Seasonal Trends, Sources, and Health Impacts of PAH-Bound PM10 in Kraków Amidst the COVID-19 Pandemic

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Abstract

This study aimed to assess the seasonal variability, sources, and health impacts of PM10-bound polycyclic aromatic hydrocarbons (PAHs) in Krakow during the COVID-19 pandemic (2020–2021). A total of 92 PM10 samples were analysed using gas chromatography-mass spectrometry (GC-MS) for 16 priority PAHs identified by the US EPA. Concentration data were used to determine pollution source profiles and health risk indicators, including toxic (TEQ), mutagenic (MEQ), and carcinogenic (CEQ) equivalents. The analyses were performed using the NOAA Air Resources Laboratory's HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) developed by the NOAA Air Resources Laboratory (National Oceanic and Atmospheric Administration. Results revealed significant seasonal differences in PAH concentrations and highlighted increased exposure risks during colder months. The findings contribute to a better understanding of urban air pollution dynamics and public health implications.

Background

Fig. 1. Low-volume sampler LV Leckel.

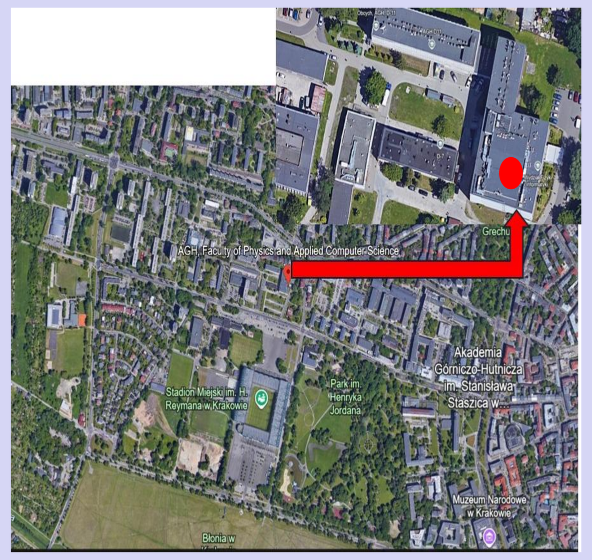

Fig. 2. Sampling site – Krakow 2020-2021 [Google Maps 2022]

- ✓ Daily PM10 samples were collected using a low-volume LV Leckel sampler on quartz fibre filters (Whatman QM-A, 47 mm) with 24-hour resolution. Sampling periods included Jan–Apr 2020, Jul–Aug 2020, and Dec 2020–Feb 2021, totaling 92 days. The sampler was located on the rooftop of a building at AGH University of Krakow. Filters were preheated (550 ± 8 °C for 6 h), conditioned (20 ± 1 °C, 50 ± 5% RH), and weighed (A&D HM-202-EC, ±0.01 mg) before and after sampling. Post-collection, filters were conditioned for 48 h and stored at −20 °C until analysis.

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Methodology

PAHs were extracted from PM10 samples using solvent extraction (dichloromethane and cyclohexane) and analysed via GC-MS (Clarus 600/600T) using the EPA 525 PAH Mix A standard. During low PM periods, filters were combined to ensure detectable PAH concentrations. Extracts were concentrated, centrifuged, and transferred to chromatographic vials. GC-MS operated in FULL SCAN and SIM modes with a capillary HP-5ms column. Calibration curves (2.5–10,000 ng/mL) showed high linearity (R^2 = 0.991–1.000). Method performance was verified by limits of detection (LOD), limits of quantification (LOQ), and recovery tests (88–97%). Analytical precision and sensitivity ensured reliable quantification of all 16 EPA-priority PAHs. Quality control included replicate analysis and correction for compound-specific recoveries.

