Particulate Oxidative Potential (OP) Associated with Fireworks Activity during Diwali at a site in the Indo-Gangetic Plain

Anita Lakhani (anita.lakhani01@gmail.com)
Dayalbagh Educational Institute Faculty of Science https://orcid.org/0000-0002-6030-0887
Isha Goyal
Dayalbagh Educational Institute Faculty of Science
Puneet Kumar Verma
Dayalbagh Educational Institute Faculty of Science
Kandikonda Maharaj Kumari
Dayalbagh Educational Institute Faculty of Science

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Abstract

The potential of the atmospheric fine aerosols ($PM_{2.5}$) to generate reactive oxygen species (ROS) during firework activity in Diwali festival was assessed by the dithiothreitol (DTT) assay at a site in the Indo-Gangetic Plain, India. The 12-h mean $PM_{2.5}$ was found to be 262.9 ±150.7 μg m^{-3} during the study period which was 4.4 times exceeded the NAAQS limits. Firework activity was also characterized by increased levels of gaseous pollutants (NOx, SO_2, CO and O_3), and trace metal concentrations like Ba, Pb, Cu, Fe, Mg, K, Al and Mn. Elevated $PM_{2.5}$-NOx slope for fireworks including traffic emissions suggested significant contribution of fireworks. The highest value of PM ROS activity, volume-based DTT value was 1.37 nmol min^{-1} m^{-3} and mass-based DTT value was 11.77 pmol min^{-1} $μg^{-1}$, found in the next morning of Diwali, suggesting stronger PM associated ROS activity due to fireworks. A positive association was found between redox-active metals like Cd, Cr, Cu, Ni, and V and DTT activity that could be due to the ability of these metals to catalyze ROS generation in ambient air, while Ba, Be and Se in atmosphere as major constituents of firecrackers were also strongly associated with DTT activity. The ozone levels were strongly correlated (r^2 = 0.87) with DTTv activity during daytime due to photochemical activities including chemical species associated with fireworks responsible for forming tropospheric O_3. Comparison of the daily DTTv activity and hazard index (HI) suggests that the HI may be a poor metric to measure the health effects by which PM exposure can induce deterioration in human health.

Highlights

- • This study focuses on the impact of oxidative properties of $PM_{2.5}$ during Diwali period.
- • DTT Assay has been used to estimate the oxidative potential (OP) of $PM_{2.5}$.
- • Transition metals in PM seem to have high oxidative activity linked with a wide range of health effects, including effects on the cardiovascular and respiratory systems.

1. Introduction

Setting off fireworks during celebrations such as Diwali in India (Prabhu et al. 2019; Singh and Srivastava 2020), Chinese Spring Festival in China (Pang et al. 2021), Independence day in USA (Jia et al. 2020), Lantern festival in Taiwan (Lin et al. 2014) Guy Fawkes in UK (Godri et al. 2010) and New Year's celebrations in many countries (Retama et al. 2019; Rindelaub et al. 2021) causes short-term debilitation of air quality. Hazardous chemicals such as KNO_3, C and S apart from an array of alloys of several metals like Sr, Ba, Na, Ti, Zr, Mg, Cu and Al are added to fireworks to develop the colourful effects (Hickey et al. 2020; Rindelaub et al. 2021). Short-term exposure to particulate matter (PM), gaseous pollutants e.g., NO_x, SO_2, CO and several metals like Al, Mn and Cd can result due to bursting of firecrackers and could pose serious health risks (Prabhu et al. 2019; Singh et al. 2019). Several research have also revealed the emission of organic pollutants during fireworks (Jia et al. 2020).

The contributions of the firework events to poor air quality have been largely reported in literature (Prabhu et al. 2019; Singh et al. 2019; Hickey et al. 2020; Singh and Srivastava 2020). The consequences of fireworks contribute including reduction in visibility (Singh et al. 2019) and enhanced particulate load during German New Year (Drewnick et al. 2006), on Independence day in U.S.A. (Jia et al. 2020) and Spain (Moreno et al. 2007), and in India (Ambade 2018; Ganguly et al. 2019; Prabhu et al. 2019; Sahu et al. 2020; Singh and Srivastava 2020) during the Diwali festival has widely been reported. Attri et al. (2001) observed a sudden increase in the concentration of O_3 in the next morning of fireworks from 9:00 p.m. to 2:00 a.m. in the air (Attri et al. 2001). The concentrations of $\sum$PAHs on

Independence day was 48.1 ng m^{-3} and the diagnostic ratios of certain PAH isomers viz. Fla/(Fla+Pyr), InP/(InP+BghiP) and InP/BghiP indicated grass, wood, and coal combustion were found on the same day (Jia et al. 2020).

In the Indian context, several studies have also shown that the fireworks could be a root cause of degradation of air quality during Diwali celebrations. Ravindra et al. (2003) observed that the concentration of SO_2 during Diwali increased approximately 10 times, whereas PM_{10}, TSP and NO_2 levels increased more than twice, in comparison to normal winter days in December 1999. The diurnal variation of PM_{10}, TSP and NO_2 also showed an increase on Diwali night (Ravindra et al. 2003). The concentrations of metals like Sr, Al, K and Ba increased by 15, 18, 25 and 1091 folds respectively than pre-Diwali. This study demonstrated that firework activities on Diwali are an immense reservoir of air pollution, contributing remarkably high levels of metals in the ambient air (Kulshrestha et al. 2004). Barman et a1. (2008) reported an average spike in levels of SO_2, NO_x and PM_{10} over pre-Diwali period by a factor of 2, 2 and 3 times respectively in comparison to an ordinary day. Further, trace metals like Co, Cu, Fe, Ca, Cd, Cr, Mn, Pb, Ni, Zn in PM_{10} samples were higher than typical days and pre-Diwali period except Fe (Barman et al. 2008). Sarkar et al. (2010) ascribed 20 to 30% of the total PM_{10} to firework emissions in Delhi and also reported the increase in levels of Ca, Mn, Al, S, Na, Mg, Sr, K, Ba and elemental carbon (EC) by factor of 1.6, 2.7, 3.2, 4, 5, 5.8, 15, 18, 264 and 4.3 respectively (Sarkar et al. 2010). Similar increase in levels of PM_{10} was also reported in Jamshedpur (Ambade 2018). The mass concentrations of PM_{10} increased up to 974.55 µg m^{-3} on Diwali followed by 787.04 µg m^{-3} on post-Diwali as compared to pre-Diwali (225.69 µg m^{-3}) and 55–73% of particles were observed in the particles size less than 1 µm (PM_1) in comparison to other size ranges. The levels of metals such as K, Al, S, Ba, and Cl during Diwali also increased significantly that contributed 34% to the total metals analyzed in comparison to pre-Diwali (<1.0%) and post-Diwali (2.0%) due to fireworks (Singh and Srivastava 2020). However, in certain metropolitan regions, contamination remains in the ambient air for a short span, but fine and ultrafine particles stay for few days (Kulshrestha et al. 2004; Singh and Srivastava 2020).

