

*Original Research*

# Suspended PM<sub>10</sub> Particles in an Urbanized Coastal Zone (Tricity Agglomeration, Poland) – a Possible Source of PAHs for Gulf of Gdańsk Sediments

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## Abstract

Polycyclic aromatic hydrocarbons (PAHs) were determined by GC/MS in suspended airborne PM<sub>10</sub> particles collected at 4 sites in the Tricity agglomeration of northern Poland. This industrialized and densely populated area with distinctly seasonally variable weather conditions is located on the southern Baltic Sea coast. Daily concentrations of  $\Sigma 12$ PAHs ranged from ~0.04 to ~60 ng/m<sup>3</sup> in the samples analyzed. The levels of particulate PAHs showed distinct seasonal changes throughout the year, with higher concentrations in the heating season. The elevated PAH concentrations recorded during the heating season were most probably due to greater emissions of PAHs from heating systems, as well as meteorological factors that restrict the dispersion of these pollutants in the atmosphere and enhance their persistence. Benzo(a)pyrene was confirmed as being a good marker of total PAHs associated with PM<sub>10</sub> particles, and concentrations of this compound during the heating season often exceeded 1 ng/m<sup>3</sup> – the threshold established in Directive 2004/107/EC. Mass concentrations of PM<sub>10</sub> particulate matter were not strongly correlated with PAH concentrations. Meteorological factors like temperature and wind speed strongly influence the distribution of particulate PAHs in the study area, but the former parameter is clearly linked to seasonal emission patterns. It has been found that atmospheric input is an important source of PAHs deposited in recent Gulf of Gdańsk sediments.

**Keywords:** PAHs, air particulate matter, PM<sub>10</sub>, Tricity agglomeration

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrophobic pollutants of great concern owing to their persistence, toxicity, and widespread occurrence in the environment [1]. PAHs always occur in the environment as complex multicomponent mixtures. Certain PAH compounds have been classified as carcinogenic to animals and

probably carcinogenic to humans [2]. As molecular weight increases, PAH carcinogenicity increases, whereas their acute toxicity decreases [3].

PAHs are especially ubiquitous in the atmosphere as they arise mainly from the incomplete combustion of organic materials being formed through pyrosynthesis and pyrolysis. Several hundred PAHs have been detected in the air, but only a dozen or so are routinely determined [4]. The majority of these pollutants are derived from anthropogenic sources (domestic, mobile, industrial, and agricultural

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emissions) [3], but natural processes like volcanic eruptions, forest, grass, and bush fires, also produce airborne PAHs.

The fate of PAHs in the atmosphere is governed both by their physicochemical properties (e.g. molecular mass, volatility, solubility in water) and by environmental factors (e.g. temperature, humidity, precipitation, wind, solar radiation, type and concentration of particles, other pollutants) [5, 6]. Overall, high molecular weight PAHs (e.g. benzo(a)pyrene) that exhibit the highest carcinogenic potency tend to be associated almost exclusively with particulate matter [3]. Therefore, studies of particulate PAHs are of great importance to environmental and health scientists. PAHs in air are usually determined in particles of diameter  $<10\ \mu\text{m}$  ( $\text{PM}_{10}$ ), as they are mainly associated with this fraction, which can be retained in the human respiratory tract [7]. PAHs bound to fine particles (esp.  $< 2.5\ \mu\text{m}$ ) can be transported over long distances and are removed from the atmosphere by wet and dry deposition or transformed *via* photooxidation and other chemical reactions [5].

Because of their adverse health effects on humans, PAHs are regarded as priority air pollutants, and many countries and international organizations have established non-mandatory air quality standards for these compounds, mainly for benzo(a)pyrene, which is the most intensively studied PAH [3].

Poland is considered a major contributor to total benzo(a)pyrene emissions in Europe [8]. The aim of this study was to assess PAH pollution levels in outdoor airborne  $\text{PM}_{10}$  particles collected at selected sites from the Tricity area, and to find relationships between PAH levels in  $\text{PM}_{10}$  particles and meteorological factors there. This densely populated area is subject to strong anthropogenic stress. Finally, the influx of these pollutants into Gulf of Gdańsk sediments was estimated.

## Material and Methods

This section presents data on materials and methods that were used in this work. The section was divided into four subsections that provide descriptions of the study area, sampling procedures, details of the analytical procedure, and statistical methods applied.

### Study Area

Three cities in northern Poland (NE Pomeranian Voivodeship) – Gdańsk, Sopot, and Gdynia – form a conurbation known as ‘Tricity’ (in Polish “Trójmiasto”). The Tricity together with adjacent towns and villages forms a larger agglomeration called the Gdańsk Metropolitan Area covering an area of  $\sim 1,400\ \text{km}^2$  [9]. Located on the coast of the Gulf of Gdańsk (southern Baltic) near the mouth of the Wisła River and surrounded by forests, this area is inhabited by over 1 million people. There is heavy motor traffic in the area. Gdańsk and Gdynia are both important Polish industrial centers where shipbuilding and shipping play important roles and their ports are important international hubs. Other major branches of industry in this area include

petroleum refining, electricity and heat generation, fertilizer manufacture, and food processing. The Tricity attracts many visitors throughout the year, especially in summer. Sopot, situated between Gdańsk and Gdynia, is a popular seaside and health resort.

