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Extreme Events of Reactive Ambient Air Pollutants and their Distribution Pattern at Urban Hotspots

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ABSTRACT

The occurrence of extreme events of air pollutant concentrations at urban hotspots is a routine phenomenon, particularly during the winter season. However, extreme events of reactive air pollutants are more frequent during the summer season. The assessment of air pollution extreme events will provide a platform to formulate an effective and efficient hotspot urban air quality management plan. The statistical distribution model (SDM) is widely used to describe the average as well as extreme air pollutant concentration in a more organized and efficient manner. In the present study, the best fit SDM has been evaluated for hourly average $PM_{2.5}$ and NO_2 concentrations at one of the busiest traffic intersections in Delhi city (air pollution hotspot 1: APH-1) and for $PM_{2.5}$ at one of the heavily trafficked road corridors in Chennai city (air pollution hotspot 2: APH -2). The SDMs were developed for different seasons to evaluate the impacts of climatic conditions on the air pollution events. Results indicate that NO_2 concentrations were best fitted with lognormal and log logistic distribution models respectively, for winter and summer seasons at APH-1. However, lognormal distribution was best fitted to $PM_{2.5}$ concentration of winter and summer seasons at both APHs.

Keywords: Extreme pollutant concentrations; Urban hotspot; Statistical distribution model; Goodness of fit test; Location and Scale parameters.

INTRODUCTION

Urban air pollution (UAP) is a major concern in both developed and developing countries. The sudden rise in vehicle exhaust emissions during peak traffic hour results into extreme air pollution events (episodic conditions) at urban hotspots (Chelani, 2013; Pant *et al.*, 2015). The air pollution episodes are typically occurs during winter periods, characterized by low wind speeds, low mixing heights and temperature inversions (Gokhale and Khare, 2007a; Tiwari *et al.*, 2012). The geography at hotspots in urban regions, especially traffic intersections and congested road surrounded by high rise buildings are leading to sudden occurrences of extreme air pollution events. The urban hotspots are severely prone to vehicular pollution, because of reduced vehicle speed due to traffic congestion and the release of more exhaust emissions (Pant and Harrison, 2013; Gulia *et al.*, 2015). Although, summer condition is favorable for air pollutant dispersion, chemically reactive air pollutants such as oxides of nitrogen (NO_x), secondary particulate matter, having an aerodynamic diameter ≤ 2.5 ($PM_{2.5}$) and ozone are found to be higher during this season. Kumar *et al.* (2015) reported that maximum hourly O_3 and NO_2 concentrations of 138.4, μg m^{-3}, 106.6 μg m^{-3} and 92.1 μg m^{-3} during summer, winter and autumn, respectively at one of the urban locations in Delhi city. Chelani (2013) has observed that 24 hour average NO_2 concentration during summer as 116 μg m^{-3} at one of the traffic location in Delhi city. Pant *et al.* (2015) have found that 12 hour average $PM_{2.5}$ concentration was observed to be 58.2 ± 35.0 μg m^{-3} with a maximum of 179.5 μg m^{-3} at an urban hotspot in Delhi city which exceeded the NAAQS value of 60 μg m^{-3}. However, DPCC (2016) has reported that 24 hour average $PM_{2.5}$ is around 300 μg m^{-3} in Delhi city during summer season. Higher concentrations of these reactive air pollutants during summer season may be due to the chemical transformation of secondary air pollutants, which is significantly influenced by the presence of their pre-cursor pollutants and favorable climatic conditions i.e., humidity and ambient temperature (Wang *et al.*, 2016). The uncertainty in defining the complex behavior of chemically reactive air pollutants in the atmosphere and occurrence of their extreme concentrations can create difficulties in assessment and prediction of air pollution load on shorter time scale (Moussiopoulos *et al.*, 2005; Sharma *et al.*, 2013a).

The statistical distribution model (SDM) can describe air

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pollutant concentrations in a more organized and efficient manner including extreme as well as average concentrations. In addition, SDM is a tool of summarizing the information contained in the entire data set in a concise manner (Lu, 2002). In the last two decades, several frequency distribution models were evaluated to satisfy the objectives of the urban air quality management (Taylor *et al.*, 1986; Jakeman *et al.*, 1988; Gokhale and Khare, 2004; Sharma *et al.*, 2013b). These are probability-based models capable of estimating the entire range of pollutant concentration distribution. The SDMs are non-causal and only the monitored air pollutant concentrations are used to develop the models. The distribution form of any pollutants can be influenced by their nature (reactive or non-reactive) and source type (point, area and line), averaging time (1 hour, 3 hour, 24 hour, weekly, seasonal and annual average), emission variation pattern (continuous or discontinuous) and prevailing meteorology (seasonal variations). SDMs can easily describe that how these values of a random variable can spread out over its range. Rumberg *et al.* (2001) reported that the 3- parameters lognormal distribution model was better represented the $PM_{2.5}$ and $PM_{8.0}$ concentration data. Chung and Fang (2002) used three theoretical distributions, namely, Lognormal, Weibull, and type V Pearson to fit the measured $PM_{2.5}$, PM_{10} and wind speed data. They found that the lognormal distribution model performed best. Gokhale and Khare (2004) reviewed the common methodologies used in statistical distribution modeling. Kan and Chen (2004) used four types of theoretic distributions (Lognormal, Gamma, Pearson V and Extreme value) to fit daily average concentration data of PM_{10}, SO_2 and NO_2 and found that the best-fit distributions for PM_{10}, SO_2 and NO_2 concentrations in Shanghai were lognormal, Pearson V, and extreme value distributions, respectively. Further, Giavis *et al.* (2009) found that out of lognormal, gamma and Weibull, only first one is the most appropriate to represent the PM_{10} distribution, while the Weibull distribution is unsuitable for this case. Papanastasiou and Melas (2010) verified that the PM_{10} concentration distribution can be adequately simulated by lognormal distribution. The probability density function (pdf) of lognormal distribution is capable to predict the number of days when the European Union (EU) air quality standards are exceeded in Volos area. In the recent past, Sharma *et al.* (2013b) provided an integrated statistical approach for evaluating the exceedences of four criteria pollutants (i.e., SO_2, NO_2, CO and PM_{10}) for Delhi mega city and concluded that pdf is a basic and essential tool for realistically evaluating the compliance of NAAQS. Table 1 summarizes some of the past studies on fitting SDMs for air quality data by comparing the types of pollutant, times average concentration and source types. However, most of them are carried for 24 hour average pollutant concentrations and for source specific and did not include $PM_{2.5}$ which is one of the critical air pollutants for health point of view.

