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COMPARISON OF BENZO(A)PYRENE CONCENTRATIONS IN THE VICINITY OF ROADS AGAINST URBAN BACKGROUND IN THE UPPER SILESIA AREA

Results of measurements of B(a)P concentrations in suspended dust collected in the close vicinity of roads are presented. The investigations were aimed at assessing the risk of short-time exposures of traffic participants to carcinogenic B(a)P present in car exhaust gases. 248 samples of dust were collected at 9 measurement points located in 6 cities of the Upper Silesian Industrial Region (southern Poland) during the period of July–December 1999. The dust was sampled at roadsides. Time of a single sample taking was 30 min. The content of B(a)P was determined in the samples of total suspended dust. A quantitative analysis was carried out using the chromatography (GC/FID). The B(a)P concentrations measured were in the range from 0 to 2175 ng/m^3. The summer and winter B(a)P mean concentrations in the vicinity of roads were compared to B(a)P concentrations in urban–industrial agglomeration (measurements made by the Provincial Sanitary and Epidemiological Station) and in urban agglomeration (annual series of measurements in the town of Żywiec). The B(a)P concentrations in the vicinity of roads were many times higher than the background values.

1. INTRODUCTION

The World Health Organization treats the carcinogenicity of benzo(a)pyrene (B(a)P) as a reference standard for all air pollutants. The health risk factor for B(a)P reaches 87×10^{-6} (ng/m^3)$^{-1}$ and is among the highest concentrations of aromatic hydrocarbons [1]. In Poland, B(a)P is the only polycyclic aromatic hydrocarbon (PAH) whose permissible concentration in the ambient air has been assessed. Its permissible annual, 24 h and 30 min concentrations are 1.0, 5.0 and 12.0 ng/m^3, respectively.

The greatest share of B(a)P in ambient air is due to fossil fuels' combustion, while that of the vehicular emission of B(a)P is much lower. However, the vehicular emission should be considered as the main hazard in centres of urban agglomerations which are beyond the influence of major energetic or industrial sources.

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The Upper Silesian Industrial Region (USIR) is an appropriate place for investigations of B(a)P immission. Exponential increase of the number of cars and many years' delays in development of road infrastructure yielded very hard conditions for traffic. In many cases, big transit arteries cross the centres of urban agglomerations. Moreover, centres of cities elsewhere functioning as trade and service centres, in the USIR are densely populated being living quarters. The western district of the region is built up with old, coal-heated houses.

B(a)P, treated as a tracer for the PAHs, is monitored in urban areas. Determinations of B(a)P in 24 h samples of suspended dust are performed by the Provincial Sanitary and Epidemiological Station (PSES). The aim of this monitoring was to assess the urban B(a)P concentrations serving later as a background in comparative analyses of vehicular PAHs. Also, the Department of Contaminants' Immission of the Institute of Environmental Engineering (DCI) has initiated investigations of B(a)P and the other PAHs content in dust from the vicinity of roads [2]. The investigations focused on the assessment of hazards caused by vehicular PAHs which were not sufficiently recognized so far.

2. MATERIALS AND METHODS

Samples of suspended dust for B(a)P determinations (and 15 other PAHs) were collected at 9 points located on roadsides, 1.5 m above the ground level. The points were located in the following cities of the central part of the USIR, at sites where high concentrations of B(a)P were supposed to appear:

Katowice – 3 sampling points; No. 1 within a traffic circle, Nos. 2 and 3 by arterial roads,

Mikołów – sampling point No. 4 by a highway,

Ruda Śląska – sampling point No. 5; point affected by a great number of heavy trucks,

Zabrze – 2 sampling points; No. 6 at crossroads in the city centre, No. 7 in the Paniówki district by the road connecting the cities of Gliwice and Mikołów,

Gliwice – sampling point No. 8 by a road near a car-park,

Bytom – sampling point No. 9 in a street canyon.

The dust was sampled from July to December 1999 (the same number of samples in summer and heating seasons) on randomly chosen day in a week and hour of a day. To assess an effect of the heating season on ambient B(a)P concentrations, 13 measurements were performed off the road system (50–200 m from the fixed measurement points) at sites affected by local domestic sources (low emission).

