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Diwali Fireworks: Early Signs of Impact on PM_{10} Properties of Rural Brahmaputra Valley

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ABSTRACT

The festival of Diwali and it associated fireworks, which were not so common in the past, are slowly penetrating into rural Brahmaputra Valley. PM_{10} monitoring was done during the 2009 Diwali festivities at a rural site in the Brahamputra Valley of Northeast India. Sampling of PM_{10} was done on a 12 hourly basis for an extended period of 13 consecutive days. The mean PM_{10} concentration during the monitoring campaign was found to be 40.88 ± 19 µg/m^3 and the maximum concentration of PM_{10} was recorded on the Pre-Diwali night. Elemental and ionic constituents of PM_{10} were analyzed by ICP-OES and Ion Chromatograph (IC), respectively. The ratio of ∑anions to ∑cations was found to be 1.26 for the study period, which is indicative of a cation deficient condition. Pearson's correlation and Principal Component Analysis (PCA) were carried out to trace the impact of Diwali celebrations. In addition, the elemental enrichments due to Diwali fireworks, which we term Diwali Induced Enrichments (DIE) were calculated for the festival day samples. DIE showed marginal enrichment of elements and ions, indicating the beginning of the impact of Diwali in the rural areas of the region.

Keywords: Diwali; PM_{10}; Inorganic ions; Diwali induced enrichment.

INTRODUCTION

Fireworks are generally associated with celebrations. Such celebrations range from small local events like birthday parties, wedding ceremonies, and victory in a sports event to huge nationwide celebrations. Diwali is one such festival of India marked with lighting of lamps and celebrations with major fireworks all over the country. The fascinating characteristic of Diwali is that every household participates in bursting firecrackers, leading to emission of huge volume of aerosols into the atmosphere in one single day. With time, Diwali celebrations are growing in magnitude and scale in large cities. This trend could be explained in terms of relative affluence of the urban population in the country. There are reports of pollution reduction after implementation of emission control measures taken prior to big events such as the World Exposition 2010 (Zhang *et al.*, 2013) and the Commonwealth Games 2010 (Kaushar *et al.*, 2013). Though some success has been achieved in terms of noise reduction on implementation of noise standards for firecrackers, such strict emission control measures are not implemented in terms of Diwali celebrations in India.

Materials used in firecrackers contain chemicals and toxic substances, burning of which release toxic gases and particulate matter of fine size to the atmosphere leading to severe health and environmental hazards (Perrino *et al.*, 2011; Rao *et al.*, 2012). Literature suggests that there is a strong relationship between air pollutants like SO_2 and NO_x and numerous health effects (Curtis *et al.*, 2006) including reproductive and developmental effects such as increased risk of preterm birth (Liu *et al.*, 2003). Inhalation of smoke from fireworks may lead to acute eosinophilic pneumonia (Hirai *et al.*, 2000).

Heavy metals that are very harmful to human health are emitted in large volumes from fireworks (Yasutake and Hirayama, 1997; Ravindra *et al.*, 2003; Vecchi *et al.*, 2008). Perchlorates used in fireworks are teratogenic and can affect thyroid functions adversely (Soldin *et al.*, 2001; Saas, 2004; Mantus, 2005; Wilkin *et al.*, 2007). Visibility reduction is also an obvious effect of fireworks due to dense cloud of smoke, dispersion of which depends on favourable meteorological condition of an area (Drewnick *et al.*, 2006; Vecchi *et al.*, 2008).

There are reports of short term rise of PM_{10} loadings by many fold and elevated levels of harmful gases and elements in the atmosphere during fireworks (Kulshrestha *et al.*, 2004; Drewnick *et al.*, 2006; Barman *et al.*, 2008; Sarkar *et al.*, 2010; Chang *et al.*, 2011). Increase in carbonaceous materials (Babu and Moorthy, 2001; Wang *et al.*, 2007; Sarkar *et al.*, 2010), ionic components of particulates during fireworks are also reported (Wang *et al.*, 2007; Chang *et al.*, 2011; Perrino *et al.*, 2011; Chatterjee *et al.*, 2013). However,

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organic emission from fireworks is reported to be less when compared with other chemical species (Drewnick *et al.*, 2006; Sarkar *et al.*, 2010; Chang *et al.*, 2011). Nishanth *et al.* (2012) reported increase of PM_{10}, O_3, NO_2, NO along with various hazardous organics in the atmosphere which are released from burning of firecrackers during traditional Vishu festival of Kerala, India. There are also studies on effects of Diwali celebrations on high ground or surface ozone concentration (Attri *et al.*, 2001; Ganguli, 2009). However, all studies reported so far on Diwali fireworks are from urban centres. Diwali is also celebrated in the rural areas but with minimal fireworks, mostly restricted to lighting of lamps and sharing of traditional cakes and sweets. The effect of Diwali celebrations on rural air quality has not gained much attention despite these areas being receptors of pollutants that are emitted from city centres.

Diwali is, essentially, a festival of the 'mainland India', which has slowly spread over whole of the country in the past few decades. For over a century there have been internal migrations from 'mainland India' to the northeastern states for trade and governance carrying the festival to the region. The dimension of festivities has been growing considerably and penetrating into the local communities.

Till date there has been no study on the effect of Diwali fireworks on air quality of the Brahmaputra Valley of India. Keeping note of this and being inspired by the findings of studies from India and other countries the present study was designed to see the impact of Diwali fireworks on air quality of a rural receptor site of the Brahmaputra Valley.

In this work, PM_{10} samples of an extended festive period were chemically characterized for elements and ions. Relationships between various species were built from Pearson's correlations and multivariate analysis – Principal Component Analysis (PCA) to trace the effect of Diwali. The enrichments of elements in PM_{10} due to Diwali festivities, which we coined as Diwali Induced Enrichments (DIE), were estimated to understand the extent of the effect.

METHODS

Site and Sample Collection

The study was conducted at Tezpur University campus, a rural receptor site situated in middle Brahmaputra Valley geographically positioned around 26°37′N and 92°50′E. The site is situated at about 15 km on the east from Tezpur city's downtown area. The study area is shown in Fig. 1. Concentration and variability of aerosols in the atmosphere depend on the source strength and prevailing meteorological condition. So, windrose for the Diwali period was plotted (Fig. 2). Prevailing wind was found to be from the north with high percentage of calm (90.35%) condition.

PM_{10} sampling was carried out using a Respirable Dust Sampler (Envirotech APM 460 BL) at a height of 10 m from the ground. Whatman glass fibre filters (8" × 10" size-GF/A Schleicher & Schuell) were used for collection of PM_{10}. Diwali was celebrated on the night of October 17, 2009 and sampling protocol was started from October 11, 2009. Day and night samples (12 hourly) were collected for 13 consecutive days in a time series. A total of 26 samples of PM_{10} were collected during the monitoring campaign. For convenience samples are divided into festive days and background days. October 16–18, 2009 were chosen to be festive days and the days prior to the event and after the festive days were taken as background days.

Chemical Analysis

For elements, aliquot of PM_{10} sample was digested in 9 mL HNO_3 in a Teflon bomb at an oven temperature of 100°C for 6-hrs. The final volume of the filtered extract was made up to 20 mL and stored in pre-washed polyethylene bottles maintaining a pH of ~2. Elements were analyzed in an ICP-OES (PerkinElmer, OPTIMA-2100 DV).

