6 μm or 1.6 and 2.5 μm and the second between 4.4 and 6.8 μm or 6.8 and 10 μm (coarse particles).
The PAH diagnostic ratio (DR) is a proportion of ambient PAH concentrations. DR, in some way characterizes the origin of the involved PAH. In the present work, DR are used to determine the effect of the combustion sources in Zabrze on the concentrations of PAH bound to some PM fractions (PM_1, $PM_{2.5}$, PM_{10} and fractions where the majority of the probability functions of size distributions of PAH or ΣPAH concentrations assume their maximum). Some DR were taken from literature (Table 2).

Emission source	[BaA]/[BaP]	[Fl]/([Py]+[Fl])	[BaA]/([Ch]+[BaA])	[BbF]/[BkF]	[Ph]/([Ph]+[An])	*ΣCPAHs/ΣPAHs
Vehicular emissions		0.4 – 0.5 [2, 3, 4] 0.44[a] [5]	0.2 – 0.35 [4]			0.41[e] [5] 0.51[f] [5]
Gasoline emissions	0.5 [1]	0.4 ± 0.08 [6] < 0.5 [7, 8]		1.1 – 1.5 [13]	0.50 [15]	
Diesel emissions	1.0 [1]	> 0.5 [7, 8] 0.6 – 0.7 [5]			0.65 [15]	
Used motor oil		0.36 ± 0.08 [6]				
Crude oil			0.16 ± 0.12 [6]		> 0.70 [6]	
Combustion (stationary sources)						0.78 ± 0.16[g] [2]
Coal combustion		> 0.5 [3, 4] 0.57 [10]	0.46 [10] 0.50[b] [11] 0.17 – 0.36 [12]	3.5 – 3.9 [14]	0.76 [15]	
Wood combustion	1.0 [1]	> 0.5 [3, 4] 0.51 [9,10]	0.40 ± 0.09 [6]	0.8 – 1.1 [14]		
Natural gas combustion		0.49 [9,10]				
Other sources				2.5 – 2.9[c] [14]	> 0.7[d] [16]	

[a] Vehicular emissions – converter equipped automobiles; [b] Coal combustion for domestic heating; [c] Smelters; [d] Associated with lubricant oil and fossil fuels; [e] Non-catalyst automobiles; [f] Catalyst-equipped automobiles; [g] General dominance of combustion sources
[1]: (Li & Kamens, 1993); [2]: (Kavouras et al., 1999); [3]: (Zencak et al., 2007); [4]: (Yunker et al., 2002); [5]: (Rogge et al., 1993a, 1993b); [6]: (Sicre et al., 1987); [7]: (Ravindra et al., 2006); [8]: (Ravindra et al. 2008); [9]: (Galarneau, 2008); [10]: (Tang et al., 2005); [11]: (Gschwend & Hites, 1981); [12]: (Dickhut et al., 2000); [13]: (Masclet et al., 1987); [14]: (Khalili et al., 1995); [15]: (Alves et al., 2001)
*ΣCPAHs/ΣPAHs=([Fl]+[Py]+[BaA]+[BbF]+[BkF]+[BaP]+[BeP]+[IP]+[BghiP])/([Acy]+[Ace]+[F]+[Ph]+[An]+[Fl]+[Py]+[BaA]+[Ch]+[BbF]+[BkF]+[BaP]+[DBA]+[BghiP]+[IP])

Table 2. PAH diagnostic ratios (DR) from literature

The effect of stationary combustion sources on the ambient PAH concentrations is characterized by the proportion ΣCPAH/ΣPAH of the PM-bound ΣCPAH and ΣPAH concentrations (Rogge et al., 1993a, 1993b; Kavouras et al., 1999; Manoli et al., 2004; Sienra et al., 2005). In Zabrze, ΣCPAH/ΣPAH indicate that in winter $PM_{0.26-0.4}$-, $PM_{0.65-1.0}$- and $PM_{1.6-2.5}$-bound PAH came from stationary combustion sources (Table 2 and 3). In winter, these fractions contained half of the mass of the PM-bound PAH and, not surprisingly, the winter PM_1-, $PM_{2.5}$- and PM_{10}-bound PAH should in general come from stationary combustion.

