



Chemical speciation of respirable suspended particulate matter during a major firework festival in India

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ABSTRACT

Ambient respirable particles ($PM \leq 10 \mu m$, denoted by PM_{10}) were characterized with respect to 20 elements, 16 polycyclic aromatic hydrocarbons (PAHs), elemental and organic carbon (EC and OC) during a major firework event—the “Diwali” festival in Delhi, India. The event recorded extremely high 24-h PM_{10} levels ($317.2\text{--}616.8 \mu g m^{-3}$, 6–12 times the WHO standard) and massive loadings of Ba ($16.8 \mu g m^{-3}$, mean value), K ($46.8 \mu g m^{-3}$), Mg ($21.3 \mu g m^{-3}$), Al ($38.4 \mu g m^{-3}$) and EC ($40.5 \mu g m^{-3}$). Elemental concentrations as high as these have not been reported previously for any firework episode. Concentrations of Ba, K, Sr, Mg, Na, S, Al, Cl, Mn, Ca and EC were higher by factors of 264, 18, 15, 5.8, 5, 4, 3.2, 3, 2.7, 1.6 and 4.3, respectively, on Diwali as compared to background values. It was estimated that firework aerosol contributed 23–33% to ambient PM_{10} on Diwali. OC levels peaked in the post-Diwali samples, perhaps owing to secondary transformation processes. Atmospheric PAHs were not sourced from fireworks; instead, they correlated well with changes in traffic patterns indicating their primary source in vehicular emissions. Overall, the pollutant cocktail generated by the Diwali fireworks could be best represented with Ba, K and Sr as tracers. It was also found that chronic exposure to Diwali pollution is likely to cause at least a 2% increase in non-carcinogenic hazard index (HI) associated with Al, Mn and Ba in the exposed population.

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1. Introduction

Fireworks are truly unique sources of atmospheric pollution that generate massive quantities of pollutants within a short span of time. They are generally associated with festivities worldwide, such as New Year's Eve celebrations, the Las Fallas in Spain, the Lantern Festival in China, Bonfire Night in UK, the 4th of July celebrations in US and Diwali (or Deepawali) festival in India. These events involve extensive use of pyrotechnics on a regional, and often, national scale. This provides scientists with a unique opportunity to study short-term degradation of air quality and its likely human health impacts.

Fireworks are associated with elevated levels of pollutant gases like SO_2 and NO_x along with high loadings of ambient particulates [1–3]. Crackers contain a variety of metal salts such as chlorates, perchlorates, nitrates, etc. along with charcoal and sulfur which is manifested in the extremely high ambient concentrations of these species during the festive days. Kulshrestha et al. [4] reported that concentrations of Ba, K, Al and Sr went up by 1091, 25, 18 and 15 times, respectively, during Diwali in Hyderabad, India. Vecchi et al.

[1] also observed high enrichment of atmospheric particulates with Sr, Mg, Ba, K and Cu during a firework episode in Milan, Italy. Pronounced signatures of New Year's Eve firework activity has been recorded in fine particulate species in Mainz, Germany [5] and in snowflakes in the Austrian Alps [6]. Primary components of firework aerosol (Ba, K, Sr, Cl^- , Pb, Mg) and secondary components such as sulfates, nitrates, oxalate, malonate, succinate and glutarate were over 5 times higher during the Lantern festival in China than normal days [7].

Chemical characterization of firework aerosol is important for two reasons. Firstly, these events give rise to extremely high levels of atmospheric pollutants that have substantial health effects. Short-term particulate pollution episodes are associated with cardiopulmonary ailments [8], while similar effects are also seen for elevated SO_2 and NO_x levels [9]. Firework smoke is known to lead to acute eosinophilic pneumonia [10]. Barium-rich aerosols released from fireworks may be responsible for a significant rise in the number of asthma cases [11]. A majority of barium compounds released from pyrotechnics are water-soluble and thus, bioavailable, which may cause even greater harm [6]. Perchlorates that are used as oxidizers in fireworks are teratogenic and can adversely affect thyroid functions [12–15]. Secondly, these episodes are important from the point of view of atmospheric chemistry as well. For example, Attri et al. [16] reported formation of O_3 without the participation of NO_x due to burning of sparkles during Diwali. The cocktail of primary

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Table 1
Meteorological parameters in Delhi during the study period.

Day	Max T ($^{\circ}\text{C}$)	Min T ($^{\circ}\text{C}$)	Mean T ($^{\circ}\text{C}$)	Rain (mm)	WS (m s^{-1})	RH-night (%)	RH-day (%)	BSS (day^{-1})	Mix depth-night (m)	Mix depth-day (m)
Background	35	16.6	25.8	0	0.8	89	19	9.4	153	1493
Pre-Diwali	33.6	17.8	25.7	0	0.7	92	35	7.9	133	1877
Diwali	32.2	15.7	24.0	0	0.9	90	27	4.2	83	1431
Post-Diwali	33	14.7	23.9	0	1	80	28	8	77	1468

Source: Integrated Agromet Advisory Services, Indian Agricultural Research Institute (IARI), New Delhi.

Max T : maximum temperature; Min T : minimum temperature; WS: wind speed; RH: relative humidity; BSS: bright sunshine hours; Mix depth: mixing depth. Mixing depth was calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model developed by the Air Resources Laboratory (ARL) of the National Oceanic and Atmospheric Administration (NOAA) [64].

pollutants released may exhibit varied interactions among themselves, and if aided by favourable atmospheric conditions, may lead to the formation of secondary pollutants. Simultaneous characterization of organic and inorganic components of ambient aerosol during firework episodes may provide important insights in this regard.

Diwali, or the “Festival of lights”, is celebrated with great enthusiasm and vigour all over India. Firework displays in Delhi, the capital of India, are known to be grand and extensive, perhaps owing to the relative affluence of the city’s population. As a result, Delhi is shrouded by an envelope of smoke on Diwali nights, reducing visibility to a minimum. With emissions from nearly 6.1 million vehicles [17], three coal-fired power plants (combined capacity of around 1100 MW) and more than 129,000 industrial units [18] located within the city limits, Delhi is already reeling under a severe air pollution crisis. An episodic pollution event such as Diwali is likely to add significantly to the existing problem. Recent findings suggest that around 30% of Delhi’s population suffers from respiratory disorders due to air pollution, and the incidence of respiratory ailments in the city is as high as 12 times the national average [19]. Moreover, Delhi has been declared as the most cancer prone area in India by the National Cancer Registry Program [20]. In such a background scenario, the added pollution caused by Diwali firework gains enormous significance and needs to be investigated. The festival is generally celebrated during October/November (17th October in 2009) which marks the onset of winter in the region. Low temperatures, calm wind conditions and shallow nocturnal mixing heights limit pollutant dispersion, thus aggravating the health impacts of firework-generated aerosols [21].

