

## AMBIENT PM<sub>2.5</sub> RELATED PAHs IN URBAN AREAS

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## WYSTĘPOWANIE WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH ZWIĄZANYCH Z PM<sub>2,5</sub> W POWIETRZU ATMOSFERYCZNYM AGLOMERACJI MIEJSKICH

Pomiary stężeń 16 wielopierścieniowych węglowodorów aromatycznych w powietrzu związanych z pyłami o frakcjach poniżej 2,5 µm prowadzono w 4 punktach pomiarowych województwa małopolskiego i śląskiego, w latach 2004–2006. Zebrany na podkładach filtracyjnych pył respirabilny pochodził z terenu reprezentatywnego dla tła miejskiego, tras komunikacyjnych oraz emisji przemysłowej. Zaobserwowano wyraźne różnice w stężeniach WWA w sezonie letnim i grzewczym. Jak wynika z pomiarów najwyższe stężenia WWA w powietrzu związanych z pyłem PM<sub>2,5</sub> zaobserwowano w Krakowie, w rejonie oddziaływania źródeł przemysłowo-komunikacyjnych, ma to miejsce zarówno w okresie letnim jak i w sezonie grzewczym. W ramach badań, w oparciu o uzyskane wyniki wyznaczono wzajemne stosunki poszczególnych WWA związanych z PM<sub>2,5</sub> w powietrzu w wybranych miastach. Uzyskane wyniki badań wskazują, że poziom zanieczyszczenia badanych pyłów PM<sub>2,5</sub> jest znaczny i zbliżony do danych uzyskiwanych z obszarów o podobnym stopniu urbanizacji i industrializacji.

### Summary

Ambient concentrations of 16 polycyclic aromatic hydrocarbons (PAHs), adsorbed on particles of PM<sub>2.5</sub>, were measured at 4 points located in Silesia and Małopolska Regions during 2004 through 2005 period. The fine dust was collected on filters at locations representing conditions of urban background, communication artery and industrial area. Distinctive differences between heating and summer season PAH concentrations were observed. The highest PM<sub>2.5</sub> related PAH concentrations were observed in Krakow, within the effect of industrial and traffic sources, equally in summer and heating seasons. For selected cities, relations between the particular PM<sub>2.5</sub> related PAHs were determined. The results show that contamination of the investigated PM<sub>2.5</sub> with PAHs is considerable and comparable with that in other areas of similar degree of urbanization and industrialization.

### INTRODUCTION

The air chemistry undergoes constant modifications, both as a result of natural processes occurring in the environment as well as a result of antropogenic influences. The main sources of emitting pollution into the air in the urban areas are industrial plants, thermal energy producers, boiler houses and individual furnaces as well as traffic. In Poland within the last twenty years, the considerable reduction of emissions from the

stationary sources took place as a result of the realization of a number of investments in the scope of air protection and industry restructuring. Its place is however being rapidly replaced by the emission from the mobile sources and the disorganized emission from the rapidly developing motorization facilities. The reduction of total dust emission observed for years in Poland does not translate into the proportional reduction of PM<sub>10</sub> and PM<sub>2.5</sub> dust concentration. This may indicate that the reduction of the emission referred mainly to the coarse particles or, that the methodology of estimating dust emission applied so far was not accurate enough. Verification of this attitude requires the appropriate data based on PM<sub>10</sub> and PM<sub>2.5</sub> dust emission, while the methodological basis for emission inventory taking of both dust fractions were created only in 2002 [5]. The suspended dust of 2.5 µm grains size can originate from many different sources. The particles smaller than 2.5 µm arise mainly as a result of combusting fuel in car engines, power plants, home furnaces, wood-burning stoves, during fires and while burning grasses and forests. Part of the particles is emitted directly from the emitters such as chimneys and cars. Some of them are generated as a result of the reaction of such gases as sulfur dioxide, nitrogen oxides, and hydrocarbons with other air components. Therefore, the dust molecules demonstrate considerable diversity both in terms of chemical and physical properties. The suspended dust, mainly the fraction of less than 2.5 µm molecules/particles dimension, can be transported to large distances during the favorable circulation of air masses, reaching even a few thousand kilometers [9]. Minute dust particles/molecules can transport different sorts of chemical compounds on their surface, such as polycyclic aromatic hydrocarbons. PAHs get into the air following the above other things:

- industrial processes particularly related with coal and petroleum combustion and with other pyrolytic processes, from the installations of the industry related with coal and petroleum processing, from production and use of tar and creosote oil, production of charcoal (coking plants, refineries, steel, aluminum and copper works);
- communal combustion processes;
- car fuels combustion;
- combustion of wastes, both industrial and communal, especially in the individual households and incineration plants of old type without the appropriate after combustion, dust collection and exhaust gas treatment systems [1].

