



Research article

Trace elements in ambient aerosols and size-resolved fog droplets: Trends, enrichment, and risk assessment

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ABSTRACT

Ambient particulate matter (PM) is composed of inorganic and organic components. The contribution of each component is impacted by various factors such as emission sources, atmospheric aging process, and size of the PM or droplets. This study mainly focuses on the effect of the PM and droplet size on trace elemental concentrations, for which various size fractions of ambient PM (PM₁, PM_{2.5}) were collected on quartz filters along with fog water (FW) samples during winter. Simultaneous, online measurements of the mass concentrations of PM₁ and PM_{2.5} were also carried out. At the time of the collection, the mass concentration of PM_{2.5} ranged from 19 to 890 μg/m³, and its mean value was 227 μg/m³. During the sampling period, 17 fog events occurred and caused a 27% reduction in the mean pre-fog PM_{2.5} concentration. All the PM and FW samples were analyzed for 12 trace elements: Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn, V. The concentrations of the various trace elements in the PM₁, PM_{2.5}, and FW samples encompassed a wide range: 10 (V)–2432 (Na) ng/m³, 34 (Mn)–13810 (Na) ng/m³, and 8 (Cr)–19870 (Ca) μg/l, respectively. The concentrations of the trace elements in the FW samples indicated a droplet-size-dependent trend: the small droplets (diameter <16 μm) had several times (3–10 times) higher concentrations than the coarser droplets (diameter >22 μm). The enrichment factor (EF) analysis revealed that the EF values for almost all the trace elements were an order of magnitude higher in the FW samples than in PM₁ and PM_{2.5}. Risk assessment based on toxic elements suggested a very high inhalation carcinogenic risk (231 per million) for the exposed population during foggy periods. This study will facilitate decision-making by policymakers regarding air quality and health concerns.

1. Introduction

Trace elements are an integral component of ambient particulate matter (PM). Owing to their catalytic activities, trace elements are expected to play significant roles in the aqueous processing of various organic and inorganic species [1]. In addition to natural sources, anthropogenic activities such as fossil fuel burning, construction/demolition activities, and biomass/trash burning also contribute significantly to PM-bound trace elements. Several anthropogenic sources also emit a variety of potentially toxic trace elements such as As, Cr, Pb, Ni, V, Cd, Co, Zn, and Cu, mostly associated with fine PM (with aerodynamic diameter ≤2.5 μm; PM_{2.5}), which can penetrate

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deep into the human respiratory tract. Prolonged exposure to these toxic elements through inhalation and/or dermal exposure can lead to several health hazards, including cancer [2–5].

The concentrations of trace elements in PM can vary significantly from one region to another based on the nature and types of natural and anthropogenic sources present in the surroundings as well as meteorological variables. In an urban environment, PM-bound trace elements could originate from a variety of sources, such as vehicular and industrial emissions, tire abrasion, waste incineration, biomass burning, road dust resuspension, and crustal weathering [6]. PM-bound trace elements also display size-dependent abundance. Crustal elements such as Ca, Fe, Mg, and Mn are mostly associated with coarser PM fractions (PM_{2.5-10}) [2, 7,8]. Certain elements, mostly the anthropogenic ones, also display more than one dominant size mode (bimodal, trimodal), indicating a variety of sources for such elements [7,8]. Earlier studies in India have reported very high concentrations of the various trace elements in PM, approximately 9–10% of the total PM_{2.5} mass [8–10,11], 10–100 times or higher than those reported from Europe or USA [12–14]. The concentrations (typically >1000 ng/m³) of crustal elements in PM_{2.5} are generally much higher when compared with anthropogenic elements (typically <500 ng/m³) [8,9,15]. However, very few studies have been carried out on aerosol-size-resolved trace elements and the associated risk assessments in India [16–18]. Enrichment factor (EF) analysis is a method that could be used to qualitatively identify the possible sources of trace elements. This analysis indicates the relative enrichment of any element in the collected samples with respect to the mean crustal composition by comparing the relative abundance against a predominantly crustal element such as Fe, Al, and Si. The EF values reported by several studies for the various elements also vary significantly, but the overall trend is mostly the same; anthropogenic elements typically have much higher EF values (EF > 100) than other mostly crustal/soil-originated elements ([9,19]).

Certain studies have also reported the trace elemental composition of bulk fog water (FW) samples from India and abroad [19–22]. Similar to aerosols, crustal elements dominate over anthropogenic elements in FW as well. However, elements such as Cu, Zn, As, and Se exhibit higher solubility (almost twice) when compared with elements such as Fe, Cr, and Al in cloud water and FW [23]. The differences in solubility often result in much higher EF values in FW than in ambient aerosols. In the national and global contexts, there have been limited studies on the concentrations of trace elements in size-resolved fog droplets. Xu et al. [24] reported the dominance of crustal elements (Al, Fe) for all droplet sizes; however, no clear droplet-size-resolved concentration trend was observed for the elements. Fomba et al. [6] reported Fe and Cu dominance (>60% of the total Cu and Fe concentrations) in medium size droplets (22 μm > diameter >16 μm), whereas Mn was mostly observed (48% of total Mn concentration) in larger droplets (diameter >22 μm). However, to the best of our knowledge, no such study on size-resolved FW trace elements has been reported from India.

Kanpur (the study site) is situated in the center of the Indo-Gangetic plain (IGP) and is one of the most polluted cities in India and the world ([25–27]). It is an industrial hub with a thriving leather industry, which, along with thermal power plants, biomass burning, waste incineration, and congested vehicular traffic, contributes significantly to the deteriorating air quality in the city [28]. Several refineries and fertilizer plants are also located near Kanpur, and aerosols transported from these regions can contribute to the air pollution in Kanpur. During winter, stable meteorology coupled with various pollution sources (biomass burning and crop residue burning) leads to elevated PM concentrations (PM₁ > 100 μg/m³) [25,29,30]. Kanpur also witnesses several moderate to long-lasting winter fog events [25,31]. The formation of fog in subsaturated conditions is initiated by the water-soluble ionic species generally present in a polluted atmosphere. The fog droplets uptake organic and inorganic gaseous components from the atmosphere owing to aqueous processing and secondary aerosol formation. Some of these more oxidized, hygroscopic, and low-volatile aerosols become a part of the existing aerosols [32], initiating the fog–smog–fog cycle. In winter, PM loading is high because of increased biomass-burning activity [33] and lower boundary layer height, providing more cloud condensation nuclei for potential fog/haze formation.

