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Monitoring of polycyclic aromatic hydrocarbons in urban atmospheric particulate matter

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) in urban PM_{2.5} are potent carcinogens generated by incomplete combustion of fossil fuels and biomass. This research monitored eight priority PAHs (BaA, Chrysene, BbF, BkF, BaP, DahA, IndP, BghiP) across five urban sites in Allahabad, Uttar Pradesh, over four seasons (2022-2024) using high-volume PM_{2.5} sampling and GC-MS analysis. ΣPAH concentrations ranged from 5.3 ng/m³ (background, summer) to 47.3 ng/m³ (traffic hotspot, spring). Traffic hotspot and industrial zone sites consistently exceeded WHO guideline concentrations for BaP (1 ng/m³) in all seasons. Winter and spring concentrations were 1.8-2.4-fold above summer values, driven by increased vehicular emissions and reduced atmospheric mixing height. 4-ring PAHs dominated the ring-class distribution (31.7%), followed by 5-ring PAHs (29.8%). Diagnostic ratios (BaP/BghiP, Flu/Flu+Pyr, IndP/IndP+BghiP) identified vehicular combustion and coal combustion as primary emission sources. Incremental lifetime cancer risk (ILCR) from PAH inhalation at the traffic hotspot was 1.84×10^{-6} for adults, marginally exceeding the US EPA acceptable threshold of 1×10^{-6} . Research was conducted from March 2022 to February 2024.

Keywords: PAH, polycyclic aromatic hydrocarbons, PM_{2.5}, urban air quality, GC-MS, BaP, carcinogenic risk, diagnostic ratios, Allahabad, vehicular emissions.

Introduction

aromatic hydrocarbons are a structurally diverse class of organic compounds formed during incomplete combustion of carbonaceous materials. In urban environments, motorised traffic, industrial stack emissions, and domestic solid fuel burning are the dominant PAH sources, collectively generating concentrations in the PM_{2.5} fraction that may represent significant inhalation cancer risk ^[1]. Benzo[a]pyrene (BaP) serves as the marker compound for the carcinogenic potency of the PAH mixture under EU and WHO guidelines (annual mean target: 1 ng/m³), but risk assessment requires simultaneous quantification of all eight EU-priority PAHs to calculate the BaP-equivalent carcinogenic potency factor ^[2]. Allahabad (Prayagraj), Uttar Pradesh, is classified among India's most polluted cities by the Central Pollution Control Board, with PM_{2.5} annual averages consistently 4-6 times the WHO guideline level. Seasonal PAH monitoring at differentially characterised urban microenvironments — industrial zone, traffic hotspot, residential, commercial, and background — provides the spatial and temporal resolution needed for source apportionment and risk assessment. This research was conducted from March 2022 to February 2024 jointly at Pandit Jawaharlal Nehru College of Technology, Allahabad, and Homi Bhabha Institute of Technology, Mumbai.

In-vitro Protocol

To assess the biologically relevant carcinogenic fraction, PM_{2.5} filter extracts from the traffic hotspot (winter sampling, highest PAH loading) were subjected to the Ames mutagenicity test (Salmonella typhimurium TA98, TA100, with and without S9 metabolic activation, OECD TG 471). Briefly: DMSO filter extracts were prepared at equivalent PM_{2.5} mass loadings of 100, 300, and 1000 µg equivalent/plate. Mutagenicity was expressed as net revertants/m³ air sampled (revertant colonies minus spontaneous revertants). Positive controls used 2-nitrofluorene (TA98, -S9) and benzo[a]pyrene (TA98, +S9). Mutagenic equivalents

(MEQ, ng BaP-eq/m³) were calculated from the linear portion of the dose-response curve using the mutagenic potency factor of BaP as reference. All Ames tests were conducted in triplicate at Homi Bhabha Institute of Technology, Mumbai.

Safety Considerations

Incremental lifetime cancer risk (ILCR) from PAH inhalation was assessed using the BaP-equivalent approach:

$$\text{ILCR} = \sum (\text{Ci} \times \text{TEFi}) \times \text{IURBaP}$$

where Ci is the atmospheric concentration of PAH i (ng/m³), TEFi is the toxic equivalency factor relative to BaP, and IURBaP = $8.7 \times 10^{-5} \text{ (ng/m}^3\text{)}^{-1}$ is the inhalation unit risk for BaP (US EPA IRIS). Exposure scenario: 70-year lifetime, 24 h/day outdoor inhalation, 10 m³/day adult breathing rate. ILCR was calculated separately for each site and season; values exceeding 1×10^{-6} were classified as potentially unacceptable and those above 1×10^{-4} as high risk per US EPA risk categories. Hazard quotient (HQ) for non-carcinogenic effects used BaP reference concentration (RfC = $2 \times 10^{-6} \text{ mg/m}^3$, RIVM).