Most studies have been devoted so far to benzo[a]pyrene (B(a)P), considered as indicative carcinogen, since it reveals the strongest cytotoxic, genotoxic, carcinogenic, teratogenic and immunotoxic properties.

Its concentration is assumed in Poland as a criterion of the PAH toxicological air pollution rate. Table 1 presents the example any average concentration of benzo[a]pyrene in the selected towns of Silesian Region in 2004 [22].

Particularly high contents of hydrocarbons are observable in the air of the municipal conurbations, with heavy industry (metallurgy, mining coke engineering, power plants, gas engineering). Urban solutions are of considerable importance too. In towns of obsolete building development the concentration of hydrocarbons in the air is much higher than in towns of more modern spatial arrangements. These pollutions are of seasonal nature, which is related with the increase of coal and other fuels use for heating the flats. The fuels combusted in the individual furnaces and also in the local coal boiler plants are of very poor quality at poor characteristics and low heating parameters.

Concentrations of PM2.5 – related PAHs and B(a)P ng/m<sup>3</sup> in air in selected cities of the world are presented in Table 2 [6].

Table 1. Summer, winter, fall and annual mean concentration of benzo[a]pyrene in the selected towns of Sillesian Region in 2004 [ng/m<sup>3</sup>] [22]

City	Period			
	Winter season	Summer season	Fall season	Year
Bielsko-Biała	20.9	1.5	15.1	10.2
Bytom	22.4	–	–	–
Chorzów	32.3	0.8	–	–
Częstochowa	18.5	3.9	14.9	10.6
Gliwice	28.6	0.1	–	–
Katowice	20.1	1.2	10.0	8.6
Rybnik	35.9	6.7	21.8	18.5
Siemianowice	21.1	2.9	20.0	12.0
Sosnowiec	22.1	1.3	26.8	13.0
Tychy	36.9	1.5	12.9	14.3
Zabrze	45.2	2.5	14.5	17.5
Zawiercie	20.9	1.0	31.2	13.5
Żory	35.4	4.7	27.0	18.6

Table 2. Concentrations of PM2.5 – related PAHs and B(a)P in air in selected cities of the world [ng/m<sup>3</sup>] [6]

Localization	Measuring period	Σ PAHs	B(a)P
Tunnel, Los Angeles, USA	1989	24.02	2.01
Traffic, Tainan, Taiwan	1995	714	28.7
Urban, Tainan, Taiwan	1995	137.2	6.94
Petrochemical industrial, Taiwan	1995	69.5	1.34
Traffic, Seoul, Korea	1999	26.25	2.56
Suburban, Houston, USA	1998	2.5	0.18
Traffic, Hung Hom, Hong Kong	2001	33.96	2.54
Industrial, Kwun Tong, Hong Kong	2001	16.72	1.44
Traffic, Guangzhou, China	2002	57.89	4.79
Harbor, Taichung, Taiwan	2005	56.12	0.84

The dust originating from the low emission is often more toxic than the dust emitted from the industrial sources; it results from the fact that low emission comes from the sources in which the fuel is not combusted completely.

PAH emission indices originating from hard coal combustion depending on the sort of furnace are presented in Table 3 [10].

Table 3. PAH emission indices originating from hard coal combustion depending on the type of furnace [10]

Type of furnace	PAHs emission factor [mg/Mg]		
	benzo[a]pyrene	carcinogenic + mutagenic PAHs	sum of PAHs
Pulverized fuel fired furnace	1	5	10
Mechanical stocker > 10 Gcal/h	25	150	220
Domestic stove	5000	50000	90000

Silesian and Małopolska provinces are the regions of biggest dust and gas emissions without carbon dioxide (respectively 22% and 20% as well as 10% and 12% of national emissions of these pollutants). Figures 1 and 2 present provinces participation in the emission of dust and gas pollution in the year 2004 [20].

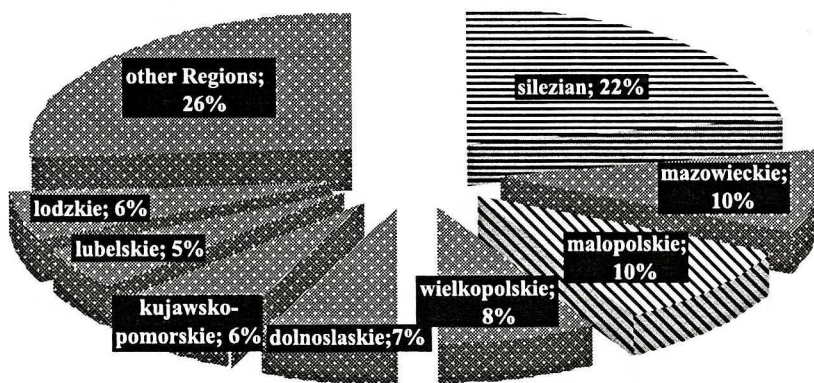


Fig. 1. Provinces participation in the emission of dust pollutions in the year 2004 [20]

