

VARIABILITY OF AIRBORNE FINE DUST CONCENTRATIONS AND
CONTENT OF PAHS IN PM_{2.5} – MEASUREMENTS IN
CZĘSTOCHOWA, POLAND

HALINA PYTA, ANDRZEJ KRASA, WIOLETTA ROGULA

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

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ZMIANY STĘŻENIA DROBNEGO PYŁU ZAWIESZONEGO I ZAWARTOŚĆ WWA
W PYLE PM_{2.5} NA PRZYKŁADZIE POMIARÓW W CZĘSTOCHOWIE

W artykule przedstawiono wyniki pomiarów stężenia pyłu PM_{2.5} (o średnicy aerodynamicznej cząstek do 2,5 μm) oraz frakcji PM_{2.5-10} (o średnicy cząstek z przedziału od 2,5 do 10 μm) na stanowisku w Częstochowie. Pomiar prowadzono od stycznia do grudnia 2005 r., w cyklach 24 h. Wykorzystano sekwencyjny, dwukanałowy pobornik pyłów z głowicą PM₁₀ i separatorem frakcji PM_{2.5} (*sharp cut cyclone*). Próbkę pyłu PM_{2.5} poddano analizie na zawartość następujących WWA: fluorantenu, benzo(a)antracenu, chryzenu, benzo(b)fluorantenu, benzo(k)fluorantenu, benzo(a)pirenu, indeno(1,2,3-c,d)pirenu, dibenzo(a,h)antracenu i benzo(g,h,i)perylenu. Wyniki pomiarów wykazały podwyższone średnioroczne stężenie pyłu PM_{2.5} – 32,3 μg/m³ oraz ponadnormatywne średnioroczne stężenie pyłu PM₁₀ – 46 μg/m³. Odnotowano wysokie stężenie WWA w pyłe PM_{2.5}, które w sezonie zimowym było od 3 do 5 razy wyższe niż w sezonie letnim. Średnioroczne stężenie benzo(a)pirenu wynosiło 3,9 ng/m³ i 4-krotnie przekraczało planowaną wartość docelową dla krajów UE.

Summary

The paper presents measurement results of two airborne dust fractions concentrations: the fine (PM_{2.5}, the particles with the aerodynamic diameter up to 2.5 μm) and coarse dust (PM_{2.5-10}, particles of diameter between 2.5 and 10 μm) at a measuring site in Częstochowa. Both fractions of dust were sampled in 24 h cycles during whole 2005 year, from January to December. The dust was collected with the use of a sequential, two channel air sampler (Dichotomous Partisol-Plus Model 2025, Ruprecht and Patashnik Co.) with the PM₁₀ head and PM_{2.5} separator (*sharp cut cyclone*). The following polycyclic aromatic hydrocarbons (PAHs) were determined in the samples of PM_{2.5}: fluoranthene, 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. The experiment proved an elevated annual concentration of PM_{2.5} (32.3 μg/m³) and annual concentration of PM₁₀ exceeding the standard (46 μg/m³). High concentrations of PAHs in PM_{2.5} were noted; in winter they were 3–5 times higher than in summer. The annual benzo(a)pyrene concentration was 3.9 μg/m³, i.e. almost 4 times the future target value for EU countries.

INTRODUCTION

Toxicological investigations of atmospheric aerosol, initiated by the US Environmental Protection Agency and the program for suspended dust monitoring, led to introducing a standard for ambient PM_{2.5} concentration in the USA. The need for imposing an upper bound on concentration of PM_{2.5} in atmospheric air in EU countries was announced in the First Daughter Directive 1999/30/EC which introduced the limit value for – among others – PM₁₀. The initial proposals for introducing annual and diurnal standards for PM_{2.5} in Europe were abandoned under influence of the World Health Organization (WHO). Investigations entrusted to WHO by the Clean Air for Europe Program (CAFE) confirmed health hazard due to ambient PM_{2.5} within urbanized areas, and also need for maintaining the PM_{2.5} concentration in air on appropriately low level but for longer periods. The health effects of PM_{2.5} high concentration episodes (short-time exposure) are not so well documented as effects of long-time exposure [33]. Finally, in the Thematic Strategy on Air Pollution and in the proposal of a new Daughter Directive, an introduction of the new annual limit value for PM_{2.5} concentration in atmospheric air, equal to 25 µg/m³, was proposed [8, 28].