This study has been undertaken to understand the aerosol–fog interactions in terms of the dependence of the concentrations and characteristics of various trace elements on aerosol size fractions and droplet sizes. The objectives are to evaluate and compare the concentration and enrichment of trace elements inside size-resolved fog droplets and various aerosol size fractions (PM₁, PM_{2.5}). Anthropogenically enriched elements are often toxic and affect health adversely. Therefore, it is necessary to study the increased health risk caused by the inhalation of fine fog droplets and PM_{2.5} for the exposed population. To investigate the impact of these pollutants on the public health of residents, this study was conducted on an academic cum residential campus.

2. Materials and methods

2.1. Sampling location and period

The sampling was carried out on the roof of the Centre for Environmental Science and Engineering (CESE) building at the Indian Institute of Technology (IIT) Kanpur (Fig. S1). IIT Kanpur is located 10 km upwind of the city center; it is an educational institute with a campus area of approximately 4.3 km² situated near a national highway with dense vehicular traffic [25,34]. A cloud droplet probe (CDP; DMT, USA) was used to identify fog episodes and determine the fog-droplet-size distribution. The fog events were identified based on the liquid water content (LWC); sampling periods with LWC >10 mg/m³ were identified as foggy periods [35]. FW samples with three different droplet-size fractions were collected using a Caltech active strand FW collector: coarse (diameter >22 μm), medium (16 μm < diameter <22 μm), and fine (4 μm < diameter <16 μm) [25,32]. A total of 63 FW samples were analyzed for trace elements in this study.

Both the PM fractions (PM₁ and PM_{2.5}) were collected on Whatman Quartz fiber filters (QM-A) using medium- and high-volume samplers [36,37] with flow rates of 175 L per minute (lpm) (APM 577, Envirotech, India) and 950 lpm (modified AAS 217NL, Eco-tech, India), respectively. The PM₁ and PM_{2.5} samples were collected on 47-mm-diameter and A4 size quartz filters (8" × 10"),

respectively. The collected filter samples were used only for chemical characterization, and no gravimetric analysis was performed. Sampling was carried out from 10 December 2014 to 30 January 2015 in slots of 4 h, mostly during late night to early morning hours from 10 p.m. to 2 a.m. and 3 a.m.–7 a.m., to capture the fog events, and 17 fog episodes were observed during the observation period. A beta attenuation monitor (E-BAM; MetOne Inc., USA) and an aerosol mass spectrometer (AMS; Aerodyne, USA) were also operated during the specified period to obtain real-time PM_{2.5} and NR-PM₁ (nonrefractory) mass concentrations, respectively. The AMS and E-BAM were operated at a sampling time resolution of 15 min.

On certain days, the PM filter sampling was interrupted owing to power failure and/or unavailability of the samplers. A total of 105 filter samples were analyzed for trace elements (50 for PM₁; 55 for PM_{2.5}). Ten field blanks (five each for PM₁ and PM_{2.5}) were also collected. The PM_{2.5} and PM₁ concentration values reported in this study were obtained using the E-BAM and AMS, respectively.

2.2. Sample preparation for elemental analysis

Elemental analysis was performed using an inductively coupled plasma–optical emission spectrometer (ICP-OES; Thermo Fisher, ICAP 6300 Duo). A circular specimen of diameter 1.5 cm was obtained from each filter sample, including the blank filters. The specimens were then digested for 2 h in a round-bottom glass vessel with 20 ml concentrated nitric acid (65%, GR Merck Supra pure) at 180 °C. The vessel was then left to cool down to room temperature and rinsed with Milli-Q water (resistivity = 18.2 MΩ cm at 25 °C). Thereafter, it was kept undisturbed for 30 min to allow the dissolution of the acid-digested filter components into the solution. After 30 min, the solution was filtered through a 0.22-μm Millipore nylon filter; using Milli-Q water, the final volume was increased to 100 ml. The FW samples were immediately filtered after collection through 0.22-μm Millipore nylon filters, and the filtered solutions were acidified using diluted nitric acid before being stored at 2 °C for further analysis.

2.3. Quality control and quality assurance

During ambient aerosol sampling, the filters were always handled using powder-free gloves and forceps to reduce the chance of contamination. Before and after handling the filters, the forceps were cleaned with ethanol followed by Milli-Q water. Immediately after collection, the filters were wrapped in aluminum foil and kept in sealed plastic bags; these bags were then stored at 2 °C in the dark until further analysis. The FW samples were also stored in similar conditions in polypropylene bottles immediately upon collection and filtration. Post sample collection, filtration (for FW samples only) and storage were usually completed within half an hour or so for both the PM and FW samples. Following each fog event, the FW Teflon collection strands were washed thoroughly with Milli-Q water. The ICP-OES calibration was performed using commercially available standards (Multielement Standard Solution, Sigma Aldrich). The standards were re-run at regular intervals to check the calibration. To assure repeatability and precision, the samples were analyzed thrice and the average values were reported. The relative standard deviations (RSDs) were calculated as follows:

$$\text{RSD} = 2 * \frac{SD}{\sqrt{3}} \quad (1)$$

Here, SD denotes standard deviation and the RSDs of the replicates and measurement uncertainties were typically <5%.

The flow rate was monitored in 30-min intervals during the 4-h sampling. All the glassware used for elemental analysis were washed with diluted (10%) nitric acid and then washed thrice with Milli-Q water; they were dried at 180 °C for 45 min to 1 h.

2.4. Enrichment factor

The EF ratio denotes the degree of enrichment of a particular element (X) in a sample (aerosol, soil, rainwater, or others) when compared with the relative abundance of that element in the Earth's crust. This comparison is usually carried out with respect to an abundant crustal element, mostly Fe, Al, or Ti; here, we opted for Fe.

$$\text{EF} = \frac{\left(\frac{X}{\text{Fe}}\right)_{\text{Aerosol}}}{\left(\frac{X}{\text{Fe}}\right)_{\text{Crustal}}} \quad (2)$$

2.5. Risk assessment methodology

Based on US EPA classification, As, Cd, Ni, Pb, and Cr are well-known or probable carcinogens that enter the body through the inhalation route; of the total amount of Cr, only Cr (VI) is a carcinogen. Based on the available literature, we assumed that only 14% (=1/7th) of the Cr was hexavalent and carcinogenic ([16,18,38,39,40]). For carcinogenic elements, the exposure concentration (EC) was calculated for the inhalation route. Thereafter, using the standard element specific inhalation unit risk (IUR) [41,42], the carcinogenic risk (CR) was computed for each element; their sum was representative of the total cancer risk of the exposed population. Other toxic elements such as Cu, Mn, Zn, and V, although not listed as carcinogens, can still harm the human health. Therefore, to assess the risk caused by their presence, a hazard quotient (HQ) parameter was used. The sum of the HQ for each element is referred to as the hazard index (HI). HI > 1 indicates that there exists a certain risk to human health from these elements; otherwise, their levels are considered safe. The risk assessment was carried out for two scenarios; aerosol only and aerosols + fog droplets. The exposure concentration (EC, μg/m³) is calculated as follows:

$$EC = \frac{C \times ET \times EF \times ED}{AT} \tag{3}$$

where C is the elemental concentration, ET is the exposure time, EF is the exposure frequency, ED is the exposure duration, and AT is the average time.

