

Polycyclic aromatic hydrocarbons (PAHs) associated with PM10 collected in Wadowice, South Poland

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Abstract. Krakow is a city in southern Poland inhabited by about 741,000 people. However, Krakow's agglomeration includes neighboring cities, hence more than 1 million people live there. The agglomeration is struggling with the problem of air pollution. In 2016, admissible average annual concentrations of PM10 ($40 \mu\text{g} / \text{m}^3$) were exceeded at all measuring points. Furthermore, daily PM10 concentrations were regularly exceeded in the winter, which is associated with increased coal combustion during this period. Fortunately, interest in the subject of air quality in the world is constantly growing. People are more often aware of the negative impact on health of chemical compounds present in particulate matter (PM) such as Polycyclic Aromatic Hydrocarbons (PAHs), which were proved to be cancerogenic and mutagenic for people. That is why it is so important to study their presence in the ambient air. PM10 collected in the center of Wadowice (22.12.2016 – 13.10.2017) were investigated. PAHs were extracted from particulate matter and analysed applying the GC/MS technique. The results are discussed in the article.

1 Introduction

Carbonaceous aerosol constitutes a large fraction of PM10 – particulate matter with an aerodynamic diameter smaller or equal than $10 \mu\text{m}$. Operationally we can divide carbonaceous fractions into two main fractions: a) elemental carbon (EC); b) organic carbon (OC). The term total carbon (TC) is also distinguished. It refers to the sum of EC and OC. Elemental carbon is a primary pollutant derived from incomplete combustion of petrol, oil, coal, residential space heating, biomass and other carbon-contained materials burning. As for primary organic carbon (POC), the origin can be natural (volcanic eruptions, forest fires, biogenic e.g. viruses, bacteria) and anthropogenic (combustion sources). Although, OC can

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also be produced by photochemical reactions involving gaseous organic precursors - secondary organic carbon (SOC) [1–3].

Organic carbon contains several groups of compounds with different properties (e.g. water solubility, vapour pressure). However, according to [3] these organic compounds constitute less than 10% of the measured mass of OC present in the air, but still, one of the components are polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons represent a group of organic compounds which are ubiquitous in the environment. They consist of ≥ 2 aromatic rings. PAHs distinguishing features among other compounds are high melting and boiling point as well as low vapor pressure and aqueous solubility [4].

Polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (NPAHs) are products of incomplete combustion of for example biomass, coal or oil. We cannot omit car exhaust emissions. They can be also released in the atmosphere by natural processes (e.g. volcanic eruptions).

PAHs occur in the atmosphere both in vapour phase (two or three benzene rings thus lower molecular weight compounds) and in particulate-bound form (four or more benzene rings thus higher molecular weight) [4, 5].

The concentration of PAHs usually depends on level of particulate matter (PM). It is also strongly associated with population density in the area. Higher number of people cause higher number of cars which cause traffic jams. We observe also seasonal variation of PAHs concentrations, especially in the areas where people are burning coal and wood in home furnaces [6–8].

PAHs are of particular concern due to their mutagenic, teratogenic and carcinogenic potential. The International Agency for Research on Cancer [9] classifies some PAHs as carcinogenic, probably carcinogenic and possibly carcinogenic to humans (Group 1, 2A, 2B, respectively). Among these, we can distinguish benzo[a]pyrene as known carcinogenic compound, dibenzo[a,h]anthracene belonging to Group 2A and chrysene, benz[a]anthracene, benzo[k]fluoranthene and benzo[b]fluoranthene belonging to Group 2B (Table 1.)

Routes of exposure to PAHs include ingestion, inhalation, and dermal contact. Therefore, there are groups of people more exposed to these compounds (e.g. street vendors, taxi drivers, mechanics, workers in mining, cigarette smokers, consumers of grilled meats) [10, 11].

Health effects from long-term exposure to PAHs might include cataracts, kidney damage, asthma symptoms, problems with immune system and lung functions with most significant – lung cancer. Whereas, contact with skin may induce skin inflammation. Too much exposure to naphthalene can be the reason of breakdown of the blood cells [11, 12].

The most common example of PAHs is benzo(a)pyrene (BaP). BaP is a 5 ring semi-volatile compound with the molar mass of $252.32 \text{ g}\cdot\text{mol}^{-1}$ which can be transported over a long distance in the atmosphere. It affects human health with its high carcinogenicity and the European Union by the Fourth Air Quality Daughter Directive 2004/107/EC established annual target value of $1 \text{ ng}/\text{m}^3$ [13–15].