On the CAFE forum, Poland objected to the proposed immision standard for PM_{2.5}, which seems impossible to be reached in majority of Polish cities due to considerable emission of dust from scattered heating sources [18]. In Poland, total emission of PM_{2.5} in 2003, assessed on the basis of new guidelines of emission inventorying, was 141 Gg, what was about 40% of PM₁₀ emission and 30% of emission of total suspended particulates (TSP). The greatest share in the total dust emission had municipal and domestic heating sources (41%), vehicular sources (18%), industrial combusting and industrial processes (11% each) energetic combustion (8%) and wastes combustion (6%). Contributions of agriculture and natural emission were 0.5% and 3%, respectively, but supposedly they are underestimated [22].

The above data on emissions of PM_{2.5} refer only to the primary emission, they do not concern the sources of secondary emission associated with conversion of gaseous precursors of dust (SO₂, NO_x, NH₃, VOCs). A potential for PM₁₀ particulate formation, expressed as PM₁₀ equivalent emissions in thousands of tons, has been evaluated as 0.88 for NO_x, 0.64 for NH₃, and 0.54 for SO₂ [19]. For PM_{2.5}, the proportion of the secondary to primary emission is even grater than for PM₁₀. Reducing emission of gaseous precursors of dust was crucial to reducing concentrations of fine dust in Europe and the USA [3, 14, 34].

Due to its capability to penetrate deeper into the respiratory tract, PM_{2.5} is considered more harmful than coarser dust fractions [7]. Effects of PM_{2.5} depend on its provenience and chemical composition [12, 31]. Dusts coming from combustion of solid fuels, wastes and engine fuels and from high-temperature conversion of energetic raw materials (coking, petrochemistry, etc.) are specially harmful. Such dusts comprise considerable amounts of polycyclic aromatic hydrocarbons (PAHs), some carcinogenic, theratogenic or mutagenic [2, 13, 20]. Although many aromatic hydrocarbons are present in ambient air, usually only 6 to 16 are determined. Among these 16 PAHs, there are 2- and 3-ring hydrocarbons as well as hydrocarbons with greater molecular weight (more than 4 rings). The latter are less volatile, less water-soluble and more lipophylic. Hydrocarbons with lower molecular weight and condensation temperature occur in gas phase only. Semi-volatile hydrocarbons (4 rings) occur in gas and solid phases in comparable amounts. Less volatile PAHs, having 5 and more benzene rings, are present in ambient air mainly adsorbed on dust [9, 30]. Although in metabolism of PAHs not all processes leading to canceration are recognized,

it is known that some of 4- to 7-ring hydrocarbons are carcinogenic, and that the PAH indicator, benzo(a)pyrene, is carcinogenic too [1]. So, in samples of atmospheric aerosol most commonly concentrations of 4- to 6-ring PAHs are investigated.

Qualitative composition of PM_{2.5} has been presented in numerous publications. They show significant regional and seasonal differentiation of this dust fraction [17, 21, 23, 30]. Some of Polish works point out that numerous and scattered hard coal fueled heating sources are the cause of higher PM_{2.5} concentrations in ambient air, higher contribution of PM_{2.5} to PM₁₀, and also higher concentrations of airborne PAHs in Poland than in other European countries [16, 23, 25].

This paper presents results of annual series of measurements of concentrations of both PM_{2.5} (fine) and the complementing (coarse) fraction PM_{2.5-10} in atmospheric air with the use of a two-channel sampler in Częstochowa. The content of nine PAHs in collected dust was examined. The work was done by an appointment of the Regional Inspectorate of Environmental Protection in Katowice (RIEP) and in cooperation with the RIEP Laboratory in Częstochowa and was financially supported by the Regional Found for Environment Protection and Water Resources Management in Katowice.