The unexpected rise in pollution level during fireworks can trigger several antagonistic health impacts including asthmatic assaults, lung infection, eye hypersensitivities, cough, fever and cardiovascular diseases (Hirai et al. 2000; Arora et al. 2018). Few investigations have also addressed the potential antagonistic health effects of exposure to fireworks emissions in India which showed that an increase of 30 to 40% cases of respiratory diseases, wheezing, and exacerbation of bronchial asthma and bronchitis patients of all ages (Liu et al. 2017). Antagonistic effects of fireworks with increase in $PM_{2.5}$ concentration, in comparison to the typical day have been observed not only at urban sites (Ravindra et al. 2003), but also at the suburban and rural sites in China (Zhang et al. 2017).

In spite of the enormous use of fireworks to celebrate special occasions worldwide, only a few studies have depicted the toxicity associated with firework PM on the respiratory system. Recently, a remarkable link was observed between particulate OP and trace metals associated with fireworks, suggesting an antagonistic impact of firework emission on human health. Generation of reactive oxygen species has been outlined following exposure to PM in various extracellular and cellular compartments, with evidence that different components (biological material, polycyclic aromatic hydrocarbons/quinones and trace metals) can cause oxidative stress through different pathways (Godri et al. 2010; Hickey et al. 2020). In a recent study, Hickey et al. measured the formation of reactive oxygen species (ROS) in bronchial epithelial airway (BEAS-2B) and human pulmonary microvascular endothelial (HPMEC-ST1.6R) cells treated with size-fractionated particles emitted from fireworks. It was concluded that significant increases in ROS in both cell types was associated with various types of fireworks and particles emitted from fireworks can be detrimental to mammalian cells and lungs (Hickey et al. 2020). In the present study, the short term variation in oxidative properties of $PM_{2.5}$ was assessed by the DTT assay during Diwali celebrations in 2019. This celebration is for a short period but it is enough to pollute the environment and to affect the human health. The period from 24-10-2019 to 26-10-2019 was considered as the pre-Diwali, 27-10-2019 and 28-10-2019 as the Diwali and 29-10-2019 to 31-10-2019 as the post-Diwali period. Air quality was measured on Diwali days and compared with normal days (pre-Diwali and post-Diwali days). This short (~ one week) measurement period provided us a peculiar opportunity to link the ambient $PM_{2.5}$ to its OP, due to firework activity.

2. Materials And Methods

2.1. Site description, sampling and extraction process

$PM_{2.5}$ samples were collected at a traffic and residential site (Bhagwan Talkies Crossing, adjacent to NH-19) at Agra, India (Fig. 1). Agra (27° 10' 47" N, 78° 01' 02" E; 168 msl) situated in Uttar Pradesh lies in the Indo-Gangetic Plain. It has an area of 188.4 km^2 and is one of the most populated cities in Uttar Pradesh with a population of nearly 1.8 million. Bhagwan Talkies Crossing is one of the busiest places in Agra. Traffic load is extremely high with approximately 10,000 vehicles per day. $PM_{2.5}$ samples were collected on 47-mm quartz fiber filters (Pallflex) using a fine particulate sampler (Envirotech, APM 550), operated at a flow rate 16.6 L min^{-1}. Sampling was performed twice a day from 8:00 a.m. to 7:55 p.m. and 8:00 p.m. to 7:55 a.m. Prior to sampling, the filter paper was pre-cleaned at 800°C for 7 h to remove volatile impurities, conditioned in a desiccator at 25°C and 40% relative humidity for 48 h, and then weighed using a microbalance (Mettler Toledo, ME 204). After sampling, the filters were again desiccated and weighed. Filters were stored at − 20°C in polyethylene zip-lock bags until analysis.

For analysis of metals, one-fourth of the loaded filter was digested in 10 ml nitric acid (69%, Merck) on a hot plate for 2 h at 90°C. After cooling, the digested solution was filtered through microporous membrane filter (Sartorious 393) and the final volume was made up to 40 ml with milli-Q water in a PTFE bottle. Then these acidic aqueous samples were analyzed for seventeen metals (Ba, Ca, Cr, Na, Ni, Cu, Be, V, Pb, Fe, Mg, Zn, Cd, K, Al, Se, Mn) using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 5110, USA). The working parameters of ICP-OES are listed in **Table S1**. The calibration of the instrument was performed by using multi-element standards (Agilent, USA). A seven-point standard curve using concentration range 0.05 to 25 ppm (0.05 ppm, 0.1 ppm, 0.5 ppm, 1.0 ppm, 5.0 ppm, 10 ppm and 25 ppm) were plotted for quantification. The linear regression coefficients of all the standard curves for individual metal were found to be greater than 0.99 ($R^2 > 0.99$). 5% HNO_3 (v/v) was used as blank and for the dilution of standards. Analysis of all the metal samples was done in triplicate, and the concentration was calculated as the average of triplicates. Field blank filters were also treated and analysed by the same procedure. The limit of detection (LOD) was determined by taking three times the standard deviation of blank concentration. LODs of metals were listed in **Table S2**. The metal concentration in field blanks was typically below or around the limit of detection for the method. Replicated analysis of selected samples and standards had the reproducibility of less than 5%. The recovery rates for the individual metals ranged from 95 to 106 percent, showing good repeatability and reliability of the extraction procedure. Blank correction is used in reporting concentrations. To avoid contamination, every glassware was washed in acid and dried in the oven.

The hourly concentrations of different criteria pollutants viz. CO, NO_2, SO_2, O_3, $PM_{2.5}$ and meteorological parameters viz. temperature (T), relative humidity (RH), wind speed (WS), rainfall (RF), solar radiation (SR) and wind direction (WD) were obtained from the online portal of Central Pollution Control Board (https://app.cpcbccr.com/ccr/#/caaqm-dashboard-all/caaqm-landing) for the study duration (from 24-10-2019 to 31-10-2019; Diwali period).

2.2. Measurement of Oxidative potential (OP) – The Dithiothreitol (DTT) Assay

The oxidative potential of water-soluble $PM_{2.5}$ was measured using the DTT assay. One-fourth of loaded quartz filters were extracted in milli-Q water followed by ultrasonication (model: USB 3.5 L H DTC, PCi Analytics) for 45 minutes (thrice, 15 minute each). Subsequently, insoluble suspended particles were removed from the extract through filtration using microporous membrane filter (Sartorious 393), and filtered extracts were incubated at 37 ºC with 100 µM DTT (≥ 98%, SRL Chem) which was made in 0.1 M phosphate buffer solution (Thermo Fisher, pH 7.4) in an amber coloured glass vial. These vials were continuously shaken in incubator with shaker (Waiometra, India). At various time intervals (0, 10, 20 and 30 minute), a known aliquot of reaction mixture was withdrawn from the vial and quenched with 10% (w/v) trichloroacetic acid (TCA, Thermo Fisher), 0.4M Tris-HCl (LOBA chemie, 20mM EDTA, pH 8.9) and 10 mM 5, 5'-dithiobis-2-nitrobenzoic acid (DTNB, SRL Chem). DTNB is immediately converted to its yellow coloured compound 2-nitro-5-thiobenzoic acid (TNB) that is stable for two hours at room temperature (Charrier and Anastasio 2012). Concentration of TNB is directly proportional to unreacted DTT concentration. Subsequently, it was measured by UV-VIS spectrophotometer (UV-1800, Shimadzu) at 412 nm. The OP response was evaluated as the depletion rate of unreacted DTT, according to the experimental procedure described in (Charrier and Anastasio 2012; Patel and Rastogi 2018a). The depletion rates were determined by linear fitting the unreacted DTT concentration as a function of time using seven experimental points (at 0, 10, 20, 30, 40, 50 and 60 min). Several blanks (n = 10) were also measured in parallel in the same way as the samples and the blank value were subtracted from measured DTT activity. All samples and blanks were run in duplicates/triplicates to maintain the quality of data, and samples were not accepted unless the relative standard deviation (RSD) values of duplicates/triplicates were within 5%. Further, to check the reproducibility of measurements, about 20% samples were repeated on different days and found to be consistent within 5–10%.