To the best of our knowledge, there have been no studies regarding simultaneous characterization of organic and inorganic components during Diwali from anywhere in India. This paper reports, for the first time, simultaneous characterization of 20 metallic and non-metallic elements, 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs), as well as elemental and organic carbon (EC and OC) in ambient aerosols collected during Diwali 2009 at three residential sites in Delhi. Relative enhancements of tracer species during the pollution episode were studied and efforts were made to justify the findings. Effects of various background activities on the observed loadings were also investigated.

2. Materials and methods

2.1. Study area

Delhi is home to a population of ~ 18 million spread over an area of 1483 km². It stretches from the latitude of 28°24′17″ to 28°53′ and from the longitude of 76°20′37″ to 77°20′37″. The area can be broadly classified into two main physiographic domains: (1) northern and central undulatory terrain (altitude between 197 and 260 m a.m.s.l) and (2) southern upland rocky region (altitude between 20 and 340 m a.m.s.l) [22]. The region is characterized by intensely hot summers (monthly mean temperatures of 32–34°C in May–June) and extremely cold winters (monthly mean temperatures of 14–16°C in December–January). The mean annual

rainfall is 612 mm, of which around 80% is received during the monsoon months (July–September). Predominant wind direction is from the north and north-west except during the monsoon season that is characterized by easterly or south-easterly winds. The months of October–November signify the onset of winter and are characterized by north-westerly winds, lower ambient temperatures and nocturnal temperature inversions. Detailed information about the meteorological parameters recorded in Delhi during the study period is presented in Table 1 while the prevalent and actual wind directions are shown in Fig. 1.

2.2. Description of the sampling sites

Three residential areas were chosen for the present study (Fig. 1). Site 1, Mayur Vihar (MV) is located in east Delhi. The sampler was located on the roof of Ahlcon International School at a height of around 12–13 m. A heavy traffic road is at a distance of about 600 m. Site 2, Mithapur (MP), lying at the extreme south-east tip of Delhi, is a sub-urban residential area with very high population density. Traffic flow in the residential colony is low, but the high-traffic Mathura Highway passes through at a distance of around 1.5 km. The sampler was located on the roof of a private household building at a height of approximately 12 m. Site 3, Jawaharlal Nehru University (JNU) campus, is a residential cum institutional area in south Delhi with good vegetation cover. Traffic flow inside the campus is very low, but it is not very far from peripheral roads that cater to a huge volume of traffic. The sampler was located on the roof of the School of Environmental Sciences building at a height of about 13 m.

2.3. Sampling protocol

In the year 2009, Diwali was celebrated on 17th October. Twenty-four hour PM₁₀ samples were collected on 9th October (designated as “Background”), 16th October (Pre-Diwali), 17th October (Diwali) and 18th October (Post-Diwali) at all the sites simultaneously. Firework activities began in the evening (around 19:00 h) and continued till late at night (03:00 h) with peak activities between 21:00 and 01:00 h. Sampling started at 07:00 h each day and continued for 24 h, which allowed for a complete overlap between firework activities and the sampling period. PM₁₀ was trapped on Whatman GF/A (8 in. \times 10 in.) Glass Fibre Filters (precombusted at 450°C for 12 h) using High-volume samplers (Respirable Dust Sampler, Model MBLRDS-002, Mars Bioanalytical Pvt. Ltd.) having a constant flow rate of 1.2 m³ min⁻¹. Filters were transported to and from the field in sealed polyethylene bags and were desiccated for 48 h before and after sampling. Utmost care was taken to avoid handling losses. Filters were stored in a refrigerator (4°C) until analysis.

2.4. Elemental analysis

Elemental composition of the samples was estimated by Wave-length Dispersive X-Ray Fluorescence Spectrometer (WDXRF), S4

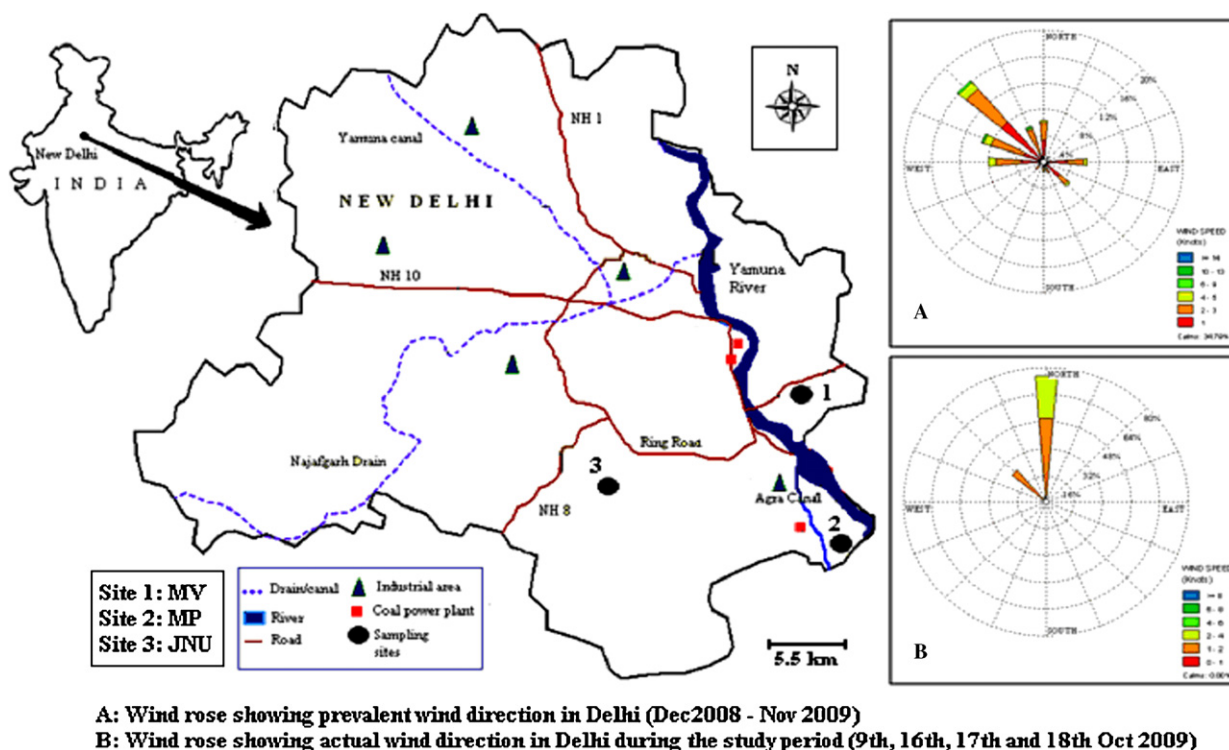


Fig. 1. Map showing the sampling sites and wind roses showing the prevalent (annual) and actual (study period) wind directions in Delhi.