Samples for determinations of content of PAHs, including B(a)P, in total suspended particulates (TSP) were collected according to the Polish Standard PN-91/Z-04030/06. An aspirator AS-50 (made by TWO-WED Zgierz, Poland) with steady flow

rate of 50 dm^3/h was applied. Time of a single sample drawing was 30 min. The total number of samples for B(a)P determinations was 248. Sampled dust was collected on Whatman GF/A Ø50 filters. The dust accumulated on the filter was extracted with the use of methylene chloride in an ultrasonic field. The fraction of aromatic compounds was separated from the extract by means of the liquid column chromatography. A quantitative analysis of the aromatic fraction was carried out by means of gas chromatography with an external reference standard, using a Varian Star 3400 CX gas chromatograph equipped with a flame ionisation detector and DB-5 capillary column (length of 30 m, diameter of 0.23 mm, film thickness of 0.32 μm). The temperatures of the detector and injector were both 320 °C; the temperature of the column changed from 60 to 290 °C at 16 °C/min [3].

The results of PAHs determination in the dust collected in Żywiec, the town with much lower anthropogenic effect than Silesia, were taken as an example of background pollution of urban air with B(a)P and were used in a comparative analysis. The single sampling point was located beyond effects of local sources. The content of B(a)P was determined in 24 h samples, collected once a month from January to December of 1999. Methods of the dust separation and all chemical analyses applied were the same as in the case of the USIR measurements [4].

3. RESULTS AND DISCUSSION

Time series of 30-min B(a)P concentrations for points 1–9 are presented in figure 1. The horizontal line represents the highest permissible in Poland 30-min B(a)P concentration, D_{30} = 12 ng/m^3 (limitations are imposed on the 99.8 percentile of annual series of measurements). In order to illustrate the wide variability of the B(a)P concentration, the logarithmic scale was used (1–10000 ng/m^3). The complete set of results of measurements is presented. The lacking bars in charts mean the concentrations of B(a)P lower than 1 ng/m^3 in the sample examined. Because of randomness of the sampling, the same measurement date occurs 2–3 times for each measurement point (for instance, the samples were taken in the morning and afternoon of the same day).

Results of measurements, averaged at each point, are presented in table 1. The results evidence a considerable variability of B(a)P concentration and B(a)P percentage in the sum of all 16 PAHs, both depending on measurement site and time. Diurnal and seasonal variability of B(a)P concentrations may be accounted for by a superposition of emission parameters (diurnal traffic variations, effect of the heating season) and meteorological conditions (air temperature, temperature inversion, humidity, wind speed). Spatial diversity of B(a)P concentrations is an effect of such characteristics of traffic as the density, fluency, shares of particular types of vehicles (e.g. cars with diesel engines emit much more particles than gasoline powered cars), as well as of