Probably, $PM_{6.8-10}$-bound PAH came in part from vehicular sources (ΣCPAH/ΣPAH=0.56). In summer, PM_1- and $PM_{2.5}$-bound PAH might also have come from vehicular sources (ΣCPAH/ΣPAH was lower than in winter) but the summer concentrations of $PM_{1.6-2.5}$-, $PM_{6.8-10}$- and PM_{10}-bound PAH were affected by stationary combustion sources as well. However, in summer, the degradation processes (oxidation, photochemical reactions) and in winter the variability of the parameters of combustion processes and the variety of used fuels limit the reliability of DR making the source apportionment uncertain (Kavouras et al., 1999; Hong et al., 2007). Nevertheless, other DR confirm these findings. [Ph]/([Ph]+[An]) indicates PAH from hard coal combustion and, in winter, from unidentified sources and crude oil (traffic). [BaA]/([BaA]+[Ch]) indicates the effect of crude oil combustion on the PAH concentrations also in summer (0.10, 0.11 and 0.08 for PM_1, $PM_{2.5}$ and PM_{10}, respectively). For $PM_{0.26-0.4}$-bound PAH, [BaA]/([BaA]+[Ch]) is 0.27 indicating car exhaust (Tables 2 and 3). The winter [BaA]/([BaA]+[Ch]) for $PM_{1.6-2.5}$-bound PAH is 0.46, for $PM_{1.6-2.5}$-bound PAH—0.53, they are higher than in summer and prove that hard coal combustion was the main source of ambient PAH in Zabrze.

The effect of vehicular sources and wood combustion on the ambient PAH concentrations is reflected by [BbF]/[BkF]. In summer [BbF]/[BkF] were slightly higher than in winter for majority of the PM fractions (Table 3). [BbF]/[BkF] allows to apportion PM_1-, $PM_{2.5}$- and PM_{10}-bound PAH to traffic in summer. In winter, except for $PM_{6.8-10}$, [BbF]/[BkF] were between 0.8 and 1.1. It indicates the contribution of wood combustion to the winter PAH concentrations. The values of [BaA]/[BaP] also indicate the contribution of wood combustion to the winter concentration of PAH in Zabrze (Tables 2 and 3).

Fraction, μm	[BaA]/[BaP]		[Fl]/([Py]+[Fl])		[BaA]/([Ch]+[BaA])		[BbF]/[BkF]		[Ph]/([Ph]+[An])		ΣCPAHs/ΣPAHs	
	S	W	S	W	S	W	S	W	S	W	S	W
$PM_{0.26-0.4}$	0.75	1.07	0.51	0.43	0.27	0.51	0.59	0.96	0.91	0.75	0.46	0.83
$PM_{0.65-1.0}$	-	1.18	0.58	0.50	-	0.53	0.34	0.94	1.00	0.81	0.50	0.82
$PM_{1.6-2.5}$	0.02	0.81	0.40	0.50	1.00	0.46	1.44	0.77	0.79	0.29	0.65	0.73
$PM_{6.8-10}$	-	-	0.31	0.43	-	-	1.03	0.67	0.82	0.77	0.81	0.56
$PM_{1.0}$	0.23	1.11	0.42	0.47	0.10	0.51	1.29	0.93	0.75	0.82	0.54	0.82
$PM_{2.5}$	0.16	1.11	0.43	0.46	0.11	0.51	1.25	0.92	0.76	0.81	0.57	0.82
PM_{10}	0.08	1.11	0.44	0.46	0.08	0.50	1.26	0.92	0.77	0.80	0.60	0.81

Table 3. PAH diagnostic ratios (DR) in summer (S) and winter (W) 2007 in Zabrze

In winter, [Fl]/([Fl]+[Py]) were close to the values characteristic of PAH coming from wood or natural gas combustion (Galarneau, 2008). In general, [Fl]/([Fl]+[Py]) were lower in summer than in winter. [Fl]/([Fl]+[Py]), oscillating about 0.4, suggest the effect of car exhaust. Relatively high summer [Fl]/([Fl]+[Py]) for $PM_{0.26-0.4}$ and $PM_{0.65-1.0}$ suggest diesel car exhaust as the source of PAH in these fractions (Rogge et al., 1993a, 1993b).

