

Health hazards from polycyclic aromatic hydrocarbons bound to submicrometer particles in Gliwice (Poland)

Barbara Kozielska^{1,*}

¹Silesian University of Technology, Faculty of Energy and Environmental Engineering, Department of Air Protection, 22B Konarskiego St., 44-100 Gliwice, Poland

Abstract. Even though there is an eminent reduction of emission of pollution, there is still a serious danger to health caused by atmospheric aerosol. Studies show that particles with aerodynamic diameters not greater than 1 μm (PM1) and 2.5 μm (PM2.5) are especially dangerous as they have the ability to easily penetrate into the alveoli and then into the circulatory system. What is more, absorbed on their surface for example persistent organic compounds, among them polycyclic aromatic hydrocarbons (PAHs) they have carcinogenic and mutagenic effects. The paper presents concentrations polycyclic aromatic hydrocarbons bound to submicrometer particles (PM1). Samples were collected at the point in southern Poland (Gliwice) with a low volume sampler. Afterwards, they were chemically analysed with a gas chromatograph equipped with a flame ionization detector (Perkin Elmer Clarus 500). The average concentration values of the PAH sum (ΣPAH) and particular PAHs; the percentages of carcinogenic PAHs in total PAHs ($\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$); toxic equivalent (CEQ); mutagenic equivalent (MEQ); TCDD-toxic equivalent (TEQ). Their high values express the significance of health hazard from PM1 and PM1-bound PAH in Silesia Region.

1 Introduction

Among the atmospheric pollutants, a particulate matter with an aerodynamic diameter of equal or less than 10 μm (PM10) has the most adverse effects on the human health [1, 2]. Dust particles PM1 (aerodynamic diameter $\leq 1 \mu\text{m}$) and PM2.5 (aerodynamic diameter $\leq 2.5 \mu\text{m}$) are especially dangerous as they have the ability to easily penetrate into the alveoli and then into the circulatory system [3-5]. According to the World Health Organization [6] prolonged exposure to PM2.5 particulate results in an increase in the incidences of lower respiratory tract diseases, cardiovascular disease, shorter life expectancy, and increases the likelihood of lung cancer [5]. Epidemiological studies have shown that there is an association between total mortality, cardiovascular mortality, respiratory mortality, hospital admissions, and ambient PM10 level [7]. Apart from the described health consequences, the absorption of dust particles by the human organisms

* Corresponding author: barbara.kozielska@polsl.pl

constitutes a significant threat with regard to its various chemical compounds that usually have toxic, carcinogenic and mutagenic effects [3, 8-10]. In addition, some components adsorbed on fine dust particles, can cause allergic reactions. Particularly dangerous are toxic metals and their compounds, sulphates, persistent organic compounds with PAHs among them and many others.

PAHs can penetrate into the body via the inhalation route through the respiratory system, via the digestive system - along with food intake, and through the skin [11]. PAHs are inhaled in the form of vapour or together with dust particles they are associated with and/or on which they are adsorbed. Depending on the fraction, dust particles may settle in different sections of the airways. The smallest particles get into the alveoli, where substances adsorbed can go into the bloodstream and spread throughout the body.

PAHs have also the ability to accumulate in adipose tissue due to their lipophilic properties. The measure of the PAHs activity level is the ability of their radical oxidation. As a result of metabolic changes in the body, PAHs form oxides of arenes, phenols, diols, and quinones [3, 8, 12-15]. When PAHs are metabolized by specific enzyme systems to epoxides, metabolites have the ability to attach to DNA, RNA, and proteins [15, 16]. Such combinations are the cause of cancer formation, inhibition and errors in protein replication, transcription and biosynthesis [3, 13, 17, 18].

Until now, however, it has not been clearly established whether individual PAHs or their sum are responsible for the formation of neoplastic changes [19-21]. It is particularly difficult to assess the impact of PAHs adsorbed on particulate matter in the air, because individual hydrocarbons can react with other components emitted from incomplete combustion processes, causing an increase or weakening of their carcinogenic properties.