1.1 Sampling site

The analysis of the composition of PM₁₀ dust samples taken from the area of Wadowice (February–September 2017) was performed. Wadowice city is located in southern Poland in Malopolska voivodeship near to its biggest city - Kraków (about 54 km) Fig.1. The population of Wadowice is about 18,000 inhabitants but each year the city is visited by about 300,000 tourists due to the fact that The Family Home of John Paul II is located here [16].

2 Methods

Quartz-fiber filters (Whatman QM-A) with a diameter of 47 mm were used for the research. The samples of the PM₁₀ fraction were collected using Atmoservice PNS-15 collector pumping averagely 54 m³. The filters were exchanged every 24 h. The flow was controlled automatically by the equipment and manually on the gas meter. The mass of PM₁₀ was computed as a difference of mean masses of filters after and before sampling, respectively.

2.1 Analysis of PAHs

To analyse Polycyclic Aromatic Hydrocarbons (PAHs) Thermo Scientific GC Trace 1310 gas chromatograph coupled with the ITQ 900 ion trap mass spectrometer and a TriPlus RSH autosampler was used. The volume of extracts were reduced up to 250 µL by the stream of argon (at 35 °C).

The remaining 150 µL of concentrate was transferred into chromatographic vial and analyzed with GC/MS technique. Concentrations of following 16 PAHs were determined: acenaphthene (Acn), acenaphthylene (Acnl), anthracene (An), benzo[b]fluoranthene (BbF), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiP), benzo[k]fluoranthene (BkF), chrysene (Ch), dibenzo[ah]anthracene (DahA), fluoranthene (Flt), fluorene (Flu), indeno[1,2,3-cd]pyrene (IP), naphthalene (Na), phenanthrene (Phen) and pyrene (Pyr).

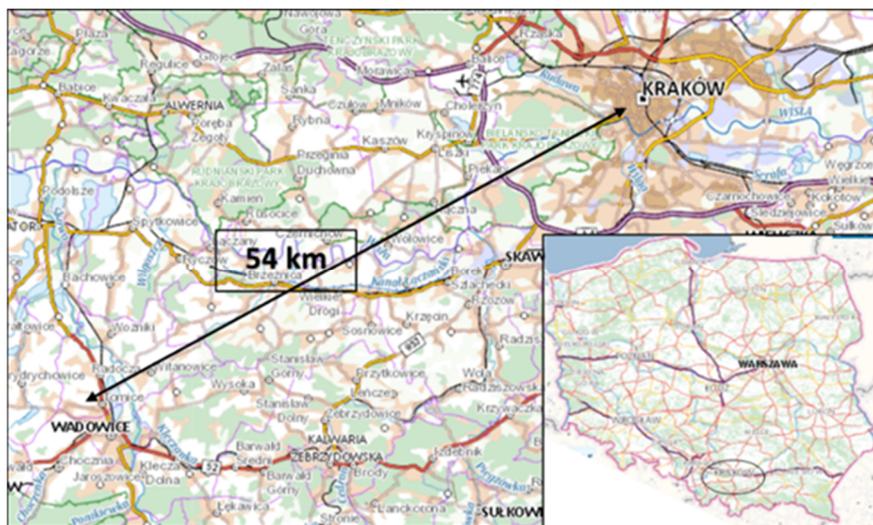


Fig.1. The sampling site.

2.2 Analysis of carbonaceous fraction and inorganic ions

The elemental carbon (EC) and organic carbon (OC) were measured with a Sunset Laboratory OCEC Aerosol Analyzer using EUSAAR2 protocol [17].

The concentration of the inorganic cations (Na^+ , NH_4^+ , Mg^{2+} , K^+ , Ca^{2+}) and anions (NO_3^- , SO_4^{2-} , PO_4^{3-} , Cl^-) were analysed with isocratic ion chromatography on an ICS-1100 instrument (by Thermo Scientific) equipped with an autosampler AS-DV and ion-exchange columns: Ion Pac AS22 (4 × 250 mm) for anions, mobile phase: 4.5 mM Na_2CO_3 + 1.4 mM NaHCO_3 ; CS16 (5 × 250 mm) for cations, mobile phase: 12 mM MSA. After electrochemical

suppression (AERS 500 (4 mm) and CERS 500 (4mm) suppressors), quantification was performed with a conductivity detector. The injection volume was 25 µL and the flow rate was 1.2 mL min⁻¹. Calibration. The method was based on [8].