Therefore, the present study is an attempt to evaluate distribution patterns of hourly average $PM_{2.5}$ and NO_2 concentrations at two different urban hotspots having different emission, meteorology and geometrical characteristics. Further, extreme event of these pollutants have been predicted and validated with observed concentrations.

EXTREME AIR POLLUTION EVENT AT DESIGNATED AREA IN MEGACITIES

Swelling urban population and increased volume of motorized traffic in cities have resulted in severe air pollution affecting the surrounding environment and human health. In developed countries, national annual average ambient air pollution levels decrease due to implementation of advanced and efficient management practices (Parrish *et al.*, 2011; EEA, 2013). However, the problem of sudden occurrence of extreme air pollution events (episode) still persists. Moussiopoulos *et al.* (2005) reported that ambient air pollution levels at urban hotspot in twenty European cities were exceeded the specified NAAQS. In the UK, out of total declared air quality management areas (AQMAs), 33% were declared due to exceedance of specified NO_x and 21% were due to exceedances of the specified PM standard (Faulkner and Russell, 2010). In European countries, the emission reductions from 1990 to 2009 has been reported to be around 54% for SO_2, 27% for NO_x, 16% for PM_{10} and 21% for $PM_{2.5}$. In spite of all these efforts in place, it observed that 18% to 49% of the population in these countries is still exposed to high levels of PM concentration (EEA, 2013). In megacities of North America namely Los Angeles, New York, and Mexico City showed declining trends in some of the criteria air pollutant concentrations

Table 1. Some of the past studies describing fitting of statistical distribution model for air pollutant.

Reference	Pollutants	Time average	Best fitted model	Source type
Simpson *et al.* (1983)	CO	1 hr.	Lognormal	Area
Taylor *et al.* (1986)	TSP ,SO_2, NO_x, O_3, CO	24 hr.	Lognormal for TSP , SO_2, NO_x; Gamma for O_3, CO	Point, area and line source
Taylor *et al.* (1987)	SO_2	24, 8, 3 & 1 hr.	Weibull	Point
Lu (2002)	PM_{10}	24 hr.	Lognormal	Line source
Kan and Chen (2004)	PM_{10}, SO_2, O_2	24 hr.	Lognormal (PM_{10}), Pearson V (SO_2), Extreme value (NO_2)	Line source
Gokhale and Khare (2005)	CO	1 hr.	Log-logistic	Line source
Papanastasiou and Melas (2010)	PM_{10}	24 hr.	Lognormal	Line source
Sharma *et al.* (2013b)	SPM, PM_{10}, NO_2,	24 hr	Lognormal for SPM and PM_{10}, Log- Logistic for NO_2	Urban area

during the last five decades. However, at some designated non- attainment areas (NAAs), the concentrations of NO_x and $PM_{2.5}$ were found to be violating NAAQS (Parrish *et al.*, 2011; USEPA, 2012). In the Asian subcontinent, few developed countries, e.g., Singapore, Japan and Hong Kong, are also facing street-level air pollution problems due to an increase in the number of motorized transport (Edesess, 2011). In developing countries, all most all mega cities are facing acute air pollution problems i.e., high levels of ambient PM and NO_2 concentrations due to rapid urbanization. In Shanghai, New Delhi, Mumbai, Guangzhou, Chongquing, Calcutta, Beijing and Bangkok, the ambient PM and NO_2 concentrations were frequently violated WHO values (CAI-Asia, 2010). In Beijing, 90% of time, PM concentrations exceed the NAAQS and WHO-AQG (Zhang *et al.*, 2016). In Indian metropolitan cities (Delhi, Mumbai, Kolkata and Chennai), ambient PM concentrations frequently violate the NAAQS as well as WHO guidelines (Guttikunda and Gurjar, 2012; Pant *et al.*, 2015). Recently, studies carried out by Yale University, USA, and WHO, have ranked Delhi as the "worst" polluted city based on an environmental performance index (Hsu and Zomer, 2014). It was observed that increase in vehicular activity as resulted in deterioration of urban air quality in both developed and developing countries (Miller *et al.*, 2006; Ravindra *et al.*, 2015; Wei *et al.*, 2016).

MATERIALS AND METHODOLOGY

Air pollutant concentration is a random variable which can be described accurately using SDM. Initially, NO_2 and $PM_{2.5}$ concentrations data were summarized and analyzed in form of descriptive statistics. These statistics provided preliminary assessment on the best fit distribution form of NO_2 and $PM_{2.5}$. The methodology for identification of the best fit distribution model was completed in three steps- (i) selection of the appropriate statistical distribution models, (ii) identification of the best fit distribution model using goodness of fit test and (iii) estimation of the associated model parameters. Based on literature, it was found that air pollutant concentrations are described by continuous distribution models such as Normal, Lognormal, Exponential, Logistic, Log-logistic, Weibull and Gamma (Taylor *et al.*, 1986; Jakeman *et al.*, 1988; Gokhale and Khare, 2007b; Sharma *et al.*, 2013b). Therefore, these SDMs were verified using three goodness of fit tests, i.e., Kolmogorov-Smirnov (KS), Anderson -Darling (AD) and Chi-square to identify the best fit (Taylor *et al.*, 1986; Gokhale and Khare, 2007b). The KS test is found more satisfactory to check the fitting of statistical distributional form of the chemical species (Kalpasanov and Kurchatova, 1976). However, AD test is found more sensitive in calculating the extreme values of concentrations towards the *tail* (Gokhale and Khare, 2007b). The Chi-square test is commonly used to verify the fitting of SDM with monitored concentration data. The maximum likelihood estimation (MLE) method was used to estimate the associated parameters of the best fit SDM (Ott and Mage, 1976). Further, best fit SDM is used to predict the exceedance of NO_2 and $PM_{2.5}$ over specified standard.