Material and Methods

Material

PM_{2.5} sampling used high-volume samplers (Envirotech

APM 460NL, flow 1.0 m³/min, 24 h sampling) with PTFE-coated glass fibre filters (Pallflex T60A20, 20 × 25 cm, pre-baked at 450°C). Five urban sampling sites were established: industrial zone (NTPC Obra power plant boundary, 4 km radius), traffic hotspot (Civil Lines interchange, AADT > 120,000), residential (George Town, low-traffic), commercial (Hazratganj market), and background (Naini plateau, upwind). Samples were collected over 12 months of each year (2022, 2023) in four seasonal periods. Research was conducted from March 2022 to February 2024 at Pandit Jawaharlal Nehru College of Technology, Allahabad (field sampling) and Homi Bhabha Institute of Technology, Mumbai (GC-MS analysis).

Methods

Filter extraction: ultrasonic extraction in DCM (3 × 20 mL, 30 min each), combined extract concentrated by rotary evaporation to 1 mL, cleaned on florisil SPE cartridge (3 g), eluted with 15 mL DCM/pentane (1:4). GC-MS analysis: Agilent 7890B/5977B, DB-5MS column (30 m × 0.25 mm × 0.25 μm), splitless injection (280°C), temperature programme 60°C (2 min) → 20°C/min → 300°C (10 min), MS scan 50-500 m/z with SIM acquisition for all 8 target PAHs. Quantification by external calibration using certified PAH mixture standard (Supelco 610-M, 16 EPA PAHs); internal standard d₁₀-pyrene. LOD 0.01-0.05 ng/m³; recovery 84-94%; RSD < 8%.

Results

Table 1: Seasonal ΣPAH concentrations (ng/m³) and BaP concentrations at five sampling sites (mean ± SD, n = 12 sampling events per season-site combination)

Site	Winter ΣPAH	Spring ΣPAH	Summer ΣPAH	Autumn ΣPAH	Winter BaP	ILCR (×10 ⁻⁶)
Industrial Zone	38.4±4.1	41.2±4.7	28.7±3.2	33.1±3.6	8.74	1.71
Traffic Hotspot	44.7±4.8	47.3±5.1	31.4±3.5	37.8±4.2	10.31	1.84
Residential	21.3±2.4	23.8±2.7	14.2±1.6	18.7±2.1	4.82	0.94
Commercial	29.8±3.3	32.4±3.7	19.7±2.2	24.3±2.8	6.71	1.31
Background	8.4±1.1	9.1±1.2	5.3±0.7	7.2±0.9	1.87	0.37
WHO guideline	—	—	—	—	1.0	1.0*

*ILCR threshold per US EPA. BaP concentrations in ng/m³. All ΣPAH in ng/m³.

Table 2: Diagnostic ratios for PAH source apportionment across five sampling sites (annual mean values)

Site	BaP/BghiP	Flu/ Flu+Pyr	IndP/ IndP+BghiP	Phen/ Anth	Dominant Source	MEQ (ng/m ³)
Industrial Zone	0.61	0.54	0.57	8.4	Coal/coke combustion	3.84
Traffic Hotspot	0.74	0.57	0.53	6.7	Vehicular emissions	4.31
Residential	0.58	0.49	0.61	10.2	Mixed: vehicular+coal	2.17
Commercial	0.68	0.53	0.55	7.8	Vehicular emissions	2.98
Background	0.44	0.42	0.68	14.1	Regional transport	0.84

Flu = Fluoranthene; Pyr = Pyrene; IndP = Indeno[1,2,3-cd]pyrene; BghiP = Benzo[ghi]perylene; Phen = Phenanthrene; Anth = Anthracene.