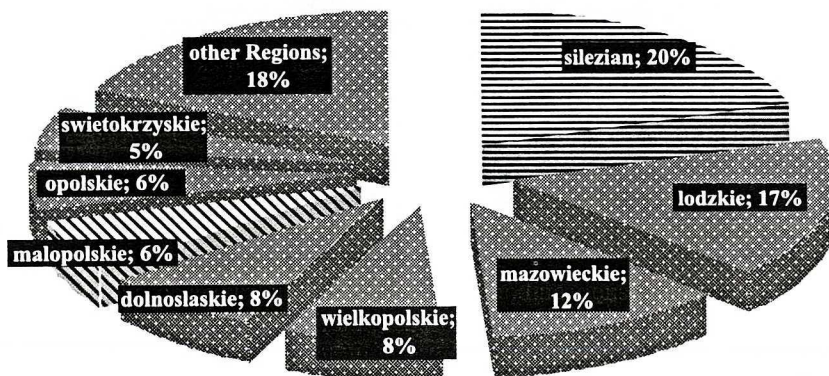


Fig. 2. Provinces participation in the emission of gas pollutions in the year 2004 [20]

The aim of this study was determination of atmospheric concentrations of 16 polycyclic aromatic hydrocarbons, i.e. naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene occurring in the fraction PM<sub>2.5</sub> of the suspended dust and particulate PAHs profiles during cold and summer weather periods. The object of this study was also determining the profiles of their concentration in this fraction considering the seasonal variability (summer and heating season), and the comparison of air pollution by PAH, including by B(a)P.

### MEASUREMENT METHODS

Samples were collected at 4 sampling sites located in Silesia and Małopolska Regions. The locations of measuring stations are show in Figures 3 and 4.

