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ORIGINAL PAPER

Short-term degradation of air quality during major firework events in Delhi, India

Shivani[1] · Ranu Gadi[1] · Mohit Saxena[2] · Sudhir Kumar Sharma[2] · Tuhin Kumar Mandal[2]

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Abstract

The effect of firework events on air quality was assessed from ambient fine particulate matter ($PM_{2.5}$) collected during the Diwali period in two consecutive years, i.e., November 2015 and October 2016. The extensive firework activities led to the short-term degradation of air quality during the Diwali days. $PM_{2.5}$ samples were chemically characterised for elements, water-soluble ionic species, organic carbon (OC) and elemental carbon (EC). Ba, K, Sr, S, Mg and Na showed significant increases in concentration on Diwali days compared to pre-Diwali days which revealed their association with firecrackers. Concentration of SO_4^{2-}, NO_3^-, Cl^-, K^+ and NH_4^+ ions contributed to the increases in $PM_{2.5}$ concentration on Diwali days. Higher OC/EC ratios indicated the formation of secondary organic carbon during the Diwali period. This study concludes that the high $PM_{2.5}$ level during Diwali 2016 was a result of contribution from fireworks on the Diwali night, trans-regional movement of pollutants due to crop residue burning, low wind speed (0.15 m s^{-1}), and high humidity. It was observed that short-term exposure to Diwali is plausible to generate 1.3% increase in non-carcinogenic hazard index due to elements Al and Ba during Diwali 2016, whereas no significant variation was observed for the carcinogenic risk due to Pb. However, in 2015, the increase in non-carcinogenic hazard index was appreciably lower as compared to 2016.

Abbreviations

NOAA	National Oceanic and Atmospheric Administration
READY	Real-time Environmental Applications and Display System
USEPA	United States Environmental Protection Agency
IMPROVE	Interagency Monitoring of Protected Visual Environment
CPCB	Central Pollution Control Board
NASA	National Aeronautics and Space Administration
UTC	Universal Time Coordinated
TSP	Total suspended particulate
ITO	Income Tax Office

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✉ Ranu Gadi
ranugadi@igdtuw.ac.in

[1] Indira Gandhi Delhi Technical University for Women, New Delhi 110006, India

[2] National Physical Laboratory, Council of Scientific and Industrial Research (CSIR), New Delhi 110012, India

1 Introduction

In Indian megacities, Delhi is one of the most polluted with respect to particulate pollution (World Bank 2004). The total population of Delhi is 16 million and decadal growth of population for Delhi is 21.2% (Census 2011). Over the last two decades, the rapid urbanisation and related industrialisation have caused an increase in a number of vehicles to 6.1 million (Transport Dept, Delhi Govt 2009) In the past, several studies have reported that the major firework event causes significant addition to the pollution levels (Sarkar et al. 2010; Singh et al. 2010; Pervez et al. 2016). This enhances the importance to study short-term degradation of air quality and its associated risk on human health. Moreover, Delhi has been declared as the most cancer prone area in India by the National Cancer Registry Program (ICMR 2005). There is a tradition of celebrating national and cultural events worldwide with firework displays. Diwali, the "Festival of Lights" is celebrated during the month of October or November in India. The peculiarity of celebrations of this festival is characterised by the lighting of lamps and candles to decorate the houses and bursting of a huge quantity of firecrackers. The extensive firework activities associated with Diwali celebrations results in emissions of trace gases, particulate matter and toxic metals into the atmosphere which causes significant short-term air quality degradation (Ravindra et al. 2003; Kulshrestha et al. 2004; Barman et al. 2008; Singh et al. 2010). The short-term variation of atmospheric air quality can result in a reduction in visibility due to the generation of a dense cloud of smoke that drifts downwind and slowly disperses (Curtis et al. 2006; Steinhauser et al. 2008; Sarkar et al. 2010; Tsai et al. 2012). The concentrations of Ba, K, Al and Sr increased up to 1091, 25, 18 and 15 times higher than the previous day of Diwali (Kulshrestha et al. 2004). The highest observed mass concentration of PM_{10} and $PM_{2.5}$ was about 20 and 27 times higher according to National Ambient Air Quality Standards (NAAQS) (Parkhi et al. 2016). SO_2, NO_2, PM_{10}, TSP increased 2–10 times higher (Ravindra et al. 2003). On Diwali night, PM_{10} and SO_2 concentrations were found to be five times higher than normal day–night time average in Kolkata city, India (Chatterjee et al. 2013). Besides the emissions of aerosols from firework displays, the formation of ozone was also observed without the participation of NO_X during Diwali in Delhi (Attri et al. 2001). The concentration of O_3 was observed to increase two times over normal days during firework displays in Kerala, by the photodissociation of NO_2 from the flash of firecrackers (Nishanth et al. 2012). A remarkable increase in the concentration of elements (Sr, Ba, Ti, Mg, Cu, K, S, V, Cl, Bi, and Ga) present in PM_{10} and $PM_{2.5}$ produced by firework displays has been reported by Perrino et al. (2011). The aerosols produced from firework activities have contributed 23–33% to ambient PM_{10} in Diwali (Sarkar et al. 2010). The concentration level of $PM_{2.5}$ was 5.74 and 2.65 times higher than the background levels at the peak hours of the firework activity for the year 2009 and 2010, respectively (Pathak et al. 2014).

All fireworks contain carbon, sulphur and a variety of metal salts such as chlorates, perchlorates, and nitrates, which is demonstrated in the high concentrations of these species during festive days (Sarkar et al. 2010; Perrino et al. 2011; Pervez et al. 2016). Several studies have revealed that firework displays during episodic events can result in serious and acute health effects on a regional scale (Perry 1999; Hirai et al. 2000; Pope III and Dockery 2006). Recent findings suggest that around 30% of Delhi population suffers from respiratory disorders due to air pollution, and the incidence of respiratory ailments in the city is as high as twelve times the national average (Pandey et al. 2005). It has been estimated that most of the cases of respiratory illness are associated with atmospheric pollution each year in Delhi (Faiz and Sturm 2000). It has been reported that inhalation of smoke from fireworks causes cough, fever and dyspnoea and leads to eosinophilic pneumonia (Hirai et al. 2000). Fireworks have potential effects on the respiratory system of healthy individuals as well as those suffering from respiratory diseases, particularly asthma and chronic obstructive pulmonary disease (Gouder and Montefort 2014). As of now, only few studies reported the chemical speciation of $PM_{2.5}$ samples during Diwali Festival for elemental, ionic content, OC and EC in Delhi region (Sarkar et al. 2010; Perrino et al. 2011). A number of news headlines highlighted the abrupt increase in $PM_{2.5}$ level during Diwali festival in 2016 (Hindustan Times 2016, Times of India 2016 and The New York Times 2016). There is increasing concern for the harmful effects of firework constituents in $PM_{2.5}$ on the human health and urban air quality. In the present study, an attempt has been made to chemically characterize and evaluate $PM_{2.5}$ samples collected during Diwali period in the years 2015 and 2016.

