

ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 39

no. 1

pp. 53 - 65

2013



PL ISSN 2083-4772

DOI: 10.2478/aep-2013-0002

© Copyright by Polish Academy of Sciences and Institute of Environmental Engineering of the Polish Academy of Sciences,
Zabrze, Poland 2012

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

WIOLETTA ROGULA-KOZŁOWSKA^{1*}, BARBARA KOZIELSKA²,
KRZYSZTOF KLEJNOWSKI¹, SEBASTIAN SZOPA¹

¹Institute of Environmental Engineering of the Polish Academy of Sciences,
M. Skłodowska-Curie 34, 41-819 Zabrze, Poland

²Department of Air Protection, Silesian University of Technology, Akademicka 2., 44-100 Gliwice, Poland

*Corresponding author's e-mail: wioletta@ipis.zabrze.pl

Keywords: PM₁, PM_{2.5}, 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 PM₁ and the PM₁-related PAH and elements were much higher than the ones of the coarse dust (PM_{2.5-10}) and the substances contained in it. The concentrations of total PAH and carcinogenic PAH were very high (the concentrations of PM₁-, PM_{2.5}-, and PM₁₀-related BaP were 16.08, 19.19, 19.32 ng m⁻³, 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 μm) 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 Al_2O_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 ng cm^{-2} for Se to 11.6 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 (CH_2Cl_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 (C_{18} , Supelco). PAH were eluted with use of dichloromethane (CH_2Cl_2). The extract of the PAH fraction was condensed in the helium atmosphere to the volume of 0.5 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 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 ⁶⁾	<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

¹⁾ 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 μm

²⁾ sum of concentrations of dust, element or compound in fractions 1.0–1.6, 1.6–2.5 μm

³⁾ sum of concentrations of dust, element or compound in fractions 2.5–4.4, 4.4–6.8, 6.8–10.0 μm

⁴⁾ average concentration from 11 January to 22 March 2008

⁵⁾ average concentration from 26 October to 27 December 2007

⁶⁾ concentrations below detection limit

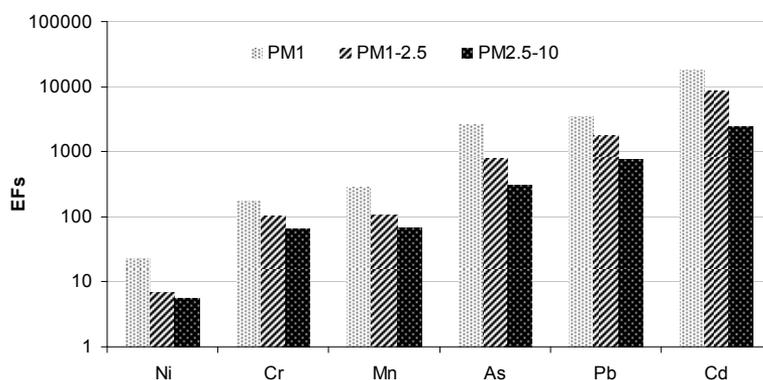
high PM_{10} concentrations during a half-year in Zabrze may mean violating this limit. The concentrations of $PM_{2.5}$ ($PM_{2.5} = PM_1 + PM_{1-2.5}$) also were high; in the winter 2007/2008 they exceeded the limit $25 \mu\text{g m}^{-3}$ [7]. $PM_{2.5}$ and PM_1 , the fractions of respirable dust, 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 ₁	2.14	0.75	2.54	59.99	0.17	23.56
		PM _{2.5}	2.63	1.02	3.65	77.25	0.21	33.1
Zabrze (Poland); urban background [41]	Jan 2006	PM ₁₀	2.98	1.16	4.98	97.91	0.27	40.6
		PM _{2.5}	-	5.5	24.3	24.6	17.7	184.7
Milan (Italy); residential-commercial area [63]	Winter 2002	PM ₁₀	-	6.9	49.7	49.8	17.3	223.6
		PM ₁	2	-	2	9	7	35
Menen (Belgium); suburban/industrial [38]	Winter 2003	PM _{2.5}	3	-	5	18	9	55
		PM _{2.5}	-	-	2.3	12	3.4	54
Athens (Greece); suburban [62]	Oct-Dec 2003	PM _{2.5}	6.83	0.70	-	-	1.59	5.45
Cartagena (Spain); suburban [35]	Jan-Mar 2005	PM _{2.5}	0.3	0.2	1.3	2.7	3.4	5.7
Seoul (Korea); residential [39]	Feb 2006	PM _{2.5}	1.7	4.0	8.4	10.4	-	58.5
		PM ₁₀	2.2	4.1	10.6	21.5	-	75.3
Barcelona (Spain); urban background [42]	2005-2006	PM ₁	0.6	0.3	1.2	4	3	17
		PM _{2.5}	-	12.6	80.5	25.6	15.3	630.8
Dehli (India), urban [55]	Nov 2007-Feb 2008	PM ₁₀	-	9.2	128.5	44.7	15.3	420.7
Ulsan (Korea), residential area [25]	Spring 2009	PM _{2.5}	-	-	3.3	4.0	97.8	275.8
		PM ₁₀	-	-	6.9	4.6	41.7	263.3