2.3 Health Risk Assessment

The cumulative health hazard from a mixture of PAH can be assessed by using the CEQ (carcinogenic equivalent), MEQ (mutagenic equivalent), or TEQ (toxic equivalent) relative to the carcinogenicity or mutagenicity of BaP, or to the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), respectively [7, 18, 19, 20]. The method is based on (Wioletta Rogulka-Kozłowska, Kozielska, and Klejnowski 2013). The equivalents were computed from the concentrations of measured PAHs and their values of TEF Eq.(1), TCDD-TEF Eq.(2) and MMC Eq.(3) (toxicity equivalence factors and TCDD-toxicity equivalence factors or minimum mutagenic concentrations, respectively) are taken from [21–23].

$$CEQ = 0,001 * ([Na] + [Ace] + [Acy] + [Flu] + [Fen] + [Fl] + [Pir]) + 0,01 * ([An] + [Ch] + [BghiP]) + 0,1 * ([BaA] + [BbF] + [BkF] + [IP]) + 1 * [BaP] + 5 * [DBA] \quad (1)$$

$$TEQ = 0,000025 * [BaA] + 0,00020 * [Ch] + 0,000354 * [BaP] + 0,00110 * [IP] + 0,00203 * [DBA] + 0,00253 * [BbF] + 0,00487 * [BkF] \quad (2)$$

$$MEQ = 0,00056 * [Acy] + 0,082 * [BaA] + 0,017 * [Ch] + 0,25 * [BbF] + 0,11 * [BkF] + 1 * [BaP] + 0,31 * [IP] + 0,29 * DBA + 0,19 * [BghiP] \quad (3)$$

Table 1. Meteorological conditions (diurnal mean values) during March and August 2017 in Wadowice.

March 2017				August 2017			
Date	Temperature [°C]	Daily Precipitation [mm]	Wind velocity [km/h]	Date	Temperature [°C]	Daily Precipitation [mm]	Wind velocity [km/h]
Ranges	6-20	0-19	6-21	Ranges	16-35	0-64	0-15
Average	11	2	13	Average	26	4	9

Table 2. Characteristics of analytes.

Compound	Formula	CAS No.	Molar mass [g·mol ⁻¹]	Boiling point [°C]	Solubility in water [µg·L ⁻¹]	IARC classification
Dibenz[a,h]anthracene	C ₂₂ H ₁₄	53-70-3	278	524	2.5	2A
Indeno[1,2,3-cd]pyrene	C ₁₂ H ₂₂	193-39-5	276	536	0.6	2B
Benzo[a]pyrene	C ₂₀ H ₁₂	50-32-8	252	438	9.4	1
Benzo[b]fluoranthene	C ₂₀ H ₁₂	205-99-2	252	481	1.5	2B
Benzo[k]fluoranthene	C ₂₀ H ₁₂	207-08-9	252	480	0.006	2B
Benz[a]anthracene	C ₁₈ H ₁₂	56-55-3	228	438	-	2B
Chrysene	C ₁₈ H ₁₂	218-01-9	228	448	2.0	2B
Pyrene	C ₁₆ H ₁₀	129-00-0	202	404	135.0	3
Phenanthrene	C ₁₄ H ₁₀	85-01-8	178	340	1150.0	3

3 Results and discussion

As is well known Poland is a country affected by coal combustion. It is noticeable in the differences between summer and winter [24, 25]. Wadowice does not seem to deviate from this trend. The results were divided into heating and non-heating season based on examples from the months of March and August, respectively. Meteorological conditions from selected months are shown in Table 1. while in Table 2. characteristic of analysed PAHs.

The difference between concentration of PM10 during heating (March) and non-heating (August) season is clearly visible in Fig.2.

