

Influence of Traffic on Particulate-Matter Polycyclic Aromatic Hydrocarbons in Urban Atmosphere of Zabrze, Poland

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Received: 26 August 2008

Accepted: 31 March 2009

Abstract

Exposure to polycyclic aromatic hydrocarbons (PAHs) of traffic-origin, adsorbed on PM10 and PM2.5 particulate matter in Zabrze, Upper Silesia, Poland, is investigated for summer 2005. Exposure levels for the particulate PAHs near the crossroads is about 66 ng/m³ and 44 ng/m³ for PM10 and PM2.5, respectively. The relative concentration increase of these compounds in road intersections compared to the concentration away from traffic emissions is equal to 189% and 237% for PAHs associated with PM10 and PM2.5, respectively. The fingerprint of PAHs contained in PM2.5 is distinctly different near the crossroads compared to the urban background site, while the fingerprints of PAHs contained in PM10 at both sites are almost the same.

Keywords: aerosol, PM10, PM2.5, traffic, motor vehicles, PAHs, Zabrze, Poland

Introduction

The definitive links between exposure to airborne particles and their adverse effects on health have been identified [1-8]. Despite insufficient knowledge on the exposure-effect relationship between PM10 and human health, PM10 (thoracic fraction) standards have been developed. In 1999 the European Commission included PM10 monitoring and limits imposed in the Air Quality Directive. It should be noticed, however, that the World Health Organization concluded that health risks are present at any level of particles [9]. For instance, an increase of PM10 concentration by 10 µg/m³ causes an increase in upper respiratory tract diseases to the exposed population by several percent, even in unindustrialized and not urbanized Polar Regions [10]. On the other hand, it is well documented that

health effects are more strongly associated with exposure to particulate matter less than 2.5 µm (PM2.5) than with the coarse fraction of PM10 [11, 12]. Recently, the U.S.Environmental Protection Agency has promulgated air quality standards for both PM10 and PM2.5, and is moving toward standards for PM2.5 and coarse particles PM (2.5-10). In the project entitled Clean Air for Europe (<http://europa.eu/scadplus/leg/en/lvb/l28026.htm>), the European Union is currently recommending the establishment of a PM2.5 standard. In Poland the first PM2.5 studies started in the mid 1990s [13]. At present, measurements of PM2.5 are being conducted in Kraków, Warsaw, Częstochowa and Zabrze.

Significant political and economic transformations in Poland during the last twenty years have changed the hierarchy of anthropogenic pollution sources. A reduction of emissions of air pollutants from the metallurgical and chemical industries has taken place, especially in Upper Silesia.

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Table 1. The number of vehicles (in thousands) registered in Poland in the years 1990-2004.

Type of vehicle	1990	1995	2000	2004
Passenger cars	5241	7517	9991	11975
Others (buses, lorries and road tractors, agricultural tractors, motorcycles)	3800	3669	4115	4726
Total	9041	11186	14106	16701

Although these traditional industrial as well as municipal emission sources are still very important there, the present sources are also related to the rapid increase of traffic. Table 1, prepared using governmental data (http://www.stat.gov.pl/opracowania_zbiorcze/maly_rocznik_stat/2006/10_mrs2006.pdf; http://www.stat.gov.pl/gus/45_737_PLK_HTML.htm?action=show_archive), shows the development of vehicles registered in Poland in the years 1990-2004. It can be seen that from 1990 to 2004 the number of cars purchased yearly in Poland increased almost two times.

Traffic has been recognized as a significant source of fine/respirable particles because fine and ultra-fine particles are mainly emitted by diesel engines, although other sources, including vehicle wear, street surface erosion, as well as dirt and materials falling down from vehicles, can be important.

Traffic is also one of the most important sources of polycyclic aromatic hydrocarbons (PAHs) in an urban environment. Other sources are fossil fuel combustion in energy and industrial processes, incinerators, domestic heating and oil refining [14]. PAHs are organic compounds that contain two or more fused benzene rings. Lighter PAHs are found predominantly in the vapor phase, whilst those with four or more rings are found to be mainly adsorbed in particulate matter [15-17]. Several studies have shown that the benzene-soluble fraction, containing 4- to 7-ring PAHs comes from the above mentioned sources [9].