The Tricity is situated in a temperate climate zone, intermediate between maritime and continental climates, where tropical air masses meet arctic air. Meteorological data show a high temporal year-to-year and day-to-day variability in weather conditions [10]. Local morphological conditions strongly impact the climate at particular sites. Because of the proximity of the Baltic Sea, winters in this area are milder and summers are cooler than in regions inland. The prevailing winds in this region are westerlies and south-westerlies, and mean monthly temperatures are below  $18^\circ\text{C}$  in July and drop below  $0^\circ\text{C}$  in winter. Annual precipitation is mostly around 550 mm, the highest monthly amounts being recorded in July and August.

Most of the air pollution in the Tricity is due to the combustion of fossil fuels in heat- and power-generating plants, small boiler-rooms, and motor vehicle emissions [11].

### Sampling Procedure

Samples of airborne particulate matter with an aerodynamic diameter smaller than  $10\ \mu\text{m}$  ( $\text{PM}_{10}$ ) were obtained from the ARMAAG Foundation (Fundacja Agencja Monitoringu Regionalnego Atmosfery Aglomeracji Gdańskie), the Agency of Regional Air Quality Monitoring in the Gdańsk Metropolitan Area.  $\text{PM}_{10}$  samples were collected at four urban stations belonging to the air quality monitoring network in the Tricity: AM3 – Gdańsk- Nowy Port, AM6 – Sopot, AM4 – Gdynia-Pogórze, AM10 – Gdynia-Port (Fig. 1). Aerosol sampling was carried out using a continuous particulate analyzer (FH 62 I-R, Eberline Instruments GmbH) at a height of 4 m above ground level and operated at a volumetric flow rate of  $1\ \text{m}^3/\text{h}$ . Samples were collected in 24-hour cycles on GF 10 glass fibre filters for 7 consecutive days (including weekends) during each campaign. Altogether, 42  $\text{PM}_{10}$  samples were taken during the heating (28 samples) and non-heating (14 samples) seasons. The characteristics of the sampling stations are given in Table 1.  $\text{PM}_{10}$  concentrations and meteorological parameters (temperature, relative humidity, solar radiation, wind speed and direction; KRONEIS GmbH) were also monitored at these sites. Wind directions were categorized according to 8 cardinal points: N, NE, E, SE, S, SW, W, NW.

### Extraction, Clean-up and Analysis of PAHs

Samples of airborne particulate matter were sonication-extracted with acetonitrile ( $5 \times 20\ \text{ml}$ ), and combined acetonitrile fractions were evaporated to dryness in a rotary evaporator. The raw extract was cleaned up by thin-layer chromatography (TLC). The TLC chromatogram was developed in the acetone:hexane (4:7 v/v) system. The fraction of PAHs detected on the TLC plate under UV light was extracted with acetonitrile.

The extracts dissolved in isooctane were analyzed by gas chromatography with an ion trap mass spectrometer detector (Varian GC/MS, Saturn 2100T). The carrier gas was helium. The extract was injected in splitless mode. The injector temperature was 310°C. Nonpolar fused silica capillary columns CP-Sil 8 CB Low Bleed/MS and VF-5ms (5% phenyl-substituted dimethylpolysiloxane phase, 0.25 mm ID×60 m, 0.25  $\mu$ m film thickness) were used. The oven temperature was held isothermally at 120°C for 2 min, then programmed at 30°C/min to 240°C, held for 4 min, next programmed at 25°C/min to 275°C, held for 19 min, programmed at 5°C/min to 280°C, and finally held for 15 min. The temperature of the ion trap was 210°C and the transfer line was kept at 280°C. 12 individual PAH compounds were determined: phenanthrene (Phen), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benzo(a)anthracene (B(a)A), chrysene (Chry), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), indeno(1,2,3-cd)pyrene (Ip), dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene (Bper). PAHs were quantified by an external standard method. Standard PAH solutions were purchased from LGC Promochem. The analytical procedure was validated on the basis of certified reference material IAEA-159.

### Statistical Analysis

The results were subjected to statistical analysis using Microsoft Office Excel and STATISTICA 6.0 software. Data were mostly normally distributed (Shapiro-Wilk test), and Pearson correlation (parametric) analysis was therefore applied to determine the strength of the linear relationship between variables. Correlation coefficients with  $p < 0.05$  were considered significant. Differences between

the arithmetic means of various groups of variables were regarded as significant for  $p < 0.05$  using the relevant statistical tests.

## Results and Discussion

The section presents results of this work and their interpretation. The section was divided into six subsections that deal with PAH concentrations in airborne  $PM_{10}$  particles. Correlations of PAHs with meteorological data were presented. In addition, atmospheric input of PAHs to the Gulf of Gdańsk was estimated.

### PAH Levels

Daily concentrations of total ( $\Sigma 12$ PAHs) and individual PAH compounds in suspended  $PM_{10}$  airborne particulates expressed as ng per air volume ( $ng/m^3$ ) are reported in Table 2. Total PAH contents varied over a broad range, depending on site and season.  $\Sigma 12$ PAHs concentrations averaged for 24-hour cycles were found to vary from  $\sim 0.04$  to  $\sim 60$   $ng/m^3$  in the samples.

The  $PM_{10}$  samples from the Tricity can be classified as moderately polluted compared with the extensive set of worldwide data listed in Table 3. However, direct comparisons with literature data should be undertaken with caution because of the specific locations of particular sites, and the differences in sampling methodology and analytical techniques employed by other authors [12]. It was found that distinctly higher maximum PAH levels were recorded in many Chinese urban areas. On the other hand, far lower PAH concentrations than in the Tricity were reported for polar regions.