3.2 Comparison of the concentrations of PM- and PM-bound PAH in Zabrze and selected sites in the world

The ambient concentrations of PAH bound to various PM fractions, especially to $PM_{2.5}$ and PM_{10}, are investigated at many sites in the world (Kavouras et al., 1999; Odabasi et al., 1999; Panther et al., 1999; Takeshi & Takashi, 2004; Mantis et al., 2005). Most often, the investigations cover short periods, results of long-term experiments are not abundant. The direct comparison of the concentrations of PM-bound PAH from various urban areas should be done cautiously. The data may be affected by the method of sampling and the technique of determination of PAH in the dust samples (Takeshi & Takashi, 2004). The local conditions, meteorological (air temperature and relative air humidity, direction and velocity of wind, precipitation) and other, neighborhood of the sampling point, a season of a year are also important (Wang X.H. et al., 2007; Evagelopoulos et.al., 2010).

Table 4 is a collation of the concentrations of the sum of 15 PAH (ΣPAH) and PM_1-, $PM_{2.5}$- and PM_{10}-bound BaP in Zabrze in 2007 and in various places in the world, mainly in Europe. BaP was selected because it is used as an air pollution indicator. The data cover the period from 2005 to 2009. In the last column of Table 4, in parentheses, the number of analyzed compounds is given. The concentration of ΣPAH was computed by summing up the concentrations of these PAH that were investigated in Zabrze. The table allows for rough evaluation of differences in the concentrations of BaP and ΣPAH bound to several PM fractions in various countries.

The ranges of the concentrations of BaP and ΣPAH are wide because of the causes mentioned above and different numbers of PAH in ΣPAH. In general, the lowest concentrations (lower than 0.1 ng m^{-3} for BaP and than 2 ng m^{-3} for ΣPAH) occurred in clean areas (not affected by vehicular or industrial sources), such as Virolahti (regional background station) in Finland (Makkonen et al., 2010) and Chréa National Park (great forest area) in Algeria (Ladji et al., 2009). In most places the BaP concentration did not exceed 1 ng m^{-3}, the limit established by the European Commission. The exceptions were the urban-traffic site in Oporto (Portugal; Slezakova et al., 2011), road tunnel in Marseille (France; El Haddad et al., 2009), urban background station in Flanders (Belgium; Vercauteren et al., 2011), measuring point in Zonguldak (Turkey; Akyüz & Çabuk, 2008) and urban background station and crossroads in Zabrze (Ćwiklak et al., 2009).

Majority of ambient PAH, especially in urbanized areas, are anthropogenic (Kulkarni & Venkataraman, 2000; Hien et al., 2007; Wang X.H. et al., 2007), and come mainly from combustion of fossil fuels, wastes or biomass and also from industry and road traffic. Most of the greatest values of BaP concentrations shown in Table 4, reaching 50 ng m^{-3}, come from sites located in industrialized and densely populated areas in Asiatic countries, such as Fushun (residential-commercial site, Kong et al., 2010), Beijing (campus site, Wang H. et al., 2009), Guiyu (electronic waste recycling site, Deng et al., 2006) in the People's Republic of China or Chennai in the Republic of India (Mohanraj et al., 2011). The concentrations of ΣPAH in these regions were also high, some times, like in Funshun, China, where the ΣPAH concentration reached 1.9 μg m^{-3}, many times higher than elsewhere in the world. In Europe, the highest BaP and ΣPAH concentrations were at traffic station in Sweden and at traffic and urban sites in Zabrze (Table 4).

BaP and ΣPAH tend to accumulate in the finest particles of PM (Table 4). Like in Zabrze, this tendency may be observed in the road tunnel in Lisbon, Portugal (Oliveira et al., 2011) and at the urban background and traffic stations in Los Angeles, USA (Phuleria et al., 2007).