For water soluble ions, aliquot of sample was soaked in ultra pure water and ultrasonicated for 20 minutes and filtered. The filtrate volume was adjusted to 20 mL in pre washed polyethylene bottles and kept at 4°C until analysis. Ions were analyzed in an Ion Chromatograph (Metrohm 882 Professional IC).

Anions were analysed by an anion column (Metrosep A Supp 5-250/4.0) with suppressor. A solution mixture of 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ was used as the eluent and the flow rate was kept at 0.7 mL/min. 50 mM H_2SO_4 was used as the regenerant in anion analysis.

Cations were analyzed by a cation column (Metrosep C 4-150/4.0). The eluent for cation analysis was prepared in ultrapure water with 1.7 mmol/L nitric acid and 0.7 mmol/L dipicolinic acid. The eluent flow rate during cation analysis was kept at 0.9 mL/min.

An inbuilt loop that measures 20 µL of sample for injection was used. Before injecting the samples in to the IC system, samples were filtered through Millipore 0.22 µm PTFE filters.

Quality Control

Whatman glass fibre filters were desiccated for 24 hours prior and after the sampling to avoid traces of moisture and attain right accuracy of measurements. To check the reproducibility, some select samples were analyzed in duplicate and the means showed a standard deviation of ± 2%. The ICP-OES was calibrated using ICP-Multi element standard solution VIII (Merck) and 2% HNO_3 (Solution-Optima Blank-Perkin Elmer Pure Plus) was used as reagent blank. To see the recovery of elements NIST SRM for Urban Particulate Matter (1648a) was used, which showed a recovery rate of 82 to 110% for the analyzed elements. For estimation of anions Multielement Ion Chromatography Anion Standard Solution (Fluka Analytical) was used to calibrate the IC. Cation standards were prepared in the laboratory with high purity reagents. Field blanks were analyzed and incorporated in the measurements. All dilutions were made in ultrapure water. Care was taken to prevent contamination of the samples. At no point sample containers were touched with bare hands to avert contamination.

RESULTS AND DISCUSSION

PM_{10}

The 12 hourly mean PM_{10} was found to be 40.88 ±

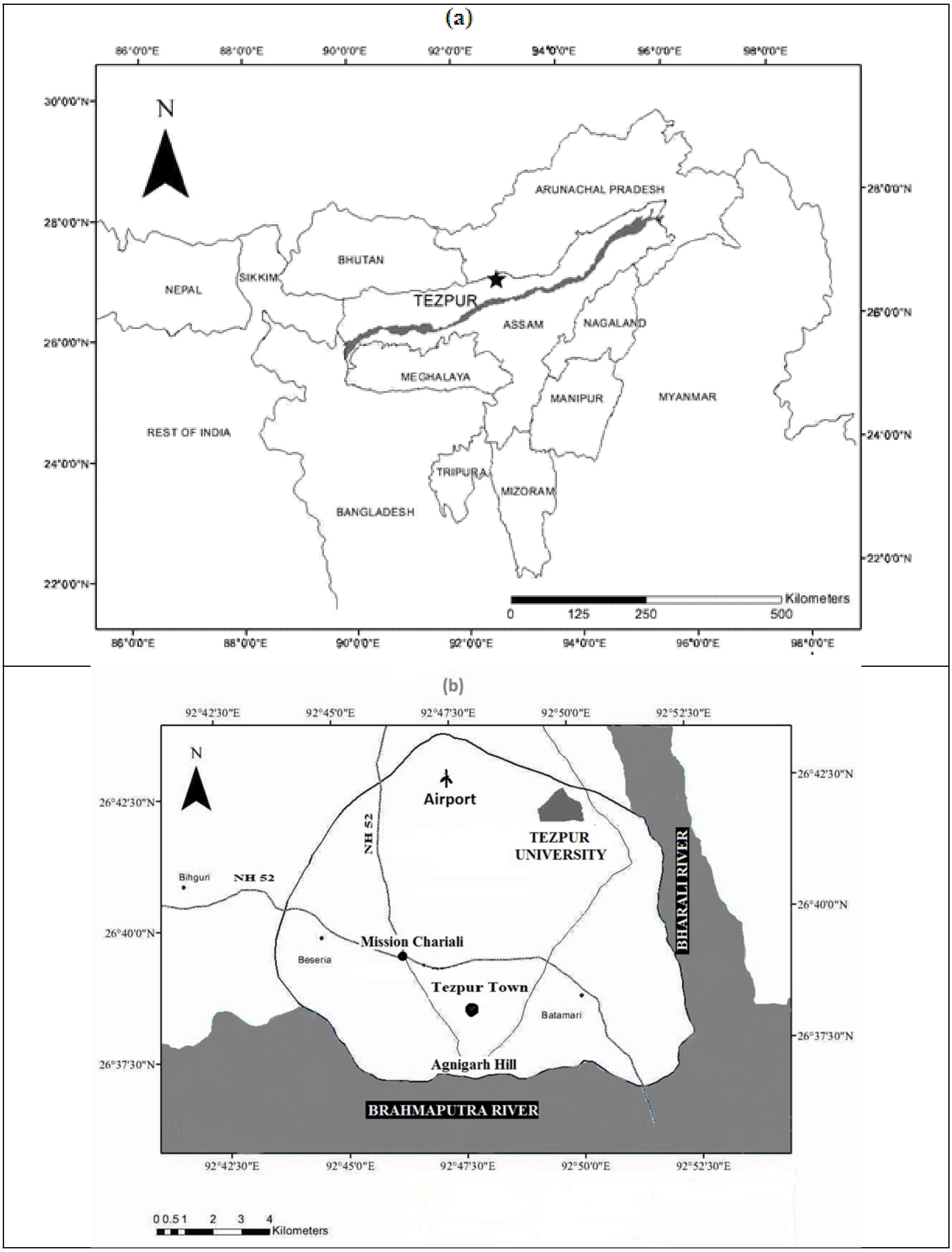

Fig. 1. Map of study area: (a) Northeast India and adjoining regions showing the position of Tezpur on the northern bank of Brahmaputra River and (b) Tezpur and surrounding areas – the sampling station, Tezpur University.

19 µg/m^3 during the monitoring period (Table 1(a)). Concentration trends of PM_{10} of the study have been illustrated in Fig. 3(a). Daytime PM_{10} was found to be the maximum on Diwali day (Fig. 3(b)), which was much on the lower side of other fireworks studies; but was comparable with the study conducted during FIFA world cup victory (Vecchi *et al.*, 2008). Nighttime PM_{10} maximum was observed on Pre-Diwali night (Fig. 3(b)), which could be due to thermal inversion at ~200 m above ground (Fig. 3(c)).

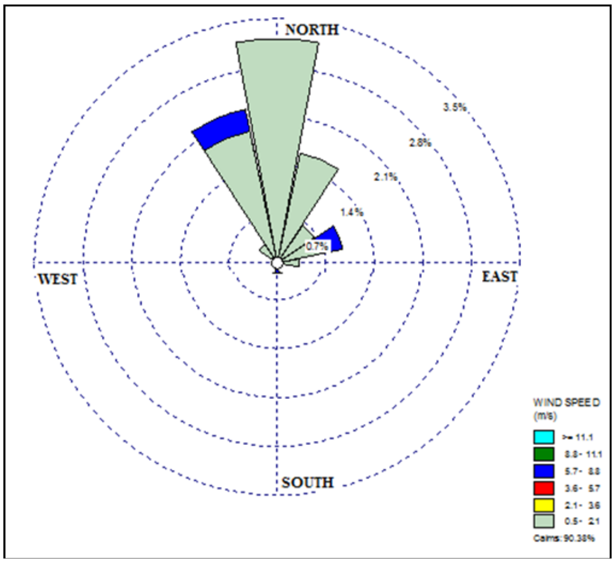

Fig. 2. Windrose of the study period.

