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

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**Abstract:** On the basis of long-term analysis (2013-2021), we reported the inter-annual and seasonal concentrations, and possible sources of trace elements (TE) in $PM_{2.5}$ over Delhi, India. In all the $PM_{2.5}$ samples, 19 major & 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 & trace elements was 17.49 ± 3.13 μg $m^{-3}$, accounting for 13.9% of $PM_{2.5}$. 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 long-term 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 principal component analysis (PCA) as crustal/soil 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 (TE) contribute a small fraction to fine mode particulate matter (PM) in comparison to the other chemical species (organic & inorganic) and affect the quality of ambient air and human well-being [1–3]. Apart from the natural sources, particulates-bound major and trace elements emitted from various anthropogenic activities such as dust particles (crustal, long-range transportation and construction activities), combustion of fuels (biomass and fossil fuels), industrial and vehicular emissions, etc. [3–6]. Majorly, the PM-bound elements are non-volatile in nature and are not affected by its transportation to or from local or other regions [1–2,5–8]. Previous studies [2,7–8] reported that on inhalation of elements like Zn, As, Fe, Hg, Mn, Pb, Cu, Cr and Ni, which can be emitted from diverse sources have 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 CSIR-National Physical Laboratory (28°38′N, 77°10′E; 218 m amsl), New Delhi from January 2013 to April 2021. Delhi experienced four distinct seasons (classified by 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 (Jain et al., 2020), the sampling location is described in detail.

$PM_{2.5}$ samples (n = 756) were collected on pre-baked quartz filters for upto 24 h by a fine particle sampler operated at a flow rate of 1 $m^3$ $h^{-1}$ (accuracy: ± 2% of FS). Wavelength Dispersive-X-ray Fluorescence Spectrometer (WD-XRF; ZSX Primus, Rigaku, 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 calibration standards used are available in Sharma et al. [3]. Principal Component Analysis (PCA) was applied to examine the possible sources of elements in Delhi.

## 3. Results and Discussion

The annual mean concentrations of $PM_{2.5}$ is depicted in Figure 1, and the time-series plots of major & trace elements of $PM_{2.5}$ are presented in Figure 2 (a&b). The mean annual concentration of $PM_{2.5}$ was 127±58 µg $m^{-3}$ with maxima of 143±70 µg $m^{-3}$ (in 2017) and 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 NAAQS (annual: 40 µg $m^{-3}$). Out of 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 $PM_{2.5}$ was 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 17% and 19% contribution of elements in $PM_{2.5}$ over Delhi.