Scenario A. Risk assessment for nonfoggy night (NFN) elemental concentrations.

Here, we assume that all the 90 winter days have NFN elemental concentrations.

$C = C_{NF}$, concentration of trace elements during nonfoggy (NF) period in $PM_{2.5}$ ($\mu\text{g}/\text{m}^3$).

Scenario B. For foggy days, $C = C_w$

The weighted elemental concentration (C_w) is estimated considering 17 foggy days during the sampling period:

$$C_w = \frac{(C_F + FW_F) \times 17 + C_{NF} \times 73}{90} \tag{4}$$

(The total number of days is 90, assuming 3 months of winter; therefore, 73 d were nonfoggy). Here, C_F and FW_F represent the concentration (in $\mu\text{g}/\text{m}^3$) of trace elements in $PM_{2.5}$ during foggy periods and fine fog droplets to obtain the air-equivalent concentrations, respectively. The aqueous elemental concentrations (mg/l) of fine droplets were converted to air-equivalent concentrations ($\mu\text{g}/\text{m}^3$) using LWC (mg/m^3) measured using the CDP. Only fine droplets were considered because their diameters were close to the range of the respirable PM fraction. The mean LWC of the fine droplets was $35 \text{ mg}/\text{m}^3$, as obtained from the CDP data. Therefore, the elemental concentrations of the fine fog droplets were multiplied by this value to obtain air-equivalent concentrations (Fig. S5).

In this study, we considered the following:

EF: 90 d/y, as this study was conducted in the winter.

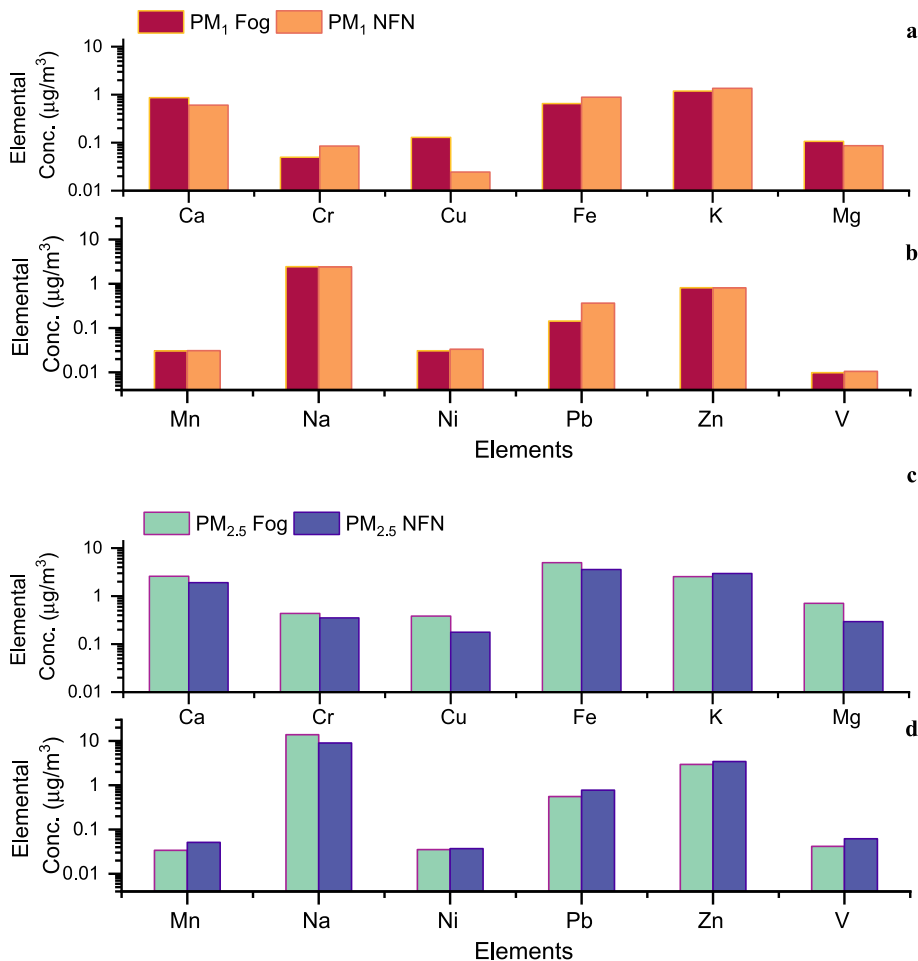


Fig. 1. Foggy and nonfoggy night (NFN) elemental concentrations for PM_1 (a and b) and $PM_{2.5}$ (c and d). The Y-axes of both the plots represent the logarithmic scale.

ED: 30 y for adults [43].

ET: 12 h/d at night.

AT: for noncarcinogens, $AT = ED \times 365 \text{ d} \times 24 \text{ h/d}$; for carcinogens, $AT = 70 \text{ y} \times 365 \text{ d/y} \times 24 \text{ h}$.

We also define $RfCi$ as the inhalation reference concentration (mg/m^3) for a noncarcinogenic element i and IUR as the inhalation unit risk ($(\mu\text{g/m}^3)^{-1}$) for carcinogens. The values of IUR were obtained from US EPA [44] and the literature (H. [39,45]). For Ni and Pb, the mean IUR values associated with the various Ni and Pb carcinogenic compounds listed in the US EPA database were considered. Using these values, the CR and noncarcinogenic risk (HQ) were calculated as follows:

$$CR = EC \times IUR \quad (5)$$

$$HQ = \frac{EC}{RfCi} \quad (6)$$

3. Results and discussion

3.1. Overall PM concentrations: foggy versus nonfoggy periods

During the study, it was noticed that the local sources of air masses impacted the PM concentration at the study site (Fig. S2). The $PM_{2.5}$ concentration ranged from 19 to $893 \mu\text{g/m}^3$, with a mean concentration of $227 \mu\text{g/m}^3$. The $PM_{2.5}$ concentration remained high ($>60 \mu\text{g/m}^3$) during most of the study period (Fig. S3). The mean night-time concentration of $PM_{2.5}$ was $251 \mu\text{g/m}^3$, whereas the mean daytime concentration of $PM_{2.5}$ was $203 \mu\text{g/m}^3$ (Fig. S4). The fog episodes observed during the sampling period mostly occurred late at night (after 9 p.m.) and lasted until sunrise. During foggy periods, the mean $PM_{2.5}$ concentration was $234 \mu\text{g/m}^3$ (S3), whereas during NFNs, the mean $PM_{2.5}$ concentration was $256 \mu\text{g/m}^3$ (the differences are statistically significant, $p < 0.001$). However, the mean $PM_{2.5}$ concentration during the prefoggy periods (the 6 h period before each fog event) was $323 \mu\text{g/m}^3$ (the prefog to fog $PM_{2.5}$ concentration differences are statistically significant, $p < 0.001$), which indicates that fog scavenging effectively reduces the $PM_{2.5}$ concentrations from the pre-fog periods by 27% (to $234 \mu\text{g/m}^3$). The mean NR- PM_1 level (nonrefractory PM_1 , obtained from AMS) during fog events was $120 \mu\text{g/m}^3$, whereas the $PM_{2.5}$ concentration during NFN was $114 \mu\text{g/m}^3$. However, the prefog NR- PM_1 level was $169 \mu\text{g/m}^3$ (the prefog to fog PM_1 concentration differences are statistically significant, $p < 0.001$), indicating that fog scavenging reduced the PM_1 concentrations by 29% (to $120 \mu\text{g/m}^3$), very similar to the magnitude of reduction for $PM_{2.5}$. Therefore, the elements present in the ambient aerosols, which acted as condensation nuclei for fog formation and other aerosols scavenged by the fog, enrich the elements in the fog droplets.

3.2. Elemental concentrations in PM_1 and $PM_{2.5}$ samples: comparison between foggy and nonfoggy periods

The overall elemental concentrations of the collected PM_1 and $PM_{2.5}$ samples are depicted in Fig. 1. The sum of elemental concentrations represented 5.9 and 5.4% of PM_1 during nonfoggy and foggy periods, respectively. In $PM_{2.5}$, the elemental contributions were 12.4 and 8.8% during the nonfoggy and foggy periods, respectively. These values are consistent with previously reported values [46,47]. The dominant elements in both PM size fractions were Ca, Fe, K, and Mg, which usually originate from crustal sources [48,49]. Owing to local biomass-/waste-burning activities during winter, higher concentrations ($>1000 \text{ ng/m}^3$) of K and Zn were also detected in both PM_1 and $PM_{2.5}$ samples. No clear trends were observed in the elemental concentrations in foggy and nonfoggy periods. Owing to higher prefog PM_1 and $PM_{2.5}$ (and most likely associated trace element) concentrations, even with fog scavenging, the elemental concentrations during the foggy periods remain comparable or higher than those during the nonfoggy periods.

A considerable amount of Na was detected in all the PM samples; although Na primarily originates from sea salt, several studies have reported anthropogenic sources of Na as well, such as refuse incineration and oil combustion. Ooki et al. [50] have described a method that calculates the contribution of anthropogenic Na (A_{Na}) using mean K/Na ratios of 0.036 and 1.50 for seawater and anthropogenic sources, respectively.

$$A_{Na} = \frac{(r[Na] - [K])}{(r - R)} \quad (7)$$

$$A_K = R \times A_{Na} \quad (8)$$

where [Na] and [K] denote the concentrations of sodium and potassium, r denotes the K/Na ratio in seawater (0.036), A_K denotes anthropogenic potassium, and R is the K/Na ratio in anthropogenic sources (1.50).

The K/Na ratio in this study was 0.80 and 0.52 for PM_1 and $PM_{2.5}$, respectively, much higher than the seawater K/Na ratio (0.036) but lower than the range of anthropogenic K/Na ratios (1.20–1.80). The K/Na ratios determined indicate that natural and anthropogenic Na are present in the study location. Higher K/Na ratios in PM_1 when compared with $PM_{2.5}$ indicate a higher presence of anthropogenic K in submicron PM. It was found that most of the K ($>90\%$) originates from anthropogenic sources, most likely from biomass burning and other activities, whereas most of the Na originates from natural sources ($>65\%$), most likely from soil and sea salt [51,52].

3.3. Elemental concentrations in FW samples

The general elemental concentrations of size-resolved FW samples are depicted in Fig. 1. Similar to ambient aerosols, the FW elemental composition was also dominated by crustal elements such as Ca, Mg, and Fe. However, the concentration of Fe was much lower (almost 10 times) when compared with other crustal elements (Ca, Mg), most likely owing to its low solubility. The concentrations of K and Na were also quite high, probably owing to their high solubility.

Among anthropogenic elements, the concentration of Zn was the highest, followed by those of Cu, Pb, Ni, V, and Cr (Fig. 2). The presence of transition elements such as Cu, Fe, and Mn, which are known for their catalytic abilities [1], indicates that fog droplets can act as an efficient medium for the oxidation of various dissolved atmospheric constituents [32,53,54,55]. It is seen that fine fog droplets are more concentrated with transition elements when compared with the other two larger droplet sizes (coarse and medium) (Fig. 2). The exact reasons for such a trend are difficult to pinpoint; several factors such as droplet volume, residence time, surface-to-volume ratio, and mass transport across the gas to liquid phase may impact the outcome. The concentration of organic components is also reported to be higher in fine droplets because secondary organic aerosol formation in the aqueous phase might occur more quickly and is less likely to be constrained by mass transfer rates of the reactants or oxidants from the gas phase [25]. Transition metals react with organic components to form complexes, leading to other oxidation reactions [56]. The air-equivalent concentrations of elements within FW samples (Fig. S5) also indicate a droplet-size-dependent trend.

3.4. Enrichment factors of elements present in ambient and FW aerosols

Enrichment factor (EF) analysis is a useful tool for gaining insights into the possible sources of elements in a broader sense (crustal or anthropogenic). The literature describes its wide use to demonstrate the potential enrichment of various elements in air and other environments.

EF values between 1 and 10 indicate that a particular element primarily originates from the Earth's crust with little/no contribution from anthropogenic sources. $EF > 100$ indicates that the element in question primarily arises from anthropogenic sources [39,40]. The EF values indicated remarkable variations from ambient PM_{10} and $PM_{2.5}$ (AP) samples to FW samples, with the values of the latter being several magnitudes higher (Fig. 3). The low EF values for Ca, Mg, and K suggest that they originate primarily from crustal/natural sources. Among the anthropogenic elements, Pb, V, Zn, Cu, and Cr had higher EF values. The highest EF value of Pb indicates that a significant amount of anthropogenic Pb persists in the aerosols ambient at the location of the study despite the ban on leaded fuel. The EF values for the elements found in FW were, on an average, 10 to 100 times greater than those found in PM_{10} and $PM_{2.5}$ samples. The EF_{FW} values of predominantly crustal origin elements such as Ca, Mg, and Mn were also much higher (>100) than 1. The higher EF values for the FW elements could also be attributed to the different solubilities of the various trace elements. It has been reported that anthropogenic elements have much higher water solubilities than predominantly crustal origin elements (such as Fe, Ca, and Mg) [23, 57,58]. The higher EF values obtained for other more soluble elements may be attributed to the fact that Fe (an element with lower solubility) was used as a representative crustal element for EF calculations (Eq. (7)).