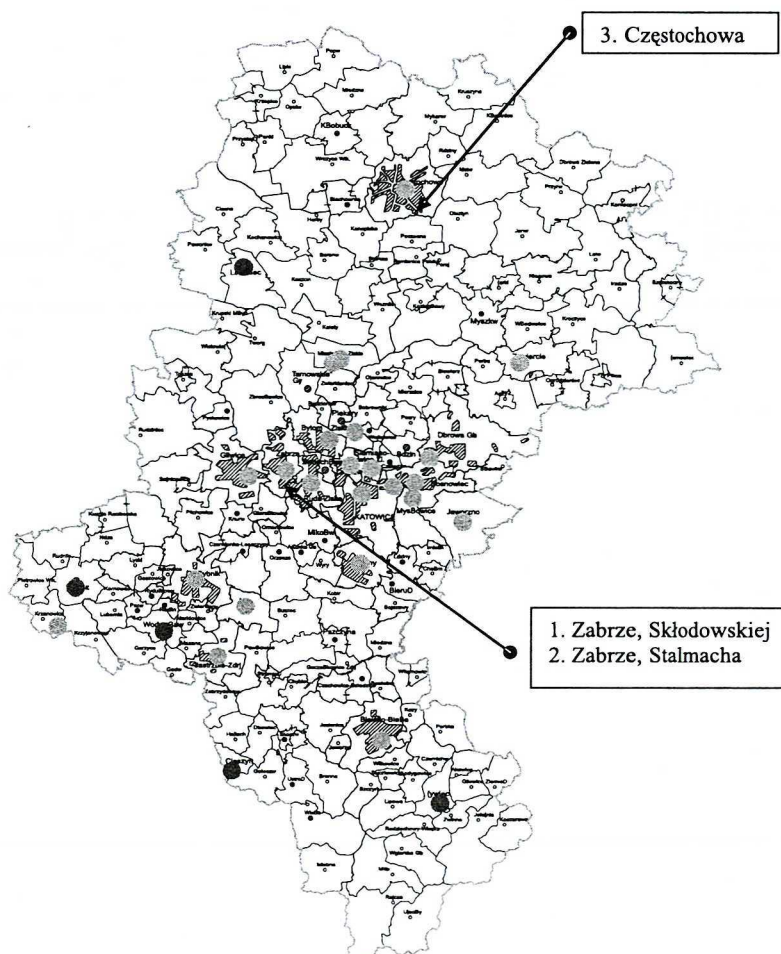


Fig. 3. The location of measuring stations in Silesia Region

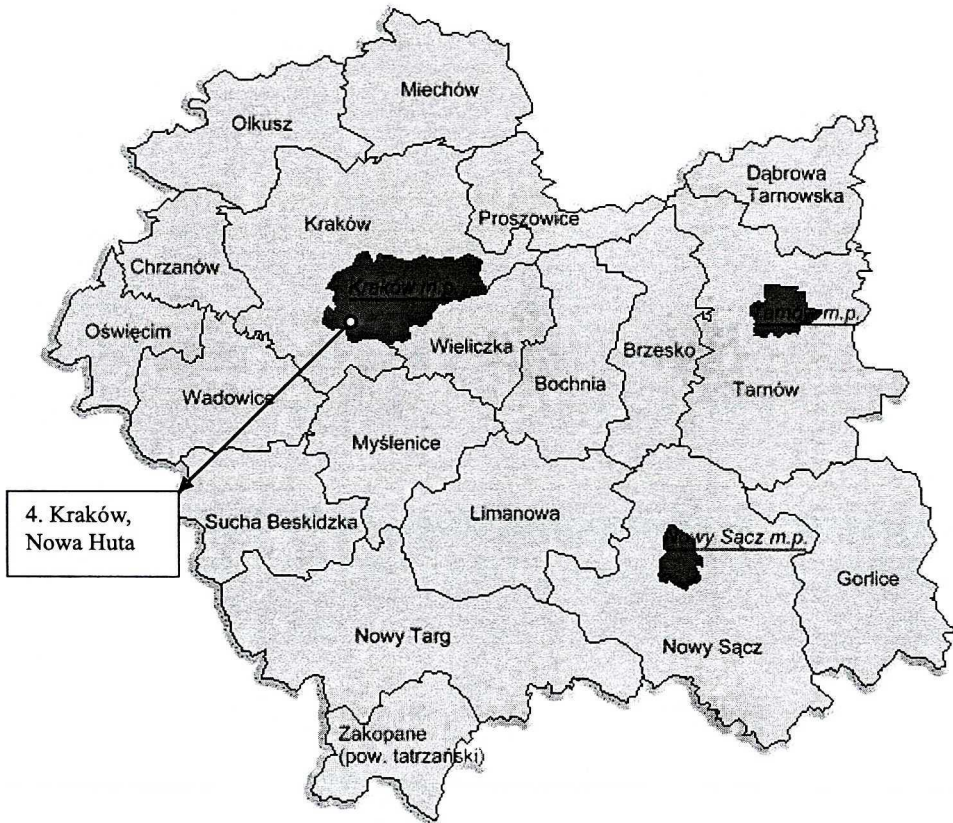


Fig. 4. The location of measuring station in Małopolska Region

### ***Point 1***

The measuring point located in the central part of Zabrze. It is located on the grounds of the Institute of Environmental Engineering of the Polish Academy of Sciences in Zabrze. The neighborhood is composed of: the national road no 88 about 500 m to the north, blocks of flats and residential houses to the east behind al. Korfantego, Zabrze city center with housing and commercial-services development to the south and south-east, and to the west there are blocks of flats of M. Skłodowska-Curie housing estate and the allotment gardens. The method of heating the surrounding flats: heating network and coal burned boilers.

### ***Point 2***

The measuring point located in the central part of Zabrze. The source of combustion gases emission: about 1200 vehicles pass by near by at the time of heaviest traffic hours. The nearest sources of industrial emission: Zabrze Heat and Power Plant, and Zabrze Coke Engineering Industrial Complex. The method of heating the nearby flats: heating network and coal burning boilers.

**Point 3**

The measuring point located in Częstochowa, on the grounds of the representation of the Provincial Environmental Protection Inspectorate within dozen or so meters from Rzaśawska street – the local medium traffic road, on the open, turfed ground. The neighboring plots are occupied by the closed down manufacturing objects. Some halls have been adopted for the warehouses. The measuring point is included in the monitoring system of air quality in the Silesian Province. The location of the measuring point can be considered as representative for the conditions of the municipal background. The ground is located within the area of direct influence of the emission from the technological, energy or motorization sources (with the exception of car park close situated).

**Point 4**

Measuring point located in Nowa Huta in Krakow on the roads crossing, at the main cross-town street going through to Sandomierz, about 2000 m to the west of Sendzimir ironworks. The station is surrounded by: allotment gardens to the north and east, transformer station building 10 m away to the south, five storey apartment building 70 m away to the west. A petrol station is located about 20 m away to the south-east.