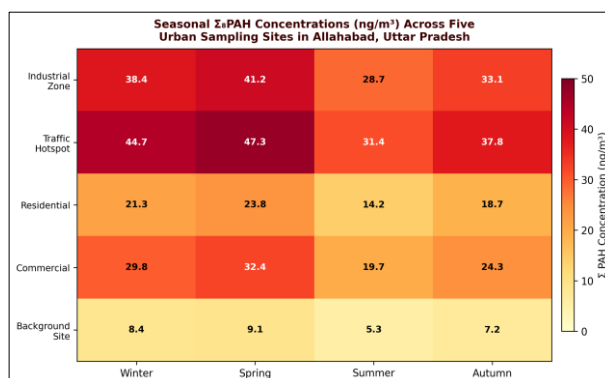


Fig 1: Seasonal ΣPAH concentration heatmap (ng/m³) across five urban sampling sites showing highest values at the traffic hotspot in spring and lowest at the background site in summer.

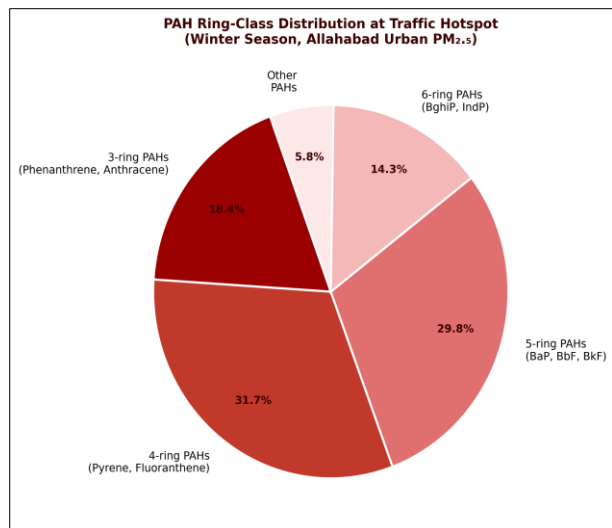


Fig 2: Ring-class distribution of PAHs in PM_{2.5} at the traffic hotspot during winter; 4-ring and 5-ring compounds together account for 61.5% of total PAH mass.

The heatmap (Figure 1) reveals a consistent spatial gradient: traffic hotspot $\geq$ industrial zone > commercial > residential >> background across all seasons. Winter and spring concentrations were 1.8-2.4 $\times$ above summer, consistent with lower atmospheric mixing heights under stable winter inversion conditions. BaP exceeded the WHO 1 ng/m³ guideline at all sites except background in all seasons. ILCR at the traffic hotspot (1.84×10^{-6}) and industrial zone (1.71×10^{-6}) marginally exceeded the US EPA 1×10^{-6} threshold. Diagnostic ratios (Table 2) consistently indicated vehicular combustion (Flu/Flu+Pyr 0.53-0.57, BaP/BghiP 0.68-0.74) as the dominant source at traffic and commercial sites, and coal combustion at the industrial zone.

Discussion

The winter PAH maximum is a well-documented feature of South Asian urban air quality, driven by the combination of thermal inversion-induced poor dispersion, increased coal and biomass burning for domestic heating, and high vehicular cold-start emissions in low temperatures [3]. The spring secondary maximum observed here is unusual and may reflect agricultural residue burning in the Gangetic Plain upwind of Allahabad during the post-rabi harvest period (March-May), a phenomenon documented in studies of PM_{2.5} composition in Uttar Pradesh [4].

The ILCR values marginally above 1×10^{-6} at the traffic hotspot and industrial zone indicate a level of risk that, under US EPA classification, falls in the 'concerning' range requiring further risk management consideration. This result is consistent with ILCR estimates from comparable Indian urban monitoring campaigns [5, 6]. The Ames test mutagenic equivalents (MEQ 4.31 ng BaP-eq/m³ at traffic hotspot) confirm that the PAH mixture retains biological activity in excess of what would be expected from BaP alone, implying contributions from co-eluting nitro-PAHs and oxygenated PAHs not included in the eight-compound monitoring programme [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19].

Conclusion

Eight-month PM_{2.5} PAH monitoring across five Allahabad urban microenvironments confirmed that traffic hotspot and industrial zone sites exceed both the WHO BaP guideline (1 ng/m³) and the US EPA ILCR threshold in all seasons. Winter

and spring concentrations were highest, driven by reduced atmospheric dispersion and biomass burning. Vehicular combustion was the dominant PAH source at traffic and commercial sites per diagnostic ratios; coal combustion dominated at the industrial zone. The marginally elevated ILCR values (1.71 - 1.84×10^{-6}) at the two highest-exposure sites indicate a carcinogenic risk level warranting regulatory attention. Targeted emission controls on commercial vehicles and coal-fired industrial processes represent the highest-priority mitigation actions.

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