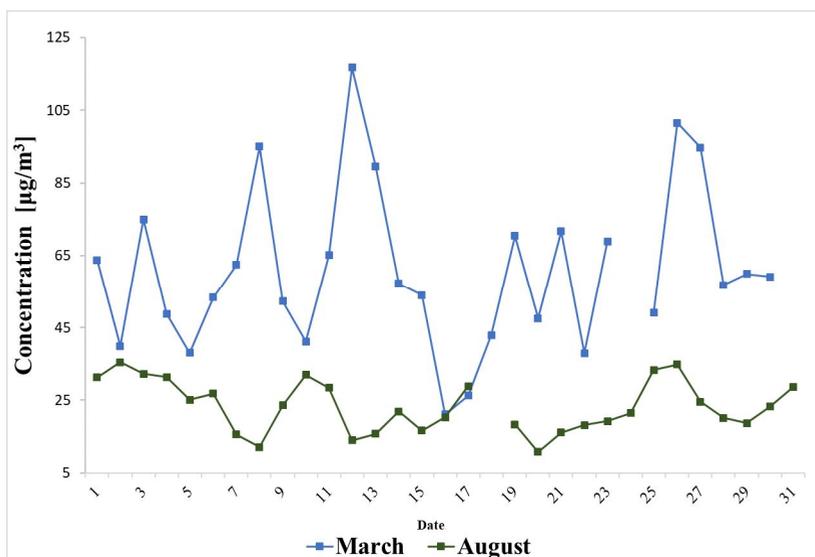


Fig. 2. Variation of concentration of PM10 during March and August 2017.

The gravimetrically measured PM10 concentration during the study period equalled 34,39 $\mu\text{g}/\text{m}^3$ on average, varying from 10,80 $\mu\text{g}/\text{m}^3$ (20th August) to 116,77 $\mu\text{g}/\text{m}^3$ (13th March). During the measurements maximum value for PM10 (50 $\mu\text{g}/\text{m}^3$) [26] was exceeded 33 times, only in March – 19 times. In this period the diurnal mean ambient temperature varied between 6-20 °C and average precipitation was equalled 1,87 mm, whereas in August 16-35 °C and 3,53 mm, respectively.

Table 3. Concentrations of selected PAHs in March and August.

Compound	Mean concentration March [$\text{ng}\cdot\text{m}^{-3}$]	Mean concentration August [$\text{ng}\cdot\text{m}^{-3}$]
Phenanthrene	2.3±1.0	0.4±0.1
Pyrene	8.2±4.4	0.8±0.7
Benzo(a)anthracene	11.9±6.4	1.2±1.1
Chrysene	10.4±5.7	1.0±0.9
Benzo(b)fluoranthene	11.1±4.9	1.6±0.8
Benzo(k)fluoranthene	5.6±2.5	0.8±0.4
Benzo(a)pyrene	11.1±5.1	1.4±1.0
Indeno(1,2,3-cd)pyrene	8.5±3.4	1.4±0.6
Dibenz(a,h)anthracene	11.5±4.8	1.9±0.8

Polycyclic aromatic hydrocarbons exhibited similar tendency to PM10. The highest concentrations of examined PAHs were reported on 13th March when the sum of analytes concentrations was equal 156,72 ng/m³. The concentrations of PAHs detected in the largest amount during selected months of heating and non-heating period are shown in Table 3.

One of the analyzed PAHs was benzo(a)pyrene (Fig.3-4). In March concentrations of BaP were noticeably higher than in August therefore in Fig.3. everyday concentrations in March are included while Fig.4. average of several days in August. Despite this, none of the cumulated concentrations from August has reached so high concentration as any single day from March. For instance, the lowest concentration of BaP were detected at 31st March (4,72 ng/m³) while in August, the highest average concentration was recorded in the last week of the month (3,17 ng/m³). The highest concentration of BaP was recorded at 13th March (19,32 ng/m³) it is clearly visible that it is more than 6 times higher than from 28-31st August. It is worth to admit that temperature on 13th March was 6 °C whereas in the mentioned last four days of August ranged between 21-30 °C.

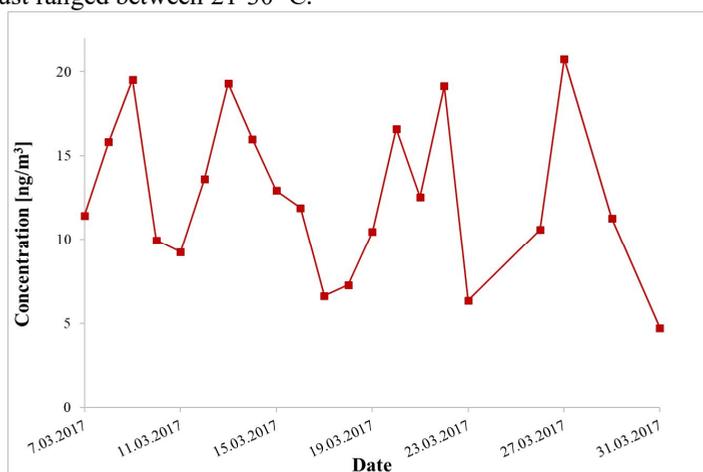


Fig. 3. Concentration of BaP (March).