### SAMPLING

The samples of suspended dust from Krakow were supplied by Provincial Environmental Protection Inspectorate in Krakow and those from Częstochowa were supplied by Department of Air Protection of the Institute of Environmental Engineering of the Polish Academy of Sciences in Zabrze. The samples from Zabrze and Częstochowa were sampled for authors. Samples from Kraków and Częstochowa were collected by low volume samplers Dichotomus Partisol Plus model 2025, manufactured by Rupprecht and Patashnick Co at air flow 0.9 m<sup>3</sup>/h. The sampler is equipped with so called “virtual impactor” that splits intake air into two streams. The dust is divided into PM<sub>2.5</sub> and PM<sub>2.5–10</sub> due to difference in inertia of smaller and greater particles. In Zabrze, dust was sampled with the use of ATMOSERVICE MVS6D aspirators, certified for compliance with the CEN EN 12341 norm. The aspirators were equipped with inlets for sampling PM<sub>2.5</sub> at air flow 2.3 m<sup>3</sup>/h. Samples were collected on Whatman’s 47 mm PTFE (Teflone) filters at all sampling points. The sampling time intervals were 24 hours, and were collected from winter 2004 to summer 2006. Multi PAHs standards were purchased from Supelco. Organic solvents of analytical grade were purchased from Merck.

### CHEMICAL ANALYSIS

To ensure that enough material was collected because of the low concentrations of PAHs the daily collected filters were grouped by three or four. After sample collection filters were extracted ultrasonically 3 times (1.5 h) with dichloromethane. Organic extract was filtered and concentrated in a rotary evaporator system to dryness. The residues were then dissolved in 20 cm<sup>3</sup> of 2-propanol:water mixture (15:85 v/v) and purified by solid phase extraction (SPE) using C18 octadecyl columns (Baker) by the method described elsewhere [4].

The qualitative and quantitative analysis of PAHs fraction was performed by gas chromatography with the Varian chromatography, model Saturn 3, equipped with a mass

detector and a capillary column V-5MS, 30 m long. The carrier gas was helium. The chromatographic conditions were as follows: injector temperature – 280°C, temperature program of analytical column – 65°C (5 min), 65–290°C at a rate of 3°C/min, 290°C (30 min). The compounds were identified by GC-MS analysis, comparing the retention times and mass spectra of the standard mixture. Blanks were analyzed and quantified to ensure that there were no significant background interferences. PAH concentration in fields blanks were not detected and data not subjected to any blank correction.

### DISCUSSING THE RESULTS

In this study, 16 PAHs bound to air dust from urban area were characterized. The qualitative analysis of aromatic fraction separated from the dust samples showed that they contain all 16 PAHs chosen by Environmental Protection Agency for monitoring in ambient air. Recoveries for the total procedures (sample preparation, extraction and SPE) ranged between 70% and 83% for individual PAHs. The quantitative analysis of suspended dust has shown that the samples collected in winter time contain much more PAHs than the samples collected in summer time. Table 4 present the seasonal distribution of concentrations of particle-associated sum of 16 PAHs.

Table 4. Mean concentrations of total PAHs adsorbed PM<sub>2.5</sub> considering the seasonal variability in air in selected towns of Silesia and Małopolska Regions [ng/m<sup>3</sup>]

Sampling point	Season	Σ 16 PAHs [ng/m <sup>3</sup> ]	Mean Σ 16 PAHs [ng/m <sup>3</sup> ]
Częstochowa, Rząsawska	winter	112.49	72.49
	summer	32.49	
Kraków, Nowa Huta	winter	147.52	98.23
	summer	48.94	
Zabrze, Skłodowska-Curie	winter	82.69	47.36
	summer	12.02	
Zabrze, Stalmacha	winter	121.96	76.67
	summer	31.37	

The average PM<sub>2.5</sub> ambient air concentrations of PAHs at Kraków sampling site were found to be 48.94 ng/m<sup>3</sup> in summer season and 147.52 ng/m<sup>3</sup> in winter season. The average seasonal concentration assume the values from 12.02 ng/m<sup>3</sup> during the summer season to 82.69 ng/m<sup>3</sup> during the heating season in the measuring point in Zabrze at Skłodowska-Curie Street, from 31.37 ng/m<sup>3</sup> during the summer season to 121.96 ng/m<sup>3</sup> during the heating season in Zabrze at Stalmacha Street, in Częstochowa from 32.49 ng/m<sup>3</sup> during the summer season to 112.49 ng/m<sup>3</sup> during the winter season. The observed concentrations were high and comparable with other studies of the world [2–4, 6, 12, 13, 16–18]. For all samples the winter time total concentration of the sum of 16 PAHs was above three times higher than one in summer (in Zabrze, Skłodowska-Curie Street – above six times). Higher concentration of PAH in the winter months is related with the higher concentration of the suspended dust and results from the increased use of fuels for heating purposes. The increased level of PAH during the winter season is also influenced by the higher emission of PAH from the vehicles combustion engines, poorer work conditions of vehicle engines by the low temperature in winter, while the influence of motor



sources rapidly decreases the greater the distance from the road [11]. Higher content of PAH in the dust, under the conditions of lower air temperature is also the effect of condensation and deposition of PAH gas fraction on the constant particle, which particularly applies to hydrocarbons of lower molecular mass (2- and 3-rings). PAH profiles were also characterized in the suspended dust for < 2.5  $\mu\text{m}$  fraction, during the summer and winter seasons (Tab. 5).

