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

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ABSTRACT

Ambient respirable particles (PM ≤ 10 μm, 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 (317.2–616.8 μg m^{-3}, 6–12 times the WHO standard) and massive loadings of Ba (16.8 μg m^{-3}, mean value), K (46.8 μg m^{-3}), Mg (21.3 μg m^{-3}), Al (38.4 μg m^{-3}) and EC (40.5 μg 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.

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 (°C)	Min T (°C)	Mean T (°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 Langrangian Integrated Trajectory (HYSPLIT) 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 km^2. 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 PM_{10} 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. PM_{10} was trapped on Whatman GF/A (8 in. × 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 m^3 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 Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF), S4