Undertaking of such investigations may be motivated by implementing the Directive 2004/107/WE of December 15, 2004 on arsenic, cadmium, mercury, nickel and PAHs in atmospheric air and by projected Directive 2005/0183 (COD) on air quality and on cleaner air for Europe, defining also the annual limit value for PM_{2.5}.

MATERIAL AND METHODS

The study area

The measurements were performed in Częstochowa, ul. Rząsawska 24–28, city quarter Wyczerpy, in the northeastern part of the city. The site was typical of the urban background conditions. The sampler was located approximately one hundred meters from Rząsawska Street – a local road with moderate traffic density – on the open, grassy yard, in front of the RIEP building. The measuring site was not affected significantly by traffic pollution and was beyond direct effects of industrial or energetic sources of pollution. There were inactive industrial facilities on the neighboring lots, some great halls adapted for warehouses. The measuring point location and the sampler view are presented in Figure 1.

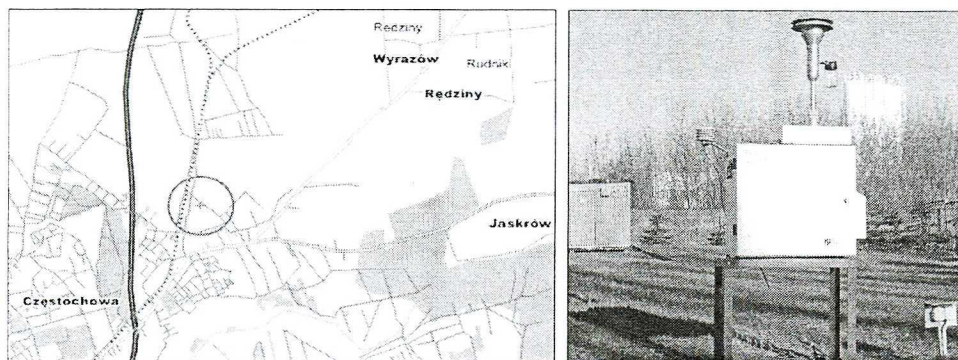


Fig. 1. Location of the measuring site; view and scheme of the dichotomous dust sampler (the base-map from www.maporama.com, ADC Worldmap was used)

Both 24 h ambient concentrations, of PM_{2.5} and PM_{2.5–10}, were measured in the period from January to December 2005. In the PM_{2.5} fraction, the concentrations of nine selected PAHs were determined.

Gravimetric measurements

Concentrations of dust in ambient air were measured by using the gravimetric method suggested by the European Committee for Standardizations CEN. The sequential, low volume Dichotomous Partisol Plus 2025 Ruprecht and Patashnik Co. sampler was used to collect dust samples. The two channel sampler, equipped with the PM₁₀ head, allows for separating the PM_{2.5} fraction from the main stream of PM₁₀. In the sampler, the stream of PM₁₀ is divided into fine PM_{2.5} and coarser PM_{2.5–10} fractions by the sharp cut cyclone (SCC). The sampler may automatically collect up to 16 samples of each of the two dust fractions (i.e., for example, work continually for 16 days taking sixteen 24 h samples during consecutive 16 days, as in the presented case). The samples of dust are collected on the filters placed in filter cassettes, the cassettes are inserted into the filter cassette magazines. The sampler automatically takes the cassettes with clean filters from the supply magazine, exposes the filters accordingly to the measurement program, and places the cassettes in the storage magazine.

The coarser dust, PM_{2.5–10}, was collected on glass fiber filters (Whatman GF/A Ø47), fine dust, PM_{2.5} – on Teflon filters (2 µm PTFE 46.2 mm filter) of finer porosity and higher filtration efficiency [6]. The minimum particle sampling efficiencies of the glass fiber and Teflon filters in collecting particles with diameters greater than 0.3 µm were 99.95% and 99.7%, respectively, which means their compliance with the standards [15, 26].

To determine concentration of dust, the filters were weighed on a microbalance before and after their exposure and the actual volume of sampled air were read from the sampler logger.

