

## HAZARDOUS COMPOUNDS IN URBAN PM IN THE CENTRAL PART OF UPPER SILESIA (POLAND) IN WINTER

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**Keywords:** PM<sub>1</sub>, PM<sub>2.5</sub>, heavy metals, PAH, benzo(a)pyrene, carcinogenicity, hazardous compounds, toxicity equivalency factor (TEF), BEQ.

**Abstract:** Thirteen fractions of ambient dust were investigated in Zabrze, a typical urban area in the central part of Upper Silesia (Poland), during a heating season. Fifteen PAH and Cr, Mn, Co, Ni, As, Se, Cd, Pb contents of each fraction were determined. The dust was sampled with use of a cascade impactor and chemically analyzed with an energy dispersive X-ray fluorescence spectrometer (PANalytical Epsilon 5) and a gas chromatograph with a flame ionisation detector (Perkin Elmer Clarus 500). The concentrations of PM<sub>1</sub> and the PM<sub>1</sub>-related PAH and elements were much higher than the ones of the coarse dust (PM<sub>2.5-10</sub>) and the substances contained in it. The concentrations of total PAH and carcinogenic PAH were very high (the concentrations of PM<sub>1</sub>-, PM<sub>2.5</sub>-, and PM<sub>10</sub>-related BaP were 16.08, 19.19, 19.32 ng m<sup>-3</sup>, respectively). The municipal emission, resulted mainly from hard coal combustion processes, appeared to be the main factor affecting the air quality in Zabrze in winter.

### INTRODUCTION

Despite clear positive statistical relations between the concentrations of ambient particulate matter (PM) and the health effects [44] the biological mechanisms of the toxic activity of PM are not entirely known [5, 11]. Still it is not definitely settled which factor, the concentration and the granularity or the chemical composition, determines the hazard from PM [1, 53]. Anyway, polycyclic aromatic hydrocarbons (PAH) and PM-related metals are considered to be the most hazardous components of PM (the most often investigated PAH are: acenaphthene (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), and metals: As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, and Se [34, 56].

The goal of the work was to determine the mass distribution of eight elements (Cr, Mn, Co, Ni, As, Se, Cd, Pb) and fifteen PAHs (Acy, Ace, F, Ph, An, Fl, Py, BaA, Ch, BbF, BkF, BaP, DBA, BghiP, IP) between three PM fractions ( $PM_1$ ,  $PM_{1-2.5}$ ,  $PM_{2.5-10}$ ) and their ambient concentrations in Zabrze, southern Poland. From the air protection point of view, Zabrze is located in the most interesting region of Poland – Upper Silesia – where the recent three decades of economic changes forced the greatest in Poland drop of industrial air pollution and where old steel works, cokeries and coal mines, together with road traffic, are responsible for high concentrations of ambient dust [40, 41, 49]. Investigations were done in a winter heating season, when the emission from combustion of fossil fuels for energy production (especially municipal) causes very high PM concentrations [41, 15].

## METHOD

The site, selected in Zabrze for the experiment, is representative of the typical air-pollution conditions in the central part of Upper Silesia – by the Directive 2008/50/EC definition [7], it is an urban background measuring point (Fig. 1). The effects of the industrial and municipal emissions on living quarters of the agglomeration are represented and may be observed very well there.



Fig. 1. Location of sampling site

Ambient dust was sampled with the use of a thirteen stage DEKATI low pressure impactor (DLPI), which collects thirteen PM fractions (0.03–0.06, 0.06–0.108, 0.108–0.17, 0.17–0.26, 0.26–0.4, 0.4–0.65, 0.65–1.0, 1.0–1.6, 1.6–2.5, 2.5–4.4, 4.4–6.8,

6.8–10.0, >10  $\mu\text{m}$ ) onto thirteen substrate filters. The principle of DLPI operating may be found in [19].

PM was sampled from 26 October 2007 to 22 March 2008 (a whole heating season). A single sample-taking lasted for about one week. The seven thirteen-substrate samples from the period 26 October – 27 December 2007 were analyzed for PAH, the remaining seven ones from the period 11 January – 22 March 2008 – for the elemental composition.