a this study

The winter ambient concentrations of total PAH (Σ PAH) in Zabrze were high – the concentrations of PM_{1-} and $PM_{2.5-}$ -related Σ PAH were 128.1 ng m^{-3} and 153.9 ng m^{-3} , respectively. PM_{1-} -related Σ PAH were 82% and $PM_{2.5-}$ -related Σ PAH were 98% of PM_{10-} -related Σ PAH. The concentrations of PM_{1-} -related Σ PAH were about 5 times greater than the concentrations of $PM_{1-2.5-}$ -related Σ PAH. All PM fractions were rich in 4- and 5-ring PAH, which were no less than 89% of Σ PAH. Among all PM-related PAH, Py, BaA and Ch had the greatest concentrations (PM_{1-} -related: 18.03 ng m^{-3} , 17.78 ng m^{-3} , 17.11 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 ($12.84\text{--}16.09 \text{ ng m}^{-3}$, PM_{1-} -related) and contributions to Σ PAH. The proportion CPAH/ Σ PAH of the concentration of CPAH (total combustion PAH: Fl, Py, BaA, BbF, BkF, BaP, BeP, IP and BghiP) to the concentration of Σ 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 Σ PAH and BaP in Zabrze are compared with the winter concentrations of Σ PAH and BaP at various sites in the world. The wide range of the concentrations of, equally, Σ 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 Σ 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 ng m^{-3} in Amsterdam (the Netherlands) to 48.00 ng m^{-3} in Prague, (the Czech Republic) [52]. In Zabrze these concentrations were several times higher. The concentrations of Σ 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 Σ PAH related to various PM fractions at various sites in the world

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

^a the number of PAH taken to compute Σ PAH concentration is in parentheses^b 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 ng m^{-3} and 31.81 ng m^{-3}), much higher than in Shanghai (15.77 ng m^{-3} ; [10]) or some Japanese cities (BEQ around 2 ng m^{-3} [58]), where the ambient PAH concentrations were very high. In Zabrze, BEQ for PM_1 was 26.73 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.

REFERENCES

- [1] Burnett, R.T., Brook, J., Dann, T., Delocla, C., Philips, O., Cakmak, S., Vincent, R., Goldberg, M.S., & Krewski, D. (2000). Association between particulate- and gas-phase components of urban air pollution and daily mortality in eight Canadian cities, *Inhalation Toxicology*, 12, 15–39.
- [2] Canepari, S., Perrino, C., Olivieri, F., & Astolfi, M.L. (2008). Characterisation of the traffic sources of PM through size-segregated sampling, sequential leaching and ICP analysis, *Atmospheric Environment*, 42 (35), 8161–8175.
- [3] De Kok, J.G., Hogervorst, J.J., Briede, M.H., van Herwijnen, L.M., Maas, E.J., Moonen, H.A., & Driee, Kleinjansz, J.C. (2005). Genotoxicity and physicochemical characteristics of traffic-related ambient particulate matter, *Environmental and Molecular Mutagenesis*, 46 (2), 71–80.
- [4] Di Filippo, P., Riccardi, C., Pomata, D., Gariazzo, C., & Buiarelli, F. (2010). Seasonal abundance of particle-phase organic pollutants in an urban/industrial atmosphere, *Water, Air, and Soil Pollution*, 211 (1–4), 231–250.
- [5] Dreher, K.L. (2000). Particulate matter physicochemistry and toxicology: in search of causality – a critical perspective, *Inhalation Toxicology*, 12, 45–57.
- [6] EC: Council Directive 2004/107/EC relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air (2004).
- [7] EC: Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (2008).
- [8] El Haddad, I., Marchand, N., Dron, J., Temime-Roussel, B., Quivet, E., Wortham, H., Jaffrezo, J.L., Baduel, C., Viosin, D., Besombes, J.L., & Gille, G. (2009). Comprehensive primary particulate organic characterization of vehicular exhaust emissions in France, *Atmospheric Environment*, 43 (39), 6190–6198.
- [9] Evagelopoulos, V., Albanis, T.A., Asvesta, A., & Zoras, S. (2010). Polycyclic aromatic hydrocarbons (PAHs) in fine and coarse particles, *Global Nest Journal*, 12 (1), 63–70.