The US EPA recognizes sixteen PM-bound PAH as priority pollutants (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[ah]anthracene and benzo[ghi]perylene).

The goal of the present study was to investigate the concentrations of PM1-bound phase of these 16 PAH in Gliwice - a city of a medium size in southern Poland. The level of the health hazard to humans from the mixture of PAH (i.e., equivalents: toxic – TEQ, mutagenic – MEQ, and cancerogenic (TCDD-2,3,7,8-Tetrachlorodibenzo-p-dioxin – CEQ) and $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$ were also determined.

2 Materials and methods

The 24-hr samples of PM1 were collected in April–June in Gliwice (Fig.1). The air temperature in the measuring period was between 7-20°C (av. 15°C). At a measuring site PM1 was sampled using Atmoservice MVS. It was sampled at an air flow rate of 2.3 m³/hr onto quartz fibre filters which earlier were conditioned in a weighing room. The weight of PM1 collected was determined gravimetrically (Radwag microbalance, resolution 1 µg).

The PM1 was extracted from filters with dichloromethane (DCM) in an ultrasonic bath. For selective purification, the solid phase of samples was extracted (SPE) in the C-18 packed columns. Finally, the PAH extracts were thickened to 0.1 cm³. The SPE extracts were analysed with the Clarus 500 Perkin Elmer gas chromatograph, equipped with a Restek RTX-5 capillary column and flame ionization detector (FID).

The extraction, the chromatography technique, and validation parameters are described in detail in [22, 23].

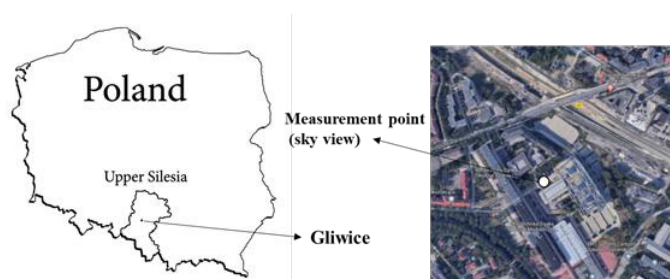


Fig. 1. Location of the measurement point in Gliwice (Map data: 2018© Google, ORION-ME).

The cumulative health hazard from a mixture of PAH can be assessed by using the TEQ, MEQ, or CEQ equivalents relative to the toxicity or mutagenicity of BaP, or to the carcinogenicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin, respectively. TEQ, MEQ, and CEQ were computed as linear combinations of the PAH concentrations and respective equivalence factors: TEF, MMC, TCDD-TEF (Table 1). Additionally, the proportion of the sum of the carcinogenic PAH ($\sum\text{PAH}_{\text{carc}}$) concentrations to the sum of the concentrations of the 16 determined PAH ($\sum\text{PAH}$) was computed.

Table 1. The value of toxicity equivalence factors TEF [24], mutagenic equivalence factors MMC [25], carcinogenic equivalence factors TCDD-TEF [26] for PAH and the carcinogenic PAH (+) [27].

Compound name	Abbrev.	TEF	MMC	TCDD-TEF	Carc
Naphthalene	Na	0.001			
Acenaphthylene	Acy	0.001	0.00056		
Acenaphthene	Ace	0.001			
Fluorene	Flu	0.001			
Phenanthrene	Ph	0.001			
Anthracene	An	0.01			
Fluoranthene	Fl	0.001			
Pyrene	Py	0.001			
Benzo[a]anthracene	BaA	0.1	0.082	0.000025	+
Chrysene	Ch	0.01	0.017	0.00020	+
Benzo[b]fluoranthene	BbF	0.1	0.25	0.00253	+
Benzo[k]fluoranthene	BkF	0.1	0.11	0.00487	+
Benzo[a]pyrene	BaP	1	1	0.000354	+
Indeno[1,2,3-cd]pyrene	IP	0.1	0.31	0.00110	+
Dibenzo[ah]anthracene	DBA	5	0.29	0.00203	+
Benzo[ghi]perylene	BghiP	0.01	0.19		