The mass of the dust collected on aluminum (PAH analyzes) and polycarbonate (elemental composition) substrates was determined by weighing the substrates before and after exposure on a Mettler Toledo balance. Before weighing, the substrates were kept in the weighing room for 48 hours (temperature  $20\pm 2^\circ\text{C}$ , relative air humidity  $48\pm 5\%$ ). 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. The samples for the PAH analysis, till analyzing, were kept in a refrigerator in tight and lightproof containers.

The elemental composition of each of the seven samples of each of the 13 PM fractions from the period 11 January – 22 March 2008 was determined by applying energy dispersive X-ray fluorescence (EDXRF). The ambient concentrations of Cr, Mn, Co, Ni, As, Se, Cd, Pb were determined and the average ambient concentrations (arithmetic means) of each element were computed for each fraction. A PANalytical Epsilon 5 was used. The measurements were done under vacuum, the analysis time for a single sample was 4800 s. The X-ray tube was adjusted depending on a secondary target used: 25 keV and 25 mA for Al, 40 keV and 15 mA for Ti, 40 keV and 15 mA for Fe, 75 keV and 8 mA for Ge, 100keV and 6mA for Zr, 100keV and 6mA for  $\text{Al}_2\text{O}_3$ . The element concentrations were determined by comparing the results with the calibration curves. Thin-layer single-element Micromatter standards were used to calibrate the apparatus [61]. Weekly measurements of the NIST SRM2873 standards (except for Co, whose recovery was 39%, recoveries of remaining elements were between 91 and 116% of the certified value) and monthly measurements of the monitor were routinely performed to control the quality of the analytical procedure. The detection limits were from  $0.2 \text{ ng cm}^{-2}$  for Se to  $11.6 \text{ ng cm}^{-2}$  for As.

For each of the 13 PM fractions, all its seven samples from the period 26 October – 27 December 2007 were extracted together in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) in an ultrasonic bath. The extract was percolated, washed and dried by evaporating in the helium atmosphere. The dry residue was diluted in propanol-2 ( $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ) and distilled water was added to receive the propanol-2 to water proportion 15/85 (v/v). For selective purification, the resulting samples were solidified (SPE) by extracting in columns filled with octadecyl ( $\text{C}_{18}$ , Supelco). PAH were eluted with use of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The extract of the PAH fraction was condensed in the helium atmosphere to the volume of  $0.5 \text{ cm}^3$ . The samples were analyzed on a Perkin Elmer Clarus 500 gas chromatograph with a flame ionization detector (FID). An RTX-5 Restek capillary  $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$  column was used to separate the sample components. The flow of the carrier gas, helium, was  $1.5 \text{ cm}^3 \text{ min}^{-1}$ . The calibration curves for the 15 PAH standards were used in the quantitative determinations. The linear correlation of the peak surfaces with the PAH concentrations was checked in the concentration range  $1\text{--}50 \text{ ng } \mu\text{l}^{-1}$ . The correlation coefficients ranged from 0.95 to 0.99. The time of the whole analysis was 40 min. FID was provided with hydrogen ( $45 \text{ cm}^3 \text{ min}^{-1}$ ) and air ( $450 \text{ cm}^3 \text{ min}^{-1}$ ). The recoveries of PAH, ranging from 85% to 93%, were determined using a standard containing the 15 PAH.

## RESULTS AND DISCUSSION

The average concentration of  $PM_{10}$  ( $PM_{10} = PM_1 + PM_{1-2.5} + PM_{2.5-10}$ ) in the last quarter of 2007 exceeded  $46 \mu\text{g m}^{-3}$ , in the first quarter of 2008 –  $38 \mu\text{g m}^{-3}$  (Table 1).