- [10] Guo, H.L., Lu, C.G., Yu, Q., & Chen, L.M. (2004). Pollution characteristics of polynuclear aromatic hydrocarbons on airborne particulate in Shanghai, *Journal of Fudan University (Natural Science)*, 43, 1107.
- [11] Harrison, R.M., & Yin, J. (2000). Particulate matter in the atmosphere: which particle properties are important for its effects on health? *Atmospheric Environment*, 249 (1–3), 85–101.
- [12] Hsiao, W.L., Mo, Z.Y., Fang, M., Shi, X.M., & Wang, F. (2000). Cytotoxicity of PM_{2.5} and PM_{2.5–10} ambient air pollutants assessed by the MTT and the comet assays, *Mutation Research*, 471, 45–55.
- [13] <http://www.lex.pl/du-akt/-akt/dz-u-10-16-87>.
- [14] Jasan, R.C., Plá, R.R., Invernizzi, R., & Dos Santos, M. (2009). Characterization of atmospheric aerosol in Buenos Aires, Argentina, *Journal of Radioanalytical and Nuclear Chemistry*, 281 (1), 101–105.
- [15] Juda-Rezler, K., Reizer, M., & Oudinet, J.-P. (2011). Determination and analysis of PM₁₀ source apportionment during episodes of air pollution in Central Eastern European urban areas: The case of wintertime 2006, *Atmospheric Environment*, 45 (36), 6557–6566.
- [16] Kavouras, I.G., Lawrence, J., Koutrakis, P., Stephanou, E.G., & Oyola, P. (1999). Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: Source reconciliation and evaluation of sampling artifacts, *Atmospheric Environment*, 33 (30), 4977–4986.
- [17] Kendall, M., Pala, K., Ucakli, S., Gucer, S. (2011). Airborne particulate matter (PM_{2.5} and PM₁₀) and associated metals in urban Turkey, *Air Quality, Atmosphere and Health*, 4 (3), 235–242.
- [18] Khalili, N.R., Scheff, P.A., & Holsen, T.M. (1995). PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions, *Atmospheric Environment*, 29 (4), 533–542.
- [19] Klejnowski, K., Pastuszka J.S., Rogula-Kozłowska, W., Talik E., & Krasa, A. (2012). Mass Size Distribution and Chemical Composition of the Surface Layer of Summer and Winter Airborne Particles in Zabrze, Poland, *Bulletin of Environmental Contamination and Toxicology*, 88 (2), 255–259.
- [20] Kliucininkas L., Martuzoviccius, D., Krugly, E., Prasauskas, T., Kauneliene, V., Molnar, P., & Strandberg, B. (2011): Indoor and outdoor concentrations of fine particles, particle-bound PAHs and volatile organic compounds in Kaunas, Lithuania, *Journal of Environmental Monitoring*, 13 (1), 182–191.
- [21] Kong, S., Ding, X., Bai, Z., Han, B., Chen, L., Shi, J., & Li, Z. (2010). A seasonal study of polycyclic aromatic hydrocarbons in PM_{2.5} and PM_{2.5–10} in five typical cities of Liaoning Province, *China Journal of Hazardous Materials*, 183 (1–3), 70–80.
