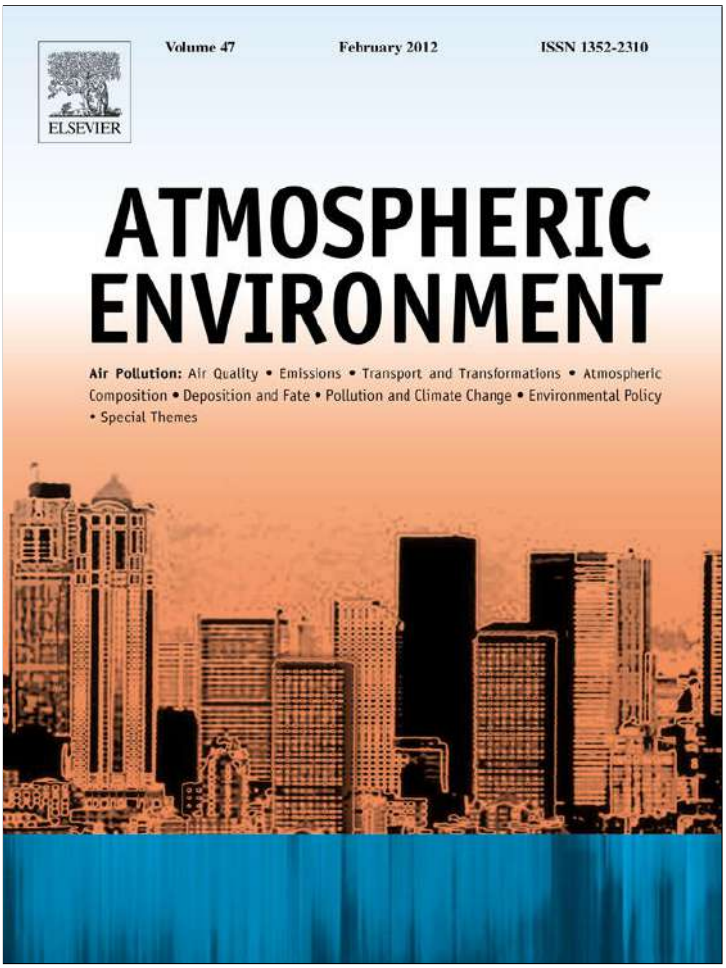

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Atmospheric pollution in a semi-urban, coastal region in India following festival seasons

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ABSTRACT

The traditional Vishu festival in the state of Kerala in South India is celebrated in April with extensive coordinated fireworks display. The influence of these celebrations on the immediate and long-term air quality and impact on the health and well being of the public needs research. The combustion clouds contain harmful fumes (sulfur dioxide, oxides of nitrogen) and particulate matter released at the surface. This study is focused on the influence of fireworks on the air quality at Kannur, India, during Vishu in April 2010 and 2011. Elevated concentrations of various air pollutants such as O_3, NO_2, NO and PM_{10} were measured during the intense usage of fireworks. Surprisingly, the organic analysis of the Particulate Matter (PM) samples collected on Vishu day revealed the emission of a variety of hazardous organic compounds during the fireworks display. One of the unique observations in this work is the nighttime production of O_3 by the photodissociation of NO_2 from the flash of firecrackers. The concentration of O_3 was observed to increase two fold over the control days of observation during the same month. Moreover, the concentrations of NO_2, and PM_{10} increased by 100%. The concentration of NO was reduced by four fold during the event. A scheme based on the organic combustion from fireworks and peroxyl radical mediation is proposed for the nighttime production of ozone. The diurnal profile of all pollutants except NO showed higher concentrations starting from the Vishu eve on April 14 to Vishu day on April 15 and this pattern repeated for years 2010 and 2011. The fireworks activities have been increasing every year and generation of pollutants at their increased levels for short duration can potentially cause adverse health impacts on a regional scale in a highly populated region.

1. Introduction

India is developing fast with rapid industrialization and economic growth. It also has many regions that remain untouched by industrial developments, but rely on culture and tourism. Kerala, the southern-most state in India is an example. Kerala is a coastal state blessed with natural beauty, lush tropical vegetation and year-round moderate climate that makes it a haven for tourists. It is rich in exuberant cultural pageants and ritualistic festivals of countless sorts. This state also takes pride in its highest literacy rate and health-care affordability among all other states in the country. It is however, the most densely populated state in India. It is also recognized that the high density of population, the increased number of motor vehicles and the severe soil erosion coupled with unregulated industrial development in recent times has created ever increasing problems of air, water and soil pollution.

Air pollution is an emerging issue in the state of Kerala. After gaining independence from Great Britain in 1947, air pollution was not an issue due to the state's focus on social advances rather than industrialization. However, the recent rapid economic advances in India have led to increased economic activity in the state. Anthropogenic contributions (automobile emissions, agricultural-related emissions, wood and waste burning), biological emissions, sea spray aerosols and indoor air pollution are presently recognized as serious issues to be addressed in the region (Bency et al., 2003; Anjaneyulu et al., 2006). It is worth noting that there exists no sustained air monitoring program in the region. Apart from the general emission sources, there are also episodic emissions from various social activities relevant only to the state. One such important source is from fireworks set off all over the state during the very large number of festivals peculiar only to the state of Kerala.

Air quality deterioration resulting from intense fireworks and its impact on health has been noted by Limaye and Salvi (2010). Attri

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et al. (2001) observed that burning of fireworks could generate ozone, a strong and harmful oxidant at ground level. Increased levels of pollutants such as SO_2, NO_2, Total Suspended Particulate Matter (TSP), trace metals, aerosol black carbon, and Polycyclic Aromatic Hydrocarbons (PAH) were observed due to fireworks (Wehner et al., 2000; Barman et al., 2008; Vecchi et al., 2008; Moreno et al., 2010; Camilleri and Vella, 2010; Drewnick et al., 2006; Godri et al., 2010; Croteau et al., 2010; Godri et al., 2010; Carranza et al., 2001). Research groups from Beijing (Wang et al., 2007) and Taiwan (Chang et al., 2011) have further established a real time analysis of ambient air quality change during fireworks on Lantern days celebrated in South East Asia. In India, it has become a practice to celebrate various occasions (weddings, birthday parties, New Year, post-election/sports results, and various festivals) by setting off fireworks. Diwali is a prominent festival in North India during which extensive fireworks are displayed that influence air quality (Babu and Moorthy, 2001; Ravindra et al., 2003; Kulshrestha et al., 2004; Ganguly, 2009; Sarkar et al., 2010; Singh et al., 2010; Thakur et al., 2010; Zhang et al., 2010; Mandal et al., 2011; Kankal and Gaikwad, 2011; Majumdar and Nema, 2011 Cinzia et al., 2011).

Vishu is a major festival celebrated throughout the state of Kerala and in parts of the adjoining state of Tamil Nadu during the first day of Medam, in the Malayalam calendar, which usually falls during the months of April–May. This coincides with the beginning of the Malayalam New Year and is celebrated irrespective of caste, creed or religion throughout the State. Hindus in several parts of South India also celebrate this under various names. The celebration is extensive and culminates in fireworks overall parts of the state. Continuous fireworks are set off from 18:00–22.00 h (IST) on the eve of Vishu on April 14th and 4:00 to 6:00 h (IST) the following day, April 15th. Such continuous fireworks display over extended periods of time impairs the air quality as well as contributes to noise pollution. The consequences of such celebratory fireworks