Actually PAHs constitute the main pollutants of major concern for human health due to their mutagenic properties [9, 18]. Certain PAHs are also classified as probable human carcinogens. There is extended literature indicating their association with lung cancer [18, 19] although benzo(a)pyrene (BaP) is the only PAH that has been fully tested for carcinogenicity after inhalation, as it produced lung tumors in experimental animals. The lung

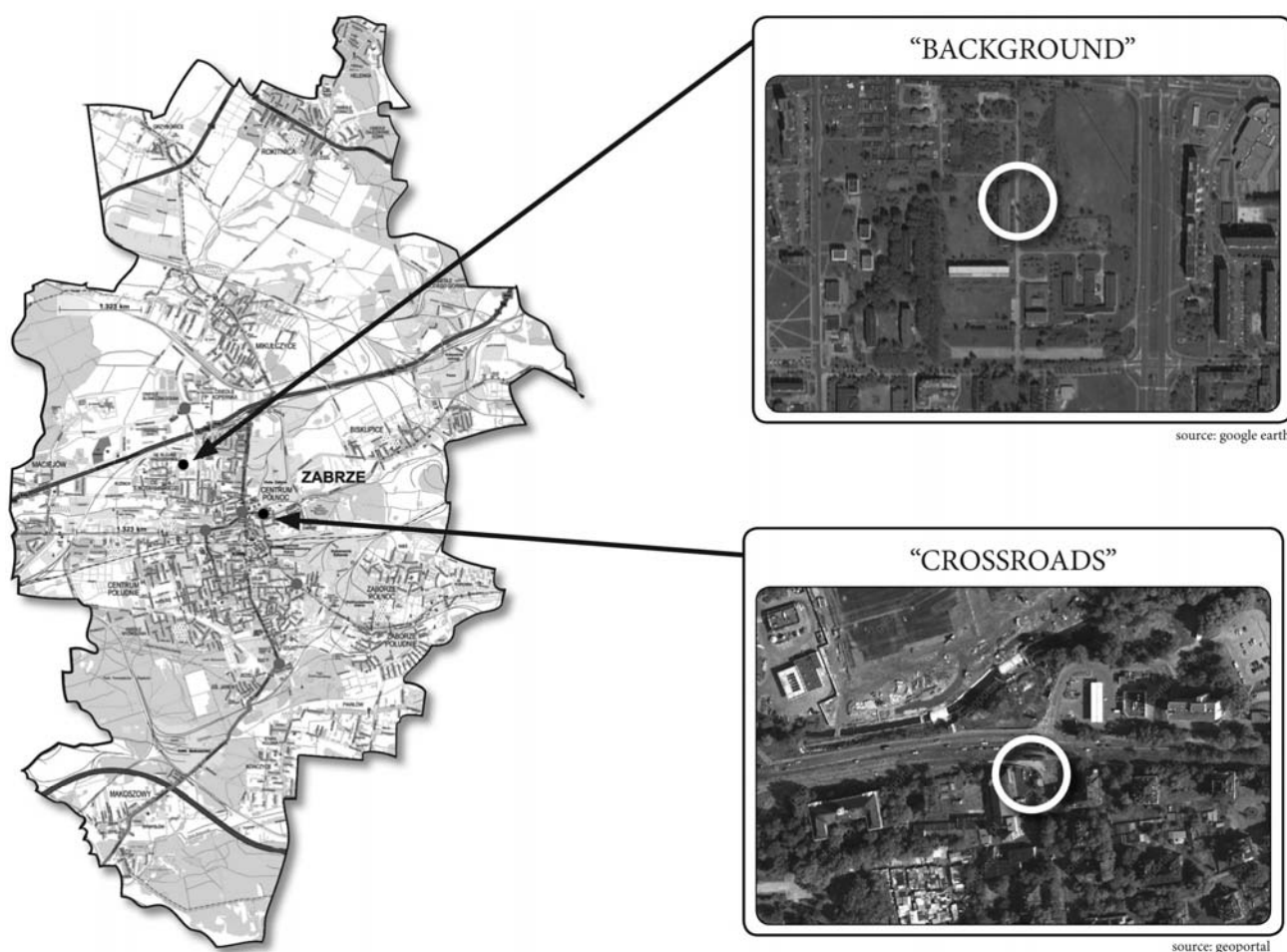


Fig. 1. Location of the "BACKGROUND" and "CROSSROADS" sampling points.

