

Article

Seasonal Variability, Sources and Markers of the Impact of PAH-Bonded PM₁₀ on Health During the COVID-19 Pandemic in Krakow

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Abstract

The main objective of this research was to evaluate the seasonal variability of PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs), their sources, and analyse their health impacts We confirmed during the COVID-19 pandemic period. The chemical composition of PM₁₀ in terms of PAH content was carried out using the gas chromatography-mass spectrometry (GC-MS) technique. PM₁₀ samples were collected in Krakow from 2020 to 2021. A total of 92 samples of particulate matter (PM₁₀ fraction) were analysed. The analyses contained 16 basic PAHs identified by the United States Environmental Protection Agency (U.S. EPA) as the most harmful. The information obtained on the concentrations of PAHs was used to determine the profiles of pollution sources, exposure profiles, and the values of toxic equivalency factors recommended by the EPA: mutagenic equivalent to B[a]P (ang. mutagenic equivalent, MEQ), toxic equivalent to B[a]P (ang. toxic equivalent, TEQ), and carcinogenic equivalent to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (ang. carcinogenic equivalent, CEQ). In Kraków, heavy PAHs accounted for over 90% of the total PAHs detected in the PM₁₀ samples. In addition, air trajectory frequency analysis was performed to obtain information on the possibility of transporting pollutants from selected areas in the vicinity of the studied site. Interpreting the trajectory results provided information on the nature of air pollution sources. Analysis of Kraków's air mass trajectory showed that the highest daily concentration of PM₁₀ in the air flow was from the southwest and east for days.

Keywords: atmospheric aerosols; PAHs; MEQ; CEQ; TEQ; pandemic; toxicity; air quality



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1. Introduction

Numerous studies conducted in the field of air quality have shown that particulate matter (PM) has a global impact on climate and human health [1–4] Long-term exposure to heavily polluted air containing particulate matter can cause respiratory diseases, problems with the immune system, Alzheimer's disease, and can contribute to the formation of cancer. For these reasons, PM is one of the pollutants that requires continuous monitoring. To design effective monitoring or PM reduction strategies, a detailed understanding of

their concentrations, sources, and chemical composition is necessary in terms of inorganic and organic compounds from various regions of the world [5].

The chemical characterisation of particulate matter is crucial information obtained from research on air pollution in relation to potential negative health effects. Due to exposure to high concentrations of PM, Poland is one of the European countries that have been struggling with this problem for a long time, especially in the southern part of the country, which is dominated by mountainous and upland landscapes, where the dispersion of pollutants is hindered. Furthermore, the south of Poland is characterised by well-developed industry and high population density, making this area more affected by poor air quality [6]. According to data from the World Health Organisation (WHO) in 2016, the number of deaths related to persistent low air quality was estimated at 68.9 per 100,000 inhabitants in Poland, giving it the 28th position among European countries [World Health Organisation 2016]. Sweden ranks first with 0.4 deaths per 100,000 inhabitants. The WHO estimates that 7,000,000 people die each year from poor air quality [7]. The latest World Health Organisation report for 2021 [7] defines the maximum allowed annual average concentrations of PM_{2.5} and PM₁₀ as 5 µg/m³ and 15 µg/m³, respectively. The daily average concentration of PM_{2.5} has been reduced from 25 µg/m³ to 15 µg/m³, and for PM₁₀ from 50 µg/m³ to 45 µg/m³. Furthermore, the amendment to the Regulation of Minister of the Environment (8 October 2019) regarding the levels of certain substances in the air changed the notification and the alert level with respect to PM₁₀ concentrations. According to the regulation, the alert level is declared when the daily average value of PM₁₀ exceeds 150 µg/m³ (previously 300 µg/m³), and the alert level is set at 100 µg/m³ (previously 200 µg/m³) [8].

Polycyclic aromatic hydrocarbons (PAHs) are important constituents of particulate matter and are known for their mutagenic and carcinogenic potential. An increase in atmospheric PAH concentrations can therefore pose serious risks to both the environment and human health [2,4]. The strongest carcinogenic compounds are benzo[a]pyrene and dibenzo[a,h]anthracene [9]. The Environmental Protection Agency [10] compiled a list of 16 PAHs, which are treated as the most toxic and are listed above in the abstract. Exposure to PAHs is assessed using the following toxic equivalency factors recommended by the EPA (Environmental Protection Agency): mutagenic equivalent to B[a]P (mutagenic equivalent, MEQ), toxic equivalent to B[a]P (toxic equivalent, TEQ), and carcinogenic equivalent to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (carcinogenic equivalent, CEQ) [10].

B[a]P is the only compound with concentration standards set by the World Health Organisation, which is established at 1 ng/m³ on an annual scale [11]. B[a]P is commonly measured in environmental analyses as a marker of the total content of PAHs. In Poland, the concentrations of B[a]P remain consistently high, significantly exceeding the permissible values. The concentration of B[a]P is high in Knurów and Łódź (Figure 1), and it has exhibited relatively high PAH levels with significant fluctuations, particularly in the mid-2000s. Other locations, such as Zielonka and Puszcza Borecka, consistently showed lower PAH concentrations throughout the period. In general, the study indicates varying PAH levels by location and year, reflecting differences in air quality between these areas over time (shown in Figure 1).

Studies conducted in many cities in Poland demonstrate that the concentrations of B[a]P significantly exceed the permissible levels. For Wadowice [1,12] and the studies conducted in 2017, the average concentration of B[a]P during the heating period was 4.98 ng/m³, and during the non-heating period, it was 1.10 ng/m³. High average daily concentrations of B[a]P were observed in studies [2,3,10] conducted in the Upper Silesia region, where busy streets with high traffic volume during peak hours recorded concentrations ranging from 7.90 to 11.10 ng/m³. The aim of this study was to provide a detailed

description of the aerosol chemistry in the Kraków metropolitan area, based on particle samples collected during the COVID-19 epidemic. The processing of these analyses enabled the extraction of statistical data, which, together with the backward trajectory of the air masses and the analysis of diagnostic ratios, enabled the identification of the sources of the emission of polycyclic aromatic hydrocarbons in the city at that time. Furthermore, the study contributes to a better understanding of the impacts of local and regional pollutants on the air quality in the area and provides valuable information on future environmental improvements.

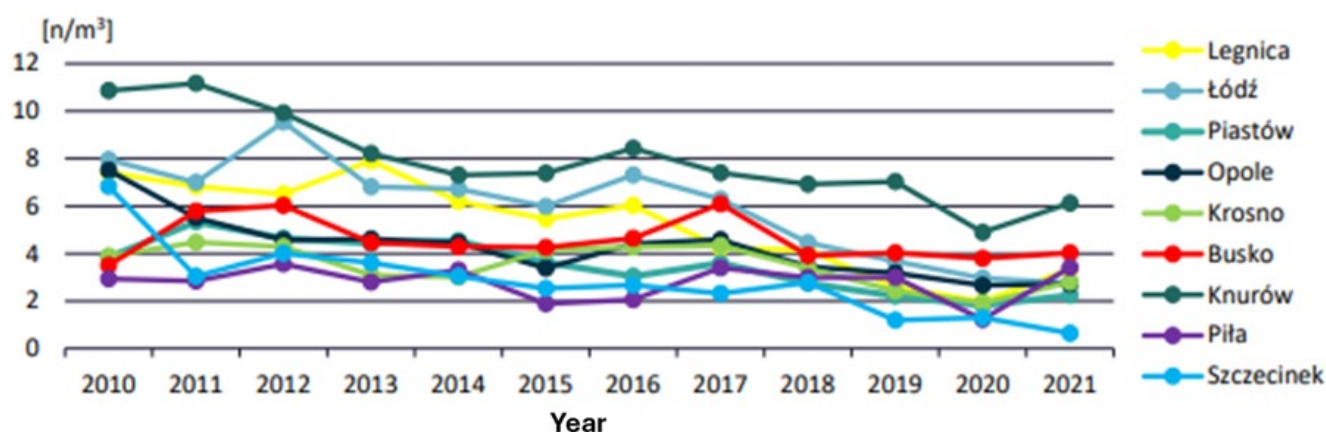


Figure 1. Mean annual concentrations of benzo[a]pyrene from 2010 to 2021 in selected cities in Poland (Source: GIOŚ/PMŚ, IOŚ-PIB).