Pioneer (Bruker AXS) equipped with a Rh X-ray tube, a 2.7 kW generator, an eight-position automatic crystal changer, a gas flow-proportional counter and a scintillation detector. The spectral data were processed with SpectraPlus software. The following elements were quantified: Na, K, Ca, Mg, Al, Ti, Mn, P, Fe, Cr, Cu, V, Br, Cl, Ba, Ni, Pb, S, Sr and Zn. Minimum detection limits (MDL) for most of the elements varied from 4–35 ng m⁻³. Some of the other elements (Co, Zr, As, Mo and Sn), although principally detectable, were found to be below the MDL.

2.5. Determination of elemental, organic and total carbon (EC, OC and TC)

Estimation of carbonaceous aerosols is associated with a number of possible sampling artifacts and analysis uncertainties. Sampling artifacts for OC could arise from the following sources: firstly, the combination of low ambient levels of particulate OC and low filter face velocity is known to increase the relative importance of field blanks [23]. However, in this study the ambient levels of OC were quite high (Section 3.3), as was the filter face velocity (49 cm s⁻¹), which is expected to reduce sampling artifacts. Secondly, a positive artifact could occur due to adsorption of gaseous carbonaceous species onto the filter during sampling. This is evidenced by the presence of carbonaceous species in a back-up filter in amounts up to 20% of that in the front filter [24]. A high filter face velocity is again likely to reduce this artifact [25,26].

In the present study, carbonaceous species were analyzed by employing the procedure described in Lin and Tai [27]. Briefly, sample filters were pre-treated by heating them at 340 °C in a muffle furnace for ~100 min in order to remove OC, and were subsequently analyzed by an elemental analyzer (EuroEA3000, EuroVector Instruments and Software) to obtain the EC content. Another portion of the filter was fed directly to the elemental analyzer without any pre-treatment to obtain the TC content. OC was calculated as the difference between TC and EC. Helium was the car-

rier gas in the elemental analyzer with a flow rate of 107 ml min⁻¹, while the fuel (ultra-pure oxygen) flow rate was 80 ml min⁻¹. The oven temperature was 980 °C; however, during actual combustion the local temperature of the reactor reached ~1800 °C. The evolved CO₂ was separated in a gas chromatography column and identified by a thermal conductivity detector (TCD). The calibration standards used were L-cystine (C–29.99%, H–5.03%, N–11.66%, O–26.63%, S–26.69%) and Acetanilide (C–71.09%, H–6.71%, N–10.36%, O–11.84%) procured from EuroVector Instruments and Software.

A possible source of uncertainty in this method is the thermal differentiation between EC and OC. Humic like substances (HULIS), being thermally rather stable, evolve at a higher temperature than other OC, leading to interferences with the EC estimation [28] causing an overestimation of EC to some extent. HULIS is typically detected in biomass smoke—a source that could have been important in this study as all the sites are in residential areas. Moreover, sample pre-treatment with HCl vapours to remove carbonates was not carried out in this study, which could also possibly lead to an overestimation of EC.

2.6. Determination of PAHs

Circular portions (Ø 8 cm) cut from each filter paper using a stainless steel punch were extracted twice in 50 ml of toluene for 15 min by ultrasonic agitation (Sonicator 3000, Misonix, Inc., USA) with a frequency of 20 kHz in a water bath (10–15 °C). Both the extracts were subsequently mixed, centrifuged for 30 min and filtered through Whatman No. 1 filter. The extracts were concentrated to 0.5–1.0 ml in a rotary evaporator (Büchi Rotavapor, Switzerland). PAHs in the concentrated extracts were fractionated by a silica gel (Silica gel 60, particle size 0.063–0.2 mm, 70–230 mesh ASTM, purchased from Merck KGaA, Darmstadt, Germany) column (4 mm i.d.). The fraction containing PAHs was again concentrated to 0.5–1.0 ml by rotary evaporation and solvent was

Table 2
Concentrations of PM₁₀ and chemical species ($\mu\text{g m}^{-3}$) observed on background, pre-Diwali, Diwali and post-Diwali days at the sites.

Species	MV				MP				JNU			
	Background	Pre-Diwali	Diwali	Post-Diwali	Background	Pre-Diwali	Diwali	Post-Diwali	Background	Pre-Diwali	Diwali	Post-Diwali
PM ₁₀	273.5	420.5	587.7	380.2	300.4	432.3	616.8	424.8	159.1	175.3	317.2	214.4
Na	2.34	7.07	15.74	7.54	2	9.01	16.04	8.32	2.64	3.01	8.63	2.91
K	2.55	21.37	57.29	25.05	1.79	25.71	63.39	26.04	3.41	6.83	19.66	6.2
Ca	9.22	8.93	22.53	10.35	11.79	11.18	15.95	13.51	10.59	9.6	10.92	7.47
Mg	3.95	7.27	26.84	8.99	4.83	10.43	27.83	13.86	2.32	5.27	9.22	2.69
Al	10.84	20.57	47.87	16.15	15.92	26.59	51.58	24.04	9.67	12.79	15.87	11.19
Ti	3.27	4.8	2.2	1.69	5.82	3.82	2.48	2.06	0.78	0.38	0.4	0.37
Mn	0.26	0.22	1.09	0.5	0.35	0.27	0.95	0.37	0.43	0.31	0.74	0.36
P	2.2	2.3	1.45	1.54	2.01	2.45	1.52	1.73	1.45	0.98	1.07	1
Fe	7.89	10.43	7.05	7.62	13.49	3.73	4.91	5.44	6.01	6.2	6.81	2.46
Cr	0.41	0.43	0.27	0.45	0.58	0.56	0.21	0.35	0.46	0.44	0.38	0.42
Cu	0.48	0.43	0.52	0.42	0.62	0.68	0.54	0.57	0.47	0.49	0.58	0.51
V	0.35	0.35	0.43	0.41	0.38	0.44	0.4	0.39	0.33	0.36	0.15	0.31
Br	0.013	0.01	0.008	0.008	0.006	0.012	0.009	0.01	0.004	0.009	0.006	0.008
Cl	2.05	2.94	6.3	6.14	3.24	4.76	6.09	6.9	0.76	1.58	5.74	0.9
Ba	0.07	1.39	21.69	7.75	0.09	2.04	18.89	6.34	0.03	1.56	9.98	1.65
Ni	0.11	0.1	0.1	0.13	0.15	0.15	0.11	0.12	0.11	0.1	0.02	0.09
Pb	0.29	0.29	0.36	0.18	0.4	0.3	0.39	0.24	0.19	0.21	0.33	0.22
S	15.54	23.85	54.55	41.74	10.75	26.53	63.89	46.41	12.31	14.15	41.09	16.41
Sr	0.01	0.02	0.19	0.06	0.01	0.03	0.15	0.04	0.01	0.01	0.09	0.02
Zn	1.38	1.65	0.95	1.07	1.99	2.36	0.85	0.97	1.96	2.16	0.67	0.86
TC	30.11	71.42	115.54	98.39	39.46	75.82	117.87	134.52	25	54.14	99.74	100.09
EC	9.66	12.76	40.8	18.28	11.51	15.11	45	23.51	7.1	10.21	35.74	14.15
OC	20.45	58.66	74.74	80.11	27.95	60.71	72.87	111.01	17.9	43.92	64	85.95