Location		Sampling period	Fraction	Concentration (ng·m^{-3})	
				BaP [a]	∑PAH [b]
Zabrze (Poland) [1]		summer 2007	PM_1	0.17	3.48 (15)
			$PM_{2.5}$	0.31	4.49 (15)
			PM_{10}	0.65	5.86 (15)
		winter 2007	PM_1	16.08	128.10 (15)
			$PM_{2.5}$	19.19	153.10 (15)
			PM_{10}	19.32	156.11 (15)
Zabrze (Poland) [2]	urban background	summer 2005	$PM_{2.5}$	*0.90*	12.80 (15)
			PM_{10}	*1.20*	21.60 (15)
	crossroads		$PM_{2.5}$	*2.10*	43.40 (15)
			PM_{10}	*4.00*	63.80 (15)
Flanders (Belgium) [3]	urban background	Oct 2006 - Mar 2007	PM_{10}	1.18	82.24 (15)
		Apr - Sep 2007	PM_{10}	0.51	74.68 (15)
	rural background	Oct 2006 - Mar 2007	PM_{10}	0.81	45.90 (15)
		Apr - Sep 2007	PM_{10}	0.41	32.23 (15)
Virolahti (Finland), regional background [4]		summer 2006	PM_1	< 0.08	1.77 (13)
			$PM_{2.5}$	< 0.08	1.77 (13)
			PM_{10}	< 0.08	1.78 (13)
		winter 2006	PM_1	0.52	7.54 (13)
			$PM_{2.5}$	0.69	14.53 (13)
			PM_{10}	0.73	13.9 (13)
Marseille (France), tunnel [5]		winter 2008	$PM_{2.5}$	2.42	74.67 (8)
			PM_{10}	6.73	108.39 (8)
Toulouse (France) [6]	traffic	Apr 2006	PM_{10}	*0.10*	18.20 (15)
	urban		PM_{10}	*0.15*	11.45 (15)
	industrial		PM_{10}	*0.80*	20.40 (15)
Thessaloniki (Greece), kerbside [7]	street level	Jan/Feb 2006	$PM_{<0.95}$	0.47	11.94 (13)
		Jan/Feb 2006	$PM_{0.95-1.5}$	0.10	2.36 (13)
		Jan/Feb 2006	$PM_{1.5-3}$	0.04	1.41 (13)
		Jan/Feb 2006	$PM_{3-7.5}$	0.02	0.98 (13)
		Jan/Feb 2006	$PM_{>7.5}$	0.02	0.80 (13)
	rooftop level	Jan/Feb 2006	$PM_{<0.95}$	0.45	11.54 (13)
		Jan/Feb 2006	$PM_{0.95-1.5}$	0.10	2.45 (13)
		Jan/Feb 2006	$PM_{1.5-3}$	0.03	1.06 (13)
		Jan/Feb 2006	$PM_{3-7.5}$	0.02	0.79 (13)
		Jan/Feb 2006	$PM_{>7.5}$	0.02	0.63 (13)
Athens (Greece), indoor samples [8]	smoking area	16-27 Jul 2007	PM_1	0.10	0.80 (15)
			$PM_{2.5}$	0.14	1.11 (15)
			PM_4	1.73	21.33 (15)
	no-smoking area		PM_1	0.03	0.44 (15)
			$PM_{2.5}$	0.05	0.65 (15)
			PM_4	0.00	5.13 (15)
	passive smokers` area		PM_4	3.58	29.04 (15)
Kozani (Greece), urban area surrounded by opencast coal mining [9]		Dec 2005 – Oct 2006	$PM_{2.5}$	0.38	4.77 (15)
			PM_{10}	0.11	1.46 (15)
Rome (Italy), downtown [10]		Apr - Jul 2007	PM_1	-	2.10 (14)
			$PM_{2.5}$	-	2.29 (14)
			PM_{10}	-	2.37 (14)