2. Materials and Methods

Krakow, with an area of 326.85 km², a population of 802,800 (2456 people/km²), and a relative elevation ranging from 188 to 383 metres altitude (as of 30 June 2022) [12], is located in the valley of the Vistula River, at the intersection of four geographic regions: the Kraków-Częstochowa upland to the north, the Sandomierz Basin to the east, the western Beskid foothills to the south, and the Oświęcim Basin to the west. The city is characterised by a continental climate, with the lowest monthly temperatures recorded in December (approximately −3 °C) and the highest in July (approximately 24 °C). The average annual precipitation is 730 mm, slightly higher in urban areas compared to the outskirts (690 mm for the Balice station). The prevailing wind direction is westward (19.7%). Frequent temperature inversions and dense urban development contribute to limited natural ventilation in the city, leading to high concentrations of pollution [13]. Through Resolution No. XVII/243/16 of the Małopolska Regional Assembly dated 15 January 2016, Krakow is subject to an absolute ban of solid fuel combustion [14]. On 24 April 2017, the Małopolska Regional Assembly passed a resolution that allows for the combustion of fuel of appropriate quality [14].

In the presented measurement campaign, daily PM₁₀ samples were collected using a low volume sampler LV (GmbH, Berlin, Germany) (Figure 2) on quartz fibre filters (Whatman QM-A 47 mm diameter) with 24 h resolution. The sampling was carried out over several periods: January–April 2020, July–August 2020, and December 2020–February 2021. The calculated average values for individual months may be unrepresentative due to the small number of measurement days in each month; the number of samples is equal to the number of days of sampling. The number shows 5 days in January, 17 days in February, 6 days in March, 7 days in April, 16 days in July, 13 days in August, 7 days in December 2020, and 13 days in January and February 2021. The sampling periods (January–April 2020, July–August 2020, and December 2020–February 2021) were intentionally selected to represent both the heating and non-heating seasons and to coincide with distinct phases of

the COVID-19 pandemic in Poland. The winter periods corresponded to strict lockdown stages with substantially reduced traffic activity and increased residential stay-at-home time, whereas July–August 2020 represented a phase of relaxed restrictions and lower heating demand. During the non-heating season, concentrations of particle-bound PAHs in single daily samples were frequently close to the analytical LOQ; therefore, 3–5 consecutive daily filters were composed to ensure reliable quantification. Compositing was applied only when daily PM_{10} concentrations were below $30 \mu\text{g m}^{-3}$ and low PAH signal was expected, while days with elevated PM_{10} were analysed individually. PAH concentrations obtained from composite extracts were subsequently normalised to daily PM_{10} mass to derive daily average concentrations.



Figure 2. Low-volume sampler LV Leckel; the right-hand side shows an internal exploded view of the main components (Krakow).

The sampler was installed on the roof of a three-story building at the Faculty of Physics and Applied Computer Science of the AGH University of Krakow (coordinates $50^{\circ}07' \text{ N}$, $19^{\circ}91' \text{ E}$, elevation 220 m above sea level), located among Kawory, Nawojki, Czarnowiejska, and Władysława Reymonta Streets (see Figure 3). All quartz fibre filters were preheated for 6 h at $550 \pm 8^{\circ}\text{C}$ and subsequently maintained at a temperature of $20 \pm 1^{\circ}\text{C}$ with a relative humidity of $50 \pm 5\%$ for a minimum of 24 h before weighing and sampling. After sampling, the filters were conditioned for 48 h, weighed using a microbalance (A&D HM-202-EC) with an accuracy of 0.01 mg, and then stored in a freezer at -20°C until analysis. The masses of the filters before and after sampling were obtained as the average of three measurements (PN-EN 12341:2006a; PN-EN 14907:2006b). This is a Polish adoption of the European gravimetric determination.

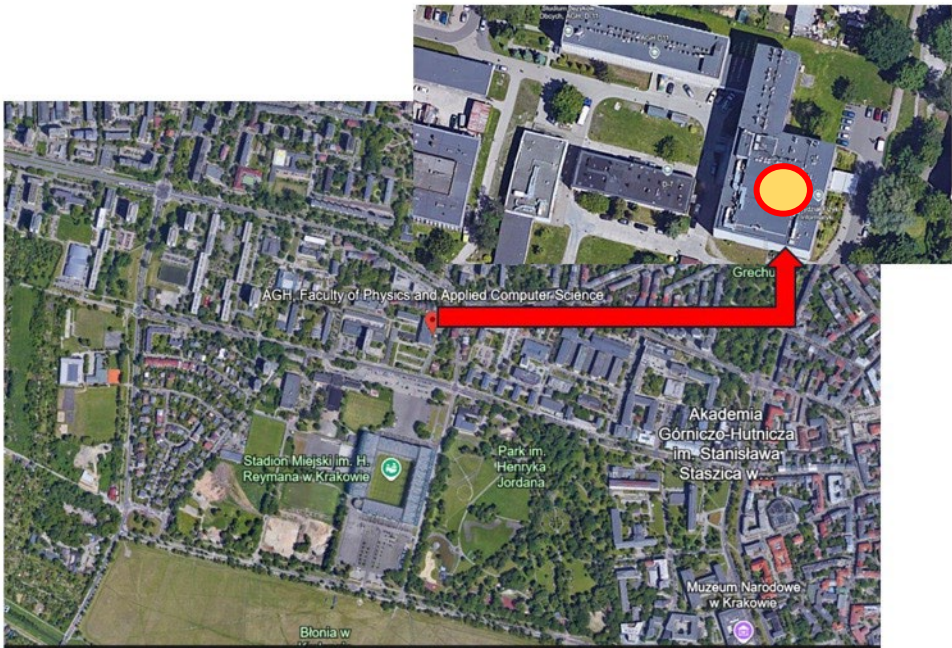


Figure 3. Sampling site: Krakow 2020–2021 (Google Maps 20225, accessed 7 February 2025) [15].

Table 1 presents detailed meteorological data for Kraków based on the statistical analysis of historical hourly weather reports available on the Weather Spark website and model reconstruction from January 1980 to 31 December 2016 [16]. The table contains the average monthly values of the following meteorological parameters: temperature, duration of precipitation, and wind speed.

Table 1. Historical meteorological data for Kraków (1980–2016) [16].

Temperature [°C]	Month											
	01	02	03	04	05	06	07	08	09	10	11	12
Max	1	3	8	14	19	22	24	24	19	14	7	3
Average	−2	0	3	9	14	17	19	18	14	9	4	0
Min	−5	−4	−1	4	9	12	14	13	9	4	0	−3
Precipitation duration [days]												
Rain	3.5	3.2	5.0	6.9	10.3	11.3	11.1	9.3	7.3	6.1	4.7	3.8
Mixed	0.7	0.9	0.8	0.3	0.0	0.0	0.0	0.0	0.0	0.1	0.5	1.0
Snow	1.2	0.8	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.9
Any	5.4	5.0	6.3	7.3	10.3	11.3	11.1	9.3	7.3	6.3	5.7	5.7
Wind speed [m/s]	4.8	4.7	4.5	3.9	3.5	3.5	3.4	3.4	3.7	3.9	4.1	4.6

3. Chemical Analysis

The calibration curves/functions were determined using a Clarus 600/600T gas chromatographer (PerkinElmer, Inc., Shelton, CT, USA) coupled with mass spectrometry (GC-MS) using standards of known concentration, specifically EPA 525 PAH mix A (Sigma Aldrich). This mixture consisted of 16 PAHs dissolved in cyclohexane: acenaphtene (Acn), acenaphthylene (Acy), anthracene (Ant), benzo[b]fluoranthene (B[b]F), benzo[a]anthracene (B[a]A), benzo[a]pyrene (B[a]P), benzo[ghi]perylene (B[ghi]P), benzo[k]fluoranthene (B[k]F), chrysene (Chry), dibenzo[ah]anthracene (D[ah]A), fluoranthene (Flt), fluorene (Flu), indeno [1,2,3-cd]pyrene (IP), naphthalene (Nap) phenanthrene (Phen), and pyrene (Pyr). The organic solvents used for the GC analysis, including dichloromethane (99.8%

purty for GC) and cyclohexane (99.0% purity for GC), were obtained from Avantor Performance Materials Poland S.A.