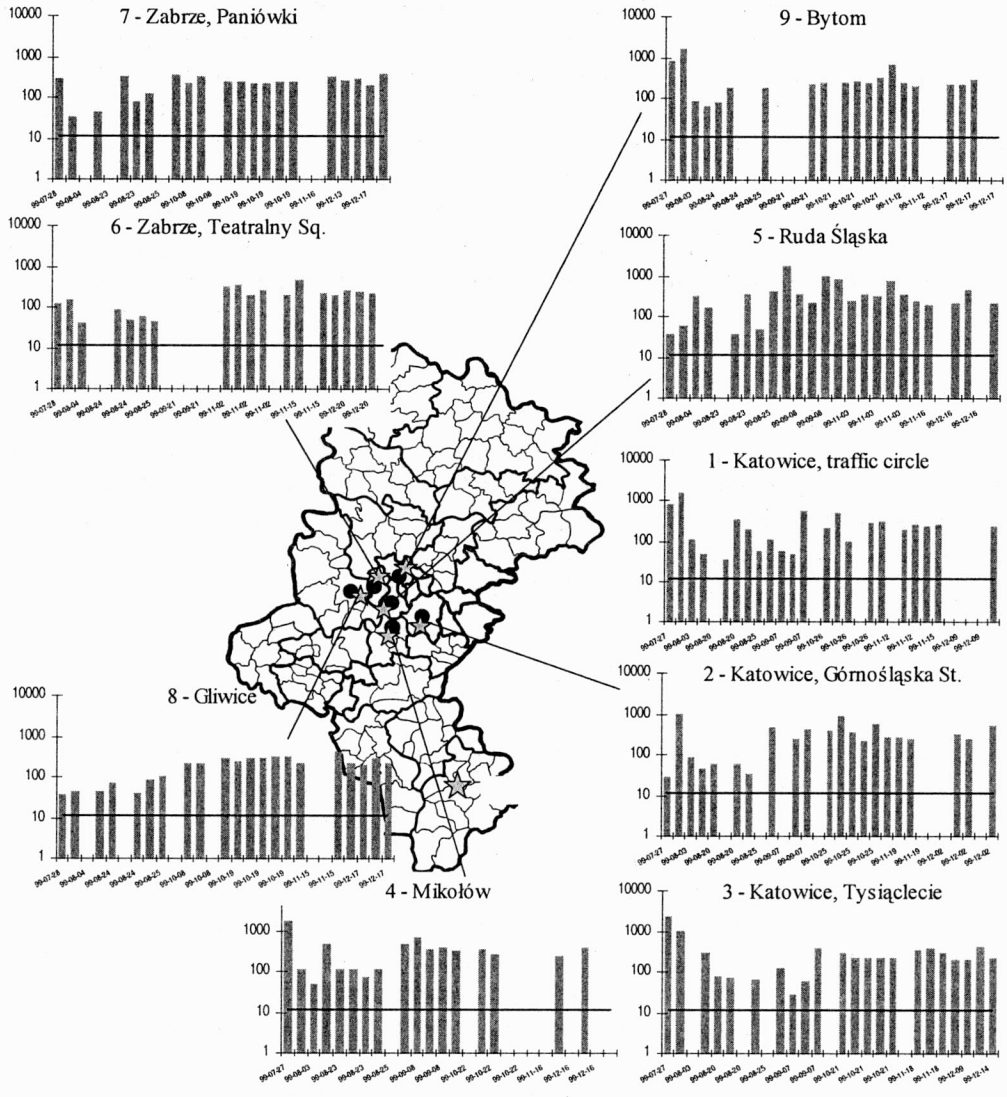

Fig. 1. Concentration of B(a)P in 30-min samples of total suspended dust in the close vicinity of roads (bar charts in log-scale). Upper Silesia Industrial Region, July–December 1999

B(a)P concentration in the vicinity of roads [ng/m^3].

—— Polish permissible 30-min B(a)P concentration, D_{30} = 12 ng/m^3.

● cities with B(a)P concentration measurements in the vicinity of roads.

☆ cities with B(a)P background concentration measurements.

Table 1

Concentrations of B(a)P and its percentage shares in the sum of the 16 PAHs at 9 measurement points

B(a)P concentration or its percentage in total PAHs	Statistical parameter	Number of measurement point									Average 1–9
		1	2	3	4	5	6	7	8	9	
Summer season											
Concentration [ng/m^3]	mean	285.8	189.2	327.2	342.7	380.5	37.8	94.8	45.7	237.1	225.9
	standard deviation	421.0	269.8	642.7	422.1	458.1	48.1	118.4	33.6	425.8	387.6
	maximum	1474.4	957.4	2175.0	1645.3	1627.9	141.6	307.0	99.5	1532.7	2175.0
Percentage [%]	mean	14.2	11.6	10.6	24.1	26.4	1.3	5.2	3.4	6.2	12.1
Winter season											
Concentration [ng/m^3]	mean	147.2	258.3	222.7	110.4	246.5	202.4	215.6	204.2	189.1	201.4
	standard deviation	148.8	240.4	115.9	158.8	194.1	128.1	114.3	124.0	180.4	160.9
	maximum	501.6	864.1	401.5	388.7	698.1	436.1	383.0	420.2	685.8	864.1
Percentage [%]	mean	4.2	9.6	8.4	3.6	9.4	7.9	8.1	7.7	6.5	7.3
Average value in measurement period											
Concentration [ng/m^3]	mean	207.3	226.1	270.9	240.5	316.0	120.1	173.8	151.4	212.3	212.6
	standard deviation	300.7	252.5	437.7	347.6	356.3	126.6	127.6	127.3	317.9	286.9
	maximum	1474.4	957.4	2175.0	1645.3	1627.9	436.1	383.0	420.2	1532.7	2175.0
Percentage [%]	mean	8.5	10.5	9.4	15.0	18.6	4.5	7.1	6.2	6.4	9.5

presence of buildings and high trees and shrubs, preventing contaminants from dispersing, or of effects of local nonvehicular B(a)P sources.

