POLYCYCLIC AROMATIC HYDROCARBONS IN PM1, PM2.5, PM10 AND TSP IN THE UPPER SILESIAN AGGLOMERATION, POLAND

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COMMUNICATION

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants, ubiquitous in the whole
environment. They are relatively well known and are still of interest due to their well documented carcino-
genic and mutagenic properties. In ambient air of urban regions they mostly occur as adsorbed to particles of
suspended dust. The richest in these compounds and therefore most hazardous to humans, fraction of dust is
the fraction of the finest particles. The paper presents results of investigations of dust sampled with use of an
impactor Dekati PM10 in Zabrze, a site typical of Upper Silesian conditions. While sampling, the impactor
segregates sampled particles into four fractions by their aerodynamic diameters. Sixteen PAHs were determined
in each fraction chromatographically. PAH content in the fraction of the finest particles, i.e. in PM1, was of
particular interest.

INTRODUCTION

Properties of ambient dust (PM, Particulate Matter), its environmental and health effects
as well as its fate in the environment depend on size of its particles [9]. Elevated health
hazard in urban areas highly polluted by the finest ambient particles has been pointed out
by many papers [3, 4, 27]. The finest particles easily penetrate into alveoli – the particles
with the diameter of 1–2 μm are arrested there with the highest efficiency. Present in the
body, such particles can cause intoxication, upper respiratory tract inflammation, bronchi-
tis, lung cancer, allergies and asthma [27, 30]. Chemical and mineralogical composition
of the dust, also that depending on the particle size fraction, affects the human health
itself. Many volatile organic compounds, metal oxides and other, often carcinogenic,
substances may be found on the particle surface [4, 11, 27]. Polycyclic aromatic hydro-
carbons (PAHs) 48 of which are carcinogens [10, 33, 35], due to their specific strong

effects on living beings are of special concern [34, 35]. Urban ambient PAHs come from combustion processes, such as production of coke, combustion of organic fuels for energy production [38], road traffic [1, 7, 13, 18] and domestic furnaces [17, 20, 21]. They occur in gas phase and are adsorbed to dust particles. In areas dominated by vehicular air pollution, up to 95% of total ambient PAHs may be in PM (in PM3 rich in elemental carbon) [28]. PM1.3 may contain 60–90% of total PAHs from PM [25, 26, 31].

The paper presents results of investigations of 16 ambient PAHs (Tab. 1) in the great Upper Silesian agglomeration, Poland, in winter. Ambient concentrations of the 16 PAHs and distribution of their mass between four PM fractions: PM1 (particles with the aerodynamic diameter less than 1.0 μm), PM1–2.5 (particles with the diameter between 1.0 and 2.5 μm), PM2.5-10 (particles with the diameter between 2.5 and 10.0 μm) and particles with the aerodynamic diameter greater than 10 μm were determined. Till now, in Poland, PAH content in ambient PM fractions has not been investigated.

Table 1. Average concentrations [ng/m³] of 16 PAHs in fractions of PM in Zabrze, winter 2006/2007