SITE CHARACTERISTICS

I.T.O. Intersection, Delhi City, APH-1

Delhi is one of the seventeen declared NAAs in India (CPCB, 2006) and having population of 22.2 million. It is located at an altitude ~215 m above mean sea level (Fig. 1) and faces heavy seasonal climatic variability. For example, temperature varies from minimum of 4–5°C during the winter (months of December–February) to maximum of 45–48°C during the summer (months of March–May) (IMD, 2010; Perrino *et al.*, 2011). The winter season faces frequent ground based inversion conditions which restrict the dispersion of pollutants. Further, the monsoon season experiences more than 80% of the annual rainfall. In Delhi city, ITO intersection is selected as study site (Air Pollution Hotspot; APH-1). It is one of the busiest traffic intersections in Delhi, located at 28°37'39.70"N and 77°14'28.60"E and surrounded by densely populated commercial and residential areas. Based on dispersion modelling and monitored data, numerous studies in past (Khare *et al.*, 2012; Kaushar *et al.*, 2013; Sharma *et al.*, 2014; Kumar *et al.*, 2015; Pant *et al.*, 2015) reported the frequent violations of NAAQS at different urban hotspots in Delhi city including ITO intersections.

Sardar Patel Road, Chennai City, APH-2

Chennai is also one of the seventeen declared NAAs in India, notified by CPCB (CPCB, 2006). It has a population of 4.6 million and located on the South East coast of India at an average altitude of six meters above mean sea level (Fig. 1). In the summer, the city experiences humid weather and strong wind with mean daily temperature reaching 36 ± 2°C. The climatic conditions are strongly affected through formation of land breeze (08:00–11:00) and sea breeze (12:00–14:00). Sea breeze controls the temperature and reduces the mixing height during afternoon, resulting in to poor dispersion of air pollutant. During winter, the ambient temperature reaches 21 ± 2°C. The monsoon experiences 90% of annual rainfall (Sivaramasundaram and Muthusubramanian, 2010). The Sardar Patel (SP) road is selected as a study site (APH-2). It is one of the busiest road corridors in the city, located at 13°00'23.94"N and 80°14'28.64"E and surrounded by densely populated institutional and residential areas. The traffic density is varied between 0.17 and 0.14 million vehicles per day, during weekdays and weekends, respectively. Ambient air quality at APH-2 was frequently reported to exceed the NAAQS (Srimuruganandam and Nagendra, 2011; Nagendra *et al.*, 2012).

AIR POLLUTION MONITORING DATA

One- hour average ambient NO_2 and $PM_{2.5}$ concentrations data for winter (December 2009–February 2010) and summer (March–May 2010) seasons of the year 2010 were collected from the ambient monitoring station located at APH-1 operated by the Central Pollution Control Board (CPCB), New Delhi. However, missing hours were present in this continuous hourly data due to malfunctioning of the

