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Proceeding Paper

Characteristics and Sources of Trace Elements in Fine Mode Aerosols in Delhi: A Long-Term Trend Analysis (2013–2021) †

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Abstract: On the basis of a long-term analysis (2013–2021), we report the inter-annual and seasonal concentrations and possible sources of trace elements (TEs) in $PM_{2.5}$ over Delhi, India. In all the $PM_{2.5}$ samples, 19 major and trace elements were extracted: Na, Al, Fe, Ti, Mg, Cu, Zn, Cr, Mn, Ni, As, Mo, Cl, P, S, Ca, K, Pb, and Br. The total annual mean concentration (∑El in $PM_{2.5}$) of major and trace elements was 17.4 ± 3.1 µg m^{-3}, accounting for 13.9% of $PM_{2.5}$. The enrichment factor (EF) and IMPROVE model analysis indicate the seasonal abundance of mineral/soil dust (Fe, Al, Ti, Na, Ca, and Mg) at the sampling location of Delhi. During the sampling period, the highest loading of trace elements was recorded in 2015 (19% of $PM_{2.5}$) and the lowest in 2020 (9% of $PM_{2.5}$), possibly due to limited activity during COVID-19 lockdown/unlock times. The major sources of elements (in $PM_{2.5}$) were extracted by a principal component analysis (PCA) as crustal/soil/road dust, vehicular traffic/industrial emissions, combustion (solid + fossil fuels), and sodium magnesium salts in Delhi.

Keywords: $PM_{2.5}$; trace elements; enrichment factor; source of elements

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1. Introduction

Trace elements (TEs) contribute a small fraction to fine mode particulate matter (PM) in comparison to other chemical species (organic and inorganic) and affect the quality of ambient air and human well-being [1–3]. Apart from natural sources, particulate-bound major and trace elements emit from various anthropogenic activities such as dust particles (crustal, long-range transportation, and construction activities); the combustion of fuels (biomass and fossil fuels); industrial and vehicular emissions, etc. [3–6]. Majorly, PM-bound elements are non-volatile in nature and are not affected by their transportation to or from local or other regions [1,2,5–8]. Previous studies [2,7,8] report that the inhalation of elements like Zn, As, Fe, Hg, Mn, Pb, Cu, Cr, and Ni, which can be emitted from diverse sources, has detrimental effects (poisonous and mutagenic) on human well-being. In this paper, we report the annual and seasonal composition of elements and their possible sources of $PM_{2.5}$ in the megacity of Delhi, India, on a long-term basis.

2. Materials and Methods

Delhi, the capital city of India, is considered one of the most polluted cities in India and the world [9]. For the long-term assessment of the elemental composition of $PM_{2.5}$, fine particulate samples ($PM_{2.5}$) were collected at the CSIR–National Physical Laboratory (28°38′ N, 77°10′ E; 218 m amsl), New Delhi, from January 2013 to April 2021. Delhi experiences four distinct seasons (classified by the India Meteorological Department): winter (January–February; JF), summer (March–May; MAM), monsoon (June–September;

JJAS), and post-monsoon (October–December; OND). In our previous publication [10], the sampling location is described in detail.

$PM_{2.5}$ samples (*n* = 756) were collected on pre-baked quartz filters for up to 24 h by a fine particle sampler operated at a flow rate of 1 m^3 h^{-1} (accuracy: ±2% of FS). A Wavelength-Dispersive X-ray Fluorescence Spectrometer (WD-XRF; ZSX Primus, Rigaku, Tokyo, Japan) was employed to identify 19 elements (Na, Al, Fe, Ti, Br, Cu, Zn, K, Mn, Cr, Ni, Mo, Mg, Cl, P, S, Pb, As, and Ca) in all the $PM_{2.5}$ samples (Mo and Ni were traced in few $PM_{2.5}$ samples). Detailed information about the estimation of elements, the working principle of the instrument, and the calibration standards used are available in Sharma et al. [3]. A principal component analysis (PCA) was applied to examine the possible sources of elements in Delhi.