3 Results and discussion

The average concentration of PM1 during spring in Gliwice was $23.9 \mu\text{g}/\text{m}^3$ (range $9.9 - 73.7 \mu\text{g}/\text{m}^3$) (Table 2). This is the value higher than the ones noted during a non-heating season in Katowice, where the mean PM1 concentrations were $18.4 \mu\text{g}/\text{m}^3$ and $20.8 \mu\text{g}/\text{m}^3$ at traffic point and urban background measurement point respectively and in Złoty Potok regional background measurement point where value $10.3 \mu\text{g}/\text{m}^3$ was observed [23]. Also in Warsaw summer concentration of PM1 were a lot lower and comprised between $5.7 \mu\text{g}/\text{m}^3$ to $22.6 \mu\text{g}/\text{m}^3$ (average $11.1 \mu\text{g}/\text{m}^3$) [28]. When compared to the other places in the world, these concentrations were substantially high. For example, summer concentrations of PM1 observed in Šlapanice and Brno (Czech Republic) in 2010 were

11.6 $\mu\text{g}/\text{m}^3$ and 12.9 $\mu\text{g}/\text{m}^3$, respectively [29], in Venice-Mestre (Italy) in the year 2014 – 6.4 $\mu\text{g}/\text{m}^3$ [30]. In Canoas (Brasil) Agudelo-Castañeda and Teixeira measured even lower PM1 concentrations (8.6 $\mu\text{g}/\text{m}^3$) [31].

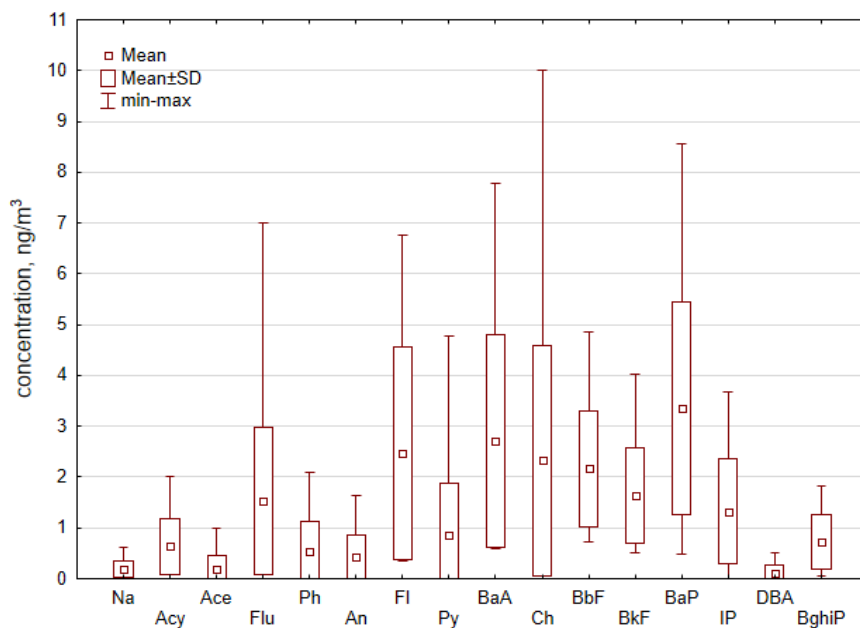


Fig. 2. The mean, mean±standard deviation, minimal, maximal concentrations of particular PM1-bound PAHs in the air in Gliwice during whole measurement period (ng/m^3).