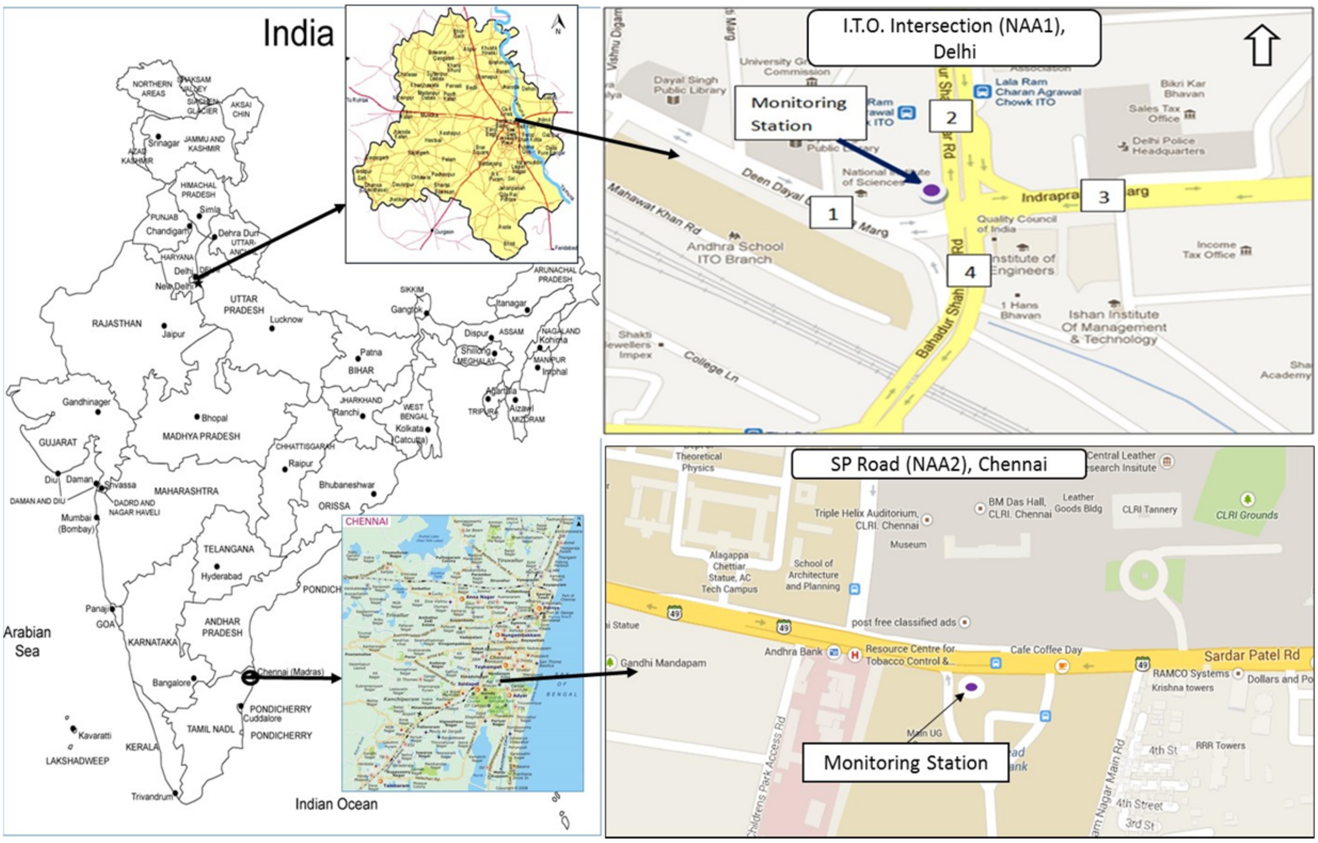

Fig. 1. Selected air pollution hotspots in Delhi and Chennai cities.

instruments. During winter, hourly $PM_{2.5}$ concentrations data were available for one week period only. The APH-1 monitoring station houses laser based particulate monitor which continually collects the data on $PM_{2.5}$ and NO_2 taking into account the effects of rains, dust storms or any other meteorological/ weather reverberations, if any. It is observed that out of total number of study hours (i.e., 2184) during the winter season, only 16 no. of hours was affected by the rain, however no dust storm was reported during the winter season. Only NO_2 concentrations were measured during the rainy hours at this station. The percentage of monitoring hours during rain and dust storm for NO_2 and $PM_{2.5}$ were 0.7% and 0%, respectively. However, in the summer season, out of total hours (i.e., 2184), only 31 no. of hours, rain were observed. Out of these hours, monitoring were carried out only for 26 and 14 no. of hours for NO_2 and $PM_{2.5}$, respectively. The dust storms were observed for 65 no. of hours during the study period out of which only 56 no. of hours, the monitoring were conducted. Therefore, the percentage of monitoring hours carried out during rain and dust storms for NO_2 and $PM_{2.5}$ are 3.8% and 3.2% respectively. The percentage of monitoring hours during rain and dust storm period are very less and does not impact the distribution patterns of pollutant concentration if removed from the data set.

The monitoring station is located at 28°37'40.83"N and 77°4'28.14"E at an altitude of 221 m above msl and at 12 meters distance from the BSZ road in west direction. The NO_2 and $PM_{2.5}$ concentrations were monitored by advanced instrumentations i.e., gas analyzer model number AC 31 (chemiluminescence based) and beta gauge based particulate matter analyzer, MP101 (Environnment S.A., 2016) as per CPCB norms (CPCB, 2011). The CPCB ensures minimum uncertainty in ambient air quality monitoring by defining stringent protocols (CPCB, 2011) for the sampling/analysis/ calibration methods and implementation of Quality Assurance /Quality Control programs (QA/QC).

At APH-2, one hour average ambient $PM_{2.5}$ concentrations data for winter (January–February, 2009) and summer (March–May, 2009) seasons were collected from IIT Madras air quality laboratory. The $PM_{2.5}$ concentrations were monitored using portable environmental dust monitor (GRIMM-107, Make GRIMM Aerosol Technik, Gmbh & CO.) at kerbside (IIT Madras gate) of SP Road. The instrument kept at kerbside of SP road (13°00'23.48"N and 80°14'28.79"E) at an altitude of 12 m above msl. The instrument is located at a distance of 10 m in the south of SP road. The ambient NO_2 concentrations data were not measured at APH-2. Further, the missing hour values were not considered in the distribution plot. No dust storm and rain were observed during the monitoring period at APH-2.

RESULT AND DISCUSSION

Status of $PM_{2.5}$ and NO_2 Level

This section describes the status and spread in $PM_{2.5}$ and NO_2 concentrations at selected urban hotspots in Delhi and Chennai cities. The mean of hourly NO_2 concentrations in winter and summer periods were found to be 84.01 ± 73.99 µg m^{-3} and 70.84 ± 62.70 µg m^{-3}, respectively, which indicate high pollution burden during winter season due to the prevalence of inversion conditions (Table 2). The skewness was 1.95 and 2.37 in winter and summer, respectively. Similarly the kurtosis value for these periods were found to be 4.14 and 7.54, respectively which indicate that data skewed more toward right side of mean. Similarly, the mean of hourly $PM_{2.5}$ concentrations in winter and summer were found to be 173.03 ± 79.20 µg m^{-3} and 129.29 ± 77.19 µg m^{-3}, respectively. The skewness and kurtosis were found to be 0.56, 1.50 and 0.77, 2.50, respectively for winter and summer seasons, indicated longer tails than the normal distribution.

Like APH-1, the mean of hourly $PM_{2.5}$ concentrations were found to be high during winter (66.90 ± 31.98 µg m^{-3}) season when compared to summer (39.28 ± 20.94 µg m^{-3}) at APH-2. This was due to poor dispersion condition in winter season. Further, skewness and kurtosis values clearly described that the distribution form have longer tails than those in the normal distribution (Table 3).