2 Materials and methods

2.1 Study area and sampling site

Delhi, the capital of India, is spread over an area of 1483 km^2 and is 160 km from the South Himalaya. It is situated at a latitude of 28°24′17″–28°53′00″N and longitude of 76°20′37″–77°20′37″E with an altitude between 213 and 305 m above mean sea level (amsl). It has an extreme climate with four distinct seasons: winter (December–March), summer (April–June), monsoon (July–September) and post-monsoon (October–November) (NAAQMS 2001). Summers are characterised by the maximum frequency of dust storms with maximum temperatures of 45–48 °C. The winter season is extremely cold with a minimum temperature around 4–6 °C. During monsoon season, the humidity is high which leads to heavy rain falls. The mean annual rainfall is 612 mm with more than 80% during the monsoon. The air is dry during the greater part of the year over Delhi region. Wind speeds are higher in the summer and the monsoon season. Yearly mean wind is in the range 0.9–2 ms^{-1} (Srivastava et al. 2009).

Sampling was carried out in the campus of the Indira Gandhi Delhi Technical University for Women, located in the east of Delhi. It is just 50 m away from the road that caters to a huge volume of traffic. The location of the site is shown in Fig. 1. The sampler was located on the rooftop of the building at a height of about 6 m above ground level. The Inter State Bus Terminal ISBT is just 400 m away from the campus, which operates bus services in Delhi and adjoining seven states. High traffic jams occur frequently during morning and evening peak hours. Lot of vehicles contribute to heavy traffic density of around 500–600 vehicles per hour (Singh et al. 2011). The meteorological parameters recorded in Delhi during the study period are presented in Table 1. There is no change in temperature during Diwali day over the sampling site for both the years. An average temperature of 23 °C and relative humidity of 32 and 42% are observed on the Diwali day for the years 2015 and 2016, respectively.

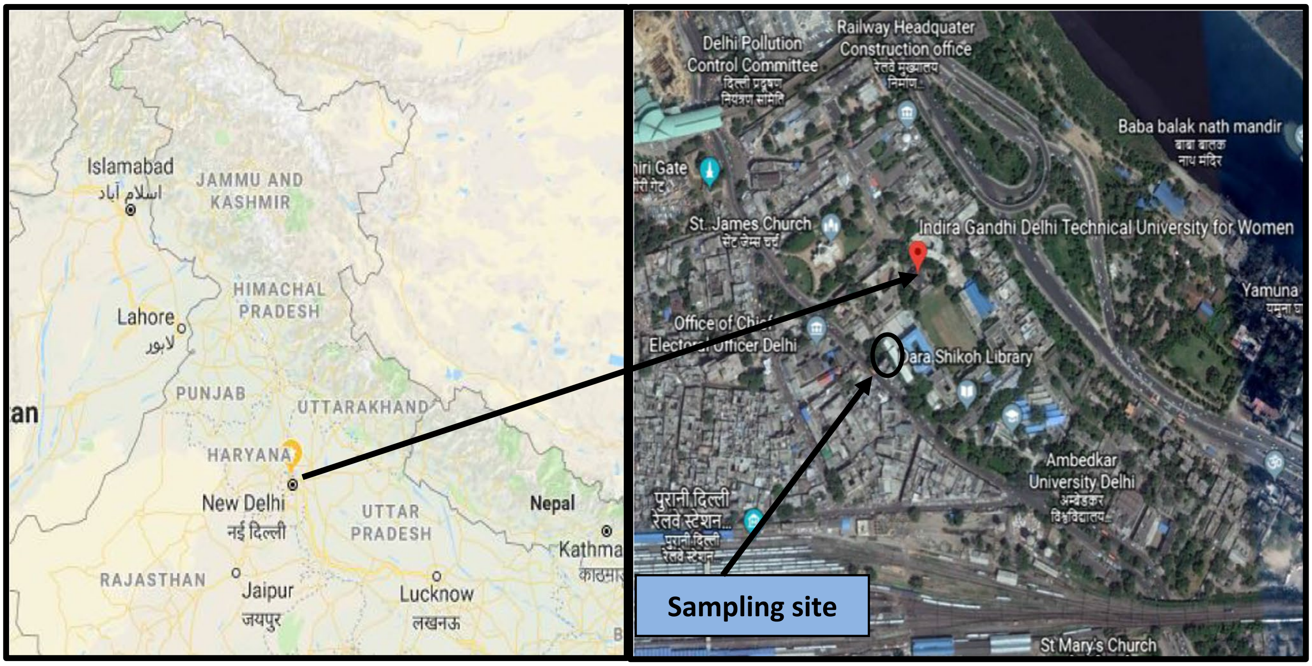

Fig. 1 Map of sampling site Delhi 28.6 N 77.2 E

Table 1 Meteorological parameters during the study period

Designated period	Temperature (°C)	Relative humidity (%)	Wind direction (°)	Wind speed (m s^{-1})
2015				
Pre-Diwali days	22.8	40.3	159.6	0.22
Diwali day	23.3	33	126.1	0.41
Post-Diwali days	21.8	29.3	201.6	0.31
2016				
Pre-Diwali days	26.2	40.5	186.3	0.89
Diwali day	23.1	42.1	178.4	0.15
Post-Diwali days	23.2	42.2	200.1	0.13

Source: DPCC (Delhi Pollution Control Committee)

Wind speed was 0.41 and 0.15 m s^{-1} for the years 2015 and 2016, respectively. There is significant variation in relative humidity and wind speed on Diwali day of both the years. The wind direction is mixed from north-east and south-west over the sampling site for the study period for both the years.

2.2 Sampling period and methodology

Diwali was celebrated on 11th November and 30th October in year 2015 and 2016, respectively. Ambient $PM_{2.5}$ samples were collected for three sampling periods designated as pre-Diwali days (29th October, 3rd, 5th and 9th day of November in 2015 and 18th, 20th, 25th, 27th day of October in 2016), Diwali days (11th November in 2015 and 30th October in 2016) and post-Diwali days (16th, 18th of November in 2015 and 2nd, 6th day of November in 2016) as given in Table 1. Firework activities began in the evening around 07:00 pm (local time GMT + 5:30) and continued till late night (01:00 am local time GMT + 5:30) with maximum burning between 08:00 and 11:00 pm (local time GMT + 5:30). Sampling for ambient $PM_{2.5}$ was performed for 24 h each day starting at 10:30 am (local time GMT + 5:30), which covered the time period for firework activities. $PM_{2.5}$ samples were collected by Fine Particulate Sampler (Envirotech Model: APM 550) (flow rate: 16.6 lpm). Quartz fibre filter (QFF) (Pallflex) (47 mm) was used for collection of $PM_{2.5}$ samples. QFFs were pre-cleaned by baking at 550 °C for 5 h before sampling. Before and after sampling, QFFs were stored in a Secador desiccator (Tarsons) under controlled temperature and 25–40% relative humidity (RH) for 24 h to prevent hydration of the filter surface. Filters were transported in cassettes, sealed in polyethene bags to and from the sampling site. The filters were weighed twice before and after sampling using microbalance with resolution ± 10 µg (Sartorius Model: GC1603S-OCE). After weighing, the filters were packed in aluminium foil to protect from sunlight and stored in the deep freezer (Haier) at − 27 °C until further analysis.