Results

Particulate matter PM_{10}

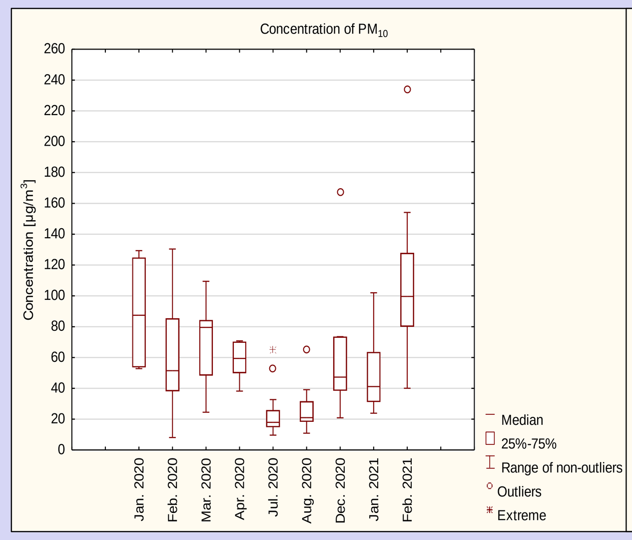

Fig. 3. Distribution of PM_{10} concentrations for Kraków 2020/2021. Values obtained for individual measurement months.

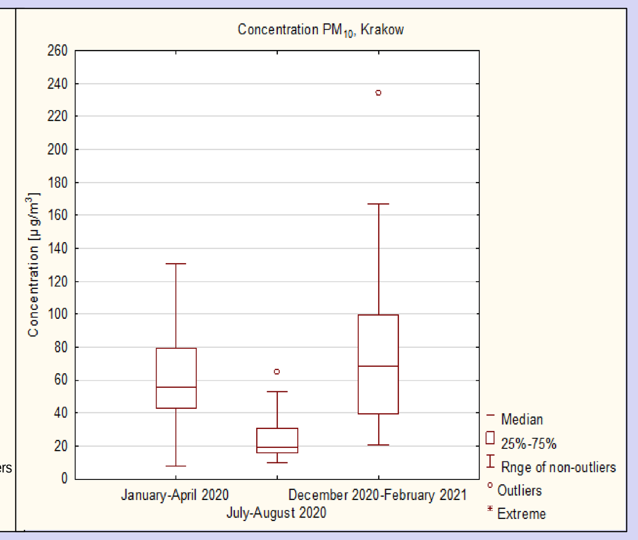

Fig. 4. Distribution of PM_{10} concentrations for Kraków in 2020/2021 considering the heating and non-heating seasons.

- ✓ PM10 concentrations during winter were approximately double those in summer, confirming a strong seasonal pattern linked to increased heating emissions, as shown in studies from Kraków (2018/2019) and Skała (2017) [Turek-Fijak et al. 2021].
- ✓ The legal daily PM10 limit of 50 µg/m³ was exceeded on a significant number of days—up to 275 days (75% of the measurement period) at Al. Krasińskiego station during 2017–2019 [Samek et al. 2021].
- ✓ Maximum daily PM10 values reached critical levels in winter, with 224 µg/m³ recorded in Kraków (March 2018) and up to 407 µg/m³ in Skała (February 2017), indicating severe pollution events [Kaleta and Kozielska 2023]..
- ✓ The problem extended across the Silesian Voivodeship, where cities like Pszczyna recorded between 94 and 139 exceedance days annually from 2018 to 2021, reflecting widespread regional air quality issues [Skiba et al., 2024d].
- ✓ During the 2020–2021 sampling period in the present study, during COVID-19, 11 days remained below the 50 µg/m³ threshold, underscoring the persistent and serious nature of PM10 pollution in Kraków.