Exceedances of $PM_{2.5}$ and NO_2

This section describes the execcedances of $PM_{2.5}$ and NO_2 concentrations over the specified air quality standards and their correlation with wind speed and direction. It was expected that the probability of occurrence of extreme pollutant event would be more during winter due to the low assimilative capacity of the atmosphere compared to summer season. The hourly average NO_2 and $PM_{2.5}$ concentrations were compared with WHO guidelines i.e., hourly average $PM_{2.5}$ = 200 µg m^{-3} (WHO, 2005) and NO_2 = 80 µg m^{-3} (Fu *et al.*, 2000; DEQ Idaho, 2001).

Fig. 2 describes the frequency of exceedences of NO_2 concentrations over 200 µg m^{-3} during winter and summer at APH-1. Hourly average NO_2 concentrations were found to be 7.5% of times exceeding the specified guidelines, out of which 7.2% were in the range of 201–400 µg m^{-3} and 0.3% in the range of 401–500 µg m^{-3}. It was also observed that the maximum frequency of *exceedences* occurred when wind speed were found to be ≤ 0.5 m s^{-1} (calm) followed by the wind speed range of 0.6–2.0 m s^{-1} blowing from northeast and east-northeast. During summer, NO_2 concentrations were found to be 5.6% of time exceeding 200 µg m^{-3}, out of which 5.3% of time were in the range of 201–400 µg m^{-3} and 0.3% in the range of 401–500 µg m^{-3}. The frequency of exceedances was found to be more when wind speed were ≤ 0.5 m s^{-1} irrespective of the wind direction and with wind speed range of 0.6–2.0 m s^{-1} (Fig. 2(b)). On the other hand, at APH-2, hourly $PM_{2.5}$ was found to be 92% of the times exceeding the specified standard during winter (Fig. 3(a)). Out of which 43% of times were in the range of 81–160 µg m^{-3}, 26% of times were in the range of 161–240 µg m^{-3} and 23% of times were in the range 241–540 µg m^{-3}. However, during summer, 72% were found to be exceeded the standards. Out which 46% of the times were in the range of 81–160 µg m^{-3}, 16% of the time were in the range of 161–240 µg m^{-3} and 10% of the time were in the range of 241–540 µg m^{-3} (Fig. 3(b)).

Highest pollutant concentrations (Fig. 1) were observed when wind were blowing from northeast, east and southeast directions and with a wind speed of ≤ 0.5 m s^{-1} (calm wind). No major polluting industries are located near monitoring station in the southeast directions because no industry are allowed to operate in Delhi city (Bentinck and Chikara, 2000). As expected, the pollutant concentration were exceeded the air quality standards more during winter compared to summer season.

At APH-2, $PM_{2.5}$ concentrations were found to be 25% of the time exceeded the standard i.e., 80 µg m^{-3}. Out of which 23% of times were in the range of 80–160 µg m^{-3} and 2% were in the range of 161–240 µg m^{-3}. However, in summer, it was 5% exceeded the specified standard which was in the range of 80–160 µg m^{-3} (Fig. 4). Therefore, $PM_{2.5}$ values were found exceeding the standard when the wind occurs from east and with low speed (calm). The percentage of exceeding was more in winter season when compared to summer season. The differences in $PM_{2.5}$ and NO_2 concentrations exceedance as observed between APH-1 and APH-2 are due to differences in emission strength of the sources and meteorology. The difference in meteorological conditions between APH-1 and APH-2 along with windrose diagram is discussed in supplementary information (SI) section S1. In addition to these parameters, the occurrence of rain, variation in temperatures and relative humidity and solar radiation can significantly influence the distribution patterns of any air pollutant. The difference in emission rate of pollutant from source and geography of the study site may also impact the distribution patterns. Gokhale and Khare (2007); McConnell *et al.* (2010); Gulia *et al.* (2015) and Sunil (2015) have described the implications of such exceedances in $PM_{2.5}$ and NO_2 concentrations over specified standards in ambient environment through analyzing various

Table 2. Summary of basic statistics of NO_2 and $PM_{2.5}$ concentrations at APH-1.

Parameters	NO_2		$PM_{2.5}$	
	Winter	Summer	Winter	Summer
Mean (µg m^{-3})	84.01	70.84	173.03	129.29
Standard Deviation (µg m^{-3})	73.99	62.70	79.20	77.19
I-Q Range (µg m^{-3})	71.2	56.8	125.5	87.00
1^{st} Q (µg m^{-3})	35.2	30.5	104.75	76.07
Median (µg m^{-3})	57.5	49.2	154.5	106.00
3^{rd} Q (µg m^{-3})	105.5	87.5	230.25	163.00
Skewness (G1)	1.95	2.37	0.56	1.50
Kurtosis (G2)	4.14	7.54	0.77	2.50

Table 3. Summary of basic statistics of $PM_{2.5}$ concentration at APH-2.

Parameters	$PM_{2.5}$	
	Winter	Summer
Mean (µg m^{-3})	66.90	39.28
Standard Deviation (µg m^{-3})	31.98	20.94
I-Q Range (µg m^{-3})	36.69	24.89
1^{st} Q (µg m^{-3})	44.13	24.801
Median (µg m^{-3})	60.42	33.86
3^{rd} Q (µg m^{-3})	80.46	49.69
Skewness (G1)	1.40	1.38
Kurtosis (G2)	2.20	2.56

scenarios and corresponding air quality management options to ensuring minimum human exposure.