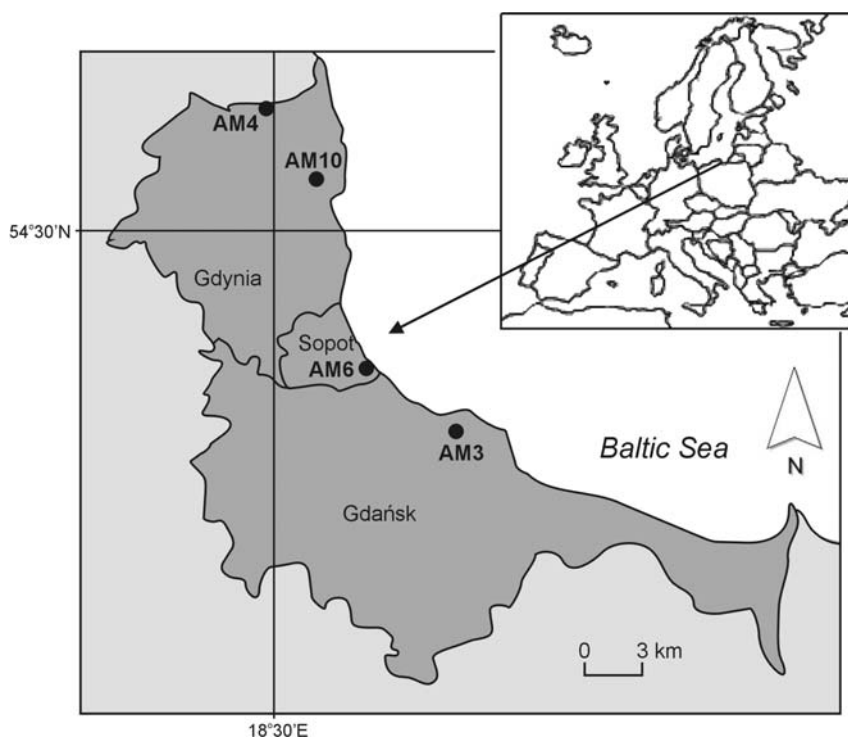


Fig. 1. Study area.

Table 1. Characteristics of the sampling stations.

Station	Coordinates	Location	Site description	Sampling period	PM <sub>10</sub> [ $\mu\text{g}/\text{m}^3$ ]	Meteorological parameters				
						t [°C]	RH [%]	SR <sup>a)</sup> [ $\text{W}/\text{m}^2$ ]	WS [m/s]	WD <sup>b)</sup>
AM4	54°33'39"N 18°29'36"E	Gdynia-Pogórze, Porębskiego, 70m ASL	residential area, high-rise buildings, in the vicinity of green areas, ~200 m from a major road, ~1.4 km from a combined heat and power plant	26.03.2004 – 1.04.2004 18.06.2004 – 24.06.2004	27.1 <sup>c)</sup> (11.2-48.1) <sup>d)</sup> 22.6 (15.9-33.9)	4.5 (1.7-6.5) 14.8 (11.7-18.0)	82.9 (73.6-92.6) 78.7 (67.3-90.6)	2,447 (580-4,402) 4,651 (2,817-5,991)	1.9 (0.9-4.2) 1.8 (1.6-2.3)	NE, SW, W, NW (each ~20%) SE (38%) S (31%)
AM10	54°31'31"N 18°32'11"E	Gdynia-Port, Wendy, 4m ASL	industrial area, close to railway lines, in the vicinity of Gdynia Harbour, ~2.5 km from Gdynia Container Terminal	26.03.2004 – 1.04.2004 18.06.2004 – 24.06.2004	45.1 (21.0-85.0) 47.3 (25.9-94.2)	3.6 (1.5-6.1) 14.4 (11.6-17.8)	78.0 (68.0-84.7) 77.9 (65.7-89.4)	2,447 (580-4,402) 4,651 (2,817-5,991)	2.2 (1.2-3.4) 2.1 (1.7-3.2)	W (43%) NW (22%) E (29%) SW (22%) S (19%)
AM6	54°25'54"N 18°34'47"E	Sopot-Dolny Taras, Bitwy pod Płowcami, 5m ASL	in the vicinity of green areas, ~180 m from a major road, ~0.45 km from the seashore	17.01.2007 – 23.01.2007	14.1 (8.5-19.4)	5.1 (-0.8-8.3)	83.0 (74.1-89.1)	519 (219-945)	3.0 (2.0-4.4)	SW (46%) W (24%)
AM3	54°24'03"N 18°39'27"E	Gdańsk-Nowy Port, Wyzwolenia, 3 m ASL	residential area, high-rise buildings, ~100 m from a road, in the vicinity of green areas, ~3 km from a combined heat and power plant, ~0.9 km from the seashore	17.01.2007 – 23.01.2007	17.2 (11.0-26.3)	3.5 (-1.9-6.5)	-	519 (219-945)	-	-

a) data from site AM6, sum of all SR values from daily measurements

b) dominant wind directions indicated

c) mean value

d) range

Abbreviations: PM<sub>10</sub> – concentration of airborne PM<sub>10</sub> particulate matter, t – temperature, RH – relative humidity, SR – solar radiation, WS – wind speed, WD – wind direction, ASL – above sea level