carcinogenicity of BaP can be enhanced by co-exposure to other carcinogenic substances such as cigarette smoke and asbestos.

Because benzo(a)pyrene (BaP) is the PAH most widely studied, the abundance of information on toxicity and occurrence of PAHs is related to this compound. Current annual mean concentrations of BaP in major European urban areas are in the range 1-10 ng/m³. In rural areas, the concentrations are less than 1 ng/m³ [9].

Previous studies of the airborne particle-associated PAHs in Upper Silesia, Poland, concerned both occupational exposure [20] and exposure to the general population [21, 22], but these data were obtained more than ten years ago in significantly different environmental conditions. Recently, Gryniewicz et al. [23] found substantial levels of PAHs in Gliwice, the town neighboring Zabrze, but these results do not reflect the exposure of PAHs to the inhabitants of Gliwice city and, in general, the population living in Upper Silesia. The reason is that these measurements were carried out in the vicinity of an extremely busy road (Pszczynska Street) under unusual conditions where all traffic of Highway A4, from Kraków and Katowice, was directed to Wrocław by that into Gliwice. The traffic density between 8 a.m. and 7 p.m. was about 1,400 cars/hour at that site. It is also important that trucks and special vehicles contributed about 20% during the day and more than 40% at night to total traffic density. As a result of such high traffic the average total concentration of PAHs contained in PM10 was more than 190 ng/m³ near the road and almost 120 ng/m³ at a distance of 100 m from the road.

The aim of this work is to compare the concentrations of PAHs adsorbed on PM10 as well as on the respirable particles (PM2.5) near a busy crossroad in Zabrze with their urban background concentrations. In this study the 16 PAH pollutants listed as priorities by the U.S. EPA are examined in the sampled airborne particles to obtain a 24-hour profile of PAHs near the city road and in the urban background.

Experimental Procedures

The aerosol particles were collected simultaneously at the roadside and in the urban background site in Zabrze, an industrial town in Upper Silesia, Poland, extending across a densely populated (with 2,363 people/km²) area of 80.5 km². The roadside site ("CROSSROADS") was located downtown at the crossing of two busy roads while the reference site ("BACKGROUND", about 1,400 m away), in the Institute of the Environmental Engineering of the Polish Academy of Sciences (Fig. 1), near the air quality monitoring station belonging to the regional network. This point is an official urban background site, although it can be influenced in specific circumstances by emissions from motorways and industries from other parts of the Upper Silesia Industrial Zone. Due to the fact that Upper Silesia is still a highly industrialized and polluted region, the urban background aerosol level is typically higher than background levels in other Polish and European towns. However, it should be mentioned that no industrial emissions affect

directly both these sites because there is no heavy industry and no power generation plant very close to these sampling points. Such emission sources are numerous in Zabrze but are located further away from these sites. Apart from vehicular traffic, which is an important source of airborne particles for the roadside sampling point, only domestic furnaces emitting pollutants from hard coal burning are significant emitters of particulate matter in the studied area.

To determine the traffic density at CROSSROADS during the first 25 minutes of each hour on the sampling days the cars passing the site were counted. The result, multiplied by a factor of 60/25, was assumed as the hourly traffic density for this hour. Such a period (25 min.) has been selected as a compromise between the intention to measure real average traffic density and the total burden of the researchers doing the field studies. The fact that traffic density at the CROSSROADS is changing periodically in the short period of time, due to the change of traffic light, has also been taken into consideration.