SDM FOR EXPOSURE ASSESSMENT

The Study Location APH-1

This section explains the distribution pattern of $PM_{2.5}$ and NO_2 concentrations, which are highly influenced by pollutant emission from source, meteorological conditions and site features. The values of KS (0.03), AD (1.98) and Chi-square (54.99) were found to be the lowest for the lognormal distribution model with a significance level of 0.05 compared to test statistics of other selected distribution model during winter (Table 4). However, in summer, these values were 0.04, 3.13 and 63.48, respectively and found to be the lowest for log-logistic distribution model. Hence, NO_2 concentrations data followed lognormal and log-logistic distribution in winter and summer, respectively, at APH-1 (Fig. 5). In one of the studies, Sharma *et al.* (2013b) have also observed that 24 hour average NO_2 concentration data of year 2003 to 2006 that include all seasons follows log-logistic distribution at one of the urban locations in Delhi city. The probability plot of NO_2 for winter and summer seasons also indicates satisfactory fitting throughout the distribution with confidence interval of 95 percent (Fig. 5).

For $PM_{2.5}$, the KS, AD and Chi-square test values of 0.08, 2.29 and 39.22, respectively, were found to be the lowest for lognormal distribution with a significance level of 0.05 compared with test statistics values of other selected distribution models (Table 5). Similarly, in summer, these values were 0.05, 5.29 and 82.83, respectively and found to be the lowest for lognormal distribution. Therefore, it is inferred that $PM_{2.5}$ concentration data follow lognormal distribution in both winter and summer seasons at APH-1.

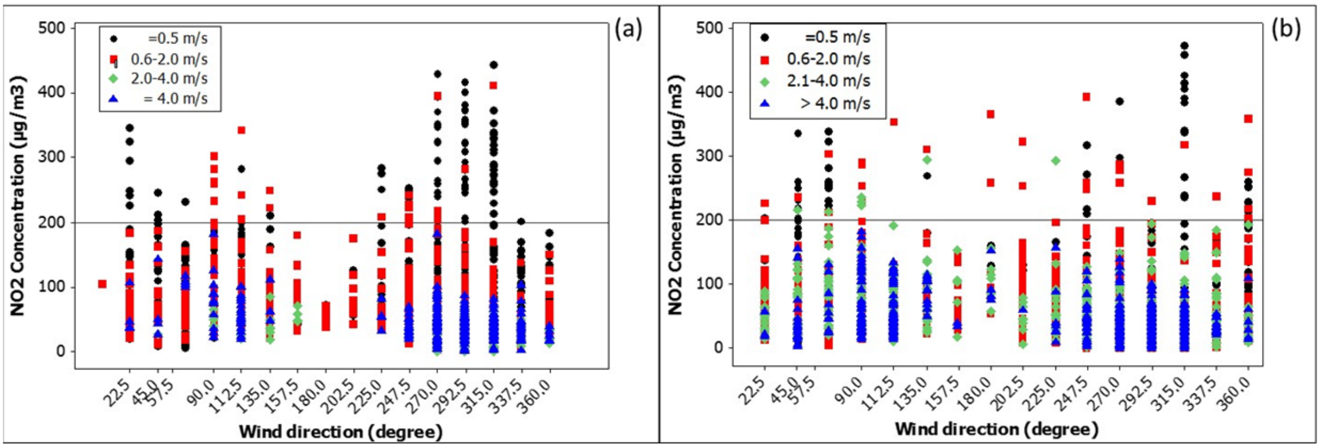

Fig. 2. Exceedance of hourly NO_2 concentrations over WHO guidelines during winter (a) and summer (b) at APH-1.

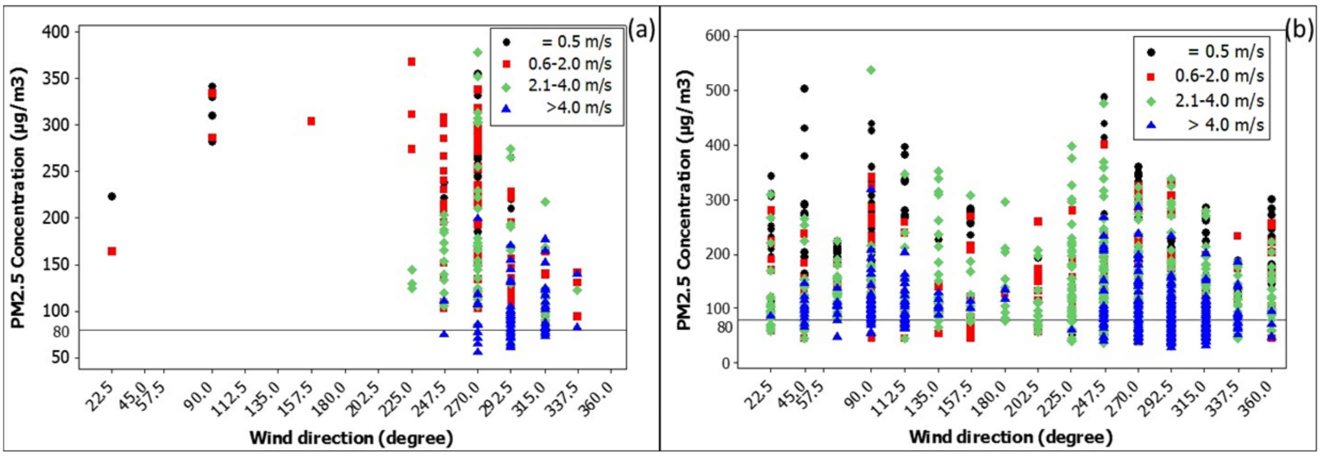

Fig. 3. Exceedance of hourly $PM_{2.5}$ concentrations over air quality standards during winter (a) and summer (b) at APH-1.