The OP was reported in terms of DTT consumption rate per cubic meter of total ambient air volume (DTTv) and DTT consumption rate per microgram of total PM mass (DTTm) collected on sampled filter. The OP was reported in terms of DTT consumption rate per cubic meter of total ambient air volume (DTTv) as Eq. 1 and DTT consumption rate per microgram of total PM mass (DTTm) collected on sampled filter as Eq. 2 (Fang et al. 2017).

$$DTTv\left(nmolmin^{-1}m^{-3}\right) = \frac{r_s\left(nmolmin^{-1}\right) - r_b\left(nmolmin^{-1}\right)}{V_t\left(m^3\right) \times A \times V}$$

1

$$DTTm\left(pmolmin^{-1}\mu g^{-1}\right) = \frac{r_s\left(pmolmin^{-1}\right) - r_b\left(pmolmin^{-1}\right)}{M_t(\mu g) \times A \times V}$$

2

where r_s and r_b are the DTT consumption rates of sample and blank, respectively. V_t and M_t are the total volume and the total particle mass of sampled air (subtracting the volume and mass of the blank filter respectively), respectively. A is the ratio of the filter paper covered with sample (A_h) and total filter paper (A_t) respectively. V is the ratio of the sample volume participating in reaction (V_s) and extraction volume (V_e) respectively. In general, the DTTv response is an extensive parameter depending on the $PM_{2.5}$ mass concentration, while the DTTm represents a measure of the intrinsic OP of the overall $PM_{2.5}$ contribution (Romano et al. 2020).

3. Results And Discussion

3.1. Mass concentration of $PM_{2.5}$ and its metallic composition

The 12-h mean $PM_{2.5}$ was found to be 262.9 ± 150.7 μg m^{-3} during the study period (Table 1). Concentration trends of $PM_{2.5}$ and meteorological conditions during the day-time and night-time of the study period have been illustrated in **Table S3**. The 12-h mean $PM_{2.5}$ (262.9 μg m^{-3}) was approximately 4.4 times higher than the National Ambient Air Quality Standards (NAAQS) of India (60 μg m^{-3}) (NAAQS 2009). A day after Diwali (October 28, 2019), particulate concentration reached to highest level of 444.3 and 508.4 μg m^{-3} in the day and night, respectively (Fig. 2) whereas, the mass concentration of $PM_{2.5}$ was 131.3 and 412.1 μg m^{-3} in day-time and night-time, respectively on Diwali days (27/10/2019). However, a day prior to Diwali (26/10/2019), the mass concentration of $PM_{2.5}$ was 108.4 and 153.2 μg m^{-3} in day-time and night-time, respectively. A comparison of pollutant concentration at different locations during fireworks is presented in Table 1. $PM_{2.5}$ mass concentration (262.9 μg m^{-3}) at the present site during the Diwali period was comparable to that observed at Beijing, China (248.9 μg m^{-3}, Zhang et al., 2017) during Chinese spring festival. $PM_{2.5}$ mass concentration at the present site was higher than various other sites around the world including urban area of Marylebone (44.3 ± 17.6 μg m^{-3}, Godri et al., 2010) and Nottingham (31.2–38.7 μg m^{-3}, Singh et al., 2015) in UK while the concentrations were lower than that reported at Shanghai, China (775 μg m^{-3}, Huang et al., 2012), Kolkata (1199.7 μg m^{-3}, Thakur et al., 2010) and Bhilai (1501.2 μg m^{-3}, Pervez et al., 2016), India. Similar increase in $PM_{2.5}$ level has been observed at Delhi (Parkhi et al. 2016) and Dehradoon (Prabhu et al. 2019) in India during Diwali. It was also observed that the $PM_{2.5}$ mass concentration was higher during night time as compared to day time due to intense firework activity during night-time (Fig. 2). Apart from the burning of firecrackers, the meteorological conditions might have contributed to delayed dispersion of pollutants too (Ganguly et al. 2019). During Diwali period low relative humidity 42% in day-time was observed which increased upto 63% in night-time while, the wind speed ranged from 0.9–1.2 m/s during day-time and 0.4–0.8 m/s in night-time resulting in decrease in boundary layer height, making the atmosphere less conducive to dispersion and dilution of pollutants. The predominant wind direction was West- north west (W-NW) during the study period (**Table S3**).

Table 1

Comparison of Ambient pollutant concentrations of normal, pre- Diwali and post-Diwali days to Diwali day with similar firework studies

Event	City, Country	Study period	Ambient pollutant concentration (μg m^{-3})						DTT Activity
			$PM_{2.5}$	PM_{10}	O_3	CO	NO_x	SO_2	DTTv (nmol min^{-1} m^{-3})/ DTTm (pmol min^{-1} $μg^{-1}$)
[a]Guy Fawkes Night (Godri et al. 2010)	Marylebone, UK	2007	44.3 ± 17.6	-	-	-	83.3 ± 3.5	23.6 ± 4.0	6.5 ± 1.5 (DTTm)
[b]Diwali (Thakur et al. 2010)	Kolkata, India	2008	1199.7	2237.2	-	-	94.5	12.3	-
[c]Chinese Spring Festival (Huang et al. 2012)	Shanghai, China	2009	775	> 900	-	-	286	438	-
[d]Commonwealth Games (Beig et al. 2013)	New Delhi, India	2010	> 2000	> 2500	-	-	-	-	-
[e]Diwali (Saha et al. 2014)	Kolkata, India	2013	-	875	-	-	190 (NO_2)	125.21	
[f]Guy Fawkes Night (Singh et al. 2015)	Nottingham, UK	2000–2012	31.2–38.7	37.4	-	-	-	-	-
[g]Diwali (Pervez et al. 2016)	Bhilai. India	2012	1501.2	-	-	-	-	-	-
[h]Diwali (Parkhi et al. 2016)	New Delhi and NCR India	2010 and 2011	1620 in 2010, 390 in 2011	2070 in 2010, 600 in 2011	> 50 ppbV	5–10 ppmV	-	-	-
[i]Chinese Spring Festival (Zhang et al., 2017)	Beijing, China	2015	248.9	-	-	-	-	57.8	-
[j]Diwali (Ambade 2018)	Jamshedpur, India	2014	-	500.5	-	-	73.4	8.6	-

[a–m]Other firework studies; 24-h average during study period

[n]Present study; 12-h average during study period.