- [22] Kozięlska, B., Rogula-Kozłowska, W., & Pastuszka, J.S. (2009). Effect of road traffic concentration of PM_{2.5}, PM₁₀ and PAHs in zones of high and low municipal emission, *Polska Inżynieria Środowiska pięć lat po wstąpieniu do Unii Europejskiej, Monografie Komitetu Inżynierii Środowiska PAN*, 58 (1), 129–137, Lublin, ISBN 978-83-89293-81-7 (in polish).
- [23] Krewski, D., Burnett, R., Goldberg, M., Hoover, B.K., Siemiatycki, J., Jerrett, M., Abrahamowicz, M., & White, W. (2003). Overview of the reanalysis of the Harvard six cities study and American Cancer Society study of particulate air pollution and mortality, *Journal of Toxicology and Environmental Health. Part A*, 66 (16–19), 1507–1551.
- [24] Ladj, R., Yassaa, N., Balducci, C., Cecinato, A., & Meklati, B.Y. (2009). Distribution of the solvent-extractable organic compounds in fine (PM₁) and coarse (PM_{1–10}) particles in urban, industrial and forest atmospheres of Northern Algeria, *Science of the Total Environment*, 408 (2), 415–424.
- [25] Lee, B.-K., & Hieu, N.T. (2011). Seasonal variation and sources of heavy metals in atmospheric aerosols in a residential area of Ulsan, Korea, *Aerosol and Air Quality Research*, 11 (6), 679–688.
- [26] Li, C.K., Kamens, R.M. (1993). The use of polycyclic aromatic hydrocarbons as sources signatures in receptor modeling, *Atmospheric Environment*, 27A, 523–532.
- [27] Li, Z., Porter, E.N., Sjödin, A., Needham, L.L., Lee, S., Russell, A.G., & Mulholland, J.A. (2009). Characterization of PM_{2.5}-bound polycyclic aromatic hydrocarbons in Atlanta-Seasonal variations at urban, suburban, and rural ambient air monitoring sites, *Atmospheric Environment*, 43 (27), 4187–4193.
- [28] Liu, D., Gao, S., & An, X. (2008). Distribution and Source Apportionment of Polycyclic Aromatic Hydrocarbons from Atmospheric Particulate Matter PM_{2.5} in Beijing, *Advances in Atmospheric Sciences*, 25 (2), 297–305.
- [29] Makkonen, U., Hellén, H., Anttila, P., & Ferm, M. (2010). Size distribution and chemical composition of airborne particles in south-eastern Finland during different seasons and wildfire episodes in 2006, *Science of the Total Environment*, 408 (3), 644–651.
- [30] Masclet, P., Bresson, M.A., & Mouvrier, G. (1987). Polycyclic aromatic hydrocarbons emitted by power stations, and influence of combustion conditions, *Fuel*, 66 (4), 556–562.