The aerosol particles were collected during the dry, warm days at low wind velocities in the period from July to September 2005, by using two MVS6D samplers (ATMOSERVICE, Poznań, Poland), certified for compliance with the CEN EN 12341 European Standard. Each sampler could collect PM10 or PM2.5, depending on the selected exchangeable sampling head, at a constant volumetric air flow of 2.3 m³/h. The sampling time was 24 hours. The samples were taken in pairs; a pair consisted of two samples of the same aerosol fraction (PM10 or PM2.5) taken simultaneously at the CROSSROADS and BACKGROUND sites. The particulate matter masses were determined gravimetrically by subtracting the initial average mass of the blank filter (Teflon for PM2.5 and glass fiber for PM10) from the final average mass of the sampled filter; the difference was then divided by the total volume of air that passed through the filter. The steps of pre- and post-sampling gravimetric mass determinations were the following: 48 hours to achieve equilibrium in the filters before weighing them at 21°C and 50%, followed by weighing them during the sampling period. The certified Mettler Toledo AG245 microbalance was used for weighing all the filters. To neutralize electrostatic charges on the filter surface the Mettler Toledo gate was applied. The PM10 particles were collected on glass fiber filters with diameter $\varnothing = 47$ mm (GF/A, Whatman Corp. USA) while respirable particles (PM2.5) were sampled on PTFE Teflon filters (Whatman Corp. USA). Both kinds of used filters meet the requirements of the standard EN 14907/2005 and PN-EN 12 341.

Days with similar meteorological patterns were selected on the basis of available weather forecasts. Basic meteorological parameters such as wind speed and direction, relative humidity and precipitation for Zabrze were taken from the web page of the Regional Inspectorate of Environmental Protection in Katowice.

Next, the filters were stored at 20°C until the time for their chemical analysis for detecting PAHs.

Multi PAH standards were purchased from Supelco. All organic solvents were of analytical grade and were supplied by Baker. To ensure that the mass of sampled

Table 2. Averaged PM_{2.5} and PM₁₀-related total PAHs and B(a)P concentrations, as well as the toxic equivalents B(a)P_{eq} in the summer season in Zabrze, Upper Silesia, Poland.

Sampling point		Concentration Σ_{16} PAHs [ng/m ³]	B(a)P [ng/m ³]	B(a)P _{eq} [ng/m ³]
BACKGROUND	PM _{2.5}	13.19±2.11	0.89±0.36	1.87
	PM ₁₀	22.68±2.36	1.22±0.14	3.15
CROSSROADS	PM _{2.5}	44.41±5.37	2.12±0.64	5.20
	PM ₁₀	65.66±6.0	3.98±0.78	7.94

aerosol particles collected on the filters was enough for the chemical analysis, the two or three daily exposed filters were grouped together. Such a group of filters was treated as one sample in the next analysis. Next, the filters were extracted ultrasonically 3 times (1.5 h) with dichloromethane. Organic extract was filtered and concentrated in a rotary evaporator system to a volume of 0.5 ml. The purification of the extract was done using solid phase extraction (SPE) using C18 octadecyl columns (Baker) by a method described elsewhere [24].

The qualitative and quantitative analysis of PAH fraction was performed by gas chromatography with a Varian chromatograph, model Saturn 3, equipped with a mass detector and a capillary column V-5MS, (30 m × 0.25 mm i.d., film thickness 0.25 μm), with helium as carrier gas. The chromatographic conditions were as follows: injector and transfer line temperatures were 310 and 300°C, respectively. The temperature program used was: 35°C for 3 min, then to 180°C at a rate of 25°C min⁻¹ and hold for 2 min, then to 200°C at a rate of 20°C min⁻¹ and hold for 2 min, then to 300°C at a rate of 2°C min⁻¹ and hold for 6.4 min, for a total duration of 70 min.