Event	City, Country	Study period	Ambient pollutant concentration (µg m^{-3})						DTT Activity
			$PM_{2.5}$	PM_{10}	O_3	CO	NO_x	SO_2	DTTv (nmol min^{-1} m^{-3})/ DTTm (pmol min^{-1} μg^{-1})
[k]Diwali (Prabhu et al. 2019)	Dehradoon, India	2017 and 2018	79.92–324.97	57.35–256.12	-	-	-	-	-
[l]Guy Fawkes Night (Rindelaub et al. 2021)	Auckland, New Zealand	2019	-	35.8	-	-	-	-	-
[m]Diwali (Singh et al. 2020)	Delhi, India	2018	-	974.55	-	-	-	-	-
[n]Diwali (Present study)	Agra, India	2019	262.9 ± 150.7	-	26.3 ± 13.0	1.4 ± 0.4	70.3 ± 26.2	15.8 ± 2.2	0.28 ± 0.46 (DTTv) and 5.05 ± 4.03 (DTTm)
[a–m]Other firework studies; 24-h average during study period									
[n]Present study; 12-h average during study period.									

Firework activity during late evening and night may cause increased emissions of metal oxides, metal salts and other inorganic species. Figure 3a illustrates the variation of trace metals such as Ba, Be, Cd, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn, whereas, the variation of crustal metals such as Al, Ca, Fe, K, Mg, and Na is represented in Fig. 3b. Among all the seventeen metals, Fe, K, Mg and Na were identified as the major metals with concentrations above 50 ng m^{-3}. Al, Ba, Ca, Cu and Zn varied from 1 to 50 ng m^{-3} while Be, Cd, Cr, Mn, Ni, Pb, Se and V and were mostly between 0.1 and 1 ng m^{-3}. The concentration of V was lowest (< 0.1 ng m^{-3}). The concentration of metals was found in the order of Na > Fe > Mg > K > Ca > Zn > Ba > Al > Pb > Cu > Be > Cr > Ni > Se > Mn > Cd > V. Ba, Ca, Cr, Ni, Se, Cu, Be, V, Mg, Zn, and Cd were found to be 5.0, 2.7, 2.4, 2.0, 2.0, 2.0, 1.8, 1.8, 1.6, 1.5, and 1.4 times higher, whereas Mn and K were moderately higher than the levels observed during pre-Diwali.

Ba, as a tracer of fireworks (Lin 2016), has the maximum contribution among these metals which could be due to the extensive use of various salts of Ba, such as barium sulphate ($BaSO_4$), barium oxalate (BaC_2O_4), barium carbonate ($BaCO_3$), barium nitrate ($Ba(NO_3)_2$), barium chlorate ($Ba(ClO_3)_2$), in the firecrackers to impart green colour to the flashes (Kulshrestha et al. 2004). Additionally, salts of Al (white), Na (yellow), Cu (blue) and Mg (bright white) contribute to creating a range of colors in the fireworks (Moreno et al. 2007), however, In contrast, Fe plays a vital role in producing sparks, while Ca enhances the intensity of colour created by other elements. Similarly, rest of the metals are also used in fireworks to add color and sparkle. Thus, the high concentration of these metals on Diwali day may be attributed to the presence of various salts of color-producing metals (Hickey et al. 2020; Rindelaub et al. 2021). It has also been found that the levels of metal were low during the pre-Diwali and post-Diwali periods, suggesting their retention period was short and weak contribution of other local sources (Kulshrestha et al. 2004). This study found similar levels of Al, Ba, Mg and other metal as previous studies conducted in China (Kong et al. 2015), Taiwan (Tsai et al. 2012), Italy (Vecchi et al. 2008), Spain (Moreno et al. 2007), and India (Kulshrestha et al. 2004; Barman et al. 2008; Perrino et al. 2011).

A backward air mass trajectory analysis can assist in determining the source and pathway of PM which may be due to the fact that PM concentrations are closely related to wind speed and direction. The 72-h backward air mass trajectories in Agra were simulated at 12:00 h (UTC) during Diwali period by using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al. 2015) and are represented in **Figure S1**. The trajectories were short which showed the firework effect is localized within a limited geographic scale during Diwali days from 26/10/2019 to 28/10/2019, suggesting potential needs for local monitoring and control programs.

Conclusion

The 12-h mean $PM_{2.5}$ was found to be 262.9 ± 150.7 µg m-3 during the study period which exceeded by the NAAQS limits by 4.4 times. Firework activity was also characterized by increased levels of gaseous pollutants (NOx, SO_2 and O_3), and trace metal concentrations (Ba, Pb, Cu, Fe, Mg, K, Al and Mn). Elevated PM2.5-NOx slope for fireworks including traffic emissions suggested significant contribution of fireworks. The highest value of volume normalized DTT (DTT_v = 1.37 nmol min^{-1} m^{-3}) and mass normalized DTT (DTT_m = 11.77 p mol min^{-1} μg^{-1}) was found in the next morning of Diwali showing the significant elevation in day time as compared to night time, suggesting stronger ROS activity associated with PM constituents due to fireworks which are retained in atmosphere. Good correlations ($r > 0.700$, $p < 0.01$) were found between redox-active metals like Cd, Cr, Cu, Ni, and V and DTT activity that could be due to the ability of these metals to catalyze ROS generation in ambient air, while Ba, Be and Se in atmosphere as major constituents of firecrackers were also strongly associated with DTT activity. The significant correlation between O_3 and PM-ROS activity was noticed which implied that the intensity of photochemical reaction including chemical species associated to fireworks is responsible for the formation of tropospheric O_3. This was also a prominent factor influencing the formation of particulate ROS in the daytime atmosphere. The daily OP and hazard index (HI) was compared to measure the health effects of fine particles which suggested that measurement of PM-associated OP is needed along with mass concentration to estimate the toxicity. From health perspective, it is required to restrict or control the fireworks activity, to mitigate human exposure that could be possible only through public awareness and emphasising on manifestation of some effective control measures during celebrations like Diwali festival.

Declarations

Ethics approval and consent to participate

The manuscript is submitted to Springer for consideration. The submitted work is unique and has never been published elsewhere, and it has been submitted solely to the journal. The data for this manuscript is taken from other sources that were clearly cited and used with permission. The data is true and not manipulated.

Consent for publication

Authors seek their consent to Springer for publication their data prior to submitting their paper to a journal.

Author's contribution

IG has made substantial contribution to analysis and interpretation of data and writing the original draft of manuscript. PKV is involved in checking all the mathematical calculations reported in the manuscript. KMK is involved in reviewing and editing the manuscript. AL has been involved in conceptualization, data curation, funding acquisition, reviewing and editing the manuscript. All authors read and approved the final manuscript.