The highest concentrations were observed at the point No. 5 which was affected by emission from heavy-duty cars (lorries, diesels) and where the conditions for pollutants' dispersion were unfavourable. Effects of both vehicular and low municipal emissions (1- or 2-storey buildings, coal heating) overlap at this point, but the contribution of domestic sources is not prevailing (concentrations in winter are clearly lower). B(a)P concentrations in the eastern part of the agglomeration (points 1–4), in the vicinity of the roads being frequently jammed with vehicles, are higher than in the western part. They are also higher in summer than in winter which is due to more frequent episodes of elevated concentration related to higher traffic and enhanced air turbulence. That is why mean concentrations of B(a)P for the nine measurement points in winter are lower than in summer by more than 10%. At the same time the standard deviation of the winter data is only 60% of the standard deviation for the summer data.

During the whole period of measurements, the mean of all B(a)P concentrations from the points in the vicinity of roads was over 200 times higher than the Polish standard for mean annual concentration $D_a = 1$ ng/m^3. For off-road samples, the mean B(a)P concentration measured in winter was 190.6 ng/m^3, its maximum was 596.5 ng/m^3, and average B(a)P part in the sum of PAHs was 11.5%.

In order to determine the regularities in the behaviour of B(a)P concentrations in the vicinity of roads, an attempt to classify the results of measurements by means of the artificial neural networks was made [5]. The Self-Organizing Map, version with 2D-visualization and colour coding (*Neural Connection* software package), was applied. This method does not require prerequisite determination of the number of classes of correlated observations, like in the *k*-means procedure of the cluster analysis. The data base consisted of the records of 30-min B(a)P concentrations, traffic density, ambient air temperature and measurement time. The temperature, which determines running conditions for car engines, and meteorological conditions affecting dispersion of pollutants appeared crucial for the classification. Three classes of the observations were obtained: summer observations, transient period (moderate temperature) observations and winter observations. In the class of summer observations, three subclasses were distinguished: one with the highest B(a)P concentrations, the second, the biggest one, with mean B(a)P concentrations, and the third with B(a)P concentrations tightly related to the highest temperature. Analogously, the class of winter observations was divided into three subclasses: of the highest B(a)P concentration, mean concentration, and that related to the lowest temperature. In each of the two classes of mean B(a)P concentrations (for summer and winter), the number of observations is almost the same for each measurement point. The class of the highest B(a)P concentrations for summer comprised no observations from these measurement points which contributed significantly to the winter class and vice versa (these classes

are disjoint). In the summer class of the highest B(a)P concentrations, the contribution of points located in areas of heavy traffic (Mikołów, Katowice) or in a street canyon (Bytom) was the greatest. In the winter class of the highest B(a)P concentrations, the measurements in the points located near the tracks of heavy duty trucks and in the vicinity of low emission sources (Ruda Śląska, Zabrze–Paniówki) have the largest share. Maximum B(a)P concentrations appeared in different hours in summer than in winter. Observations belonging to the summer class of the highest B(a)P concentrations came from afternoon hours, while the winter class consisted mainly of the morning observations (morning rush hours, frequent temperature inversions).

Regularities obtained by means of the neural network analysis are confirmed by the box-plot in figure 2. The plot presents distribution of B(a)P concentration at nine measurement points in the vicinity of roads and average concentration off the road system, denoted as the "10". The box represents concentrations between the 25th and 75th percentiles (the thick, horizontal line denotes median). Circles denote outliers, i.e. values set farther than 1.5 box-lengths from a box.