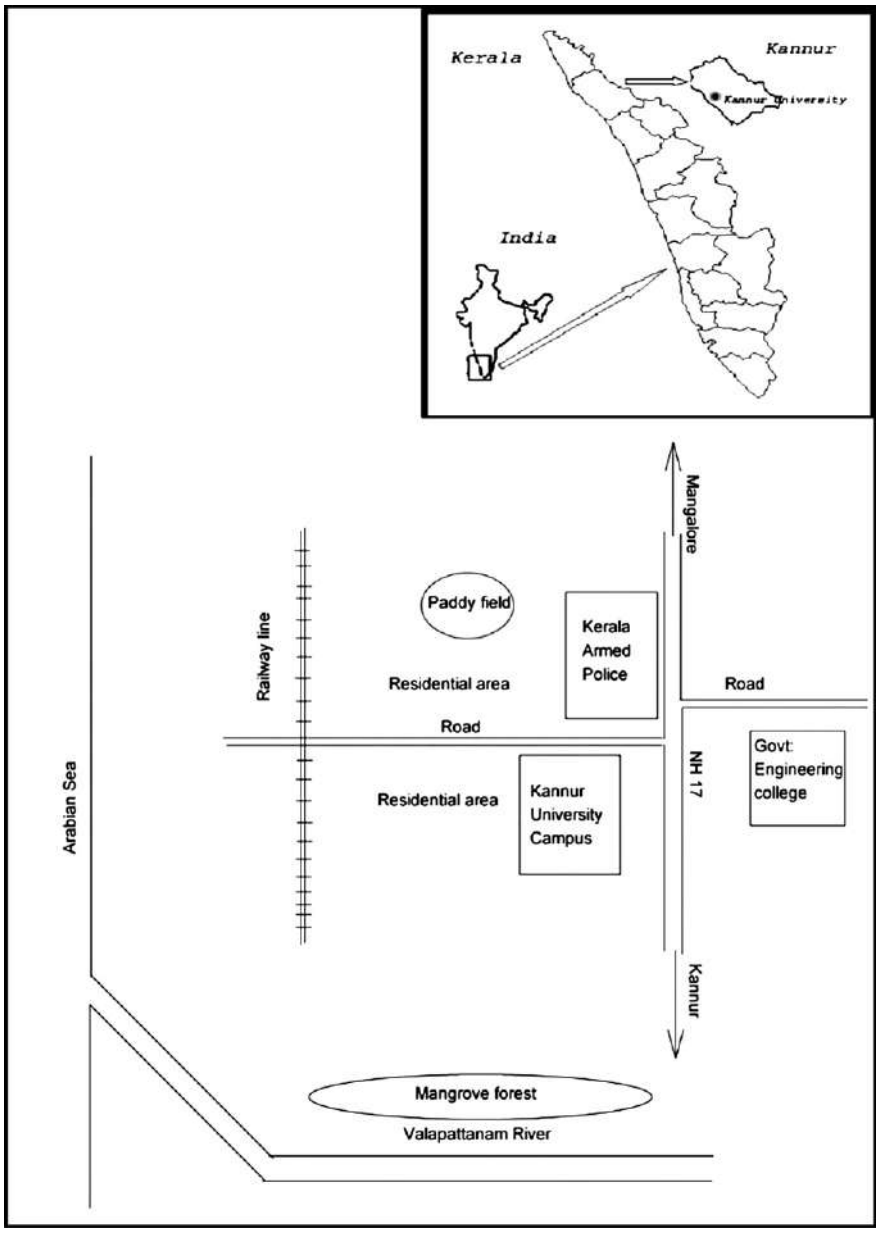

Fig. 1. Schematic layout of the observation site.

among a region with a very high population density such as Kerala need to be evaluated. Therefore, a sustained program to understand the overall air quality and potential adverse health impacts is being undertaken in which this work is the first in a series of studies.

2. Experimental

2.1. Area description and sampling site

The impact of firecrackers on the air quality over Kannur district in North Kerala was carried out at the Kannur University Campus (11.9 N, 75.4 E), situated 15 km north from Kannur town, a location lying along the coastal belt of the Arabian Sea in the west-coast region of the Indian subcontinent. This site is close to a National Highway (NH 17) and the Arabian Sea and is 5 m above mean sea level. A schematic layout of the location of Kannur University is shown in Fig. 1. The land area of Kannur District is about 3000 km^2 with an average population density of around 1000 per square kilometer. Kannur is industrially backward except for a few small scale industries like plywood, textiles, tiles and stone crushers. Kannur being one of the highly populated regions in Kerala, any significant change in the air quality can induce dramatic influence in the social picture for this region. We focused on changes in the air quality during the fireworks associated with Vishu festival on April 14th and 15th for two consecutive years, 2010 and 2011. Measurements of O_3, NO_x ($NO_2 + NO$), PM_{10}, and organic compounds were made. The meteorological parameters like temperature, relative humidity and wind speed were acquired from the local automatic weather station, which is one of the stations run by the Meteorological and Oceanographic Satellite Data Archival Centre (MOSDAC) established by the Indian Space Research Organization (ISRO).

2.2. Sampling

Air inlet sample hood is placed at a height of 10 m above the ground to collect ambient air into the respective gas analyzers. The concentrations of O_3 and NO_x were continuously monitored since 2009 November at the Kannur University Campus. O_3 and NO_x mixing ratios have been successfully measured with the aid of ground based O_3 and NO_x analyzers obtained from Environment SA, France. Ozone present in the ambient air is measured by the analyzer which is working on the principle of strong absorption of UV radiation at 253.7 nm by ozone molecules. The analyzer incorporates corrections due to changes in temperature, pressure in the absorption cell and drift in the intensity of the UV lamp. Previously we studied the solar eclipse of 2010 induced variations in the air quality over this location using this set up (Nishanth et al., 2011a, 2011b). The details of the detection method and specifications for the analyzers are described in Table 1. The NO_x analyzer is working on the principle of chemiluminescence effect produced by the oxidation of NO by O_3 molecules, which peaks at 630 nm radiation. In the present study NO_2 is measured by converting it into NO using the thermal conversion method using a heated molybdenum converter. The molybdenum converter is found to have higher sensitivity and ~100% conversion efficiency (Winer et al., 1974; Finlayson-Pitts and Pitts, 1986). It has been realized that molybdenum converter also converts other species such as Peroxy Acetyl Nitrate (PAN), Nitric acid (HNO_3) etc; however PAN is thermally unstable at temperature above 30–35 C and its concentration is may be very small at the surface level. Since NO_x analyzer does not have a blue light converter to distinguish between NO_2 present in the ambient air and NO_2 produced in the molybdenum converter by the oxidation of PAN, HNO_3 etc; NO_x represents the total NO_x measured at this site.

Table 1
Details of detection schemes of O_3 and NO_x.

Analyzer	Primary operation principle	Response time (s)	Lower detection limit (ppbv)	Zero Drift
O_3	O_3 absorption of UV radiation (253.7 nm)	30	0.4	Less than 0.5 ppb/24 h less than 1 ppb/7 days
NO_x	Chemiluminescence from the O_3–NO reaction	30	0.4	Less than 0.5 ppb/24 h less than 1 ppb/7 days

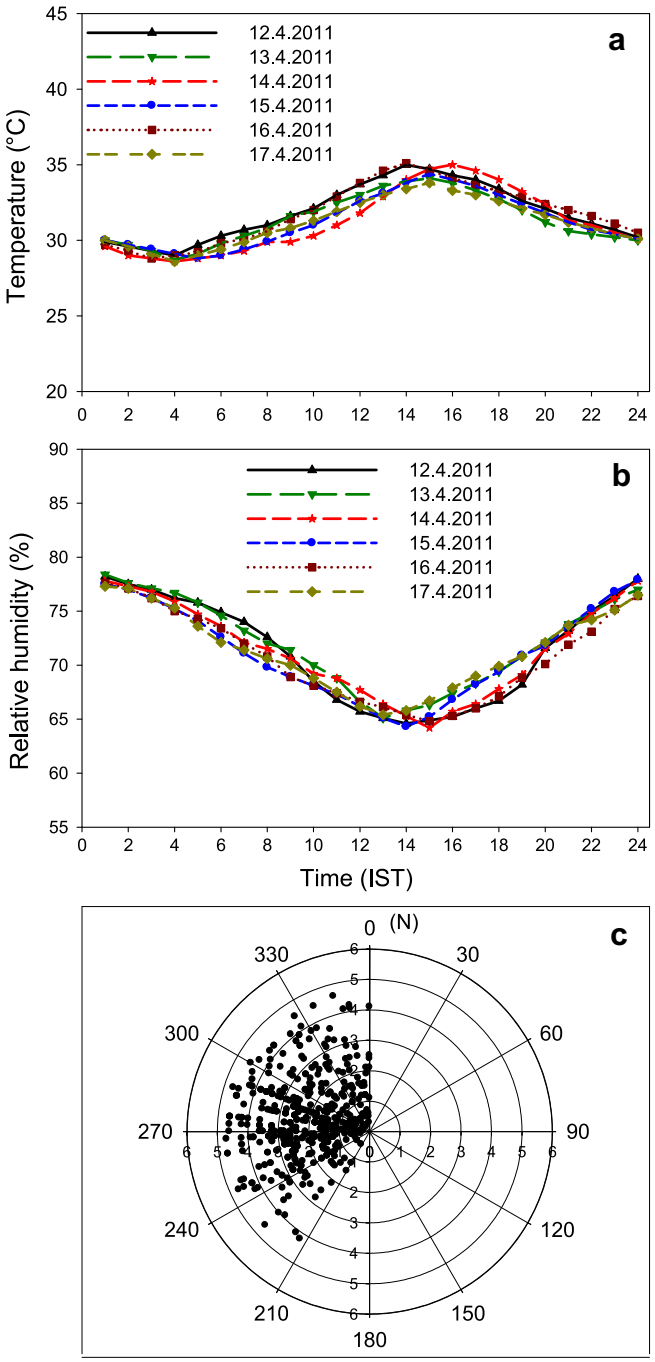

Fig. 2. Temporal profiles of meteorological parameters at Kannur during the period of observation. Diurnal variations of (a) temperature, (b) relative humidity and (c) polar diagram showing wind speed and direction.