The 16 PAHs were quantified in SIM mode according to their elution orders as follows: naphthalene (Nap, m/z = 128), acenaphthylene (Ace, m/z = 152), acenaphthene

(Acen, m/z = 154), fluorene (Flu, m/z = 166), phenanthrene (Phen, m/z = 178), anthracene (An, m/z = 178), fluoranthene (Fluo, m/z = 202), pyrene (Pyr, m/z = 202), benzo(a)anthracene (BaA, m/z = 228), chrysene (Chry, m/z = 228), benzo(b)fluoranthene (BbF, m/z = 252), benzo(k)fluoranthene (BkF, m/z = 252), benzo(a)pyrene (BaP, m/z = 252), indeno(1,2,3-cd)pyrene (Indeo, m/z = 276), dibenzo(a,h)anthracene (DiBa, m/z = 278), and benzo(ghi)perylene (BgP, m/z = 276). The quantifications were performed using the external standard method.

Blank samples were also analyzed and quantified to make sure that there was no significant background interference.

Results and Discussion

The daily concentrations of PM₁₀ and PM_{2.5} for both studied sites are shown in Figs. 2 and 3. It can be seen that traffic significantly elevates both PM_{2.5} and PM₁₀ levels at the CROSSROADS site. The average measured increment of PM₁₀ concentration between CROSSROADS and BACKGROUND was 15.52 μg/m³ (44.92%). The mean concentration for PM_{2.5} was 18.64 μg/m³ and 27.45 μg/m³ for BACKGROUND and CROSSROADS, respectively. The average measured increment of PM_{2.5} concentration between the two sites was 8.81 μg/m³, (46.94%). More detailed comparison of the concentrations of PM₁₀ and PM_{2.5} near the crossroads and in the background site in Zabrze, based on a much greater set of data, has been made by Rogula-Kozłowska et al. [25] and indicated the road-side/background ratio 1.5 for both PM₁₀ and PM_{2.5}. The results obtained in Zabrze fit very well, especially the British data. Harrison et al. [26] in London and Birmingham, UK, examined the differences between road-side and corresponding urban background aerosol samples, obtained average mass increments of 11.5 μg/m³ for PM₁₀ and 8.0 μg/m³ for PM_{2.5}. It can be calculated from their data that the concentration of PM₁₀ near the street is 1.5 times higher than for background level, while the street level of PM_{2.5} is 1.6 times higher than the background one.

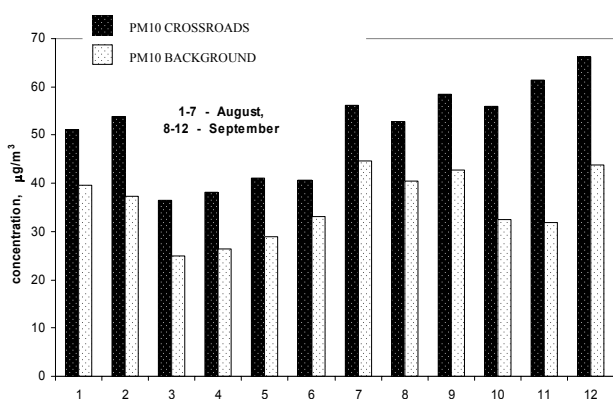


Fig. 2. Concentration of PM₁₀ at both sampling sites in the summer season.

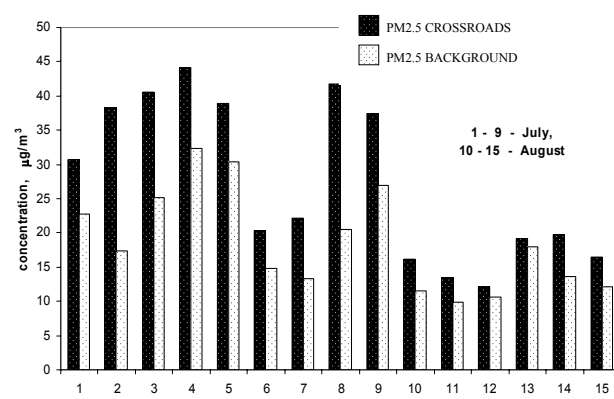


Fig. 3. Concentrations of PM_{2.5} at both sampling sites in the summer season.