The isolation and enrichment of PAHs from the filters were conducted through solvent extraction. Initially, an 18 mm diameter punch was taken from each filter. During the non-heating season, to address the low concentration of particulate matter (PM) and achieve PAH concentrations above the limit of quantification (LOQ), punches from multiple filters were combined to create average samples collected over several days. Based on the concentrations measured for the PM₁₀ fraction of particulate matter, several daily filters were chosen for aggregation, and the PAH concentrations were analysed in the combined samples. The daily PAH values for these samples were calculated using the average PAH concentration of the aggregated sample and the PM₁₀ concentration of the corresponding daily sample. This included data from 5 days in January, 17 days in February, 6 days in March, 7 days in April, 16 days in July, 13 days in August, 7 days in December 2020, and 13 days in January and February 2021.

The individual punch or combination of punches was placed in separate 20 mL vials. Samples were extracted twice with 3 mL of dichloromethane and 2 mL of cyclohexane for 40 min using a horizontal shaker set at 50 rpm. The combined extract volume was reduced to 200 µL in a thermoblock (AccuBlock Digital Dry Bath Labnet, Woodbridge, VA, USA) by applying a gentle stream of argon at 30 °C. The extracts were then centrifuged at 12,000 rpm to remove solid impurities that had formed during the extraction and volume reduction process. Finally, the concentrates were transferred to chromatographic vials for analysis using GC-MS. Table 2 presents the parameters of the GC-MS analysis.

Table 2. Operating conditions and instrumental parameters for GC-MS analysis (FULL SCAN and SIM modes) using an HP-5 ms capillary column.

Operating Mode	FULL SCAN and SIM
GC column	Capillary column HP—5 ms 30 m × 0.25 mm—0.25 µm I—60 °C for 1 min II—from 60 °C to 300 °C at 15 °C/min III—300 °C for 13 min
Temperature program	
Temperature of injection port	250 °C
Temperature of ion source	250 °C
Temperature of transfer line	250 °C
Ionisation energy	Positive electron ionisation: 70 eV
Volume of injections	1 µL
Split ratio	1:10
Carrier gas	He, 1 mL/min (99.9999%)
Total analysis time	30 min

Data were collected, analysed, and processed using TurboMass software (version 5.4, PerkinElmer) using SCAN and SIM (Single Ion Mode) modes. Retention times, characteristic ions of tested analytes, and validation parameters of the method are shown in Table 3.

Data quality was assessed by evaluating the limits of detection (LOD), limits of quantification (LOQ), and the linearity of the calibration curve. Limits of detection (LOD) were obtained on the signal to noise ratio of 3:1. Limits of quantification (LOQ) were calculated as LOQ 3× LOD. Linearity was determined by analysing calibration points within the concentration range of 2.5 to 10,000 ng/mL. The calibration curves for all organic compounds demonstrated a high degree of linearity, with R² values ranging from 0.991 to 1.000. The percent recoveries for all target compounds were tested using 4-fold repetition of analyses for samples with a known amount of analyte (1000 ng, 500 ng, 100 ng, and 50 ng).

The percentage recoveries for all PAHs were in the range of 88 to 97%. In the calculations of PAH concentrations, the value of percent recoveries for each PAH was considered. To determine the LOQ, the value of the peak area of a given analyte was assumed to be 3 times smaller than the smallest peak area obtained from the calibration curve.

Table 3. Chromatographic and mass spectrometric characterisation of target analytes: retention time, mass of characteristic ions, limits of detection (LOD), and limits of quantification (LOQ).

Compound	Precursor	Retention Time [min]	LOD [$\mu\text{g}/\text{m}^3$]	LOQ [$\mu\text{g}/\text{m}^3$]	RSD (%)
Naphthalene	128	6.11	0.58	1.74	6.36
Acenaphthylene	152	8.45	1.09	3.27	4.57
Acenaphthene	153	8.77	0.72	2.16	8.38
Fluorene	166	9.72	0.63	1.89	6.08
Phenanthrene	178	11.68	4.59	13.77	3.23
Anthracene	178	11.79	1.50	4.50	4.49
Fluoranthene	202	14.32	1.34	4.02	4.63
Pyrene	202	14.82	0.28	0.84	2.87
Benzo[a]anthracene	228	17.60	0.13	0.39	3.37
Chrysene	228	17.69	0.21	0.63	4.95
Benzo[b]fluoranthene	252	19.95	0.51	1.53	3.74
Benzo[k]fluoranthene	252	20.01	0.14	0.42	2.76
Benzo[a]pyrene	252	20.60	0.29	0.87	6.68
Indeno[1,2,3-cd] pyrene	276	22.98	0.57	1.71	3.82
Dibenzo[ah]anthracene	278	23.06	1.87	5.61	3.45
Benzo[ghi]perylene	276	23.64	0.25	0.75	4.41

4. Results and Discussion

4.1. Particulate Matter PM_{10}

The distribution of the average monthly concentrations of PM_{10} in Kraków is shown in Figure 4. To better reflect the statistical distribution of the results, charts containing a set of data for the heating and non-heating seasons for Krakow were prepared (Figure 5). The study period coincided with the COVID-19 pandemic, which substantially altered human activity and therefore emission patterns. During the strict lockdown phases in 2020 and winter 2020/2021, traffic intensity in Kraków was markedly reduced due to mobility restrictions, remote work, and closure of educational institutions. At the same time, residential energy demand increased because people spent more time at home. The predominance of high-molecular-weight PAHs and elevated B[a]P levels observed in the heating seasons suggests that emissions from domestic solid-fuel combustion remained the dominant source of particulate-bound PAHs despite the concurrent reduction in traffic. In contrast, during July–August 2020, when restrictions were relaxed, PAH concentrations were lower overall and diagnostic ratios indicated a relatively higher contribution from traffic-related sources. The highest average monthly concentration of PM_{10} was recorded in February 2021 at $106 \mu\text{g}/\text{m}^3$, while the lowest was recorded in July 2020 at $23 \mu\text{g}/\text{m}^3$.

The highest concentration of PM_{10} was recorded on 24 February 2021, while the lowest concentration was recorded on 11 February 2020, respectively $234 \mu\text{g}/\text{m}^3$ and $8.1 \mu\text{g}/\text{m}^3$. The concentration in the heating season (January–April) ranged from $8.1 \mu\text{g}/\text{m}^3$ (11 February 2020) to $130 \mu\text{g}/\text{m}^3$ (8 February 2020) with an average daily PM_{10} concentration of $65 \mu\text{g}/\text{m}^3$. In the 2020/2021 winter season (December 2020, January and February 2021), these values ranged from $21 \mu\text{g}/\text{m}^3$ (13 December 2020) to $234 \mu\text{g}/\text{m}^3$ (24 February 2021) with the average daily concentration of PM_{10} equal to $75 \mu\text{g}/\text{m}^3$. During the non-heating season (July, August 2020), the range of PM_{10} concentrations was $9.6 \mu\text{g}/\text{m}^3$ (23 July 2020) to $65 \mu\text{g}/\text{m}^3$ (29 August 2020), while the daily average concentration was $23 \mu\text{g}/\text{m}^3$. This study has several limitations. Measurements

were performed at a single urban background site and therefore may not have captured the full spatial heterogeneity within the city. The number of samples was limited during some months, and several filters were composed in summer to exceed the LOQ, which may have reduced temporal resolution. Only particle-bound PAHs were analysed; gas-phase species were not included, potentially underestimating the total PAH exposure, particularly for low-molecular-weight compounds.

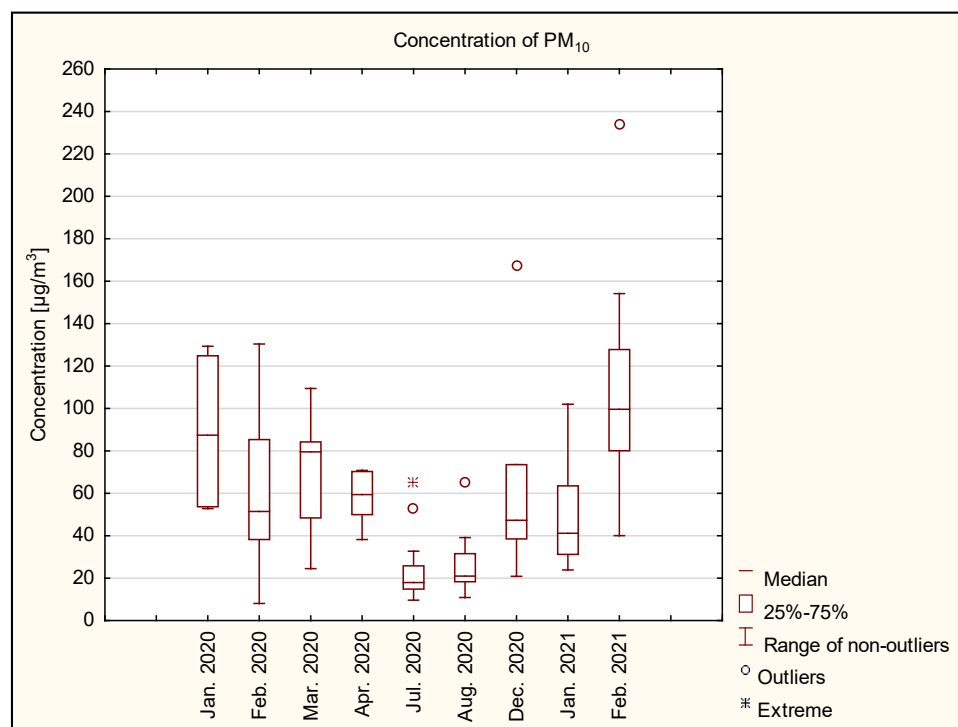


Figure 4. Distribution of PM₁₀ concentrations for Krakow 2020/2021. Values obtained for individual measurement months.

