Chemical characterization of PM$_{2.5}$ bound species during the Diwali fireworks in Delhi: An insight from source apportionment and airborne hazardous elements

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Abstract

Diwali is among the most important Indian festivals, and elaborate firework displays mark the festivities in the evening. This study assesses the impact of Diwali on the concentration, composition, and sources of ambient PM$_{2.5}$. The total PM$_{2.5}$ concentrations were observed to rise by $\sim$16 times their pre-firework levels, while each of the elements, organics, and black carbon were augmented by a factor of 12.3, 1.6, and 2.3, respectively. Concentration levels of species like K, Al, Sr, Ba, S, and Bi displayed distinct peaks during the firework event, and were identified as tracers for the same. The average concentrations of potential carcinogens like As, exceeded US EPA screening levels for industrial air by a factor of $\sim$9.6, while peak levels reached up to 16.1 times the screening levels. The source apportionment study, undertaken using positive matrix factorization, revealed the fireworks to account for 95% of the total elemental PM$_{2.5}$ during Diwali. The resolved primary organic emissions, too, were enhanced by a factor of $\sim$8 during Diwali. Delhi has encountered serious haze events following Diwali in recent years, this study highlights that it is the biomass burning emissions rather than the fireworks that dominate Delhi’s air quality in the days following Diwali.

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1. Introduction

Enhancement of heavy metal concentrations in the environment has been recognized to pose a severe threat to the ecosystem and human health, from impacting the microbiological balance in soils (Barbieri, 2016) to an adverse effect on human health (Singh et al., 2011). Intensified metal loading in aerosols, especially fine particulate matter (PM$_{2.5}$), has been a pressing concern taking into account the increased risk of exposure and ease of bioaccumulation (Tchounwou et al., 2012). Past studies have noted that exposure to high metal concentrations can have a severe detriment to human health, such as increased neurotoxic impairment, respiratory ailment, and carcinogenic impact from metals like Mn, Cu, Pb, Cr (Santos-Burgoa et al., 2001; Wang et al., 2006).

Advances in measurement technology and increased use of statistical tools to apportion the particulate-bound metallic species to real-world sources like traffic emissions, industrial plumes, and mining operations have enabled policymakers to make more informed decisions (Csavina et al., 2011). However, relatively less attention has been drawn towards episodic anthropogenic activities, which can lead to much more metalliferous particulate matter concentrations in ambient air. Fireworks are often an essential component in recreational activities, celebrations, and festivities across the globe, the New Year’s Eve, Las Fallas festival in Spain, the Lantern Festival and Chinese New Year in China, and Diwali in India (Moreno et al., 2007).

Along with particulate matter rich in metallic elements, fireworks are also known to cause high levels of black carbon and generate gaseous pollutants like oxides of carbon, sulfur, and nitrogen (Barman et al., 2008). Diwali is a Hindu religious festival celebrated every year around October-November in most parts of India, and the celebrations are prominently marked by fireworks displays and firecracker burning during the night. Multiple studies in the past have worked to delineate the after-effects of these festivities on ambient air quality. Babu and Moorthy, (2001) studied the effects of the use of fireworks during Diwali in Thiruvananthapuram, India, and recorded a three-fold increase in the mass concentration of atmospheric black carbon during Diwali when compared with ambient levels during regular days. In Hisar, India a study, undertaken by Ravindra et al., (2003) reported a 2x to 10x increase in mass concentrations of PM$_{10}$, TSP, NO$_x$, and SO$_2$ during the Diwali festival as compared to a typical winter day with no firework display.
Kulshrestha et al., (2004) were the first in India to study variation in particle-bound metal concentration engendered by Diwali and found Ba, K, Al, and Sr to increase by 1091, 25, 18, and 15 times, about a typical day in Hyderabad. Barman et al., (2008) based their study in Lucknow, India, investigating the effect of Diwali on ambient air quality and reported Cu and Ni to rise by 272% and 149% following the fireworks event. Chatterjee et al., (2013) reported K, Mg, and Ca to rise by a factor of 30, 20, and 14 times in terms of 12-hr averaged concentration levels during the Diwali night. Rastogi et al., (2019) documented that organic aerosols were the dominant contributor (~85%) followed by sulfate (~13%), chloride (~4%), nitrate (~4%), and ammonium (~2%) to non-refractory PM$_1$ on the Diwali night at Ahmedabad, India.

Delhi is regarded as one of the world’s most polluted cities (Cropper et al., 1997; IQAir World Air Quality Report, 2018) and despite the increasing intensity of pollution levels following Diwali in the recent years (Schultz and Raj, 2019), the number of studies focusing on the impact of Diwali in Delhi is found to be very limited. Sarkar et al., (2010) studied the effect of Diwali on the ambient air quality in Delhi and found Ba, K, Sr, and Na in PM$_{10}$ to increase by a factor of 264, 18, 15, and 5, respectively, based on 24-hr averages. Perrino et al., (2011) attributed the rise in ambient PM$_{2.5}$ levels in Delhi to a commensurate increase in the concentrations of Mg, Al, Ti, V, Cr, Mn, and Ga concentrations during Diwali. Kulshrestha et al., (2014) made a first attempt at characterizing the elements measured during the Diwali event into principal factors using PCA to segregate and quantify the contribution of firecrackers as a separate factor. During the regular days with no firework displays, the principal components were identified as crustal, vehicular, and industrial, while during the fireworks event, vehicular and firecrackers emerged as the predominant sources. However, most of the studies noted above are limited by the time resolution of their analysis, mainly due to the offline methods employed for processing the samples. Aerosol concentrations averaged over larger intervals of time often undermine the peak pollutant levels, which become of greater importance while analyzing episodic events like Diwali. In addition to quantifying peak concentrations, higher time resolutions are also essential to better analyze the health risks to the population exposed to metalliferous aerosols during firework events based on the time and pollutant concentrations associated with the exposure.

The present study overcomes these limitations by employing an online XRF-based near the real-time metal monitor, Xact 625i (Cooper Environmental Services, Tigard, Oregon, USA), for highly resolved continuous measurement and characterization of ambient PM$_{2.5}$. The study is placed towards the end of October, enabling...
us to analyze the impact of Diwali and comparing it with the ordinary days, with no firework events. We further focus on the source apportionment of the elemental PM$_{2.5}$ data to quantify the impact of Diwali on ambient air quality in Delhi. We also measure and apportion the organic fraction of total PM$_{2.5}$ to assess the time variation of sources contributing to organic and elemental PM$_{2.5}$ around the Diwali event. In addition to the organic and elemental fractions of PM$_{2.5}$, the inorganic ions (sulfate, nitrate, and ammonium) and black carbon concentrations are also measured to account for the impact of the fireworks on total PM$_{2.5}$ and its composition. This is also the first study in India to utilize not one but two Xact 625i monitors located at different sites, around 15 km apart, in Delhi. The source apportionment analysis is applied independently to the data from both these instruments, enabling us to evaluate the local variability of the sources contributing to elemental PM$_{2.5}$ both during the firework event and the regular days.

2. Materials and Methods

2.1 Sampling Location and Instrumentation

The present study is based in the National Capital Territory (NCT) Delhi, spread over an expanse of 1483 km$^2$, lies at an elevation varying between 213 and 305 m above sea level, at a distance of approximately 1400 km from the nearest coast (Govt. of NCT of Delhi, 2018). The capital city is house to a population of 19 million with a registered vehicle population of around 10.75 million, as of 2018 (Transport Department, 2018). However, some studies suggest that the number of registered vehicles might actually be overestimated as compared to the number of vehicles on the road, as the vehicles are often not de-registered once they are decommissioned (Goel et al., 2016).

The climate in Delhi is regarded as an overlap between monsoon-influenced humid subtropical and semi-arid and is mainly influenced by its inland position and the prevalence of continental air during most of the year. The present study is placed towards the end of October, which, in the context of Delhi, is regarded as a transitional month into the cold season following the monsoon. It is marked by an increase in the average sunshine alongside a decrease in the amount of rainfall. Humidity drops to an average of 29% in October, as does the average temperature to a low of 19°C (66.2°F) and a high of 31°C (87.8°F). The wind is mostly northwesterly, with the speeds dropping down to an average of 7.6 km/h (4.7 mph) (India Metrological Department, 2011).
The present study spans over a period of 12 days from 20th October 2019 to 31st October 2019, with the Diwali festival on 27th October 2019. In order to account for the immediate effect of the firecracker burning, we focus on a six-day interval around the Diwali fireworks event and subdivide it into three phases Pre-Diwali (PD) (25th October 2019 24:00 IST – 27th October 2019 18:00 IST), During Diwali (DD) (27th October 2019 18:00 IST – 28th October 2019 6:00 IST), and Following Diwali (FD) (28th October 2019 6:00 IST – 31st October 2019 24:00 IST). The DD phase was structured to coincide approximately with the start of the firecracker burning on the evening of the Diwali day, leading to a surge in PM$_{2.5}$ concentrations during the night, and end around the point when the pollution levels fall back to nearly normal levels when the boundary layer height starts to increase in the morning following the Diwali night. However, in the case of the elemental PM$_{2.5}$ (denoted using PM$_{2.5}^{el}$) levels and its apportioned sources discussed in sections 3.1 and 3.2, respectively, the enhancement in concentration in the DD phase is referenced against an extended Pre-Diwali phase (ePD) (20th October 2019 24:00 IST – 27th October 2019 18:00 IST).