Table 5. Profiles of determined PM<sub>2.5</sub> – related PAHs in selected towns of Silesia and Małopolska Regions [ng/m<sup>3</sup>]

Compound	Sampling point							
	Zabrze, Skłodowska-Curie		Zabrze, Stalmacha		Kraków, Nowa Huta		Częstochowa, Rzasańska	
	Concentration [ng/m <sup>3</sup> ]							
	winter	summer	winter	summer	winter	summer	winter	summer
Naphtalene	1.72	0.3	2.87	1.12	2.11	1.20	3.33	2.3
Accnaphtylenc	1.45	0.79	3.76	2.22	3.45	1.96	1.8	0.99
Accnaphtenc	1.19	0.25	1.99	0.76	2.89	1.24	1.79	0.49
Fluorcne	5.67	0.41	10.87	3.27	12.21	2.12	8.35	1.06
Phenanthrene	10.45	1.48	12.74	4.98	14.21	3.68	12.88	2.61
Anthracene	5.73	1.07	7.3	4.32	7.21	2.54	8.88	1.67
Fluoranthene	10.05	0.89	10.87	1.76	14.24	4.21	14.15	3.33
Pyrene	4.58	0.13	6.11	1.97	8.32	2.89	7.28	0.74
Benzo(a)anthracenc	10.37	0.98	11.78	1.76	14.21	5.21	12.36	3.09
Chrysenc	9.62	2.17	13.66	1.22	14.25	5.34	12.52	3.07
Benzo(b)fluoranthene	7.9	0.54	12.84	0.76	16.23	0.94	6.9	3.6
Benzo(k)fluoranthene	1.97	1.17	6.12	1.12	8.32	3.51	3.07	3.09
Benzo(a)pyrcne	4.35	0.89	8.99	1.89	16.32	2.65	6.55	1.95
Indeno(1,2,3-cd)pyrcne	2.92	1.12	3.72	2.12	4.21	0.58	4.92	2.42
Dibenz(ah)anthracene	0.56	0.11	1.23	0.32	1.10	0.28	1.55	0.72
Benzo(ghi)pcrylcnc	4.16	0.89	7.11	1.78	8.24	3.21	6.16	1.36

The analysis of PAH profile in < 2.5  $\mu\text{m}$  dust fraction in the selected towns proved that the dominant hydrocarbons during the heating season in Krakow Nowa Huta were hydrocarbons 3- and 4-rings. They constituted above 60% of total content of the determined PAHs. The dominating hydrocarbons during the summer season were benzo(a)anthracene, chrysene, benzo(b)fluoranthene, with their average concentration equaling respectively 5.21, 5.34 and 6.32 ng/m<sup>3</sup>. In Zabrze at Skłodowska-Curie Street the dominating hydrocarbons during the heating season were 3- and 4-ring hydrocarbons, such as phenanthrene, fluoranthene, chrysene, benzo(a)anthracene, while during the summer season the dominating 3-ring hydrocarbons were phenanthrene, anthracene and chryse- ne, in Zabrze at Stalmacha Street the dominating hydrocarbons were also 3- and 4-ring such as fluorene, phenanthrene, chrysene, benzo(a)anthracene, during the summer season dominating 3-ring hydrocarbons – fluorene, phenanthrene, anthracene. In Częstochowa,

the dominating hydrocarbons during the winter season were 3- and 4-ring hydrocarbons, such as phenanthrene, fluoranthene, chrysene and benzo(a)anthracene. They constituted above 46% of the total mass of the selected PAHs. The highest concentration of fluoranthene – 16.02 ng/m<sup>3</sup> – was observed in December 2004. The participation of 5- and 6-ring hydrocarbons was considerably smaller – amounting in total 29% of PAH mass. During the summer season the concentration of all hydrocarbons was lower. The change of proportion of the individual PAH groups were observed. Hydrocarbons 4- and 5-ring were dominating. The participation of hydrocarbons of lower molecular mass was relatively higher than during the winter season. The average concentration of PAH total was 3.5-times lower in summer than during the winter months. It appears from the data available in literature that 5- and 6-ring hydrocarbons originate mainly from the processes of high temperature combustion (industrial processes), while 3- and 4-ring hydrocarbons – most often from the incomplete combustion of solid fuels [7], it can be thus concluded that the main source of PAH in the analyzed dust samples was the coal combustion processes in home furnaces and other low capacity energy sources. The results of benzo(a)pyrene concentration in the air related with PM<sub>2.5</sub> dust in the subject towns are presented in Table 6.