Elements and Ions

Fireworks carry specific elemental signatures. Firecrackers contain large amount of nitrates and sulphates of lead, cadmium, potassium, ammonium and magnesium (Rao *et al.*, 2012). Wang *et al.* (2007) had used K and Cl as the elements for fireworks indicators. Sarkar *et al.* (2010) proposed Ba, K and Sr as tracers of Diwali fireworks. Various elements like Na and K as metal oxidizers, Al, Mg, Cu and Sr as color and sparkle emitters are used in firecrackers (Attri *et al.*, 2001). Ba gives green color, Ca deepens the colors and Fe helps to produce spark in fireworks (Kulshrestha *et al.*, 2004). Calcium chlorides and sulphates give rise to orange flames (Moreno *et al.*, 2007). Firecrackers lead to an increased level of these elements and ions in atmospheric particulate during fireworks.

A comparative account of elemental concentrations of PM_{10} of the present study along with fireworks studies from India and elsewhere has been put up in Table 1(a). Elemental concentrations during Diwali day were found to be above mean concentrations of the elements during the monitoring campaign, which are otherwise of much lower concentrations as compared to other reported studies on fireworks. However, Cr concentration of the Diwali day was extraordinarily high as compared to other elements, which was also much on the higher side than studies elsewhere except one reported by Sarkar *et al.* (2010) and attributed to vehicular and industrial activities. Enhanced vehicular movement on the Diwali day is an added characteristic of the roads on Diwali, which adds up to the normal levels of metals in the PM_{10}. Reports on Diwali from Delhi often have higher levels of particulate matter and heavy metals. Rajarathnam *et al.* (2011) reported PM_{10} concentrations of as high as 1200 $\mu g/m^3$ in Delhi during Diwali celebrations. When compared to such studies, increased level of elements in the present study from fireworks was found to be marginal.

Anion concentrations of PM_{10} were showing a decreasing order of $SO_4^{2-} > Cl^- > NO_3^- > F^-$ and cations in the order of $Mg^{2+} > Na^+ > Ca^{2+} > NH_4^+ > K^+$ during the study period (Table 1(b)). There are not many studies on ionic composition of PM_{10} during fireworks as compared to studies focusing on elements yet a few researchers had reported many fold increase in the levels of ions during fireworks events in comparison to normal day samples. In a study on Yanshui Lantern Festival Chang *et al.* (2011) reported 143, 69, 38, 6, 4 and 3.8 times increase for K^+, Cl^-, Mg^{2+}, Na^+, Ca^{2+} and SO_4^{2-}, respectively. However, they had not noticed any increase in the concentrations of NO_3^- and NH_4^+. Again, Chatterjee *et al.* (2013) conducted an experiment during Diwali in Kolkata and reported many fold increase in metal and ionic concentrations than normal days. They had found 1.6–6 times higher concentration of ionic species on Diwali night with remarkable increase for K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} in PM_{10}. In the present study, except for K^+ and NO_3^-, higher concentrations of ionic species were recorded on the Post-Diwali night (Figs. 4(c) and 4(d)). Nitrate is the main constituent of firecrackers. There are studies (e.g., Drewnick *et al.*, 2006; Chang *et al.*, 2011) where researchers did not notice any remarkable increase in NO_3^- and NH_4^+ concentrations during fireworks. Apparently all nitrates in fireworks quantitatively get converted into NO_x, concentration of which is often seen to rise during fireworks (Wehner *et al.*, 2000; Ravindra *et al.*, 2003; Mandal *et al.*, 2012). Contrary to this, however, many fold raise in the concentrations of SO_4^{2-}, K^+ and Cl^- during fireworks had been reported.

Comparison of the levels of ions found in the present study was made with a few studies elsewhere (Table 1(b)). Drewnick *et al.* (2006) reported much higher levels of SO_4^{2-}, NO_3^- and NH_4^+ during New Year celebrations in Mainz, Germany. Rao *et al.* (2012) also reported ionic constituents of PM_{10} collected during Diwali celebrations. They reported much higher levels of SO_4^{2-}, NO_3^- and Mg^{2+} than the levels of the present study. However, Na^+ concentration of the present study was found to be higher. As such, ionic enhancement of PM_{10} due to Diwali in the rural Brahmaputra Valley was found to be marginally above the mean concentration levels during the monitoring campaign, which was also much on the lower side compared to other studies.

Diurnal Variability

Diurnal variation of PM_{10} concentrations has been illustrated in Fig. 3(a). Nighttime PM_{10} concentrations were found to be higher than the daytime concentrations during the study period. The probable reason behind this could be the shrinkage of boundary layer towards the evening which is not conducive for particulates dispersion and dilution. During daytime, in the presence of sunlight, pollutants get more space to disperse due to elevation of boundary layer height. Also, fireworks activity is more intense during night.

Diurnal variations of elements and ions are put up in Fig. 4. All the elements manifest an increase on the Diwali night, which was, again, not seen in the case of Mn (Figs. 4(a) and 4(b)). The maximum concentration of Cl^- and SO_4^{2-} were recorded on the post-Diwali night (Fig. 4(c)). As Cl^- and SO_4^{2-} are constituents of firecracker emission, post-event maximum would mean that aged particulates laden with secondary ions were reaching the site. This observation has been further stressed upon in the later section while appreciating enrichments.

Table 1. (a) PM_{10} (μg/m^3), elemental concentrations (ng/m^3) and a comparison with studies elsewhere; (b) inorganic ionic concentration (μg/m^3) and a comparison with studies elsewhere (NA- data not available and nd-not detectable; NM-not mentioned).

(a)

Event, year	Diwali, 2009[1a]	Diwali, 2009[1b]	Diwali, 2009[2]	Diwali, 2005[3]	Diwali, 2009[4]	Lantern festival, 2006[5]	FIFA world cup, 2006[6]	Yanshui, 2008[7]
Location	Present study	Present study	Delhi, India	Lucknow, India	Delhi, India	Beijing, China	Milan, Italy	Tainan, Taiwan
PM_{10} (μg/m^3)	40.88 ± 19 (15.20–87.45)	49.83	507.2	NA	620	466.2	63.9	NA
Cr	176.18 ± 151 (8.51–660.60)	216.26	290	42.1	100	NA	11	10
Mn	106.68 ± 87 (6.70–344.94)	77.42	930	83.9	170	400	30	80
Fe	2462.08 ± 1530 (142.58–5424.98)	2353.65	6300	747.23	3900	5000	1731	410
Co	6.62 ± 8 (0.21–26.07)	4.44	NA	78.69	NA	NA	NA	NA
Ni	143.57 ± 108 (6.32–439.76)	150.94	70	41.47	13	NA	5	
Cu	19.93 ± 15 (0.26–59.74)	30.84	550	454.03	100	600	105	50
Pb	17.70 ± 5 (0.52–83.55)	12.55	360	307.54	940	1100	57	100

[1a] Present study; 12-h average of whole monitoring campaign.
[1b] Present study; 24-h average on Diwali day.
[2] Sarkar *et al.* (2010). 24-h average of three sites on Diwali day.
[3] Barman *et al.* (2008). 24-h mean of four sites on Diwali day.
[4] Perrino *et al.* (2011). 24-h average on Diwali day.
[5] Wang *et al.* (2007). 12-h night time sample, Values are approximate (ascertained from graphs).
[6] Vecchi *et al.* (2008). 4-h sampling duration, 12 am-4 am, 10-07-2006.
[7] Do *et al.* (2012). 11-h sampling duration, 8 am–7 pm, 22-02-2008.