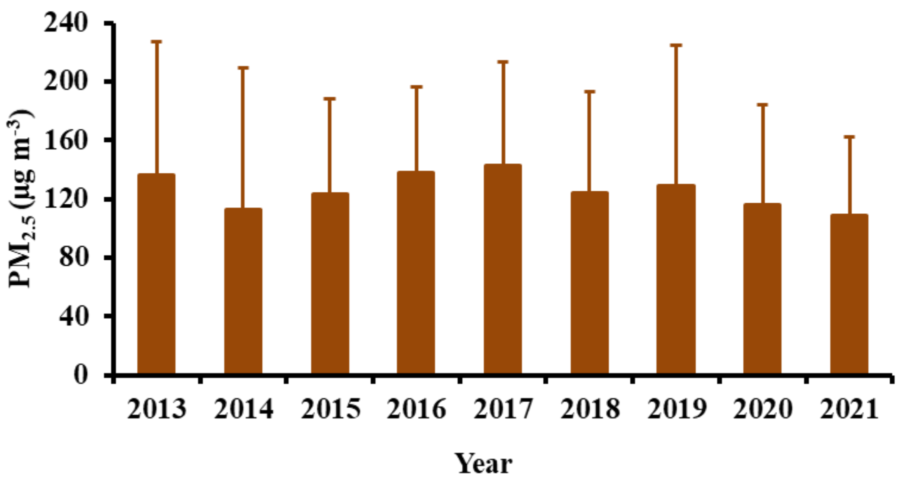


**Figure 1.** Annual mean concentrations of $PM_{2.5}$ in Delhi, India.

Seasonal elemental concentrations (Al, Fe, Ti, Cu, As, Zn, Mn, Cr, Ni, P, Mo, Na, Mg, Cl, S, K, Pb, Br and Ca) of $PM_{2.5}$ depicted in Figure 3, whereas seasonal percent contribution of elements in $PM_{2.5}$ is illustratedin Table 1. The percentage of elements contributing to $PM_{2.5}$ during winter, summer, monsoon, and post-monsoon seasons was computed as 12.9%, 16.9%, 16.6%, and 11.7%, respectively. Higher loading of elements in $PM_{2.5}$ during summer (16.9%) and monsoon (16.6%) seasons are due to occasional dust storms, higher wind speed, 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 PM2.5 found during all the seasons at the sampling site is attributrable to mineral/soil dust [14–16]. During post-monsoon, a higher concentration of Cl was found, which could be attributed to combustion of coal and burning of wood, plastic, paper, diesel fuels, etc. [14, 17– 18].