2.3 Chemical analysis of $PM_{2.5}$ samples

The sampled QFFs were analysed for elemental species, water-soluble ionic species and temperature-resolved organic (OC1, OC2, OC3, OC4, OP) and elemental (EC1, EC2, EC3) carbonaceous fractions. Filters were analysed by energy dispersive X-ray fluorescence (EDXRF-Epsilon 5) for quantification of elements and subsequently used for water-soluble ionic components, since EDXRF is a non-destructive technique. For monitoring and controlling the operation of the instruments, standards were run routinely. Samples were run in duplicate to maintain precision. Field blank levels were determined and elemental concentrations were corrected by subtracting the corresponding elemental concentration in blank filters.

The QFFs were analysed for determination of the water-soluble ions components (WSIC) by Ion Chromatograph (Model: DIONEX-ICS-3000, USA). The extraction of water-soluble ionic species from sampled QFFs was performed using ultrasonicator (Citizen, Model: CUB 5, capacity 5 L) with a frequency of 40 kHz. One-fourth of each filter was extracted in 10 ml of de-ionized water (having resistivity of 18.2 MΩ-cm) for 45 min. The process was repeated three times and extracts were made up to final volume of 30 ml after filtration through nylon membrane filters (0.22 µm pore size, supplied by Millipore). The filtered extract was then transferred to polypropylene sample bottles. These bottles were cleaned thoroughly by first keeping them dipped in 2% nitric acid overnight and then in deionised water, overnight. Four anions (SO_4^{2-}, Cl^-, F^-, NO_3^-) were determined by Ion Chromatograph (IC) using an Ion Pac-AS11-HC analytical column, ASRS-300 4 mm anion micro-membrane suppressor, 20 mM NaOH (50% w/w) as eluent. Five cations (Na^+, Mg^{2+}, K^+, Ca^{2+}, NH_4^+) were determined using a separation column with a guard column, suppressor CSRS-300 and 5 mM MSA (methane sulphonic acid) as eluent. National Institute of Standards and Technology (NIST, USA) traceable calibration standards were used for calibration of these ionic species. The data was collected at 5 Hz and resulting chromatographs were processed using Chromeleon software. Blank filters were analysed in the same way and corrections incorporated accordingly. Samples were analysed in duplicates to ensure precision.

~0.54 cm^2 area of QFFs was analysed for the eight carbon fractions by OC/EC analyzer (Model: DRI: 2001A; Make: Atmoslytic Inc., Calabasas, CA, USA) following the USEPA IMPROVE protocol with negative pyrolysis area zeroed. The IMPROVE method separates carbon in PM collected on a quartz fibre filter into eight carbon peaks (OC1, OC2, OC3, OC4, OP, EC1, EC2, EC3). The sample is heated to four temperature plateaus (140, 280, 480 and 580 °C) in pure helium and three temperature plateaus (580, 740 and 840 °C) in 98% helium and 2% oxygen. Different atmosphere is required on the basis of the fact that the OC can be volatilized in a non-oxidizing helium atmosphere, while EC must be combusted by an oxidizer. Relative standard deviation of duplicate samples was less than 5% for elements, water-soluble ionic species, OC and EC.

3 Results and discussion

3.1 Fine particulate concentrations

24 h averaged concentration of $PM_{2.5}$ aerosols were determined before, during and after the Diwali festival in two consecutive years, i.e., November 2015 and October 2016. The average concentration of $PM_{2.5}$ was 308.8 µg m^{-3} on Diwali 2015 (11th November 2015) and 766.5 µg m^{-3} on 2016 (30th October 2016), respectively. Increased level of atmospheric $PM_{2.5}$ concentrations was observed on the Diwali day as compared to pre-Diwali and post-Diwali days (Fig. 2). The concentration of $PM_{2.5}$ observed during Diwali day was 2 and 6 times higher than the pre-Diwali days for the years 2015 and 2016. For Diwali 2015, the increase in $PM_{2.5}$ mass concentration was found to be comparable with the earlier reported $PM_{2.5}$ mass during Diwali 2009 (365 µg m^{-3}) (Perrino et al. 2011) and 2011 (390 µg m^{-3}) (Parkhi et al. 2016). $PM_{2.5}$ concentration of 766 µg m^{-3} on Diwali day in 2016 was found to be comparable with the CPCB reported value for ITO, 797 µg m^{-3} (Central Pollution Control Board Delhi 2016). During Diwali 2015 and 2016, the $PM_{2.5}$ mass concentrations were about 7.7 (308.8 µg m^{-3}) and 19 (766.5 µg m^{-3}) times higher than NAAQ standards. The high wind speed (0.41 m s^{-1}) and comparatively low moisture content observed during 2015 on Diwali day contributed to lower $PM_{2.5}$ concentration. In

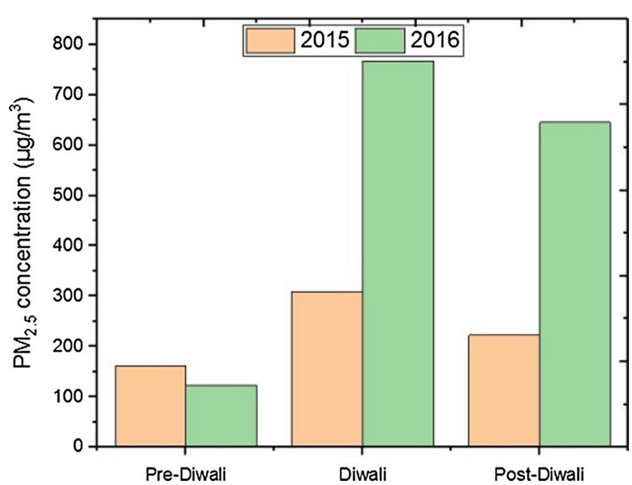

Fig. 2 Comparison of $PM_{2.5}$ levels during pre-Diwali days, Diwali day and post-Diwali days for the year 2015 and 2016

addition to the adverse meteorological parameters observed for the year 2016, the westerly winds from adjacent states of Delhi carried smoke released from stubble burning towards Delhi during Diwali period. As per the NASA report, the 2016 crop residue fires were the most severe in the Northern India since 2002 in regards to the number of fire hot spots detected (NASA 2017). The study also reported that the crop fires detected over Punjab and Haryana showed 2016 to be an anomalous year, with the highest number of crop residue fires (18,707) in relation to the fires in all other years over the region. The smoke emanating from crop residue burning combined with the pollutants emitted on Diwali day accentuated the pollution level.