- [31] Massolo, L., Muller, A., Tueros, M., Rehwagen, M., Franck, U., Ronco, A., & Herbarth, O. (2002). Assessment of Mutagenicity and Toxicity of Different-Size Fractions of Air Particulates from La Plata, Argentina, and Leipzig, Germany, *Environmental Toxicology*, 17 (3), 219–231.
- [32] Mohanraj, R., Solaraj, G., & Dhanakumar S. (2011): PM_{2.5} and PAH concentrations in urban atmosphere of Tiruchirappalli, India, *Bulletin of Environmental Contamination and Toxicology*, 87 (3), 330–335.
- [33] Mooibroek, D., Schaap, M., Weijers, E.P., & Hoogerbrugge, R. (2011). Source apportionment and spatial variability of PM_{2.5} using measurements at five sites in the Netherlands, *Atmospheric Environment*, 45 (25), 4180–4191.
- [34] Na, K., & Cocker, D.R. (2009). Characterization and source identification of trace elements in PM_{2.5} from Mira Loma, Southern California, *Atmospheric Research*, 93 (4), 793–800.
- [35] Negral, L., Moreno-Grau, S., Moreno, J., Querol, X., Viana, M.M., & Alastuey, A. (2008): Natural and anthropogenic contributions to PM₁₀ and PM_{2.5} in an urban area in the western Mediterranean coast, *Water, Air, and Soil Pollution*, 192 (1–4), 227–238.
- [36] Nisbet, I.C.T., & LaGoy, P.K. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regulatory Toxicology and Pharmacology*, 16 (3), 290–300.
- [37] Norramit, P., Cheevaporn, V., Itoh, N., & Tanaka, K. (2005). Characterization and carcinogenic risk assessment of polycyclic aromatic hydrocarbons in the respirable fraction of airborne particles in the Bangkok Metropolitan area, *Journal of Health Science*, 51 (4), 437–446.
- [38] Pakkanen, T.A., Kerminen, V.-M., Loukkola, K., Hillamo, R.E., Aarnio, P., Koskentalo, T., & Maenhaut, W. (2003). Size distributions of mass and chemical components in street-level and rooftop PM₁ particles in Helsinki, *Atmospheric Environment*, 37 (12), 1673–1690.
- [39] Park, K., Park, J.Y., Kwak, J.-H., Cho, G.N., & Kim, J.-S. (2008). Seasonal and diurnal variations of ultrafine particle concentration in urban Gwangju, Korea: Observation of ultrafine particle events, *Atmospheric Environment*, 42 (4), 788–799.
- [40] Pastuszka, J.S., Wawroś, A., Talik, E., & Paw, U.K.T. (2003). Optical and chemical characteristics of the atmospheric aerosol in four towns in southern Poland, *Science of the Total Environment*, 309 (1–3), 237–251.
- [41] Pastuszka, J.S., Rogula-Kozłowska, W., & Zajusz-Zubek, E. (2010). Characterization of PM₁₀ and PM_{2.5} and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes, *Environmental Monitoring and Assessment*, 168 (1–4), 613–627.
- [42] Pérez, N., Pey, J., Querol, X., Alastuey, A., López, J.M., & Viana, M. (2008). Partitioning of major and trace components in PM₁₀-PM_{2.5}-PM₁ at an urban site in Southern Europe, *Atmospheric Environment*, 42 (8), 1677–1691.
- [43] Pietrogrande, M.C., Abbaszade, G., Schnelle-Kreis, J., Bacco, D., Mercuriali, M., & Zimmermann, R. (2011). Seasonal variation and source estimation of organic compounds in urban aerosol of Augsburg, Germany, *Environmental Pollution*, 159 (7), 1861–1868.
- [44] Pope, C.A., Burnett, R.T., Thun, M.J., Cale, E.E., Krewski, D., Ito, K., & Thurston, G.D. (2002). Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution, *Journal of American Medical Association*, 287 (9), 1132–1141.
- [45] Pope, C.A., & Dockery, D.W. (2006). Health effects of fine particulate air pollution: lines that connect, *Journal of the Air & Waste Management Association*, 56 (6), 709–742.
- [46] Rajšić, S., Mijić, Z., Tasić, M., Radenković, M., & Joksić, J. (2008). Evaluation of the levels and sources of trace elements in urban particulate matter, *Environmental Chemistry Letters*, 6 (2), 95–100.
- [47] Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., & Simoneit, B.R.T. (1993). Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: Roads as sources and sinks, *Environmental Science and Technology*, 27 (9), 1892–1904.
- [48] Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., & Simoneit, B.R.T. (1993). Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, *Environmental Science and Technology*, 27 (4), 636–651.
- [49] Rogula-Kozłowska, W., Pastuszka, J.S., & Talik, E. (2008). Influence of vehicular traffic on concentration and particle surface composition of PM₁₀ and PM_{2.5} in Zabrze, Poland, *Polish Journal of Environmental Studies*, 17 (4), 539–548.
- [50] Rogula-Kozłowska, W., Klejnowski, K., Krasa, A., & Szopa, S. Concentration and elemental composition of atmospheric fine particles in Silesia Province, Poland, [in] *Environmental Engineering III*, Pawłowski, Dudzińska & Pawłowski (eds.), Taylor & Francis Group, London 2010, 75–81.

