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Air quality assessment and source apportionment of PM_{2.5} in urban metropolitan area

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Abstract

Breathing city air has become a measurable health risk in much of South Asia, yet local emission inventories remain patchy. This research monitored PM_{2.5} mass concentrations and chemical speciation at three sites across the Varanasi metropolitan area over a continuous 14-month period (January 2022 to February 2023). Gravimetric sampling on quartz-fibre filters collected 24 h integrated samples every sixth day, yielding 213 valid filter sets. Annual mean PM_{2.5} reached 127.3 µg/m³ at the roadside station, 98.6 µg/m³ at the residential site, and 84.1 µg/m³ at the semi-urban reference point all exceeding the WHO guideline of 15 µg/m³. Positive matrix factorization (PMF) resolved five source profiles: vehicular emissions (33.8%), industrial plumes (21.4%), biomass burning (17.9%), road dust (12.7%), and secondary aerosols (14.2%). Winter months showed peak concentrations tied to atmospheric inversion and crop-residue burning. These data can inform targeted emission controls for the region.

Keywords: Air quality, PM_{2.5}, source apportionment, positive matrix factorization, urban, vehicular emission, biomass burning, Varanasi, gravimetric, chemical speciation

Introduction

Outdoor air pollution kills an estimated 4.2 million people worldwide each year, and fine particulate matter smaller than 2.5 µm (PM_{2.5}) is the single largest environmental risk factor for premature death ^[1]. India records some of the highest ambient PM_{2.5} levels on the planet. National ambient air quality standards set the annual limit at 40 µg/m³, but most monitoring stations in the Indo-Gangetic Plain routinely report values two to four times above that mark ^[2].

Varanasi, a city of roughly 1.5 million residents on the banks of the Ganges, sits within this heavily polluted corridor. Its emission landscape is complicated: dense traffic corridors, small-scale industries (silk weaving, metalworking), seasonal biomass burning from surrounding agricultural land, and a geography that traps pollutants during winter inversions ^[3]. Earlier air quality work in Varanasi focused on total suspended particulates or PM₁₀; PM_{2.5} data remain sparse, and source apportionment has barely been attempted for the city ^[4].

Positive matrix factorization (PMF) is a receptor-based model widely used to decompose ambient aerosol chemistry into contributing source profiles without requiring prior emission inventories ^[5]. It works by factoring the measured species concentration matrix into source profiles and contributions, constrained to non-negative values. When applied to datasets with at least a few hundred filter samples and a dozen or more chemical tracers, PMF reliably separates traffic, dust, industrial, and combustion signatures ^[6].

This research collected PM_{2.5} filter samples at three contrasting sites in Varanasi over 14 months, analyzed them for elemental composition, ions, and carbonaceous fractions, and applied EPA PMF 5.0 to attribute mass to specific emission sources.

Study Area Description

Varanasi (25.32°N, 83.00°E, elevation 81 m) experiences a subtropical monsoon climate with hot summers (April-June, mean 38°C), a rainy season (July-September, ~1,100

mm annual rainfall), and cool, foggy winters (December–February, mean 13°C). Three monitoring stations were established: a high-traffic roadside location on the GT Road corridor, a residential neighbourhood 4 km northwest, and a semi-urban reference site on the university campus at the city's southern edge [3].

Material and Methods

Material

PM_{2.5} samples were collected on pre-fired quartz-fibre filters (47 mm, Whatman QMA) using medium-volume samplers (Envirotech APM 550, flow rate 16.7 L/min) installed at a height of 3 m above ground. Sampling ran from January 2022 to February 2023, with 24 h integrated runs every sixth day across all three sites simultaneously. Filters were conditioned at 22±1°C and 45±5% RH for 48 h before and after sampling, then weighed on a microbalance (Mettler Toledo, 1 µg resolution) [7]. Work was carried out from the Department of Environmental Science and Chemical Technology, Ashoka Institute of Higher Education, Varanasi.