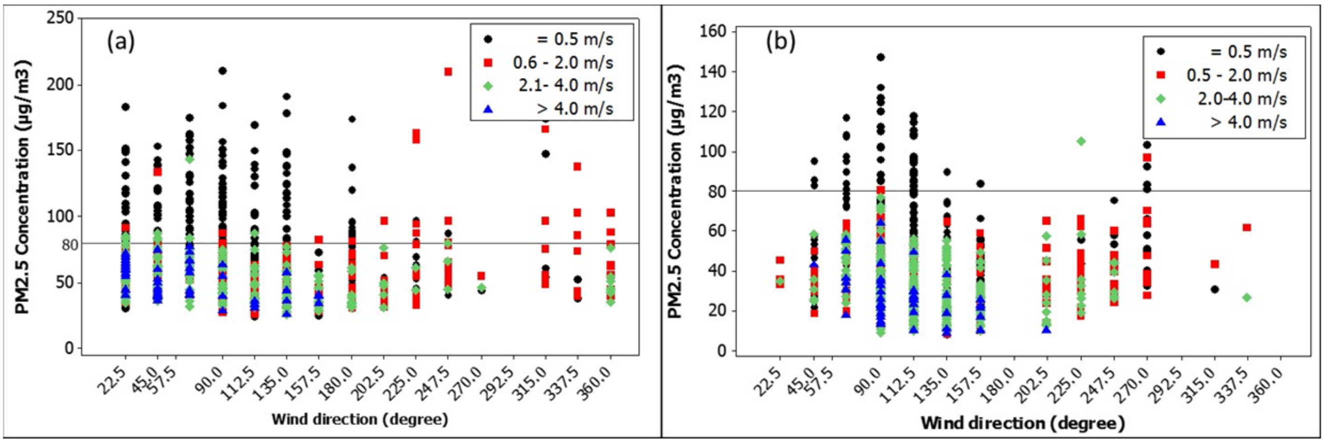

Fig. 4. Exceedance of hourly $PM_{2.5}$ concentrations over air quality standards during winter (a) and summer (b) at APH-2.

Table 4. Goodness of fit test statistics for NO_2 concentrations at APH-1.

Distribution Model	Winter period			Summer period		
	K-S	A-D	Chi-square	K-S	A-D	Chi-square
Normal	0.154	63.713	788.909	0.175	108.42	1395.64
Lognormal	0.032	1.988	54.99	0.055	4.623	56.38
Logistic	0.335	45.893	-	0.353	63.189	-
Log-logistic	0.050	3.396	105.158	0.041	3.127	63.48
Gamma	0.076	11.327	95.330	0.092	15.461	164.4
Weibull	0.079	16.371	122.918	0.09	23.359	192.987
Exponential	0.118	59.53	90.67	0.102	61.902	15.77

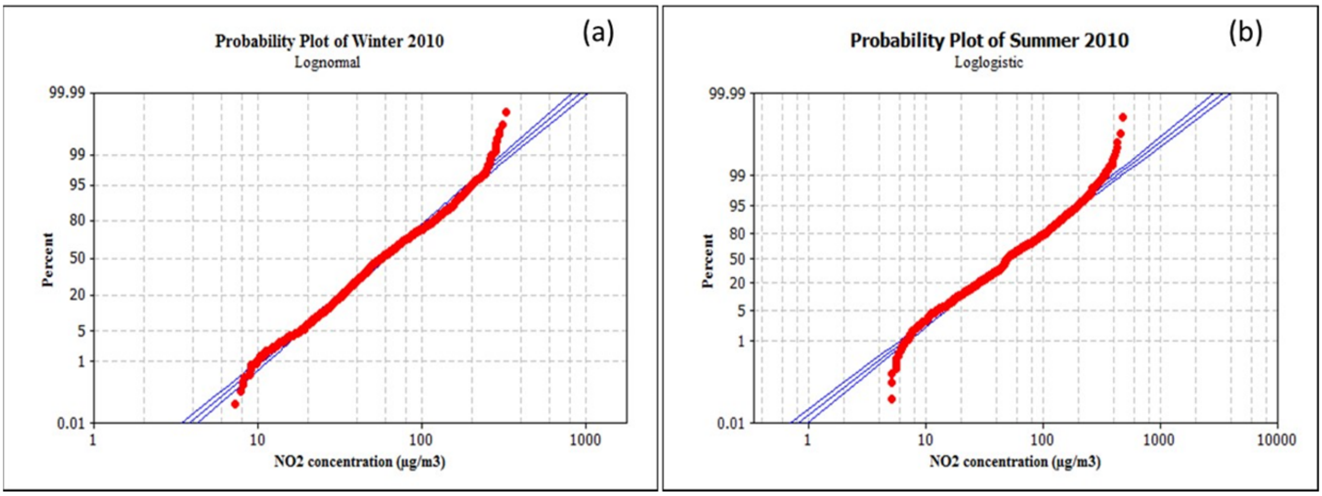

Fig. 5. Probability plot of NO_2 concentration in winter (a) and summer (b) at APH-1.

In the past, the studies (Kan and Chen, 2004; Giavis *et al.*, 2009; Papanastasiou and Melas, 2010; Sharma *et al.*, 2013b) were reported that daily average of ambient PM concentrations best fit the lognormal distribution. The probability plot of lognormal distribution of $PM_{2.5}$ also indicates satisfactory fitting throughout the distribution with confidence interval of 95 percent (Fig. 6).

The Study Location APH-2

The KS, AD and Chi-square values of 0.03, 1.89 and 39.70, respectively, were found to be the lowest for lognormal distribution with significance level of 0.05 compared with test statistics of other selected SDMs in winter. Similarly, in summer, these values were 0.039, 1.42 and 28.91, respectively and found to be the lowest for lognormal distribution. Hence, lognormal distribution was fitted to be the best to hourly $PM_{2.5}$ concentrations in winter as well as summer seasons (Table 6). The probability plot of lognormal distribution of $PM_{2.5}$ also indicates satisfactory fitting throughout the distribution with confidence interval of 95 percent (Fig. 7).

It is observed that $PM_{2.5}$ concentration distributions at

Table 5. Statistical distribution models for $PM_{2.5}$ concentrations at APH-1.