In most European countries the yearly  $PM_{10}$  concentration has been limited for about twenty years (in Poland since 1998) and its highest permissible value is  $40 \mu\text{g m}^{-3}$ . The

Table 1. Concentrations of ambient dust (PM,  $\mu\text{g m}^{-3}$ ), and of 15 PAH and 8 elements (ng  $\text{m}^{-3}$ ) related to three fractions of ambient dust in Zabrze, in the central part of Upper Silesia, Poland, in winter

	$PM_1^{1)}$	$PM_{1-2.5}^{2)}$	$PM_{2.5-10}^{3)}$
$PM^{4)}$	25.55	7.79	5.18
$PM^{5)}$	33.65	7.66	4.98
Cr	2.54	1.11	1.33
Mn	59.99	17.26	20.66
Co	<DL <sup>6)</sup>	<DL	<DL
Ni	0.17	0.04	0.06
As	2.14	0.49	0.35
Se	<DL	<DL	<DL
Cd	0.75	0.27	0.14
Pb	23.56	9.54	7.50
Acy	0.19	0.10	<DL
Ace	0.33	0.05	<DL
F	1.36	0.17	0.38
Ph	4.07	0.95	0.51
An	0.88	0.28	0.25
Fl	15.80	3.49	0.08
Py	18.03	4.50	0.12
BaA	17.78	3.57	0.05
Ch	17.11	3.78	0.16
BbF	12.84	2.09	0.24
BkF	13.76	2.41	0.27
BaP	16.09	3.11	0.13
DBA	0.73	0.09	<DL
BghiP	3.01	0.36	<DL
IP	6.12	0.86	<DL

<sup>1)</sup> sum of concentrations of dust, element or compound in fractions 0.03–0.06, 0.06–0.108, 0.108–0.17, 0.17–0.26, 0.26–0.4, 0.4–0.65, 0.65–1.0  $\mu\text{m}$

<sup>2)</sup> sum of concentrations of dust, element or compound in fractions 1.0–1.6, 1.6–2.5  $\mu\text{m}$

<sup>3)</sup> sum of concentrations of dust, element or compound in fractions 2.5–4.4, 4.4–6.8, 6.8–10.0  $\mu\text{m}$

<sup>4)</sup> average concentration from 11 January to 22 March 2008

<sup>5)</sup> average concentration from 26 October to 27 December 2007

<sup>6)</sup> concentrations below detection limit

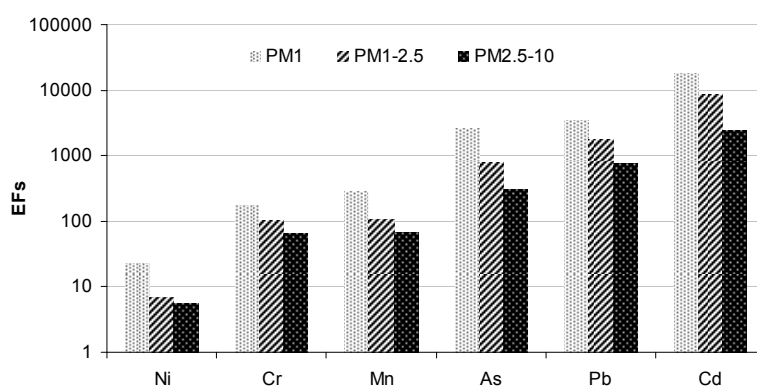
high  $PM_{10}$  concentrations during a half-year in Zabrze may mean violating this limit. The concentrations of  $PM_{2.5}$  ( $PM_{2.5} = PM_1 + PM_{1-2.5}$ ) also were high; in the winter 2007/2008 they exceeded the limit  $25 \mu g m^{-3}$  [7].  $PM_{2.5}$  and  $PM_1$ , the fractions of respirable dust, contributed no less than 89 and 72% to  $PM_{10}$ , respectively.

The average concentrations of the eight toxic elements in Zabrze in the period 11 January – 22 March 2008 were low compared to their permissible values both domestic and EU ones, [6,13]. All, except the Cd concentration, were at least 10 times lower than their yearly limits. Because in summer the concentrations of PM and of the PM-related elements are usually lower, their yearly concentrations are not expected to exceed the yearly limits. The concentrations of Co and Se for each PM fraction were very low, lower than their detection limits:  $0.1 ng m^{-3}$  for Se and  $0.2 ng m^{-3}$  for Co.