According to a study carried out in Korea [59], for Asian aerosols, elements such as Mg and Mn are 20–40 times more water soluble than Fe. However, the EF_{FW} values for Mg and Mn are 200–1000 times higher than the EF_{AP} values (Fig. 3). This indicates that solubility differences are not the only cause of elevated EF_{FW} values, and the trace elements were enriched to a certain extent within the fog droplets, as explained in Section 3.2. Further, the EF_{FW} values are comparable to those reported for rainwater samples and water-soluble aerosols in some other studies [23,60].

Also, the trends of elemental EF values in FW are very similar when compared with AP (Fig. 3), with higher EF values associated with Zn and Pb. The droplet-size-resolved EF values for many elements have not revealed any clear trend similar to those for their

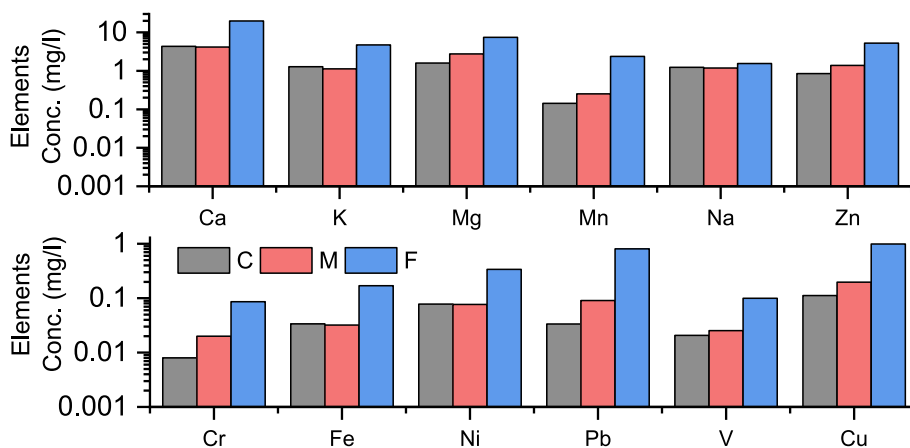


Fig. 2. Droplet-size-resolved elemental concentrations for fog-water (FW) samples. C, M, and F denote coarse, medium, and fine droplet samples, respectively.

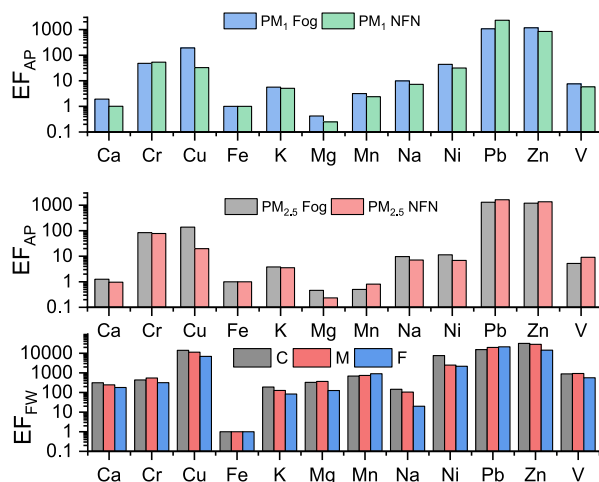


Fig. 3. Enrichment factor (EF) values of various elements in ambient PM (AP; PM₁, PM_{2.5}) and FW samples. F, M, and C denote fine, medium, and coarse droplets, respectively. PM₁/PM_{2.5} fog/NFN represents PM₁/PM_{2.5} filter samples collected during fog events/NFNs (PM₁ collected during foggy and nonfoggy days are denoted as PM₁ fog and PM₁ NFN, respectively).

concentrations. This could be attributed to relatively higher Fe levels in fine droplets (Fig. 2), thus reducing the EF values of other trace elements in fine droplets. As mentioned earlier, in India, only a few bulk FW studies have been carried out so far, and these are mostly confined to measuring the concentrations of alkali metals such as Na, Ca, Mg and K [20,21]. Table S1 presents a comparison of the FW elemental concentrations calculated in this study with those calculated in other studies.

3.5. Assessment of health risk owing to ambient aerosols and FW

Assessments of health risks caused by the inhalation of ambient aerosols during foggy periods have been reported from India and abroad. However, none of the studies have considered contributions from trace elements dissolved in fog droplets. It can be seen from Table 1 that carcinogenic risk based only on ambient PM_{2.5} is higher than the acceptable range of 10⁻⁴–10⁻⁶ [16] and warrants immediate regulatory action to safeguard the exposed population. These risks are much higher than those reported in China and elsewhere (Table S2).

This combined aerosol + FW CR value (Table 2) is 6% higher when compared with nonfoggy periods (Table 1), whereas the HI value is also higher but within the acceptable limit (<1). This clearly indicates that fog episodes and inhalation of enriched fog droplets could increase the overall carcinogenic and noncarcinogenic risk to the exposed population. To the best of our knowledge, this is the first report of combined aerosol and fog droplet risk assessment based on trace metals. In the current study, several other carcinogenic elements have not been included, and only inhalation exposure risk is considered; otherwise, the carcinogenic risks may have been even higher. We have considered only the winter exposure period (90 days), but the EC values and corresponding CR values may change (they are likely to be higher) based on the annual mean trace elemental concentrations and year-long exposure. Further, RfC values for other elements such as Zn and Cu are not available in the US EPA database. Hence, we were unable to calculate their associated HQ values. Therefore, in reality, the noncarcinogenic risk is also higher than the values presented here.

4. Conclusions

The concentrations of trace elements measured in the ambient PM during the winters in Kanpur, India, revealed a substantial

Table 1
Estimation of PM_{2.5} inhalation exposure concentrations and risk assessment for the nonfoggy period.

Risk (carcinogenic)	EC (ng/m ³)	IUR (ng/m ³) ⁻¹	CR
Ni	1.96	2.4 × 10 ⁻⁷	0.5 × 10 ⁻⁶
Cr (VI)	2.61	8.4 × 10 ⁻⁵	219 × 10 ⁻⁶
Pb	40.87	3.4 × 10 ⁻⁸	1.4 × 10 ⁻⁶
			Sum = 221 × 10⁻⁶
Risk (noncarcinogenic)	EC (ng/m ³)	RfCi (ng/m ³)	HQ
Ni	4.57	24	0.19
Cr	6.08	100	0.06
Mn	6.34	50	0.13
V	7.61	100	0.08
			Sum, HI = 0.46

Table 2Estimation of combined (PM_{2.5} and fog droplets) inhalation exposure and risk assessment for foggy periods.