exchanged with acetonitrile for further chromatographic analysis. Samples were analyzed on a High Performance Liquid Chromatography (HPLC) system (Waters, USA), equipped with a tunable absorbance UV detector (254 nm) and Waters PAH C₁₈ column (4.6 mm × 250 mm, particle size 5 μm). The mobile phase was a gradient of acetonitrile and degassed water (50% acetonitrile held for 5 min; linear gradient to 100% acetonitrile in 5–20 min; 100% acetonitrile held till 28 min and linear gradient to 50% acetonitrile from 28 to 32 min; flow rate: 1.5 ml min⁻¹). Quantification of PAHs was done by internal calibration method and their identification was carried out by comparing their retention times with those of authentic standards (EPA 610 Polynuclear Aromatic Hydrocarbons Mix and Semivolatile Internal Standard Mix, both procured from Supelco, USA). Filters were spiked with internal standard solution prior to extraction in order to monitor procedural performance and matrix effects. Surrogate compounds were represented for the analyses as follows: Naphthalene-d₈ for Naphthalene (Naph); Acenaphthene-d₁₀ for Acenaphthylene (Acy), Acenaphthene (Acen) and Fluorene (Flu); Phenanthrene-d₁₀ for Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Flan) and Pyrene (Pyr); Chrysene-d₁₂ for Benz[a]anthracene (B[a]A) and Chrysene (Chry); Perylene-d₁₂ for Benz[b]fluoranthene (B[b]F), Benz[k]fluoranthene (B[k]F), Benz[a]pyrene (B[a]P), Dibenz[a,h]anthracene (DB[ah]A), Benz[ghi]perylene (B[ghi]P) and Indeno[1,2,3-cd]pyrene (IP).

2.7. Analytical quality control

Instruments were calibrated using at least five standards covering the range of concentrations encountered in ambient air work. The calibration curves were linear in the concentration range with linear regression coefficients (R^2) > 0.995 for linear least-squares fit of data. Samples were analyzed in triplicates to ensure precision. Relative Standard Deviations (RSD) of replicate samples were less than 10%, 8% and 10% for PAHs, EC/OC, and elements, respectively. Field blanks and reagent blanks were analyzed to determine analytical bias. Concentrations of target PAHs and carbonaceous compounds were very low (<5%) in the blanks as compared to real samples. Elemental concentrations reported in this study were blank-corrected by subtracting the corresponding elemental load-

ing on blank filters. Recovery efficiencies of PAHs were determined by spiking the filters with deuterated standards as described in Section 2.6. Recoveries of reported PAHs ranged from 81% to 98%.

3. Results and discussion

3.1. PM₁₀ loadings

Twenty-four hour PM₁₀ concentrations on the background date were 273.5, 300.4 and 159.1 $\mu\text{g m}^{-3}$ at MV, MP and JNU, respectively, which are 1.6–3 times the 24-h PM₁₀ National Ambient Air Quality Standard (NAAQS: 100 $\mu\text{g m}^{-3}$) of the Central Pollution Control Board (CPCB) of India. The overall mean PM₁₀ concentration on the background day (244.3 $\mu\text{g m}^{-3}$) was quite comparable to the annual mean PM₁₀ (April 2008–March 2009) measured at 40 locations across Delhi (231 $\mu\text{g m}^{-3}$) [29] as well as to the mean PM₁₀ in October 2008 (216 $\mu\text{g m}^{-3}$). As such, the background day can be thought of being representative of any typical day in Delhi in terms of particulate loading. On Diwali, the values registered at MV, MP and JNU were 587.7, 616.8 and 317.2 $\mu\text{g m}^{-3}$, respectively. These values are 3–6 times higher than the NAAQS and a staggering 6–12 times the 24-h Air Quality Guideline (AQG) (50 $\mu\text{g m}^{-3}$) set by the World Health Organization [30]. PM₁₀ concentrations on pre-Diwali (420.5, 432.3 and 175.3 $\mu\text{g m}^{-3}$ for MV, MP and JNU, respectively) and post-Diwali (380.2, 424.8 and 214.4 $\mu\text{g m}^{-3}$ for MV, MP and JNU, respectively) days were intermediate between these two extremes.

3.2. Elemental concentrations

3.2.1. Relative abundances and enrichment in ambient aerosol

Concentrations of 20 major and trace elements observed during the study period are presented in Table 2. A first inspection suggests that metal concentrations in the background sample of Delhi (7 days prior to Diwali, with no impact of firework activities) are much higher than what is reported from European or US cities [31–38]. Previous studies have attributed high metal concentrations in Delhi's air to vehicular activities, industrial emissions, coal combustion and crustal resuspension [39–42].

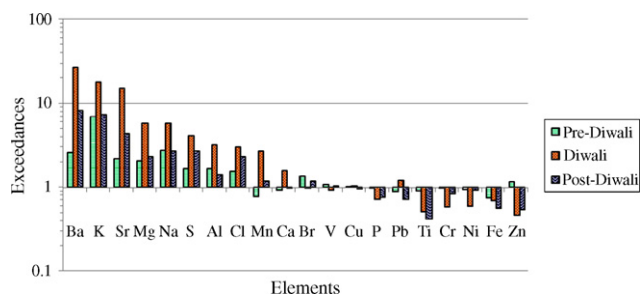


Fig. 2. Mean elemental exceedances (number of times over background values) on pre-Diwali, Diwali and post-Diwali days.