3.2 Elemental concentrations

Ambient $PM_{2.5}$ samples collected during Diwali period were chemically characterised for elements. The concentration of individual elements during pre-Diwali, Diwali and post-Diwali are reported in Table 2 for the years 2015 and 2016. It appears that the concentration of a number of species showed a marked increase during both festivals in both years (Fig. 3). Major increase was recorded for seven elemental species in $PM_{2.5}$ samples (Al, S, K, Ba, Sr, Na, Mg) on Diwali day as compared to samples from pre- and post-Diwali days. This result is in line with findings of previous firework-related studies (Kulshrestha et al. 2004; Wang et al. 2007; Sarkar et al. 2010; Perrino et al. 2011; Tsai et al. 2012; Pervez et al. 2016). K, S, Al, Ba, Sr, Na, Mg showed a significant increase in concentration on Diwali day for both the years which was due to bursting of firecrackers (Vecchi et al. 2008). The fire crackers usually contain potassium salts such as potassium nitrate, chlorates and perchlorates. Na and K are used as metal oxidizers, whereas Al, Cu are used as colour and sparkles in firecrackers (Pervez et al. 2016), and S is used as a propellant in the firecrackers (Tandon et al.

Table 2 Concentration of $PM_{2.5}$, elements, ions, OC and EC observed on pre-Diwali, Diwali and post-Diwali days (in μg m^{-3})

Species	2015			2016		
	Pre-Diwali	Diwali	Post- Diwali	Pre- Diwali	Diwali	Post-Diwali
$PM_{2.5}$	160.76	308.82	222.02	122.15	766.51	645.18
Mg	1.52	2.13	1.61	0.96	5.93	3.17
Na	2.26	4.51	1.51	1.95	9.76	6.80
Al	10.46	23.79	17.71	17.26	67.55	14.64
S	22.88	33.55	10.33	15.01	107.46	59.91
K	4.22	35.74	4.72	6.49	124.61	19.89
Ba	0.92	8.51	0.00	0.82	25.7	1.04
Sr	0	0.91	0.00	0	0.99	0.00
Cl	7.09	17.29	19.84	17.23	65.98	78.23
Ca	4.62	11.06	5.55	3.59	9.82	10.97
Ti	0.07	0.22	0.16	0.25	1.18	0.38
Mn	0.09	0	0.08	0.10	0.07	0.09
Fe	0.50	0.46	0.83	1.56	1.64	1.06
Ni	0.05	0.04	0.03	0.02	0	0.00
Cu	1.01	0.26	0.26	0.24	1.09	0.27
Zn	1.59	0.66	2.91	1.02	0.50	0.86
Mo	0.14	0.13	0.15	0.17	0.10	0.14
Pb	1.68	0.59	0.54	0.65	2.27	0.94
F^-	0.31	2.67	0.31	0.29	1.92	1.99
Cl^-	1.76	9.00	3.75	1.92	29.34	25.08
SO_4^{2-}	3.61	10.48	2.28	2.09	84.64	35.84
NO_3^-	6.43	33.38	19.98	7.56	51.41	90.89
Na^+	1.27	3.86	1.41	1.01	8.92	5.81
NH_4^+	1.37	0.10	2.20	1.17	6.53	25.38
K^+	1.49	9.24	1.86	1.62	77.3	12.80
Mg^{2+}	0.62	1.56	0.67	0.58	4.88	2.21
Ca^{2+}	3.80	10.25	4.91	3.02	9.63	10.60
OC	31.83	48.34	38.63	36.25	64.15	106.28
EC	10.83	5.73	9.39	8.14	8.34	14.83

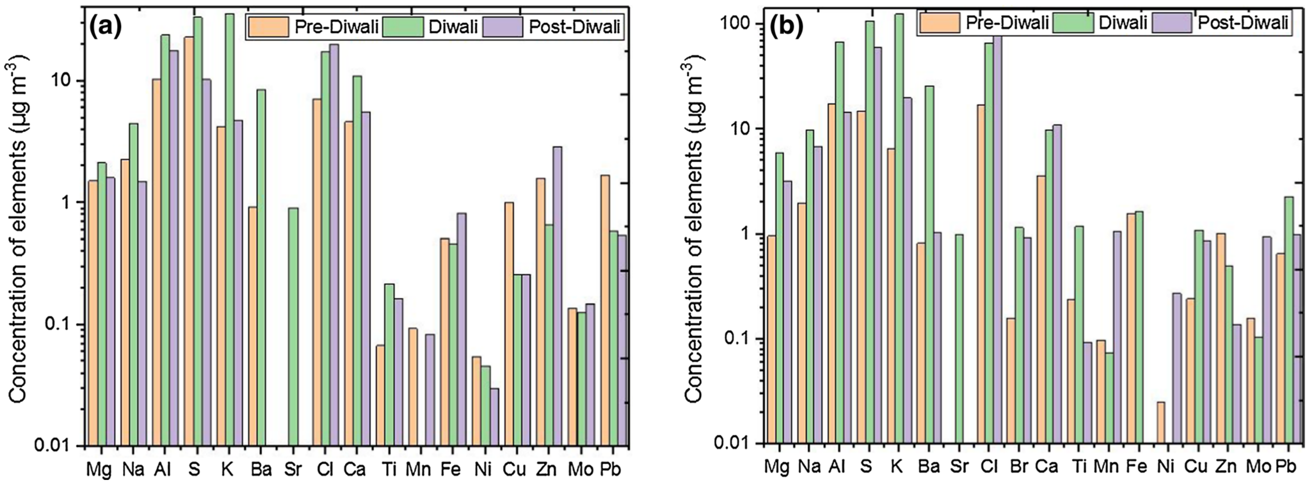

Fig. 3 Elemental concentrations in $PM_{2.5}$ during pre-Diwali days, Diwali day and post-Diwali days of **a** 2015 and **b** 2016 year

2008). Calcium chlorides and sulphates give rise to orange flames, potassium nitrate, sulphur and potassium chlorate or perchlorates are a component of the black powder, the combustible material (Moreno et al. 2007). The concentrations of Ca, Mn, Ni, Cu and Zn overall decreased on Diwali day for both years, as compared to the results obtained for pre- and post-Diwali days. This may be attributed to the fact that Diwali is observed as a national holiday, due to which there is low traffic on the roads leading to lower possibility for road dust resuspension (Sarkar et al. 2010).