Risk (carcinogenic)	EC (ng/m ³)	IUR (ng/m ³) ⁻¹	CR
Ni	2.07	2.4×10^{-7}	0.5×10^{-6}
Cr	2.73	8.4×10^{-5}	229×10^{-6}
Pb	38.98	3.4×10^{-8}	1.3×10^{-6}
			Sum = 231×10^{-6}
Risk (noncarcinogenic)	EC (ng/m ³)	RfCi (ng/m ³)	HQ
Ni	4.82	24	0.20
Cr	6.37	100	0.06
Mn	7.78	50	0.16
V	7.19	100	0.07
			Sum, HI = 0.49

presence of various toxic elements and very high enrichment factor values, indicating their anthropogenic origins. Despite the ban on leaded fuel, the ambient PM still has a substantial concentration of Pb, indicating that owing to the prolonged use of leaded fuel, Pb has become a part of the crustal dust and/or other sources of Pb present at this location of study. The trace elemental composition of FW samples indicated even higher enrichment (compared to PM₁ and PM_{2.5}) for all the elements inside fog droplets, indicating FW contamination caused by anthropogenic pollution. The elemental concentrations in FW were found to be impacted by fog-droplet-size distribution, with fine droplets being more concentrated with the various elements. The substantial quantity of transition elements such as Cu, Fe, and Mn inside the fog droplets indicates that fog can act as an effective oxidizing agent for various inorganic and organic species. Risk assessment for toxic trace elements in ambient aerosols revealed a very high carcinogenic risk for the exposed population. However, the risk was increased further during foggy periods owing to the combined exposure to PM_{2.5} and fine fog droplets. Polluted fog with more fine droplets poses a greater risk to the exposed population. This is the first study to demonstrate that exposure to fog droplets can increase health hazards; therefore, steps should be taken to curb pollution at this location. However, in this study, we have selected inhalation as the only route of exposure, whereas exposure to toxic elements through other routes (ingestion, dermal absorption) is also plausible. Certain parameters are fixed, such as the adult's weight at 70 kg. These parameters and hypotheses can lead to an underestimation or overestimation in the assessment. To overcome such limitations, a multiseasonal study with higher spatiotemporal coverage is required for more accurate estimates of health risks. The analyses and addition of other toxic species, such as polyaromatic hydrocarbons (PAH), could provide further insights into the risk estimation of the exposed population.

Author contribution statement

Abhishek Chakraborty: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Tarun Gupta: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Anil mandaria: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Shruti Tripathi: Analyzed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of competing interest

I confirm that all the co-authors have read, and approved the manuscript, and there is no conflict of interests, and declares that none of the material has been published or is under consideration elsewhere.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e16400>.

References

- [1] C. Giorio, S. D'Arco, V. Marco, D. Badocco, F. Battaglia, L. Solda, P. Pastore, A. Tapparo, Emerging Investigator Series: Aqueous-phase Processing of Atmospheric Aerosol Influences Dissolution Kinetics of Metal Ions in an Urban Background Site in Po Valley, vol. 24, Royal Society of Chemistry, 2022, pp. 884–897, <https://doi.org/10.1039/D2M0023G>.