Compound	Dust fraction							
	< 1 μm	1–2.5 μm	2.5–10 μm	> 10 μm	PM1	PM2.5	PM10	TSP
PM [μg/m³]	38.84	8.86	3.40	1.32	38.84	47.70	51.10	52.42
Naphthalene	0.00	0.26	0.06	0.00	0.00	0.26	0.32	0.32
Acenaphtylene	0.07	0.12	0.00	0.00	0.07	0.19	0.19	0.19
Acenaphtene	0.19	0.09	0.15	0.00	0.19	0.28	0.43	0.43
Fluorene	0.22	0.29	0.23	0.00	0.22	0.51	0.74	0.74
Phenanthrene	2.69	0.68	1.20	0.00	2.69	3.37	4.57	4.57
Anthracene	0.56	0.21	0.46	0.00	0.56	0.77	1.23	1.23
Fluoranthene	3.33	0.63	0.36	0.00	3.33	3.96	4.32	4.32
Pyrene	3.78	0.43	1.11	0.00	3.78	4.21	5.32	5.32
Benzo(a)anthracene	7.83	0.98	1.10	0.00	7.83	8.81	9.91	9.91
Chrysene	8.56	1.31	2.45	0.00	8.56	9.87	12.32	12.32
Benzo(b)fluoranthene	4.30	0.23	1.08	0.00	4.30	4.53	5.61	5.61
Benzo(k)fluoranthene	4.36	0.25	0.20	0.00	4.36	4.61	4.81	4.81
Benzo(a)pyrene	5.82	0.45	0.89	0.00	5.82	6.27	7.16	7.16
Indeno(1,2,3.cd)pyrene	2.09	1.67	0.50	0.00	2.09	3.76	4.26	4.26
Dibenzo(ah)anthracene	0.28	0.00	0.00	0.00	0.28	0.28	0.28	0.28
Benzo(ghi)perylene	2.27	0.00	0.29	0.00	2.27	2.27	2.56	2.56
∑ PAHs	46.35	7.60	10.08	0.00	46.35	53.95	64.03	64.03

METHOD

Dust was sampled from December 2006 to February 2007 in the central part of Zabrze (Fig. 1) by taking 48 hour samples with use of a Dekati PM10 four stage impactor. The sampling site is representative of the Upper Silesian ambient air quality conditions and it was characterized in [12]. The impactor collects dust from ambient air and segregates particles into four fractions: PM1, PM1–2.5, PM2.5–10 and particles greater than 10 μm. The finest dust was collected on a glass fiber after filter, the other fractions – on aluminium plates. The inlet of the impactor was 7 m above the ground level – the altitude

precluding effects of the secondary emission. The detailed description of the impactor is in [12]. In total, there were 30 samples taken.

Fig. 1. Location of the sampling point

Concentrations of the dust fractions were determined gravimetrically. Prior to each weighing, before and after exposing, all substrates were conditioned in the weighing room for 48 hours.

The collected dust was extracted from the after-filter and plates in a dichloromethane (CH_2Cl_2) ultrasonic bath. The extract was percolated, washed and dried by evaporating in the helium atmosphere. The dry residue was diluted in propanol-2 $(CH_3CH(OH)CH_3)$ and distilled water was added (proportion of propanol-2 to water – 15/85, v/v). For selective purification, the samples were extracted to solid phase (SPE) in columns filled with octadecylsilane $(C_{18}$, Supelco). The columns were pre-conditioned in the extraction setting by washing, first with methanol, next with the 15/85 propanol-2/water mixture. They were kept wet during the whole conditioning. Directly before the extraction, 5 cm³ of the propanol-2/water mixture was percolated through each column in normal conditions (no vacuum). The samples were percolated under vacuum, rinsed with the propanol-2/water mixture and dried under vacuum. PAHs were eluted with use of dichloromethane. The extract of PAHs was condensed in the helium atmosphere to the volume of 0.5 cm³.

A Perkin Elmer Clarus 500 gas chromatograph, with a flame ionization detector (FID), was used. An RTX-5 (Restek) 30 m x 0.32 mm x 0.25 μm capillary column with nonpolar stationary phase was used to separate the sample components. The flow of carrier gas, helium, was 1.5 cm³/min.

Calibration curves for the 16 PAH standards were used in quantitative determinations. Linear correlation of peak surfaces with PAH concentrations was checked in concentration range 10–40 ng/mm³. The samples were introduced into a split/splitless injector. Temperatures of the vaporizer and detector were 240 and 280°C, respectively. The temperature of the column was 60°C during the first 4 min of the analysis and increased at 10°C/min up to 280°C, at which the column was maintained for 14 min. The whole analysis lasted 40 min. The rates of providing the detector with hydrogen, air and helium were 45 cm³/min, 450 cm³/min and 30 cm³/min, respectively.