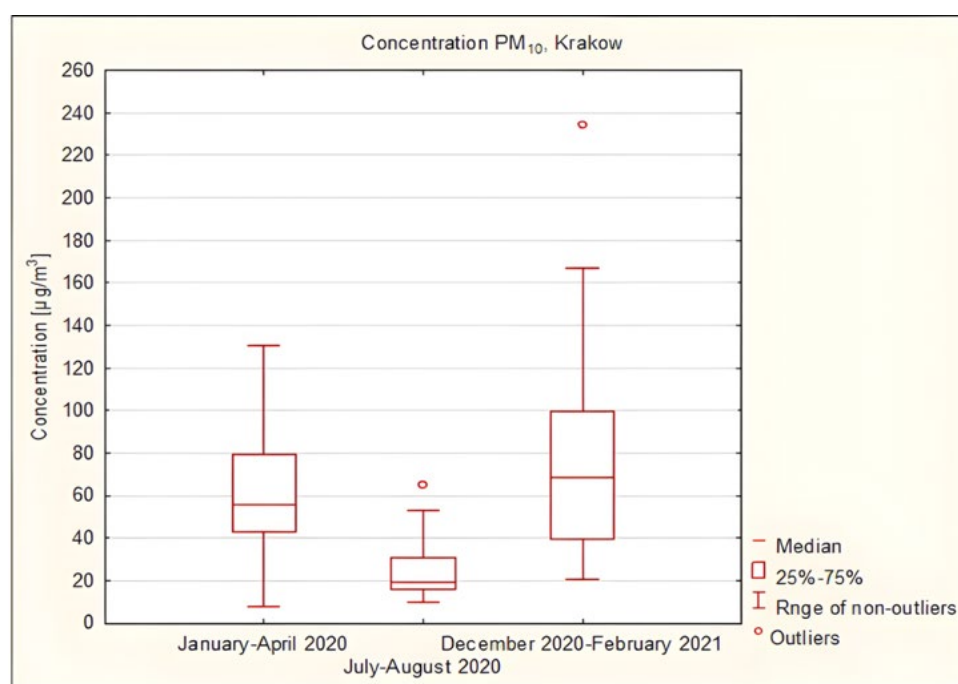


Figure 5. Distribution of PM₁₀ concentrations for Krakow in 2020/2021 considering the heating and non-heating seasons.

In [17,18], measurements were taken before the ban on burning solid fuels for Kraków in 2018/2019 for two measuring stations: Al. Krasinskiego and Zloty Rog, with similar seasonal differences in PM_{10} . The average daily concentrations of PM_{10} were twice higher in the winter season than in the summer season. In the summer season, the average daily concentrations of PM_{10} did not exceed $50 \mu\text{g}/\text{m}^3$, while in the winter season, the highest recorded values of the average daily concentrations of PM_{10} were $157 \mu\text{g}/\text{m}^3$ and $132 \mu\text{g}/\text{m}^3$ for Al. Krasinskiego and Zloty Rog, respectively. Research [19] on PM_{10} concentrations in Krakow, carried out in 2014, showed the highest average daily concentrations of particulate matter in the winter season: 3 February 2014— $136.6 \mu\text{g}/\text{m}^3$, 4 February 2014— $153.8 \mu\text{g}/\text{m}^3$, and 6 February 2014— $112.9 \mu\text{g}/\text{m}^3$. The lowest daily concentration of PM_{10} was recorded in summer— $23.5 \mu\text{g}/\text{m}^3$. The authors of [19,20] presented the percentage share of days with an exceedable average daily concentration of PM_{10} ($50 \mu\text{g}/\text{m}^3$). Research was carried out in the months of September 2017–April 2018 and September 2018–April 2019 for 7 measurement stations located in Krakow. At the Al. Krasinskiego measuring station, the permissible level was exceeded for 275 days, which was 75% of all measurement days for this station. For the Piastow station, it was 127 days, Wadow 115 days, Zloty Rog 176 days, Kurdwanow 163 days, Dietla 185 days, and Bulwarowa 151 days. The highest average daily concentration of PM_{10} was recorded at Aleje Krasinskiego station on 5 March 2018 of $224 \mu\text{g}/\text{m}^3$. In the study by [20] carried out for the city of Skala, located about 20 km north of Kraków, in winter (24 January–20 February; 28 sampling days) 2017, the daily concentration of PM_{10} ranged from $43 \mu\text{g}/\text{m}^3$ to $407 \mu\text{g}/\text{m}^3$, while the average concentration in the measurement period was $174 \mu\text{g}/\text{m}^3$. Throughout the sampling period in Krakow reported in this study, for only 11 days did the average daily concentration of PM_{10} not exceed the average daily concentration level ($50 \mu\text{g}/\text{m}^3$). High concentrations of particulate matter have also been recorded for Slask Voivodship [21]. In the years 2018–2021, 113 days with an exceedingly permissible level of PM_{10} were recorded for Dabrowa Gornicza in 2018, 69 days in 2019, 49 days in 2020, and 65 days in 2021. For Czestochowa, it was 72 days, 39 days, 20 days, and 40 days, respectively, while for Katowice, it was 93 days (2018), 72 days (2019), 48 days (2020), and 52 days (2021), respectively. The highest number of days with a concentration greater than $50 \mu\text{g}/\text{m}^3$ was observed in Pszczyna: 2018—139 days, 2019—116 days, 2020—96 days, and 2021—94 days.

4.2. Polycyclic Aromatic Hydrocarbons Bonded to PM_{10}

The distributions of the concentrations of polycyclic aromatic hydrocarbons in the sampling months and in the heating and non-heating seasons in Krakow are presented in Figures 6 and 7.

PAH concentrations throughout the sampling period ranged from $0.01 \text{ ng}/\text{m}^3$ to $18.85 \text{ ng}/\text{m}^3$. The highest daily concentrations were detected for phenanthrene ($18.85 \text{ ng}/\text{m}^3$ —27 February 2020), benzo[b]fluoranthene ($16.95 \text{ ng}/\text{m}^3$ —24 February 2020), and pyrene ($16.61 \text{ ng}/\text{m}^3$ —27 February 2020). The highest average daily concentration in the first (January–April 2020) and second (December 2020–February 2021) heating season was characterised by benzo[b]fluoranthene ($2.06 \text{ ng}/\text{m}^3$ and $7.64 \text{ ng}/\text{m}^3$, respectively). In the non-heating period, the highest average daily concentration was also recorded for benzo[b]fluoranthene ($0.14 \text{ ng}/\text{m}^3$) and phenanthrene ($0.09 \text{ ng}/\text{m}^3$). In summer, the concentration values for many compounds were below the LOQ.