Table 6. Mean concentrations of B(a)P adsorbed on PM<sub>2.5</sub> considering the seasonal variability in air in selected towns of Silesia and Małopolska Regions [ng/m<sup>3</sup>]

Sampling Point	Season	Concentration B(a)P [ng/m <sup>3</sup> ]	Mean B(a)P [ng/m <sup>3</sup> ]
Częstochowa	winter	6.55	4.25
	summer	1.95	
Kraków, Nowa Huta	winter	16.32	9.4
	summer	2.65	
Zabrze, Skłodowska-Curie	winter	4.35	2.62
	summer	0.89	
Zabrze, Stalmacha	winter	8.99	5.44
	summer	1.89	

The observed concentrations of PM<sub>2.5</sub> – related benzo(a)pyrene were high, but comparable to other studies of the world (Tab. 2) [6], the mean concentrations of benzo(a)pyrene ranged from 2.62 ng/m<sup>3</sup> for Skłodowska-Curie Street to 9.4 ng/m<sup>3</sup> in Kraków. Winter time total concentrations of benzo(a)pyrene in PM<sub>2.5</sub> fraction were from three to six times higher than adequate concentration in summer season. The lowest concentrations of benzo(a)pyrene during the heating season were observed in Zabrze at Skłodowska-Curie Street – 4.35 ng/m<sup>3</sup>, the highest in Kraków – 16.32 ng/m<sup>3</sup>. Several studies from European cities reported lower benzo(a)pyrene concentrations than those recorded in this study. They ranged between a mean concentration of 4.4 ng/m<sup>3</sup> in winter in Denmark [15], 1.38 ng/m<sup>3</sup> in Italy [14], and 0.22 ng/m<sup>3</sup> in Germany [19]. The average concentrations of benzo(a)pyrene in PM<sub>2.5</sub> fraction announces with high probability the exceeding of planned middle year allowable concentration in dust PM<sub>10</sub> – 1 ng/m<sup>3</sup>. The average concentration of benzo(a)pyrene for PM<sub>2.5</sub> fraction was a few times higher than the limit in PM<sub>10</sub>.

The percentage participation of benzo(a)pyrene in the total content of PAH in the individual measuring points was following: Częstochowa 5.82%, Kraków 11.06%, Za-

brze, Stalmacha Street 7.37%, Zabrze, Skłodowska-Curie Street 5.26%. Similarly as in the case of the concentration of total polycyclic aromatic hydrocarbons, the highest concentrations were observed in Kraków and then in Zabrze at Stalmacha Street. The highest concentration of benzo(a)pyrene in the Kraków was due to localization of sampling point (the roads crossing, about 2500 vehicles pass nearby at the time of heaviest traffic hours, i.e. 48% higher than at Stalmacha Street), and also direct neighborhood of petrol station, periodical accumulation of vehicles, and domestic emission in the heating season. Simultaneously with higher concentrations of total PAHs, the higher concentrations of fine dust were observed (above 60  $\mu\text{g}/\text{m}^3$  in heating seasons). Relatively high concentrations of total PAHs and also benzo(a)pyrene were observed in Częstochowa and could be the result of repair works (wood combustion) performed a short distance away from the sampling point during measurements in summer season. The lowest concentrations of total PAHs and benzo(a)pyrene during both, the heating and summer seasons in Skłodowska-Curie Street were result of the greatest distance from the road and other emission sources.

These results, obtained in different locations with differential local sources (industrial, traffic, domestic) and meteorological conditions indicate significantly impact of these elements on total concentrations of PAHs and also concentrations of B(a)P in aerosols. The composition of PAHs in association with airborne particles changes significantly according to their emission sources, particularly traffic or other processes of combustion.