Recoveries of the 16 PAHs were calculated by using the internal standard method. They ranged from 85% to 93%. The detection limit was 0.1 ng/mm³.

RESULTS AND DISCUSSION

The measurement results are presented in Table 1. Concentrations of dust fractions are averages of 30 measurements (10 measurements per one month from December 2006 to February 2007). Each ambient PAH concentration is an average of nine measurements, three from each month. In this period, the average TSP concentration was almost equal to average PM10 concentration. PM1 was more than 74% of TSP; average content of PM1 in PM2.5 was 81.4%. It proves combustion and transformation of gaseous precursors contributing greatly to ambient PM. The average concentration of PM10 (Tab. 1) exceeds 40 μg/m³, the limit value defined in [24]; the PM2.5 concentration exceeds 25 μg/m³, the European Commission's proposal for the limit value for yearly ambient PM2.5 concentrations [4]. However, the summer concentrations of PM in this area are much lower (averages of 48 hour PM10 and PM2.5 concentrations in summer 2006 were 38 and 32 μg/m³, respectively [12]) and yearly concentrations of PM also may be lower than these presented in Table 1.

Concentrations of particular PAHs belong to a wide interval. They are high – concentration of B(a)P, the compound expressing carcinogenicity of PM, differs from 1 ng/m³, the standard for yearly average from the Regulation [24], by one order (in fact, the concentrations should not be compared but the comparison is very figurative). B(a)P and other US EPA carcinogens – benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo(ah)anthracene and indeno[1,2,3-cd]pyrene – are 72, 64 and 62% of the total mass of the 16 PAHs in PM1, PM1–2.5 and PM2.5–10, respectively. High contribution of these seven compounds (over 33 ng/m³) to PM1 is of special significance. These PAHs adsorbed on such fine particles may penetrate human body very deeply.

Pyrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene – 4- and 5-ring hydrocarbons prevailed in PM1 and, in PM1, their concentration was about 60% of total concentration of the 16 PAHs (Tab. 1).

Considerable amounts of total and particular PAHs were found in PM1 (Tab. 1). There were no PAHs in the fraction of particles with diameters greater than 10 μm. It is probably due to low mass of the analyzed sample (in average 30 times lower than the mass of PM1, Table 1) and mechanical origin of these particles.

Total PAHs from PM1 had the greatest ambient concentration, and consequently the greatest mass (all the fractions were in the same volume of air), next were PAHs from PM2.5–10 and PAHs from PM1–2.5 had the lowest ambient concentration. In some conditions there are more 4-, 5-, 6- and 7-ring ambient PAHs in particles with aerodynamic diameter 7 µm than in particles with the diameter 3 µm [28]. It corresponds very well with the obtained results.