### Temporal Trends

At stations AM4 (Gdynia-Pogórze) and AM10 (Gdynia-Port), PAH contents were distinctly higher in samples taken in March/April 2004 than in June 2004 (Table 2). Mean  $\Sigma$ 12PAHs concentrations for weekly series at station AM4 were equal to 19.7 ng/m<sup>3</sup> in the heating season and only 2.6 ng/m<sup>3</sup> in the non-heating one, and they were statistically different (Kolmogorov-Smirnov test –  $p < 0.05$ ). Similar temporal trends were recorded for site AM10 (15.5 ng/m<sup>3</sup> – winter; 2.6 ng/m<sup>3</sup> – summer; statistically significant differences – Cochran-Cox test –  $p < 0.05$ ). Weekly means of  $\Sigma$ 12PAHs concentrations recorded during the 2004 heating season at stations AM4 and AM10 were not statistically different (Student's t-test –  $p > 0.05$ ), as was the case at sites AM6 and AM3 in 2007. Although the highest concentrations of  $\Sigma$ 12PAHs in airborne particulate matter were reported in the heating season, there were significant changes in PAH levels for particular sampling campaigns, e.g. the  $\Sigma$ 12PAHs concentration at station AM3 was found to be 60 ng/m<sup>3</sup> on 23<sup>rd</sup> January 2007, but only 5 ng/m<sup>3</sup> on 19<sup>th</sup> January 2007. Total PAH concentrations in daily samples during each campaign do not reflect the weekly variations in vehicular traffic volume because  $\Sigma$ 12PAHs contents were in general similar during weekdays and at the weekend.

The distinctly higher PAH contents in the air particles found in the heating season can probably be attributed to the high intensity of emissions from the domestic low-energy combustion of solid fuels (coal, wood). In addition, at low temperatures car engines emit more PAHs because of the less efficient combustion of fuels (the 'cold start effect'). Furthermore, lower doses of solar radiation reduce the rate of photochemical transformation, and low temperatures favor the enhanced condensation of these compounds in the gas phase and its sorption to particulate matter [3]. The higher PAH concentrations noted during the heating season also result from the reduced dispersion of pollutants during cold periods because of the lower mixing heights in comparison with the non-heating season [13].

Other authors recognized similar seasonal trends. By using artificial neural networks, Wesolowski et al. [14] demonstrated significant changes in PAH levels (8 PAH compounds) in the city of Gdańsk between the heating and non-heating seasons between 1997 and 2001. Within the framework of air quality monitoring conducted in the province of Pomerania, an increased content of benzo(a)pyrene in PM<sub>10</sub> outdoor dust was also reported in the heating season, whereas in summer it was mostly below the level of quantification [15]. Higher concentrations of PAHs associated with airborne particulate matter were also recorded during winter by other researchers in different areas worldwide, where there are significant seasonal changes in weather conditions [3, 16]. For example, Huang et al. [17] recorded a 16-fold greater content of high molecular weight PAHs in winter than in summer in the air of Beijing (China).

### Proportions of n-Ring PAHs

The highest proportions of 4-ring PAHs in  $\Sigma$ 12PAHs were found in airborne PM<sub>10</sub> samples collected during the heating season (Fig. 2). The mean proportions of these compounds ranged from 40.4 to 44.6%, which agrees well with the results reported for 6 urban sites in Europe (41–47%) by Saarnio et al. [18]. The contents of the sum of 3-ring PAHs were distinctly lower than for other groups of 4, 5, and 6-ring PAHs, most probably due to their higher volatility. It should be stressed that the mean proportions of particular groups of n-ring PAHs were similar at all the sites.

### Benzo(a)pyrene

Benzo(a)pyrene is widely recognized as a marker of air pollution by PAH compounds [19]. For PM<sub>10</sub> samples collected in the heating season, a strong correlation ( $r = 0.98$ ,  $p < 0.05$ ) between the content of benzo(a)pyrene and  $\Sigma$ 12PAHs was recorded, which makes this compound a good indicator of PAH pollution levels in the PM<sub>10</sub> particles examined in the present research. Correlation coefficients of benzo(a)pyrene with other, individual PAH compounds for the heating period varied from 0.76 to 0.99 and were statistically significant, with the exception of anthracene, which implies that PAH composition patterns were similar at the sites studied.

Benzo(a)pyrene is the most widely investigated PAH compound, and different approaches have been developed to assess the carcinogenicity of particular PAHs based on their relative potency to benzo(a)pyrene [20]. Benzo(a)pyrene equivalent concentrations (B(a)P-eq) were calculated for  $\Sigma$ 12PAHs (Table 2) on the basis of toxic equivalency factors (TEFs), following the cancer risk estimate by Nisbet and LaGoy [21]. Mean weekly B(a)P-eq values exceeded 1 ng/m<sup>3</sup> at all the sites during the heating season (5.3–6.6 ng/m<sup>3</sup>), but were significantly lower in the

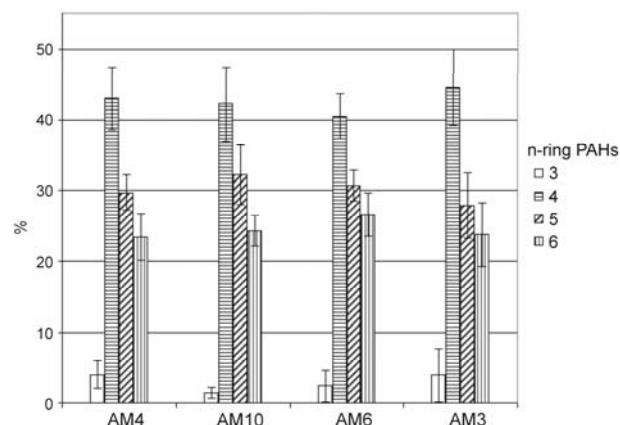


Fig. 2. Percentages of 3-, 4-, 5-, and 6-ring PAHs in  $\Sigma$ 12PAHs in airborne PM<sub>10</sub> samples collected in the Tricity agglomeration during the heating season.