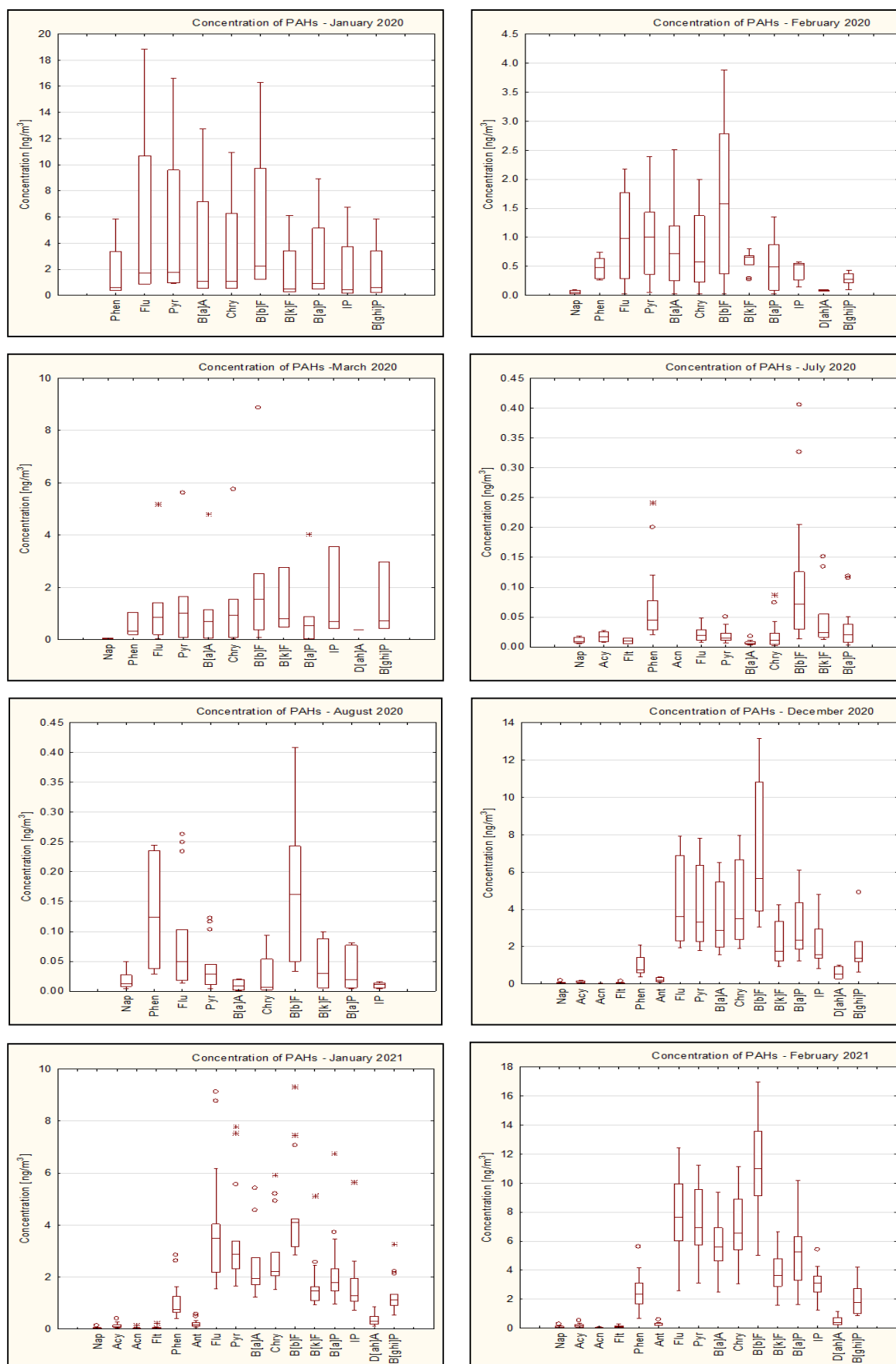


Figure 6. Distribution of PAH concentrations for Krakow (2020/2021) (—median, □—values between 25% and 75%, T i l —non-outliers, ○—outliers, *—extreme).

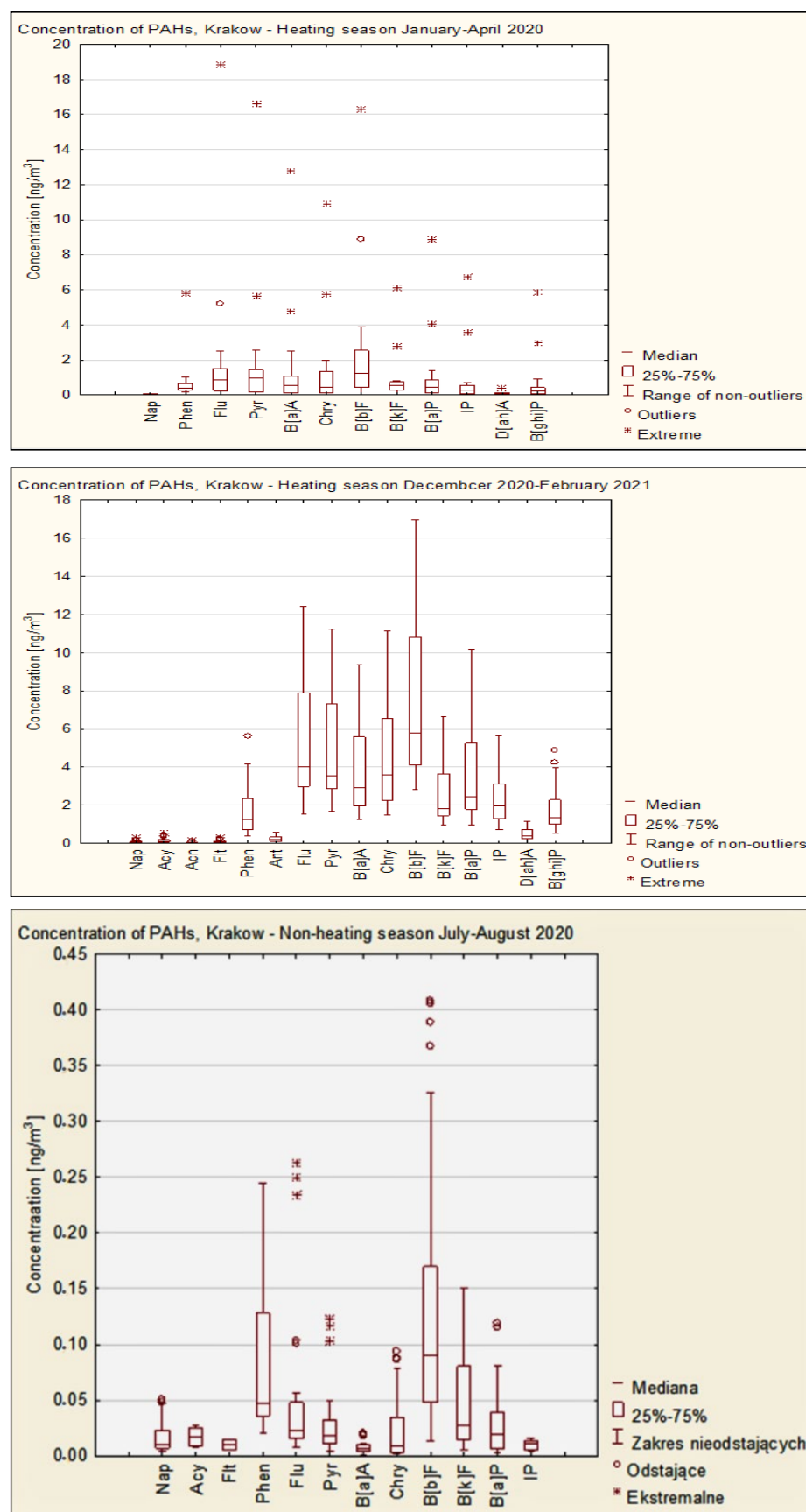


Figure 7. Distribution of PAH concentrations for Kraków (2020/2021) considering the heating and non-heating seasons with range of non-outliers (—median, □—values between 25% and 75%, —non-outliers, ○—outliers, *—extremes).

Figure 8 shows the distribution of benzo[a]pyrene concentration in Kraków.

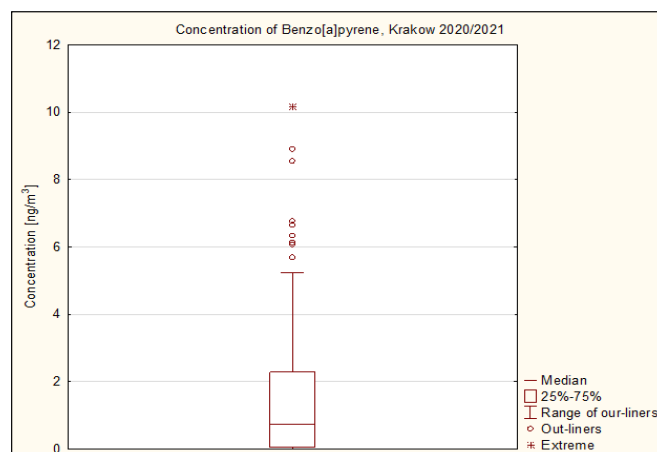


Figure 8. Distribution of B[a]P concentrations for Krakow (July 2020/February 2021).