3.3 Ionic species of $PM_{2.5}$

The concentrations of water-soluble ionic species during pre-Diwali days, Diwali day and post-Diwali days are shown in Fig. 4. The concentration of ions followed the order of $NO_3^- > SO_4^{2-} > Cl^- > F^-$ and $SO_4^{2-} > NO_3^- > Cl^- > F^-$ among anions and $K^+ > Ca^{2+} > NH_4^+ > Na^+ > Mg^{2+}$ and $K^+ > NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+}$ among cations during Diwali day of 2015 and 2016, respectively. The increase in $PM_{2.5}$ mass concentrations during Diwali day was mainly due to SO_4^{2-}, NO_3^-, Cl^-, K^+ and NH_4^+ ions produced from firework activities. Potassium and sulphate were present in high quantities during Diwali day as compared to pre- and post-Diwali days. The ratio of microequivalents of Cl^- to Na^+ increased from 0.91 in pre-Diwali to 1.53 on Diwali day of 2015 and from 1.26 to 2.16 in 2016, which indicates the enrichment of Cl^- in $PM_{2.5}$. This can be attributed to the high chlorine content emitted from firework activities. The high concentrations of SO_4^{2-}, NO_3^- and NH_4^+ ions in the atmosphere during Diwali period indicate the formation of these ions as secondary inorganic aerosols. These ions are considered to be the secondary fine particles produced from gas to particle

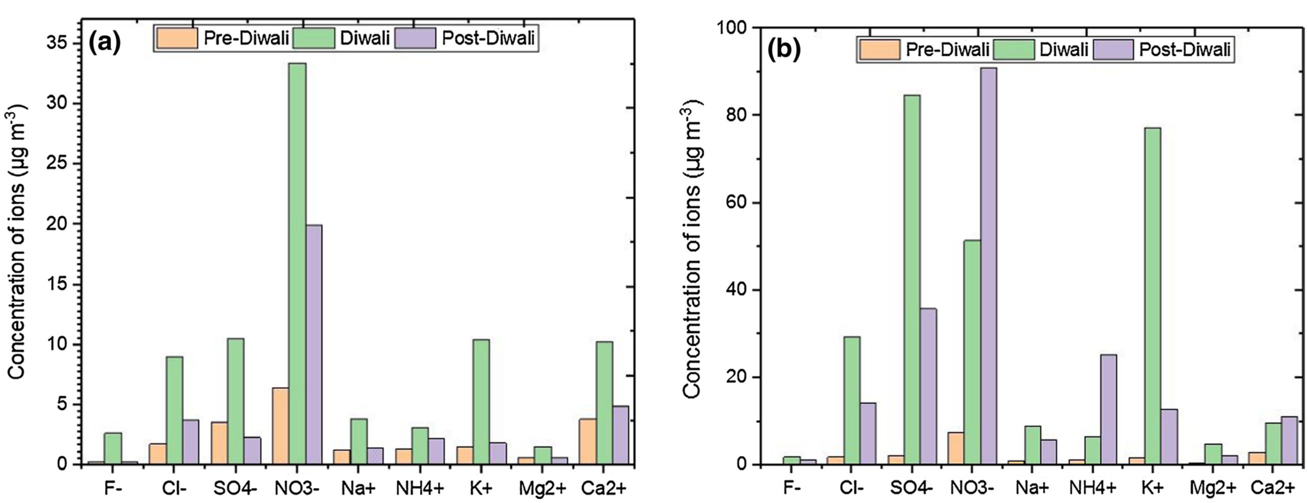

Fig. 4 Ionic species concentrations in $PM_{2.5}$ during pre-Diwali days, Diwali day and post-Diwali days of **a** 2015 and **b** 2016 year

conversion of NO_x, and SO_x. These species are released during the burning of firecrackers which can easily get converted to SO_4^{2-}, NO_3^- and NH_4^+ ions by chemical reaction.

In the year 2016, NO_3^-, SO_4^{2-}, K^+ and NH_4^+ ions showed a marked difference in concentrations than that in the year 2015. The observed increase in concentration for both SO_4^{2-} and K^+ ions was almost eight times than the concentration in 2015. Increase in NH_4^+ and NO_3^- ions concentration during post-Diwali days as compared to Diwali day was observed in 2016, in contrast to the trend observed in 2015. It was reported that NH_4NO_3 can be formed if the molar ratio of NH_4^+/SO_4^{2-} is greater than 1.5 (Huang et al. 2011; Pathak et al. 2009). The molar ratio of NH_4^+/SO_4^{2-} less than 1.5 during post-Diwali days in 2015 (ratio: 1.1), indicates that ammonium nitrate would not have formed. Molar ratio of NH_4^+/SO_4^{2-} above 1.5 as observed during post-Diwali days in 2016 (ratio: 3.7) could be treated as ammonium rich condition, showing that NH_4NO_3 would be produced effectively after the formation of $(NH_4)_3H(SO_4)_2$ (Ge et al. 2017). Elemental and ionic concentrations were comparable for Na, Mg and Ca. However, appreciable difference in elemental and ionic forms of K and Cl were observed, for which relevant explanation could not be proposed.

3.4 Carbonaceous fraction of $PM_{2.5}$

Carbon fractions (OC1, OC2, OC3, OC4, OP, EC1, EC2, and EC3) present in $PM_{2.5}$ samples during the study period are presented in Fig. 5. It was observed that the OC concentration rose by 1.3 times on Diwali day as compared to pre-Diwali days in 2015. A previous study in Delhi reported that during Diwali, the OC rate was 1.4 times higher than the pre-Diwali days (Sarkar et al. 2010). OC levels increased 1.8 times as compared to pre-Diwali days in 2016. In contrast to 2015, the OC levels were higher during post-Diwali days than Diwali day in 2016. The low wind speed along with high humidity during Diwali period in 2016 led to increase in concentration of pollutants in the lower atmosphere. Furthermore, low temperature and high humidity during the period may have lead to the formation of secondary organic carbon. In addition to this, as mentioned above, the westerly winds from adjacent states of Delhi carried smoke released from stubble burning towards Delhi during Diwali period which might be the cause for the high levels of OC on post-Diwali days. These findings are in line with the results reported during Diwali in Delhi (Sarkar et al. 2010) and lantern festival in Beijing (Wang et al. 2007).

EC levels were lower for both the years on Diwali day compared to the pre- and post-Diwali days. Since EC is extensively used as a tracer for vehicular emissions, the lower traffic density on Diwali day being a national holiday accounted for lower levels of EC. This is in accordance with the above mentioned observation for Zn and Ni vehicular tracers. In 2015, OC/EC ratio showed the increasing trend from pre-Diwali days (OC/EC: 3) to Diwali days (OC/EC: 8.4) and then dropped for post-Diwali days (OC/EC: 4). OC/EC ratio increased from pre-Diwali days to Diwali day and remained same in post-Diwali days during 2016. OC2, OC3, OC4 showed two times increase in concentration during Diwali day compared to pre-Diwali days for the both the years. In 2016, OC1, OC2, OC3 and OC4 showed higher levels in post-Diwali samples than the Diwali day. EC1, EC2 and EC3 have shown a different pattern. EC1 was higher during Diwali day compared to pre- and post-Diwali days during 2015, while it was lower than the post-Diwali days during 2016. EC1 level is marginally higher than EC2 and EC3 fraction for both the years which solely depends on the source strength of EC.