Table 2. Concentrations of PAH compounds and benzo(a)pyrene equivalent concentrations for  $\Sigma 12$ PAHs [ng/m<sup>3</sup>] in airborne PM<sub>10</sub> samples from the Tricity agglomeration.

Station	Date of sampling	Phen <sup>a</sup>	Ant <sup>a</sup>	Fla <sup>a</sup>	Py <sup>a</sup>	B(a)A <sup>b</sup>	Chry <sup>b</sup>	B(b)F <sup>c</sup>	B(k)F <sup>c</sup>	B(a)P <sup>c</sup>	Ip <sup>d</sup>	DBA <sup>e</sup>	Bper <sup>f</sup>	$\Sigma 12$ PAHs	B(a)P-eq	
AM4 Gdynia- Pogórze	26.03.2004 (Fri.) - 1.04.2004 (Thu.) heating season	Min	<0.02	0.33	0.17	0.10	0.52	0.24	0.17	0.32	<0.50	<0.50	<0.50	2.2	0.4	
		Max	<0.04	5.44	5.03	3.78	4.23	4.30	2.10	2.79	3.84	2.10	2.10	3.45	36.5	14.5
		Median	<0.04	2.1	1.62	1.62	1.99	2.40	1.17	1.34	2.42	<1.40	<1.40	1.96	18.1	5.4
													MEAN	19.6	6.0	
													SD	12.5	5.2	
AM10 Gdynia-Port	18.06.2004 (Fri.) - 24.06.2004 (Thu.) non-heating season	Min	<0.04	0.04	<0.02	<0.90	<0.80	<0.60	<0.40	<0.80	<1.80	<1.90	<1.90	0.04	0.0	
		Max	<0.04	0.55	0.28	<0.90	<0.80	1.27	0.80	0.94	2.39	<1.90	<1.90	<1.80	6.7	1.4
		Median	<0.04	0.19	<0.02	<0.90	<0.80	0.79	0.52	<0.80	<1.80	<1.90	<1.90	<1.80	1.8	0.1
													MEAN	2.6	0.4	
													SD	2.2	0.6	
AM6 Sopot	26.03.2004 (Fri.) - 1.04.2004 (Thu.) heating season	Min	<0.02	0.76	0.52	0.30	0.81	0.58	0.28	0.40	0.71	<0.50	<0.50	4.7	0.6	
		Max	<0.03	2.56	2.45	3.34	3.43	4.34	2.04	2.94	4.31	1.44	1.44	3.63	30.8	11.6
		Median	<0.03	1.33	1.15	1.16	1.35	1.69	0.82	0.90	1.64	0.70	0.70	1.32	12.3	4.7
													MEAN	15.5	5.3	
													SD	9.8	4.6	
AM3 Gdańsk- Nowy Port	18.06.2004 (Fri.) - 24.06.2004 (Thu.) non-heating season	Min	<0.04	0.29	<0.02	<0.90	<0.80	0.66	0.47	<0.80	<1.80	<1.90	<1.90	1.7	0.1	
		Max	<0.04	0.73	0.18	<0.90	<0.80	1.13	0.68	0.84	2.29	<1.90	<1.90	<1.80	5.9	1.3
		Median	<0.04	0.38	<0.02	<0.90	<0.80	0.83	0.55	<0.80	<1.80	<1.90	<1.90	<1.80	2.1	0.1
													MEAN	2.6	0.4	
													SD	1.5	0.5	
AM6 Sopot	17.01.2007 (Wed.) - 23.01.2007 (Tue.) heating season	Min	<0.05	0.47	0.52	0.37	0.49	0.63	0.25	0.20	0.75	0.38	0.38	4.8	2.3	
		Max	1.99	4.98	4.67	3.99	3.87	4.39	1.61	2.68	5.41	1.43	1.43	3.46	38.7	11.5
		Median	0.20	1.23	1.16	0.94	1.20	1.53	0.75	0.77	2.00	0.58	0.58	1.53	12.1	4.4
													MEAN	15.1	5.3	
													SD	12.0	3.3	
AM3 Gdańsk- Nowy Port	17.01.2007 (Wed.) - 23.01.2007 (Tue.) heating season	Min	<0.05	1.07	0.69	0.31	0.42	0.79	0.21	0.13	0.72	<0.25	<0.25	5.0	0.4	
		Max	3.35	7.73	7.65	6.86	6.13	5.47	2.39	5.15	7.88	1.78	1.78	5.44	60.2	16.4
		Median	0.54	1.90	1.45	1.12	1.45	1.90	0.77	0.85	1.84	0.76	0.76	1.49	14.0	5.3
													MEAN	21.7	6.6	
													SD	19.5	6.1	

Phen – phenanthrene, Ant – anthracene, Fla – fluoranthene, Py – pyrene, B(a)A – benzo(a)anthracene, Chry – chrysene, B(b)F – benzo(b)fluoranthene, B(k)F – benzo(k)fluoranthene, B(a)P – benzo(a)pyrene, Ip – indeno(1,2,3-cd)pyrene, DBA – dibenzo(a,h)anthracene, Bper – benzo(ghi)perylene,  $\Sigma 12$ PAHs – sum of 12 PAH compounds, B(a)P-eq – benzo(a)pyrene equivalent concentration; Min – minimum value, Max – maximum value, SD – standard deviation;

a – 3-ring PAHs, b – 4-ring PAHs, c – 5-ring PAHs, d – 6-ring PAHs.