During winter, the average monthly concentration of benzo[a]pyrene was 1.56 ng/m^3 . The highest values were determined on 24 February 2021 (10.16 ng/m^3) and 27 February 2020 (8.91 ng/m^3). Most measurements fell within the 25% to 75% distribution range. Similar seasonal variations have been observed for many large cities in Poland and around the world. In 2014–2018, the Voivodeship Inspectorate for Environmental Protection reported high concentrations of B[a]P in many cities in Poland. The highest average annual concentration of B[a]P was observed at the station in Brzeszcze, measuring 22.70 ng/m^3 in 2017, while the lowest concentration was found at the station in Muszyna-Złockie, at 2.00 ng/m^3 in 2018. The permissible levels of B[a]P were exceeded in resort areas. In the Krakow Agglomeration, the average annual concentrations of B[a]P varied between 3.60 ng/m^3 and 8.30 ng/m^3 . In the Lesser Poland Voivodeship, the maximum concentrations recorded in specific years were at the following stations: Nowy Targ (15.20 ng/m^3 , 2014), Nowy Sącz (12.00 ng/m^3 , 2015), Nowy Sącz (9.70 ng/m^3 , 2016), Brzeszcze (22.70 ng/m^3 , 2017) and Nowy Targ (18.30 ng/m^3 , 2018) [22–25]. In research [4] in Upper Silesia [22], in areas characterised by high traffic intensity, the range of B[a]P concentrations was 7.90 ng/m^3 – 11.10 ng/m^3 . Analyses made for Warsaw and Gliwice [23] also showed high concentrations of B[a]P in closed rooms: Warsaw— 1.11 ng/m^3 , and Gliwice— 3.27 ng/m^3 . In many studied cases, B[a]P constituted 1–20% of all PAHs [22,24,26]

4.3. Diagnostic Ratios

The ambient concentration of specific air pollutants depends on their emission sources. Because the research covered pandemics, for example, there was a small share of car traffic, especially on those dates when there had been a lockdown (Table 4). In many studies as well as in this article, most PAHs are classified as heavier hydrocarbons (4 rings and more) [3,22]. The presence of heavier PAHs in the air indicates the emission of pollutants from sources such as transport (combustion of fuels in engines) and heating houses with low-calorific fuel (Table 4) [24,27,28]. The contribution of individual PAHs and their relationship to each other can be used to estimate the origin of particulate matter. PAH concentration ratios are referred to as diagnostic indicators. For example, PHE, FLT, and PYR are mostly considered as carbon-burning markers. B[a]P and FLU are emitted during wood processing (Table 4) [29]. Flu, Pyr, BbF, and BkF are characteristic of fuel combustion in diesel engines [30,31]. Table S1 (in the Supplementary Materials) presents the characteristic diagnostic ratios (DR) derived from various sources.

Table 4. Characteristic diagnostic indicators from different sources.

No.	Ratio	Value Range	Source	Refs.
1.	$Flu / (Flu + Pyr)$	<0.50 >0.50	Petrogenic emission Petrogenic emission (combustion)	[27,30,31].
2.	$Fla / (Fla + Pyr)$	<0.50 >0.50	Petrogenic emission Coal, wood burning	
3.	$B[b]F / B[k]F$	~0.92	Wood burning	
		~1.26	Vehicles	
		2.50–2.90	Smelters	
4.	$Pyr / B[a]P$	3.50–3.90	Coal/coke	
		0.90 ± 0.40	Gasoline exhaust	
		0.80 ± 0.90	Diesel exhaust	
5.	$B[a]P / (B[a]P + Chr)$	0.70	Wood combustion	
		0.08–0.39	Wood burning	
		<0.50	House heating	
		>0.50	Mobile sources	
		~0.18	Car	
6.	$IcdP / (IcdP + B[ghi]P)$	~0.37	Diesel exhaust	
		~0.32	Gasoline vehicles	
		~0.32	Natural gas combustion	
		~0.36	Oil combustion	
		~0.56	Coal	
7.	$B[a]A / (B[a]A + Chr)$	~0.64	Wood burning	
		~0.50	Vehicles	
		~0.73	Gasoline and diesel exhaust	

Table 5 presents the percentage participation of emission sources based on the average daily concentrations in samples taken in Krakow in 2020/2021. Values that exceeded the ranges of indicators in (Table 5) were assigned to a separate source category (other).

Table 5. Diagnostic ratios for samples of PM₁₀ for Krakow in 2020/2021.

No.	Ratio	Source	%
(1)	$Flu / (Flu + Pyr)$	Petrol emission	92
		Diesel emission	4
		other	4
(2)	$Fla / (Fla + Pyr)$	Petrogenic emissions	100
		Coal, wood burning	0
		other	0
		Wood burning	0
(3)	$B[b]F / B[k]F$	Vehicles	4
		Smelters	0
		Coal/coke	0
		other	96
		Gasoline exhaust	1
(4)	$Pyr / B[a]P$	Diesel exhaust	2
		Wood combustion	8
		other	89
		Wood burning	0
(5)	$B[a]P / (B[a]P + Chr)$	House heating	65
		Mobile sources	29
		other	6
		Car	0
		Diesel exhaust	0
		Gasoline vehicles	0
(6)	$IcdP / (IcdP + B[ghi]P)$	Natural gas combustion	0
		Oil combustion	0
		Coal	41
		Wood burning	11
		other	48

Table 5. Cont.

No.	Ratio	Source	%
(7)	$B[a]A/(B[a]A + Chr)$	Vehicles	61
		Gasoline and diesel exhaust	11
		other	28

Indicators (1), (2), and (7) indicate transport as the main source of pollution, mainly fuel combustion in internal combustion engines. Similar observations were made for places closely related to street transport [27]. No specific source information was obtained for indicator (3) was 96%, therefore, the results were classified as ‘other’ unknown sources. Similar assumptions were made for indicator (4). Indicator (5) most often facilitates the identification of sources, such as heating and mobile sources. In this study, it indicates the dominance of heating sources during the heating season. Because a significant part of the results concerned the colder months, 65% of the results indicated that house heating was the main source of these pollutants. In the remaining period (summer), transport dominated as the main source. Similar data were obtained for (6), where 41% of the days corresponded to coal burning and 1% to wood burning. For indicator (6), it was impossible to identify the source of pollutants with high probability due to the high percentage contribution of the ‘other’ unknown sources.

4.4. Health Risk Assessment

For a more accurate analysis of air quality, exposure profiles were determined considering the percentage of PAH content depending on the number of rings (their mass). Figure 9 shows the percentage of PAH particulates depending on the number of rings in the heating/non-heating season.

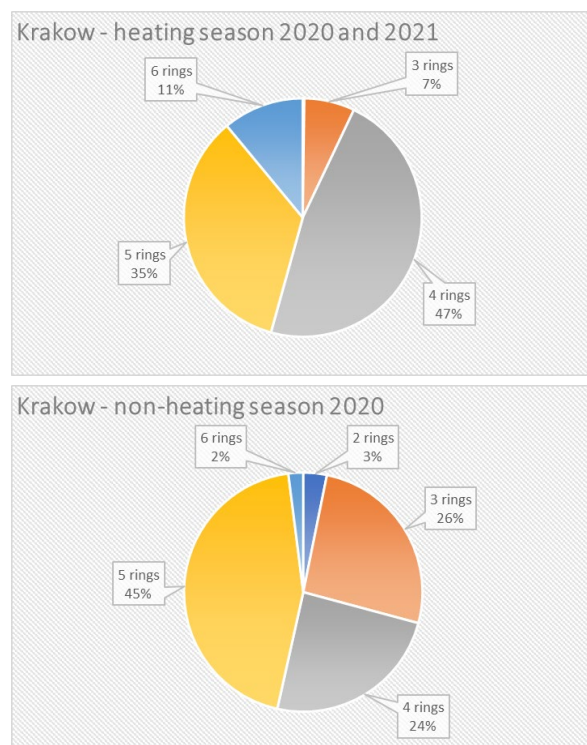


Figure 9. Percentage participation of PAHs in terms of the number of rings for Krakow in 2020/2021, considering the heating and non-heating seasons.