- [2] N.V. dos Santos, C.L.Z. Vieira, P.H.N. Saldiva, C.D.S. De André, B.P. Mazzilli, M. de Fátima Andrade, C.H. Saueia, M. Saiki, M.M. Veras, P. Koutrakis, Accumulation of trace element content in the lungs of Sao Paulo city residents and its correlation to lifetime exposure to air pollution, *Sci. Rep.* 12 (1 12) (2022) 1–7, <https://doi.org/10.1038/s41598-022-15048-2>, 2022.
- [3] M. Kampa, E. Castanas, Human health effects of air pollution, *Environ. Pollut.* 151 (2008) 362–367, <https://doi.org/10.1016/j.envpol.2007.06.012>.
- [4] P. Wild, E. Bourgard, C. Paris, Lung cancer and exposure to metals: the epidemiological evidence, *Methods Mol. Biol.* 472 (2009) 139–167, https://doi.org/10.1007/978-1-60327-492-0_6.
- [5] Y.-S. Wu, G.-C. Fang, W.-J. Lee, J.-F. Lee, C.-C. Chang, C.-Z. Lee, A review of atmospheric fine particulate matter and its associated trace metal pollutants in Asian countries during the period 1995–2005, *J. Hazard Mater.* 143 (2007) 511–515, <https://doi.org/10.1016/j.jhazmat.2006.09.066>.
- [6] K.W. Fomba, D. van Pinxteren, K. Müller, Y. Iinuma, T. Lee, J.L. Collett Jr., H. Herrmann, Trace metal characterization of aerosol particles and cloud water during HCCT 2010, *Atmos. Chem. Phys.* 15 (2015) 8751–8765, <https://doi.org/10.5194/acp-15-8751-2015>.
- [7] B. Jia, Y. Tian, Y. Dai, R. Chen, P. Zhao, J. Chu, X. Feng, Y. Feng, Seasonal variation of dissolved bioaccessibility for potentially toxic elements in size-resolved PM: impacts of bioaccessibility on inhalable risk and uncertainty, *Environ. Pollut.* 307 (2022), 119551, <https://doi.org/10.1016/j.envpol.2022.119551>.
- [8] P. Pant, S.J. Baker, R. Goel, S. Guttikunda, A. Goel, A. Shukla, R.M. Harrison, Analysis of size-segregated winter season aerosol data from New Delhi, India, *Atmos. Pollut. Res.* 7 (2016) 100–109, <https://doi.org/10.1016/j.apr.2015.08.001>.
- [9] R. Das, B. Khezri, B. Srivastava, S. Datta, P.K. Sikdar, R.D. Webster, X. Wang, Trace element composition of PM_{2.5} and PM₁₀ from Kolkata – a heavily polluted Indian metropolis, *Atmos. Pollut. Res.* 6 (2015) 742–750, <https://doi.org/10.5094/APR.2015.083>.
- [10] S.K. Sharma, T.K. Mandal, Elemental composition and sources of fine particulate matter (PM_{2.5}) in Delhi, India, *Bull. Environ. Contam. Toxicol.* 110 (2023) 60, <https://doi.org/10.1007/S00128-023-03707-7>.
- [11] Rajput et al., 2014.
- [12] J. Boman, M.J. Gatari, S. Janhäll, A.S. Shannigrahi, A. Wagner, Elemental content of PM_{2.5} aerosol particles collected in Göteborg during the Göte-2005 campaign in February 2005, *Atmos. Chem. Phys.* 9 (2009) 2597–2606, <https://doi.org/10.5194/acp-9-2597-2009>.
- [13] C. Petaloti, A. Triantafyllou, T. Kouimtzi, C. Samara, Trace elements in atmospheric particulate matter over a coal burning power production area of western Macedonia, Greece, *Chemosphere* 65 (2006) 2233–2243, <https://doi.org/10.1016/j.chemosphere.2006.05.053>.
- [14] L. Xia, Y. Gao, Characterization of trace elements in PM_{2.5} aerosols in the vicinity of highways in Northeast New Jersey in the US East Coast, *Atmos. Pollut. Res.* 2 (2011) 34–44, <https://doi.org/10.5094/APR.2011.005>.
- [15] V. Bangar, A.K. Mishra, M. Jangid, P. Rajput, Elemental characteristics and source-apportionment of PM_{2.5} during the post-monsoon season in Delhi, India, *Front. Sustain. Cities* 3 (2021) 18, <https://doi.org/10.3389/frsc.2021.648551/BIBTEX>.
- [16] S. Izhari, A. Goel, A. Chakraborty, T. Gupta, Annual trends in occurrence of submicron particles in ambient air and health risk posed by particle bound metals, *Chemosphere* 146 (2016) 582–590, <https://doi.org/10.1016/j.chemosphere.2015.12.039>.
- [17] D.D. Massey, A. Kulshrestha, A. Taneja, Particulate matter concentrations and their related metal toxicity in rural residential environment of semi-arid region of India, *Atmos. Environ.* 67 (2013) 278–286, <https://doi.org/10.1016/j.atmosenv.2012.11.002>.
- [18] D.K. Singh, T. Gupta, Source apportionment and risk assessment of PM₁ bound trace metals collected during foggy and non-foggy episodes at a representative site in the Indo-Gangetic plain, *Sci. Total Environ.* 550 (2016) 80–94, <https://doi.org/10.1016/j.scitotenv.2016.01.037>.
- [19] X.H. Liu, K.M. Wai, Y. Wang, J. Zhou, P.H. Li, J. Guo, P.J. Xu, W.X. Wang, Evaluation of trace elements contamination in cloud/fog water at an elevated mountain site in Northern China, *Chemosphere* 88 (2012) 531–541, <https://doi.org/10.1016/j.chemosphere.2012.02.015>.
- [20] K. Ali, G.A. Momin, S. Tiwari, P.D. Safai, D.M. Chate, P.S.P. Rao, Fog and precipitation chemistry at Delhi, North India, *Atmos. Environ.* 38 (2004) 4215–4222, <https://doi.org/10.1016/j.atmosenv.2004.02.055>.
- [21] M. Kulshrestha, J. Monika, R. Sekar, D. Krishna, A.K. Hazarika, N.C. Dey, P.G. Rao, Deposition fluxes of chemical components of fog water at a rural site in north-east India, *Tellus B* 57 (2005) 436–439, <https://doi.org/10.1111/j.1600-0889.2005.00165.x>.
- [22] D.J. Straub, J.W. Hutchings, P. Herckes, Measurements of fog composition at a rural site, *Atmos. Environ.* 47 (2012) 195–205, <https://doi.org/10.1016/j.atmosenv.2011.11.014>.
- [23] T. Li, Y. Wang, W.J. Li, J.M. Chen, T. Wang, W.X. Wang, Concentrations and solubility of trace elements in fine particles at a mountain site, southern China: regional sources and cloud processing, *Atmos. Chem. Phys.* 15 (2015) 8987–9002, <https://doi.org/10.5194/acp-15-8987-2015>.
- [24] Xu et al., (2018).
- [25] D.S. Kaul, T. Gupta, S.N. Tripathi, V. Tare, J.L. Collett Jr., Secondary organic aerosol: a comparison between foggy and nonfoggy days, *Environ. Sci. Technol.* 45 (2011) 7307–7313, <https://doi.org/10.1021/es201081d>.
- [26] M. Mohan, S. Payra, Influence of aerosol spectrum and air pollutants on fog formation in urban environment of megacity Delhi, India, *Environ. Monit. Assess.* 151 (2009) 265–277, <https://doi.org/10.1007/s10661-008-0268-8>.
- [27] National ambient air quality standards, National Ambient Air Quality Status & Trends in India-2010 Central Pollution Control Board, GOI, 2012.
- [28] U. Gupta, Valuation of Urban Air Pollution: A Case Study of Kanpur City in India, 2006.
- [29] D. Bhattu, S.N. Tripathi, CCN closure study: effects of aerosol chemical composition and mixing state, *J. Geophys. Res. Atmos.* 120 (2015) 766–783, <https://doi.org/10.1002/2014JD021978>.
- [30] A. Chakraborty, D. Bhattu, T. Gupta, S.N. Tripathi, M.R. Canagaratna, Real-time measurements of ambient aerosols in a polluted Indian city: sources, characteristics and processing of organic aerosols during foggy and non-foggy periods, *J. Geophys. Res. Atmos.* 120 (2015) 9006–9019, <https://doi.org/10.1002/2015JD023419>.
- [31] D.S. Kaul, T. Gupta, S.N. Tripathi, Source apportionment for water soluble organic matter of submicron aerosol: a comparison between foggy and nonfoggy episodes, *Aerosol Air Qual. Res.* 14 (2014) 1527–1533, <https://doi.org/10.4209/aaqr.2013.10.0319>.
- [32] A. Chakraborty, B. Ervens, T. Gupta, Sachchidan. Tripathi, Characterization of organic residues of size-resolved fog droplets and their atmospheric implications, *J. Geophys. Res. Atmos.* 121 (2016) 4317–4332, <https://doi.org/10.1002/2015JD024508>.
- [33] C. Bray, W. Battye, V. Aneja, The role of biomass burning agricultural emissions in the Indo-Gangetic Plains on the air quality in New Delhi, India, *Atmos. Environ.* 218 (2019), 116983, <https://doi.org/10.1016/j.atmosenv.2019.116983>.
- [34] A. Chakraborty, P. Rajeev, P. Rajput, T. Gupta, Water soluble organic aerosols in indo gangetic plain (IGP): insights from aerosol mass spectrometry, *Sci. Total Environ.* (2017) 599–600, <https://doi.org/10.1016/j.scitotenv.2017.05.142>.
- [35] Kim et al., 2022.
- [36] A. Kumar, T. Gupta, Development and laboratory performance evaluation of a variable configuration PM₁/PM_{2.5} impaction-based sampler, *Aerosol Air Qual. Res.* 15 (2015) 768–775, <https://doi.org/10.4209/aaqr.2014.11.0307>.
- [37] A. Kumar, T. Gupta, Development and field evaluation of a multiple slit nozzle-based high volume PM_{2.5} inertial impactor assembly (HVIA), *Aerosol Air Qual. Res.* 15 (2015) 1188–1200, <https://doi.org/10.4209/aaqr.2015.01.0050>.
- [38] Y. Li, Z. Zhang, H. Liu, H. Zhou, Z. Fan, M. Lin, D. Wu, B. Xia, Characteristics, sources and health risk assessment of toxic heavy metals in PM_{2.5} at a megacity of southwest China, *Environ. Geochem. Health* 38 (2016) 353–362, <https://doi.org/10.1007/s10653-015-9722-z>.
- [39] H. Li, Q. Wang, M. Shao, J. Wang, C. Wang, Y. Sun, X. Qian, H. Wu, M. Yang, F. Li, Fractionation of airborne particulate-bound elements in haze-fog episode and associated health risks in a megacity of southeast China, *Environ. Pollut.* 208 (2016) 655–662, <https://doi.org/10.1016/j.envpol.2015.10.042>.
- [40] S. Taner, B. Pekey, H. Pekey, Fine particulate matter in the indoor air of barbeque restaurants: elemental compositions, sources and health risks, *Sci. Total Environ.* 454 (2013) 79–87, <https://doi.org/10.1016/j.scitotenv.2013.03.018>. –455.
- [41] USEPA, Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment), Office of Superfund Remediation and Technology Innovation Environmental Protection Agency I, 2009, pp. 1–68. EPA-540-R-070-002.
- [42] USEPA, Regional Screening Level (RSL) Summary Table (TR=1E-06, HQ=1) November 2015, USEPA, 2022.
- [43] USEPA, Supplemental Risk Assessment of Potential Air Emissions from the Confined Disposal Facility for the Indiana Harbor and Shipping Canal Sediment Dredging and Disposal Project, vol. 5, US EPA Region, 2006, <https://doi.org/10.1017/CBO9781107415324.004>.