The analyzers have been calibrated by using sample gases on a regular basis. Calibration procedure is based on the photometric assay of ozone concentration in a dynamic flow system. The concentration of ozone in the absorption cell of the analyzer is determined from the estimation of the intensity of 253.7 nm radiation absorbed by the sample. In practice, a stable ozone generator is used to produce ozone concentrations over the required range. Calibration of NO_x analyzers is performed by using permeation tube oven. In this gas analyzer, the flow volume is controlled at the specified level so that the pressure in the reaction chamber is maintained at a constant value. Generally, a standard gas of NO_2 is commonly used to check the performance of the converter efficiency as described by Rehme (1976).

A Respirable Dust High Volume Air Sampler (ENVIROTECH, India Model APM 460 NL) was placed on top of the building at a height of 10 m from the ground to collect dust particles that are less than PM_{10} in the ambient air. The sampler used an improved cyclone (with cutoff- D_{50} at 10 microns) to separate the coarser particles (>10 microns) from the air stream before filtering it on a glass microfiber filter. The in-built manometer provided precise flow rate of air through the filter. The timer attached with this sampler accurately measured the duration of airflow through the filter.

2.3. Organic chemical analysis of particulate matter and vapor samples

2.3.1. Sample collection of organics bound to PM

For the analysis of organic chemicals bound to the particulate matter (PM_{10}), a fraction (approximately one quarter) of the glass fiber filter paper used for the PM measurement was cut out and extracted using HPLC grade dichloromethane in an ultrasonic bath at room temperature. Three sequential extractions were performed with 20, 10 and 10 mL of extraction solvent respectively. Each batch of the extract was filtered using a funnel packed with a small amount of pre-cleaned glass fiber filter. The extract was concentrated using a gentle stream of high purity nitrogen to a volume of about 2 mL, which was then transferred to a vial and sealed for GC–MS analysis.

2.3.2. Sample collection of organics in vapor phase

Vapor phase organics were collected using an air sampling tube (1/4 inch glass tube) filled with about 200 mg of XAD-2 (Supelpak-2 from Sigma Aldrich). The samples were collected over an interval of 24–36 h in the period before and after the sparklers event. Air was drawn through the sampling tube at a flow rate of about 1 L min^{-1}. The tubes were sealed at both ends and stored until extraction. The contents of the tube were transferred to a 10 mL vial. About 5–6 mL of dichloromethane was added to the XAD-2 adsorbent. The mixture was then allowed to equilibrate overnight. 2 mL of the extract was transferred to a vial and stored for GC–MS analysis.

2.3.3. Chromatographic analysis

The extracts were injected into a gas chromatography (GC) instrument fitted with a mass spectrometer (MS) and an auto injector (Shimadzu QP2010 Plus) and using an HP-5ms column. Several method and solvent blanks were also analyzed. The temperature program was allowed to reach a high temperature of

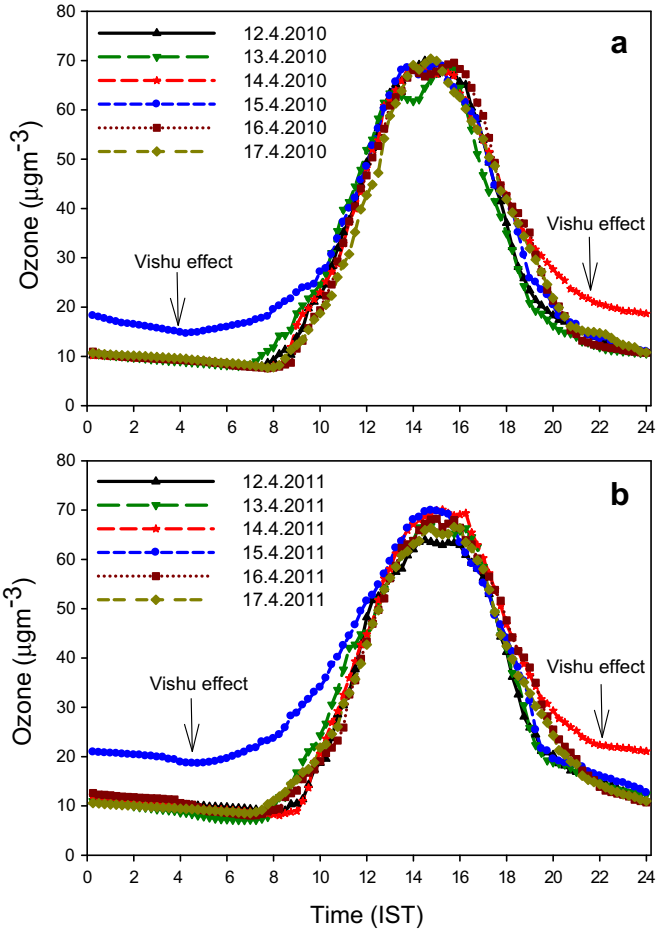

Fig. 3. Diurnal profiles of O_3 on Vishu days (14th and 15th of April) in (a) 2010 and (b) 2011 at Kannur University Campus.

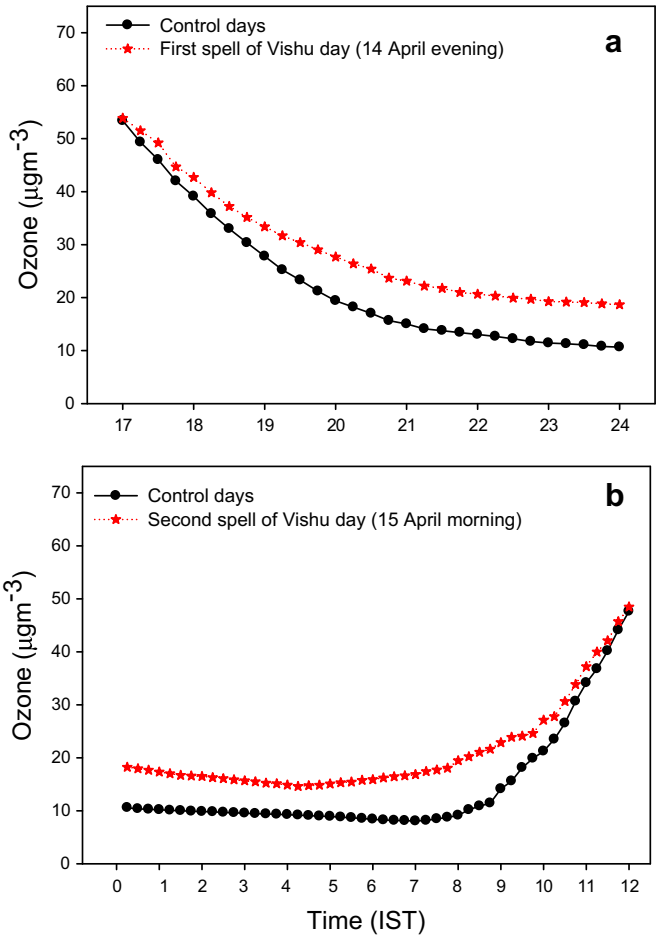

Fig. 4. Temporal variation of O_3 concentration during Vishu eve of 2010 (a) evening spell on April 14 and (b) morning spell on April 15.

280 C, until benzo-ghi-perylene eluted in a 16-PAH standard, which was used to evaluate the separation efficiency. The chromatograms of the method and solvent blanks were subtracted from the samples.

2.4. Meteorological parameters

The meteorological parameters recorded at an hourly resolution during the period of observation and the average values are shown in Fig. 2, from which it is evident that the atmospheric condition remained unaltered as far as the parameters like temperature, humidity and wind speed are concerned. During the monitoring period, the sky remained clear with a few scattered clouds. A maximum daytime temperature of 35 °C at 16:00 h and a minimum temperature of 28.6 °C at 04:00 h were observed on Vishu day. During the control days, the maximum and minimum average temperatures were 34.5 °C and 28.7 °C respectively. The maximum humidity of 77.8% was observed at midnight and a minimum of 64.2% at 15:00 h in the afternoon on Vishu day. The maximum and minimum average values of relative humidity observed during control days were 77.9% and 64.9% respectively indicating little variation in relative humidity. The sunshine hours were from 6:40 h to 18:05 h on all days of observation. The average wind speed ranged from 2 m s^{-1} to 4.5 m s^{-1} confined in the northwest direction. Since the wind speed remains unaltered, the transport of pollutants by advection is likely not affected during fireworks. Thus the O_3 formation can be attributed to the chemistry imparted by the fireworks in the atmosphere.