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Competing interest

The authors declare that they have no competing interests.

Availability of data and materials

The authors declare that all data supporting the findings of this study are available within the article and its supplementary information files.

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Tables 2 And 3

Table 2. Concentrations of particulate matter and trace gases on pre-Diwali, Diwali and post-Diwali day

Pollutants	Concentration					
	pre-Diwali		Diwali		post-Diwali	
	Day	Night	Day	Night	Day	Night
$PM_{2.5}$ (μgm^{-3})	52.7 ± 17.1	65.6 ± 9.2	63.0 ± 9.6	116.3 ± 23.6	97.6 ± 35.0	97.6 ± 15.9
NOx (μgm^{-3})	41.6 ± 2.4	78.9 ± 13.4	51.1 ± 5.8	108.1 ± 11.6	50.9 ± 6.2	97.6 ± 6.0
SO_2 (μgm^{-3})	14.1 ± 3.3	16.9 ± 3.1	14.7 ± 0.4	15.9 ± 1.7	16.2 ± 1.7	16.6 ± 1.4
CO (mgm^{-3})	0.8 ± 0.2	1.3 ± 0.3	1.3 ± 0.1	1.7 ± 0.2	1.6 ± 0.4	1.8 ± 0.2
Ozone (μgm^{-3})	28.6 ± 4.6	16.9 ± 4.3	49.9 ± 12.2	15.4 ± 1.7	35.9 ± 4.6	15.1 ± 0.2

Table 3. Correlation coefficients (r) of volume-based DTT activity (DTTv) with trace gases during Diwali period

Trace Gases	DTTv	
	r (Day-time)	r (Night-time)
NO_2	0.28	**0.65**
SO_2	0.32	0.32
CO	**0.68**	0.23
O_3	**0.92**	**0.49**