(b)

Event, year	Diwali, 2009[1a]	Diwali, 2009[1b]	Diwali (NM)[2]	Diwali, 2009[3]	New Year, 2005[4]
Location	Present study	Present study	Nagpur, India	Delhi, India	Mainz, Germany
F^-	0.05 ± 0.02 (0.02–0.11)	0.063	NA		NA
Cl^-	6.28 ± 4.20 (1.36–21.78)	5.81	NA	16	5.13
NO_3^-	0.84 ± 0.70 (0.05–2.58)	1.23	16	11	6.48
SO_4^{2-}	8.05 ± 2.68 (2.68–13.72)	8.05	19.9	44	36.17
Na^+	4.43 ± 2.19 (0.97–11.27)	4.47	NA	1.6	NA
NH_4^+	1.13 ± 1.23 (0.01–0.92)	0.14	16.8	0.64	2.39
K^+	0.15 ± 0.20 (0.10–6.22)	1.15	26	Nd	33.15
Mg^{2+}	5.10 ± 1.55 (1.55–7.83)	5.85	29.6	5.1	NA
Ca^{2+}	1.26 ± 0.42 (0.42–2.53)	1.28	NA	6.2	NA

[1a] Present study; 12-h average of whole monitoring campaign.
[1b] Present study; 24-h average on Diwali day.
[2] Rao *et al.* (2012); 24-h average on Diwali day.
[3] Perrino *et al.* (2011); 24-h average on Diwali day.
[4] Drewnick *et al.* (2006); sampling time covers 23.45 of 31-12-04 until 8.00 0f 01-01-05.

On the other hand maximum concentration of NO_3^- was found on the Pre-Diwali night (Fig. 4(c)). NO_3^- being secondary product of NO_x emission from vehicles, enhanced vehicular traffic during the period could have brought about this change. F^- levels in the PM_{10} were quite low and consistent yet a marginal rise was observed on the Diwali day. F^- is often considered to be a constituent of emission from coal combustion. Brick kilns which are coal fed in nearby localities could be the likely source of F^- (Mouli *et al.*, 2006; Salve *et al.*, 2007).

Among cations, maximum concentrations were recorded on the Post-Diwali night for Na^+, NH_4^+, Ca^{2+} and Mg^{2+} (Fig. 4(d)). On the Diwali night, K^+, an important tracer of firework, was found to be maximum. When concentrations

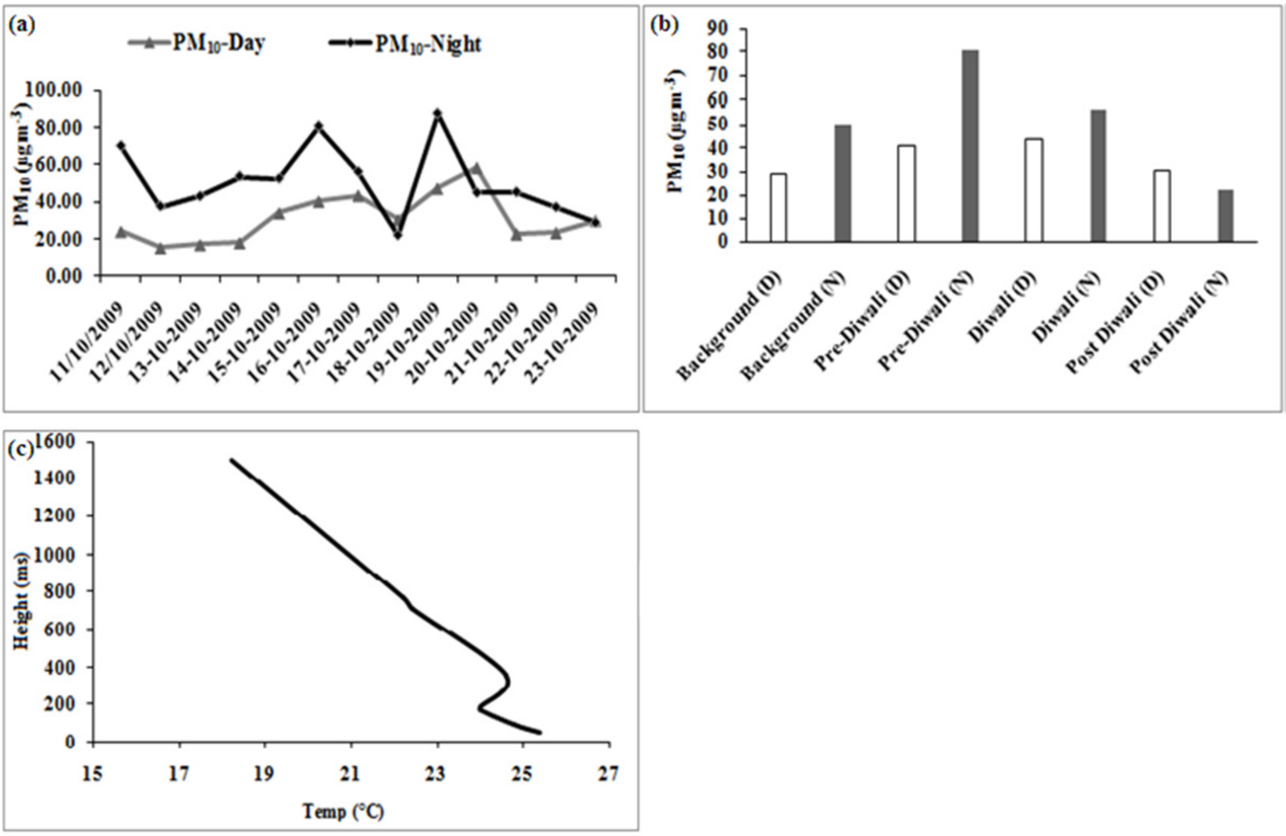

Fig. 3. PM_{10} trends and atmospheric condition. (a) Concentration of PM_{10} during the monitoring period (b) Diurnal variation of PM_{10} during the festive days [D~Day and N~Night] (c) Thermal inversion prevalent at about 200 m above ground on Pre-Diwali (profile computed from the free temperature database of Department of Atmospheric Science, University of Wyoming of the nearest station).