Most of the 16 PAHs (acenaphtene, phenanthrene, anthracene, pyrene, benzo(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, Tab. 1 and Fig. 2) behaved like the sum of PAHs. Some of the rest (fluoranthene, benzo(k) fluoranthene, indeno(1,2,3.cd)pyrene), like PM (Fig. 3), had concentrations increasing along with decreasing diameters defining the fractions. Naphthalene was entirely comprised in PM1–2.5 and PM2.5–10 (probably majority of this compound in the air, especially its gas phase, comes from its vapor condensed on surfaces of greater particles) and dibenzo(ah)anthracene did not occur in particles greater than 1 µm at all – Figure 3.
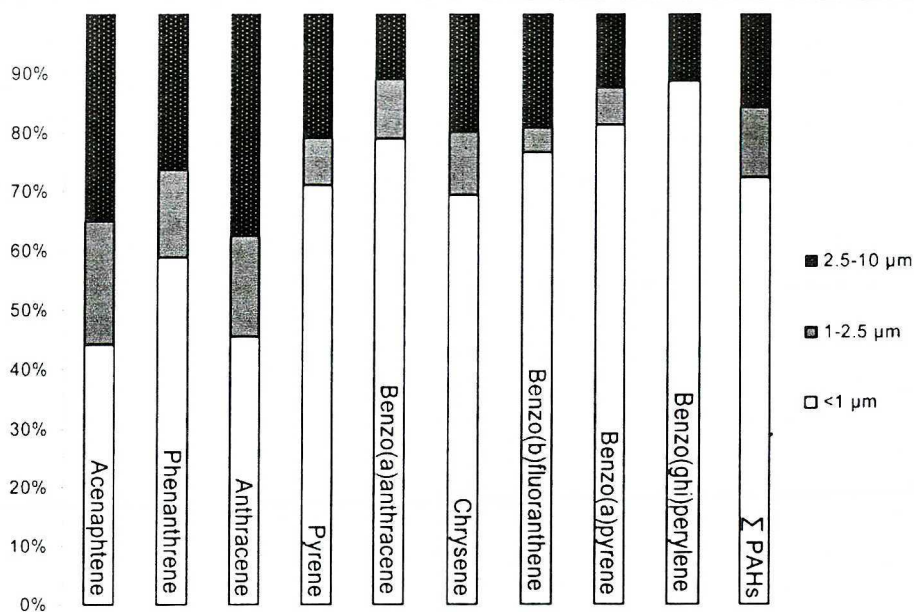

Fig. 2. Mass distribution of nine PAHs among dust fractions

Some combinations of PAHs may be characteristic of their sources [2, 6, 8, 15, 16, 19, 32, 37]. Chrysene, and benzo(k)fluoranthene are markers of coal combustion, benzo(ghi)perylene, coronene and phenanthrene – of car engine emission, phenanthrene, fluoranthene, pyrene are connected with absorbing vehicular gaseous PAHs particles from salted (in winter) roads, pyrene, fluoranthene, phenanthrene – with incinerators, volatile PAHs (fluorene, fluoranthene, pyrene, benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene) are tied with oil combustion.
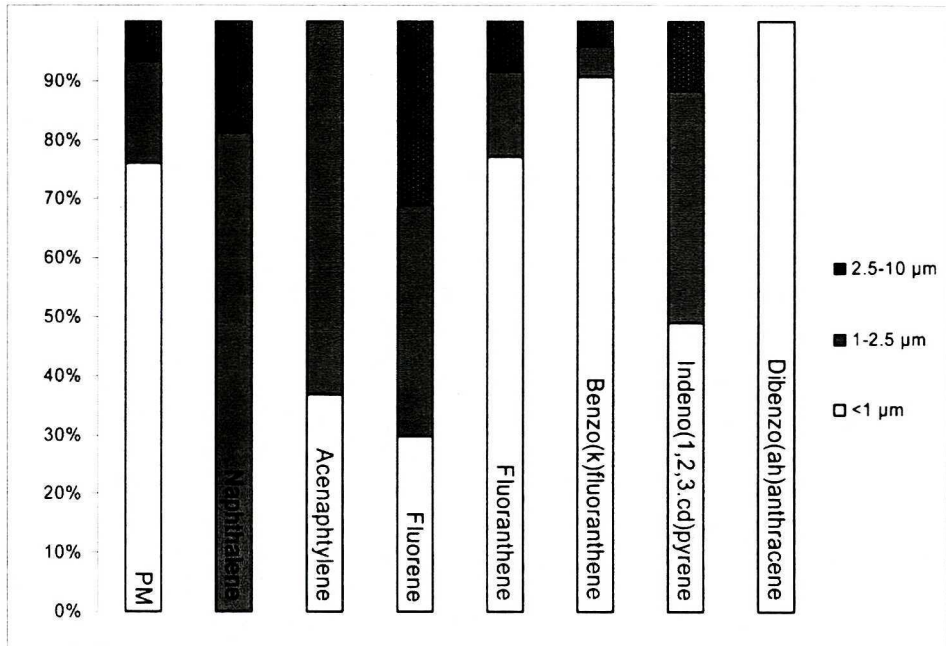
Fig. 3. Mass distribution of dust and seven PAHs among dust fractions