Figures

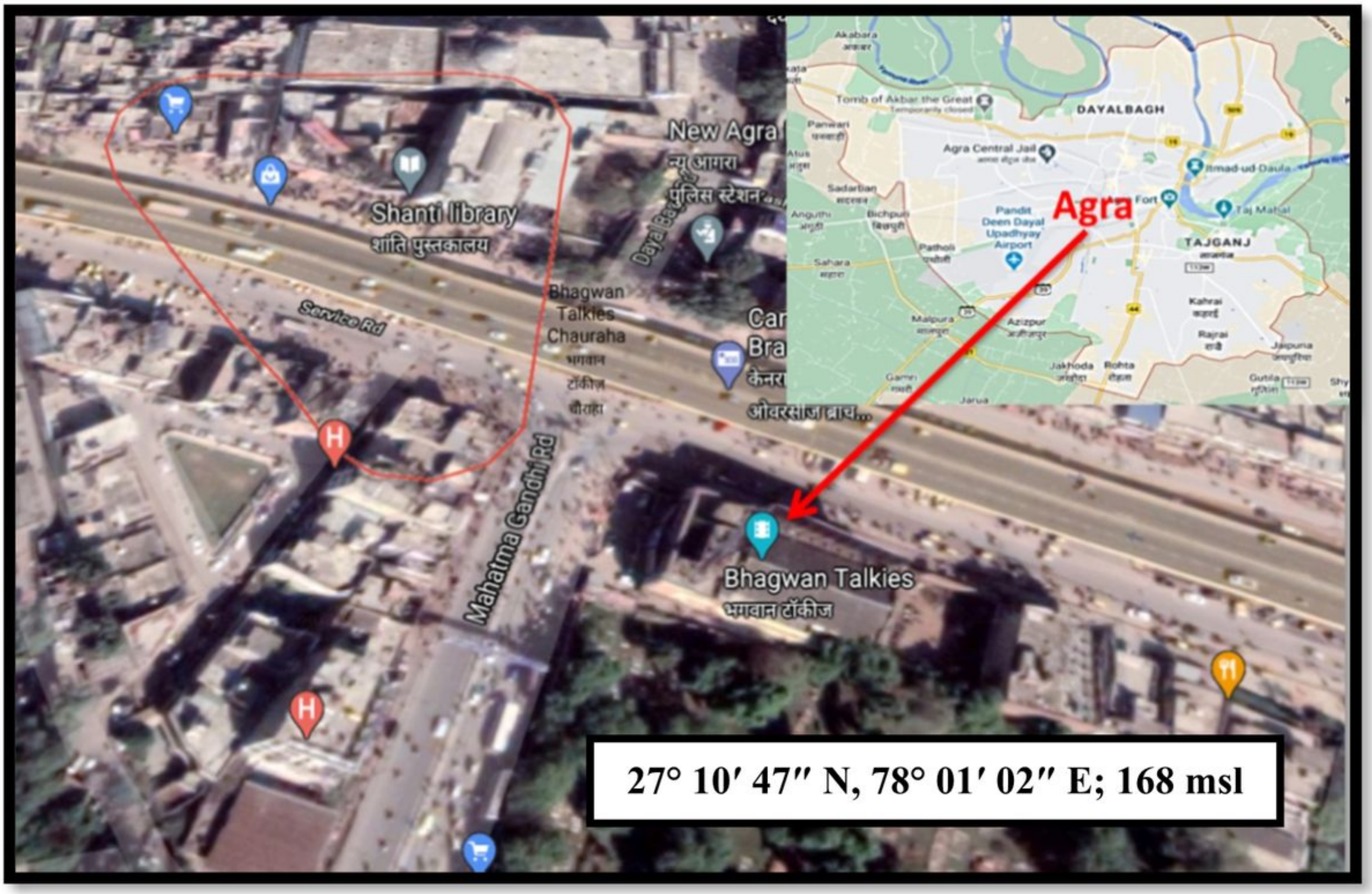

Figure 1

Location of PM2.5 sampling site at Agra

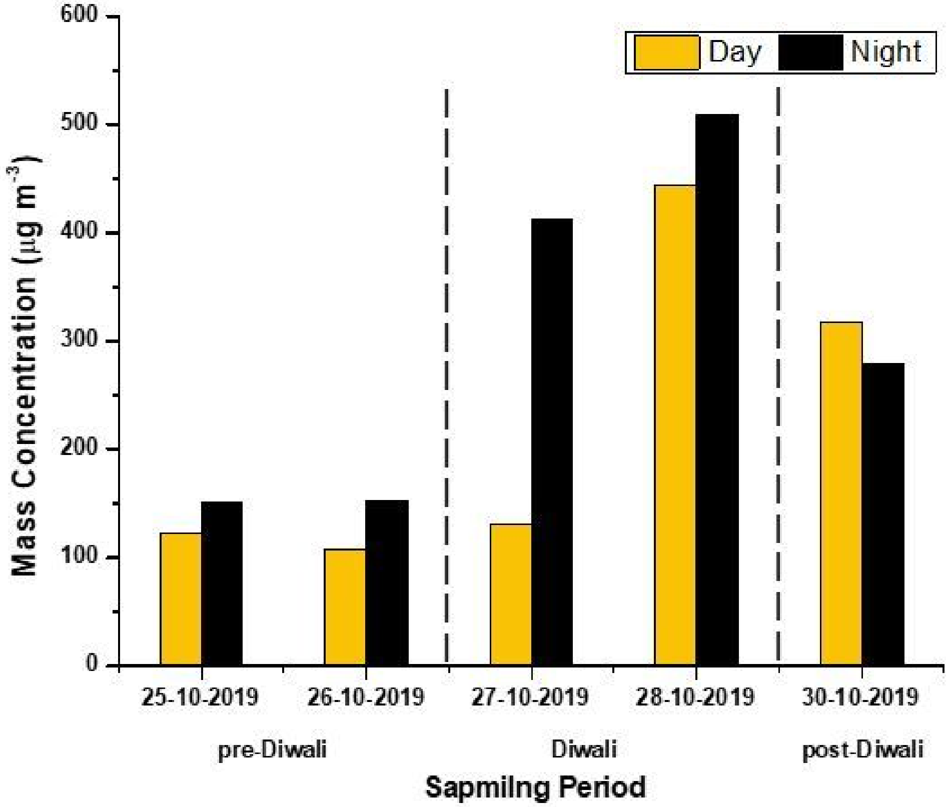

Figure 2

Day night variation of PM2.5 mass concentrations during Diwali 2019

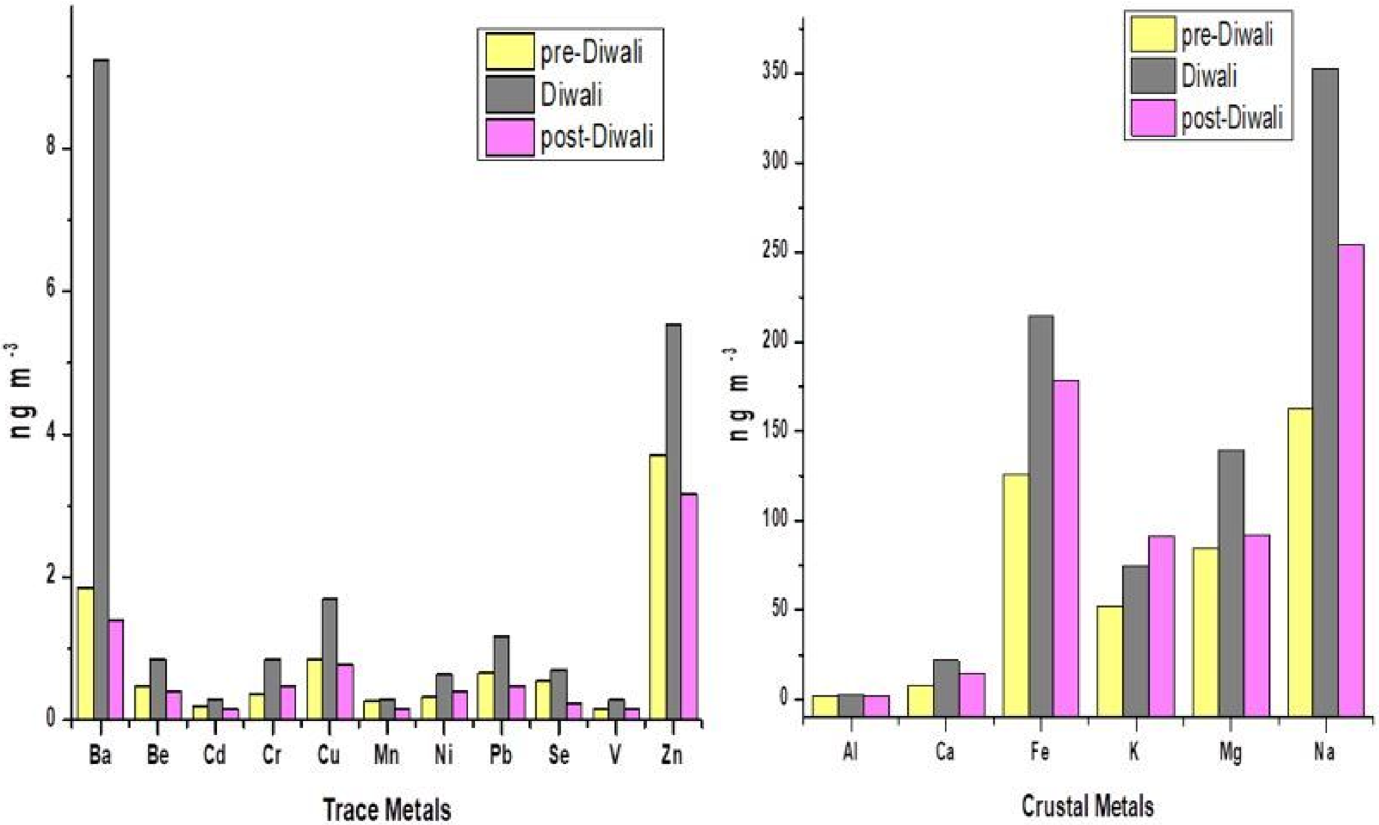

Figure 3

Variation of trace and crustal metal during pre-Diwali, Diwali and post-Diwali period