3. Results and Discussion

The annual mean concentrations of $PM_{2.5}$ are depicted in Figure 1, and the time-series plots of major and trace elements of $PM_{2.5}$ are presented in Figure 2a,b. The mean annual concentration of $PM_{2.5}$ was 127 ± 58 µg m^{-3} with a maxima of 143 ± 70 µg m^{-3} (in 2017) and a minima of 109 ± 53 µg m^{-3} (in 2021) during the entire sampling period. The non-significant decreasing trend ($y = -1.63x + 133.9$; $R^2 = 0.15$) in annual concentrations of $PM_{2.5}$ was observed from 2013–2021. The annual mean concentrations of $PM_{2.5}$ was recorded more than three times that of National Ambient Air Quality Standards (NAAQS, annual level: 40 µg m^{-3}). Out of the 19 elements, the higher concentrations of major elements such as K, Al, Fe, Ca, Na, Mg, and S in $PM_{2.5}$ were recorded in Delhi. Other studies also reported similar observations [1,5,10–14]. The highest loading of elements was recorded in 2015 (19% of $PM_{2.5}$), and the lowest in 2020 (9% of $PM_{2.5}$) might be due to limited activity during COVID-19 lockdown/unlock times. The total concentrations (∑El) of elements in $PM_{2.5}$ accounted for 13.9% of $PM_{2.5}$ during 2013–2021 in Delhi. Similar observations were reported by Jain et al. [10] and Rai et al. [1] with a 17% and 19% contribution of elements in $PM_{2.5}$ over Delhi.

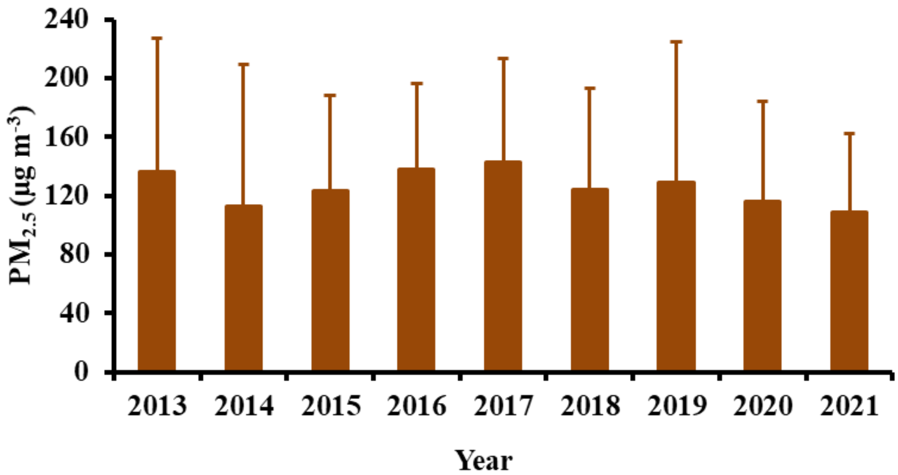
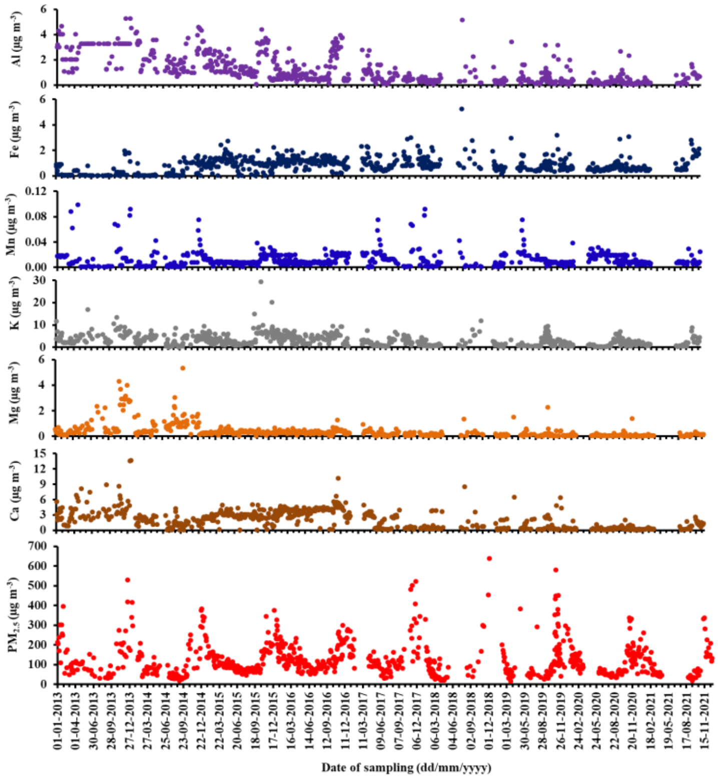
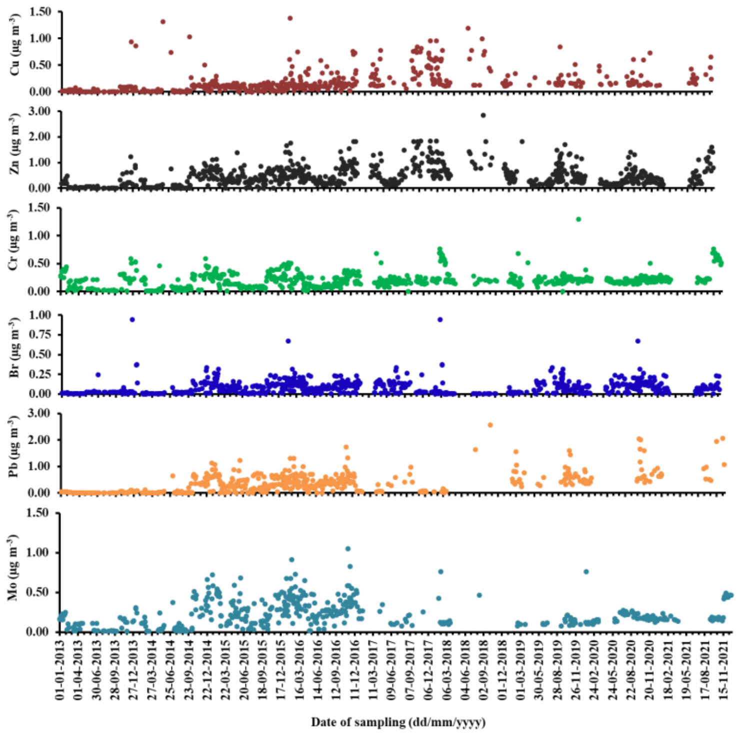