As discussed earlier, sampling was conducted at two sites approximately 15 km apart (figure S1). The first site was the campus of the Indian Institute of Tropical Meteorology, Delhi (IITMD), located in Central Delhi (28.6304° N, 77.1751° E). The location is surrounded by an expansive green stretch of the Pusa forest, and no primary industrial sources are located within a 5 km radius. However, a biomass incineration plant is located around 4 km west of the facility. The instruments were placed in a temperature-controlled facility on the 2nd floor of the complex, while the sampling inlet extended to the rooftop around 15 m from ground level. The second site was at the Indian Institute of Technology, Delhi (IITD) campus, located in South Delhi (28.5450° N, 77.1926° E). The instruments were housed in a temperature-controlled laboratory on the top floor of a four-story building on campus. The nearest source of local emissions is an arterial road outside the campus, located about 150 m from the building.

The Xact 625i Ambient Metal Monitor, installed with a PM$_{2.5}$ inlet for sampling, was employed to measure PM$_{2.5}^{el}$ concentrations, with a half-hourly time resolution for the entire study period. From the PD to the FD phase, the existing instruments at the IITMD site were supplemented with a multi-channel Aethalometer (Magee Scientific Model AE33, Berkeley, CA) for measuring black carbon at a one-minute time resolution. Also, a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR ToF AMS, Aerodyne Inc., MA, USA), measuring the non-refractory fraction of PM$_{2.5}$ (NR-PM$_{2.5}$), i.e., the fragments that flash vaporize at 600°C, was
deployed at the IITMD site. The HR ToF AMS measures the organic fraction of total PM$_{2.5}$ along with inorganic ions like sulfate, nitrate, ammonium (SNA), and chloride. A time resolution of two minutes was used for the AMS. It is essential to note that while both the AMS and Xact measure Cl concentrations, the chlorine fraction reported in this study is based on the Xact 625i values, as AMS only measures the non-refractory ions, and thus total Cl reported by AMS is always found to be less than or equal to the Xact reported levels.

Further details on the instrumentation and data quality assurance or quality control (QA/QC) checks for each instrument are provided in the supplementary information (SI) section S1.

2.2 Source Apportionment

2.2.1 Positive Matrix Factorization

Positive Matrix Factorization (PMF) is an essential multivariate factor analysis technique widely used for source apportionment of particulate matter constituents (Sharma et al., 2016; Ulbrich et al., 2009; Vossler et al., 2016). The PMF model attempts to best express the covariance of the multivariate input data set in terms of a set of time-invariant factor/source profiles and their time-varying contribution, as shown in eq. (1):

\[ X = GF + E \quad \ldots \quad (1) \]

Where \( X \) is an \( m \times n \) input data matrix with a measured concentration of \( n \) species at \( m \) time steps, \( G \) is a \( m \times p \) fractional contribution matrix quantifying the fractional contribution of \( p \) source profiles at each of the \( m \) time steps. \( F \) is a time-invariant matrix representing a set of \( p \) factor profiles/vectors constituted by \( n \) elements, where the user selects the number of factors, i.e., \( p \). \( E \) is a \( m \times n \) matrix of residuals corresponding to the difference \((e_{ij})\) between each element of the input matrix \( X \) and the product of matrices \( G \) and \( F \).

The PMF algorithm implements non-negativity constraints on each of the solution matrices to prevent negative factor concentrations. The elements constituting the matrices \( G \) and \( F \) are iterated to minimize the object function or the Q-value given by eq. (2):

\[ Q = \sum_i \sum_j \left( \frac{e_{ij}}{s_{ij}} \right)^2 \quad \ldots \quad (2) \]

Here, the term \( s_{ij} \) represents the uncertainty associated with each element \( x_{ij} \) of the input data matrix \( X \). Thus, the PMF algorithm allows each input data point to be weighted individually, enabling the user to alter the impact
of each data point on the final solution, depending on the confidence in the associated measurement. Hence, low confidence measurements like for the case of concentrations below method detection limits can be down-weighted w.r.t the other measurements. The PMF algorithm was implemented using EPA PMF 5.0, which is, in turn, built on the ME-2 solution model (Paatero, 1999). Further details on the model are discussed in past studies (Paatero, 1997; Paatero and Tapper, 1994). Further details w.r.t the present study in terms of pmf input preparation, factor selection and uncertainty quantification has been reported in SI section S2.

3. Results and Discussions

In the present work, we focus our attention on quantifying the impact of the extensive firework displays/firecracker burning on the ambient air quality. Section 3.1 presents the variation in levels of total PM$_{2.5}$ in the Diwali period as well as the change in its composition during each phase from PD to FD. We further pivot our discussion about constituents of PM$_{2.5}$$_{el}$ augmented during the DD phase and the possible role of fireworks in the enhancement of these species, which are further observed to mark the firework event. In section 3.1.1 we discuss the potential health risks associated with the firework-related emissions during Diwali. In order to quantify the contribution of firework displays to the organic and elemental fractions of PM$_{2.5}$, we perform a source apportionment study using PMF presented in sections 3.2 and 3.3. The PMF analysis successfully resolves a separate emission profile corresponding to fireworks in case of elemental PM$_{2.5}$ source apportionment, presented in section 3.2.4, also the time variation of the resolved primary organic aerosol source is observed to have a distinct peak marking the firework event (section 3.3.1).

3.1 Variation in PM$_{2.5}$ and its constituents during Diwali

As discussed in section 2.1 earlier, from the PD up till the FD phase, we commissioned an extra set of instruments at the IITMD site to get a broader image of the impact of the firecracker event on total PM$_{2.5}$. We must note that each of the instrument is designed to measure partial rather than total PM$_{2.5}$, measuring each of the elemental, organic, inorganic ions, and black carbon components. While none of these instruments can measure refractory ions like sodium, magnesium, oxides, and fluorides, the residual mass we obtained comparing the instrument total PM$_{2.5}$ and total PM$_{2.5}$ from a Beta Attenuation Monitor (BAM) is negligible. The instrument total was regressed against the BAM measurements, and an appreciable correlation (Pearson R = 0.953) between their time variation was recorded (figure S2).
Figure 1(a) presents the time variation of the instrument total PM$_{2.5}$ from the PD to the FD phase; we note that the firework event results in a sharp rise in the instrument total PM$_{2.5}$, with the average concentration in the DD phase (around 192 µg/m$^3$) increasing by 408% compared to the PD phase. The peak concentrations observed within the DD phase (around 606 µg/m$^3$) are more than 16 times (or 1500 % rise) w.r.t the PD phase. After the fireworks event, the FD phase shows a significant dip in the particulate concentrations. However, the average particulate concentrations remain higher than the PD phase by a factor of ~2, which suggests that either some effect of the fireworks remain in the FD phase or the background PM$_{2.5}$ levels start rising due to some other sources; this will be discussed further in section 3.2 and 3.3.

The variation in the composition of the PM$_{2.5}$ across the 3 phases is shown in figure 1(b); we observe that similar to the total PM$_{2.5}$, each of its constituent fractions increases during the DD phase; however, the percentage rise in each component is highly disproportionate. The organics, BC, and SNA fractions increase by approximately 1.6, 2.3, and 2.5 times the PD concentrations, respectively. The chloride fraction (measured using Xact 625i) increases by 640% or 7.4 times during the DD phase, while the metallic fraction rises to around 19.4 times the PD value. During the FD phase, all fractions reduce considerably but remain higher than the PD levels. BC during FD remains around 30% higher than PD, while metals and chloride remain at around 3.5 and 3 times their PD levels. However, it is essential to note that SNA remains around 2.1 times the PD concentrations, reducing by only 15% compared to the average in the DD phase, signaling towards either the lasting impact of the Diwali event on the inorganic ionic concentrations or some other anthropogenic or meteorological cause leading to the increase, this will be discussed further in section 2. Again for the organic fraction (figure 1(b)), it is interesting to note that the levels in the FD phase average around 2.2 times the PD phase and are, in turn, 37% higher than even the DD phase; this behavior is discussed further in section 3.3 when the organic fraction is subjected to source apportionment, to identify possible reasons that lead to this increase.

Figures 1 (c-d) present the variation of PM$_{2.5}$$_{el}$ (PM$_{2.5}$$_{el}$ = Metals + Cl + S), measured using Xact 625i at both the sampling sites, i.e., IITMD and IITD, throughout the study period, while figures 1 (e - j) present the variation of each element constituting PM$_{2.5}$$_{el}$ at IITD and IITMD through each of ePD, DD, and FD. As expected, the variation of PM$_{2.5}$$_{el}$ is in-sync with the variation of the metallic fraction of PM$_{2.5}$ at IITMD observed in figure 1(b). At IITMD, PM$_{2.5}$$_{el}$ rises by 12.4 times compared to ePD and stays at around 2.8 times the ePD value in FD, while at IITD, PM$_{2.5}$$_{el}$ rises to 12 times the ePD levels and remain at around twice the ePD concentrations.
in FD. However, the average PM$_{2.5}$ concentration remains ~155 µg/m$^3$ during the DD phase at both the IITD and IITMD sites.