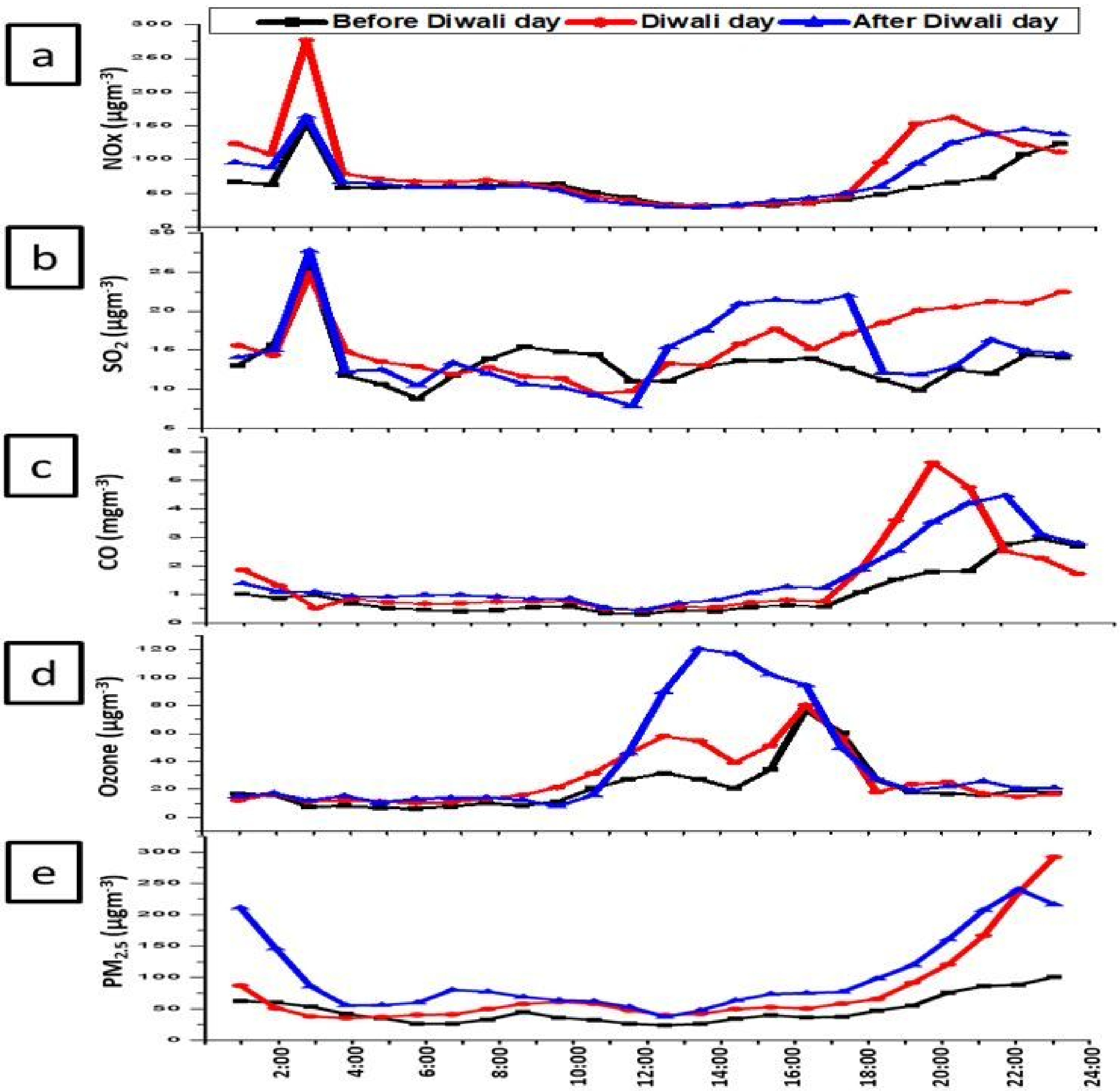

Figure 4

Diurnal profile of (a) NOx, (b) SO2, (c) CO, (d) O3 and (e) PM2.5 mass concentration