Table 3. Concentrations of PAHs in ambient airborne particulate matter in various areas worldwide.

Area	Survey year	PM type	N	ΣNPAHs [ng/m <sup>3</sup> ]	B(a)P [ng/m <sup>3</sup> ]	Reference
Gdańsk, Sopot, Gdynia (Poland)	2004-07	PM <sub>10</sub>	12	0.04-60.2	0.13-5.15	This work
Preila, Curonian Spit (Lithuania)	1980-1994	-	-	-	0.02-25.08	[32]
Prague (Czech Republic)	2000-01	PM <sub>10</sub>	13	11-343	0.1-8.9	[33]
Rügen (Germany)	1996	-	-	0.03-8.77	-	[34]
Berlin (Germany)	2000	PM<7.1 μm	12	up to 15.87	up to 1.07	[35]
Athens (Greece)	2003	-	14	0.44-13.2	0.02-1.36	[25]
Heraklion (Greece)	2000-02	-	24	3.2-44.9	0.11-3.07	[12]
Eastern Mediterranean Sea	2001-02	-	24	0.2-7.27	0.004-0.363	[36]
Venice (Italy)	2003	PM <sub>10</sub>	-	-	0.02-3.22	[37]
Turin (Italy)	2002-04	PM <sub>2.5</sub>	-	-	0.015-2.354	[38]
Rome (Italy)	1996-98	PM <sub>10</sub>	11	1.3-17.3	-	[7]
Zaragoza (Spain)	2001-02	PM <sub>10</sub>	17	0.4-30.22	0.03-2.11	[22]
Gothenburg, traffic tunnel (Sweden)	2000	-	29	35-330	0.48-2.8	[23]
Zagreb (Croatia)	1998	-	-	-	0.01-14.17	[39]
6 towns in Europe	2002-03	PM <sub>10</sub>	32	2.93-55.1	0.05-3.15	[18]
Vienna (Austria)	1995-96	-	16	2-113	-	[40]
forest in Finland	2003	-	17	1-6.3	-	[41]
6 sites in Flanders (Belgium)	2001-03	-	16	0.7-14.1	0.01-1.27	[42]
London (U.K.)	1995-96	TSP	16	0.23-32.04	0.01-2.88	[43]
Lake Balaton (Hungary)	2002-03	TSP	13	0.3-52	0.02-4.3	[44]
Tianjin (China)	-	TSP	16	7-2165	1.22-219	[45]
Beijing (China)	2005-06	PM <sub>2.5</sub>	16	5-1062	-	[46]
Nanjing (China)	2004	PM <sub>2.5</sub>	17	12-178	0.6-12	[47]
Hong Kong (China)	2000-01	PM <sub>10</sub>	16	2-297	0.07-15.49	[48]
Shanghai (China)	2002-03	PM <sub>2.5</sub>	-	1.3-125.6	-	[49]
Guangzhou (China)	2001	PM <sub>10</sub>	>16	7.4-159.4	0.52-15.38	[50]
Wajima, Ishikawa (Japan)	2004-05	-	9	0.12-0.52	0.01-0.03	[51]
Higashi Hiroshima (Japan)	2006-07	PM <sub>10</sub>	13	up to ~5.5	0.52+/-0.42	[6]
Shizuoka (Japan)	2001-02	PM <sub>2.5</sub>	21	1.0-8.4	0.08-0.903	[52]
Seoul (Korea)	1992-94	TSP	20	7.74-265	0.55-4.15	[53]
Kuala Lumpur (Malaysia)	1997	-	-	48	-	[54]
central Taiwan	2004	-	21	13.5-33	0.285-0.510	[55]
Ho Chi Minh City (Vietnam)	2005-06	-	11	7.6-19	0.6-1.4	[56]
Jakarta (Indonesia)	1992-94	TSP	20	13.3-177	0.83-10.2	[53]
Bangkok (Thailand)	1992-94	TSP	20	4.97-74	0.18-2.44	[53]
Mumbai (India)	1996	PM <sub>10</sub>	7	24.5-38.8	-	[57]
Tehran (Iran)	2004-05	PM <sub>10</sub>	16	44.1-130	1.41-3.82	[58]
Algiers (Algeria)	1998	PM <sub>10</sub>	11	5.5-43.4	0.07-2.1	[59]

Table 3. Continued.