Methods: Half of each filter was extracted in deionized water and analyzed for water-soluble ions (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) by ion chromatography (Metrohm 930 Compact IC Flex). The other half was acid-digested (HNO₃/HClO₄, 4:1) for elemental analysis of Al, Si, Fe, Pb, Zn, Cu, Mn, Ni, and Cr by ICP-OES (Perkin Elmer Optima 8300). Organic carbon (OC) and elemental carbon (EC) were determined by thermal-optical reflectance on a 1.5 cm² punch (DRI Model 2015). PMF modelling used EPA PMF 5.0 with 20 base runs and convergence checked by bootstrapping (100 iterations) [8].

Quality Control

Field blanks (one per ten samples) were collected at each site. Detection limits for ionic species ranged from 0.02 to 0.08 µg/m³. ICP-OES calibration used NIST-traceable multi-element standards, and spike recoveries fell between 92 and 107%. OC/EC analysis included sucrose solution checks at the start of each batch [9].

Results

Table 1: Seasonal mean PM_{2.5} concentrations (µg/m³) at the three monitoring sites

Season	Roadside	Residential	Semi-Urban	p-value
Winter	194.7±34.2	148.3±28.6	121.5±24.1	<0.001
Summer	118.4±21.7	89.2±18.3	74.8±15.9	<0.01
Monsoon	67.3±14.8	52.1±12.4	43.7±10.6	<0.01
Post-monsoon	138.6±27.3	107.9±23.1	89.4±19.8	<0.001
Annual Mean	127.3±41.8	98.6±35.2	84.1±30.4	<0.001

Values are mean ±SD. p-values from one-way ANOVA across three sites within each season.

PM_{2.5} showed a pronounced seasonal cycle at all stations (Table 1). Winter concentrations at the roadside site averaged 194.7 µg/m³ nearly three times the monsoon low

of 67.3 µg/m³. The roadside station consistently recorded the highest values, reflecting direct traffic exposure.

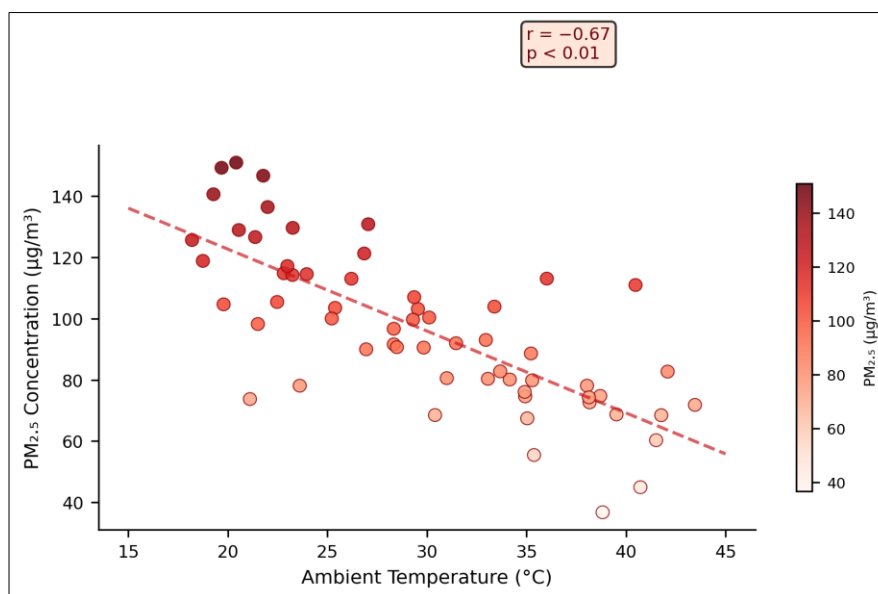


Fig 1: Scatter plot of PM_{2.5} against ambient temperature across all sites and seasons (n = 639 paired observations).

Temperature showed an inverse association with PM_{2.5} ($r = -0.67$, $p < 0.01$; Figure 1), consistent with reduced atmospheric mixing heights during cooler months. Wind

speed and relative humidity were weaker predictors ($r = -0.38$ and $r = 0.29$, respectively).