3. Observations

Concentrations of surface ozone, NO_2, NO and PM_{10} were continuously monitored from 12th to 17th April in 2010 and 2011 at the observational site. Burning of sulfur nitrates, Mg, Ba, Al and gunpowder produce air pollution during Vishu festival. However, O_3, NO_2, NO and PM_{10} are of special interest, as they are the major air pollutants.

3.1. Ozone

Fig. 3 shows the diurnal variation of surface ozone at the site with a sharp increase in ozone concentration from the evening of April 14th to morning of Vishu day on April 15th for two consecutive years 2010 and 2011. The increase in O_3 concentration shows two maxima, between 18:00 and 22:00 h on April 14th and between 04:00 and 08:00 h of April 15th. The increase in ozone concentration observed at 18:00 and 22:00 h on the control days in 2010 was 3.01 μg m^{-3} and 7.5 μg m^{-3} and that in 2011 was 3.4 μg m^{-3} and 7.4 μg m^{-3} respectively. Likewise, O_3 concentration observed in the early morning of 15th of April 2010 at 04:00 h and 08:00 h exceeds the control day average by 5.6 μg m^{-3} and 10.5 μg m^{-3} and that in 2011 was 9.1 μg m^{-3} and 14.3 μg m^{-3} respectively. The increase in O_3 concentration is matched with the two spells of intense fire bursts. In 2010, the O_3 concentration was restored to its normal level after 10:00 h while in 2011 this was realized at 13:00 h. The temporal variation of O_3 during the evening

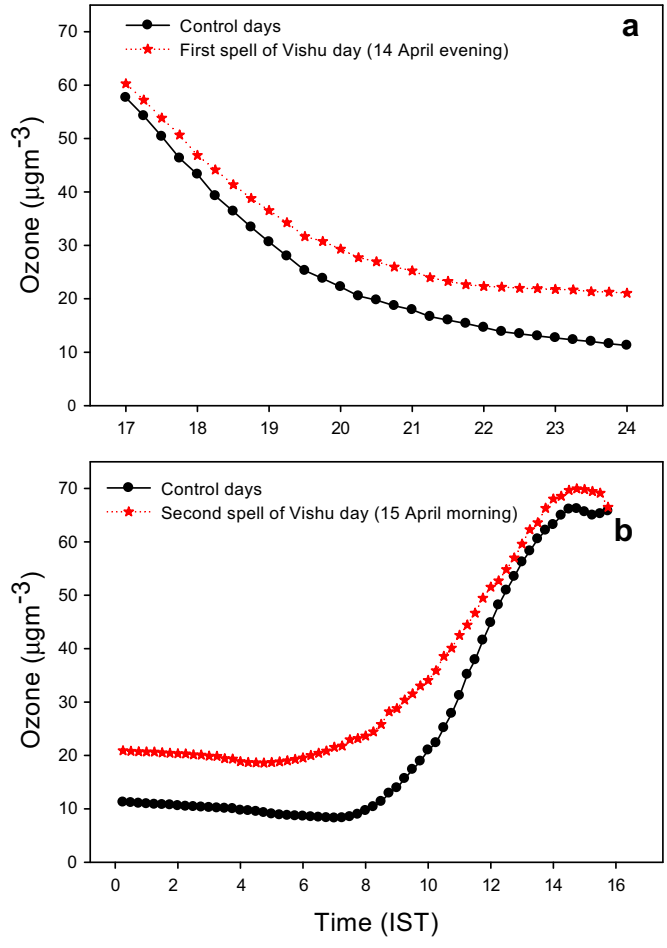

Fig. 5. Temporal variation of O_3 concentration during Vishu eve of 2011 (a) evening spell on April 14 and (b) morning spell on April 15.

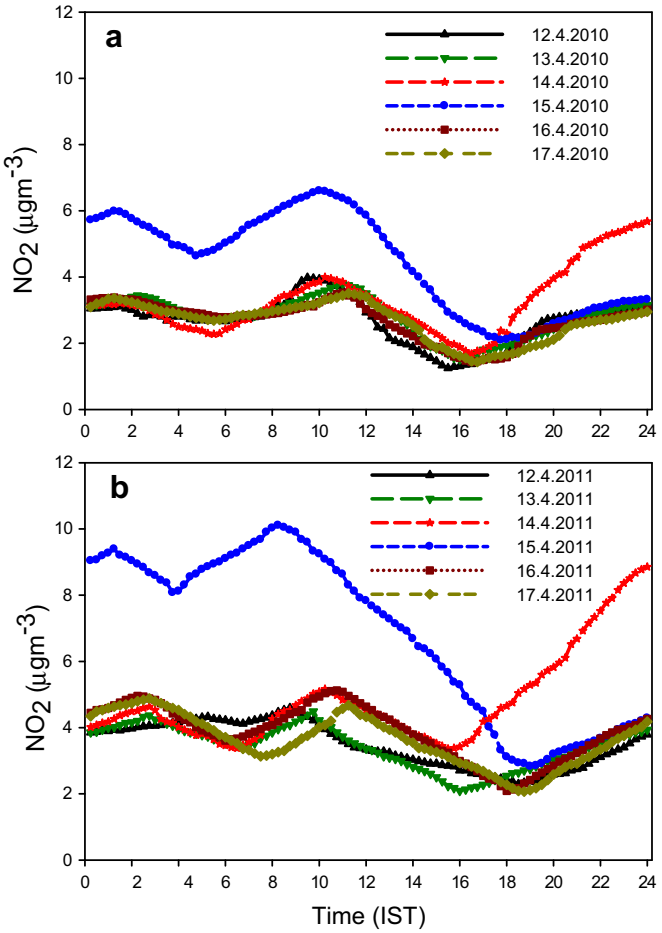

Fig. 6. Diurnal variation of NO_2 concentration observed in (a) 2010 and (b) 2011.

spell (April 14th) of Vishu eve from the mean values of the control days in 2010 and 2011 are shown in Figs. 4 and 5. There is a significant variation in air quality on Vishu days, but the overall variations are similar in both years.

3.2. NO_2, NO and PM_{10}

From the diurnal variation of NO_2 shown in Fig. 6, it was found that nighttime average concentration of NO_2 on control days of 2010 and 2011 were 2.74 and 3.23 μg m^{-3} respectively. But the nighttime average concentrations observed in 2010 and 2011 April 14th were 4.7 and 7.1 μg m^{-3} respectively. The daytime average NO_2 concentrations observed during the control days in 2010 and 2011 were 2.9 and 3.9 μg m^{-3} respectively, while during the morning of April 15th, their magnitudes were 5.5 and 9.3 μg m^{-3} respectively. Thus, the increase in NO_2 resulted from fireworks corresponds to the two spells of fire bursting. It is clear that the enhancement in the NO_2 concentrations during the event corresponds to the increase in the production of O_3 during the firework display. The two peaks found in the diurnal profile of NO_2 correlates with the two distinct spells of increase in O_3. Fig. 7a and b illustrate the change in NO_2 concentration on 14th April evening and 15th April morning in 2010 and 2011 for comparison. Another distinctive feature observed is a sharp reduction in NO concentration during the event for 2 years as shown in Fig. 8.

Fig. 9a and b depict the variations of NO concentration observed during the control days and Vishu day for comparison. It is clear that NO concentration starts declining from 18:00 h to a minimum at 22:00 h, gradually increasing to a maximum at 02:30 h and, then gradually becoming a minimum at 08:30 h the next morning. Thus, the NO concentration shows an inverse behavior compared to NO_2 during the two spells of fire bursting. The average concentration of NO during the control night in 2010 was 1.64 μg m^{-3} and that observed in 2011 was 1.8 μg m^{-3}. But on April 14th of 2010 and 2011, the average magnitudes between 18:00 and 22:00 h were 0.9 and 0.8 μg m^{-3} respectively. Likewise, the average value of NO concentrations on the morning of the control day in 2010 was 2.2 μg m^{-3} and 2.7 μg m^{-3} in 2011. During the day of Vishu on April 15th in 2010 and 2011, the same were 1.5 and 1.4 μg m^{-3} respectively.

The variation in PM_{10} during the Vishu festival days is shown in Fig. 10.The vertical bars represent one sigma standard deviation. It is obvious that the particle loading was higher on 14th and 15th of April. The mean concentration of PM_{10} during the daytime and the night following the control day was 56 μg m^{-3} while it was elevated to 118 μg/m^3during the night of Vishu on April 14th. In general, particle concentration approximately doubled during the festival days. This large amount of particulate matter emitted in a short span of time can impact public health (Moreno et al., 2007; Gurjar et al., 2010).