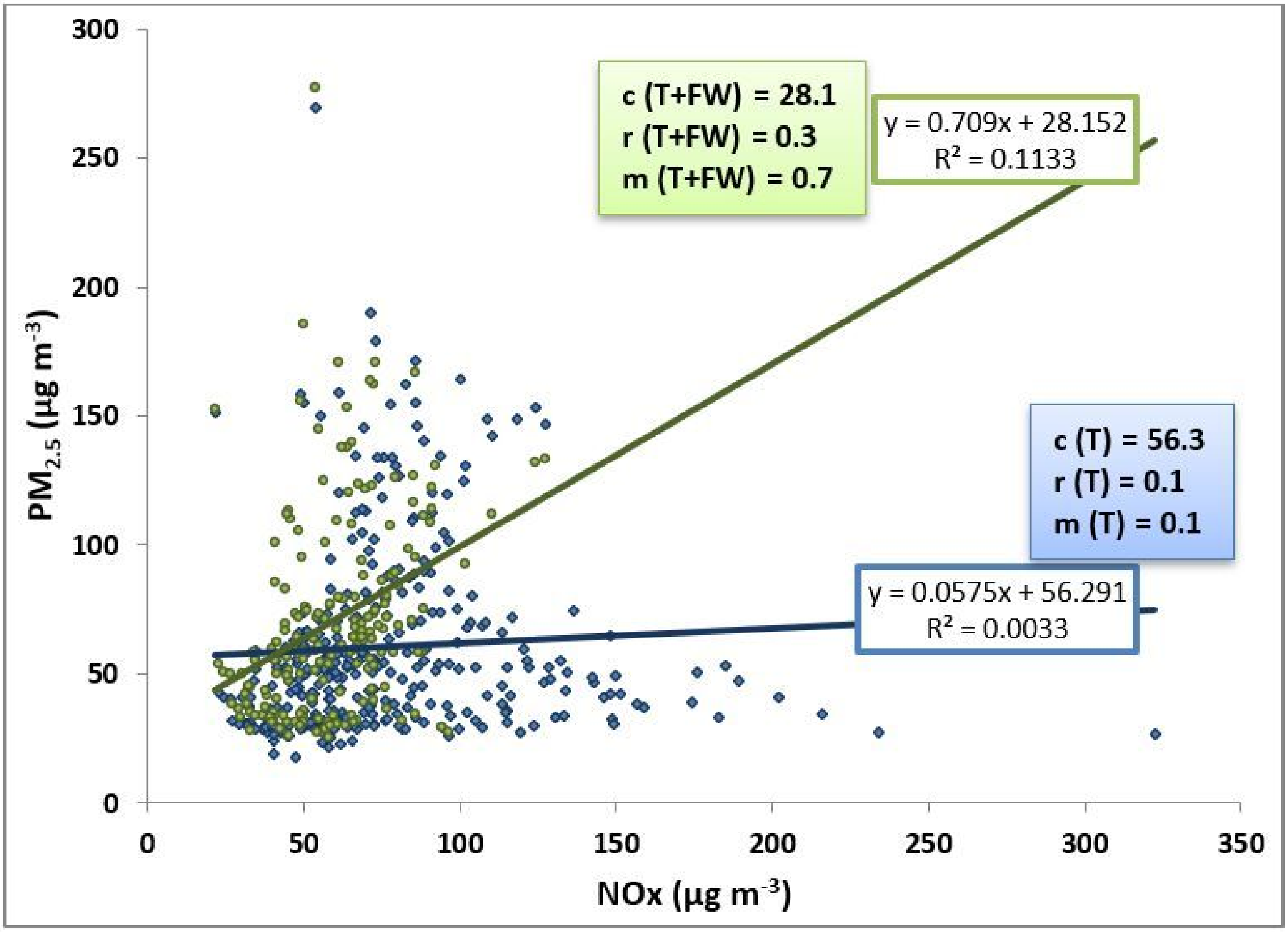

Figure 5

Regression curve of NOx-PM2.5

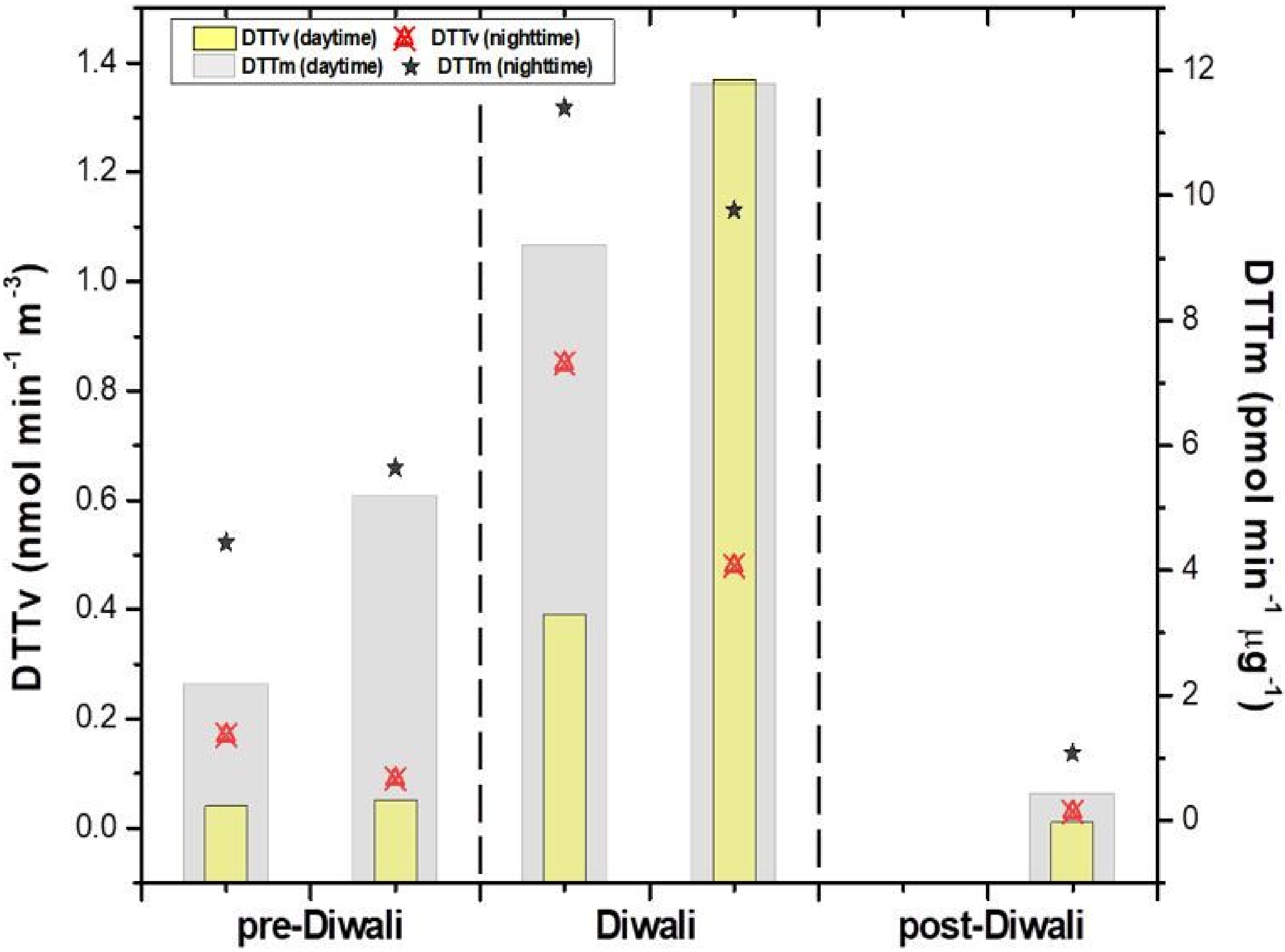

Figure 6

Diurnal Variation in OP values during pre-Diwali, Diwali and post-Diwali.

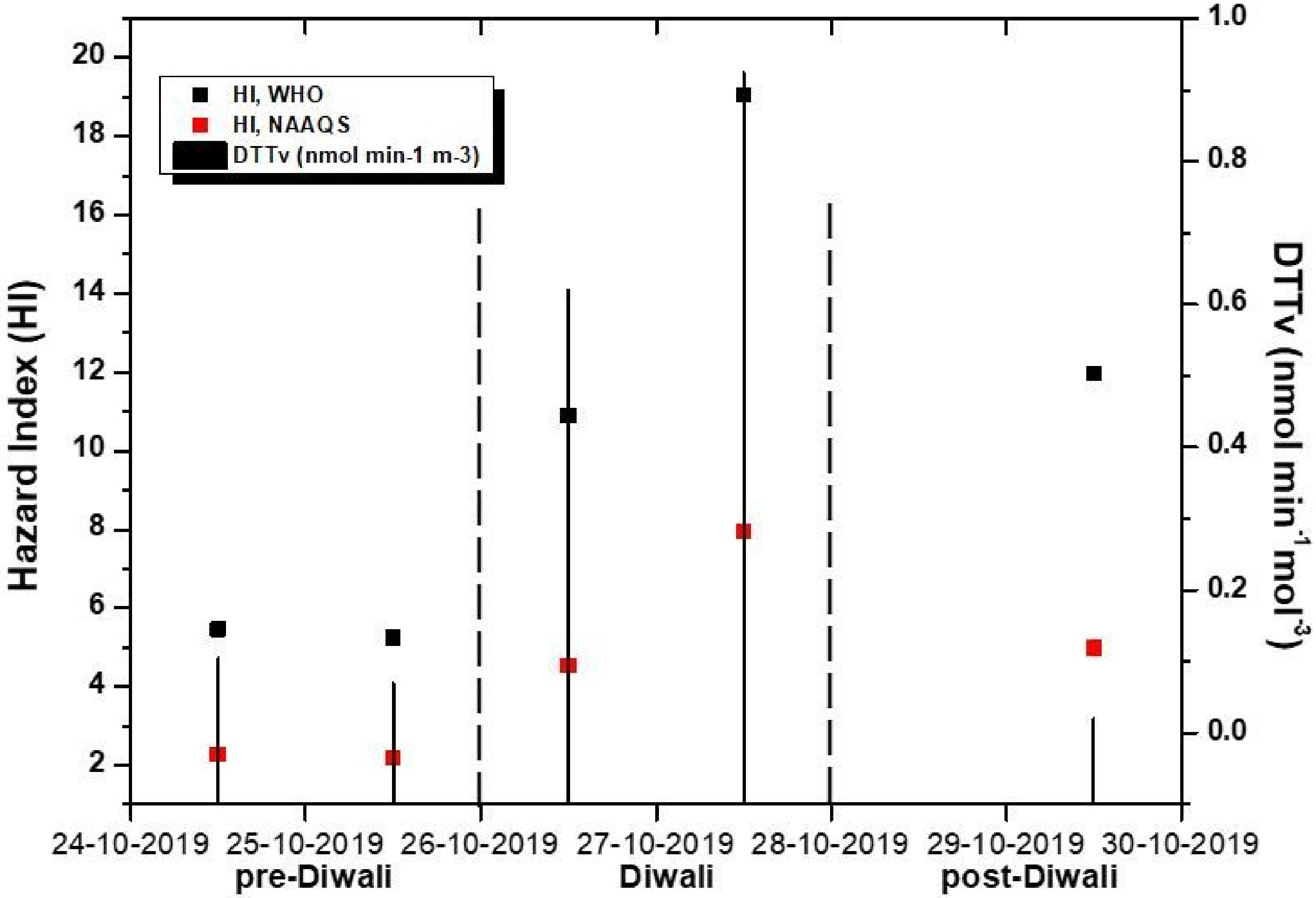

Figure 7

Daily variations in the measured DTTv and HI during Diwali period

Supplementary Files

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