In terms of the elemental variation at both the sites during each phase (figure 1 (e-j)), we note that elements like Al, Ba, Cl, K, Sr, and S are recorded in considerable concentrations at both locations during the study period and rise significantly in the DD phase. Aluminum rises by 69.6 and 97.3 times in the DD phase w.r.t ePD at IITMD and IITD sites, respectively, with an average concentration of 44.2 µg/m$^3$ (IITMD) and 48.8 µg/m$^3$ (IITD) during the DD phase. Similarly, during the DD phase, Ba concentration averages at 15.4 µg/m$^3$ (IITMD) and 14.3 µg/m$^3$ (IITD), Cl at 11.4 µg/m$^3$ (IITMD) and 9 µg/m$^3$ (IITD), K at 48.2 µg/m$^3$ (IITMD) and 53.2 µg/m$^3$ (IITD), Sr at 1.5 µg/m$^3$ (IITMD) and 1.1 µg/m$^3$ (IITD), and S at 25.3 µg/m$^3$ (IITMD) and 23 µg/m$^3$ (IITD). In terms of the increment in concentration during the DD phase, Ba rises by 190.4, 123.4 times, Cl by 4.7, 6.5 times, K by 22.5, 19.8 times, Sr rises by 145, 87.2 times and S by 6.3, 5.1 times at IITMD and IITD sites respectively when comparing the DD to the ePD average concentrations. However, there are certain species where the concentration was close to the MDL in ePD and rose substantially in the DD phase. At IITMD, Vanadium and Bismuth averaged around 0.0007 µg/m$^3$ and 0.0004 µg/m$^3$ in the ePD phase while rising to 0.43 µg/m$^3$ and 0.13 µg/m$^3$ respectively in DD, thus increasing ~608 and ~321 times their ePD concentrations.

From Figures 1 (e-j), we notice that while the firecracker burning leads to a considerable rise in the concentration of certain species, other species remain mostly unaffected. It is also noted that during the DD phase, the correlation between the multiple elemental constituents of PM$_{2.5}$ increases significantly as compared to the ePD and FD phase (figure S3). Numerous studies in the past have recognized this disproportionate behavior pointing to the emissions specific to firework events and identified these elements as a marker for the fireworks. Figures 2 (a-f) present the elemental markers that were found to have distinct peaks during the DD phase at both our sampling locations.

Multiple studies around the world have recognized potassium as a reliable marker for particulate emissions from firecracker burning events (Shon et al., 2015; Tanda et al., 2019; Tian et al., 2014; Yang et al., 2014). K is a significant component of the black powder fuel, which is a common raw material in most fireworks and is present in the form of KClO$_3$ or KNO$_3$ (Drewnick et al., 2006; Dutcher et al., 1999). However, in India, the period of October – November, during which Diwali usually occurs, witnesses a rise in the stubble and biomass burning events (Jethva et al., 2019) also, as it coincides with the crop harvesting season and the onset of winters.
Potassium is also widely accepted as a tracer for the biomass and the stubble burning events (Pant and Harrison, 2012); thus, such activities may impose background disturbances when considering K as a sole marker in the context of Diwali.

Similar to K, nitrate, and perchlorate salts of Ba are used as oxidizers in fireworks to facilitate rapid combustion (Do et al., 2012). Metals like Al, Ba, and Sr are often used as coloring agents for fireworks; Al salts have been known to emit white and silver sparkles, while Ba gives green as chlorates, white as carbonates and nitrates, while Sr salts are known to emit red (Kulshrestha et al., 2004; QW et al., 2018). Bi compounds (Bi$_2$O$_3$, (BiO)$_2$CO$_3$) are mostly used to produce crackling stars in fireworks (Perrino et al., 2011; Tanda et al., 2019).

Sulfur, similar to potassium, is another component of the black powder fuel used in firecrackers and is used as a reducing agent (Drewnick et al., 2006; Dutcher et al., 1999).

Apart from elemental markers, we also observe a marked trend in BC concentrations (figure 2 (h)) in the DD phase, with the average levels rising to about 2.2 times the PD concentrations, while peak concentrations around 5.6 times the average PD levels. Similar observations were made in past studies, which recorded a 3 to 4 times rise in BC concentrations during Diwali (Babu and Moorthy, 2001; Majumdar and Gavane, 2017). The BC emissions from firecrackers are usually traced back to the combustion of the carbonaceous matter, which acts as a reducing agent, in the black powder fuel (Babu and Moorthy, 2001; Dutcher et al., 1999).

Some past studies have also noted elevated SO$_4$ to NO$_3$ ratios (figure 2 (g)) to mark a firework event (Drewnick et al., 2006; Feng et al., 2012; Li et al., 2017); in our case, we observe this ratio to increase by around 2.1 times the PD levels. The primary reason possible for such behavior, as presented by past studies, rests on the hypothesis that SO$_4$ is directly emitted from firecracker burning due to oxidation of sulfur present in the black powder fuel, thus supplementing the sulfate from SO$_2$ oxidation from the atmosphere. At the same time, nitrate continues to remain in the photo-stationary state with O$_3$ and NO$_x$ for oxidation (Feng et al., 2012).

While these species or characteristic ratios have been identified as reliable tracers for firework-related emissions in different parts of the world, it is important to note that the trace metal concentrations observed during Diwali are significantly higher than those observed during similar events across the globe (Singh et al., 2019). In a recent study, Tanda et al., (2019) studied the impact of firework displays during the New Years’ Eve (NYE) on PM (ranging from 15nm to 10 µm) at Brno, Czech Republic, and Graz, Austria. At Brno, the average concentrations during the NYE for each of Al, Ba, K, Sr, and Bi were reported to be 54, 23, 381, 6.1, and 2.8
ng/m³ respectively. Similarly, at Graz, average concentrations for each of Al, Ba, K, Sr, and Bi were found to be 29, 14, 460, 4.8, and 1.2 ng/m³ respectively. Thus, while the study by Tanda et al., (2019), accounts for heavier particles (>2.5 µm) as compared to the present study, the average concentration of trace metals remain 2-3 orders of magnitude lower than the present study, when compared to not only the DD phase but also the ePD phase. Similar conclusions have been reached upon by an extensive review of such studies conducted by Lin, (2016). While the degree of enhancement in concentrations and the average concentration levels of individual metals recorded by us are similar to those reported by some past studies focusing on some of these metals during Diwali across different parts of India (Chatterjee et al., 2013; Perrino et al., 2011; Sarkar et al., 2010), it is essential to take note that none of these studies have been able to provide a holistic view of a variation of PM$_{2.5}$ at a time resolution and level of chemical speciation as in the present study, majorly due to the limitations associated with filter-based techniques employed by these studies. However, a few studies in different parts of the world have employed high-time resolution equipment similar to ours to quantify the impact of firework events, enabling them to comment on total PM$_{2.5}$ QW et al., (2018), focused on the Spring festival in Chengdu, China, to quantify the impact of fireworks on PM$_{2.5}$; however, the average PM$_{2.5}$ concentration recorded during the fireworks event was recorded to be 24.1 µg/m³, which is still much lower than the average levels in the present study (155 µg/m³), further highlighting the intensity of emissions associated with the firecracker burning associated with the Diwali event.