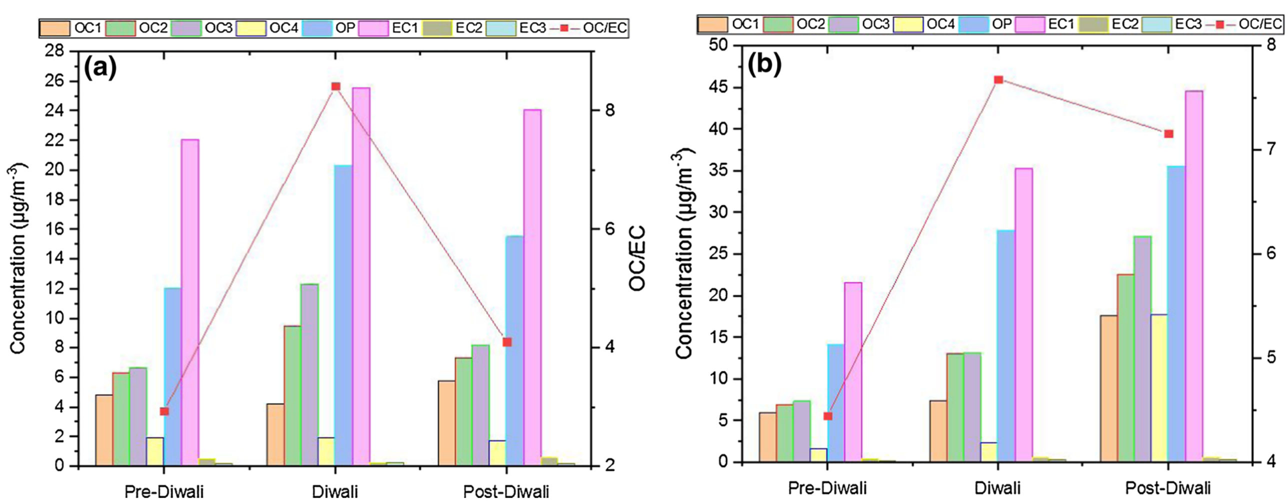

Fig. 5 Carbon fractions levels in $PM_{2.5}$ during pre-Diwali days, Diwali day and post-Diwali days of **a** 2015 and **b** 2016 year

3.5 Health risk assessment

3.5.1 Deposition flux of trace elements in the human respiratory tract

The deposition flux (DF, μg h^{-1}) of trace elements in the human respiratory tract was calculated using the following equation (Lyu et al. 2017)

$$\mathrm{DF} = \sum (\mathrm{DE}_i \times C_i) \times \mathrm{V} \tag{1}$$

where DE is the particle deposition efficiency in the size range for Dpi = 2.5 μm (mean diameter of the particle), C_i is the trace element concentration (μg m^{-3}) and V is the inhalation rate (m^3 h^{-1}). The inhalation rate under normal conditions was assumed to be 0.45 m^3 h^{-1} (Lv et al. 2016).

The deposition efficiency, DE, adopted from Lyu et al. (2017) is 0.63 for particle size 2.5 μm. The total deposition flux for selected trace elements was quantified using above equation for pre-Diwali, Diwali and post-Diwali days (Fig. 6). DF value was in the range of 0.012–10 and 0.021–35 μg h^{-1} for Diwali day in 2015 and 2016, respectively. Highest deposition flux in the human respiratory tract was reported for K (10.1 and 35.3 μg h^{-1}) on Diwali day in 2015 and 2016. The most carcinogenic and toxic elements Pb and Ni showed non-zero deposition in the respiratory tract on Diwali day for both years. Pb showed 0.16 and 0.64 μg h^{-1} deposition flux during Diwali day in 2015 and 2016 which was much higher than the value 0.071 μg h^{-1} reported in the study for non-ferrous metal smelting in China (Lyu et al. 2017).

The deposition flux of elements for head, tracheobronchial and pulmonary region in the respiratory tract were calculated to compare the deposition rates of elements during Diwali, pre-Diwali and post-Diwali days (listed in Table 3). Highest contribution to the total deposition flux was made in the head region for all elements. The high deposition flux of the elements in the head region was due to the combined effect of impaction, sedimentation and diffusion deposition mechanisms (Lippmann 2011). Al and K have shown the highest deposition, while Ni, Ti and Mn showed lowest flux in the head region.

3.5.2 Estimation of carcinogenic and non-carcinogenic risk

To determine the excess health risk to an individual associated with the elevated levels of elements during Diwali, hazard index (HI) and cancer risk (CR) were calculated. For this calculation, hazard index was calculated for two events I and II. In event I, cumulative hazard index due to firework tracers Al and Ba was obtained using their base concentrations for annual period (365 days). Event II involved the calculation for two parts: in first part, HI was estimated for 360 days (365 days minus 5 days for Diwali period) using the base concentration of Al and Ba. In the second part of calculation, HI was obtained for 5 days; assuming that the pronounced effect of firework emissions remained in the air for approximately 5 days from the day of Diwali. Hazard index for event II was obtained by adding these HI for two parts. Excess risk associated with these elements due to Diwali was estimated by comparing the cumulative HI for event II with the HI for event I. The hazard quotient (HQ) was estimated for Al and Ba using the following equation (Gurjar and Mohan 2003; Lim et al. 2009)

$$\mathrm{HQ} = \frac{\mathrm{DI}}{\mathrm{RfD}} \tag{2}$$

where DI is the daily intake (mg kg^{-1} day^{-1}), RfD is the inhalation chronic reference dose (mg kg^{-1} day^{-1}). DI in