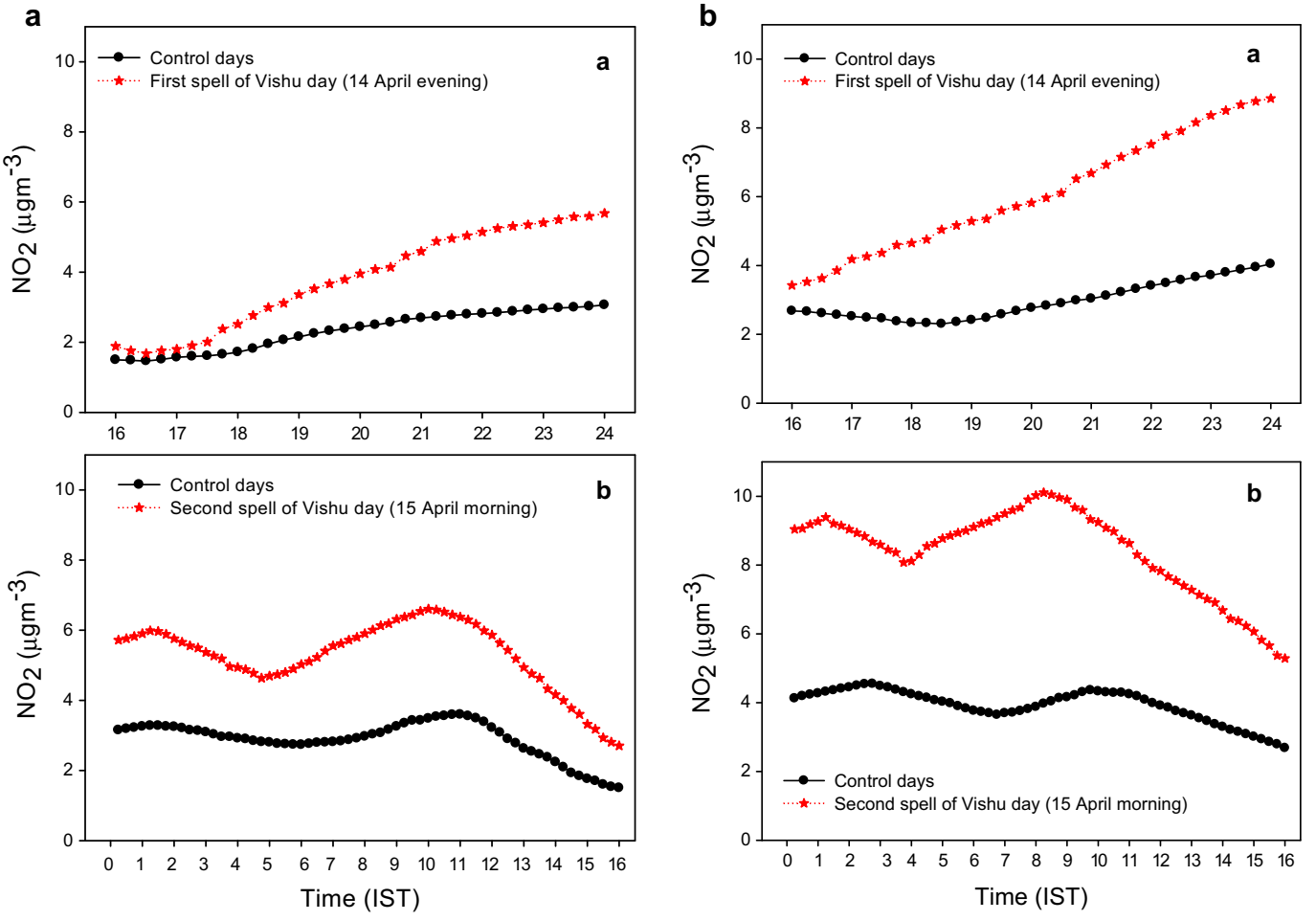

Fig. 7. a. Temporal variation of NO_2 concentration during Vishu eve of 2010 (a) evening spell on April 14 and (b) morning spell on April 15 b. Temporal variation of NO_2 concentration during Vishu eve of 2011 (a) evening spell on April 14 and (b) morning spell on April 15.

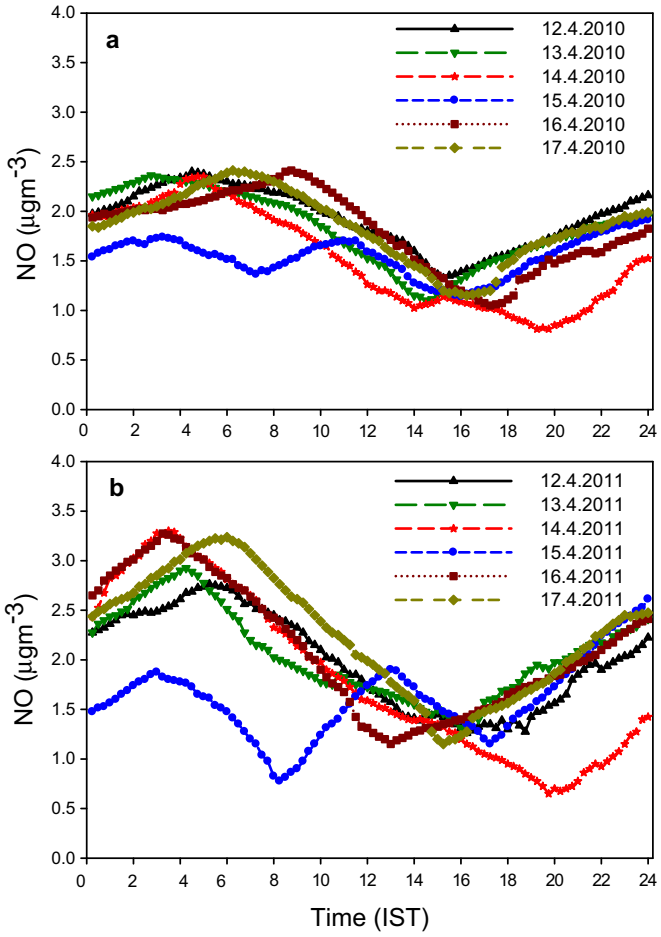

Fig. 8. Diurnal profiles of NO concentration as observed in (a) 2010 and (b) 2011.

4. Results and discussion

Fireworks contain several compounds that give it radiant color bursts. Fireworks activation is a combustion reaction involving a mixture of potassium nitrate (75%), charcoal (15%) and sulfur (10%). Black powder is used even today as an explosive charge and as a propellant (Conkling, 1985; Russell, 2009). Upon ignition, the gaseous mixture expands in volume as it explodes and propels the container just as a rocket. In order to sustain the combustion, oxygen is required and is supplied in the form of nitrates, chlorates or perchlorates. A reducing agent capable of burning in the presence of oxygen is also required; sulfur or charcoal is used for this purpose. In order to bind the oxidizer and reducer, one uses starch dextrin or gum Arabic to make the mixture more homogeneous. The sparkling colors require the addition of other metallic compounds into the black powder. Upon ignition, the mixture can reach temperatures as high as 1000–3000 °C. Metallic compounds at such temperatures emit radiation covering the visible region of the light spectrum. There is evidence that metals at high temperature also emit colors in the ultraviolet region of the spectrum at wavelengths less than 240 nm. This high energy UV radiation has been speculated to lead to the splitting of molecular oxygen into O radicals, and produce ozone, a powerful atmospheric oxidant (Fishman et al., 1979; Brasseur and Solomon, 2005).

$$O_2\ (\lambda < 240\ \text{nm}) \rightarrow O + O \quad \text{(R1)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}$$

However, surface ozone is generally produced only during daytime by the photodissociation of NO_2 in the presence of sun light ($\lambda < 420$ nm). Thus, the natural diurnal variation of O_3 shows a maximum concentration in the afternoon to be removed during night through the following closed set of reactions:

$$NO_2 \rightarrow NO + O \quad \text{(R3)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R4)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R5)}$$

The most interesting feature of our present observation is the increase in ozone concentration during the night of April 14th even in the absence of sun light. This increase is well correlated with fireworks and occurred in two spells, late evening of April 14th and early morning of April 15th each year. Thus, the ozone generated was primarily at the expense of the light flash from the firecrackers. The emission spectra of commonly used firecrackers was recorded by a UV–Visible Spectrophotometer (Maya 2000 series, Ocean Optics) operating between 175 nm and 1100 nm with a resolution of 0.035 nm (FWHM) and are shown in Fig. 11. The emission spectra of three different sparklers and powders were analyzed and the emission wavelengths of all samples were found in the visible region extending from 390 nm to 1100 nm. Further, it was found that UV wavelengths were absent in the emission spectra of all six samples which were commonly ignited in the fireworks. This rules out the possibility of O_3 formation by the reactions (R1) and (R2) as suggested by Attri et al. (2001). Since the emission is mainly confined in the visible and near infrared region, we believe that O_3 production was via photolysis of NO_2 around 420 nm. The O_3 formation by photodissociation of NO_2 via reactions (R3) and (R4) is a distinct possibility. The excess NO_2 required for the enhancement of O_3 was formed from some other species produced during this event. This fact is qualitatively explained on the basis of peroxy radical formation from alkanes, aldehydes etc detected during the episode by the reactions:

$$NO + HO_2 \rightarrow NO_2 + OH \quad \text{(R6)}$$

$$NO + RO_2 \rightarrow NO_2 + RO \quad \text{(R7)}$$

Thus, we tentatively attribute reactions (R3)–(R5) along with reactions (R6) and (R7) as the reasons for the observed enhancement of NO_2 and the sharp decline in NO during the nighttime episodes.