### 3.1.1 Potential health hazards associated with the Diwali fireworks

It has been well accepted that increased exposure to respirable particulate matter can have deleterious impact on human health (WHO, 2013). Past studies have also noted that elderly and children, and those with past history of heart or lung diseases are more susceptible to the pernicious health effects (Schwartz et al., 1996). It comes as a natural consequence that enhanced PM$_{2.5}$ concentrations observed during Diwali (Figure 1(a)) leads to an increased health risk for the exposed population. However, as noted earlier, in the case of Diwali the rise in the PM$_{2.5}$ levels stems from the escalated concentrations of certain elemental species (Figure 1 (e-f) & Figure 2) originating from firework displays. It is essential to take note that most of these elemental species are toxic in nature and pose a severe health risk to the exposed population, ranging from cardiopulmonary and respiratory disorders to neurological impact. Inorganic species like Al, Sr, Ba, Bi and BC were identified as tracers to mark the fireworks event in the present study (Figure 2). Past studies have noted potential role of increased exposure
to aluminum in development of Alzheimer’s disease and other neurological disorders (Niu, 2018), while exposure to increased levels of strontium have been noted to impact respiratory and bone health (Agency for Toxic Substances and Disease Registry, 1999). Exposure to barium salts have associated with neurological, musculoskeletal and respiratory effects (Effiong and Neitzel, 2016), prolonged exposure to bismuth compounds have been recognized to lead to neurotoxicity and nephrotoxicity (Wang et al., 2019); past toxicological studies have also associated BC exposure with cardiopulmonary morbidity (Janssen et al., 2013). However, it is important to note that, while past studies affirm the toxic nature of most species emitted from firecracker burning, the carcinogenic/non-carcinogenic health risks associated with these species, are mostly based on prolonged exposures at ambient pollutant levels, whereas in the case of firework events like Diwali, the pollutant levels are much higher, but the duration of exposure is much shorter. Similar concerns have been put forth by a number of recent review articles focusing on firework related emissions across the globe (Lin, 2016; Singh et al., 2019). While some studies have employed traditional risk assessment techniques to quantify the hazardous impact associated with firework related emissions during Diwali (Sarkar et al., 2010), such metrics would highly undermine the actual risks associated with short-lived but high intensity exposures associated with firework events (Lin, 2016; Singh et al., 2019). Licudine et al., (2012), utilized the EPA Risk-Based Concentration (RBC) tables (or the Generic Regional Screening Levels (RSLs) to reference against the trace metal concentrations observed during the New Years’ Eve fireworks in Pearl City, Hawaii, USA. Table 1 provides a comparison between the elemental concentrations recorded during the DD phase and the EPA generic RSLs (United States Environmental Protection Agency, 2020) for both residential and industrial air, for each of the elements measured for which the RSLs were available. We note that, for metals like Al and Ba, which were recognized as markers for the Diwali event in this study, with the 12-hr average levels exceeding the SLs not only for the residential air quality but also the industrial air standard by 1-2 orders of magnitude respectively. The average levels of Al during the DD phase exceeded the industrial air SL by a factor of ~2 at both the IITMD and IITD sites, whereas the maximum levels reached up to 5.2 and 8.1 times the industrial SL at the IITD and the IITMD sites respectively. Similarly, for Ba the average and maximum levels exceeded the industrial SLs by a factor of 6.5, 16 at the IITD site and 7, 29 at the IITMD site. In case of potential carcinogens like As, both the 12-hr average and the maximum levels during the DD phase at both the sampling locations exceeded the industrial air SLs by a factor of 4.8 and 16.1 respectively (taking a mean across the two sites), further signifying the intensity of emissions associated with Diwali fireworks. Similar behavior was displayed by other elemental species like
chlorine, and lead, with the maximum concentrations exceeding the SLs by more than order of magnitude. However, in the case of manganese the observed concentrations exceeded the residential air SL, but were under the industrial air SL, while in case of nickel, selenium and vanadium, the measured concentrations remain below the residential air SL. These observations warrant the need of further study focused on evaluating the health impact of firework events like Diwali on human health and quantifying the risks associated with high intensity, limited duration exposures characteristic of such events.

3.2 Source apportionment of elemental PM$_{2.5}$

In order to shed light on the variation sources contributing to the ambient PM$_{2.5}$ before, during and after Diwali, the elemental constituents of total PM$_{2.5}$ measured using Xact 625i at both the IITMD and IITD sites were individually subjected to source apportionment utilizing PMF. The input dataset was found to be best represented by a seven-factor solution at both the sampling locations. The real-world sources associated with each of the resolved factors were determined based on the species dominating each factor profile. The species contribution in each factor was quantified in terms of both the percentage of factor total (% FT) (concentration of species of interest as a fraction of total factor concentration) and the percentage of species sum (%SS) (ratio of the concentration of species of interest in the factor of interest to the total species concentration across all factors).

A detailed description of the resolved seven-factor solution and its time variation during the study period (figure 3 - 4) is as follows:

3.2.1 Industrial Emissions

At the IITMD site, the particulate matter apportioned to the industrial plumes (figure 3(a)) is dominated by S (57% of FT), followed by Zn (26% of FT) and K (10% of FT). In terms of % SS, the industrial plumes contribute to 66% of Zn, 29% of each Br and V, 18% of Se, and 16% of Cr, while around 13% of total S. At the IITD site, the resolved factor (figure 4 (a)) is dominated by S (44% of FT), followed by K (18% of FT) and Zn (10% of FT). In terms of % SS, the factor at IITD is found to contribute to 48% of total Cu, 44% of As, and 25 % of Zn.

While both these independently calculated profiles present some disparities in terms of the % SS that the factor accounts for, it is essential to note that both factors were found to be dominated by Zn, K, and S in terms of %
FT. The dissimilarities seem to be indicative of effects localized to each receptor site, like local wind direction or some localized industrial sources specific to each location, leading to the disparities.

Some past studies have noted elements like Zn, K, As, and V to be makers for iron and steel industries (Duan and Tan, 2013; Vincent and Passant, 2013). A study by Negi et al., (1987) differentiated between non-ferrous industrial emissions( Zn, Cu, Mn), textile emissions (V, Br), and oil refinery emissions (S, Cu, V). Shridhar et al., (2010) characterize Zn, Cu, Cr to originate from industrial emissions, while Mouli et al., (2006) traced Se to originate from metallurgical industries. The overlap and the ambiguity between the tracers proposed by various past studies to mark different kinds of industries have led us to define the factor to be associated with industrial emissions rather than attempting to characterize it to the type of industry further.

In terms of the temporal variation of this factor at the IITMD (figure 3 (b-c)) and IITD (figure 4(b-c)), there seems to be no consistent behavior observed at any of the two sites in terms of the variation during the ePD to FD phase, while the factor concentration decreases in the DD phase at IITMD, it increases at the IITD site. However, the factor concentration in the FD phase is lower than the ePD phase at both the sites, which could possibly stem from limited industrial activities during a period of extended festivities (that lasts up to 2-3 days following Diwali). These difference in the time variation of this factor at both the sites further supports the hypothesis of localized sources/meteorological conditions affecting the factor profiles. The diurnal behavior (figure S5 (a & b)) of this source at both sites is found to be coherent with each other, and 2 sharp peaks around midnight and early morning (6:00 IST) are observed. The increasing concentrations around midnight may result from the lowering boundary layer height (BLH) at night, while the early morning peak followed by a rapid decline in levels indicates the role of gas-particle partitioning.

3.2.2 Coal Combustion

At the IITMD site, the resolved coal combustion source profile is dominated by S (34% of FT) followed by Pb (28% of FT), while in terms of %SS, coal combustion accounts for 71% of total Pb, 41% of As, 22% Cu and 15% of total Se. Again at the IITD site, in terms of %FT, the factor is dominated by S (44% of FT), followed by Pb (28% of FT), while in terms of %SS, it contributes to 82% Pb and 60% Se.

Se and As are well accepted as tracers for coal combustion by many studies both in India and across the world (Hien et al., 2001; Lee et al., 2008; Sharma et al., 2007). While commercially available coal is limited in Pb-
content, past studies have noted Pb levels to be higher in domestic coals (Negi et al., 1987). However, local coal in northern India is known to have low sulfur content due to aged deposits; the high sulfur levels in the resolved factors may indicate the use of sulfur-rich coal from northeastern India (Chandra and Chandra, 2004; Sarkar, 2009). However, it is also known that power plants utilize blends of domestic and imported coal to get a balance between low ash content and high sulfur content (Central Electricity Authority, 2012; Chandra and Chandra, 2004), signaling the possible reception of coal-burning associated aerosols from thermal power plants. Again, the real world source to such a factor profile may also correspond to small scale industries. Some studies have reported Pb aerosol levels to be enhanced during lead smelting which may mix with coal combustion related particulate matter from the same plants to result in the profile resolved in this study.

While the time variation associated with coal combustion (figure 3(b)) & figure 4(b)) displays peaks of different intensities at both the sites; however, the diurnal variation (figure S5 (c & d)) shows the factor to reach peak values around 6:00 IST at both locations. Similar to the industrial emissions, the diurnality seems to be influenced by the lower temperatures and decreased volatility at night, leading to condensation of aerosols in the particulate phase and rising in concentration until early morning when temperature and, in turn, volatility starts to increase, and the aerosols evaporate back from the particle phase.

### 3.2.3 Vehicular Emissions

The vehicular emissions factor at the IITMD site is dominated by K (24% of FT), followed by Cl (17% of FT), S (16% of FT), Si (12% of FT), and Fe (10% of FT), whereas in terms of the %SS the vehicular emissions factor accounts for 76% of total Cr, 61% of Mn, 55% of Ni, 43% of Ti, 27% of Fe, 23% of Si and 22% of Ca. At the IITD site, the vehicular emissions are dominated by Ca (19% of FT), Si and Fe (18% each by FT), S (16% of FT), and Zn (15% of FT), looking at the %SS this factor contributes to 83% of total Cr, 48% of Ni, 32% of Zn, 23% of Mn, 22% of Ca and 21% of Fe.

Potassium is known to be used as an additive in engine oil as well as an anti-freeze inhibitor. In addition to that, K is also recognized to be present in almost all unleaded fuels (Spencer et al., 2006). Chlorine-based lubricating oils are used in the form of dispersants, which are used to protect the engine by retaining dirt in suspension (Dyke et al., 2007). Sulfur is known to occur naturally in crude oil. As per the currently applicable emission standards in India, i.e., BS-IV, diesel fuels are permitted to contain up to 50 ppm of sulfur (Transport Policy, 2015). Also, some past studies have pointed out the use of sulfur in engine oil anti-wear additives (Fitch, 2019).
Calcium is known to be added to engine lubricants to serve as a base to neutralize acids and to stabilize highly polar compounds formed in the engine as combustion by-products (Lyyränen et al., 1999; Rudnick, 2017).