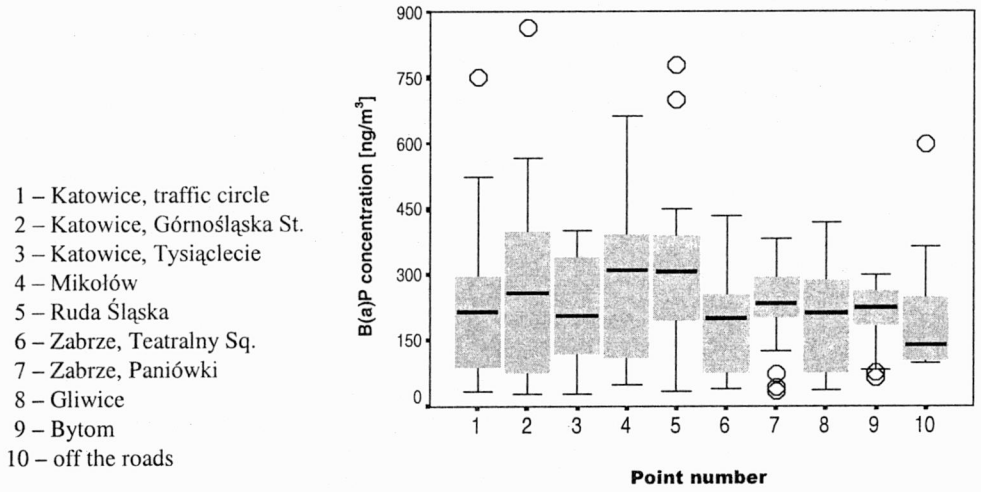

Fig. 2. Box-plot of B(a)P concentrations at points near roads (1–9) and off roads (10)

Low concentrations of B(a)P predominated at the point 10 (off the roads); the lowest median value could be observed in this case. Similarity among the distributions of concentration for crossroads is clear (points 1, 6, 8), especially if confronted with street canyons (9 – high buildings, 7 – low buildings). Low concentrations for street canyons are denoted as outliers, while at other measuring points they prevail. The outlying concentrations at most of the points were high, usually of the order of hundreds of ng/m^3. These concentrations, higher than results of 24 h determinations reported in literature [6]–[8], fall into intervals defined by occasional short-term

measurements of PAHs [9]. It should be stressed that samples were taken close to the exhaust gas sources (line of the kerb) and that B(a)P concentration in these gases reaches the values up to 10–20 $\mu g/m^3$ [10].

The most considerable variability of concentration was observed at the points with the heaviest traffic (points 1–4). The highest value of median, shifted towards higher concentrations, was calculated for a two-lane road with the heaviest traffic (point 4) and for a road used by the greatest number of cars with diesel engines (point 5).

In table 2, the mean of 30 min B(a)P concentrations measured in the vicinity of roads are compared to background concentrations in urban–industrial agglomeration (USIR) and in urban environment (Żywiec) [4]. The results of B(a)P determinations in dust samples collected by the PSES were taken as urban–industrial background concentrations. Each sample of TSS was collected continuously for 24 h. Content of B(a)P was determined by means of the gas chromatography. The PSES carries out systematic measurements at 28 points within the USIR. The averaged PSES' winter and summer measurements from the downtown quarters of Katowice, Mikołów, Ruda Śląska, Zabrze, Gliwice, and Bytom were used in this paper [11]. As the urban background the results obtained by the DCI during 24 h B(a)P measurements from Żywiec, averaged over summer (April–September) and winter, were used [12].

Mean B(a)P concentration in the closest vicinity of roads is many times higher than the background concentrations. To confirm this regularity emerging from comparison of the results of two environmental experiments differing in the dust sampling duration (30 min and 24 hours), site and time of sampling, and which have been performed with the use of the methods differing in details (DCI method, PSES method), further investigations should be carried out.

Table 2

Concentrations of B(a)P in suspended air in summer and winter in the vicinity of roads and in the backgrounds in urban–industrial (USIR) and urban agglomerations (Żywiec)

Season	B(a)P concentrations [ng/m^3]		
	Roads	USIR background	Żywiec background
Summer	225.9	3.4	7.8
Winter	201.4	29.7	8.9

4. CONCLUSIONS

The results of investigations prove that high level of toxic components of exhaust gases, including carcinogenic B(a)P, poses a serious hazard for the USIR inhabitants. The instantaneous high concentrations people are exposed to, for instance on the way to or back from the work or while crossing a street, were assessed. Polish guidelines

concerning air quality control, as well as EU laws, comprise no instructions of how to monitor the concentration of vehicular aerosols, especially those of B(a)P and other PAHs. The measurements showed alarmingly high, if compared to these in typical urban or urban–industrial agglomerations, level of B(a)P concentration in the vicinity of roads. It is highly probable that the Polish standards for B(a)P concentration are exceeded.

In an urban environment, the vehicular B(a)P emission may play more important role than the emission of B(a)P from energetic sources. This fact justifies pressing need for installing stationary street stations measuring B(a)P concentrations to carry out regular investigations confirming regularities observed during these screening experiments. Further investigations should be undertaken to determine the dependence of B(a)P concentration on distance from the street and height above the ground level, or on aerosol particles' size and averaging time. Based on the estimation of real proportion between municipal and vehicular emissions we should decide on priorities for environmental investments allowing reduction of PAHs emission in the USIR area.