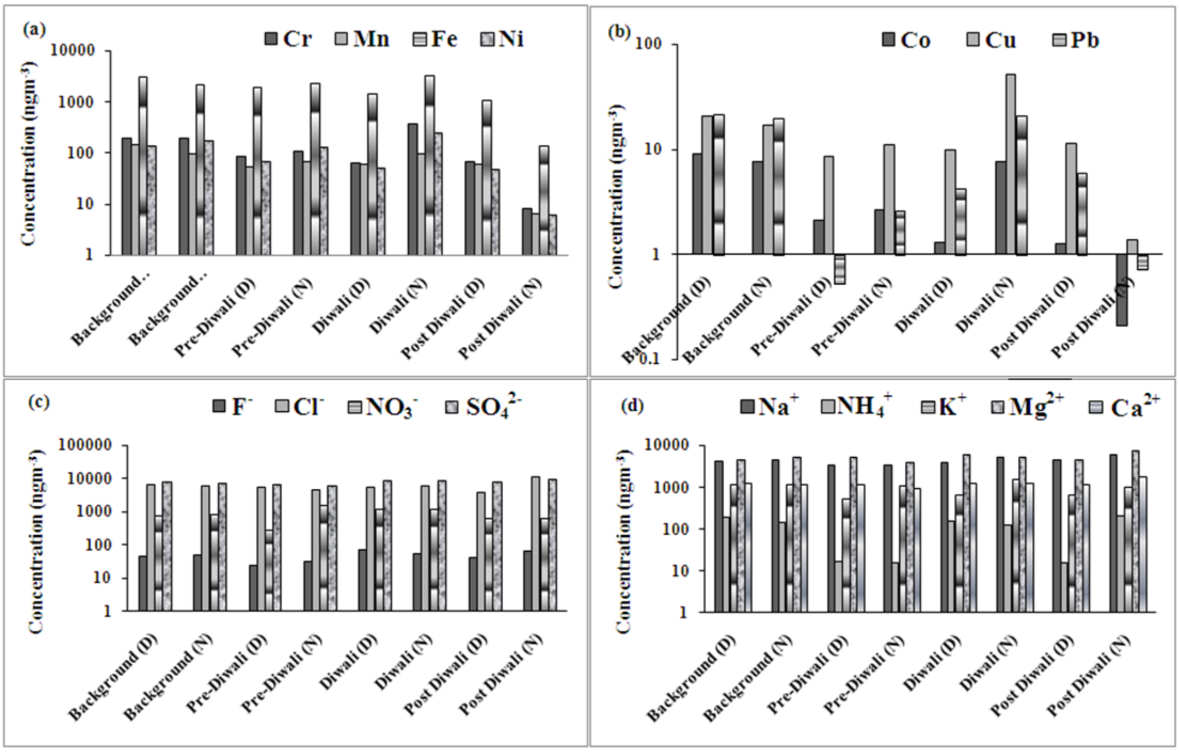

Fig. 4. Diurnal variations during the study period: (a) and (b) – elements; (c) anions and (d) cations (D~Day and N~Night).

of the ions for the entire monitoring campaign and the concentrations during festive days were compared, it was found that there was only marginal increase of ions. Marginal increase of elemental and ionic concentrations indicated the beginning of the effect of Diwali on PM_{10} in the Brahmaputra Valley.

Probable Sources and Effects of Diwali

Ionic Ratios

The calculated ratio of ∑anions to ∑cations for the study period was found to be 1.26, which was indicative of a cation deficient condition. This would mean that either all the contributing cations were not estimated in the study or, on the other hand, the atmosphere was cation deficient indicating probability of acid rain in this region. A strong correlation (R^2 = 0.89) between anionic and cationic components of PM_{10} was, of course, found (Fig. 5), but the slope was less than unity indicating for cation deficiency in PM_{10} samples.

Sulphur and nitrogen in the atmosphere originate from both stationary like and mobile sources. Arimoto *et al.* (1996) used the mass ratio of $[NO_3^-]/[SO_4^{2-}]$ as an indicator of relative importance of stationary versus mobile sources of sulphur and nitrogen in the atmosphere. High $[NO_3^-]/[SO_4^{2-}]$ mass ratios indicate the predominance of mobile source over stationary source of pollutants. In the present study, this ratio was found to be 0.10 indicating of stationary sources to be dominant for nitrate and sulphate. Diwali and coal fed brick kilns are two main stationary sources what would have impact on the PM_{10} properties, like the concentrations of NO_3^- and SO_4^{2-} during the study period.

Inter Species Correlations

Pearson's correlations were built to find associations between chemical species (Table 2(a)). In principle, the chemical species pairs having good significant correlations are assumed to have come from similar sources, or having similar chemical behaviour. Good significant correlations were obtained between element pairs Cr and Fe (r = 0.52), Cr and Ni (r = 0.60), Cr and Pb (r = 0.58), Co and Pb (r = 0.73), Mn and Pb (r = 0.66) and Fe and Pb (r = 0.65) at a significant level of $p < 0.01$.

Elements of crustal origin, Mn and Fe showed a good correlation with Pb which could mean that the source of Pb could be from resuspended soil/dust. Vehicular Pb has been phased out in India over a decade ago. It was interesting to note that good correlations existed between Mn and Co (r = 0.92; $p < 0.01$) and Fe and Co (r = 0.88; $p < 0.01$) indicating probable source of Co to be crustal.

F^- was showing good correlations with Cl^- (r = 0.66), Na^+ (r = 0.67), K^+ (r = 0.52), NH_4^+ (r = 0.60) and Ca^{2+} (r = 0.65) and Cl^- with all cations except Mg^{2+}. These relationships could indicate vegetation/biomass burning and, as such, use of biomass as fuel in the kitchens is a common practice in the rural areas of this region (e.g., Li *et al.*, 2003; Sillapapiromsuk *et al.*, 2013).

Good correlation between SO_4^{2-} and NO_3^- (r = 0.65; $p < 0.01$) was also found, which could indicate their similar chemistry of formation as both of them originate as secondary product in the atmosphere. Na^+ was well correlated with Mg^{2+} and Ca^{2+}. Mg^{2+} and Ca^{2+} are known constituents of mineral dust and, interestingly, SO_4^{2-} was showing better correlation with Na^+ (r = 0.72), Mg^{2+} (r = 0.65) and Ca^{2+} (r = 0.67) at a significant level of $p < 0.01$ than with NH_4^+ (0.41; $p < 0.05$). This could explain that in neutralization of SO_2 crustal materials played a greater role than NH_4^+. Similarly, NO_3^- was correlated with Mg^{2+} (r = 0.43; $p < 0.05$) indicating neutralization by cations of mineral dust.

A varied relationship was found when Pearson's correlations were calculated for the festive days only viz. Pre-Diwali, Diwali and Post-Diwali days (Table 2(b)). All the elements were showing good inter element correlations. Similarly, most of the ionic species especially Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} well correlated with one another. These chemical species are important constituents of fireworks (Attri *et al.*, 2001; Kulshreshtha *et al.*, 2004; Moreno *et al.*, 2007; Wang *et al.*, 2007; Sarkar *et al.*, 2010). This could explain that the effect of Diwali could be traced; however, for a very short duration.

Principal Component Analysis (PCA)

PCA was executed on normalized data to find factors that could identify contributing sources of particulates for the entire monitoring campaign and for the festive days separately. By extracting the eigenvalues and eigenvectors

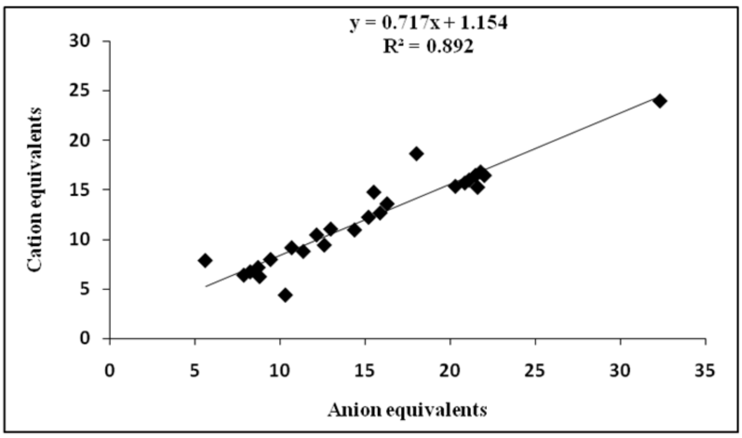

Fig. 5. Correlation between anion and cation equivalents of PM_{10}.