Figure 1. Annual mean concentrations of $PM_{2.5}$ in Delhi, India.

Seasonal elemental concentrations (Al, Fe, Ti, Cu, As, Zn, Mn, Cr, Ni, P, Mo, Na, Mg, Cl, S, K, Pb, Br, and Ca) of $PM_{2.5}$ are depicted in Figure 3, whereas the seasonal percentage contribution of elements in $PM_{2.5}$ is illustrated in Table 1. The percentage of elements contributing to $PM_{2.5}$ during the winter, summer, monsoon, and post-monsoon seasons was computed as 12.9%, 16.9%, 16.6%, and 11.7%, respectively. A higher loading of elements in $PM_{2.5}$ during the summer (16.9%) and monsoon (16.6%) seasons is due to occasional dust storms, higher wind speeds, and long-distance transit of pollutants from the Thar desert and neighboring areas to the receptor site of Delhi [4,15,16]. The higher loading of Al, Fe, Ti, Ca, and Na in $PM_{2.5}$ found during all the seasons at the sampling site is attributable to mineral/soil dust [14–16]. During the post-monsoon season, a higher concentration of Cl was found, which could be attributed to the combustion of coal and the burning of wood, plastic, paper, diesel fuels, etc. [14,17,18].



(**a**)



(**b**)

Figure 2. (**a**). Time-series plots of major elements present in $PM_{2.5}$ in Delhi from 2013–2021. (**b**). Time-series plots of trace elements present in $PM_{2.5}$ at Delhi from 2013–2021.