The qualitative analysis of aromatic fractions separated from the airborne particle samples showed that they all contain 16 PAHs selected by the US Environmental Protection Agency for monitoring ambient air. Concentrations of PAHs in the ambient air were calculated by multiplying the determined mass contents of PAH in the collected airborne particles (ng/g) by the concentration of these particles in the air. The result, presented in Table 2, indicates that the average concentration of the sum of 16 analyzed PAHs in PM2.5 and in PM10 near CROSSROADS has been elevated 3.4 times and 2.9 times, respectively, compared to the urban background level. Similar results were found in other studies [27-32].

On the other hand, these data are significantly lower than the results obtained previously in Upper Silesia. Bodzek et al. [21] reported the average winter-summer concentration in the range 109.5-486.7 ng/m³, but they determined the content of polycyclic aromatic hydrocarbons in the total suspended particles (TSP) only. Besides, as we mentioned, their study was performed twelve years ago when the industrial emission of pollutants, generated mainly due to incomplete coal combustion, was extremely high in this region. In fact, also recently Gryniewicz-Bylina et al. [23] found very high concentrations of PAHs in PM10

near the road in Gliwice (191.56 ng/m³), but the airborne particles were collected during unusually high traffic density.

Attendance of BaP in collected airborne particles is assumed to be an indicator of ΣPAHs in the atmosphere. Its high concentration in the air indicates, as a rule, the high concentration of total polycyclic aromatic hydrocarbons. Therefore, it is important to note that the average concentrations of PM2.5-related benzo(a)pyrene was 0.89 ng/m³ at the BACKGROUND and 2.12 ng/m³ at the CROSSROADS (Table 2) sites. The average concentration of PM10-related benzo(a)pyrene was 1.22 ng/m³ in the background area and 3.98 ng/m³ at the crossroads. This result suggests that the annual mean of the BaP concentration exceeds the Polish national standard for benzo(a)pyrene contained in PM10 (1 ng/m³).

In the last column of Table 2 the equivalent benzo(a)pyrene B(a)P_{eqs} of the individual PAHs based upon their relative carcinogenic potential [33] is presented. The B(a)P_{eqs} were calculated by multiplying the concentration of the individual PAHs by the toxic equivalence factors (TEFs) proposed by Nisbet and La Goy [34]. They constituted a multiplication factor of 1 attributed to benzo(a)pyrene and assumed that this factor ranges from 0.001 to 5. It can be seen that the highest B(a)P_{eq} value equal to 7.94 ng/m³ occurred for PM10 near CROSSROADS, while the lowest value (1.87 ng/m³) was derived for PM2.5 at BACKGROUND. Comparing these calculated B(a)P_{eq} values with data from literature, it might be concluded that they were much lower than in newly industrialized Chinese cities, for example in Shanghai 15.77 ng/m³ [30]. But the same level of B(a)P_{eq} (1.91 ng/m³) was found in some Japanese cities [32].

PAH profiles (fingerprints), depending on the particle fraction and location of the sampling points, are presented in Figs. 4 and 5. The analysis of PAH profile, in particles PM10 (Fig. 4) prove that the dominant hydrocarbons during the measuring period at both sites were hydrocarbon 3-rings. The highest concentrations appeared for phenanthrene and anthracene. At the CROSSROADS the third compound was benzo(k)fluoranthene, while at the BACKGROUND benzo(a)anthracene.

Analysis of Fig. 5 shows that in the urban background air the highest concentration of the specific PAHs compound, carried by fine particles (PM2.5), was found for chrysene 2.17 ng/m³ and for phenanthrene 1.48 ng/m³. They contributed 16.5% and 11.2% to the sum of all 16 analyzed PAHs, respectively. The lowest level, equal to 0.11 ng/m³, (0.8% of the total PAHs) was observed for the dibenz(ah)anthracene. Generally, PM2.5 at the BACKGROUND site contains mainly hydrocarbons having 3 and 4 rings. They constituted 30.33 and 31.61% of the total content of the determined PAHs, respectively.