The Mettler Toledo microbalance with a resolution of 2 µg was used to weigh filters and the Haug U-ionizer was used to neutralize electrostatic charges on filters. Air temperature and relative humidity in the weighing room were maintained at 20°C and 50%, respectively. Usually, the mass of collected dust was very small (tenths of milligram) so it was important to assure the same conditions of weighing for clean and exposed filters. It was done by equilibrating the filters for 48 hours, before and after exposition, in the darkened weighing room. Each filter was weighed three times and an arithmetic mean of the three received results was assumed as its weight.

Analytical procedure

The fine dust (collected on the Teflon filters) was analyzed in the RIEP Laboratory in Częstochowa to determine content of PAHs in PM_{2.5}. Two analyses were performed monthly: one of the dusts collected in the first half of a month, the second – of the dust collected during the second half of a month. Concentrations of fluoranthene, benz(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 were determined in PM_{2.5}. They are the same 9 PAHs that were determined in PM₁₀ by the Regional Sanitary and Epidemiological Station (RSES) within the Silesian Region. PM_{2.5} was analyzed by applying the RIEP Laboratory own procedures developed on the basis of the Polish Norm [27]. The analysis was divided into the sample preparation and the chemical analysis of separated compounds with the use of the High Performance Liquid Chromatography (HPLC).

Błaszczyk presented detailed description of the sample preparation [4]. The Teflon

filters with PM_{2.5} from one half of a month were placed in Erlenmayer flasks shielded from light. PAHs were desorbed from PM_{2.5} by using a solvent. About 100 cm³ of cyclohexanone was put into the flasks and the flasks were placed in an ultrasonic bath for about 45 min. The purified and concentrated extract was analyzed by using HPLC. To preclude changes in retention times of PAHs, the extract was evaporated dry in a nitrogen stream at temperature of 37°C before the analysis. Finally, 0.5 cm³ of acetonitrile, used with water as a mobile phase, was added to the flasks. The actual chemical analysis consisted in determining the concentration of PAHs in the extract through separation with the use of reversed phase HPLC with fluorescence detection. The particular PAHs were identified by comparing their retention times with the retention times of standard solutions and by their specific fluorescence. The quantitative analysis was performed by using calibration coefficients determined with the use of the standard solutions. To determine possible effects of factors not related directly with the experiment (filter material, filter transportation, etc.) 15 filters were used as field blanks. Their analyses showed negligible PAHs concentrations.

A Waters LC-1 liquid chromatograph with SupelcosilTM LC-PAH column (15 cm x 4.6 mm x 5 µm) and with WatersTM 475 SFD fluorescence detector was used. Detailed description of the analytical method (the pump and detector adjustment parameters, instrumental analysis program) has been presented by Błaszczuk [5].

The limits of detection and expanded uncertainty for determinations of PAHs for a coverage factor $k=2$ and 95% confidence interval, computed by the RIEP Laboratory, are presented in Table 1. The detection limit was computed by analyzing standard solution of low concentration of PAHs several times. In Table 1 the detection limit is given in nanograms per 1 cm³ of the analyzed solution and recalculated to nanograms per 1 m³ of air passed through analyzed filters.

Table 1. Limits of detection and expanded uncertainty for determinations of PAHs in PM_{2.5}

Compound	Limit of detection		Expanded uncertainty $k=2$, for $P=95\%$ [%]
	[ng/cm ³]	[ng/m ³]	
Fluoranthene	1.6	0.07	25
Benzo(a)anthracene	3.2	0.15	25
Chrysene	3.2	0.15	25
Benzo(b)fluoranthene	2.8	0.13	25
Benzo(k)fluoranthene	2.4	0.11	25
Benzo(a)pyrene	2.8	0.13	25
Dibenzo(ah)anthracene	3.2	0.15	25
Benzo(ghi)perylene	3.2	0.15	25
Indeno(1,2,3-cd)pyrene	2.8	0.13	25

RESULTS AND DISCUSSION

Concentrations of PM_{2.5} and PM_{2.5-10}

Measured concentrations of PM_{2.5} and PM_{2.5-10}, as well as of their sum, i.e. concentration of PM₁₀, are presented in Table 2. Mean month concentrations of PM_{2.5} and PM_{2.5-10} are shown in Figure 2. There were 228 diurnal measurements performed in the whole year and the time of measurements covered 65% of the year.