		Oct 2007 - Feb 2008	PM_1	-	6.70 (14)
			$PM_{2.5}$	-	7.77 (14)
			PM_{10}	-	7.98 (14)
Lisbon (Portugal), roadway tunnel [11]		Oct 2008	$PM_{0.49}$	6.98	113.80 (15)
			$PM_{0.49-0.95}$	0.35	14.70 (15)
			$PM_{0.95-2.5}$	0.17	7.33 (15)
			$PM_{2.5-10}$	0.19	2.66 (15)
Oporto Metropolitan Area (Portugal), urban-traffic [12]		Dec 2008	PM_{10}	2.02	20.67 (15)
			$PM_{2.5}$	1.88	18.96 (15)
Umeä (Sweden), traffic [13]		autumn 2009	$PM_{2.5}$	25.00	196.45 (12)
Zonguldak (Turkey), industrial city [14]		summer 2007	$PM_{2.5}$	0.40	5.70 (14)
		winter 2007	$PM_{2.5}$	15.70	152.70 (14)
		summer 2007	$PM_{2.5-10}$	0.20	1.60 (14)
		winter 2007	$PM_{2.5-10}$	0.70	10.50 (14)
Kabul (Afganistan), urban [13]		autumn 2009	$PM_{2.5}$	6.70	55.97 (12)
Mazar-eSharif (Afganistan), urban [13]			$PM_{2.5}$	0.09	2.19 (12)
Beijing (China); campus site [15]		summer 2005-2007	$PM_{2.5}$	1.19	39.28 (15)
			$PM_{2.5-10}$	1.14	24.87 (15)
		winter 2005-2007	$PM_{2.5}$	19.82	360.71 (15)
			$PM_{2.5-10}$	5.09	102.00 (15)
Guiyu (China), electronic waste recycling site [16]		AugI - Sep 2004	TSP	15.40	144.85 (15)
			$PM_{2.5}$	8.85	99.26 (15)
Xiamen (China) [17]	industrial-traffic intersection site	summer 2005	PM_{10}	0.10	5.24 (15)
		autumn 2005	PM_{10}	1.40	37.10 (15)
	residential site	summer 2005	PM_{10}	0.00	1.69 (15)
		autumn 2005	PM_{10}	1.50	26.60 (15)
Fushun (China) [18]	urban background	2004-2005	$PM_{2.5}$	10.71	261.82 (13)
			$PM_{2.5-10}$	1.98	72.44 (13)
	residential-commercial		$PM_{2.5}$	48.44	1899.36 (13)
			$PM_{2.5-10}$	3.44	166.92 (13)
Jinzhou (China) [18]	urban background		$PM_{2.5}$	13.61	190.86 (13)
			$PM_{2.5-10}$	1.13	20.78 (13)
	residential		$PM_{2.5}$	6.61	106.94 (13)
			$PM_{2.5-10}$	0.77	16.40 (13)
Chennai City (India) [19]	urban-residential	Dec 2009 – Feb 2010	$PM_{2.5}$	6.50	365.30 (11)
		Apr - Aug 2009	$PM_{2.5}$	7.40	326.90 (11)
	industrial/traffic site	Dec 2009 – Feb 2010	$PM_{2.5}$	8.10	681.80 (11)
		Apr - Aug 2009	$PM_{2.5}$	10.60	456.60 (11)
	urban-commercial	Dec 2009 – Feb 2010	$PM_{2.5}$	16.20	448.00 (11)
		Apr - Aug 2009	$PM_{2.5}$	2.50	313.90 (11)
Ho Chi Minh (Vietnam), roadside [20]		dry season, Jan-Feb 2005	TSP	*2.00*	39.80 (9)
		rainy season, Jul 2005	TSP	*5.70*	58.70 (9)

Boumerdes (Algeria), urban traffic congestion [21]		PM_1	0.11	1.53 (14)
		PM_{1-10}	0.02	0.33 (14)
Rouiba-Réghaia (Algeria), industrial zone [21]	Oct 2006	PM_1	0.30	2.70 (14)
		PM_{1-10}	0.04	0.59 (14)
Chréa National Park (Algeria), forest ecosystem [21]		PM_1	0.02	0.28 (14)
		PM_{1-10}	0.002	0.10 (14)
Golden (British Columbia, Canada), residential [22]	spring 2006	$PM_{2.5}$	0.14	1.76 (15)
	winter 2007	$PM_{2.5}$	2.67	31.39 (15)
Long Beach, California (USA), coastal city [23]	Jan – Mar 2005	$PM_{0.25}$	0.17	0.94 (10)
		$PM_{0.25-2.5}$	0.03	0.43 (10)
		$PM_{2.5-10}$	0.00	0.01 (10)
Los Angeles (USA) [24]	Jan 2005	$PM_{0.108-2.5}$	0.03	0.31 (9)
background		$PM_{>2.5}$	0.16	1.45 (9)
freeway		$PM_{0.108-2.5}$	0.04	0.38 (9)
		$PM_{>2.5}$	0.17	1.82 (9)