The dominance of chrysene and benzo(k)fluoranthene suggests coal combustion being the main source of the dust [5, 14, 22, 23, 29]. Their distribution among the PM fractions (almost all ambient PAHs are in PM1) and high content of PM1 in PM reflect the structures of air pollution in Zabrze – majority of houses in the centre of Zabrze are heated by furnaces burning hard coal very inefficiently. The sum of concentrations of acenaphtene, fluoranthene and pyrene is in average 21, 23 and 28% of the total PAH concentrations in PM1, PM1–2.5 and PM2.5–10, respectively. It means that in Zabrze PM, these compounds may come from adsorption of their gas phase by particles of dust [8]. Their content in – having greater mass – coarse fractions is relatively higher. In PM1, oil combustion markers – benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene – occur in high concentrations. Only several of the 16 PAHs came from other than hard coal burning sources – among them very clearly naphthalene.

REFERENCES

[1]   Borstel R. von, B. Georgi, M. Bahadir: *Size-fractioned sampling of particulate Diesel emissions and determination of particle bound PAH*, Staub, Reinhaltung der Luft, **55**(5), 199–203 1995

[2]   Bzdusek P.A., E.R. Christensen, A. Li, Q.M. Zou: *Source apportionment of sediment PAHs in Lake Calumet, Chicago: application of factor analysis with nonnegative constraints*, Environmental Science & Technology, **38**, 97–103 (2004).

[3]   Commission staff working paper, Impact Assessment of the thematic strategy on air pollution and the Directive on *Ambient Air Quality and Cleaner Air for Europe*, Commission of the EC, Brussels, 21 September 2005, SEC1133.

[4]   Dockery D., C.A. Pope, X. Xu, J. Spengler, J. Ware, M. Fay, B. Ferris, F. Speizer: *An Association between Air Pollution and Mortality in Six US Cities*, The New England Journal of Medicine, **329**, 1753–1759 (1993).

[5]   Duval M.M., S.K. Friedlander: *Source resolution of polycyclic aromatic hydrocarbons in the Los Angeles atmosphere-application of a CMA with first order decay*, US EPA Report EPA-600/2-81-161 (1996).

[6]   Esen F., Y. Tasdemir, N. Vardar: *Atmospheric concentrations of PAHs, their possible sources and gas-to-particle partitioning at a residential site of Bursa, Turkey*, Atmospheric Research, **88**, 243–255 (2008).

[7]   Grynkiewicz-Bylina B., B. Rakwic, J.S. Pastuszka: *Assessment of exposure to traffic- related aerosol and to particle- associated PAHs in Gliwice, Poland*, Polish Journal of Environmental Studies, **1**, 117–123 (2005).

[8]   Harrison R.M., D.J.T. Smith, L. Luhana: *Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK*, Environmental Science & Technology, **30**, 825–832 (1996).

[9]   Hinds W.C.: *Aerosol Technology, Properties, Behavior, and Measurement of Airborne Particles*, Second Edition, John Wiley & Sons Inc., New York 1998.

[10]   Holland M.R., H.H. Jones, J. Berdowski, A. Bleeker, A.J.H. Visschedijk: *Economic Evaluation of Air Quality Targets for PAHs*, Final report for European Commission DG Environment, 2001.

[11]   Katsouyanni K., G. Touloumi, E. Samoli, A. Gryparis, A. Le Tertre, Y. Monopolis, G. Rossi, D. Zmirou, F. Ballester, A. Boumghar, H.R. Anderson, B. Wojtyniak, A. Paldy, R. Braunstein, J. Pekkanen, C. Schindler, J. Schwartz: *Confounding and Effect Modification in the Short-Term Effects of Ambient Particles on Total Mortality: Results from 29 European Cities within APHEA2 Project*, Epidemiology, **12**, 521–531 (2001).