A closer inspection of the data reveals that a group of elements (Na, K, Ca, Mg, Al, Cl, Ba, S, Sr) exhibits a common temporal trend of increasing progressively from background date to Diwali (when their abundances peak) and then show a drop on post-Diwali. This group clearly represents the firework-related elements. Potassium compounds (in the form of nitrate, perchlorate or chlorate) act as the main oxidizer during burning [43]. Other components of the black powder used in fireworks include charcoal and sulfur. Barium compounds (carbonate, chlorate and nitrate) are used as colouring agents and stabilizers, where carbonate and nitrate create white effects while chlorates are associated with green colouration [1,43]. Strontium and Cu salts produce red and blue colourations, respectively. Magnesium is used as a fuel and also to produce sparks and crackling stars (in the form of a 50:50 Mg:Al alloy, magnalium) [44]. Calcium chlorides and sulfates give rise to orange flames [43]. The abruptly high emissions of these elements due to firework-burning activity during Diwali explain their high concentrations in atmospheric aerosol. Fig. 2 presents the mean elemental exceedances on pre-Diwali, Diwali and post-Diwali days (number of times over background values). Concentrations of Ba, K, Sr, Mg, Na, S, Al, Cl, Mn and Ca were higher by factors of 264, 18, 15, 5.8, 5, 4, 3.2, 3, 2.7 and 1.6, respectively, on Diwali compared to background. It

seems then that Ba, K and Sr can be conveniently used as tracers of Diwali fireworks in the future. Table 3 shows a comparison of PM₁₀ and associated elemental concentrations observed in this study and those from other firework events. The values reported in this study are often more than an order of magnitude greater than those from outside India. This is the first time that such high concentrations of ambient elements (especially metals) have been reported for a firework pollution event.

Although the Diwali festival is a single-day event, celebrations tend to spill over to the preceding and succeeding days in the form of sporadic firework burnings. This is confirmed by the abundances of tracer species on pre- and post-Diwali days; however, the magnitude and extent of pyrotechnic displays is greatest on the festival day itself, as is evident from Fig. 2. Although firework aerosol is relatively transient in the atmosphere and dissipates quickly to the ground [4], a fraction of it may be resuspended at a later time due to wind action or vehicular turbulence.

In sharp contrast to the firework tracers, concentrations of Zn, Ni, V and Cr dropped on Diwali. These metals are generally considered tracers for vehicular (fuel combustion, brake and tyre abrasion) and industrial sources [45–47]. Traffic on Diwali remains exceptionally low [3] as offices are closed (the day being a National Holiday) and people tend to stay home to celebrate the festival with their families. Crackers are very often burnt on the streets, which forces people to stay off the road. The observed decrease is perhaps due to low traffic and industrial activities on that day. Concentrations of Cu rose only slightly (from 0.52 to 0.55 $\mu\text{g m}^{-3}$) from background to Diwali. Lesser use of Cu-emitting blue fireworks is probably the reason in this case. Further, any rise may have been offset by the relatively lower contribution of Cu by vehicular and industrial sources on Diwali as compared to other days.

An attempt was made to determine the composition of the background and the firework aerosol. For this purpose, the species quantified in this study were classified into five groups, namely, “crustal”, “fireworks”, “anthropogenic”, “OC/EC” and “others”. The groups were represented as follows: (1) crustal—Na, K, Mg, Al, Ba,

Table 3

Comparison of PM₁₀ and elemental ($\mu\text{g m}^{-3}$) concentrations observed during various firework events from across the world.

	Present study	Barman et al. [2] ^a	Kulshrestha et al. [4] ^b	Moreno et al. [43] ^c	Vecchi et al. [1] ^d	Wang et al. [7] ^e
Event, yr	Diwali, 2009	Diwali, 2005	Diwali, 2002	Las Fallas, 2005	FIFA World Cup victory, 2006	Lantern Festival, 2006
Location	Delhi, India	Lucknow, India	Hyderabad, India	Valencia, Spain	Milan, Italy	Beijing, China
PM ₁₀	507.2	0.75	NR ^f	79	63.9	466.2
Na	13.5	NR	0.4	0.2	NR	4
K	46.8	NR	58	3.8	0.99	50
Ca	16.5	3.2	0.25	1.2	0.65	7
Mg	21.3	NR	0.25	0.3	0.6	6
Al	38.4	NR	35	1.5	0.68	10
Fe	6.3	0.75	1.2	0.4	1.7	5
Ti	1.7	NR	NR	0.04	0.05	NR
Cl	6	NR	NR	NR	0.23	20
P	1.4	NR	NR	0.05	NR	0.3
S	53.2	NR	NR	NR	1.18	40
Mn	0.93	0.08	0.1	NR	0.03	0.4
Cr	0.29	0.04	NR	0.003	0.01	NR
Cu	0.55	0.45	0.18	0.06	0.11	0.6
V	0.33	NR	0.01	0.01	<0.006	NR
Br	0.007	NR	NR	NR	0.009	NR
Ba	16.8	NR	15	0.24	0.16	4.5
Ni	0.07	0.04	0.008	0.003	0.005	NR
Pb	0.36	0.31	NR	0.25	0.06	1.1
Sr	0.14	NR	0.5	0.03	0.14	0.8
Zn	0.82	0.54	NR	0.08	0.19	3

NR: not reported.

^a Values reported are mean of four sites, 12-h sampling, values reported as 24-h.

^b 8-h sampling, values reported are approximate (ascertained from graphs).

^c 24-h sampling, Al reported as Al₂O₃.

^d Values reported are for 4-h resolution sample, 12 am–4 am on 10th July 2006.

^e Values reported are for 12-h night-time sample, values are approximate (ascertained from graphs).

^f PM₂₅ samples collected.

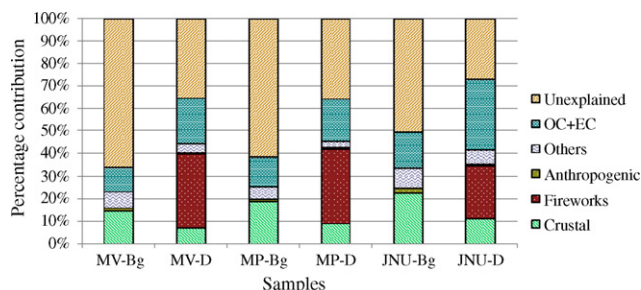


Fig. 3. Composition of ambient aerosol on the background and Diwali days at the three sites. MV-Bg, MP-Bg and JNU-Bg refer to the background aerosol at MV, MP and JNU, respectively while MV-D, MP-D and JNU-D refer to the Diwali aerosol at MV, MP and JNU, respectively.