Table 2. Statistical parameters of series of 24h measurements of PM2.5 and PM2.5-10 concentrations, Częstochowa 2005

Measurement season	Concentration [$\mu\text{g}/\text{m}^3$]	PM2.5	PM2.5-10	PM10
I quart. of 2005	Mean	46.4	6.7	53.0
	Minimum	17.6	0.2	23.0
	Maximum	106.4	17.1	123.5
II quart. of 2005	Mean	33.8	14.1	48.0
	Minimum	1.1	0.9	10.1
	Maximum	139.6	72.0	140.5
III quart. of 2005	Mean	22.3	17.3	39.6
	Minimum	2.7	1.4	6.4
	Maximum	69.3	139.8	153.5
IV quart. of 2005	Mean	42.4	9.2	51.6
	Minimum	9.7	1.5	12.2
	Maximum	98.6	28.7	113.5
Winter season (I and IV quart. of 2005)	Mean	43.1	8.8	51.9
	Minimum	9.7	0.2	12.2
	Maximum	106.4	28.7	123.5
Summer season (II and III quart. 2005)	Mean	27.6	15.9	43.4
	Minimum	1.1	0.9	6.4
	Maximum	139.6	139.8	153.5
For whole data series 2005	Mean	32.3	13.7	46.0
	Standard deviation	23.8	13.1	27.0
	Maximum	139.6	139.8	153.5
	Number of measurements	228		

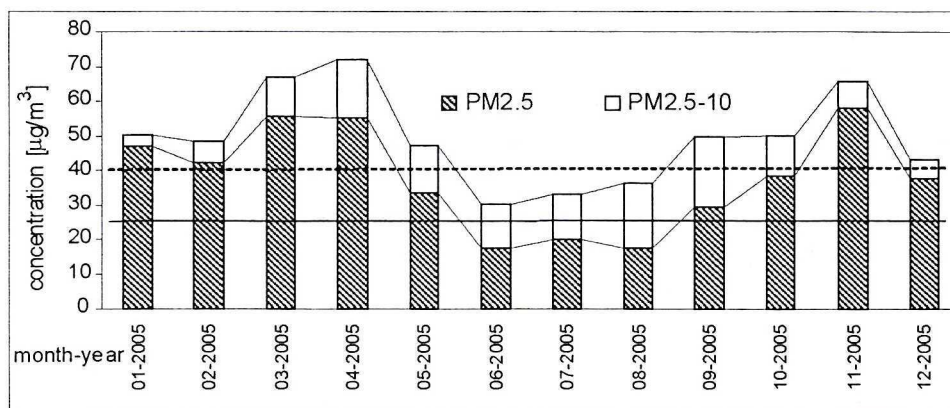


Fig. 2. Average month's PM2.5 and PM2.5-10 concentrations, Częstochowa 2005
horizontal solid line – planned annual limit value for PM2.5 – 25 $\mu\text{g}/\text{m}^3$;
horizontal dotted line – actual annual limit value for PM10 – 40 $\mu\text{g}/\text{m}^3$.

The mean annual concentration of PM_{2.5} (32.3 µg/m³) exceeded the annual limit value (25 µg/m³) planned to be introduced in EU countries by 30%. The heating season was responsible for such a level of PM_{2.5} in ambient air. The mean winter PM_{2.5} concentration was 43.1 µg/m³ and was higher than the summer concentration by 30%. In summer, the mean PM_{2.5} concentration was 27.6 µg/m³ and did not differ from the background concentration of a European agglomeration. Mean annual PM₁₀ concentration was 46 µg/m³ (51.9 µg/m³ mean summer and 43.4 µg/m³ mean winter concentration). It means that the admissible annual PM₁₀ concentration 40 µg/m³ was exceeded.

Using the two channel sampler enabled also evaluation of the contribution of the fine fraction PM_{2.5} to PM₁₀. The contribution of PM_{2.5} to PM₁₀ depends on local emission, meteorological factors and atmospheric air circulation. In Częstochowa, the average mass PM_{2.5} contribution to PM₁₀ was 67.2%. In summer and winter it was 60.5% and 82.2%, respectively.