Table 2. Pearson's correlations of elemental and inorganic ionic species of PM_{10}: (a) entire monitoring period (n = 26); (b) festive days (n = 6).

(a)

	Cr	Mn	Fe	Co	Ni	Cu	Pb	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}
Cr	1.00															
Mn	0.16	1.00														
Fe	0.52**	0.86**	1.00													
Co	0.25	0.92**	0.88**	1.00												
Ni	0.60**	0.30	0.52**	0.46*	1.00											
Cu	0.41*	–0.22	0.09	–0.23	0.29	1.00										
Pb	0.58**	0.66**	0.65**	0.73**	0.40*	–0.25	1.00									
F^-	–0.05	–0.17	–0.28	–0.14	–0.11	–0.04	0.08	1.00								
Cl^-	–0.11	–0.32	–0.39	–0.29	–0.22	–0.08	–0.05	0.66**	1.00							
NO_3^-	–0.12	–0.30	–0.28	–0.35	–0.15	0.35	–0.36	0.03	–0.03	1.00						
SO_4^{2-}	–0.18	–0.41*	–0.48*	–0.43	–0.33	0.23	–0.25	0.35	0.46*	0.65**	1.00					
Na^+	–0.30	–0.42*	–0.55*	–0.42	–0.30	0.05	–0.25	0.67**	0.88**	0.29	0.72**	1.00				
K^+	–0.25	–0.35	–0.44*	–0.40	–0.33	0.04	–0.31	0.52**	0.75**	0.32	0.55**	0.83**	1.00			
NH_4^+	–0.23	–0.33	–0.40	–0.36	–0.24	0.03	–0.28	0.60**	0.83**	0.12	0.41*	0.87**	0.92**	1.00		
Mg^{2+}	–0.15	–0.46*	–0.53**	–0.41	–0.19	0.18	–0.19	0.48*	0.34	0.43*	0.65**	0.49*	0.16	0.08	1.00	
Ca^{2+}	–0.27	–0.44*	–0.55*	–0.41	–0.33	0.01	–0.19	0.65**	0.92**	0.15	0.67**	0.94**	0.74**	0.76**	0.57**	1.00

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

(b)

	Cr	Mn	Fe	Co	Ni	Cu	Pb	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}
Cr	1.00															
Mn	0.80	1.00														
Fe	0.86*	0.91*	1.00													
Co	0.97**	0.84*	0.93**	1.00												
Ni	0.99**	0.81	0.89*	0.98**	1.00											
Cu	0.99**	0.79	0.80	0.93**	0.98**	1.00										
Pb	0.95**	0.74	0.68	0.86*	0.92*	0.98**	1.00									
F^-	–0.04	–0.22	–0.36	–0.16	–0.09	0.06	0.20	1.00								
Cl^-	–0.22	–0.74	–0.54	–0.30	–0.23	–0.20	–0.16	0.47	1.00							
NO_3^-	0.33	0.46	0.43	0.49	0.35	0.31	0.31	0.24	–0.20	1.00						
SO_4^{2-}	0.07	–0.28	–0.43	–0.13	0.00	0.19	0.35	0.82*	0.58	–0.12	1.00					
Na^+	0.11	–0.38	–0.41	–0.06	0.05	0.19	0.32	0.58	0.74	–0.19	0.90*	1.00				
K^+	–0.02	–0.43	–0.38	–0.15	–0.06	0.05	0.13	0.89*	0.80	0.09	0.79	0.71	1.00			
NH_4^+	0.77	0.38	0.51	0.78	0.77	0.76	0.76	0.16	0.28	0.50	0.28	0.46	0.31	1.00		
Mg_2^+	–0.27	–0.70	–0.61	–0.43	–0.31	–0.22	–0.15	0.72	0.88*	–0.29	0.72	0.68	0.91*	0.03	1.00	
Ca_2^+	–0.22	–0.73	–0.61	–0.38	–0.25	–0.17	–0.10	0.55	0.95**	–0.41	0.73	0.82*	0.81	0.16	0.94**	1.00

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

Table 3. Principal Component Analysis of PM_{10} attributes during the monitoring period (n = 26).

	1	2	3	4	5
Cr	–0.10	0.22	**0.88**	–0.13	0.03
Mn	–0.20	**0.93**	–0.03	–0.06	–0.21
Fe	–0.28	**0.80**	0.37	–0.05	–0.30
Co	–0.20	**0.93**	0.08	–0.15	–0.11
Ni	–0.16	0.31	**0.72**	–0.15	–0.07
Cu	0.00	–0.15	**0.75**	**0.45**	0.00
Pb	–0.03	**0.78**	0.30	–0.31	0.23
F^-	**0.71**	0.04	0.02	–0.09	**0.46**
Cl^-	**0.93**	–0.11	–0.03	–0.11	0.19
NO_3^-	0.03	–0.19	0.00	**0.91**	0.11
SO_4^{2-}	**0.45**	–0.18	–0.09	**0.67**	**0.42**
Na^+	**0.89**	–0.20	–0.13	0.24	0.23
K^+	**0.87**	–0.20	–0.14	0.28	–0.18
NH_4^+	**0.94**	–0.20	–0.07	0.07	–0.20
Mg^{2+}	0.19	–0.27	–0.02	0.32	**0.86**
Ca^{2+}	**0.85**	–0.21	–0.12	0.10	0.36
Eigenvalues	4.97	3.47	2.15	1.91	1.62
% of variance	31.08	21.69	13.42	11.92	10.13
Cumulative %	31.08	52.77	66.19	78.11	88.24
Possible sources	Mix source	Soil	Fossil fuel combustion	Brick kilns & soil	Brick kilns & soil

from the correlation matrix, principal factors with eigenvalues > 1 were chosen. The initial eigenvalues extracted were 'cleaned up' by means of Varimax rotation with Keiser Normalization.

PCA of the chemical species did exhibit 5 components explaining 88.24% of variance (Table 3). PC1 accounted for 31% of total variance and was loaded with F^-, Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+ and Ca^{2+} indicating a mix source (*soil, biomass burning, livestock and agricultural activities, fireworks*). Mn, Fe, Co and Pb were placed in PC2, explaining 21.69% of variance. Higher loadings of Co, Mn, Fe and Pb explain that resuspension of soil as mineral dust from agricultural land and loosely bound sediment of riverine areas could have sufficient influence on the PM_{10} loading.

PC3 has high loadings of Cr, Ni and Cu, explaining 13.42% of variance, which could be attributed to fuel combustion (Swaine, 2000; Allen *et al.*, 2001). PC4 was loaded with Cu, NO_3^- and SO_4^{2-} explaining 11.92% of variance and PC5 with F^-, SO_4^{2-} and Mg^{2+} explaining 10.13% of variance. As discussed, NO_3^- and SO_4^{2-} could be mainly from stationary sources. This indicates brick kilns and soil as the possible sources of these chemical species. F^- may be attributed to coal fed brick kilns and Mg from soil (Mouli *et al.*, 2006; Salve *et al.*, 2007). Some NO_3^- and SO_4^{2-} could also have come as contributions from soil (Wang *et al.*, 2003; Tare *et al.*, 2006).