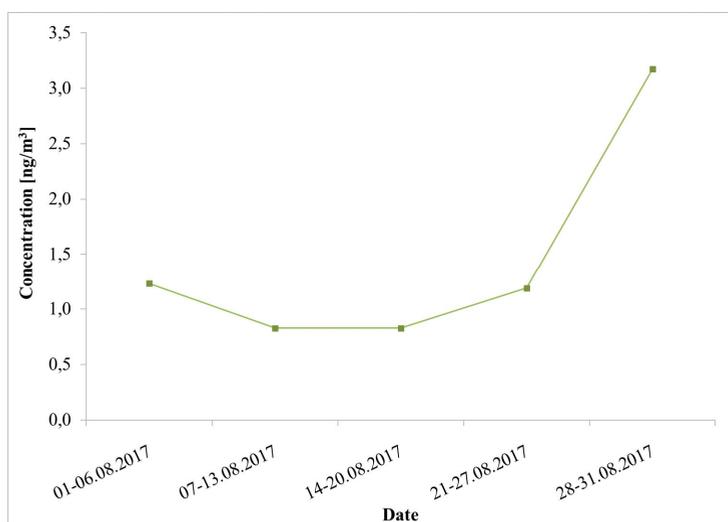


Fig. 4. Concentration of BaP (August).

The highest concentrations of OC and EC in heating season (March) ($39,32 \mu\text{g}/\text{m}^3$ and $6,78 \mu\text{g}/\text{m}^3$) were observed on 13th and 4th March, whereas the highest concentrations in non-heating season (July/August) ($9,87 \mu\text{g}/\text{m}^3$ and $2,77 \mu\text{g}/\text{m}^3$) on 2nd August and 21st July, respectively (Fig.5-6). Minimum value for OC and EC obtained during non-heating season were $4,48 \mu\text{g}/\text{m}^3$ and $1,67 \mu\text{g}/\text{m}^3$, respectively. On the 3rd March, when the wind velocity reached $18,75 \text{ km}/\text{h}$ (the month average: $13,14 \text{ km}/\text{h}$), the lowest concentrations of OC and EC were observed ($6,41 \mu\text{g}/\text{m}^3$ and $2,02 \mu\text{g}/\text{m}^3$).

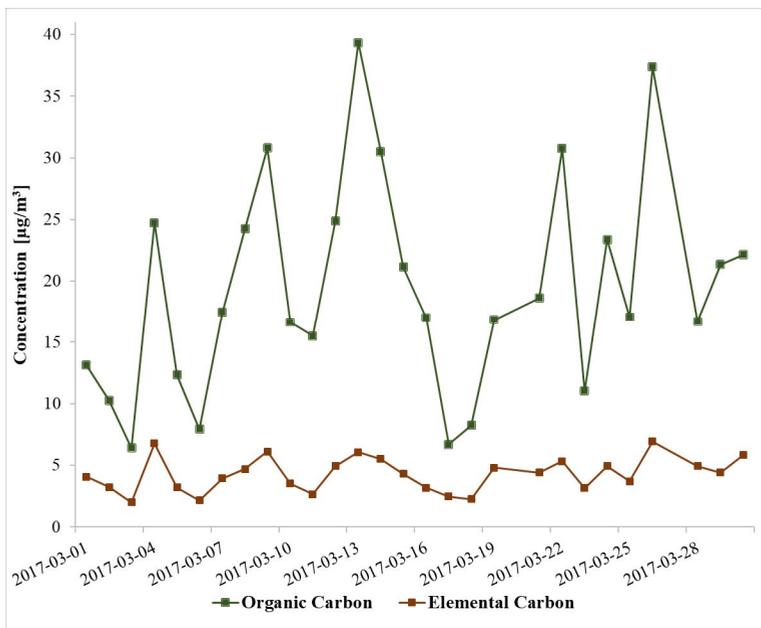


Fig. 5. Concentration of OC and EC (March).