Sr, Fe, Ti, Ca and Mn; (2) fireworks: Na, K, Mg, Al, Ba, Sr, S; (3) anthropogenic: Ni, Pb, Cr, Cu, V, Zn; (4) OC/EC: organic and elemental carbon; (5) others: P, Br, Cl, S. It was assumed that Na, K, Mg, Al, Ba and Sr had two major sources: crustal and fireworks while Fe, Ti, Ca and Mn were predominantly crustal. Ambient sulfur had two sources: fireworks and others (all other sources except fireworks). The “anthropogenic” group represented traffic and industrial sources. The contributions of firework aerosol to the firework-related elements (group 2) were then calculated by subtracting their background concentrations from those measured on Diwali. This method, however, has some uncertainties associated with it. Firstly, the assumption that Na, K, Mg, Al, Ba and Sr had only two contributing sources—crustal and firework is not strictly true. Ambient K is often associated with biomass burning, a source that could be important in residential areas such as those chosen in this study (in the form of domestic fuel use). Moreover, Ba could also be sourced from traffic. Secondly, the representativeness of the other groups is also not absolute. For example, Mn, although chosen as a purely crustal element, has a traffic and a firework source, while Cu has a possible firework source that has been ignored. Thirdly, it has also been assumed that crustal contributions to Na, K, Mg, Al, Ba and Sr on the background and Diwali days were the same, which might not have been true. And lastly, EC was not chosen as a firework tracer (despite its high concentrations on Diwali; see Section 3.3) because most of its other sources (traffic, industries, domestic, etc.) varied in magnitude over the study period. This might lead to a somewhat incomplete characterization of the firework aerosol and a possible underestimation of its contribution; however, it will suffice as a gross estimate. Composition of the background and firework aerosol at each of the three sampling sites is shown in Fig. 3. Fireworks contributed 33% to the aerosol load at both MV and MP

on Diwali, while the contribution was 23% at JNU. The unexplained mass could be attributed to inorganic salts, organic species containing hetero-atoms and moisture. Firework contribution of 50% to PM_{10} mass (4-h resolution) has been reported from Milan, Italy [1] while a much lower contribution of ~15% to PM_{10} (12-h resolution) has been reported from Beijing, China [7].

It is readily seen from Table 2 that concentrations of firework tracers were 2–3 times lower at JNU as compared to MV and MP while the contribution of firework aerosol to ambient PM_{10} was around 30% lower at JNU compared to the other two sites (Fig. 3). This is a direct consequence of the nature of the sites. Both MV and MP are engaged actively in firework displays while JNU has negligible firework activity inside the campus. Firework aerosol at JNU was mainly due to the diffused and advected smoke cloud from neighbouring areas such as Vasant Kunj, Vasant Vihar, and Munirka. This demonstrates that although advected firework smoke can provide vital information about the composition and relative abundance of tracer species, it often underestimates the actual concentration, and hence, potential exposure to population residing in active firework zones.

Firework metals exhibited significant positive correlations between themselves, pointing towards their common source (Fig. 4). Zinc, Cr and Ni were negatively correlated with firework tracers, showing that vehicular and industrial emissions decreased during Diwali. Strong positive correlations observed between Cl and firework tracers ($r > 0.7$, $p < 0.01$) suggested that chlorate salts of Ba, K, etc. were probably used in the fireworks [1,48]. Ambient sulfur concentrations were extremely high on Diwali and were significantly correlated ($r > 0.9$, $p < 0.01$) with firework metals as sulfur is a major constituent of the black powder used in crackers. In fact, SO_2 levels on Diwali night 2009 were higher than the previous 2 yrs (measured at 40 locations across Delhi) [49], which probably were due to the extensive use of freely imported crackers enriched with sulfur compounds.

3.3. Levels and distribution of carbonaceous aerosol

Non-metallic fuel used in fireworks contains charcoal and it seems logical to expect an impact of these events on ambient EC. Pollution gases (SO_2 , NO_x , etc.) emitted during these events may be oxidized to secondary organic and inorganic components that may remain adsorbed onto particles [7].

EC, OC and TC levels observed at the study sites over the four chosen days are presented in Table 2. Mean EC levels rose from $9.4 \mu g m^{-3}$ on background day to $40.5 \mu g m^{-3}$ on Diwali, and then dropped to $18.6 \mu g m^{-3}$ on post-Diwali. The mean EC level on

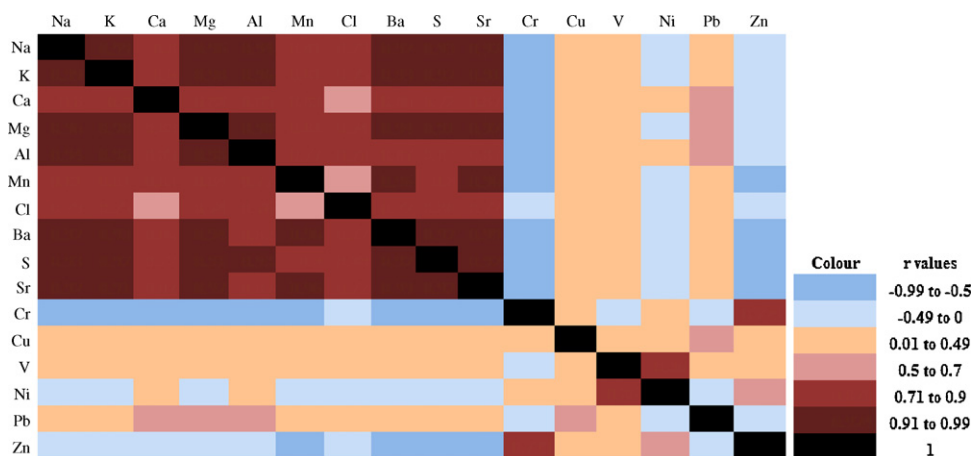


Fig. 4. Colour code diagram showing correlations between selected elements over the study period. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

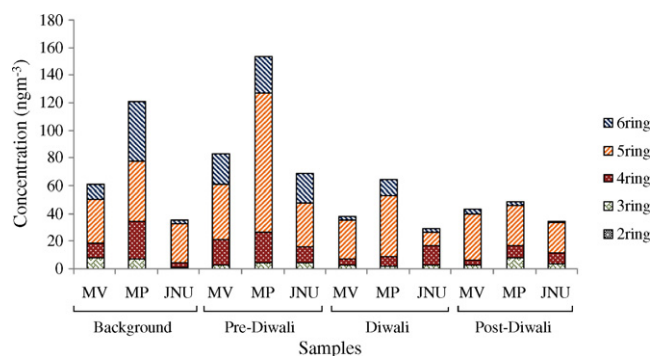


Fig. 5. Ring-wise distribution (shaded areas) and \sum_{16} PAH concentrations (column heights) observed in this study.

Diwali was 4.3 times higher than the background value. Babu and Moorthy [50] reported a 3- to 4-fold increase in aerosol BC during Diwali at Thumba, India while Wang et al. [7] observed a 5 times increase in BC during the Lantern Festival in China. Vecchi et al. [1] reported an increase of 3.1 times in aerosol EC during a firework episode in Milan, Italy.