The identification of organics emitted by fireworks revealed the presence of a variety of alkanes, alkenes, aldehydes and other organic species at this location. Elevated levels of alkanes found in the gas phase during fireworks may react with the OH radical to form alkyl radicals, which react rapidly with O_2 to form alkyl peroxy (RO_2) radicals through the following reaction (Atkinson, 1997, Atkinson et al., 2006):

$$OH + RH \rightarrow H_2O + R \quad \text{(R8)}$$

$$R + O_2 \rightarrow RO_2 \quad \text{(R9)}$$

RO_2 can further react with NO_3 radicals to form NO_2, which is the general reaction path way during nighttime (Atkinson, 1998a,b).

$$RO_2 + NO_3 \rightarrow RO + NO_2 + O_2 \quad \text{(R10)}$$

Thus the peroxy radicals efficiently convert NO into NO_2, regenerating OH. The NO_2 thus formed is photolyzed in the presence of the flash of firecrackers to generate O_3. This scheme

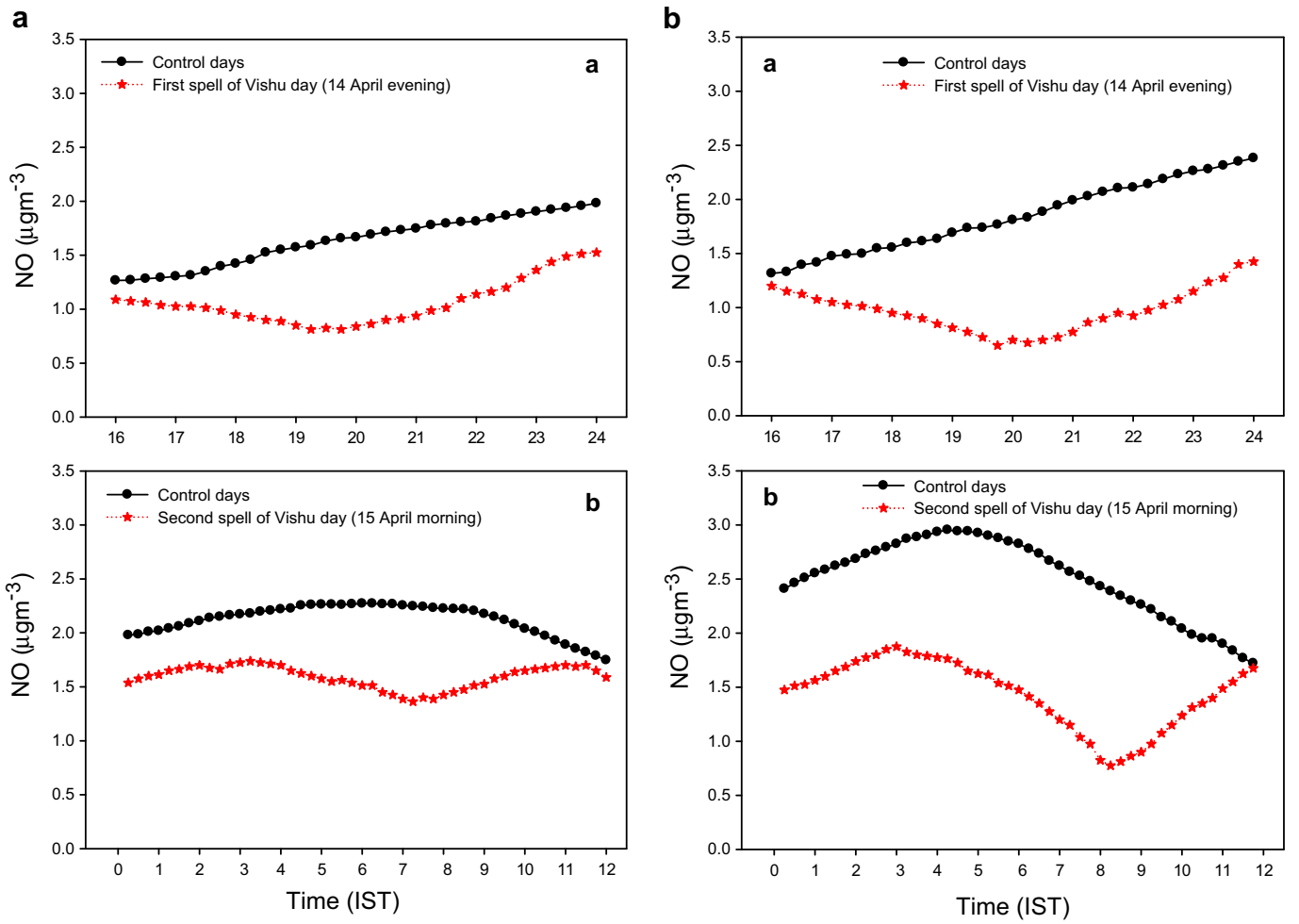

Fig. 9. a. Temporal variation of NO concentration during Vishu eve of 2010 (a) evening spell on April 14 and (b) morning spell on April 15. b. Temporal variation of NO concentration during Vishu eve of 2011 (a) evening spell on April 14 and (b) morning spell on April 15.

proposed for nighttime production O_3 by fireworks is in concurrence with the nighttime chemistry of O_3 and its production efficiencies from a variety of organic species (Finlayson-Pitts and Pitts, 1997). Moreover, the photolysis of $ClNO_2$ formed out of the abundant sea salt aerosols present over the coastal belt can also generate surface O_3 (von Glasow, 2008).

A correlation was made between the changes in the concentration of O_3 and NO_2 produced during Vishu eve and Vishu day.

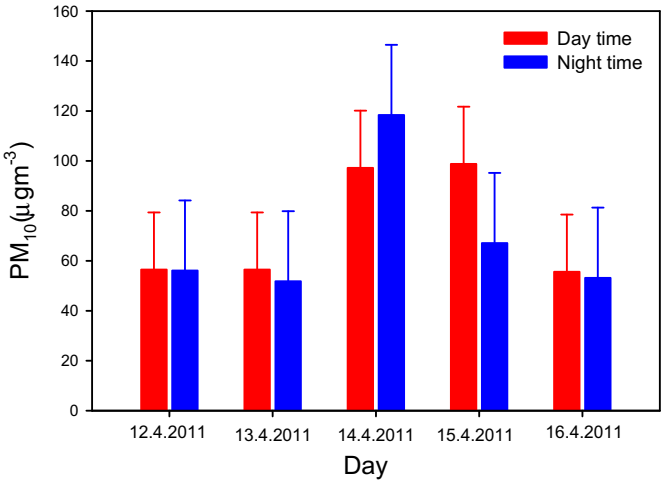

Fig. 10. Variation of PM_{10} concentration during Vishu festival.

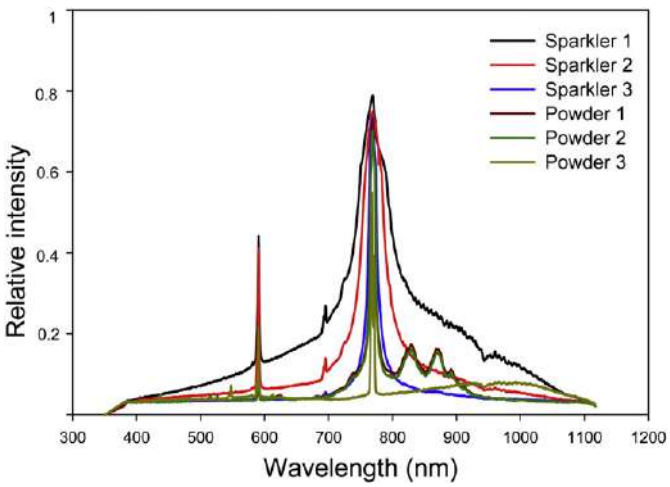

Fig. 11. Emission spectra of sparklers and powders used in firecrackers.