Results

Polycyclic aromatic hydrocarbons binded to PM_{10}

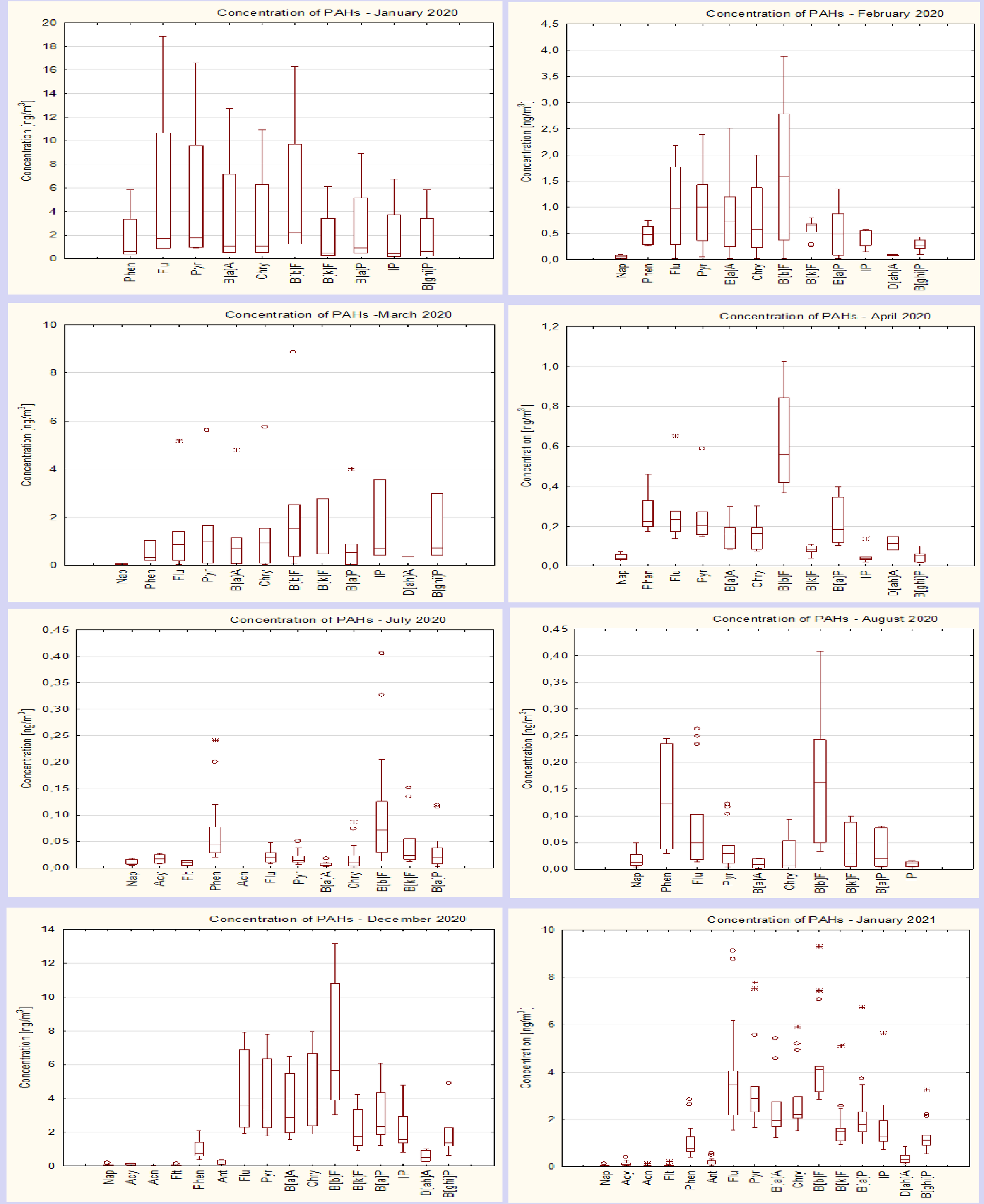

Fig. 5. Distribution of PAHs concentrations for Kraków (2020/2021)

(− - median, □ – values between 25 % - 75 %, ⊤ i ⊥ - non-outliners, ○ - outliners, * - extreme)

Naph (Naphthalene), **Ace** (Acenaphthene), **AcPy** (Acenaphthylene), **Flu** (Fluorene), **Phe** (Phenanthrene), **Ant** (Anthracene), **Flt** (Fluoranthene), **Pyr** (Pyrene), **BaA** (Benzo[a]anthracene), **Chr** (Chrysene), **BbF** (Benzo[b]fluoranthene), **BkF** (Benzo[k]fluoranthene), **BaP** (Benzo[a]pyrene), **DahA** (Dibenzo[a,h]anthracene), **IcdP** (Indeno[1,2,3-cd]pyrene), and **BghiP** (Benzo[ghi]perylene).

- ✓ PAH concentrations ranged from 0.01 to 18.85 ng/m³ during the entire sampling period.
- ✓ The highest daily concentrations were observed for phenanthrene (18.85 ng/m³), benzo[b]fluoranthene (16.95 ng/m³), and pyrene (16.61 ng/m³), all in late February 2020.
- ✓ Benzo[b]fluoranthene showed the highest average daily concentration in both heating seasons: 2.06 ng/m³ (Jan–Apr 2020) and 7.64 ng/m³ (Dec 2020–Feb 2021).