In the period 11 January – 22 March 2008, the concentrations of  $PM_1$  were high, the eight elements assumed the greatest concentrations as the  $PM_1$ -related ones (Table 1). In Zabrze all these elements come probably from combustion and occur in  $PM_1$  in metal oxides, sulfates and chlorides. The enrichment coefficients [14, 51, 66], presented in Figure 2, confirm the fact. Only EF for  $PM_{1-2.5}$ - and for  $PM_{2.5-10}$ -related Ni are lower than 10. EF for the rest of the elements are very high, for  $PM_1$ -related Cr and Mn higher than 100, for As and Pb higher than 1000. It reflects a strong anthropogenic effect on the winter concentrations of these PM-related elements in Zabrze.

Seeming not very high compared to the air quality standards, the winter ambient concentrations of the toxic elements in Zabrze are higher than their winter concentrations in other regions of Europe (Table 2).

The high concentrations of Pb, Cd, As, the lower than in other regions concentration of Ni (tracer of combustion of oil in typical European urban areas, [65]) and the results from the investigations of the smog episode in Zabrze in January 2006 [41] suggest the combustion of low-quality coal in domestic furnaces (municipal emission) as the source of these elements in Zabrze in winter.



$EF_x$  for the element  $x$  is referred to the concentration  $C_{Si}$  of Si, a marker element for the Earth crust- $EF_{Si}=1$  (average Si concentrations in Zabrze in January–March 2009 were:  $122.8 ng m^{-3}$  for  $PM_1$ ,  $94.9 ng m^{-3}$  for  $PM_{1-2.5}$ ,  $172.6 ng m^{-3}$  for  $PM_{2.5-10}$ ). The chemical characterization of the Earth upper continental crust is taken from Wedepohl; 1995 [66]

Fig. 2. EF for PM-related elements in Zabrze in winter 2008

Table 2. Ambient concentrations of elements related to various PM fractions at various sites in the world

Location	Sampling period	Fraction	As	Cd	Cr	Mn	Ni	Pb
Zabrze (Poland); urban background a	Jan-Mar 2008	PM <sub>1</sub>	2.14	0.75	2.54	59.99	0.17	23.56
		PM <sub>2.5</sub>	2.63	1.02	3.65	77.25	0.21	33.1
		PM <sub>10</sub>	2.98	1.16	4.98	97.91	0.27	40.6
Zabrze (Poland); urban background [41]	Jan 2006	PM <sub>2.5</sub>	-	5.5	24.3	24.6	17.7	184.7
		PM <sub>10</sub>	-	6.9	49.7	49.8	17.3	223.6
Milan (Italy); residential-commercial area [63]	Winter 2002	PM <sub>1</sub>	2	-	2	9	7	35
		PM <sub>2.5</sub>	3	-	5	18	9	55
Menen (Belgium); suburban/industrial [38]	Winter 2003	PM <sub>2.5</sub>	-	-	2.3	12	3.4	54
Athens (Greece); suburban [62]	Oct-Dec 2003	PM <sub>2.5</sub>	6.83	0.70	-	-	1.59	5.45
Cartagena (Spain); suburban [35]	Jan-Mar 2005	PM <sub>2.5</sub>	0.3	0.2	1.3	2.7	3.4	5.7
		PM <sub>1</sub>	1.7	4.0	8.4	10.4	-	58.5
Seoul (Korea); residential [39]	Feb 2006	PM <sub>10</sub>	2.2	4.1	10.6	21.5	-	75.3
Barcelona (Spain); urban background [42]	2005-2006	PM <sub>1</sub>	0.6	0.3	1.2	4	3	17
		PM <sub>2.5</sub>	-	12.6	80.5	25.6	15.3	630.8
Dehli (India), urban [55]	Nov 2007-Feb 2008	PM <sub>10</sub>	-	9.2	128.5	44.7	15.3	420.7
		PM <sub>2.5</sub>	-	-	3.3	4.0	97.8	275.8
Ulsan (Korea), residential area [25]	Spring 2009	PM <sub>10</sub>	-	-	6.9	4.6	41.7	263.3