For Krakow, over 90% participation of heavy PAHs (PAHs containing ≥ 4 aromatic rings) was recorded in relation to all PAHs determined in the PM₁₀ samples. This is due to the adsorption and condensation of heavy PAHs on the surface of the particle matter. In the heating season, the share of heavy PAHs was about 93%, while in the non-heating season, it was 71%. In similar environmental studies [22,32], an analogous participation of PAHs with a 4–6 ring structure was observed, and the participation of heavy PAHs was estimated at 90% throughout the sampling period. In most cases, the values for light PAHs do not exceed 10%. A much smaller share of light PAHs is the result of their presence mainly in the gas phase. In warmer seasons, light PAHs dominate the total PAH mass, while heavy PAHs contribute less due to their lower presence in the gas phase.

Table 6 presents a profile considering the percentage of carcinogenic hydrocarbons in relation to the total concentration of all PAHs in the PM₁₀ fraction of particulate matter.

Table 6. Participable of cancerogenic PAHs, Krakow 2020/2021.

Heating Seasons 2020 and 2020/2021		Ref.
Total average monthly concentration of carcinogenic PAHs	15.98 ng/m ³	[33]
Total average monthly concentration of all PAHs	25.92 ng/m ³	
Percentage participable of carcinogenic PAHs	63%	
Non-Heating Season 2020		
Total average monthly concentration of carcinogenic PAHs	0.27 ng/m ³	
Total average monthly concentration of all PAHs	0.51 ng/m ³	
Percentage participable of carcinogenic PAHs	53%	

In Krakow, highly carcinogenic hydrocarbons accounted for 63% of all PAHs in the heating season and a 53% share in the non-heating season. Despite the lower total average of monthly concentrations of PAHs in summer periods, highly carcinogenic hydrocarbons accounted for more than 50% of all PAHs. In Katowice, for measurements of particulate matter fractions PM₁–PM₁₀, it was 55% for the winter season and 63% for the summer season [22]. One of the important reasons for the observation of this type of dependence in most cities in Poland is the dominant role of the emission source, that is, transport [3].

The relative impact of the PAH mixture on human health can be determined using different types of approaches, such as the CEQ, (MEQ), and TEQ. The values of these indicators are estimated using formulas with specific factors assigned to a given compound that consider its carcinogenic and mutagenic potential. The following are the formulas for individual indicators.

Equation (1). Mutagenic equivalent MEQ [23]

$$\text{MEQ} = 0.00056 \cdot [\text{Acy}] + 0.082 \cdot [\text{B[a]A}] + 0.017 \cdot [\text{Chry}] + 0.25 \cdot [\text{B[b]F}] + 0.11 \cdot [\text{B[k]F}] + 1 \cdot [\text{B[a]P}] + 0.31 \cdot [\text{IP}] + 0.29 \cdot [\text{D[ah]A}] + 0.19 \cdot [\text{B[ghi]P}] \quad (1)$$

Equation (2). Carcinogenic equivalent CEQ [23]

$$\text{CEQ} = 0.001 \cdot ([\text{Acy}] + [\text{Acn}] + [\text{Flu}] + [\text{Phen}] + [\text{Flt}] + [\text{Pyr}]) + 0.01 \cdot ([\text{Ant}] + [\text{Chry}] + \text{B[ghi]P}) + 0.1 \cdot ([\text{B[a]A}] + \text{B[b]F} + [\text{B[k]F}] + [\text{IP}]) + 1 \cdot [\text{B[a]P}] + 5 \cdot [\text{D[ah]A}] \quad (2)$$

Equation (3). Toxic equivalent TEQ [23]

$$\text{TEQ} = 0.000025 \cdot [\text{B[a]A}] + 0.0002 \cdot [\text{Chry}] + 0.000354 \cdot [\text{B[a]P}] + 0.0011 \cdot [\text{IP}] + 0.00203 \cdot [\text{D[ah]A}] + 0.00253 \cdot [\text{B[b]F}] + 0.00487 \cdot [\text{B[k]F}] \quad (3)$$

Table 7 presents the MEQ, CEQ, and TEQ values obtained for samples taken from Krakow and other places in Poland and around the world. These health-risk indicators (MEQ, CEQ, TEQ) were calculated assuming adult inhalation exposure with standard default parameters ($20 \text{ m}^3 \text{ day}^{-1}$ inhalation rate, 70 kg body weight, lifetime exposure duration). These indicators express the mixture toxicity in terms of benzo[a]pyrene equivalents and were compared to the regulatory guideline of 1 ng m^{-3} B[a]P. Results were therefore interpreted as screening-level indicators of potential health concern, and not exact quantitative risk estimates.

Table 7. MEQ, CEQ, and TEQ.

Location	Measurement Period	PM Fraction	MEQ [ng/m^3]	CEQ [ng/m^3]	TEQ [pg/m^3]	Refs.
Krakow, Poland	Non-heating season 2020	PM ₁₀	0.08	0.06	0.62	[1,22,33,34]
	Heating season 2020/2021		4.65	5.33	24.10	
Wadowice, Poland	Non-heating season 2017	PM ₁₀	3.05	11.27	14.00	
	Heating season 2017		22.08	72.23	94.00	
Katowice, Poland	Summer 2012	PM ₁₀	2.06	2.43	128	
	Spring 2012		3.54	4.16	413.9	
	Summer 2007/2008		7.87	23.09	42.82	
Delhi, India	Winter 2007	PM ₁₀	20.07	59.75	106.42	
	Summer 2007		0.14	0.10	0.56	
Zagrzeb, Croatia	Winter 2008	PM ₁₀	4.91	3.64	16.12	
	Summer 2009		0.09	0.12	0.43	
Madrid, Spain	Winter 2009	PM ₁	0.51	0.51	2.55	
	January–March 2004		0.53	0.48	2.19	
Atlanta, USA	October–December 2004	PM _{2.5}	0.97	0.90	3.52	

For all examined sites, much lower indicators were obtained during the summer periods or during non-heating seasons. Analysis of the results of this study and data collected from other cities in Poland and the world [1,22,33,35,36] shows that regardless of the measurement season (summer/winter, heating/non-heating) and the fraction of particulate matter, there is a high risk for humans generated by the presence of polycyclic aromatic hydrocarbons in the air. The greatest danger occurs in densely populated areas (e.g., India), with a high share of transport and burning solid fuels as the main sources of pollution [37].

4.5. Evaluation of the Direction of Pollutant Transport

To obtain information on the possibility of transporting pollutants from selected areas in the vicinity of the study sites, frequency analyses of the directions of air mass inflow were performed. Analyses were performed using the NOAA Air Resources Laboratory HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) developed by the NOAA Air Resources Laboratory [38–40]. Due to the analyses performed on a regional scale, data prepared by the GFS (Global Forecasting System) operational system with a resolution of $0.25^\circ/0.25^\circ$ and 127 layers were used as input to the model. These are data with the highest available resolution covering the analysed areas. GFS is a short- and medium-term weather forecasting system developed by the National Centres for Environmental Prediction (NCEP). NCEP data include information on wind speed and direction, temperature, humidity, pressure, altitude, precipitation, cloud cover, etc. The GFS data have a time resolution of 3 h. As base data, GFS.v2 was used (0.25 degrees, global system, data collected from June 2019) [39]. The simulation consisted of 24 generated backward trajectories with a duration of 12 h. The starting point was Krakow: $50^\circ 10' \text{ N}$, $19^\circ 90' \text{ E}$. The days with the highest daily concentration of PM₁₀ were selected for the backward trajectory analysis (Figure 10).