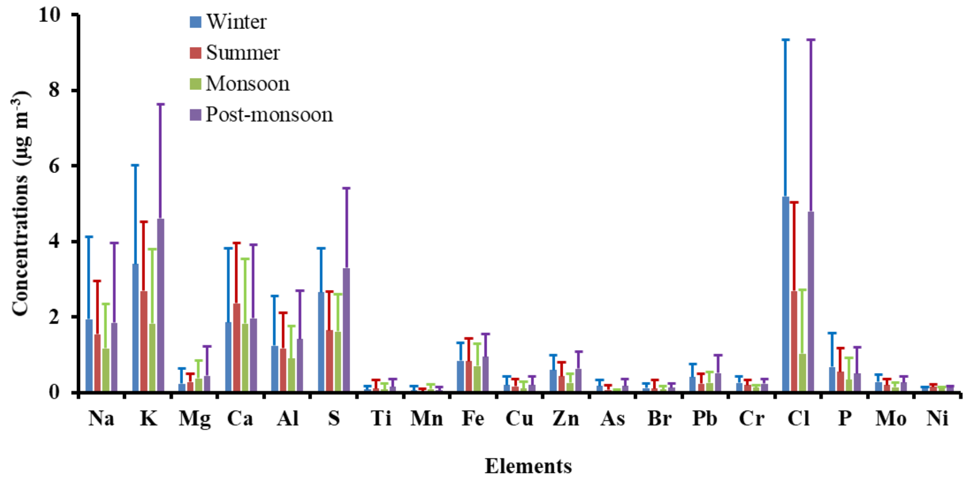


Figure 3. Pooled seasonal mean concentrations (2013–2021) of major and trace elements (TEs) in $PM_{2.5}$ during all seasons in Delhi.

Table 1. Total elemental concentrations (∑El) of $PM_{2.5}$ (in µg m^{-3}) in Delhi, India.

Parameters	Winter (JF)	Summer (MAM)	Monsoon (JJAS)	Post-Monsoon (OND)
Total elements ∑El	20.4 ±2.5	15.5 ± 1.5	11.2 ± 1.6	22.3 ± 2.3
$PM_{2.5}$	158 ± 70	92 ± 44	67 ± 32	192 ± 110
% of ∑El in $PM_{2.5}$	12.9%	16.9%	16.6%	11.7%

± standard variation.

For the source apportionment of $PM_{2.5}$, a PCA was used and identified the five sources of $PM_{2.5}$ in Delhi. During all the seasons, the heavy loading of crustal elements (Al, Na, Ca, Ti, Fe, and Mg) indicated crustal/soil/road dust as the first factor of $PM_{2.5}$. An IMPROVE model analysis and EFs suggest an abundance and crustal origin of these elements (Al, Na, Ca, Fe, Ti, and Mg) [16,19]. The second factor extracted the combustion source (biomass burning + fossil fuel combustion) of $PM_{2.5}$ due to the substantial loading of K, S, and Cl [3,17,18]. The third factor indicated the relatively heavy loading of Pb, Cu, Mn, and Zn and was extracted as a source of vehicular emissions (VEs) [4,16,20]. The fourth factor of $PM_{2.5}$ was examined as industrial emissions (IEs) due to the elevated loading of Cr, Cu, Zn, Ni, Fe, Br, and Ti [10,21,22]. The fifth factor of $PM_{2.5}$ was resolved as soil dust + VEs + IEs [10,19].

4. Conclusions

This paper presents the seasonal, long-term annual concentrations and sources of major & trace elements in $PM_{2.5}$ over Delhi, India. During the entire study period, 19 elements (Na, Mg, Ca, Mn, Al, Fe, Ti, Cu, Zn, Cr, Ni, As, Mo, Cl, P, S, K, Pb, and Br) were extracted from $PM_{2.5}$ samples, which accounted for 13.9% of the $PM_{2.5}$ mass concentration (127 ± 58 µg m^{-3}). An IMPROVE model analysis implies the seasonal accumulation of soil dust (SD) in the sampling location of Delhi. Crustal/soil/road dust, vehicular traffic/industrial emissions, combustion (solid + fossil fuels), and sodium magnesium were resolved as the major sources of elemental concentrations of $PM_{2.5}$ in Delhi. This long-term study on the elemental composition of $PM_{2.5}$ will be useful for policymakers in mitigating and improving the ambient air quality and human health.

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Conflicts of Interest: The authors declare no conflicts of interest.

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