a this study

The winter ambient concentrations of total PAH ( $\Sigma$ PAH) in Zabrze were high – the concentrations of  $PM_1$ - and  $PM_{2.5}$ -related  $\Sigma$ PAH were  $128.1 \text{ ng m}^{-3}$  and  $153.9 \text{ ng m}^{-3}$ , respectively.  $PM_1$ -related  $\Sigma$ PAH were 82% and  $PM_{2.5}$ -related  $\Sigma$ PAH were 98% of  $PM_{10}$ -related  $\Sigma$ PAH. The concentrations of  $PM_1$ -related  $\Sigma$ PAH were about 5 times greater than the concentrations of  $PM_{1-2.5}$ -related  $\Sigma$ PAH. All PM fractions were rich in 4- and 5-ring PAH, which were no less than 89% of  $\Sigma$ PAH. Among all PM-related PAH, Py, BaA and Ch had the greatest concentrations ( $PM_1$ -related:  $18.03 \text{ ng m}^{-3}$ ,  $17.78 \text{ ng m}^{-3}$ ,  $17.11 \text{ ng m}^{-3}$ , respectively). Fl, BbF, BkF, BaP – the compounds whose presence and high concentrations in atmospheric air indicate stationary combustion had also great ambient concentrations ( $12.84$ – $16.09 \text{ ng m}^{-3}$ ,  $PM_1$ -related) and contributions to  $\Sigma$ PAH. The proportion CPAH/ $\Sigma$ PAH of the concentration of CPAH (total combustion PAH: Fl, Py, BaA, BbF, BkF, BaP, BeP, IP and BghiP) to the concentration of  $\Sigma$ PAH, expresses the effect of stationary combustion on the PAH concentrations [47, 48, 54]. In Zabrze it was equal to 0.82 for  $PM_1$ , 0.79 for  $PM_{1-2.5}$  and 0.41 for  $PM_{2.5-10}$  – in winter  $PM_1$ - and  $PM_{1-2.5}$ -related PAH come from stationary combustion and  $PM_{2.5-10}$ -related PAH – from combustion of fuels in car engines [47, 48].

The diagnostic ratios (selected proportions of the concentrations of PAH) for  $PM_1$ - and  $PM_{1-2.5}$ -related PAH ( $[BaA]/([BaA]+[Chry])$  equal to 0.51 for  $PM_1$  and 0.49 for  $PM_{1-2.5}$  or  $[BaA]/[BaP]$  equal to 1.11 for  $PM_1$  and 1.15 for  $PM_{1-2.5}$ ) show that  $PM_1$ - and  $PM_{1-2.5}$ -related PAH came mainly from coal combustion [59,67,68]. According to some authors [26], the winter  $[BaA]/[BaP]$  for  $PM_1$  and  $PM_{1-2.5}$  in Zabrze are indicative of wood burning. Also  $[BbF]/[BkF]$  equal to 0.93, 0.87 and 0.89 for, respectively,  $PM_1$ ,  $PM_{1-2.5}$  and  $PM_{2.5-10}$  suggest wood burning [30]. In turn, the proportions  $[BaA]/[BaP]$ ,  $[BaA]/([BaA]+[Chry])$ ,  $[Ph]/([Ph]+[An])$  for  $PM_{2.5-10}$ -related PAH (0.38, 0.24, 0.67) suggest combustion of gasoline and oil in car engines as the  $PM_{2.5-10}$ -related PAH origin [18,26,67] – in winter, at low air temperatures, the gaseous PAH from car engines tend to rapidly condense on big dust particles. The values of  $[BbF]/[BkF]$  equal to 0.74, 0.44 and 0.40 for, respectively,  $PM_1$ ,  $PM_{1-2.5}$  and  $PM_{2.5-10}$  suggest the vehicular origin of not only  $PM_{2.5-10}$ -related but also of  $PM_1$ - and  $PM_{1-2.5}$ -related PAH in Zabrze in winter [16,47,48,67,68].