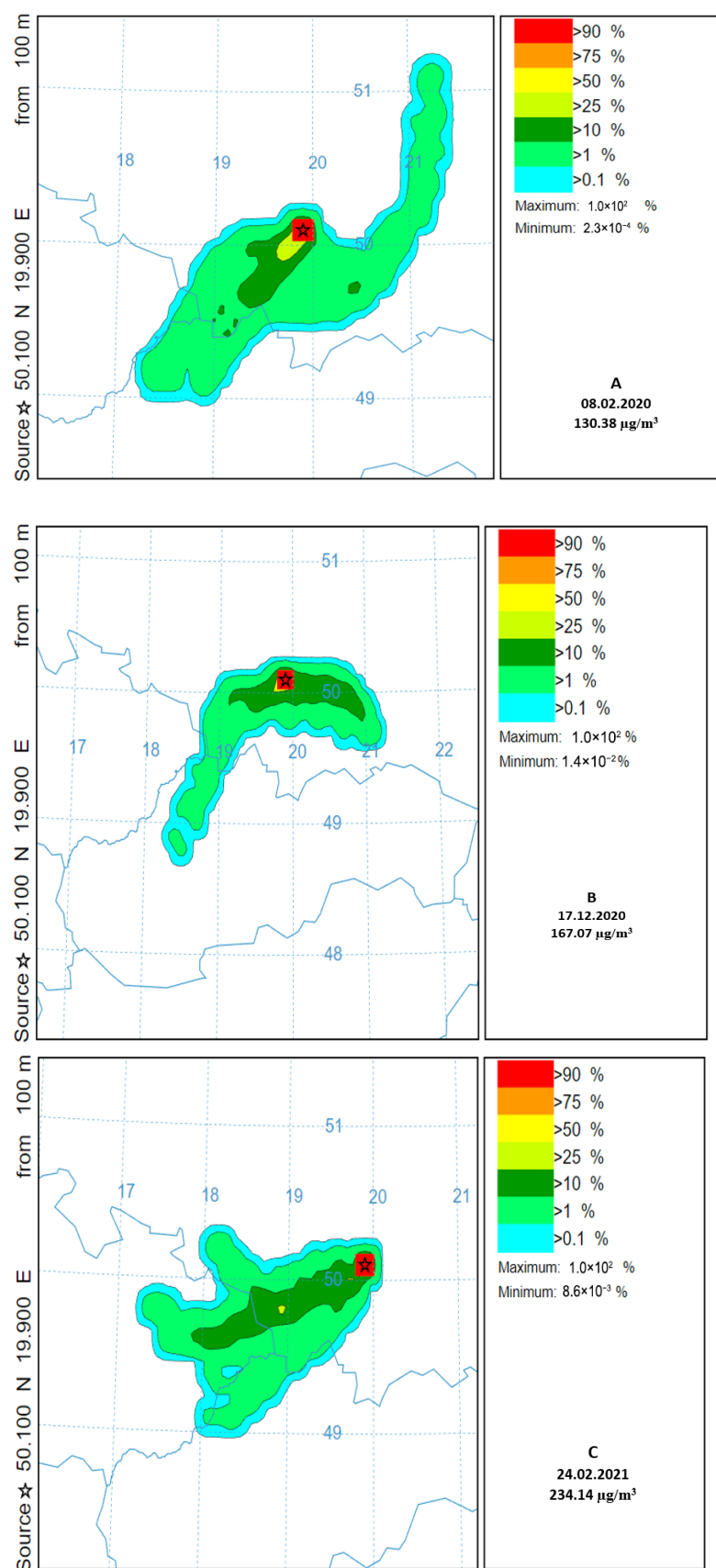


Figure 10. Frequency maps of backward trajectories for the selected days in Krakow: 8 February 2020 (A), 17 December 2020 (B), and 24 February 2021 (C). The colour scale corresponds to the percentage of the trajectory that crosses a given point.

Table 8 presents the average daily concentrations of PM₁₀, PAHs, B[a]P, and information on the daily meteorological conditions for the analysed cases.

Table 8. Meteorological conditions and ambient air pollutant concentrations (PM₁₀, total PAHs, and benzo[a]pyrene, B[a]P) during the selected sampling periods.

Fig.	Date	Wind Direction	Wind Speed [m/s]	Air Temperature [°C]	PM ₁₀ Concentration [µg/m ³]	PAHs Concentration [ng/m ³]	B[a]P Concentration [ng/m ³]
10A	20 February 2008	SW	0.7	0.4	130.38	4.78	0.10
10B	20 December 2017	E	1.2	2.3	167.07	67.24	6.11
10C	21 February 2024	SW	0.7	8.2	234.14	83.67	10.16

Analysis of the air mass trajectory for Kraków for days with the highest daily concentration of PM₁₀ showed the inflow of air masses from the south-west and east. These areas are characterised by a high population density: east direction—Tarnow, 1463 people/km² (as of 31 December 2021), Brzesko, 1421 people/km² (as of 31 December 2019) [37]; south-west direction—Bielsko Biala, 1352 people/km² (as of 31 December 2021), Wadowice, 1729.6 people/km² (as of 30 June 2021) [37]. The reports of the Chief Inspectorate of Environmental Protection rank these towns as high on the list of towns with the highest daily concentrations of particulate matter and benzo[a]pyrene in Poland [41–44]. The highest daily concentration of PM₁₀ was recorded in the south-west areas on 24 February 2021 and in the eastern areas on 17 December 2020 of 234.14 µg/m³ and 167.07 µg/m³, respectively. On 8 February 2020, the south-west direction of the retrograde trajectories also showed, despite the high daily concentration of PM₁₀ (130.38 µg/m³), that the daily PAHs and B[a]P were low, at 4.78 ng/m³ and 0.10 ng/m³, respectively. A factor influencing this type of observation is the terrain. Areas from south-west to south (SW/S) are characterised by upland and a mountain topography and lower population density such as Beskid Maly, Beskid Makowski, and Beskid Wyspowy [45]. In these areas, pollutants accumulate in the valleys because of the hindered natural ventilation process and the hindered movement of air masses. The areas south-east to west (SE/W) [46] are the areas of the valley stretching from Bielsko-Biala, Oswiecim to Jastrzebie-Zdroj. A similar shape dominates eastward from Krakow, Niepolomice, Bochnia, and Tarnow. These areas are characterised by a high population density, where house heating dominates, which has a major impact on air quality. The air monitoring carried out in these cities shows high daily concentrations of PM₁₀ and B[a]P [34,46].

5. Conclusions

This work presents a detailed chemical characterisation of PM₁₀ in Krakow for a period of 9 months. Analyses were performed on 92 samples obtained during the collection campaign. Seasonal variability was observed in the concentrations of PM₁₀, and 16 PAHs was observed. The highest average daily concentration of PM₁₀ in Krakow was 234.14 µg/m³ (11 February 2020). The lowest values of the average daily concentrations of PM₁₀ were recorded in non-heating seasons. The average monthly concentration of B[a]P was 1.56 ng/m³. The highest values were determined on 24 February 2021 (10.16 ng/m³) and 27 February 2020 (8.91 ng/m³). The reports of the Krakow Regional Inspectorate of Environmental Protection have shown that many Polish cities are characterised by poor air quality, where B[a]P concentrations significantly exceed the permissible level (average annual value of 1 ng/m³), and the compound itself can account for up to 20% of all PAHs. The highest daily concentrations were detected for phenanthrene (18.85 ng/m³—27 February 2020), benzo[b]fluoranthene (16.95 ng/m³—24 February 2020), and pyrene (16.61 ng/m³—

27 February 2020). The highest average daily concentrations for benzo[b]fluoranthene were recorded in both non-heating and heating periods.

In this study, various values of diagnostic ratios were shown. These indicators are ratios of specific concentrations of PAHs that can be used to estimate the origin of particulate matter. Transport as a source of pollution had the highest percentage share. A typical seasonal variation of emission sources was observed in the heating season (apart from transport) where house heating dominated (coal and wood burning sources), while in the non-heating season, it was mainly transport. Information on PAH concentration levels was used to determine the profiles of the pollution sources, exposure profiles, and the values of toxic equivalency factors recommended by the EPA: B[a]P mutagenic equivalent (MEQ), B[a]P (toxic equivalent of B[a]P, TEQ), and carcinogenic equivalent to 2,3,7,8-tetrachlorodibenzo-p-dioxin (carcinogenic equivalent, CEQ). Elevated carcinogenic equivalent (CEQ), the mutagenic equivalent (MEQ), and the toxic equivalent (TEQ) values signify a substantial presence of carcinogenic compounds that pose a serious threat to human health and well-being. Immediate targeted actions are necessary to decrease the concentrations of these harmful substances in the atmosphere, and most importantly, eliminate their emission sources. Deterministic models allowed us to estimate the possibility of a pollutant influx from neighbouring areas of the studied site. In the cases analysed, it can be concluded that the high concentrations of pollutants come from areas located in the vicinity of Krakow. The highest concentrations of particulate matter were recorded on days when the wind was mostly from the SW and E directions of pollution inflow. Despite these constraints, the study's strengths lie in its detailed chemical analysis, seasonal emission assessment, and integration of atmospheric transport modelling, making it a valuable contribution to air pollution research and policy development.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atmos17020120/s1>.

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