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#### REFERENCES

- [1] Bilek M.: *Zanieczyszczenie powietrza WWA*, <http://www.wsse.krakow.pl>.
- [2] Bodzek D., K. Luks-Betlej, L. Warzecha: *Determination of particle-associated polycyclic aromatic hydrocarbons in ambient air samples from the Upper Silesia region of Poland*, *Atmospheric Environment*, **27A**, 759 (1993).
- [3] Ćwiklak K., H. Pyta: *Występowanie wielopierścieniowych węglowodorów aromatycznych w pyłe PM<sub>2,5</sub> i PM<sub>2,5-10</sub> na stanowisku pomiarowym w Częstochowie*, *Ochrona powietrza i problemy odpadów*, **44**, 5, 141–148 (2006).
- [4] Ćwiklak K., E. Surowicz: *Przemiany chemiczne WWA zaadsorbowanych na pyłach pod wpływem promieniowania słonecznego*, *Ochrona powietrza i problemy odpadów*, **39**, 5, 149–156 (2005).
- [5] Dębski B., J. Fudała, S. Hławiczka, M. Cenowski, K. Olcndrzyński: *Analiza metodok inwentaryzacji pyłu drobnego możliwych do zastosowania na potrzeby Konwencji w sprawie transgranicznego zanieczyszczenia powietrza na dalekie odległości*, KCIE, IOŚ, Warszawa 2002.
- [6] Fang G., Y. Wu, C. Chang, T. Ho: *A study of polycyclic aromatic hydrocarbons concentrations and source identifications by methods of diagnostic ratio and principal component analysis at Taichung chemical Harbor near Taiwan Strait*, *Chemosphere*, **64**, 7, 1233–1242, 2006.
- [7] Fernandes M.B., M.-A. Sicre, A. Boircau, J. Tronczynski: *Polyaromatic Hydrocarbon (PAH) Distributions in the Seine River and its Estuary Marine*, *Pollution Bulletin*, **34**, 857–867 (1997).
- [8] Guor-Cheng F., Ch. Kuan-Foo, L. Chungsyng, B. Hsunling: *Estimation of PAHs dry deposition and BaP toxic equivalency factors (TEFs) study at Urban, Industry Park and rural sampling sites in central Taiwan*, *Taichung*, *Chemosphere*, **55**, 6, 787–796 (2004).
- [9] Koniecznyński J., B. Koziełska, J. Żeliński, J. Staisz, A. Pasoń-Koniecznyńska: *Skład ziarnowy oraz zawartość i profile wielopierścieniowych węglowodorów aromatycznych w pyłach emitowanych z obiektów energetyki komunalnej i zakładowej*, Wydawnictwo Politechniki Śląskiej, Gliwice 2003.
- [10] Koniecznyński J., A. Pasoń-Koniecznyńska: *Scalony wskaźnik emisji substancji zanieczyszczających po-*

- wietrze w procesie spalania węgla, Archives of Environmental Protection, **25**, 29–40 (1999).
- [11] Lee W.J.; Wang Y.F.; Lin T.C.; Chen Y.Y.; Lin W.C.; Ku C.C.; Cheng J.T.: *PAH characteristics in ambient air traffic source*, Science of the Total Environment, 185–200, 1995
- [12] Lenicek J., M. Sckyra, K. Citkova, I. Holoubek: *Determination of polycyclic aromates, chlorinated insecticides and polychlorinated biphenyls in the air of North Bohemian Region*, Central European Journal of Public Health, **1**, 113 (1993).
- [13] Maliszewska-Kordybach B.: *Sources, Concentrations, Fate and Effects of polycyclic Aromatic Hydrocarbons (PAHs) in the Environment, Part A, PAHs in Air*, Polish Journal of Environ. Studies, **8**(3), 131–136 (1999).
- [14] Menchini E., F. Monfredini, F. Merli: *The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome 1993–1998*, Atmos. Environ., **33**, 3739–3750 (1999).
- [15] Nielsen T., H.E. Jørgensen, J.Ch. Larsen, M. Poulsen: *City air pollution of polycyclic aromatic hydrocarbons and other mutagens: occurrence sources and health effects*, Sci. Total Environ., **189/190**, 41–49 (1996).
- [16] Pastuszka J.S.: *Study of PM10 and PM 2.5, Concentrations in southern Poland*, J. Aerosol Sci., **28**, 1, 227–228 (1997).
- [17] Pleil J., A. Vette, S. Rappaport: *Assaying particle-bound polycyclic aromatic hydrocarbons from archived PM<sub>2.5</sub> filters*, Journal of Chromatography A, **1033**, 1, 9–17 (2004).
- [18] Pyta H., A. Krasa, W. Rogula: *Variability of Airborne Fine Dust Concentration and Content of PAHs in PM2.5 – Measurements in Częstochowa, Poland*, Archives of Environmental Protection, **32**, 4, 314 (2006).
- [19] Schnelle-Kreis J., I. Gebeftügi, G. Welzl, T. Jaensch, A. Kettrup: *Occurrence of particle-associated polycyclic aromatic compounds in ambient air of the city of Munich*, Atmos. Environ., **35**, S71–S81 (2001).
- [20] Szymańska-Kubicka L., R. Zbrojkiewicz: *Raport o stanie środowiska 2004*, <http://www.katowice.pios.gov.pl>.
- [21] Ximci H., Z. Guoshun, S. Yele, A. Zhisheng: *Characteristics and sources of polycyclic aromatic hydrocarbons and fatty acids in PM<sub>2.5</sub> aerosols in dust season in China*, Atmospheric Environment, **40**, 18, 3251–3262 (2006).
- [22] *Zanieczyszczenie atmosfery w województwie śląskim w latach 2003–2004*, Wojewódzka Stacja Sanitarno-Epidemiologiczna w Katowicach, Katowice 2005.

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