In Table 3, the winter concentrations of  $PM_1$ -,  $PM_{2.5}$ - and  $PM_{10}$ -related  $\Sigma$ PAH and BaP in Zabrze are compared with the winter concentrations of  $\Sigma$ PAH and BaP at various sites in the world. The wide range of the concentrations of, equally,  $\Sigma$ PAH and BaP is due to the differences in the number of PAH, meteorological conditions, local PAH sources etc. Nevertheless, the greatest concentrations of  $PM_{2.5}$ -related BaP and  $\Sigma$ PAH occur in Poland (Zabrze and Bytom, Upper Silesia). In other European cities, at the sites beyond the effect of vehicular and industrial emissions like in Zabrze, the concentrations of  $PM_{2.5}$ -related BaP were from  $0.33 \text{ ng m}^{-3}$  in Amsterdam (the Netherlands) to  $48.00 \text{ ng m}^{-3}$  in Prague, (the Czech Republic) [52]. In Zabrze these concentrations were several times higher. The concentrations of  $\Sigma$ PAH and BaP in Asiatic cities, such as Fashun (China) [21], Delhi (India) [55] and Tiruchirappalli (India) [32], were much greater than in Europe and closer to the winter concentrations in Zabrze.

The hazard for humans from an individual ambient PAH is expressed relative to the hazard from BaP, whose toxicity is well characterized as the toxicity equivalency factor (TEF). TEF for BaP is equal to 1, TEF equal to 0 means lack of carcinogenicity of a compound. The hazard from a mixture of PAH is expressed as the BaP equivalent

Table 3. Ambient concentrations of BaP and  $\Sigma$ PAH related to various PM fractions at various sites in the world

Location	Sampling period	Fraction	Concentration, ng·m <sup>-3</sup>	
			BaP	$\Sigma$ PAH <sup>a</sup>
Zabrze (Poland), urban background <sup>b</sup>	Oct – Dec 2007	PM <sub>1</sub>	16.08	128.10 (15)
		PM <sub>2.5</sub>	19.19	153.10 (15)
		PM <sub>10</sub>	19.32	156.11 (15)
Bytom (Poland), urban background (T1) [22]	Feb – Mar 2007	PM <sub>2.5</sub>	6.49	85.52(16)
		PM <sub>10</sub>	11.12	120.69(16)
Bytom (Poland), city center (T2) [22]	Feb – Mar 2007	PM <sub>2.5</sub>	6.49	80.36(16)
		PM <sub>10</sub>	19.84	128.64(16)
Duisburg (Germany), urban background [52]	Sep – Nov 2002	PM <sub>2.5</sub>	1.05	12.63 (32)
		PM <sub>10</sub>	1.10	15.76 (32)
Prague (Czech Republic), urban background [52]	Nov 2002 – Jan 2003	PM <sub>2.5</sub>	3.03	48.00 (32)
		PM <sub>10</sub>	3.15	55.11 (32)
Amsterdam (Netherlands), urban background [52]	Jan – Mar 2003	PM <sub>2.5</sub>	0.33	7.25 (32)
Bangkok (Thailand), urban [37]	Nov 2002 – Apr 2003	PM <sub>10</sub>	1.3	12.59 (16)
Atlanta (USA), urban [27]	Oct – Dec 2004	PM <sub>2.5</sub>	0.27	2.86 (28)
		PM <sub>2.5</sub>	3.18	21.23 (6)
Zagreb (Croatia), urban [57]	Winter 2004	PM <sub>10</sub>	3.04	21.78 (6)
		PM <sub>2.5</sub>	10.71	261.82 (13)
Fushun (China); urban background [21]	Dec 2004 – Feb 2005	PM <sub>10</sub>	12.69	334.26 (13)
		PM <sub>1</sub>	0.52	7.54 (13)
Virolahti (Finland), regional background [29]	Winter 2006	PM <sub>2.5</sub>	0.69	14.53 (13)
		PM <sub>10</sub>	0.73	13.9 (13)
		PM <sub>10</sub>	1.18	82.24 (15)
Flanders (Belgium), urban background [64]	Oct 2006 – Mar 2007	PM <sub>10</sub>	1.18	82.24 (15)
Rome (Italy), downtown [4]	Oct 2007 – Feb 2008	PM <sub>1</sub>	-	6.70 (14)
		PM <sub>2.5</sub>	-	7.77 (14)
		PM <sub>10</sub>	-	7.98 (14)
Dehli (India), urban [55]	Nov 2007 – Feb 2008	PM <sub>2.5</sub>	9.9	96 (16)
		PM <sub>10</sub>	6.9	81.5 (16)
Augsburg, (Germany) urban aerosol [43]	Feb – Mar 2008	PM <sub>2.5</sub>	0.83	11 (11)
Kaunas (Lithuania), urban [20]	location 1 location 2 Winter 2009	PM <sub>2.5</sub>	3.2±1.0	32.7±11.8 (13)
			6.2±3.9	75.1±32.7 (13)
Tiruchirappalli (India), urban atmosphere [32]	Dec 2009 – Feb 2010	PM <sub>2.5</sub>	8.7-24.1	136-371.5 (9)