The sudden rise in EC on Diwali despite low contributions from vehicular and industrial sources on that day obviously points to its source in firework burnings. This is confirmed by the high correlation coefficients between EC and the firework tracers ($r=0.91, 0.89, 0.75, 0.89, 0.82, 0.85, 0.89, 0.96$ and $0.94, p < 0.01$, between EC and Na, K, Ca, Mg, Al, Cl, S, Ba and Sr, respectively). In contrast, OC increased on Diwali by a smaller margin. The pre-Diwali sample showed considerably higher OC than the background value, which may be linked to increased emissions due to a large influx of traffic from neighbouring regions into Delhi during this time due to the shopping rush [51]. Post-Diwali OC levels were higher than Diwali whereas EC levels dropped. Low wind speed and low mixing heights help in trapping pollution gases near the surface and high humidity along with low ambient temperatures may aid in their secondary transformation and subsequent condensation onto pre-existing aerosol. As a result, concentrations of secondary components may be high in the post-firework period as observed by Wang et al. [7]. Meteorological conditions over Delhi were favourable for secondary transformation on the night of Diwali and on the following day (Table 1). Considering a wind speed of 1 m s^{-1} , it would have taken 12 h for the pollution gases to travel $\sim 43 \text{ km}$ (roughly equal to the north-south extent of Delhi), thus providing sufficient time for secondary transformation. It seems plausible, then, that enhanced OC levels in the post-Diwali samples could have been due to high levels of secondary organic carbon (SOC); however, this remains subject to confirmation as secondary components were not measured separately in this study. Apart from influencing secondary transformation, prolonged residence of the pollution plume over the city is bound to cause greater inhalation exposure.

3.4. Polycyclic aromatic hydrocarbons

\sum_{16} PAH concentrations (sum of 16 PAHs analyzed) along with corresponding ring-wise distributions observed in this study are represented in Fig. 5. Mean \sum_{16} PAH levels rose from background (72.8 ng m^{-3}) to pre-Diwali (102.6 ng m^{-3}) and then fell sharply on Diwali (44.3 ng m^{-3}), followed by a further small decline on post-Diwali (42.6 ng m^{-3}). However, Harrad and Laurie [52] observed significantly enhanced levels of PAHs during Bonfire Night festival in UK, while Dyke and Coleman [53] observed high levels of ambient dioxins during the same festival. This seeming contradiction can be rationalized by keeping in mind the fundamental differences in the nature of the two firework events in question. The Bonfire

Night festival, as the name suggests, involves lighting numerous bonfires, in addition to fireworks, which amounts to large-scale wood burning. Enhanced levels of PAHs during such events are expected, since wood combustion is widely recognized as a major source of atmospheric PAHs [54–56]. In fact, Fleischer et al. [57] found nominal levels of PCDD/Fs during lab-scale combustion of pyrotechnics, and concluded that high levels of dioxins observed by Dyke and Coleman [53] were probably from bonfires, not from fireworks. Our results indicate that Diwali fireworks are not major sources of particulate PAHs in the atmosphere.

We believe that the sharp drop in PAH levels on Diwali was linked to the dearth of traffic on that day more than anything else. High PAH levels on pre-Diwali coincided with the rush of pre-Diwali traffic [51]. \sum_{16} PAHs were either uncorrelated or negatively correlated with firework metals (Na, K, Mg, Al, Ba, Sr) indicating that firework is not a major source of PAHs, but were positively correlated with industrial and vehicular markers (Zn, V, Ni, Cr, Cu; $r > 0.5$) suggesting their common origin. Concentrations of DB[ah]A, B[ghi]P and IP, all of which are known traffic markers, fell by 82%, 76% and 83%, respectively, on Diwali as compared to pre-Diwali values. This strengthens our assumption that reduced traffic was the main cause of low PAH levels on Diwali. Low \sum_{16} PAH concentration in the post-Diwali sample (Sunday) was again due to low traffic. In this context, Li et al. [58] observed that total PAH levels fell from 95.9 to 58.9 ng m^{-3} during the Chinese Spring Festival (also a firework event) in Beijing, and attributed it to the reduced industrial and vehicular emissions.

The overall PAH profile at the study sites was dominated by B[b]F, which contributed $\sim 22\%$ (16.8 – 26.7%) to \sum_{16} PAHs. This was followed by B[a]P (13.9%), DB[ah]A (11.8%), B[ghi]P (9.8%) and B[k]F (9.3%). Ring-wise distribution showed dominance of 5-ring species (57%, overall mean), followed by 4-ring (18%), 6-ring (15%) and 3-ring species (8%). The seven carcinogenic PAHs—B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A and IP [59] contributed 73% (overall mean; range: 41–88%) to total PAHs implying considerable carcinogenic exposure to the population. Concentrations of B[a]P, the most carcinogenic of the priority PAHs, varied from 3 to 20.2 ng m^{-3} at the sites, with a considerably high overall mean of 8.6 ng m^{-3} .

Values of the molecular diagnostic ratios Flan/Flan+Pyr, IP/IP+B[ghi]P, B[a]A/Chry and B[a]P/B[ghi]P for the individual days are presented in Table 4. The ratios gave fingerprints of coal combustion and vehicular emission as the chief sources of atmospheric PAHs during the study period. Two coal-fired power plants (Rajghat Power Plant, 135 MW and Indraprastha Power Plant, 247.5 MW) are present around 4–4.5 km upwind of MV site while Badarpur Power Plant (720 MW, coal-fired) is present at about 2.5 km upwind of MP site. Apart from these, the use of low-grade coal for cooking purposes, especially around MP and JNU, serves as a source of coal combustion at the study sites. On the other hand, traffic, varying from moderate to heavy, is present in the vicinity of all the sites. This explains the dominance of these two sources as revealed by diagnostic ratios. In this context, it was interesting to note the variation of B[a]P/B[ghi]P over the study period. On the background and pre-Diwali days, the ratio indicated dominance of vehicular emissions, presumably due to the pre-Diwali rush. However, the values shifted markedly to the coal combustion domain on Diwali and post-Diwali days, which could be best explained by the dearth of traffic on these 2 days. Comparatively lower contributions by the vehicular source on these days were very likely translated into the dominance of the coal source.

3.5. Health risk assessment of chronic exposure to Diwali firework aerosol

An attempt was made to quantify the excess chronic health risk to an individual due to Diwali fireworks. For this purpose,

Table 4
Molecular diagnostic ratios (mean of the three sites) of PAHs for the background, pre-Diwali, Diwali and post-Diwali days in Delhi.