Area	Survey year	PM type	N	ΣNPAHs [ng/m <sup>3</sup> ]	B(a)P [ng/m <sup>3</sup> ]	Reference
16 sites in Canada	2000-01	-	9	0.7-66.2	-	[60]
Chicago (USA)	1995-97	-	14	4.4-89.3	-	[61]
Galveston Bay, Texas (USA)	1995-96	-	>39	0.217-4.811	0.006-0.3	[62]
Baltimore, Chesapeake Bay (USA)	1997	-	23	0.137-8.26	0.004-0.641	[26]
Mexico (Mexico)	1997	PM <sub>10</sub>	15	4.85-9.40	0.44-2.50	[63]
Rio de Janeiro (Brazil)	1999	TSP	16	22.5-24.4	0.94-1.52	[64]
Porto Alegre (Brazil)	2001-02	PM <sub>10</sub>	-	-	0.012-10.99	[65]
São Paulo (Brazil)	2002	PM <sub>2.5-10</sub>	13	5.41-20.8	0.33-3.28	[66]
Melbourne (Australia)	1992-94	TSP	20	1.68-21.53	0.02-0.83	[53]
North Pacific and Arctic Ocean	2003	TSP	15	0.02-4.38	0.003-0.61	[67]
Spitzbergen Island (Norway)	1998-99	PM <sub>10</sub>	13	0.6-2	<0.1	[68]
Ross Sea coast (Antarctica)	1991-93	PM <sub>10</sub>	13	0.01-0.7	<0.0004-0.055	[69]

PM – particulate matter, N – number of PAH compounds analysed, B(a)P – benzo(a)pyrene, TSP – total suspended particles

Table 4. Pearson correlation coefficients between Σ12PAHs contents in airborne PM<sub>10</sub> and meteorological variables for samples collected in the heating season.

Station	N		t [°C]	RH [%]	SR [W/m <sup>2</sup> ]	WS [m/s]	Frequency of wind directions							
							N	NE	E	SE	S	SW	W	NW
AM4	7	Σ12PAHs	0.41	-0.18	0.02	-0.52	-0.12	-0.36	-0.61	0.78*	0.75	0.09	0.55	-0.24
AM10	7		0.52	0.27	0.48	-0.94*	0.38	0.28	0.77*	-0.11	-	-0.36	-0.11	-0.37
AM6	7		-0.85*	0.46	0.42	-0.81*	-	-	-	0.15	-0.28	-0.34	0.19	0.72
AM3	7		-0.88*	-	0.49	-	-	-	-	-	-	-	-	-
all sites	28		-0.47*	0.16	0.10	-0.67*	0.05	-0.06	0.17	0.17	0.05	-0.15	0.14	-0.11

\* statistically significant (p < 0.05)

N – number of samples, t – temperature, RH – relative humidity, SR – solar radiation, WS – wind speed, N-NW – wind directions

non-heating season (0.4 ng/m<sup>3</sup>). The B(a)P-eq index relates to the whole PAH fraction and is a better measure of carcinogenicity than the concentration of just benzo(a)pyrene, which is especially liable to photodegradation [22].

In this study, no strong relationship was found between the concentrations of benzo(a)pyrene and PM<sub>10</sub> particles (r=0.45, p<0.05); only for station AM10 (Gdynia-Port) was the relationship clear (r=0.93, p<0.05). Therefore, it is not possible to reliably predict the level of PAH pollution solely on the basis of *in situ* measurements of PM<sub>10</sub> concentration. The mass concentration of airborne particulates is an important index of air quality, but other characteristics, such as particle size distribution, morphology, and detailed chemical speciation, including PAH levels, are necessary to evaluate the potential health hazards [23]. The lack of seasonality in PM<sub>10</sub> concentration contrasts markedly with the distinct seasonal trend in PAH contents in samples

from the Tricity. Similar observations were reported in Mediterranean Europe [5].

Directive No. 2004/107/EC of the European Union [24] set the average annual target of the benzo(a)pyrene content in the airborne PM<sub>10</sub> fraction at 1 ng/m<sup>3</sup>. This directive envisages that this air quality criterion should be achieved by 31<sup>st</sup> December 2012, where this is technically possible and economically justified. During the heating season, there were 2 to 5 cases of daily B(a)P concentration that exceeded the 1 ng/m<sup>3</sup> threshold at particular stations, but in the non-heating season this threshold was not exceeded.

#### Correlations of PAHs with Meteorological Data

Table 4 lists Pearson correlation coefficients between Σ12PAHs contents and meteorological variables for samples taken in the heating season. Concentrations of individ-



ual PAH compounds were mostly below quantification levels for samples collected during the non-heating period, so these samples were excluded from correlation analysis. Taking into account all four sites examined in this study, the  $\Sigma 12\text{PAHs}$  concentration was negatively correlated with ambient temperature ( $r = -0,47$ ,  $p < 0,05$ ). A similar relationship was also found in other areas worldwide, where distinct seasonal changes in outdoor temperature are recorded throughout the year, e.g. in a suburban area of Athens [25] and at Higashi Hiroshima in Japan [6]. Surprisingly, however, at sites AM4 and AM10 this correlation was positive and not statistically significant, most probably because of the smaller differences in temperature at these stations compared to stations AM6 and AM3 and/or different PAH sources.

On the basis of a correlation matrix we notice that the relationship between the PAH pollution level of PM<sub>10</sub> particles and such parameters as relative humidity and solar radiation is not clear, in contrast to the study conducted in Zaragoza (Spain) by Callén et al. [22]. In general, a distinct negative correlation was found between  $\Sigma 12\text{PAHs}$  contents and wind speed. This relationship is consistent with the findings of other authors [25], who observed that stable weather conditions (i.e. low wind speed) lead to elevated PAH concentrations in ambient air; the dispersion of PAHs in the atmosphere is more intensive as wind speed increases. Moreover, higher wind speed accelerates the volatilization of PAHs, which leads to higher gas-phase concentrations [26].