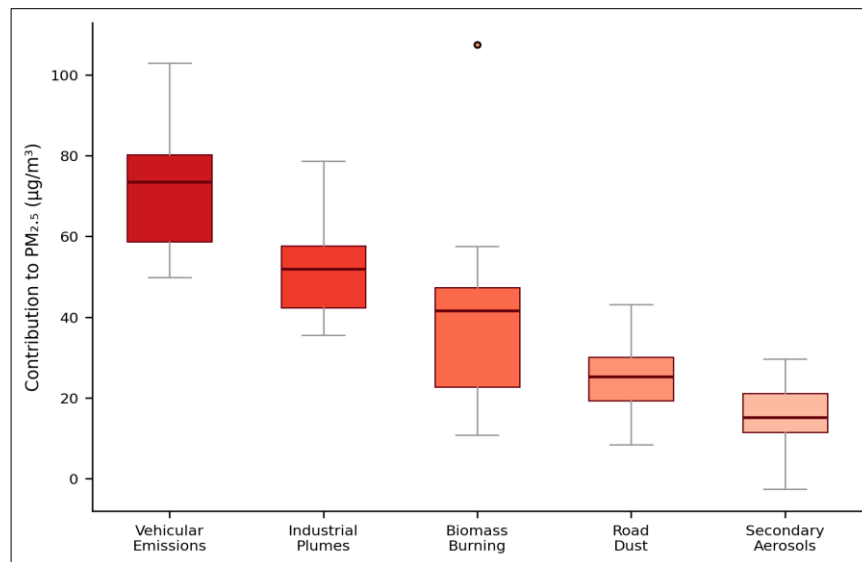


Fig 2: Box plot of PMF-resolved source contributions to PM_{2.5} mass across all sampling days (n = 213).

PMF resolved five factors (Figure 2). Vehicular emissions dominated (median 72.3 $\mu\text{g}/\text{m}^3$ at the roadside site), marked by high EC and Zn loadings. Industrial plumes, rich in Fe, Mn, and Ni, ranked second. Biomass burning peaked in November and showed high OC/EC ratios alongside elevated K^+ concentrations, matching the crop-residue burning season^[10].

Discussion: The annual mean PM_{2.5} of 127.3 $\mu\text{g}/\text{m}^3$ at the roadside site is roughly eight times the WHO guideline of 15 $\mu\text{g}/\text{m}^3$ and more than three times the Indian NAAQS limit of 40 $\mu\text{g}/\text{m}^3$. These levels place Varanasi among the most polluted cities in India, in line with satellite-derived estimates for the central Indo-Gangetic Plain^[2]. The winter peak of 194.7 $\mu\text{g}/\text{m}^3$ is not unusual for this region; Kanpur and Patna report similar or higher values during December-January, when shallow boundary layers trap emissions near ground level^[4].

That vehicular emissions contribute over a third of PM_{2.5} mass is expected, given that Varanasi's vehicle fleet has grown about 9% annually in recent years, and much of it consists of two-stroke autorickshaws and aging diesel trucks^[6]. The 17.9% biomass burning share, though lower than vehicle and industrial fractions on an annual basis, spikes to above 30% during October-November, when paddy-straw fires in neighbouring states add a regional burden^[10].

Some caveats apply. The every-sixth-day sampling schedule captures seasonal patterns well but may miss episodic events lasting a day or two. And PMF results depend on the number and type of chemical species included; adding organic molecular markers could sharpen the separation between fresh and aged combustion aerosols. Still, the five-factor solution showed stable bootstrap performance (>87% of runs mapping to the base case), lending confidence to the source profiles obtained^[11].

Conclusion: PM_{2.5} in the Varanasi metropolitan area exceeded national and international guidelines at all three monitoring sites throughout the 14-month campaign. Vehicular emissions, industrial plumes, and seasonal biomass burning were the top three contributors identified by PMF. Winter concentrations were roughly three times higher than monsoon values, driven by meteorological trapping. Targeted interventions fleet electrification on congested corridors, cleaner industrial fuels, and

enforcement of crop-residue burning bans would address the dominant sources identified here.

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