Ratios	Sources and values	Background	Pre-Diwali	Diwali	Post-Diwali
Flan/Flan + Pyr	Coal/wood: >0.5 ^a Gasoline: 0.4 ^b Petroleum: <0.4 ^a	0.25	0.68	0.83	0.5
IP/IP + B[ghi]P	Gasoline: 0.22 ^c Diesel: 0.5 ^c Petroleum: 1.3 ^c	0.37	0.37	0.23	0.35
B[a]A/Chry	Vehicles: 0.53 ^d Coal: 1.11 ^d	1.08	1.5	1.5	1.24
B[a]P/B[ghi]P	Coal: 0.9–6.6 ^b Vehicles: 0.3–0.78 ^b	0.88	0.87	3.45	4.09

^a Yunker et al. [65].

^b Simcik et al. [66].

^c Yassaa et al. [67].

^d Dickhut et al. [68].

Table 5
Estimation of non-carcinogenic health risk.

Species	RfC ^a	RfD ^b	Scenario I	Scenario II	
			HQ1	HQ2a	HQ2b
Al	5.00 E–03	1.43 E–03	2.33	2.31	0.04
Mn	5.00 E–05	1.43 E–05	6.64	6.58	0.09
Ba	5.00 E–04	1.43 E–04	0.12	0.12	0.13
		HI	9.09	9.01	0.26

HQ1 refers to the hazard quotient for exposure to Al, Mn and Ba for 350 days/yr at their respective background concentrations. HQ2a refers to the hazard quotient for exposure to Al, Mn and Ba for 347 days/yr at their respective background concentrations. HQ2b refers to the hazard quotient for exposure to Al, Mn and Ba for 3 days/yr at their respective concentrations during Diwali (mean of pre-Diwali, Diwali and post-Diwali). Here, inhalation rate (IR) = 20 m³ day⁻¹; exposure frequency (EF) = 350, 347 and 3 days/yr for Scenario I, first part of Scenario II and second part of Scenario II, respectively; Exposure Duration (ED) = 60 yrs; body weight (BW) = 70 kg; average lifetime (LT) = 60 yrs × 365 days, i.e. 21,900 days.

^a Source: The Risk Assessment Information System (www.ra.is.ornl.gov).

^b Calculated from RfC.

we considered two scenarios. Scenario I involved calculating the cumulative Hazard Index (HI) due to some firework tracers (Al, Mn and Ba) for an annual period (350 days) utilizing their background concentrations (this study) as a surrogate for their annual means. Scenario II involved two separate calculations: firstly, to find out the HI for Al, Mn and Ba for 347 days (350 days minus 3 days for Diwali) using their background concentrations and secondly, to calculate the HI for the 3 days of Diwali (using the mean of pre-Diwali, Diwali and post-Diwali values). These were then added to get the cumulative HI for Scenario II, which was then compared with the HI from Scenario I to get the excess risk due to Diwali.

The non-carcinogenic health risk to an individual due to exposure to a chemical is given by [60,61]

$$\text{Hazard Quotient (HQ)} = \frac{D_i}{\text{RfD}}$$

where D_i = Daily intake dose (mg kg⁻¹ day⁻¹), RfD = Inhalation chronic reference dose (mg kg⁻¹ day⁻¹). Further, D_i can be calculated as

$$D_i = \frac{CC \times IR \times EF \times ED}{BW \times LT}$$

where CC = contaminant concentration (mg m⁻³), IR = inhalation rate (m³ day⁻¹), EF = exposure frequency (days/yr), ED = exposure duration (yrs), BW = body weight (kg) and LT = average lifetime (days) i.e. age (yr) × 365 days/yr.

RfD can be calculated as RfD = (RfC × inhalation rate)/body weight [62], where RfC is the Inhalation chronic reference concentration (mg m⁻³).

Adverse non-carcinogenic health effects are expected if this quotient exceeds unity. A different HQ is estimated for each contaminant and sometimes for each pathway if pathway specific

reference doses are known [60]. The HQs are combined to form HI which assumes that the effects of the different chemicals are additive.

$$HI = \sum_i (HQ)_i$$

where i is the contaminant and/or pathway index, and $(HQ)_i$ is the hazard quotient for contaminant or pathway i .

The parameters used for calculating health risks and results of the assessment are presented in Table 5. The cumulative HI for Scenario I is very high (9.09) indicating significant health effects at the background levels of the chosen contaminants. Including Diwali in this calculation (Scenario II) further raises the HI to 9.27. This translates into a 2% rise in health effects due to chronic lifetime exposure to Al, Mn and Ba alone during Diwali. We stress at this point that the actual effects, however, should be far more severe due to chronic exposure to high levels of other pollutants such as PM₁₀, SO₂, NO_x, EC, etc., in addition to the acute effects of the said pollutants.

4. Conclusions

This paper shows that atmospheric pollution due to the Diwali firework event comes primarily from very high concentrations of respirable particulates and associated metals (Ba, K, Na, Al, Sr) along with EC. Extremely high PM₁₀ loadings (6–12 times the WHO limit) on Diwali is bound to affect sensitive groups of the exposed population. Concentrations of Ba, K, Sr and Na increased by factors of 264, 18, 15 and 5, respectively, commensurate with the abundant use of these metals in pyrotechnic compositions. Very high concentration of Ba in atmospheric aerosol (mean 16.85 μg m⁻³) on Diwali is particularly of concern from the health effects point of view. Fire-

work aerosol contributed 23–33% to the ambient aerosol loads on Diwali. Metals having primarily a vehicular and industrial origin (Zn, Cr, V and Ni) showed lower abundances on Diwali, presumably due to lower traffic and industrial activities. The firework event was also characterized by an increase in the EC levels by a factor of 4.3, which agrees well with previous studies. OC levels were higher on post-Diwali compared to Diwali, which may be due to secondary transformation of pollutant gases released during firework burning under favourable meteorological conditions. We observed significantly low PAH levels on Diwali, and thereby confirm that fireworks are not major sources of particulate PAHs. Instead, PAH levels correlated well with the traffic trend during Diwali, indicating its major source as vehicular emissions. The analysis of molecular diagnostic ratios corroborated this argument and identified vehicular emissions and coal combustion as predominant sources of atmospheric PAHs. It was estimated that chronic exposure to Diwali pollution is likely to cause at least a 2% increase in non-carcinogenic hazard index associated with Al, Mn and Ba in the exposed population.

Overall, we conclude that the festival of Diwali adds significantly to the existing pollution problem in Delhi, albeit for a short period of time. In general, people's perception of Diwali pollution is centered on criteria pollutants like ambient particulates, SO₂, NO_x, etc. It is, however, vitally important to characterize specific tracers emitted during firework episodes to get a better understanding of the actual scenario. Although SO₂ and NO_x levels on Diwali 2009 were well below stipulated standards [63], the present study reveals that the event generates enormous quantities of other pollutants (metals, EC, etc.) that pose a high health risk. As Clark [21] has noted, regulating or banning such events would be socially unacceptable; however, adequate knowledge of the scenario is vital to ensure that the sensitive populace takes precautionary measures.

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