In Gliwice average concentration of the 16 PAH sum (ΣPAH) was 21.2 ng/m^3 with the maximum amounting 52.4 ng/m^3 (Table 2). This average is comparable to the one noted in Złoty Potok in a non-heating – 18.6 ng/m^3 , and approx. 2.6 times lower than in Katowice at traffic point – 56.0 ng/m^3 [23]. One should mention that in summer average concentrations of ΣPAH in the other sites in Poland or Europe are lower. For example average concentrations of PM1-bound PAHs in Zabrze was 3.5 ng/m^3 [37], in Brno and Šlapanice (Czech Republic) were 1.7 ng/m^3 and 1.5 ng/m^3 , respectively [29], and in Virolahti (Finland) 1.8 ng/m^3 [32] alike. A bit lower ΣPAH concentrations in the summer than in winter can be caused by high ambient insolation, air temperatures and ozone concentrations favorable to the intense PAH conversion, and to the evaporation of light PAH from PM and their staying in gaseous form in the air [33]. The mean concentrations of 16 PAHs were in the decreasing order BaP > BaA > Fl > BbF > BkF > Flu > IP > Py > BghiP > Acy > Ph > An > Ace > Na > DBA (0.11–3.35 ng/m^3) (Fig 2). In Gliwice BaP, BaA, Fl, BbF and BkF constituted 61.6% of the ΣPAH mass.

Among investigated compounds, BaP is the one of a great interest considering its well known carcinogenic and mutagenic properties. The concentration of PM1-bound BaP was in the range of 0.49 to 8.57 ng/m^3 (average 3.35 ng/m^3) which was the highest values among the whole PAHs under interest (Table 2). For the examined point BaP was 4.7%–20.5% (average 15.9%) in ΣPAH over the whole measurement period. The ambient concentration of the PM10-bound BaP has the formal limit that should not be exceeded; the yearly permissible ambient concentration of PM10-bound BaP is 1 ng/m^3 [34]. The high BaP concentrations are observed in Poland not only in the heating season but also in the remaining part of the year [22, 23, 35]. Such a situation was not the case in other European regions where concentrations in summer are substantially lower e.g in Czech Republic,

Spain, Portugal (Table 3). On the other hand the summer concentrations of PM1-bound BaP in Chennai City (India) was similar to the Polish ones or even higher (6.2 ng/m³ – 25.6 ng/m³) [36].

Table 2. Mean concentrations along with ±standard deviation (SD), min, max of PM1, ΣPAH, BaP and TEQ, MEQ, CEQ, PAH_{canc}/ΣPAH in the air in Gliwice.

	Mean±SD	Min	Max
PM1, □g/m ³	23.921±14.94	9.873	73.723
ΣPAH, ng/m ³	21.158±11.58	8.870	52.446
BaP, ng/m ³	3.349±2.08	0.487	8.566
TEQ, ng/m ³	4.753±3.24	1.021	13.156
MEQ, ng/m ³	4.912±2.94	1.308	12.129
CEQ, pg/m ³	16.863±9.55	5.751	40.641
PAH _{canc} /ΣPAH	0.630±0.08	0.507	0.795

Table 3 presents BaP concentrations and the following indicators of the exposure to the PAH mixture: toxic equivalent (TEQ), mutagenic equivalent (MEQ), carcinogenic equivalent (CEQ), and share of seven PAHs, with carcinogenic influence revealed in a table 1 in the ΣPAH. Additionally, the measurements results from other locations, taken from the publications quoted in Table 3, are shown.

Table 3. The concentration of BaP, equivalents TEQ, MEQ, CEQ and the share of carcinogenic PAH in ΣPAH for PM1-bound PAH in Poland and other locations in non-heating season or summer.