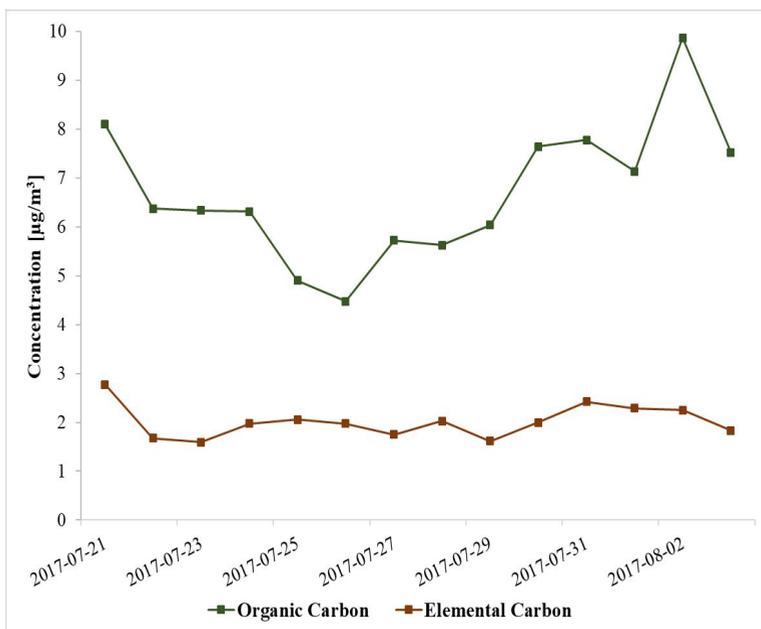


Fig. 6. Concentration of OC and EC (July/August).

Table 4. shows average concentrations and standard deviations of ions in August and March. In both months SO_4^{2-} concentration is dominant ($5,39 \mu\text{g}/\text{m}^3$ and $6,50 \mu\text{g}/\text{m}^3$, respectively). The average values obtained from most cations are visibly smaller than for anions (except Cl in August $0,28 \mu\text{g}/\text{m}^3$, which grows significantly in March to $3,36 \mu\text{g}/\text{m}^3$). The highest average concentrations of cations are detected for Na^+ and NH_4^+ both in heating (March) and non-heating (August) seasons and are equal to $2,40 \mu\text{g}/\text{m}^3$ and $2,06 \mu\text{g}/\text{m}^3$ (March), $2,03 \mu\text{g}/\text{m}^3$ and $0,74 \mu\text{g}/\text{m}^3$ (August), respectively. The results obtained for PO_4^{3-} on both months are similar - $2,23 \mu\text{g}/\text{m}^3$ (August) and $2,25 \mu\text{g}/\text{m}^3$ (March), whereas the difference between average concentrations of NO_3^- is noticeable - $1,47 \mu\text{g}/\text{m}^3$ and $3,50 \mu\text{g}/\text{m}^3$, respectively. The highest values in heating season were observed for secondary pollutants NO_3^- , SO_4^{2-} and NH_4^+ , which can either be produced on a local and regional scale, or can come from the long range transport. Their presence point to emission sources such as fossil fuels combustion. The presents the dependence of the equivalent concentration of sum of nitrate and sulphate ions on the equivalent concentration of the ammonium ions. The correlation coefficient is accounted for $R^2 = 0.9821$. It confirms that this ions are associated with each other and have the common source in the total mass of the PM10. Furthermore concentrations of particulate chloride are elevated in heating season, what confirms that particulate matter was affected by emissions from coal combustion. The average OC and EC contribution to the total PM10 mass equals 84% and 8,3%, respectively. The EC/OC ratio is rather constant with an average of 0.09 and 0.30 in heating and non-heating season, respectively. The small variation of these ratios give and evidence for similar emission patterns during the sampling period. Very high contribution of OC in March is strongly correlated with combustion of solid fuels.

Table 4. Concentrations of ions in heating (March) and non-heating season (August) in Wadowice.