<sup>a</sup> the number of PAH taken to compute  $\Sigma$ PAH concentration is in parentheses<sup>b</sup> this study



(BEQ), which is the sum of the products of the concentrations of individual PAH in the mixture and their TEF [36].

In Zabrze, BEQ for  $PM_{2.5}$  and  $PM_{10}$  were very high in winter ( $31.70 \text{ ng m}^{-3}$  and  $31.81 \text{ ng m}^{-3}$ ), much higher than in Shanghai ( $15.77 \text{ ng m}^{-3}$ ; [10]) or some Japanese cities (BEQ around  $2 \text{ ng m}^{-3}$  [58]), where the ambient PAH concentrations were very high. In Zabrze, BEQ for  $PM_1$  was  $26.73 \text{ ng m}^{-3}$ .

## CONCLUSIONS

In Zabrze, in winter, the greatest parts of the PM-related PAH and elements accumulate in the finest PM fractions. The ambient fine particles occur in much greater amounts than coarse particles ( $PM_{2.5-10}$ ), and the ambient concentrations of the toxic substances they contain, especially carcinogenic PAH, are very high. After penetration into the respiratory system, the finest particles ( $PM_1$ ) reach the pulmonary alveoli where 60–80% of the elements brought with them pass into blood [45]. This is why the toxicity related to PAH [12] and transitive metals [60] is greater for fine than for coarse dust. The correlations between PAH content and cytotoxicity, mutagenity and DNA reactivity are higher for fine than coarse dust [3, 12, 31]. Such high winter concentrations and toxic component content of  $PM_1$  cause health hazard for the inhabitants of Zabrze, yet more serious because of its periodic occurrence and several months' duration.

## ACKNOWLEDGMENTS

*The work was partially supported by grant No. N N523 564038 from the Polish Ministry of Science and Higher Education.*

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NIEBEZPIECZNE ZWIĄZKI W MIEJSKIM PYLE ZAWIESZONYM W CENTRALNEJ CZĘŚCI  
GÓRNEGO ŚLĄSKA W ZIMIE

Próbki trzynastu frakcji pyłu zawieszonego były pobierane w Zabrze w okresie grzewczym (centralna część Górnego Śląska, Polska). Punkt poboru jest charakterystyczny dla obszaru miejskiego. Zbadano zawartość 15 WWA oraz Cr, Mn, Co, Ni, As, Se, Cd, Pb w każdej frakcji pyłu. Do poboru pyłu zastosowano impaktor kaskadowy, a do analizy chemicznej – spektrometr fluorescencji rentgenowskiej z dyspersją energii (PANalytical Epsilon 5) oraz chromatograf gazowy z detektorem płomieniowo-jonizacyjnym (Perkin Elmer Clarus 500). Zarówno stężenia pyłu  $PM_{10}$  jak i stężenia związanych z nim WWA i pierwiastków były znacznie wyższe niż stężenia pyłu grubego ( $PM_{2.5-10}$ ) i związanych z nim substancji. Stężenia sumy WWA, a w szczególności kancerogennych związków tej grupy były bardzo wysokie (np. stężenia dla BaP związanego z  $PM_{10}$  i  $PM_{2.5-10}$  oraz  $PM_{10}$  – wynosiły odpowiednio: 16.08, 19.19, 19.32  $ng\ m^{-3}$ ). Na podstawie uzyskanych wyników badań dla ww. zanieczyszczeń stwierdzono, że za stan jakości powietrza w Zabrze, w zimie, odpowiedzialna jest emisja komunalna – stacjonarne źródła spalania, głównie spalanie węgla.