Location	BaP	TEQ	MEQ	CEQ	PAH _{canc} /ΣPAH
	ng/m ³			pg/m ³	
Gliwice - this study	3.35	4.75	4.91	16.86	0.63
Katowice, UB [23]	2.97	5.29	4.23	13.71	0.59
Katowice, traffic point [23]	4.73	15.46	6.45	20.42	0.55
Złoty Potok, RB, [23]	2.46	4.50	4.29	13.80	0.50
Zabrze, UB [37]	0.17	0.62	0.38	3.33	0.43
Katowice, city center [35]	1.48	2.06	1.69	96.1	0.62
Brno, Czech Republic, large city [29] Bląd! Nie zdefiniowano zakładki.]	0.15	0.45	0.29	0.83	0.54
Šlapanice, Czech Republic, small town [28]	0.15	0.35	0.27	0.79	0.59
Madrid, Spain, UB [38]	0.02	0.10	0.05	0.26	0.57
North of Portugal [39]	0.05	2.45	0.29	1.69	0.70
	0.12	2.69	0.42	2.20	0.52

UB - urban background, RB - regional background

In these studies, the mean TEQ, MEQ and CEQ were 4.75 ng/m³ (range: 1.02 – 13.16 ng/m³), 4.91 ng/m³ (range: 1.31 – 12.13 ng/m³) and 16.89 pg/m³ (range: 5.75–40.64 pg/m³), respectively (Table 2). They were unquestionably high and comparable to the ones obtain in [23] except the traffic point in Katowice, where TEQ were three times higher than observed during this investigations. In the European cities, the TEQ, MEQ, CEQ values were lower than in Gliwice (Table 3).

The values of TEQ, MEQ, CEQ obtained for Asian cities (e.g., Chennai City and Delhi in India) were as high as or higher than those observed in Poland. For example, the values of TEQ, MEQ, CEQ observed for Chennai City in the urban area in summer were 44.3 ng/m³, 77.4 ng/m³ and 246.7 pg/m³, respectively [23, 36].

Also the more general tendency can be pointed - regardless of the season these values are generally higher in Poland than, in the European cities and similar or lower Asian cities.

The sum of seven carcinogenic PAHs concentrations were in the range of 5.04 ng/m³ to 33.18 ng/m³. The average value of $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$ was 0.63. In other regions of Silesia this value is usually lower (Table 3).

4 Summary and conclusions

The PM₁ samples were collected from April to June. This period excluded the heating season, when in Gliwice occurs intensive emissions of PM and PAH from domestic coal-fired stoves and heating plants, coal-fired as well. It also didn't include summer season which is characterized by a strong insolation, high ambient temperatures and ozone concentrations and the presence in the atmosphere other compounds favorable to the PAH transformations. In these conditions, PAHs three and less aromatic rings have the tendency to evaporate from PM surface into the air in the gaseous form. Despite this common tendency, average concentrations of PM₁ and $\sum\text{PAH}$ were unexpectedly high reaching in the air in Gliwice area values 23.92 µg/m³ and 21.16 ng/m³, respectively. In the same time mass percentage of four- and five-ring PAHs in $\sum\text{PAH}$ was up to 77%.

High percentage of BaP in the $\sum\text{PAH}$ (4.7% – 20.5%) and high ambient concentrations of the PM₁-bound BaP may pose a serious threat to the inhabitants of the City. Also values of subsequent equivalents TEQ (4.47 ng/m³), MEQ (4.91 ng/m³), CEQ (16.86 pg/m³) indicate the serious health hazard for humans. They are higher than observed in other places in Poland and Europe, and similar or lower than noted in Asian cities during comparable measurement periods.

The concentrations proportion of the $\sum\text{PAH}_{\text{carc}}$ to $\sum\text{PAH}$ was 0.63. This value belongs to the highest noted in the world in a summer period (the closer this value is to 1, the more hazardous $\sum\text{PAH}$ to human's health).

Generally, the health hazard from the 16 US EPA PM₁-bound PAHs in Gliwice is greater than in majority of cities where such hazard was evaluated. On the base of other available investigations [22, 23] one can assume with a high possibility that this threat will be much higher during the heating seasons.

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