Thus, PCA did not show the influence of Diwali explicitly as did for other sources.

Diwali Induced Enrichment (DIE)

For better understanding of incremental effect of Diwali, Diwali Induced Enrichments (DIEs) were calculated (Table 4). DIE for each chemical species was calculated as $[X_{ij}/\overline{X_i}]$, where X_{ij} is the mass concentration for i^{th} species (i = 1–16) in j^{th} sample (j = 1–6; only festive days) and $\overline{X_i}$ is the mean mass concentration. We did not incorporate the data beyond Post-Diwali days for calculation of DIE as Agarwal (2011) proved that the atmospheric residence time of fireworks particulates is just 1.5 days. Also, Pearson's correlations and PCA did not reveal any effect of Diwali for a longer period. To avoid bias $\overline{X_i}$ was calculated separately for day and night samples. $\overline{X_i}$ was calculated for an element present in first two and last two day/night samples of the time series assuming effects of firework to be least in these samples. DIE > 1 was assumed to the indication of Diwali impact.

DIE > 1 was observed for Cr, Fe, Ni, Cu and Pb on the Diwali night. For ions, NO_3^- had a DIE value of 1.91 on Pre-Diwali night and 1.41 on Diwali Day. K^+ had maximum DIE on Diwali night (1.41). However, Cl^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+} had DIE of 1.90, 1.23, 1.28, 1.4, 1.48 and 1.52, respectively on Post-Diwali night. Tandon *et al.* (2008) had also calculated Enrichment Factor (EFi) for different chemical species during Diwali study in Delhi. They had reported 1–58 times enrichment of various elements. In the present context, the enrichments were just marginally greater than 1 indicating that effect of Diwali in the rural areas of Brahmaputra Valley was weak and short-lived.

CONCLUSIONS

The study revealed that the impact of Diwali fireworks on PM_{10} characteristics in the rural Brahmaputra Valley could be traced; however, the impact could be noticed for a very short period with very marginal increase of the associated chemical species - elements and ions. The incremental effect of Diwali was also very marginal as compared to the events in the 'mainland India'. The study also revealed that PM_{10} in the atmosphere of rural Brahmaputra Valley could

Table 4. Diwali Induced Enrichment (DIE) – DIE > 1 are in bold; D~Day and N~Night.

	Cr	Mn	Fe	Co	Ni	Cu	Pb	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Pre-Diwali (D)	0.52	0.59	0.93	0.31	0.40	0.50	0.04	0.53	0.98	0.31	0.86	0.77	0.11	0.47	**1.03**	**1.07**
Pre-Diwali (N)	0.55	0.71	**1.04**	0.35	0.73	0.66	0.13	0.62	0.78	**1.91**	0.80	0.73	0.11	0.96	0.75	0.80
Diwali (D)	0.39	0.67	0.68	0.20	0.30	0.58	0.32	**1.60**	0.99	**1.41**	**1.12**	0.89	0.98	0.55	**1.23**	**1.07**
Diwali (N)	**1.91**	0.99	**1.45**	0.99	**1.39**	**3.07**	**1.06**	**1.08**	**1.03**	**1.41**	**1.14**	**1.11**	0.84	**1.41**	**1.03**	**1.08**
Post-Diwali (D)	0.42	0.68	0.52	0.19	0.28	0.67	0.45	0.92	0.71	0.72	**1.11**	**1.05**	0.10	0.58	0.90	1.00
Post- Diwali (N)	0.04	0.07	0.06	0.03	0.04	0.08	0.04	**1.29**	**1.90**	0.80	**1.23**	**1.28**	**1.40**	0.91	**1.48**	**1.52**

be cation deficient which could also mean acidic nature of the particulates. As mentioned by Ocskay *et al.* (2005), water soluble fraction of particulate matter determines their bioavailability, their effect on human health, and their role in the radiative forcing it is imminent to have more studies on ionic constituents of aerosol together with precipitation chemistry of the region to have better understanding of these effects.

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REFERENCES

Agrawal, A., Upadhyay, V.K. and Sachdeva, K. (2011). Study of Aerosol Behavior on the Basis of Morphological Characteristics during Festival Events in India. *Atmos. Environ.* 45: 3640–3644.

Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M. and Greenwood, J.C. (2001). Size Distributions of Trace Metals in Atmospheric Aerosols in the United Kingdom. *Atmos. Environ.* 35: 4581–4591.

Arimoto, R., Duce, R.A., Savoie, D.L., Prospero, J.M., Talbot, R., Cullen, J.D., Tomza, U., Lewis, N.F. and Ray, B.J. (1996). Relationships among Aerosol Constituents from Asia and the North Pacific during PEM-West A. *J. Geophys. Res.* 101: 2011–2023.

Attri, A.K., Kumar, U. and Jain, V.K. (2001). Formation of Ozone by Fireworks. *Nature* 411: 1015.

Babu, S.S. and Moorthy, K.K. (2001). Anthropogenic Impact on Aerosol Black Carbon Mass Concentration at a Tropical Coastal Station: A Case Study. *Curr. Sci.* 81: 1208–1214.

Barman, S.C., Singh, R., Negi, M.P. and Bhargava, S.K. (2008). Ambient Air Quality of Lucknow City (India) during Use of Fireworks on Diwali Festival. *Environ. Monit. Assess.* 137: 495–504.

Chang, S.C., Lin, T.H., Young, C.Y. and Lee, C.T. (2011). The Impact of Ground-level Fireworks (13 km long) Display on the Air Quality during the Traditional Yanshui Lantern Festival in Taiwan. *Environ. Monit. Assess.* 172: 463–479.

Chatterjee, A., Sarkar, C., Adak, A., Mukherjee, U., Ghosh, S.K., Raha, S. (2013). Ambient Air Quality during Diwali Festival over Kolkata – A Mega-City in India. *Aerosol Air Qual. Res.* 13: 1133–1144.

Curtis, L., Rea, W., Smith-Willis, P., Fenyves, E. and Pan, Y. (2006). Adverse Health Effects of Outdoor Air Pollutants. *Environ. Int.* 32: 815–830.

Do, T., Wang, C., Hsieh, Y. and Hsieh, H. (2012). Metals Present in Ambient Air before and after a Firework Festival in Yanshui, Tainan, Taiwan. *Aerosol Air Qual. Res.* 12: 981–993.

Drewnick, F., Hings, S.S., Curtius, J., Eerdekens, G. and Williams, J. (2006). Measurement of Fine Particulate and Gas-Phase Species during the New Year’s Fireworks 2005 in Mainz, Germany. *Atmos. Environ.* 40: 4316–4327.

Ganguli, N.D. (2009). Surface Ozone Pollution during the Festival of Diwali, New Delhi, India. *Earth Sci. India* 2: 224–229.

Hirai, K., Yamazaki, Y., Okada, K., Furuta, S. and Kubo, K. (2000). Acute Eosinophilic Pneumonia Associated with Smoke from Fireworks. *Int. Med.* 39: 401–403.

Kaushar, A., Chate, D., Beig, G., Srinivas, R., Parkhi, N., Satpute, T., Sahu, S., Ghude, S., Kulkarni, S., Surendran, D., Trimbake, H. and Trivedi, D.K. (2013). Spatio-Temporal Variation and Deposition of Fine and Coarse Particles during the Commonwealth Games in Delhi. *Aerosol Air Qual. Res.* 13: 748–755.