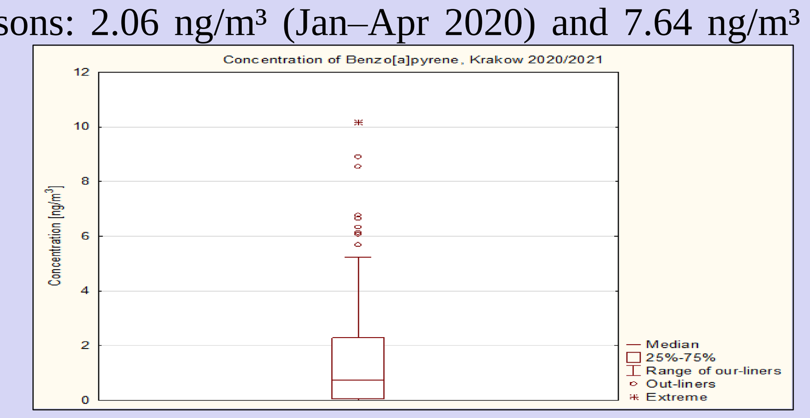

Figure 6. Distribution of B[a]P concentrations for Krakow (July 2020/ February 2021)

Health risk assessment

- ✓ Heavy PAHs (4–6 rings) dominated the PAH profile in Kraków, comprising over 90% of total PAHs in PM10, especially during the heating season (93%) compared to the non-heating season (71%).
- ✓ This dominance is linked to the stronger adsorption and condensation of heavy PAHs onto particulate matter, while light PAHs, mainly present in the gas phase, contributed less than 10%.

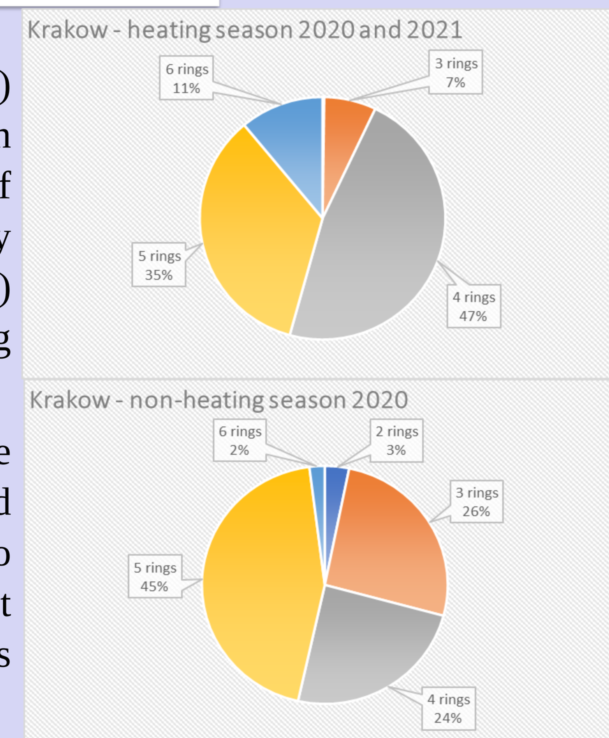

Figure 9. Percentage participation of PAHs in terms of the number of rings for Krakow

Heating seasons 2020 and 2020/2021	
Total average monthly concentration of carcinogenic PAHs	15.98 ng/m-3
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 %

Conclusions

- ✓ Significant seasonal differences in PM10 and PAHs concentrations were observed, with peak values during the heating season attributed to increased residential combustion of coal and wood.
- ✓ The average monthly concentration of B[a]P (1.56 ng/m³) exceeded the EU annual limit (1 ng/m³), with daily maxima of 10.16 ng/m³, underscoring chronic exposure risks.
- ✓ Molecular diagnostic ratios (e.g., Flt/(Flt+Pyr), IP/(IP+B[ghi]P)) indicated vehicular emissions as the predominant PAH source year-round, with a substantial contribution from residential heating in winter.
- ✓ High toxic equivalency values (TEQ, MEQ, CEQ) reflect the elevated presence of carcinogenic PAHs in PM10, confirming their potential health hazard based on EPA risk assessment guidelines.
- ✓ HYSPLIT trajectory analysis revealed that elevated PM10 levels were associated with air mass inflow from the southwest and east, suggesting regional pollution transport into Kraków.

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