- [51] Rogula-Kozłowska, W., Błaszczak, B., & Klejnowski, K. (2011). Concentrations of PM_{2.5}, PM_{2.5-10} and PM-related elements at two heights in an urban background area in Zabrze (Poland), *Archives of Environmental Protection*, 37 (2), 31–47.
- [52] Saarnio, K., Sillanpää, M., Hillamo, R., Sandell, E., Pennanen, A.S., & Salonen, R.O. (2008). Polycyclic aromatic hydrocarbons in size-segregated particulate matter from six urban sites in Europe, *Atmospheric Environment*, 42 (40), 9087–9097.
- [53] Saldiva, P.H.N., Clarke, R.W., Coull, B.A., Stearns, R.C., Lawrence, J., Murthy, G.G.K., Diaz, E., Koutrakis, P., Suh, H., Tsuda, A., & Godleski, J.J. (2002). Lung inflammation induced by concentrated ambient air particles is related to particle composition, *American Journal of Respiratory and Critical Care Medicine*, 165 (12), 1610–1617.
- [54] Sienra, M. del.R., Rosazza, N.G., & Préndez, M. (2005). Polycyclic aromatic hydrocarbons and their molecular diagnostic ratios in urban atmospheric respirable particulate matter, *Atmospheric Research*, 75 (4), 267–281).
- [55] Singh, D.P., Gadi, R., & Mandal, T.K. (2011). Characterization of particulate-bound polycyclic aromatic hydrocarbons and trace metals composition of urban air in Delhi, India, *Atmospheric Environment*, in press.
- [56] Swaine, D.J. (2000). Why trace elements are important, *Fuel Processing Technology*, 65–66, 21–33.
- [57] Šišović, A., Vadić, Z., Šega, K., Bešlić, I., & Vadić, V. (2005). Comparison between PAH mass concentrations measured in PM₁₀ and PM_{2.5} particle fractions, *Bulletin of Environmental Contamination and Toxicology*, 75 (1), 121–126.
- [58] Takeshi, O., Takashi, A. (2004). Spatial distributions and profiles of atmospheric polycyclic aromatic hydrocarbons in two industrial cities in Japan, *Environmental Sciences and Technology*, 38 (1), 49–55.
- [59] Tang, N., Hattori, T., Taga, R., Igarashi, K., Yang, X., Tamura, K., Kakimoto, H., Mishukov, V.F., Toriba, A., Kizu, R., & Hayakawa, K. (2005). Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries, *Atmospheric Environment*, 39 (32), 5817–5826.
- [60] Tong, Y., Ni, X., Zhang, Y., Chen, F., Zhang, G., & Ye, S. (2002). Study of the toxicological mechanism of acidified aerosols, *Biological Trace Element Research*, 85, 149–156.
- [61] US EPA.: Compendium of Methods for the Determination of Inorganic Compounds In Ambient Air. Compendium Method IO-3.3: Determination of metals in ambient particulate matter using X-Ray Fluorescence (XRF) Spectroscopy, Cincinnati, June 1999.
- [62] Vasilakos, C., Pateraki, S. Veros, D. Maggos, T., Michopoulos, J. Saraga, D., & Helmis, C.G. (2007): Temporal determination of heavy metals in PM_{2.5} aerosols in a suburban site of Athens, Greece, *Journal of Atmospheric Chemistry*, 57 (1), 1–17.
- [63] Vecchi, R., Marazzan, G., Valli, G., Ceriani, M., & Antoniazzi, C. (2004). The role of atmospheric dispersion in the seasonal variation of PM₁₀ and PM_{2.5} concentration and composition in the urban area of Milan (Italy), *Atmospheric Environment*, 38 (27), 4437–4446.
- [64] Vercauteren, J., Matheeußen, C., Wauters, E., Roekens, E., van Grieken, R., Krata, A., Makarovska, Y., Maenhaut, W., Chi, X., & Geypens, B. (2011). Chemkar PM₁₀: An extensive look at the local differences in chemical composition of PM₁₀ in Flanders, Belgium, *Atmospheric Environment*, 45 (1), 108–116.
- [65] Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, S., Szidat, A.S.H., Prévôt, C., Hueglin, H., Bloemen, P., Wählin, R., Vecchi, A.I., Miranda, A., Kasper-Giebl, W., Maenhaut, W., & Hitzenberger, R. (2008). Source apportionment of particulate matter in Europe: A review of methods and results, *Journal of Aerosol Science*, 39 (10), 827–849.
- [66] Wedepohl, K.H. (1995). The composition of the continental crust, *Geochimica et Cosmochimica Acta*, 59 (7), 1217–1232.
- [67] Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition, *Organic Geochemistry*, 33 (4), 489–515.
- [68] Zencak, Z., Klanova, J., Holoubek, I., & Gustafsson, Ö. (2007). Source apportionment of atmospheric PAHs in the western balkans by natural abundance radiocarbon analysis, *Environmental Science and Technology*, 41 (11), 3850–3855.

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.