[12]   Klejnowski K., A. Krasa, W. Rogula: *Seasonal variability of concentrations of total suspended particles (TSP) as well as PM10, PM2.5 and PM1 modes in Zabrze, Poland*, Archives of Environmental Protection, **33**(3), 15–29 (2007).

[13]   Kristensson A., Ch. Johansson, R. Westerholm, E. Swietlicki, L. Gidhagenb, U. Wideqvist, V. Vesely: *Real-world traffic emission factors of gases and particles measured in a road tunnel in Stockholm, Sweden*, Atmospheric Environment, **38**, 657–673 (2004).

[14]   Li A., J.K. Jang, P.A. Scheff: *Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago*, Environmental Science & Technology, **37**, 2958–2965 (2003).

[15]   Liu D., S. Gao, X. An: *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 (2008).

[16]   Nielsen T.: *Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city*, Atmospheric Environment, **30**, 3481–3490 (1996).

[17]   Nikolao K., P.M. Masclet, G. Mouvier: *Sources and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere – a critical review*, Science of the Total Environmental, **32**, 102–132 (1984).

[18]   Niles R., Y.L. Tan: *Determination of polynuclear aromatic hydrocarbons and mononitrated derivatives in air and diesel particulates*, Analytica Chimica Acta, **221**, 53–63 (1989).

[19]   Rajput N., A. Lakhani: *Measurements of polycyclic aromatic hydrocarbons at an industrial site in India*, Environmental Monitoring Assessment, **150**, 273–284 (2009).

[20]   Ramdahl T., J. Alfheins, A. BjÖrseth: *PAH emission from various sources and their evolution over the last decades in mobile sources emission including organic species*, D. Reidel ed., Publ. Comp., 1983.

[21]   Ramdahl T., G. Becher: *Characterization of polynuclear aromatic hydrocarbon derivatives in emission from wood and cereal straw combustion*, Analytica Chimica Acta, **144**, 83–91 (1982).

[22]   Ravindra K., E. Wauters, R. van Grieken: *Spatial and temporal variations in particulate polycyclic aromatic hydrocarbon (PAH) levels over Menen (Belgium) and their relation with air mass trajectories*, [in:] C. Borrego, *et al.* (Eds.), Air Pollution Modeling and its Application XVIII Developments in Environmental Sciences Series, **6**, 838–841 (2007).

[23]   Ravindra K., E. Wauters, R. van Grieken: *Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses*, Science of The Total Environment, 396(2-3), 100–110 (2008).

[24]   Rozporządzenie Ministra Środowiska z dnia 5 grudnia 2002 r. w sprawie wartości odniesienia dla niektórych substancji w powietrzu, Dz. U. Nr 1/2003, poz. 12.

[25]   Sanderson, E.G., J-P. Farant: *Atmospheric size distribution of PAHs: Evidence of a high-volume sampling artifact*, Environmental Science and Technology, **39**(19), 7631–7637 (2005).

[26]   Schönbuchner H., G. Guggenberger, K. Peters, H. Bergmann, W. Zec: *Particle-Size Distribution of PAH in the Air of a Remote Norway Spruce Forest in Northern Bavaria*, Water, Air and Soil Pollution **128**(3-4), 355–367 (2001).

[27]   Schwartz J., W. Dockeryd, L.M. Neas: *Is daily mortality associated specifically with fine particles?*, Journal of the Air and Waste Management Association, **46**(10), 927–939 (1996).

[28] Sheu L., W.J. Lee, C.C. Su, C.C. Chao, Y.C. Fan: *Dry deposition of polycyclic aromatic hydrocarbons in the ambient air of both urban and petrochemical-industry areas*, Journal of Environmental Engineering ASCE, 1101–1109 (1995).