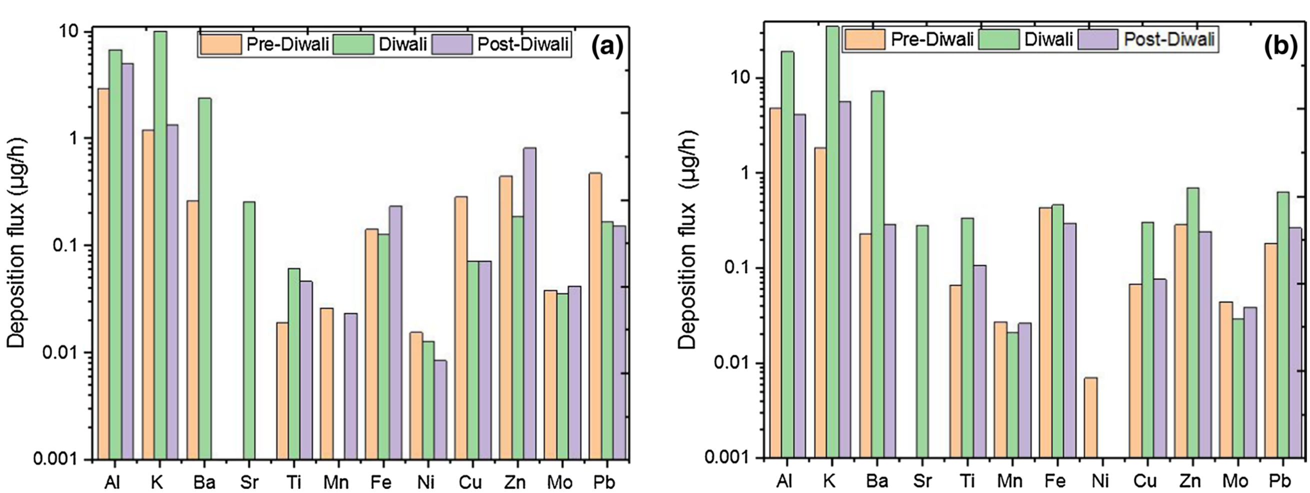

Fig. 6 Deposition flux of elements in the human respiratory tract during pre-Diwali, Diwali and post-Diwali days in **a** 2015 and **b** 2016

Table 3 Deposition flux (in µg h^{-1}) of elements in the head, tracheobronchial and pulmonary region of the human respiratory tract during pre-Diwali, Diwali and post-Diwali days

	Pre-Diwali			Diwali			Post-Diwali		
	Head	Tracheobronchial	Pulmonary	Head	Tracheobronchial	Pulmonary	Head	Tracheobronchial	Pulmonary
2015									
Al	2.118	0.282	0.847	4.817	0.642	1.927	3.586	0.478	1.434
K	0.855	0.114	0.342	7.238	0.965	2.895	0.956	0.127	0.382
Ba	0.187	0.025	0.075	1.723	0.230	0.689	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.184	0.025	0.074	0.000	0.000	0.000
Ti	0.014	0.002	0.005	0.044	0.006	0.018	0.033	0.004	0.013
Mn	0.019	0.003	0.008	0.000	0.000	0.000	0.017	0.002	0.007
Fe	0.102	0.014	0.041	0.093	0.012	0.037	0.168	0.022	0.067
Ni	0.011	0.001	0.004	0.009	0.001	0.004	0.006	0.001	0.002
Cu	0.205	0.027	0.082	0.052	0.007	0.021	0.052	0.007	0.021
Zn	0.321	0.043	0.128	0.134	0.018	0.054	0.588	0.078	0.235
Mo	0.028	0.004	0.011	0.026	0.003	0.010	0.030	0.004	0.012
Pb	0.341	0.045	0.136	0.119	0.016	0.048	0.110	0.015	0.044
2016									
Al	3.496	0.466	1.398	13.679	1.824	5.471	2.965	0.395	1.186
K	1.314	0.175	0.526	25.233	3.364	10.093	4.027	0.537	1.611
Ba	0.166	0.022	0.066	5.239	0.698	2.095	0.210	0.028	0.084
Sr	0.000	0.000	0.000	0.202	0.027	0.081	0.000	0.000	0.000
Ti	0.048	0.006	0.019	0.239	0.032	0.096	0.076	0.010	0.031
Mn	0.020	0.003	0.008	0.015	0.002	0.006	0.019	0.003	0.008
Fe	0.316	0.042	0.126	0.332	0.044	0.133	0.214	0.028	0.085
Ni	0.005	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000
Cu	0.049	0.007	0.020	0.221	0.029	0.088	0.055	0.007	0.022
Zn	0.207	0.028	0.083	0.506	0.067	0.202	0.174	0.023	0.069
Mo	0.032	0.004	0.013	0.021	0.003	0.008	0.028	0.004	0.011
Pb	0.132	0.018	0.053	0.460	0.061	0.184	0.190	0.025	0.076

the above formula can be calculated using the following equation

$$\mathrm{DI} = \frac{C \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{IR}}{\mathrm{BW} \times \mathrm{LT}} \tag{3}$$

where C is concentration of pollutant in mg m^{-3}, EF is exposure frequency in days $year^{-1}$, ED is exposure duration in years, IR is inhalation rate in m^3 day^{-1}, BW is body weight in kg and LT is average lifetime in days.

Assuming that the effects of pollutants are additive, the HQs for two events were summed to obtain HI for event I and II. Adverse health effects due to non-carcinogenic elements Al and Ba are pronounced if the HQ value exceeds unity.

Cancer risk (CR) was calculated for the carcinogenic element lead, Pb present in the Diwali samples. CR was calculated using the following formula

$$\mathrm{CR} = \mathrm{DI} \times \mathrm{CSF} \tag{4}$$

where CSF is the cancer slope factor (mg kg^{-1} $day^{-1})^{-1}$

From Table 4, it was concluded that the cumulative hazard index for event I and II in 2015 are low, 3.93 and 3.96 as compared to 5.32 and 5.39 in 2016. The values for the background, event I, revealed their significant effects on health due to Al and Ba. HI for the event II including Diwali was 1.4 times in 2016 as compared to 2015 value. The excess risk due to chronic lifetime exposure to Al and Ba was 0.7 and 1.3% for the years 2015 and 2016 during Diwali, respectively. In contrast, CR value for Pb was lower than the Environment Protection Agency (EPA) acceptable range (10^{-6}–10^{-4}) which indicated that the carcinogenic risk is negligible.

3.6 Air mass trajectory analysis: long-range transport

To study the large difference in concentration of $PM_{2.5}$ for the years 2015 and 2016 during Diwali period, air mass backward trajectories were calculated. The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT),

Table 4 Estimation of carcinogenic and non-carcinogenic risk

	RfD[a]	Event I		Event II			
		2015	2016	2015	2016	2015	2016
		HQ1	HQ1	HQ2a	HQ2a	HQ2b	HQ2b
Al	1.43E−03	2.09	3.68	2.06	3.63	0.06	0.11
Ba	1.43E−04	1.84	1.63	1.82	1.61	0.02	0.04
		3.93	5.32	3.88	5.24	0.08	0.15
	CSF	Event I		Event II			
		2015	2016	2015	2016	2015	2016
		CR1	CR1	CR2a	CR2a	CR2b	CR2b
Pb	0.5	6.57E−05	7.60E−05	6.48E−05	7.49E−05	1.12E−05	3.15E−05