High PM_{2.5} concentration, deciding on excessive PM₁₀ concentration, is hazardous to health of inhabitants. In Figure 3, classification of the health hazard due to PM_{2.5} concentrations in ambient air, according to the six threshold scale of the air quality index (AQI), is presented [32]. For 74% of time covered by measurements, conditions classified by EPA as good or moderate occurred. For the remaining 26% of the measurement time, unhealthy for sensitive groups or unhealthy conditions occurred. For 31% of measuring time in summer the quality of air was good and so for 8% in winter. Conditions unhealthy for sensitive groups or for whole population occurred for 18% of measuring time in summer and for 42% in winter. Neither the situation very unhealthy nor hazardous to health was ever noted.

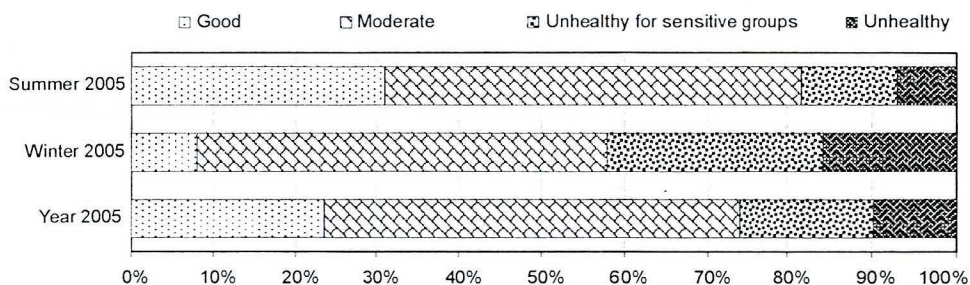


Fig. 3. Air Quality Index for PM_{2.5} according to U.S. EPA, Częstochowa 2005

Concentrations of PAHs

Accordingly to the Directive 2004/107/EC [11], seven PAHs have to be monitored in ambient air. This monitoring concerns: benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, and dibenzo(a,h)anthracene in airborne PM₁₀. Among all these compounds only one has an annual target value – benzo(a)pyrene; it is equal to 1 ng/m³. Assessing content of PAHs in PM_{2.5} is not obligatory; however appearance of such an obligation should be expected as soon as the limit value for PM_{2.5} is established. Therefore, Częstochowa measurements were of explorative character; they were performed to identify the hazard due to PAHs occurring in the fine fraction of dust. Nine PAHs, having from 4 to 6 benzene rings, were analyzed. These PAH concentrations were monitored in the Silesian Region for years by

the RSES. Average PAH concentrations in PM_{2.5} and range of variability of concentrations of the monitored PAHs are presented in Table 3. If carcinogenic benzo(a)pyrene is to be assumed as the indicative hydrocarbon for PAHs then the PAH concentration in atmospheric air around the measuring site show hazard for health. Average concentration of benzo(a)pyrene, equal to 3.94 ng/m³, was almost four times the planned target standard for this compound [11]. Ambient concentration of each of the 9 investigated PAHs was higher in winter than in summer – for PAHs with higher molecular weights, i.e. benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene, more than 3 times, and for 4-ring fluoranthene more than 5 times (Fig. 4). Average concentrations of 4- and 5-ring PAHs and of the total PAHs were 18 ng/m³, 15 ng/m³ and 72 ng/m³, respectively. Results received by the RIEP Laboratory in Częstochowa were similar to ones received by the Institute of Environmental Engineering for 4-, 5- and 6-ring PAHs from among EPA's 16 PAHs determined in PM_{2.5}, despite of differences in the analytical procedures applied [10].