Past studies have attributed Fe, Mn, and Zn to brake and engine wear emissions, citing their abundance in brake lining and brake pads (Gianini et al., 2012; Grigoratos and Martini, 2015; Thorpe and Harrison, 2008). Some studies have also attributed Ti and V to brake and tire wear (Gerlofs-Nijland et al., 2019). Ni and Cr emissions have been associated with Ni-Cr based catalytic converters employed for controlling toxic vehicular emissions (Negi et al., 1987; Srivastava et al., 2016).

Looking at the variation in concentration and contribution of this factor at both the locations (figure 3(b)) & figure 4(b)), we note that the vehicular emissions at both sites decrease by more than 95% on average during the DD phase as compared to the ePD phase and remain lower than the ePD values even in the FD phase. This decrease can be attributed to reduced mobility due to holidays in educational and most commercial establishments from the DD phase to the FD phase. In terms of diurnal behavior, the source resolved at the IITMD site (figure S5(e)) displays distinct rush-hour peaks around 6:00 IST to 9:00 IST in the morning and 18:00 IST to 21:00 IST during the evening. However, at the IITD site (figure S5(f)), the most prominent peak is observed between 3:00 IST to 6:00 IST, indicating the role of heavy motor vehicle traffic possibly due to the vicinity of the site to National Highway (NH) - 48 (around 8 km NW). Other than this, the diurnal behavior is not as distinct as observed for IITMD, while peaks are observed at potential rush hours, i.e., 9:00 IST, 16:00 IST, and 19:00 IST, but the characteristic rush hour trend is suppressed by the presence of multiple busy roads around the IITD site and limited (12-day) sampling period.

3.2.4 Fireworks

At the IITMD site, the fireworks source profile is dominated by K (31% of FT), Al (30% of FT), and S (20% of FT), while based on the %SS, this factor contributes about 91% of Ba, 87% of Bi, 86% of Sr, 80% of Al, 59% of Ga, 54% of K and 43% of V. At the IITD site the factor profile is again dominated by K (37% of FT), followed by Al (30% of FT) and S (20% of FT), in terms of the %SS the fireworks contribute to 87% of Ba, 85% of Bi, 85% of Al, 83% of Sr, 56% of V, 55% of Ga and 48% of K.

Most of the dominating species noted above, including K, Al, S, Ba, Bi, and Sr, have already been recognized as constituents of firecrackers and, in turn, tracers for marking firework events and have been discussed in detail.
in section 3.1. However, Ga and V, as discussed in section 3.1, remained near MDL for most of the non-Diwali period and raised to considerable concentrations only in the DD phase. However, limited studies in the past have observed increment in Ga and V concentrations during a fireworks event (Dutcher et al., 1999; Perrino et al., 2011).

It is a usual practice in India that the firecrackers are burst not only on the Diwali day but also in limited numbers on a day prior and a day later to Diwali; this trend is clearly evident from the temporal variation associated with this factor at both the sites (figure 3(b) & figure 4(b)) as well as the diurnal profile (figure S5 (g & h)). The average concentration at the IITMD site in the DD phase is around 390 times the ePD values, while the peak concentrations are ~1576 times the average ePD levels, whereas, at IITD, the average concentrations in the DD phase were around 178 times, while the peak concentrations around 332 times the average ePD values. It is interesting to note the change in PM$_{2.5}^\text{el}$ composition during DD, while the average contribution of fireworks to PM$_{2.5}^\text{el}$ was just 3% at IITMD and 6% at IITD, in the ePD phase, it rose to 94% and 92% in the DD phase at IITMD and IITD respectively. While the peak concentrations plummet within ~12 hours following the firework event, the firecracker burning in the day following Diwali and to some extent, the residual firework-related particulate content from the Diwali day cause this factor account for around 54.3 % of total PM$_{2.5}^\text{el}$ at the IITMD site and 29.5% of total PM$_{2.5}^\text{el}$ at the IITD site during the FD phase. However, it’s important to note that some technical difficulties caused disruption in sampling on 29th October at the IITMD site, and thus the limited measurement in the FD phase at IITD is partially responsible for the inflation in percentage contribution of the fireworks source at IITD, as compared to IITMD in the FD phase.

It is also interesting to note that PM$_{2.5}$ or fine mode particulate matter are often associated with longer residence time in the atmosphere, but as for the total PM$_{2.5}$ levels in the present study and the underlying fireworks source (figure 3b and figure 4b), both display and rapid downfall in concentration following the maxima around midnight. Similar observations were made by Hoyos et al., (2020), studying the impact of NYE fireworks on ambient air quality in Colombia. Hoyos et al., (2020) hypothesized that the seemingly anomalous behavior occurred due to and atmospheric instability caused by a weak thermal inversion due to firecracker burning, leading to the rapid dispersion of aerosols and their episodic escape across the boundary layer. Hoyos and co-workers supported this hypothesis, using ceilometer based backscattering intensity (BI) measurements, and observed anomalous BI readings marking the atmospheric instability following the fireworks event. Similar
atmospheric behavior may be the reason behind the observations of the present study, however, the present study lacks any ceilometer-based or similar measurements to justify similar atmospheric behavior and leave this question open for further investigation in the future.

3.2.5 Dust-Related

The dust-related factor at the IITMD site is dominated by Si (26% of FT), Ca (24% of FT), Al (16% of FT), and Fe (12% of FT), while in terms of %SS, the factor accounts for 46% of total Ca, 34% of Si, 24% of Fe, 23% of V. At the IITD site the dust-related factor is dominated by Si (34% of FT), Ca (26% of FT), and Fe (24% of FT). In contrast, in terms of % SS the dust-related factor contributes around 70% of total Ca, 64% each of Si and Fe, 61% of Mn, 49% of Ti, 35% of Ni, and 36% of Cu. It is important to note that while the dust-related factor at IITD seems to account for 50% of total measured Ti, the average total Ti concentrations are of the order of ~0.05 μg/m³.

Multiple studies across the globe have used crustal elements including Ca, Al, Si, Ti, and Fe, as tracers to soils dust or crustal re-suspension (Jaeckels et al., 2007; Kothai et al., 2008; Lough et al., 2005; Rai et al., 2020; Stone et al., 2010). However, elements like Ni, Cu, and V may have contaminated the crustal dust over time, with actual origins related to coal fly ash, or vehicular emissions, as suggested by Mouli et al., (2006).

While the dust-related factor seems to follow no discernable trend in terms of time variation (figure 3(b)) & figure 4(b)) or the diurnal profiles (figure S5 (i & j)), at the IITMD or IITD sites, it is evident that this factor remains mostly unaffected by the Diwali event.

3.2.6 Biomass Burning

At the IITMD site, this factor is dominated by S(51% of FT) and K (25% of FT), while in terms of %SS, the factor contributes to around 66% of Se, 51% of Ti, 46% of S, 43% of V and 32% of Br. At the IITD site, the biomass burning source profile is dominated by S (50% of FT) and K (34% of FT), whereas in terms of %SS, it accounts for 58% of Br, 55% each of S and As, 39% of Se and 37% of K.

Potassium has been a widely accepted marker for biomass burning by several past studies (Khare and Baruah, 2010; Pant and Harrison, 2012; Reche et al., 2012; Shridhar et al., 2010). A study by Li et al., (2003) concluded that for fresh biomass burning plumes, much of the potassium content exists as KCl or, to a degree KBr, while in the case of aged plumes, the chloride and bromides are partially substituted by sulfates, thus supporting the
resolved profile in our case for high S and Cl concentrations in conjunction with K in the biomass burning source profile. Prior studies have found selenium to reach significant levels in biomass grown in Se-rich soils (Goldstein, 2018), which in turn are typical to northern India (Sharma et al., 2009). Observations similar to Se have been made for Ti, for enrichment through the soil; however, in relatively lesser concentrations (Tlustoš et al., 2011). Pyrolysis of fibers in biomass, like cereal, grass, and straw, has been noted to emit silicon (Obernberger et al., 2006). Toxic elements like V and As while representing considerable quantities in terms of % SS, but the actual concentration associated with the factor profiles are of the order of $10^{-4}$ $\mu g/m^3$ and $10^{-3}$ $\mu g/m^3$ respectively, such traces concentration may result from some amount of anthropogenic contamination, similar toxic metal concentrations in biomass emissions have been noted by past studies (DEMİRBAŞ, 2003).

As discussed earlier in section 3.1.1, the October to November period in India coincides with crop harvesting season in northern India and witnessed a rise in biomass/stubble burning events (Jethva et al., 2019). The time variation corresponding to this factor displays a positive trend throughout the study period (figure 3(b) & figure 4(b)). In terms of the diurnality (figure S5 (k & l)), we observe elevated concentrations at both the sites after 18:00 IST until early morning; this behavior may stem from increased emissions from stubble burning events at night, and increased use of domestic biomass for heating purposes due to the cold weather, along with decreasing BLH after sunset. From the variation in percentage contribution (figure 3(c) & figure 4(c)), we take note that the factor falls in concentration from the ePD to the DD phase; however, it rises back in the FD phase to a concentration higher than the ePD phase. Past studies (Wang et al., 2012) have proposed the use of Delta-C (the difference between the Aethalometer measurements at 880nm and 370 nm, respectively) as a marker for biomass and wood burning. In the present study, we note a Pearson R correlation of 0.67 (figure S4 (a)) between the PM$_{2.5}$ apportioned biomass burning source and Delta-C.