[a] Underlined italics mark the values read from a chart; [b] The number of PAH taken to compute ΣPAH concentration is in parentheses

[1]: (this study); [2]: (Ćwiklak et al., 2009); [3]: (Vercauteren et al., 2011); [4]: (Makkonen et al., 2010); [5]: (El Haddad et al., 2009); [6]: (Dejean et al., 2009); [7]: (Chrysikou et al., 2009); [8]: (Saraga et al., 2010); [9]: (Evagelopoulos et al., 2010); [10]: (Di Filippo et al., 2010); [11]: (Oliveira et al., 2011); [12]: (Slezakova et al., 2011); [13]: (Wingfors et al., 2011); [14]: (Akyuz & Cabuk, 2008); [15]: (Wang et al., 2009); [16]: (Deng et al., 2006); [17]: (Hong et al., 2007); [18]: (Kong et al., 2010); [19]: (Mohanraj et al., 2011); [20]: (Hien et al., 2007); [21]: (Ladji et al., 2009); [22]: (Ding et al., 2009); [23]: (Krudysz et al., 2009); [24]: (Phuleria et al., 2007)

Table 4. Comparison of the PM and PM-bound PAH concentrations at various sites in the world

Like in Zabrze in 2007, at some other sites in the world the BaP and ΣPAH concentrations depend on a season of a year and are higher in cold seasons. One of the most obvious causes of the seasonal variability of the PAH concentrations is home heating, central or individual, that is important, if not the most important, source of air pollutants in winter. Moreover, the meteorological conditions in winter (shallow mixing layer) are favorable for local occurrences of high air pollution, like in Zabrze, Zonguldak (Turkey) and in Golden (Canada). Instead, in summer, higher air temperatures and solar radiation intensify desorption of PAH from PM particles and their photochemical decomposition (Odabasi et al., 1999; Hong et al., 2007). Therefore, lower in summer than in winter concentrations of PM-bound PAH may also be due to releasing of PAH from PM particles. To prove it in Zabrze, the gas phase of ambient PAH would have to be investigated. In summer, more favorable conditions for dispersion and dilution of air pollutants (Mantis et al., 2005) and washing out of particles (with adsorbed PAH) by precipitation occur.

The concentrations of BaP and ΣPAH in Zabrze in summer 2007 were lower than in 2005 (Table 4). It may be due to the differences in the sampling periods (long sampling periods in 2007, 24-hour sampling in 2005), in the method of sampling (cascade impactor in 2007, manual sampler with a separating head in 2005) and in the method of PAH determination (combining of extracts for a season and GC-FID in 2007, averaging of diurnal concentrations in a season and GC-MS in 2005) (Ćwiklak et al., 2009).

Nevertheless, the concentrations at two measuring points in Zabrze in summer 2005, several times lower than in winter 2007, suggest that the municipal emission in Silesian Agglomeration may be much greater problem than the traffic emission. Instead, in other European cities, the greatest problem is the traffic emission. The ΣPAH concentrations in Zabrze in 2007 were higher than in other European cities except for the traffic sites (road tunnels) in Marseille (France) and Lisbon (Portugal).

3.3 Health hazard from PAH in Zabrze

Ambient PAH endanger human health by their mutageneity and carcinogenicity. Their strong adverse biological effect is documented by numerous works (Grimmer et al., 1986; White, 2002; Yan et al., 2004).

The risk from the exposure to particular PAH is expressed in terms of the most cancerogenous PAH, BaP, as the toxicity equivalence factor (TEF). The carcinogenicity of a combination of PAH, the BaP equivalence (BEQ), is computed as the linear combination of the concentrations of PAH entering the PAH combination and their TEF (Nisbet & LaGoy, 1992). BEQ for the 15 PAH discussed in this paper is:

$$\begin{aligned} BEQ = &[Acy] \times 0.001 + [Ace] \times 0.001 + [F] \times 0.001 + [Ph] \times 0.001 + [An] \times 0.01 + \\ &+[Fl] \times 0.001 + [Py] \times 0.001 + [BaA] \times 0.1 + [Ch] \times 0.01 + [BbF] \times 0.1 + [BkF] \times 0.1 + \\ &+[BaP] \times 1 + [DBA] \times 5 + [BghiP] \times 0.1 + [IP] \times 0.1 \end{aligned} \quad (1)$$