- [44] US EPA, (2022).
- [45] V. Romanazzi, M. Casazza, M. Malandrino, V. Maurino, A. Piano, T. Schilirò, G. Gilli, PM10 size distribution of metals and environmental-sanitary risk analysis in the city of Torino, *Chemosphere* 112 (2014) 210–216, <https://doi.org/10.1016/j.chemosphere.2014.04.034>.
- [46] R. Das, B. Khezri, B. Srivastava, S. Datta, P.K. Sikdar, R.D. Webster, X. Wang, Trace element composition of PM2.5 and PM10 from Kolkata—a heavily polluted Indian metropolis, *Atmos. Pollut. Res.* 6 (2015) 742–750, <https://doi.org/10.5094/APR.2015.083>.
- [47] L. Xu, X. Chen, J. Chen, F. Zhang, C. He, J. Zhao, L. Yin, Seasonal variations and chemical compositions of PM 2.5 aerosol in the urban area of Fuzhou, China, *Atmos. Res.* 104–105 (2012) 264–272, <https://doi.org/10.1016/j.atmosres.2011.10.017>.
- [48] A. Chakraborty, T. Gupta, Chemical characterization and source apportionment of submicron (PM1) aerosol in Kanpur region, India, *Aerosol Air Qual. Res.* 10 (2010) 433–445, <https://doi.org/10.4209/aaqr.2009.11.0071>.
- [49] T. Gupta, A. Mandariya, Sources of submicron aerosol during fog-dominated wintertime at Kanpur, *Environ. Sci. Pollut. Control Ser.* 20 (2013) 5615–5629, <https://doi.org/10.1007/s11356-013-1580-6>.
- [50] A. Ooki, M. Uematsu, K. Miura, S. Nakae, Sources of sodium in atmospheric fine particles, *Atmos. Environ.* 36 (2002) 4367–4374, [https://doi.org/10.1016/S1352-2310\(02\)00341-2](https://doi.org/10.1016/S1352-2310(02)00341-2).
- [51] P. Rajeev, P. Rajput, T. Gupta, Chemical characteristics of aerosol and rain water during an El Niño and PDO influenced Indian summer monsoon, *Atmos. Environ.* 145 (2016) 192–200, <https://doi.org/10.1016/j.atmosenv.2016.09.026>.
- [52] S. Tiwari, A.K. Srivastava, D.S. Bisht, T. Bano, S. Singh, S. Behura, M.K. Srivastava, D.M. Chate, B. Padmanabhamurty, Black carbon and chemical characteristics of PM10 and PM 2.5 at an urban site of North India, *J. Atmos. Chem.* 62 (2009) 193–209, <https://doi.org/10.1007/s10874-010-9148-z>.
- [53] B. Ervens, B.J. Turpin, R.J. Weber, Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.* 11 (2011) 11069–11102, <https://doi.org/10.5194/acp-11-11069-2011>.
- [54] S.N. Pandis, J.H. Seinfeld, C. Pilinis, Chemical composition differences in fog and cloud droplets of different sizes, *Atmos. Environ., Part A* (1990), [https://doi.org/10.1016/0960-1686\(90\)90529-V](https://doi.org/10.1016/0960-1686(90)90529-V).
- [55] D.K. Singh, T. Gupta, Role of transition metals with water soluble organic carbon in the formation of secondary organic aerosol and metallo-organics in PM1 sampled during post monsoon and pre-winter time, *J. Aerosol Sci.* 94 (2016) 56–69, <https://doi.org/10.1016/j.jaerosci.2016.01.002>.
- [56] T. Gupta, P. Rajeev, R. Rajput, Emerging major role of organic aerosols in explaining the occurrence, frequency, and magnitude of haze and fog episodes during wintertime in the Indo Gangetic Plain, *Am. Chem. Soc.* 7 (2) (2022) 1575–1584, <https://doi.org/10.1021/acsomega.1c05467>.
- [57] W. Birmili, A.G. Allen, F. Bary, R.M. Harrison, Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic, *Environ. Sci. Technol.* 40 (2006) 1144–1153.
- [58] L. Deguillaume, M. Leriche, K. Desboeufs, G. Mailhot, C. George, N. Chaumerliac, Transition metals in atmospheric liquid phases: sources, reactivity, and sensitive parameters, *Chem. Rev.* 105 (2005) 3388–3431, <https://doi.org/10.1021/cr040649c>.
- [59] R.M. Duvall, B.J. Majestic, M.M. Shafer, P.Y. Chuang, B.R.T. Simoneit, J.J. Schauer, The water-soluble fraction of carbon, sulfur, and crustal elements in Asian aerosols and Asian soils, *Atmos. Environ.* 42 (2008) 5872–5884, <https://doi.org/10.1016/j.atmosenv.2008.03.028>.
- [60] D.R. Samayamantula, C. Sabarathinam, N.A. Alayyadhi, Trace elements and their variation with pH in rain water in arid environment, *Arch. Environ. Contam. Toxicol.* 80 (2021) 331–349, <https://doi.org/10.1007/S00244-020-00787-Y>.