### 3.2.7 Secondary Chloride

The secondary chloride factor is solely dominated by Cl, accounting for 78% and 72% of FT at the IITMD and IITD sampling sites, respectively. In terms of the %SS, the source profile at the IITMD site contributes to 62 % of total Cl and 32% of total Br, while the factor resolved at IITD accounts for 53% of total Cl and 26% of total Br.

A similar factor has been resolved by some past source apportionment studies based in Delhi. Jaiprakash et al., (2017) observed a similar source profile while studying sources of PM$_1$ levels in Delhi and speculated this factor
to emerge as HCl fumes transported from metal processing plants to the northwest of Delhi, reacting with high NH$_3$ concentrations in Delhi to condense in particulate phase as NH$_4$Cl (Warner et al., 2017). In a recent study based in Delhi, Gani et al., (2019), reached similar conclusions for the high particulate-phase chloride concentrations observed by them.

In the present study, focusing on the temporal variation and changes in the percentage contribution associated with this factor (figure 3(b-c)) & figure 4b(c)), we note that the secondary chloride factor is actually enhanced in terms of concentration in the DD phase, suggesting some influence of the fireworks event in augmenting the concentrations associated with this factor. These enhanced concentrations could result from a scenario when excess aqueous ammonia (Warner et al., 2017) replaces the metallic cation from the primary aerosols released from the combustion of perchlorate oxidants present in the fireworks as discussed in section 3.1. It is essential to take note that while some portion of the total chlorine emissions from fireworks, which doesn’t react with the excess ammonia is apportioned to fireworks, while the portion which undergoes secondary reactions with ammonia leads to the enhancement of secondary chloride. A similar situation is possible in the case of biomass burning; while KCl is regarded as a primary emission from biomass burning (Li et al., 2003), the biomass burning accounts for less than 15% of total chlorine concentrations. The increasing biomass burning levels during the FD phase, observed in section 3.2.6, may thus be the reason behind the elevated levels of secondary chloride in the FD phase as compared to the ePD phase at both the sampling sites (2.87 times at IITMD and 4.58 times at IITD). The diurnal variation associated with the factor (figure S5 (m & n)) displays a sharp peak around 6:00 IST, very similar to the expected diurnal trend for NH$_4$Cl (Warner et al., 2017), stemming from low saturation vapor pressure at lower temperatures at night leading to condensation of NH$_4$Cl in the particulate phase leading to accumulation in the particle phase and thus the early morning peak, followed by the consequent increase in saturation vapor pressure in the morning responsible for the sharp decline in species concentration.

**3.3 Source Apportionment of organic PM$_{2.5}$**

The organic fraction of total PM$_{2.5}$ measured using the AMS at the IITMD site was subjected to source apportionment using PMF analysis. The variation in the mass spectra was best described by a set of 3 factors, i.e., one primary organic aerosol (POA) and two oxygenated organic aerosols (OOA) profiles. These results are similar to the results obtained by Bhandari et al., (2020), wherein a POA and an OOA factor were resolved during the winters of 2017 and 2018. The resolved factors were identified based on the resolved mass spectra,
which was further characterized using AMS reference profiles from Aiken et al., (2009) and Ng et al., (2011). The detailed description for each of the resolved factor profiles is as follows:

3.3.1 Primary Organic Aerosol (POA)

The POA mass spectra (figure 5(a)) is marked by distinct peaks of \( m/z \) 55 and \( m/z \) 57, which are characteristic of primary organic emissions like traffic and cooking-related emissions (Zhang et al., 2005; Zhu et al., 2018). The resolved mass spectra have a significant correlation with the hydrocarbon-like organic aerosol (HOA) reference profiles from both Aiken et al., (2009) (Pearson R = 0.92) and Ng et al., (2011) (Pearson R = 0.89). Past studies have often employed BC as a tracer for POA emissions (Schmidt and Noack, 2000; Zhu et al., 2018), as BC is mainly derived from incomplete combustion products. In the present study, a significant correlation (Pearson R = 0.89) between BC and POA was observed (figure S4 (b)). The diurnal characteristics (figure S6 (a)) present variation characteristic to POA (Zhu et al., 2018), with a strong dependence on BLH, resulting in a distinct peak around 24:00 IST with reducing intensity with increasing in BLH towards the morning.

In terms of the time variation of this factor presented in figure 5(b) as well as the change in percentage contribution to total organic content (figure 5(c)), we observe a steep rise in POA concentrations during the DD phase, indicating that the POA factor captures the direct organic emissions from the firecracker burning during Diwali. The average factor concentrations during the DD phase are around 7.8 times the PD levels; however, the concentrations remain around 5 times higher than the average PD levels in the FD phase. This behavior may arise from the primary organic emissions associated with the increasing biomass burning concentrations towards the FD phase as observed in section 3.2.6 during the PM\(_{2.5}\) source apportionment; the appreciable correlation observed between POA and BC bolsters this hypothesis further as biomass burning is known to contribute significantly to total BC (Pant and Harrison, 2012), and BC-like POA continues to increase in the FD phase.

3.3.2 Oxygenated Organic Aerosols (OOA-1 and OOA-2)

The OOA-1 and OOA-2 mass spectra are marked by distinct peaks of \( m/z \) 44 or \( \text{CO}_2^{+} \) which are tracer fragments used to mark Oxygenated Organic Aerosol (OOA) (Aiken et al., 2009; Li et al., 2019). The mass spectra associated with both OOA-1 & 2 display significant correlation with reference OOA profiles from Aiken et al., (2009) (Pearson R = 0.92, 0.95 for OOA-1, OOA-2 respectively) and also reference LVVOOA profiles from Ng
et al., (2011) (Pearson R = 0.80, 0.84 for OOA-1, OOA-2 respectively). Both the factors show diurnal profiles (figure S6 (b & c)), with a sharp peak in concentration during noon, which is characteristic of OOA diurnal behavior (Aiken et al., 2009), due to enhanced photochemical aging of POA during noon.

In terms of the time variation of the OOA factors presented in figure 5(b) as well as the change in percentage contribution to total organic content figure 5(c), we observe a slight increment in the OOA concentrations during the DD phase, suggesting a slight immediate impact of the fireworks on the OOA concentrations. OOA-1 concentrations during the DD phase rose by around 30%, while OOA-2 concentrations rose by around 22% as compared to the PD averages. However, we note that there is a steep rise in the OOA concentrations in the FD phase, while OOA-1 rises by around 50% compared to its PD levels. The average OOA-2 in the FD phase rises about 186% as compared to the PD phase. While the Diwali event may have some contribution to this rise in OOA levels due to oxidation of the organic aerosols emitted on the Diwali night, however, the increased OOA levels may also indicate an increased influx of aged aerosol from biomass burning activities rising during the period affecting both organic and inorganic fractions of total PM$_{2.5}$.

The steep rise in OOA-1 and OOA-2 following Diwali, along with increasing elemental biomass burning contributions as noted in section 3.2.6, together account for the increasing background PM$_{2.5}$ levels, observed in Figure 1 (a-b), following Diwali.

**Conclusions**

The festival of Diwali is celebrated with great joy and enthusiasm in most parts of India; however, the increase in haze events in weeks following the festival in the past few years has raised serious health concerns. While the firework displays during Diwali are only concentrated over a short period, the firework-related emissions are a significant source of metal-rich aerosols, which can have a detrimental impact on human health. The present study reports near real-time variation of elemental compositions of PM$_{2.5}$ at two sites (IITMD and IITD) at New Delhi during a 12-day period around Diwali. The results indicate that the degree of enhancement in the concentration of species associated with fireworks displays is localized spatially, and considerable variability was observed between the two sampling sites in the present study. At IITMD Al, Ba, K, S, Bi, and Sr were recorded to rise by a factor of 69.6, 190.4, 22.5, 6.3, 320.7, and 145 respectively in the DD phase w.r.t ePD, while at IITD Al, Ba, K, S, Bi, and Sr were observed to increase by a factor of 97.3, 2.4, 19.8, 5.1,62.3 and 1.35
respectively, when compared to the ePD levels. Average BC levels increased by a factor of 2.3, while inorganic ions or SNA were enhanced by a factor of 2.5 during DD as compared to PD. The enhanced elemental concentrations also pose a severe health hazard to the exposed population, species like aluminum, barium, chlorine, lead and manganese were noted to exceed the EPA risk-based concentration levels, by an order of magnitude, for not only the peak levels, but also the average levels during the DD phase. Also, potential carcinogens like As, were found to exceed the risk-based concentrations at both the IITD and the IITMD sites by an order of magnitude.