In winter, BEQ for $PM_{0.17\text{-}0.26}$-, $PM_{0.26\text{-}0.40}$-, $PM_{0.40\text{-}0.65}$-, $PM_{0.65\text{-}1.0}$-, and $PM_{1.0\text{-}1.6}$-bound PAH were 2.85 ng m^{-3}, 7.09 ng m^{-3}, 14.65 ng m^{-3}, 11.07 ng m^{-3} and 5.28 ng m^{-3}, respectively (Table 5). The five fractions contain 78% of the mass of PM_{10} and 96% of PM_{10}-bound ΣPAH (Table 1). The summer BEQ of PAH in these fractions do not exceed 1 ng m^{-3}. BEQ for the remaining eight fractions do not exceed 1 ng m^{-3} in both seasons. PAH in the seven fractions contained in $PM_{0.108\text{-}2.5}$ have BEQ higher, often several times, in winter than in summer.

BEQ for PAH in $PM_{2.5}$ and PM_{10} in summer 2007 in Zabrze were 0.79 ng m^{-3} and 1.16 ng m^{-3}, respectively. They were two or almost three times lower than Ćwiklak et al. (2009) determined in summer 2005 at the urban background site in Zabrze. They are comparable with other, foreign, values (Xiamen: 0.85 ng m^{-3} and 0.92 ng m^{-3} for PM10 and PM2.5 bound PAH; Hong et al., 2007). Instead, the winter BEQ for PAH in PM2.5 and PM10 are very high, 41.72 ng m^{-3} and 41.91 ng m^{-3}, and they are higher than BEQ computed for PAH in these fractions in areas with very high PAH concentrations, such as in Shanghai (BEQ equal to 15.77 ng m^{-3}; Guo et al., 2004) or in some Japanese cities (BEQ about 2 ng m^{-3}; Takeshi & Takashi, 2004).

The closer $\Sigma PAH_{carc}/\Sigma PAH$ to 1 are the more hazardous to humans ambient PAH are (Hong et al., 2007). In Zabrze, in summer, the values of $\Sigma PAH_{carc}/\Sigma PAH$ were between 0.17 and 0.74 (Table 5). They are dispersed owing to differentiation of the PAH profiles (Table 1). The winter $\Sigma PAH_{carc}/\Sigma PAH$ are close to or higher than 0.5. In general, in Zabrze, the values of $\Sigma PAH_{carc}/\Sigma PAH$ were high, much higher than ones determined for other urban areas (Bourotte et al., 2005; Sienra et al., 2005). They are comparable with the values received by Chen et al. (2004) for dust emitted from coal combustion.

Fraction		BEQ, ng m^{-3}	*∑PAH$_{carc}$/∑PAH
PM$_{0.03-0.06}$	W	0.07	0.44
	S	0.32	0.70
PM$_{0.06-0.108}$	W	0.02	0.37
	S	0.06	0.39
PM$_{0.108-0.17}$	W	0.20	0.57
	S	0.10	0.39
PM$_{0.17-0.26}$	W	2.85	0.69
	S	0.07	0.17
PM$_{0.26-0.40}$	W	7.09	0.67
	S	0.03	0.39
PM$_{0.40-0.65}$	W	14.65	0.66
	S	0.02	0.34
PM$_{0.65-1.0}$	W	11.07	0.65
	S	0.01	0.63
PM$_{1.0-1.6}$	W	5.28	0.62
	S	0.02	0.74
PM$_{1.6-2.5}$	W	0.50	0.62
	S	0.15	0.39
PM$_{2.5-4.4}$	W	0.02	0.23
	S	0.12	0.70
PM$_{4.4-6.8}$	W	0.10	0.43
	S	0.18	0.55
PM$_{6.8-10.0}$	W	0.07	0.48
	S	0.07	0.63
PM$_{> 10.0}$	W	0.10	0.39
	S	0.14	0.54
PM$_{1}$	W	35.93	0.66
	S	0.62	0.43
PM$_{1-2.5}$	W	5.78	0.62
	S	0.17	0.47
PM$_{2.5-10}$	W	0.19	0.39
	S	0.37	0.61
PM$_{2.5}$	W	41.72	0.65
	S	0.79	0.44
PM$_{10}$	W	41.91	0.65
	S	1.16	0.48