Correlation analysis shows that it is difficult to find a direct link between the PAH pollution of airborne particles and the frequency of occurrence of particular local wind directions at the sites investigated. Similar findings were obtained by St-Amand et al. [27] in the vicinity of Ottawa, Canada. However, correlation coefficients were high, e.g. at station AM4 for a SE wind, but wind from this direction was reported for only two days. Interestingly, local wind directions could be different from those recorded at a greater height, which are associated with the long-range transport of pollutants. Using the atmospheric HYSPLIT model, Lewandowska et al. [28] estimated for the atmosphere over Gdynia that the directions of air masses at 500 m and 1000 m largely coincided and usually differed from the masses measured at 20 m in September 2007. This indicates that local wind patterns recorded at 10 m above ground level relate to local sources of PAHs and should not be uncritically correlated with distant sources.

Finally, it should be emphasized that the study of the relationship between PAH levels in airborne particles and meteorological data cannot be carried out properly without considering other factors, like seasonality in emission patterns.

### Influx of Airborne PAHs to the Gulf of Gdańsk

The annual direct atmospheric input of PAHs associated with PM<sub>10</sub> particles into the waters of the Gulf of Gdańsk (area 4,940 km<sup>2</sup>) from the land area located on the western side of the Gulf was estimated using a simple box approach. The frequency of directions of wind (~ 46%) and its relevant average speed (~ 4.3 m/s) conducive to this atmos-

pheric transport were determined on the basis of the meteorological data given by Kwiecień [10]. Assuming that particle-bound PAHs (with average concentrations equal to ~ 5 ng/m<sup>3</sup> for  $\Sigma 12\text{PAHs}$  and ~ 0.35 ng/m<sup>3</sup> for benzo(a)pyrene) pass through an air section 50 km wide and 50 m high, one can estimate that the annual atmospheric influx toward the sea amounts to ~800 kg (~160 g/km<sup>2</sup>/year) of  $\Sigma 12\text{PAHs}$  and ~55 kg (~11 g/km<sup>2</sup>/year) of benzo(a)pyrene. These assessed inflows account for ~21% of  $\Sigma 12\text{PAHs}$  and ~15% of B(a)P of the total annual load deposited in sediments (total loads of  $\Sigma 12\text{PAHs}$  (760 g/km<sup>2</sup>/year) and B(a)P (72 g/km<sup>2</sup>/year) were taken from [29]), provided that all PM<sub>10</sub> particles entering the investigated section sink within the area of the Gulf and that the return flux (i.e. from sea to land) is negligible. For comparison, Lewandowska et al. [28] found that atmospheric carbon input accounts for up to 18% of total carbon fluxes into Baltic coastal waters. The estimated values of dry deposition of benzo(a)pyrene to surface waters that may be transferred to bottom sediments are in agreement with those modeled within the framework of EMEP (Co-operative Program for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe) modeling studies. EMEP assessed that the annual deposition flux of airborne benzo(a)pyrene to Gulf of Gdańsk varied from 5 to 20 g/km<sup>2</sup>/year in 2006 [8].

However, the results obtained in our work may be underestimated, because average annual concentrations of benzo(a)pyrene recorded during the monitoring program conducted by the regional inspectorate for environmental protection in the period 2005-09 were significantly higher (0.8-3.4 ng/m<sup>3</sup>) [15]. Moreover, the assumed height of the air section seemed to be too low, given the fact that the mixing layer height, which is crucial to the transport and dispersion of pollutants, is of the order of 10<sup>2</sup>-10<sup>3</sup> meters for the area in question [30]. On the other hand, it should be noted that small (especially <2.5  $\mu\text{m}$ ) airborne particles (with associated pollutants) can be transported over long distances, e.g. the horizontal advection scale over Baltic Sea for marine aerosol particles of radius 1  $\mu\text{m}$  can be as high as 10<sup>2</sup>-10<sup>3</sup> km, according to calculations carried out by Petelski [30], whereas the Gulf stretches no farther than 10<sup>2</sup> km from the Tricity shoreline.

The dry deposition flux ( $F$ ) of contaminants from the atmosphere to the Earth's surface can be determined indirectly as the product of dry deposition velocity ( $V_d$ ) and the ambient concentration ( $c$ ) of a given pollutant (i.e.  $F = V_d \times c$ ) [31]. Based on the above-mentioned formula, and assuming that wet deposition is negligible and the average concentration of B(a)P over the Gulf of Gdańsk is equal to ~0.3 ng/m<sup>3</sup> [8], we may calculate that the mean dry deposition velocity of particle-bound benzo(a)pyrene varies from ~0.05 to ~0.21 cm/s.

### Conclusions

This study reveals that PAH pollution of ambient airborne PM<sub>10</sub> particles is a serious problem in the Tricity area. The major conclusions to be drawn are as follows:

- a) there are distinct seasonal fluctuations of particulate PAH concentrations in the air, with the highest levels being found in the heating season
- b) benzo(a)pyrene is a good marker of the whole group of PAHs associated with PM<sub>10</sub> particles, and concentrations of this compound during the heating season often exceeded the air quality guidelines set by the European Union
- c) mass concentrations of PM<sub>10</sub> particulate matter proved to be an inadequate measure of PAH pollution
- d) ambient temperature and wind speed strongly affect the distribution of particulate PAHs in the study area
- e) atmospheric input is an important source of PAHs deposited in the sediments of the Gulf of Gdańsk.

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