The Diwali festival often coincides with the crop harvesting season, and the ambient air quality is seriously affected by increased stubble burning events. These coinciding events make it difficult to ascertain the impact of either of the two on ambient air pollution. The current study presents source apportionment results for highly time-resolved elemental and organic fractions of PM$_{2.5}$. The PM$_{2.5}^{el}$ source apportionment was performed on the datasets from both the sampling sites separately, and both the analysis resulted in seven source profiles, i.e., industrial emissions, coal combustion, vehicular emissions, fireworks, dust-related emissions, biomass burning, and secondary chloride. At both the sampling sites, the fireworks are most prominent only during the expected firecracker burning period. During the DD phase, the fireworks account for ~94% and ~92% of the total PM$_{2.5}^{el}$ at the IITMD and IITD sites, respectively; it is also important to note that the PM$_{2.5}^{el}$ levels at both sites were increased by a factor of ~12 in the DD phase as compared to the ePD levels. The coal combustion and dust-related sources remained mostly unaffected from the PD to the FD phase, whereas sources like industrial emissions, biomass burning, and vehicular emissions reduced by more than 50% at both the sites during the DD phase as compared to ePD mainly due to the reduced human mobility on the festival day. However, in the FD phase, industrial emissions and vehicular emissions trend back towards the ePD levels while remaining lower than the ePD average values majorly due to 2-3 days of official holidays for the festivities. It is important to note that biomass burning related emissions rise steeply in the FD phase and the average values increase by more than twice as compared to the ePD phase. In terms of the source apportionment of the organic fraction, the primary organic emissions display a distinct rise in concentrations in the DD phase. Also, both the POA and the two OOA factors display a considerable rise in the FD phase, hinting towards the role of biomass related emissions towards the rise in primary organic emissions and, in turn, their aged products.
This is the first study to quantify the impact of fireworks on ambient PM$_{2.5}$ levels, the variability in firework associated emissions across different locations, and the actual duration for which the average population is exposed to enhanced PM concentrations due to the firework events. It is also the first study to delineate the potential impact of firecracker burning and the concurrent rise in stubble burning events on the aerosol levels following the Diwali night. These results pose important implications for guiding informed policies and control strategies to prevent/alleviate future haze events.

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| Species     | IITD Site (µg/m³) | IITMD Site (µg/m³) | US EPA Generic RSLs (µg/m³) | Potential Health Risk             |
|-------------|-------------------|--------------------|-----------------------------|-----------------------------------|
|             | Average           | Maximum            | Average                      | Maximum                          | Residual Air | Industrial Air | Carcinogenic / Non-Carcinogenic |
| ALUMINIUM   | 48.8146 (114.8407)| 44.2154 (178.3848) | 5.2                          | 22                               | None / Neurological |
| ARSENIC     | 0.0105 (0.0365)   | 0.0172 (0.0570)    | 0.0007                       | 0.0029                           | Respiratory Cancer/Developmental |
| BARIUM      | 14.3015 (35.0304) | 15.4308 (63.9083)  | 0.52                         | 2.2                              | None / Cardiac |
| CHLORINE    | 9.0537 (17.7699)  | 11.4043 (34.9752)  | 0.15                         | 0.64                             | None / Respiratory |
| LEAD        | 0.6325 (1.4244)   | 0.8219 (2.9588)    | 0.15                         | NA                               | None / Developmental |
| MANGANESE   | 0.0735 (0.1654)   | 0.1004 (0.4222)    | 0.052                        | 0.22                             | None / Neurological |
| NICKEL      | 0.0018 (0.0046)   | 0.0030 (0.0114)    | 0.012                        | 0.051                            | Lung Cancer/Immunological |
| SELENIUM    | 0.0004 (0.0013)   | 0.0005 (0.0021)    | 21                           | 88                               | None / Neurological |
| VANADIUM    | 0.0238 (0.0701)   | 0.4305 (3.8841)    | 0.1                          | 0.44                             | None / Respiratory |

Table 1: Average and Maximum concentration levels of various inorganic species during the DD phase at the IITD and IITMD site, corresponding Generic Regional Screening Levels (RSLs) as suggested by US EPA and Potential Health Hazards
Figure 1: (a) Time variation of instrument total PM$_{2.5}$ at IITMD; (b) Variation in total PM$_{2.5}$ compositions in the PD, DD and FD phases; (c-d) Temporal Variation of PM$_{2.5}$ at the (left to right) IITMD (green) and IITD
sites respectively; (e-j) Variation in constituents of PM$_{2.5}$ through each of (top to bottom) PD, DD and FD phase at the IITMD (green) and IITD (yellow) sites

Figure 2: Temporal Variation of marker species for the fireworks event during Diwali at the IITMD (green) and IITD (yellow) sites; (a) Potassium; (b) Aluminum (c) Strontium; (d) Barium; (e) Sulfur; (f) Bismuth at the two sites using Xact 625i; (g) Sulfate to Nitrate (SO$_4$/NO$_3$) ratio measured using HR-ToF-AMS at IITMD site; (h) Black Carbon measured using Aethalometer AE33 at IITMD site
Figure 3: Source apportionment results for elemental PM$_{2.5}$ at the IITMD site (a) resolved factor profiles; (top to bottom) industrial emissions, coal combustion, vehicular emissions, fireworks, dust-related, biomass burning, secondary chloride; (b) temporal variation of each resolved factor; (top to bottom) (top to bottom) industrial emissions, coal combustion, vehicular emissions, fireworks, dust-related, biomass burning, secondary chloride; (c) phase-wise composition of organic PM$_{2.5}$; (left to right) Pre-Diwali (PD), During Diwali (DD), Following Diwali (FD)
Figure 4: Source apportionment results for elemental PM$_{2.5}$ at the IITD site (a) resolved factor profiles; (top to bottom) industrial emissions, coal combustion, vehicular emissions, fireworks, dust-related, biomass burning, secondary chloride; (b) temporal variation of each resolved factor; (top to bottom) (top to bottom) industrial emissions, coal combustion, vehicular emissions, fireworks, dust-related, biomass burning, secondary chloride; (c) phase-wise composition of organic PM$_{2.5}$; (left to right) Pre-Diwali (PD), During Diwali (DD), Following Diwali (FD)
Figure 5: Source Apportionment Results of Organic PM$_{2.5}$ at IITMD (a) resolved factor profiles; (top to bottom) primary organic aerosol (POA), oxygenated organic aerosol - 1 (OOA-1), oxygenated organic aerosol – 2 (OOA-2); (b) temporal variation of each resolved factor; (top to bottom) primary organic aerosol (POA), oxygenated organic aerosol - 1 (OOA-1), oxygenated organic aerosol – 2 (OOA-2); (c) phase-wise composition of organic PM$_{2.5}$; (left to right) Pre-Diwali (PD), During Diwali (DD), Following Diwali (FD)
Supplementary Information for “Chemical characterization of PM$_{2.5}$ bound species during the Diwali fireworks in Delhi: An insight from source apportionment and airborne hazardous elements”

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S1. Quality Assurance and Quality Control (QA/QC) Procedures

For the duration of the study period, the Xact 625i at both the sites operated at a half-hourly time-resolution, sampling ambient PM$_{2.5}$ at the standard airflow rate of 16.7 lpm. Automated quality assurance checks were performed by the instrument every midnight for the elements Cr, Cd, and Pd. Other than the automated checks, XRF and flow calibration, along with leak and flow checks, were performed as per the maintenance routine advised by the manufacturer.

NR-PM$_{2.5}$ was analyzed using an HR-ToF-AMS operating at a standard flow rate of around 0.1 lpm, while sampling and analyzing at a 2-min interval, with background air allowing for continuous air beam correction. The collection efficiency (CE) was determined for the mass spectra for an optimum collection considering inlet humidity, particle composition, and aerosol acidity, as described by Middlebrook et al. (2012). A monodisperse supply of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ aerosols, selected through a differential mobility analyzer (DMA) and

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counted using a condensation particle counter (CPC), was used to calculate the ionization efficiency (IE) of NO\textsubscript{3} and relative ionization efficiencies (RIE) of NH\textsubscript{4} and SO\textsubscript{4} as suggested by Crenn et al. (2015).

Near real-time concentrations of Black Carbon were recorded using a multichannel Aethalometer operated at a unit time resolution and a 5 lpm ambient air flow rate. The readings were monitored continuously for any instrument warnings, noise/spikes, as well as BC vs. attenuation values for any required compensation. Other than that, regular flow rate checks, inspection, and cleaning of the optical chamber and insect screen assembly were conducted as a part of routine maintenance.

**S2. Positive Matrix Factorization**

**S2.1 PMF Input preparation**

The present study employed the Xact 625i for measuring PM\textsubscript{2.5} at both the sampling sites, i.e., IITMD and IITD. Both the instruments were configured to measure 43 elements in total (Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pt, Au, Hg, Tl, Pb, and Bi) with a half-hourly time resolution. For the duration of the study, the concentration levels of 18 elements (P, Sc, Co, Ge, Y, Mo, Ag, Cd, In, Sn, Te, Cs, La, Ce, Pt, Au, Hg, Tl) were found to remain below the Minimum Detection Limit (MDL) for more than 50% of the readings and were thus ignored for the PMF analysis (Polissar et al., 1998). The uncertainty \( s_{ij} \), associated with every data point is reported by the ADAPT software module, on-board the Xact 625i. The reported uncertainty accounts for the measurement uncertainty, as well as the spectral deconvolution uncertainty (Tremper et al., 2018), and the same has been employed for preparing the PMF input uncertainty matrix in the present study. The datasets from both the instruments were subjected to PMF individually.