Table 3. Determined content of selected PAHs in PM_{2.5}, Częstochowa 2005

Measurement season	Statistic parameter	Concentration [ng/m ³]								
		Fluoranthene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Dibenzo(ah)anthracene	Benzo(ghi)perylene	Indeno(1,2,3-cd)pyrene
Winter season (I and IV quart. 2005)	Mean	13.311	11.056	10.900	10.089	3.933	6.844	1.526	7.633	4.233
	Minimum	3.10	3.10	3.70	4.30	1.70	2.40	0.52	1.60	2.00
	Maximum	23.00	25.00	24.00	16.00	6.40	12.00	2.70	14.00	6.20
Summer season (II and III quart. 2005)	Mean	2.533	2.228	2.273	2.977	1.098	1.929	0.442	2.323	1.280
	Minimum	0.54	<0.15 *	<0.15 *	0.37	0.16	0.19	<0.15 *	0.36	<0.13 *
	Maximum	9.50	9.50	8.70	10.00	3.70	6.70	2.00	8.00	4.70
Whole year 2005	Mean	6.942	5.840	5.802	5.886	2.258	3.940	0.885	4.495	2.488
	Standard deviation	7,791	7,393	7,147	5,379	2,120	3,820	0,850	4,279	2,144
	Minimum	0.54	<0.15 *	<0.15 *	0.37	0.16	0.19	<0.15 *	0.36	<0.13 *
	Maximum	23.00	25.00	24.00	16.00	6.40	12.00	2.70	14.00	6.20
	Number of measurements	22								

*) incomplete sample from the second half of May, 2005, (May 30 and 31, 2005) with too small amount of dust

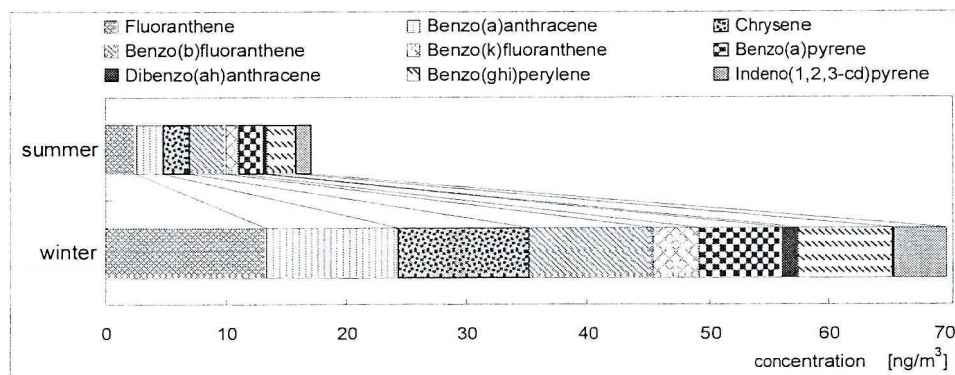


Fig. 4. PAHs concentration in PM_{2.5} in summer and winter season, Częstochowa 2005

CONCLUSIONS

In spite of moderate winter of 2004/05 and delayed heating season of 2005, the results from Częstochowa confirmed elevated, hazardous to human health, level of PM_{2.5}. If the risk was to be evaluated with the use of the AQI index, then conditions unhealthy to sensitive groups of people or to whole population lasted for 36% of the time of measurements. The annual concentration of PM_{2.5} – 32.3 $\mu\text{g}/\text{m}^3$ – exceeded the future, planned for EU countries, annual limit value of 25 $\mu\text{g}/\text{m}^3$ by 30%. So, the proposed by the Working Group on Particulate Matter limit value for PM_{2.5} may appear much harder to be kept than the one for PM₁₀.

Implementation of a system disseminating data about airborne PM_{2.5} health hazard and radical action against high concentrations of fine aerosols in atmospheric air are highly advisable. The detailed inventory of primary sources of PM_{2.5}, made by inquiring, and analysis of the contribution of secondary sources to airborne PM_{2.5} formation should serve a basis for effective dust emission preventing.

High concentrations of benzo(a)pyrene and other PAHs in PM_{2.5} were noted, especially in winter. Average concentration of benzo(a)pyrene was four times higher than its target limit for its concentrations in PM₁₀. Concentration of each of 9 PAHs was 3–5 times higher in winter than in summer. Exceeding of the target limit by benzo(a)pyrene in dust sampled on the city border suggests future common need for Air Protection Programs in urbanized areas due to the above-limit concentrations of this hydrocarbon.

Experiences of EU countries, producing energy from solid fuels, prove that without solving the low emission problem and without replacing hard coal with more ecological fuel wherever it is economically motivated, limiting concentrations of PM_{2.5} and PAHs in atmospheric air in Poland will be impossible.

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