Kulshrestha, U.C., Rao, T.N., Azhaguvel, S. and Kulshrestha, M.J. (2004). Emissions and Accumulation of Metals in the Atmosphere due to Crackers and Sparkles during Diwali Festival in India. *Atmos. Environ.* 38: 4421–4425.

Li, J., Pósfai, M., Hobbs, P., Buseck, P.R. (2003). Individual Aerosol Particles from Biomass Burning in Southern Africa 2. Compositions and Aging of Inorganic Particles. *J. Geophys. Res.* 108: 8484.

Liu, S., Krewski, D., Shi, Y., Chen, Y. and Burnett, R.T. (2003). Association between Gaseous Ambient Air Pollutants and Adverse Pregnancy Outcomes in Vancouver, Canada. *Environ. Health Perspect.* 111: 1773–1778.

Mandal, P., Prakash, M. and Bassin, J.K. (2012). Impact of Diwali Celebrations on Urban Air and Noise Quality in

Delhi City, India. *Environ. Monit. Assess.* 184: 209–215.

Mantus, E.K. (2005). Health Implications of Perchlorate Ingestion, In *Preprints of Extended Abstracts Presented at the ACS National Meeting*, Vol. 45, American Chemical Society, Division of Environmental Chemistry, p. 873.

Moreno, T., Querol, X., Alastuey, A., Minguillón, M.C., Pey, J., Rodriguez, S., Miró, J.V., Felis, C. and Gibbons, W. (2007). Recreational Atmospheric Pollution Episodes: Inhalable Metalliferous Particles from Firework Displays. *Atmos. Environ.* 41: 913–922.

Mouli, P.C., Mohan, S.V. and Reddy, S.J. (2006). Chemical Composition of Atmospheric Aerosol (PM_{10}) at a Semi-arid Urban Site: Influence of Terrestrial Sources. *Environ. Monit. Assess.* 117: 291–305.

Nishanth, T., Praseed, K.M., Rathnakaran, K., Kumar, M.K.S., Krishna, R.R. and Valsaraj, K.T. (2012). Atmospheric Pollution in a Semi-urban, Coastal Region in India following Festival Seasons. *Atmos. Environ.* 47: 295–306.

Ocksay, R., Salma, I., Wang, W. and Maenhaut, W. (2006). Characterization and Diurnal Variation of Size-resolved Inorganic Water-soluble Ions at a Rural Background Site. *J. Environ. Monit.* 8: 300–306.

Perrino, C., Tiwari, S., Catrambone, M., Torre, S.D., Rantica, E. and Canepari, S. (2011). Chemical Characterization of Atmospheric PM in Delhi, India, during Different Periods of Year including Diwali Festival. *Atmos. Pollut. Res.* 2: 418–427.

Rajarathnam, U., Seghal, M, Nairy, S, Patnayak, R.C., Chhabra, S.K., Kilnani and Santhosh Ragavan, K.V. (2011). Part 2. Time-series Study on Air Pollution and Mortality in Delhi. In *Public Health and Air Pollution in Asia (PAPA): Coordinated Studies of Short-Term Exposure to Air Pollution and Daily Mortality in Two Indian Cities*, Research Report 157. Health Effects Institute, Boston, MA.

Rao, P.S., Gajghate, D.G., Gavane, A.G., Suryawanshi, P., Chauhan, C., Mishra, S., Gupta, N., Rao, C.V.C. and Wate, S.R. (2012). Air Quality Status during Diwali Festival of India: A Case Study. *Bull. Environ. Contam. Toxicol.* 89: 376–379.

Ravindra, K., Mor, S. and Kaushik, C.P. (2003). Short-term Variation in Air Quality Associated with Firework Events: A Case Study. *J. Environ. Monit.* 5: 260–264.

Saas, J. (2004). U.S. Department of Defense and White House Working Together to Avoid Cleanup and Liability for Perchlorate Pollution. *Int. J. Occup. Environ. Health* 10: 330–334.

Salve, P.R., Krupadam, R.J. and Wate, S.R. (2007). A Study on Major Inorganic Ion Composition of Atmospheric Aerosols. *J. Environ. Biol.* 28: 241–244.

Sarkar, S., Khillare P.S., Jyethi, D.S., Hasan, A. and Parween, M. (2010). Chemical Speciation of Respirable Suspended Particulate Matter during a Major Firework Festival in India. *J. Hazard. Mater.* 184: 321–330.

Sillapapiromsuk, S., Chantara, S., Tengjaroenkul, U., Prasitwattanaseree, S. and Prapamontol, T. (2013). Determination of PM_{10} and Its Ion Composition Emitted from Biomass Burning in the Chamber for Estimation of Open Burning Emissions. *Chemosphere* 93: 1912–1919.

Soldin, O.P., Braverman, L.E. and Lamm, S.H. (2001). Perchlorate Clinical Pharmacology and Human Health: A Review. *Ther. Drug Monit.* 23: 316–331.

Swaine, D.J. (2000). Why Trace Elements are Important. *Fuel Process. Technol.* 65–66: 21–33.

Tandon, A., Yadav, S. and Attri, A.K. (2008). City-wide Sweeping a Source For Respirable Particulate Matter in the Atmosphere. *Atmos. Environ.* 42: 1064–1069.

Tare, V., Tripathi, S.N., Chinnam, N., Srivastava, A.K., Dey, S., Manar, M., Kanawade, V.P., Agarwal, A., Kishore, S., Lal, R.B. and Sharma, M. (2006). Measurements of Atmospheric Parameters during Indian Space Research Organization Geosphere Biosphere Program Land Campaign II at a Typical Location in the Ganga Basin: 2. Chemical properties. *J. Geophys. Res.* 111: D23210.

Vecchi, R., Bernardoni, V., Cricchio, D., D'Alessandro, A., Fermo, P., Lucarelli, F., Nava, S., Piazzalunga, A. and Valli, G. (2008). The Impact of Fireworks on Air Particles. *Atmos. Environ.* 42: 1121–1132.

Wang, G., Wang, H., Yu, Y., Gao, S., Feng, J., Gao, S. and Wang, L. (2003). Chemical Characterization of Water-soluble Components on PM_{10} and $PM_{2.5}$ Atmospheric Aerosols in Five Locations of Nanjing, China. *Atmos. Environ.* 37: 2893–2902.

Wang, Y., Zhuang, G., Xu, C. and An, Z. (2007). The Air Pollution Caused by the Burning of Fireworks during the Lantern Festival in Beijing. *Atmos. Environ.* 41: 417–431.

Wehner, B., Wiedensohler, A. and Heintzenberg, J. (2000). Submicrometer Aerosol Size Distributions and Mass Concentration of the Millenium Fireworks 2000 in Leipzig, Germany. *J. Aerosol Sci.* 31: 1489–1493.

Wilkin, R.T., Fine, D.D. and Burnett, N.G. (2007). Perchlorate Behavior in a Municipal Lake Following Fireworks Displays. *Environ. Sci. Technol.* 41: 3966–3971.

Yasutake, A. and Hirayama, K. (1997). Animal Models, In *Handbook of Human Toxicology*, Massaro, E.J. (Ed.), Boca Raton, CRC, New York.

Zhang, M., Chen, J., Chen, X., Cheng, T., Zhang, Y., Zhang, H., Ding, A., Wang, M. and Mellouki, A. (2013). Urban Aerosol Characteristics during the World Expo 2010 in Shanghai. *Aerosol Air Qual. Res.* 13: 36–48.

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