The non-refractory fraction of PM\textsubscript{2.5} (NR-PM\textsubscript{2.5}) was studied using the HR-ToF-AMS, which determines the quantitative mass spectra (MS) of NR-PM\textsubscript{2.5} up to a mass to charge (\( m/z \)) ratio of 200. The measured MS is further resolved into the sulfate, nitrate, ammonium, chloride, and organic fractions using a library of pre-determined fragmentation characteristics, as employed by Allan et al., (2004). The uncertainty values \( s_{ij} \) associated with the species measured using the AMS were calculated using the standard HR-ToF-AMS data access software, following the procedure documented by Ulbrich et al., (2009) and Ng et al., (2011a).
The MDL values for each elemental species measured using the Xact were provided by the manufacturer, i.e., Cooper Environmental Services (CES), while the MDLs for the organic MS measured using the HR-ToF-AMS were determined according to Drewnick et al. (2009). The missing data values caused by power failure and maintenance shutdown were neglected from the PMF input (Rai et al., 2020).

The input measurements corresponding to each species \( j \) were screened further on the basis of the signal-to-noise ratio (S/N) computed within the EPA PMF 5.0 software module (Norris et al., 2014). For each entry \( x_{ij} \) in the input data matrix and its corresponding uncertainty \( s_{ij} \), the difference between the two is regarded as the signal, such that

\[
    d_{ij} = \left( \frac{x_{ij} - s_{ij}}{s_{ij}} \right) \quad \text{if} \quad x_{ij} > s_{ij} \quad \ldots \ldots (1)
\]

\[
    d_{ij} = 0 \quad \text{if} \quad x_{ij} < s_{ij} \quad \ldots \ldots (2)
\]

The S/N ratio is then given by the following equation:

\[
    \left( \frac{S}{N} \right)_j = \frac{1}{n} \sum_{1}^{n} d_{ij} \quad \ldots \ldots (3)
\]

Based on the S/N value, each input species is further characterized as strong, weak, or bad (Norris et al., 2014). The species with \( S/N > 1 \) were categorized as strong, and input concentration and uncertainty were used for further analysis with no alteration. The species with the S/N ratio between 0.5 and 1 were categorized as weak; for such a case, the input uncertainty values were augmented by a factor of four and used along with the input concentration for further analysis. Finally, the species with an S/N ratio of less than 0.5 were classified as bad signals and were excluded from further analysis.

In the present study, in the case of the Xact-based PMF Rb, Sb and Pd were identified as bad signals and were ignored from the PMF input. However, none of the \( m/z \) signals measured using the HR-ToF-AMS fell into the category of bad signals.
S2.2. Factor Selection and Uncertainty Quantification

The quality of source profiles resolved using the PMF analysis often relies on the number of factors deemed optimal, for representing the input dataset, by the user. However, the PMF algorithm is focused on minimizing the sum of weighted residual errors for a linear fitting problem. A singular solution is seldom possible for such a scenario as there can be several possible solutions with similar residuals; this led multiple past studies to conclude that mathematical diagnostics alone are insufficient for deciding on the right number of factors (Canonaco et al., 2013; Rai et al., 2020). Thus, the present study explores the physical realizability of each resolved factor by comparing its temporal variation with recognized external tracers, evaluating for observed diurnal behavior, known elemental or m/z dominance in the factor profile, in addition to the established diagnostics like Q-value, Q/Q_{exp} (Canonaco et al., 2013) and scaled residuals for each species.

The solution space corresponding to the input measurements is assessed with a set of initial base runs, wherein the number of factors is varied from 2 to 10 with 10 seeds each (number of PMF runs with pseudorandom starting points). The same procedure is adopted for all 3 datasets analyzed in the present study (2 Xact-based + 1 AMS-based). The vicinity of a plausible solution, i.e., the optimal number of factors resulting in the lowest Q-value and no significant change in Q-value by further increasing the number of factors, is further explored by repeating the PMF runs with 50 seeds each.

The solution corresponding to the number of factors deemed optimal after the base run is tested for rotational ambiguity using the DISP analysis available within the EPA PMF 5.0 module. The DISP technique assesses the maximum possible variation in the source profile obtained as the results of the base run, without an appreciable change in the base Q-value. In EPA PMF 5.0, the DISP tool perturbs each species, one at a time, in the source profile resolved from the optimal base run, and following each alteration, the PMF run is repeated to evaluate changes in the source profile due to each perturbation, such that the change in the Q-value w.r.t the base run remains under a pre-determined maximum change dQ_{max} (dQ_{max} = 4,8,15,25). These perturbations, at times, may lead to a switch in the identity of the factor profile w.r.t the base run, i.e., a particular base factor after displacement may be better correlated with another base factor than the original base profile, such a case is noted to be a factor swap. These swaps are accounted for using uncentered cross-correlations between the original and the displaced factor profiles.
No factor swaps were observed in the present study for both the Xact and AMS-based datasets. In the present study, the maximum decrease in Q-value for the IITMD Xact dataset was observed to be 0.027 with % dQ change as 0.0021%; in the case of the IITD Xact dataset, the maximum decrease in Q-value was found to be 0.038 with % dQ change as 0.0039%, while for the IITMD HR-ToF-AMS dataset the largest decrease in Q-value was observed to be 1.486 with % dQ change as 0.00363%. Past studies have established % dQ change within 1% to represent acceptable DISP solutions (Norris et al., 2014).

The optimal base-run solutions were further subjected to controlled rotations via variation in f-peak values from -1 to +1 with an increment of 0.1, to evaluate the impact of rotations on parameters like the fraction of variance explained by each factor, the mutual correlation between the time series of resolved factors, correlation of factor profile with reference profiles and correlation of factor time series with external tracers (Bhandari et al., 2020; Rai et al., 2020; Ulbrich et al., 2009). The range of the f-peak value was limited to ensure that the % change in Q-value between the rotated and base factor profile is small. In the case of the IITMD and IITD Xact based datasets, a minimal effect of factor rotation was observed in terms of the mutual correlation between the factors and correlation with external tracers; thus, in both the cases, the base solution was considered optimal. However, for the IITMD HR-ToF-AMS dataset, f-peak variations were found to reduce mutual correlations between the factor time series and improve correlations between factor profiles and reference MS from Ng et al. (2011). The solution corresponding to fpeak value of +0.2 was found to best improve the correlations with minimal change in Q-value, thus was chosen as the optimal solution (Bhandari et al., 2020; Rai et al., 2020).

Further, the bootstrap (BS) randomized resampling strategy was employed to evaluate the effect of random error on the solution (Brown et al., 2015). Similar to the DISP analysis, the BS analysis is effected through the EPA PMF module; it works by creating a randomized input matrix of size equal to the original input matrix, using non-overlapping blocks of input measurements, where the user determines the block size. The new input matrix is subjected to PMF, and the BS factors are mapped back to the base factors based on the uncentered correlations exceeding a user-defined threshold. In case a BS factor fails to have an uncentered correlation with any of the base factors, greater than the threshold, then that BS factor is deemed unmapped. The BS results act as a proxy to understand the uncertainty associated with the resolved factors and the species associated with each factor profile. In the present study, the optimal base/f-peak solutions were subjected to 800 BS runs, with an uncentered correlation threshold of 0.8. In both Xact based and AMS based datasets, none of the BS factors remained
unmapped. In the case of the IITMD Xact dataset, 738 BS runs, for the IITD Xact dataset, 721 runs, and for the IITMD HR-ToF-AMS dataset, 742 BS runs were deemed reasonable solutions, i.e., the BS factor was mapped back to the original base factor.

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Figure S1: Location of the sampling sites in the present study: 1. Indian Institute of Tropical Meteorology, Delhi (IITMD) (green); 2. Indian Institute of Technology, Delhi (IITD) (yellow)
Figure S2: Linear regression analysis comparing Instrument Total PM$_{2.5}$ (Xact 625i + HR ToF AMS + Aethalometer AE33) (y-axis) with Beta Attenuation Monitor (BAM) measured PM$_{2.5}$ (x-axis)
Figure S3: Pearson R Correlation statistics among the constituents of PM$_{2.5}$ measured at (a-c) IITMD through the phases (top to bottom) ePD, DD and FD; (d-f) IITD through the phases (top to bottom) ePD, DD and FD
Figure S4: Correlation of PMF resolved sources with independent external markers (a) Xact-derived Biomass burning with Delta-C (from Aethalometer); (b) AMS derived primary organic aerosol (POA) with black carbon (from Aethalometer)
Figure S5: Diurnal Variation for sources resolved from apportionment of PM$_{2.5}$ ($\mu$g/m$^3$): (a,b) industrial emissions at (left to right) IITMD, IIITD; (c,d) coal combustion at (left to right) IITMD, IIITD; (e,f) vehicular emissions at (left to right) IITMD, IIITD; (g,h) fireworks at (left to right) IITMD, IIITD; (i,j) dust-related at (left to right) IITMD, IIITD; (k,l) biomass burning at (left to right) IITMD, IIITD; (m,n) secondary chloride at (left to right) IITMD, IIITD.
Figure S6: Diurnal Variation for sources resolved from apportionment of organic PM$_{2.5}$ measured at IITMD: (a) primary organic aerosols (POA); (b) oxygenated organic aerosol-1 (OOA-1); (c) oxygenated organic aerosol-2 (OOA-2)