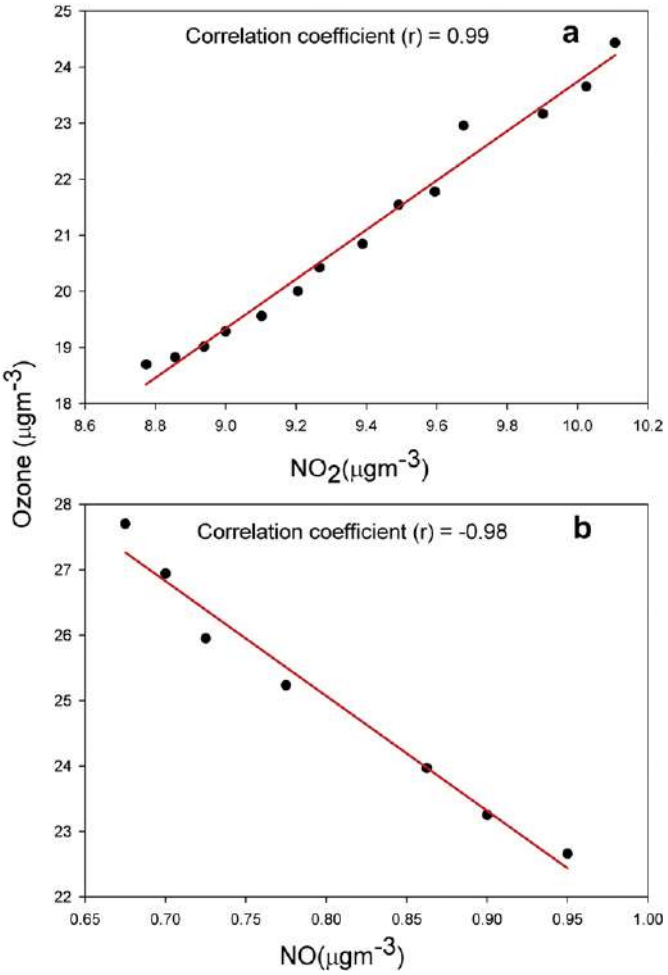

Fig. 12. Correlation between changes in the concentrations of O_3 and NO_2 (a) and O_3 versus NO (b) observed during Vishu.

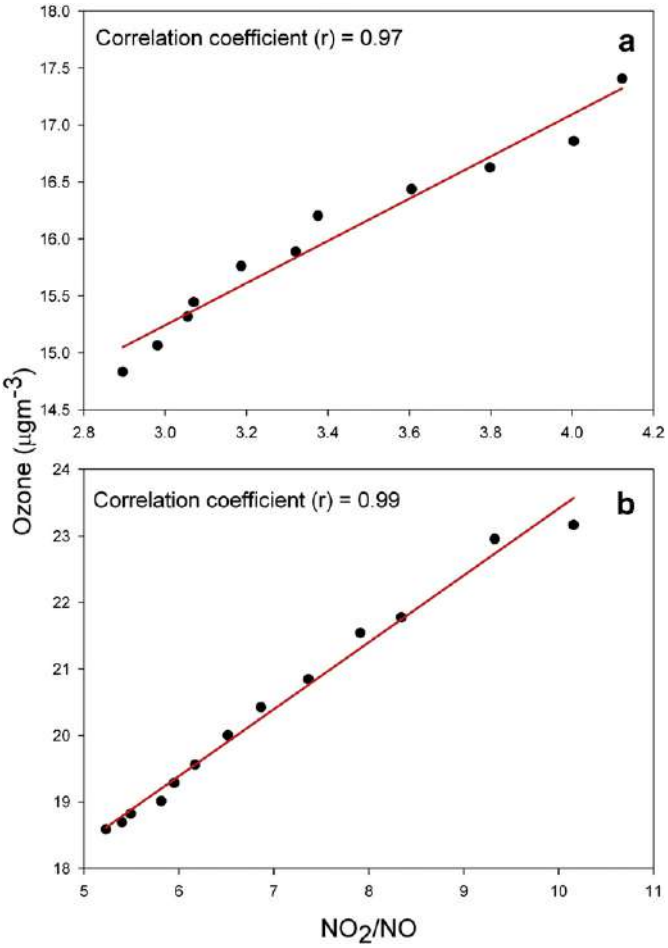

Fig. 13. Correlation between O_3 and NO_2/NO in (a) 2010 and (b) 2011 during the morning spell between 04:00 h and 07:30 h (IST).

Fig. 12(a)shows a positive correlation with a correlation coefficient of 0.99. This shows that O_3 was produced mainly from the photolysis of NO_2 since the emission wavelengths from the flash of firecrackers are mostly in the visible region. A strong negative correlation between O_3 and NO is shown in Fig. 12(b) with a correlation coefficient of 0.98. Thus the decline observed in the concentration of NO during this episode may further reduce the removal of O_3 by the titration process. A correlation between NO_2/NO and O_3 during the early morning of April 15 in 2010 and 2011 depicted in Fig. 13 reveals the enhancement of O_3 produced in tune with the similar change in NO_2 induced by the flash of fireworks. A more focused experimental work in the laboratory is necessary to shed further light into the suggested mechanisms of O_3 formation at night during the Vishu fireworks events. Statistical analysis (student's *t*-test) was conducted and the correlation coefficient is found to be significant at 99% confidence level.

4.1. Organics

Fleischer et al. (1999) and Ahn et al. (2006) reported organic air pollutants at two locations in Germany and Korea respectively. Our study also identified a variety of organic compounds associated with the particulate matter and vapor phase samples collected during the festival over a period of three days (Tables 2, 3a, b, c). The number of compounds detected in the vapor phase was larger than

Table 2
Organics detected as associated with the particulate matter in air during fireworks display.

Aliphatic compounds and derivatives	Pentane, 2,3,3-trimethyl-	Dodacane, 2,6,111-trimethyl-
	Heptane, 3,3,5-trimethyl-	Tetradecene
	Nonadecane	Tetrapentacontane
	Octane, 2,6-dimethyl-	1-Hexene, 3,3-dimethyl-
	Octane, 2,3-dimethyl-	2-Pentene, 2,3,4-trimethyl-
	Octane, 3,3-dimethyl-	2,4,4- Trimethyl-1-hexene
	Octadecene	Cyclotetradecane
Halogenated Aliphatic	Butane, 1-bromo-2-methyl-	Dodecane, 1-iodo-
	Octane, 1-iodo-	
Organic Acids/Ester	Phosphorous acid, tris(2-ethylhexyl) ester	Methyl 2-hydroxydecanoate
	Valeric anhydride	2-Propenoic acid, 2-methyl-, octyl ester
	1,2-Benzenedicarboxylic acid, diheptyl ester	
Alcohols/Ketones	4-Tetradecanol	3-Heptanol, 2,6-dimethyl-
	2-Buten-1-ol, 2-methyl-	3,3,6-Trimethyl-1, 5-heptadien-4-ol
	1-Pentanol, 2-ethyl-4-methyl-	1-Penten-3-ol, 3-methyl-
	1-Hexanol, 3,5,5-trimethyl-	3-Heptanone, 4-methyl-
	3,3,5,5-Tetramethylcyclohexanol	
Others	Caprolactam	Diallyl carbonate
	Bis(2-ethylhexyl) hydrogen phosphite	

Table 3a
Aliphatic compounds and derivatives and Aromatic chemicals detected in the vapor phase.

Aliphatic compounds and derivatives		
Dodecane, 4.6 dimethyl-	Pentane, 1,1′- oxybis-	2,3- Dimethyl-1-hexene
Pentane, 2,2,3,4-tetramethyl-	Heptane,3-methyl-	2-Pentene, 4,4-dimethyl-,(Z)
Hexane, 2,3,4-trymethyl-	Undacane, 4-methyl-	1-Pentene, 4-methyl-
Hexane, 3,3,4-trymethyl	Dodecane, 4-methyl-	3-Heptene, 2,6-dimethyl-
Pentadecane	Tridecane, 6-methyl-	1-Hexene, 3,3-dimethyl-
Butane, 2,2-dimethyl	Heptane, 3,3-dimethyl-	2-Octane, 2,6-dimethyl-
Hexane, 2,4,4-trymethyl-	Pentane, 3-ethyl-2,2-dimethyl-	3,3-Diethoxy-1-propyne
Dodecane	Pentane, 3-ethyl-2,4-dimethyl-	1,5-Hexadien-3-yne, 2-methyl-
Pentane, 2,2-dimethyl-	Cyclopentane, 1,1,3,4-tetramethyl-,cis	Cyclohexane, 1,1-dimethyl-
Neopentane	Hexadecane	Cyclopropane, 1,1,2,2-tetramethyl-
Hexane, 3,3-dimethyl-	Decane, 3,8-dimethyl-	Pentanenitrile, 4-methl-
Diazene, bis(1,1-dimethylethyl)-	Pentane,2,3,4-trimethyl-	Carbon Tetrachloride
Undecane, 3-methyl-	Heptane, 4-ethyl-	Cycloheptane
Decane, 3-methyl-	Heptacosane	Butane, 2,3-dimethyl-2, 3-dinitro-
Dodecane, 2,6,11-trymethyl-	Octane,4-ethyl-	Undecane, 4-methyl-
Heptane, 2,5,5-trymethyl-	Nonanae, 3-methyl-	1-Hexene, 3,5,5-trimethyl-
Nonane, 5-butyl-	Heptane, 3,3,5-trimethyl-	1-Azabicyclo[3.1.0]hexane
Hexane, 2,4-dimethyl-	Decane, 5,6-dimethyl-	Cyclopropane, 1,1,2-trimethyl-
Tridecane	Heptane, 3,4,5-trimethyl-	1,3,5-Cycloheptatriene
Undecane, 5-methyl-	2-Hexene, 5, 5-dimethyl-,(Z)-	
Aromatic chemicals		
Naphthalene	Naphthalene, 1-methyl-	Benzene, 1-azido-4-methoxy-
Toluene		

Table 3b
Halogenated Aliphatic compounds and Aldehydes/Alcohols/Ketones detected in the vapor phase.