HQ1 hazard quotient for exposure to Al and Ba for 365 days year^{-1} at their background concentrations, *HQ2a* hazard quotient for exposure to Al and Ba for 360 days year^{-1} at their background concentrations, *HQ2b* hazard quotient for exposure to Al and Ba for 5 days year^{-1} at their concentrations during Diwali (mean of Diwali and post-Diwali). Here, inhalation rate (IR) = 20 m^3 day^{-1}; exposure frequency (EF) = 365, 360 and 5 days year^{-1} for event I, first part of event II and second part of event II, respectively; exposure duration (ED) = 60 years (average); body weight (BW) = 70 kg (average); average lifetime (LT) = 60 years × 365 days, i.e. 21,900 days, *CR1* cancer risk for exposure to Pb for 365 days year^{-1} at their background concentrations, *CR2a* cancer risk for exposure to Pb for 360 days year^{-1} at their background concentrations, *CR2b* for exposure to Pb for 5 days year^{-1} at their concentrations during Diwali (mean of Diwali and post-Diwali)

[a]Source: The Risk Assessment Information system (http://www.rais.ornl.gov)

GDAS (Global Data Assimilation System) meteorological data and Trajstat software are used to study air mass backward trajectories (Draxler and Rolph 2003). The 5-day air mass backward trajectories terminated at the sampling site at 5:00 h (UTC) were calculated at an elevation of 500 m above ground level (AGL). Figure 7 shows the HYSPLIT 5 day back trajectories on Diwali days of November 2015 and October 2016. These trajectories reveal that during Diwali days for both the years, pollutants are carried from the area of Indo-Gangetic plains (Uttar Pradesh, Punjab and Haryana and surrounding areas) towards Delhi. Earlier studies over Delhi have also shown that the air mass was transported from the area of IGP region, Iran, Afghanistan and Pakistan and surrounding areas (Sharma et al. 2015). The air mass approaching the receptor site at Delhi from the area of IGP region carried a stream of smoke released from stubble burning (George et al. 2013). Farmers set fire to crop residue left after harvesting rice every year in October and November to quickly prepare the fields for the wheat crop. The smoke emanating from crop residue fires in Uttar Pradesh, Punjab and Haryana combined with urban pollution and fireworks emissions increase the $PM_{2.5}$ concentration in the capital city during Diwali period. Figure 7 shows the air mass trajectory from IGP region and

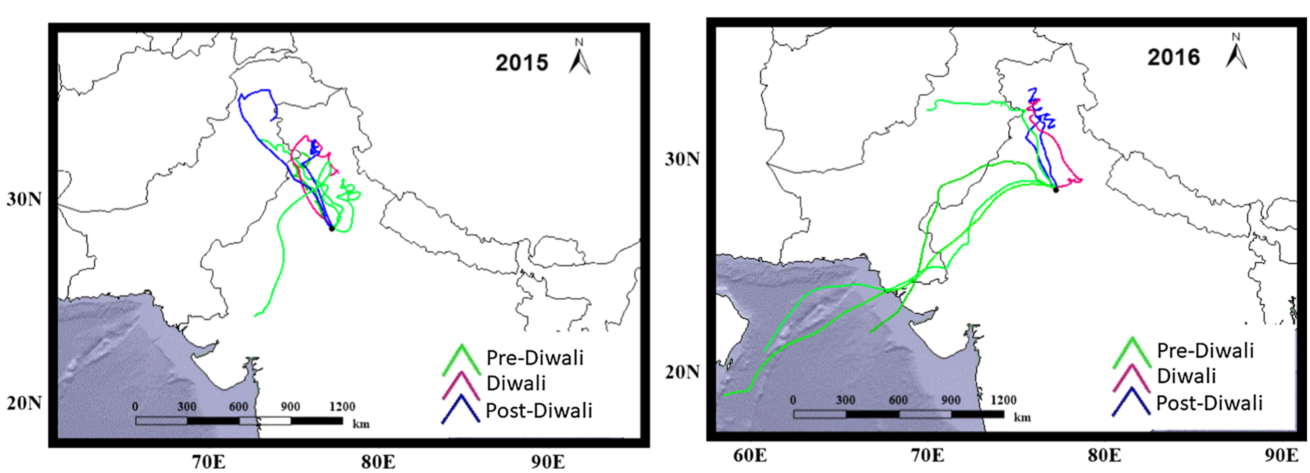

Fig. 7 Air mass 5 day back trajectories (using HYSPLIT model) at 500 m AGL over Delhi on Diwali days for the year 2015 and 2016

Rajasthan most of the time during study period in 2015, whereas in 2016, the origin of trajectories was from Arabian sea and long-range transport through the states of Rajasthan and Gujarat during pre-Diwali days and from IGP region during rest of the period.

4 Conclusion

This study showed appreciably high $PM_{2.5}$ mass concentrations during Diwali festival. $PM_{2.5}$ concentrations observed on Diwali day, exceeded the NAAQ standards, 308.8 and 766.5 µg m^{-3} for the years 2015 and 2016, respectively. The higher $PM_{2.5}$ concentration (766.5 µg m^{-3}) in 2016 than that in 2015 (308.8 µg m^{-3}) is probably due to lower wind speed (0.15 m s^{-1} in 2016 and 0.41 m s^{-1} in 2015) and high humidity (42% in 2016 and 33% in 2015) in the air. The firework tracers (Al, K, S, Na, Mg, Ba, Sr) constituting the $PM_{2.5}$ on Diwali day were appreciably higher than those found during pre-and post-Diwali days in 2015 and 2016, respectively. The increase in $PM_{2.5}$ mass concentrations on Diwali day was mainly due to SO_4^{2-}, NO_3^-, Cl^-, K^+ and NH_4^+ ions produced by firework activities. The increase in Cl^- to Na^+ ratio revealed that a high content of chlorine was present in firework material. OC levels increased to 1.3 and 1.8 times on Diwali day compared to pre-Diwali days during 2015 and 2016. Air mass backward trajectory showed that the pollutants are carried from the area of Indo-Gangetic plains (Uttar Pradesh, Punjab and Haryana and surrounding areas). The deposition flux of elements for head, tracheobronchial and pulmonary region was calculated and the highest contribution to the total deposition flux was made in the head region for all elements. The deposition flux of elements in the human respiratory tract was calculated and found higher for K (10.1 and 35.3 µg h^{-1}) on Diwali day in 2015 and 2016. The excess risk due to chronic lifetime exposure to Al and Ba was 0.7 and 1.3% for the year 2015 and 2016 during Diwali, respectively, whereas the carcinogenic risk due to lead is negligible.

The festival adds significantly to the existing air pollution problem in Delhi for a short period of time. The findings of this study highlighted the negative impact of this activity on environment and health. Therefore, there is a need to replace the firecrackers with environment-friendly alternatives. Farmers should also be made aware of the problems due to crop residue burning. Suitable mitigation options should be implemented by government to manage the waste after harvesting practices.

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