Ion	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}	NO_3^-	SO_4^{2-}	PO_4^{3-}	Cl
Mean concentration (March) [$\mu\text{g}\cdot\text{m}^{-3}$]	2.40±0.40	2.06±1.31	0.52±0.32	0.52±0.09	0.76±0.43	3.50±2.45	6.50±2.46	2.25±0.61	3.36±2.24
Mean concentration (August) [$\mu\text{g}\cdot\text{m}^{-3}$]	2.03±0.22	0.74±0.43	0.19±0.15	0.61±0.18	0.49±0.33	1.47±0.60	5.39±1.93	2.23±0.50	0.28±0.15

Analysis of correlations has shown many dependencies between the PAHs with PM10 concentrations. Apart from strong correlation for PM10, a high correlation with the high concentrations of chlorine and SO_4^{2-} were found. The presence of those components suggests that main source of PAHs for PM10 in heating season might be connected to incomplete combustion processes, outworn residential heating systems and coal combustion. Three risk indicators

The results for the sample months - March and August are presented in Fig.7. The data from Krakow was also compared to the different cities [7, 18, 19]. It is noticeable that only in Teheran (Iran) we can see higher values of equivalents than from March in Wadowice, CEQ is equal to $111,31 \text{ ng}/\text{m}^3$, MEQ - $31,13 \text{ ng}/\text{m}^3$, TEQ - $226,60 \text{ pg}/\text{m}^3$, whereas in Wadowice the results are $72,23 \text{ ng}/\text{m}^3$, $22,08 \text{ ng}/\text{m}^3$ and $94,38 \text{ pg}/\text{m}^3$, respectively. (CEQ, TEQ, MEQ) were computed using Eqs.(1)-(3).

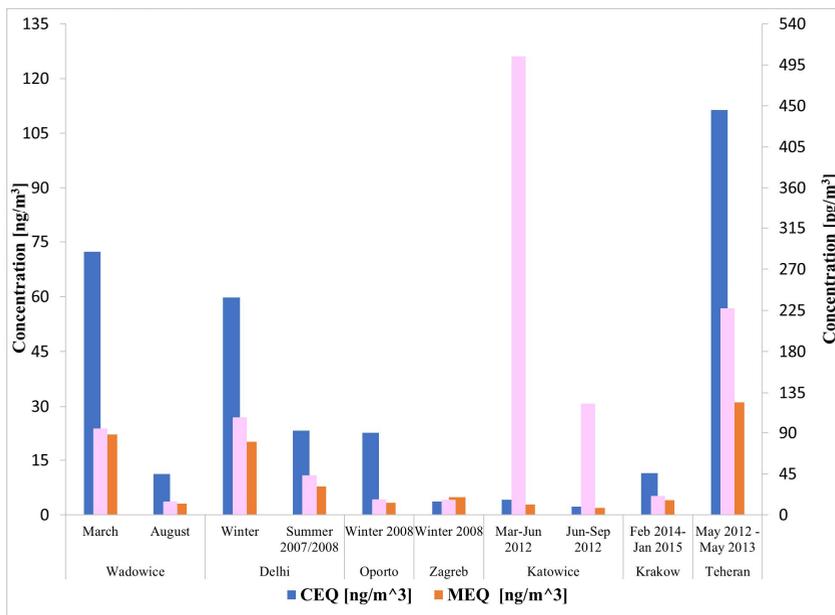


Fig. 7. Mean values of the three risk indicators (CEQ, MEQ and TEQ) in Wadowice and other cities.

The results from August (CEQ: 11,27 ng/m³, MEQ: 3,05 ng/m³, TEQ: 14,15 pg/m³) are lower than from both seasons in Delhi (India) – e.g. summer 2007/2008: 23,09 ng/m³, 7,87 ng/m³ and 42,82 pg/m³, respectively, but comparable to the rest of the cities, except from high values of TEQ (503,85 pg/m³) from Mar-Jun 2012 period in Katowice (Poland).

4 Conclusions

Wadowice is a city strongly affected by air pollution. Maximum value for PM10 (50 µg/m³) only in March was exceeded 19 times. The concentration of PM10 is strongly connected with concentration of PAHs (within widely discussed BaP) also with organic and elemental carbon.

The problem with air pollution in Wadowice is associated with coal and biomass combustion during the winter time, what was proved on the example of March (heating season) and August (non-heating season).

Three risk indicators – carcinogenic, mutagenic and toxic equivalents (CEQ, MEQ, TEQ) reached high values in Wadowice, especially in heating season (March). The long term exposure to PAHs might result with many dangerous diseases including cancer. That is why it is so important to take steps to counteract air pollution in this city.

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