*PAH$_{carc}$/ΣPAH=([BaA]+[BaP]+[BbF]+[BkF]+[Ch]+[DBA]+[IP])/([Acy]+[Ace]+[F]+[Ph]+[An]+[Fl]+[Py]+[BaA]+[Ch]+[BbF]+[BkF]+[BaP]+[DBA]+[BghiP]+[IP])

Table 5. BEQ and ∑PAH$_{carc}$/∑PAH for PM-bound PAH In the PM fractions in Zabrze in winter (W) and summer (S) 2007

4. Conclusion

In Zabrze, the winter PM-bound BaP concentrations are 19 times greater than the limit for the yearly average BaP concentrations (1 ng m^{-3}). Both PM-bound BaP and Σ15PAH concentrations are much greater than the concentrations in other European cities. Despite the general improvement of the air quality in the Silesian Agglomeration during the last thirty years (decrease of the concentrations of ambient coarse particles and PAH related

with this fraction), the concentrations of PM-bound BaP and Σ15PAH are high. On the local scale, in winter, the most important sources of fine particles and particle-bound PAH are municipal sources (hard coal, wood and garbage combustion), and/or electric power and heat production from coal; in summer it is vehicular emission. At the urban background measuring point in Zabrze, the vast differences in the seasonal ambient concentrations of PAH and in PAH profiles refute the supposition on industry affecting mostly the air quality in the Silesian Agglomeration. However, DR applied in determination of probable PAH sources are not reliable and their application may give contradictive results (Simcik et al., 1999; Sienra et al., 2005; Evangelopoulos et al., 2010; Dvorská et al., 2011). The exact apportionment of PAH to sources needs measuring of the diurnal PM-bound PAH concentrations and some statistical reasoning must be done (e.g. multivariate factor analysis to apportion combinations of PAH to sources). The data base containing the intervals of DR determined for the specific conditions in the Silesian Agglomeration in vicinities of real PAH sources would appear very helpful. Also, the measurements of ambient gaseous PAH concentrations are necessary.

The high ambient PAH concentrations and the high five- and six-ring PAH content of total PAH are hazardous to the Zabrze population, especially in winter. The concentrations of the carcinogenic PAH was never lower than 50% of the ΣPAH concentration in winter, and BEQ for PM_1, $PM_{2.5}$ and PM_{10} were 35.93 ng m^{-3}, 41.72 ng m^{-3} and 41.91 ng m^{-3}, respectively.

In winter, all the four-, five- and six-ring PAH and ΣPAH had two- or trimodal distributions with one maximum between 0.26 and 0.4 μm, the second usually between 0.65 and 1.0 μm and the third between 4.4 and 10 μm. The greatest BEQ and $\Sigma PAH_{carc}/\Sigma PAH$ found for $PM_{0.17\text{-}1.6}$ suggest elevated toxicity of very fine particles, which are the core mass of PM, in Zabrze in winter. In summer, the distribution of ΣPAH and particular PAH with respect to the aerodynamic diameter of particles they are bound to, the values of BEQ and $\Sigma PAH_{carc}/\Sigma PAH$ were similar to those from other sites in the world (Chen et. al., 2004; Akyüz & Çabuk, 2008). The contribution of PM_1- and $PM_{2.5}$-bound ΣPAH to ΣPAH was in Zabrze, like elsewhere (Chrysikou et al., 2009; Kong et al., 2010; Makkonen et al., 2010; Oliveira et al., 2011), very high (99 and 82% in winter and 77 in 69% summer, respectively).

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6. References

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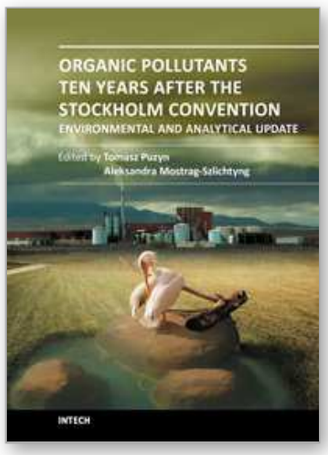
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Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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