It is interesting that near the CROSSROADS the highest concentration was obtained for phenanthrene (Fig. 5). Its level increased up to 4.98 ng/m³, but its relative content remained exactly the same (11.2%). The second concentration level was for anthracene – 4.32 ng/m³ (9.7% of total

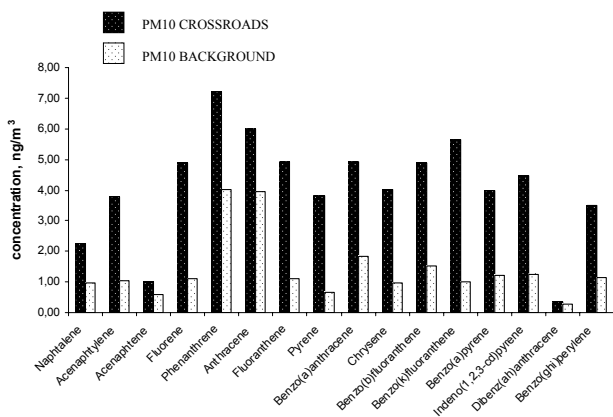


Fig. 4. Profiles of PM10-related PAHs in the summer season at both sampling sites.

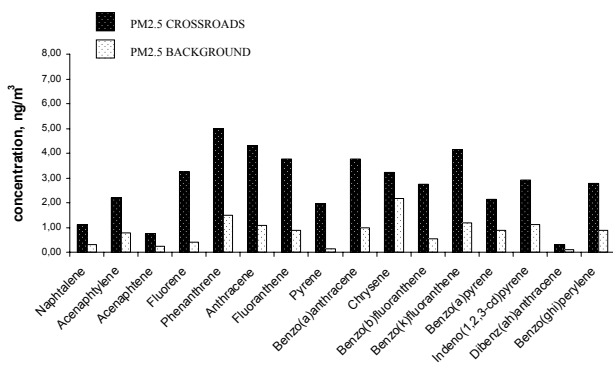


Fig. 5. Profiles of PM2.5-related PAHs in the summer season at both sampling sites.

PAHs). The lowest level was observed again for dibenz(ah)anthracene. The concentration of chrysene was higher at CROSSROADS than at BACKGROUND, but its contribution to total PAHs was lower than in the BACKGROUND (only 7.2%).

Concentration of BaP adsorbed on fine particles near CROSSROADS was 2.4 times higher than at the BACKGROUND site, but its contribution to total PAHs was 4.8%, i.e. less than in the BACKGROUND site case (6.7%). The obtained results agree well with previous data [27-32] where ΣPAHs ranged between 2.5 ng/m³ and 714 ng/m³, while the BaP level ranged from 0.18 ng/m³ to 28.7 ng/m³ and BaP/ΣPAHs was from 1.5% to 14.33%.

Conclusions

Daily PM₁₀ and PM_{2.5} samples were collected simultaneously near the CROSSROADS site and in the site representing the urban background in Zabrze, Upper Silesia, Poland. Selected samples were analyzed for 16 PAH species by GC-MS.

The obtained results indicate that the general population living in Zabrze is exposed in the summer to the particulate phase PAHs reaching the mean level of about 23 ng/m³ and 13 ng/m³ for the PAHs adsorbed on PM₁₀ and PM_{2.5}, respectively.

Near the CROSSROADS the concentration levels of PAHs are elevated up to about 66 ng/m³ and 44 ng/m³ for PM₁₀ and PM_{2.5}, respectively; this means that the relative increase of these compounds due to traffic emissions is 189% and 237% for PAHs adsorbed on PM₁₀ and PM_{2.5}, respectively.

The fingerprint of PAHs detected in fine particles was distinctly different near CROSSROADS compared to the BACKGROUND site, while the fingerprints of PAHs contained in PM₁₀ at both sites were almost the same.

Acknowledgements

Our work was founded within the framework of grant No. 3 T09D10628 financed in 2005-06 by the Polish Government, and was partially supported by grant No. N207 068 31/3307 from the Polish Ministry of Science and Higher Education.

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