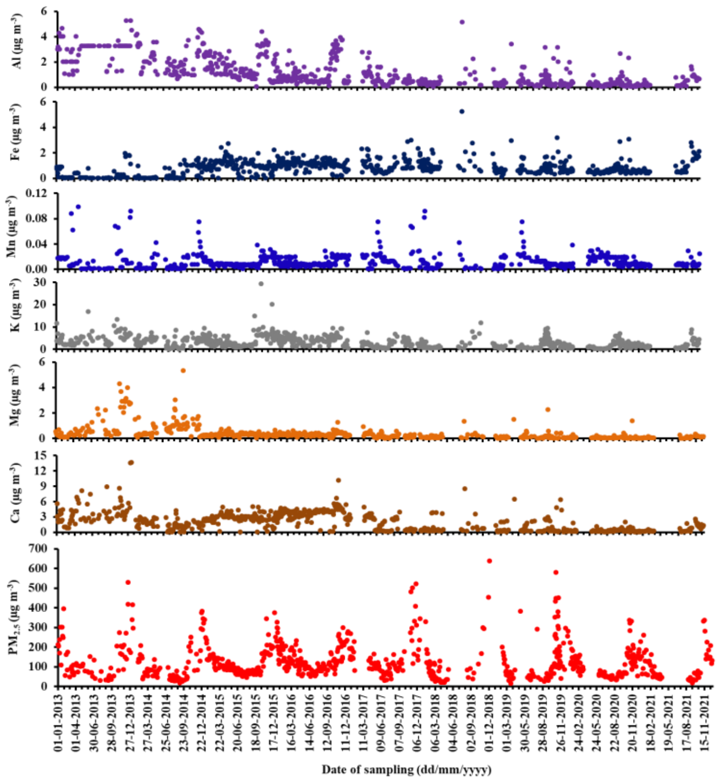


**Figure 2. a**. Time-series plots of major elements present in $PM_{2.5}$ in Delhi from 2013-2021.

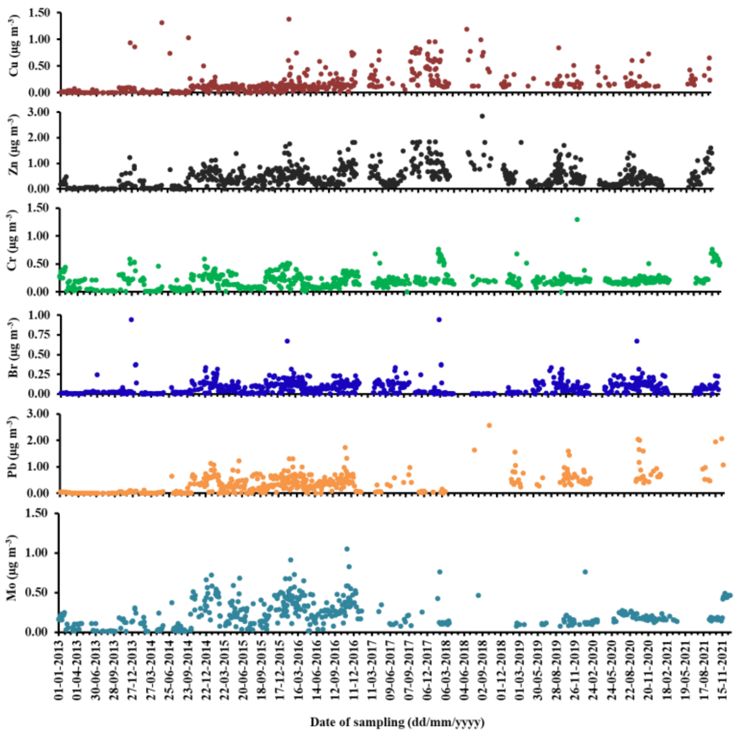


**Figure 2. b**. Time-series plots of trace elements present in $PM_{2.5}$ at Delhi from 2013-2021.

**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

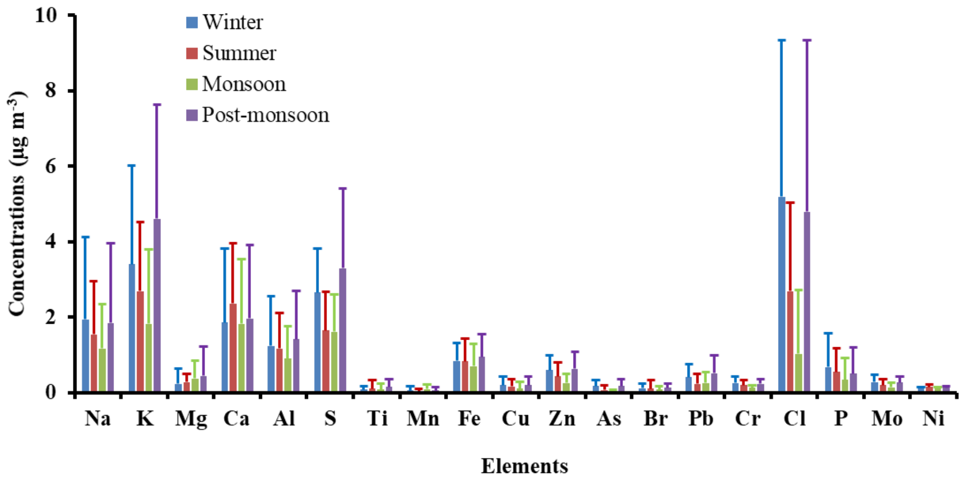


**Figure 3.** Pooled seasonal mean concentrations (2013-2021) of major and trace elements (TE) in $PM_{2.5}$ during all seasons in Delhi.

For the source apportionment of $PM_{2.5}$, PCA was used and identified the 5 sources of $PM_{2.5}$ in Delhi. During all the seasons, the heavy loading of indicator elements (Al, Na, Ca, Ti, Fe, and Mg) indicated the crustal/soil/road dust as the first factor of $PM_{2.5}$. IMPROVE model analysis, and EFs suggest the 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 substantial load of K, S and Cl [3,17–18]. The third factor indicated the relatively heavy loading of Pb, Cu, Mn, and Zn and extracted as a source of vehicular emissions (VE) [4,16,20]. The fourth factor of $PM_{2.5}$ is examined as industrial emissions (IE) due to the elevated loading of Cr, Cu, Zn, Ni, Fe, Br, and Ti [10, 21–22]. The fifth factor of $PM_{2.5}$ is resolved as soil dust+vehicular emissions+industrial emissions [10,19].

## 3. Conclusions

The paper presents, the seasonal, long-term annual concentrations and sources of 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 in $PM_{2.5}$ samples which is accounted 13.9% of $PM_{2.5}$ mass concentration (127±58 µg $m^{-3}$). IMPROVE model analysis implies the seasonal accumulation of soil dust 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 conflict of interest.

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