[29] Smith D.J.T., R.M. Harrison: *Polycyclic aromatic hydrocarbons in atmospheric particles*, [in:] R.M. Harrison, R. van Grieken (Eds.), Atmospheric Particles, Wiley, 1998.

[30] Spurny K.R.: *Chemical Mixtures in Atmospheric Aerosols and Their Correlation to Lung Diseases and Lung Cancer Occurrence in the General Population*, Toxicology Letters, **88**, 271–277 (1996).

[31] Tang X.L., X.H. Bi, G.Y. Sheng, J.H. Tan, J.M. Fu: *Seasonal Variation of the Particle Size Distribution of n-Alkanes and Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Aerosol of Guangzhou, China*, Environmental Monitoring and Assessment, **117**, 193–213 (2006).

[32] Tian F., J. Chen, X. Qiao, Z. Wang, P. Yang, D. Wang, L. Ge: *Sources and seasonal variation of atmospheric polycyclic aromatic hydrocarbons in Dalian, China: Factor analysis with non-negative constraints combined with local source fingerprints*, Atmospheric Environment, **43**(17), 2747–2753 (2009).

[33] White P.A.: *The genotoxicity of priority polycyclic aromatic hydrocarbons in complex mixtures*, Mutation Research, **515**, 85–98 (2002).

[34] Wu S.P., S. Tao, W.X. Liu: *Particle size distributions of polycyclic aromatic hydrocarbons in rural and urban atmosphere of Tianjin, China*, Chemosphere, **62**, 357–367 (2006).

[35] Yan J., L. Wang, P.P. Fub, H. Yu: *Photomutagenicity of 16 polycyclic aromatic hydrocarbons from the US EPA priority pollutant list*, Mutation Research, **557**, 99–108 (2004).

[36] Yang H.H., C.F. Chiang: *Size distribution and dry deposition of road dust PAHs*, Environment International, **25**(5), 585–597 (1999).

[37] Yunker M.B., R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre: *PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition*, Organic Geochemistry, **33**, 489–515 (2002).

[38] Zou L.Y, W. Zhang, S. Atkiston: *The characterizations of polycyclic aromatic hydrocarbons emissions from burning of different firewood species in Australia*, Environmental Pollution, **124**, 283–289 (2003).

WIELOPIERŚCIENIOWE WĘGLOWODORY AROMATYCZNE ZWIĄZANE Z PM1, PM2.5, PM10 I CAŁKOWITYM PYŁEM ZAWIESZONYM W AGLOMERACJI GÓRNOŚLĄSKIEJ

Wielopierścieniowe węglowodory aromatyczne (WWA) należą do grupy trwałych zanieczyszczeń organicznych obecnych we wszystkich elementach środowiska. Są licznie reprezentowane i stosunkowo dobrze poznane, a ich udokumentowane własności mutagenne i kancerogenne sprawiają, że nadal są w centrum zainteresowań. W powietrzu atmosferycznym obszarów zurbanizowanych najczęściej występują w postaci zaadsorbowanej na cząstkach pyłu zawieszonego. Najbogatszą w te związki, i stąd najniebezpieczniejszą, jest frakcja cząstek najdrobniejszych. Przedmiotem badań był pył zawieszony pobrany impaktorem Dekati PM10 w punkcie charakterystycznym dla Aglomeracji Górnośląskiej w Zabrzu. Impaktor umożliwia rozdział pyłu zawieszonego na cztery frakcje, każda o cząstkach mających średnice aerodynamiczne w innym z czterech przyległych rozłącznych przedziałów. W każdej z frakcji oznaczono zawartość szesnastu WWA metodą chromatograficzną. Uzyskane wyniki umożliwiły ocenę zawartości WWA, a za szczególnie interesujące uznano wyniki zawartości WWA w pyle PM1.