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REFERENCES

[1] WHO, *Air quality guidelines for Europe*, 2nd edition, WHO Regional Publications, European Series, 2000, No. 91, 92–96.

[2] IEE PAS, *Assessment of the air contamination with aromatic hydrocarbons from vehicular sources*, Techn. Report on the II stage, IEE PAS, Zabrze, 2000 (unpublished work).

[3] CZAPLICKA M., WĘGLARZ A., KLEJNOWSKI K., *Analysis of organic contaminants adsorbed on particulate matter from motor vehicles*, Chemia Analityczna, 2001, 46, 677–686.

[4] IEE PAS, *Air and soil investigations within Żywiec city*, Techn. Report. IEE PAS, Zabrze, 1999 (unpublished work).

[5] PYTA H., *Benzo(a)pyrene air pollution from vehicle emissions. Exploratory analysis using self-organizing neural networks*, Chemia i Inżynieria Ekologiczna, 2001, 8, 101–114.

[6] CECINATO A., *Atmospheric pah in Italy: experience and concentration levels*, Fresenius Envir. Bull., 1999, 8, 586–594.

[7] SANDELL E., KIVIRANTA A., TUOMINEN J., AARNIO P., *Concentration levels of polycyclic aromatic hydrocarbons (PAHs) in ambient air in Finland*, Fresenius Envir. Bull., 1999, 8, 567–575.

[8] BECK E., *Ambient air concentrations of polycyclic aromatic hydrocarbons in Germany*, Fresenius Envir. Bull., 1999, 8, 602–608.

[9] ZABRZESKI J., MUSIALIK-PIOTROWSKA A., TYLUS W., *Główne źródła zanieczyszczenia powietrza – motoryzacja*, [in:] Proc. of the 4th Sci. Conf. *Problemy ochrony powietrza w aglomeracjach miejsko-przemysłowych*, Ustroń, 2001, 317–325.

[10] BERNHARDT M., MICHAŁOWSKA J., RADZIMIRSKI S., *Motoryzacyjne skażenia powietrza*, WKŁ, Warszawa, 1976.

[11] PSE Station, Katowice, *The air pollution in the Silesian Voivodship in 1998–1999*, PSES, Katowice, 2000.

[12] KLEJNOWSKI K., ŻAK M., WĘGLARZ A., WITOSZEK J., *Contamination of Air by PAHs and Some Volatile Compounds from Transportation Sources*, [in:] Proc. of the 3th Intern. Sci. Conf. *Air Protection in Theory & Applications*, Zabrze, 2000, Vol. 1, 51–53.

PORÓWNANIE WYNIKÓW BADAŃ STĘŻENIA B(a)P W SĄSIEDZTWIE DRÓG Z WARTOŚCIĄ TŁA W AGLOMERACJI GÓRNOŚLĄSKIEJ

Przedstawiono wyniki pomiarów stężenia benzo(a)pirenu w pyle zawieszonym w powietrzu, pobieranym w bliskim sąsiedztwie dróg. Celem badań była ocena narażenia uczestników ruchu na krótkotrwałe ekspozycje na kancerogenny benzo(a)piren obecny w spalinach samochodów. W 9 stałych punktach zlokalizowanych w 6 miastach GOP-u, w okresie od lipca do grudnia 1999 pobrano 248 prób pyłu. Pył pobierano przy krawędzi jezdni. Czas poboru prób – 30 min. Zawartość B(a)P oznaczano w całkowitym pyle zawieszonym (TSP). Analizę ilościową wykonano metodą GC/FID. Otrzymano wartości stężenia benzo(a)pirenu w granicach 0–2175 ng/m^3 (stężenie średnie – 201.4 ng/m^3). Stężenie B(a)P przy drogach, uśrednione w sezonie letnim i zimowym, zestawiono z tłem zanieczyszczenia B(a)P dla aglomeracji miejsko-przemysłowej (pomiary sanitarne na terenie GOP-u) i miejskiej (roczna seria pomiarów w Żywcu). Wartości stężenia przy drogach okazały się wielokrotnie wyższe od wartości tła.