Halogenated Aliphatic		
Dodecane, 1-iodo-	Heptane, 1-iodo-	Heptane, 3-(bromomethyl)-
Propane, 1-chloro-2, 2-dimethyl-	Pentane, 3-(bromomethyl)-	2-Butene, 1-chloro-3-methyl-
Octane, 1-iodo-	Butane, 1-chloro-3,3-dimethyl-	Propane, 2-bromo-2-methyl-
Nonane, 1-iodo-	Butane, 2,3-dichloro-2-methyl-	Propane, 1,1,1,3,3,3-hexafluoro-
Ethane, iodo-		
Aldehydes/Alcohols/Ketones		
2,2-Dimethyl-3-hydroxy-propionaldehyde	(6Z)-Nonen-1-ol	3-Pentanone, 2-methyl-
Paraldehyde	2-Pentanol	3-Hexanone, 2,2-dimethyl-
Propanal, 2,2-dimethyl-	3-Buten-2-ol	3-Heptanone, 2,4-dimethyl-
Butanal	1,3-Benzenediol, monobenzoate	Acetophenone
1-Hexanol, 2-ethyl-	4-Heptanone, 3-methyl-	Ethanone, 1-cyclopropyl-
3-Hexanol, 2-methyl-	3-Hexanone, 2,5-dimethyl-	3-Penten-2-one, (E)-
4-Methyl-1, 6-heptadien-4-ol	3-Heptanone, 2-methyl-	3,4-Hexanedione
1-Pentyn-3-ol, 3-methyl-	3-Hexanone	2-Propanone, 1-phenyl-, oxime
2-Pentanol, 4-methyl-	3-Hydroxy-3-methyl-2-butanone	4-Heptanone, 2-methyl-
1-Pentanol, 3-methyl-	3-Penten-2-one	3-Butyn-2-ol, 2-methyl-
Ethanol, 2-nitro-	3-Hexen-2-one	Methyl vinyl ketone
Isopropyl Alcohol	2,3-Pentanedione	1-Penten-3-one
3-Nonen-1-ol, (Z)-		

Table 3c
Organic Acids/Esters and other organic detected in the vapor phase.

Organic Acids/Esters		
2-Butenedioic acid (Z)-, dibutyl ester	Propanoic acid, 2-hydroxy-2-methyl-, methyl ester	2-Propenoic acid, 2-methyl-, ethenyl ester
Bis(2-ethylhexyl) phthalate	Dibutyl phthalate	Butanoic acid, 2-propenyl ester
1,2-Benzenedicarboxylic acid, dihexyl ester	Propanoic acid, 2-hydroxy-2-methyl-	Dodecanoic acid, propyl ester
Propanoic acid, ethenyl ester	Aminocyanoacetic acid	1,2-Benzenedicarboxylic acid, diheptyl ester
Acetic acid, 2-ethylhexyl ester	Butanoic acid, (tetrahydro-2-furanyl) methyl ester	1-Butanol, 3-methyl-, propanoate
Methyl 2-hydroxy-decanoate	2-Propenoic acid, 2-methyl-	Benzoic acid, 4-ethoxy-, ethyl ester
2-Propenoic acid, 2-methyl-, octyl ester	3-Amino-1,2,4-triazole-5-carboxylic acid	2-Methylbutanoic anhydride
Others		
Acetyl valeryl	1,2-Propanediamine	4-Fluoroveratrole
Di-tert-butyl peroxide	2,4,5-Trihydroxy-pyrimidine	2-Hydroxy-2-methyl-butyric acid
2,2′-Bioxirane, (R*,R*)-(±)-	Ethylamine	Methacrylic anhydride
Glycidol	2,2′-Bioxirane	Butanenitrile
Formamide	Binapacryl	Propane, 1-nitro-
2-Butenoyl chloride	Cyclopropanamine, 2-phenyl-, trans-	1-Propanesulfonyl chloride
1,2-Ethanediamine, N,N,N′,N′-tetraethyl-	3-Amino-s-triazole	

that on the particle phase, while a few were found in both phases. A large number of alkanes, alkenes and halogenated aliphatic compounds were present in the vapor phase. It was also observed that the concentration on the particulate matter on 14 and 15th of April was much higher than that measured before the festival. This indicates that a large number of organic chemicals found in the particulate matter were specifically associated with the fireworks. Vapor sampling was conducted with samples collected from April 13–17. Table 4 shows the list of the compounds whose magnitude was slightly higher on April 14–15 as compared to the other days. This implied that these chemicals were probably associated with

Table 4
Chemicals in the vapor phase found in relatively higher magnitude on the days of the festival.

Pentane, 2,2,3,4-tetramethyl-
Hexane,3,3,4-trimethyl
Pentane, 2,2-dimethyl-
Dodecane, 2,6,11-trimethyl-
Undecane, 5-methyl-
Hexadecane
3,3- Diethoxy-1-propyne
Pentanenitile, 4-methyl-
Carbon tetrachloride
Undecane, 4-methyl-
Undecane, 1-iodo
Heptane, 1-iodo
Acetic acid, 2 ethylhexyl ester
Propenoic acid, 2 methyl-, octy ester
Propanoic acid, 2 hydroxy-2 methyl-, methyl ester
1-Hexanol, 2 ethyl
3- Hexanol, 2 methyl-
4-Methyl-1,6-heptadien-4-ol
4-Heptanone, 3 methyl-
3- Hydroxy-3-methyl-2-butanone
3-Penten-2-one
3-Hexanone, 2,2-dimethyl-
Acetyl valeryl
Di-tert-butyl peroxide
2,2′-Bioxirane, (R*,R*)-(±)-

the fireworks (both the active explosive component and the packing material associated with the fireworks). The organic compounds included aldehydes, ketones and aliphatics which can all generate peroxy radicals that may enhance O_3 production through (R6) and (R7) (Kleinman et al., 1995).

5. Summary and conclusion

This study revealed the impact of extended fireworks episodes during Vishu festival in the atmosphere over Kannur. Emission of visible radiation from the intense flash produced by the fireworks could generate O_3 in the atmosphere even during the nighttime and can affect both indoor and ambient air quality. The concentrations of O_3 and PM_{10} were doubled, while NO_2 increased by 2.5 times as the firecrackers were set off. Further, the smoke from fireworks consisted mainly of fine dusts (particulate matter) that can cause respiratory problems in sensitive segments of the population (Hoeek et al., 1998; Mortimer et al., 2002; von Klot et al., 2002). In addition to this, the smoke from the combustion of fireworks contains a mixture of sulfur–coal compounds, traces of heavy metals, and other toxic organic chemicals and gases. A detailed organic analysis revealed the finger prints different toxic organic compounds that emitted into the atmosphere which can severely deteriorate ambient air quality and cause serious health impacts. Subsequently, the widespread fireworks display that occurs on the night of Vishu provides a large amount of toxic pollutants and fine particles into the atmosphere that accumulates on the surface. This can be problematic in a valley such as Kerala due to the shallow boundary layer existing till noontime the following day. Therefore, it is important to explore the impact of widespread fireworks on the health of a local community within a high population density region such as in Kerala. This study explored for the first time to reveal the spontaneous changes in the air quality induced by widespread fireworks at a rural location confined along the coastal belt of the Arabian Sea. It has been observed that the amount and duration of fireworks used for celebration have been increasing in the last few years. If this trend continues, certainly the joyous celebrations may also impact the overall health of the community in this region. Thus, this study illuminates some of the projected health issues to be addressed during such elaborate long-duration festivals in Kerala.

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