Distribution model	Winter period			Summer period		
	K-S	A-D	Chi-square	K-S	A-D	Chi-square
Normal	0.113	4.679	58.214	0.155	58.38	555.208
Lognormal	0.089	2.294	39.22	0.052	5.297	82.83
Logistic	0.301	4.571	-	0.332	41.755	-
Log-logistic	0.111	2.687	54.126	0.059	6.301	149.581
Gamma	0.090	2.57	39.96	0.090	16.059	107.121
Weibull	0.092	2.992	35.976	0.107	27.039	190.114
Exponential	0.113	30.148	50.198	0.140	148.88	188.436

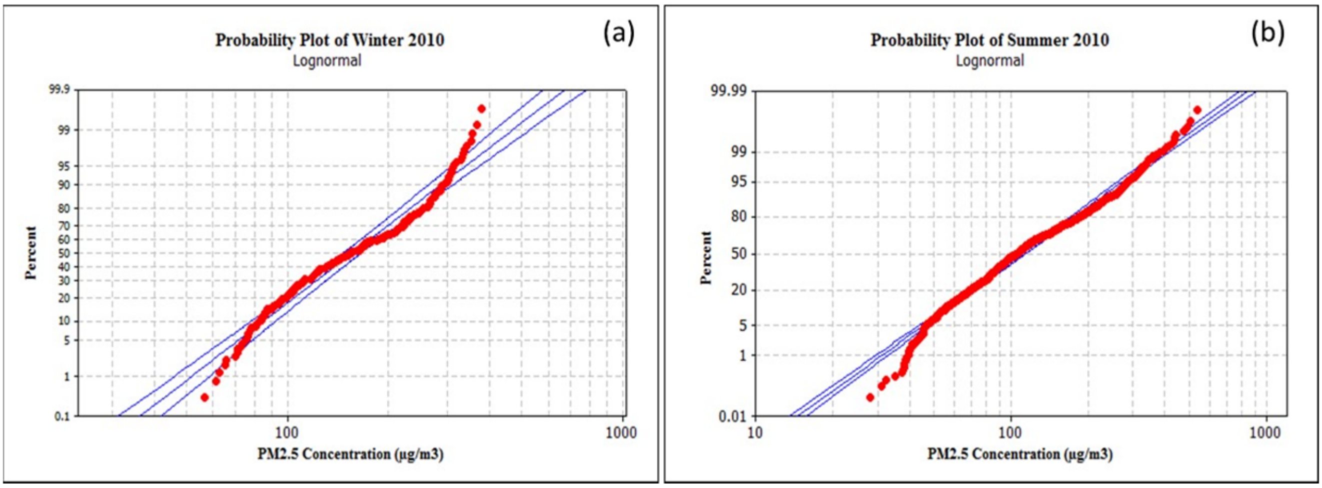

Fig. 6. Probability plot of $PM_{2.5}$ concentration in winter (a) and summer (b) at APH-1.

Table 6. Statistical distribution models for $PM_{2.5}$ concentrations at APH-2.

Distribution model	Winter period			Summer period		
	K-S	A-D	Chi-square	K-S	A-D	Chi-square
Normal	0.112	23.938	204.046	0.104	23.56	281.102
Lognormal	0.039	1.890	39.701	0.039	1.42	28.914
Logistic	0.093	13.833	183.135	0.301	14.24	-
Log-logistic	0.044	2.298	66.046	0.059	2.13	54.898
Gamma	0.052	5.741	47.708	0.065	3.229	169.864
Weibull	0.087	15.046	112.555	0.095	10.371	303.293
Exponential	0.203	126.386	256.247	0.219	120.55	237.34

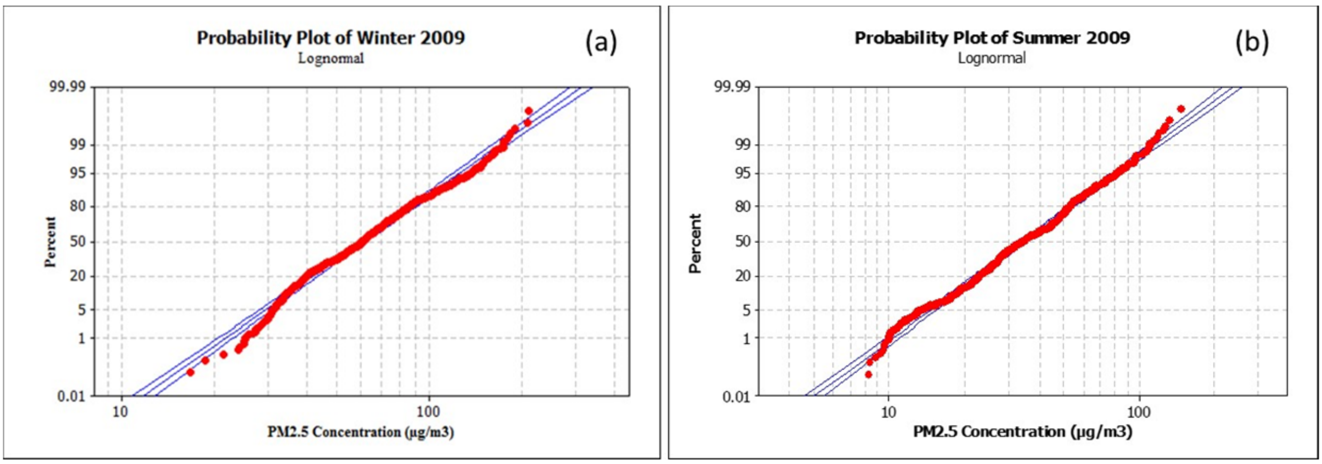

Fig. 7. Probability plot of $PM_{2.5}$ concentration in winter (a) and summer (b) at APH-2.

APH-1 and APH-2, are similar irrespective of seasons, i.e., lognormal. Sharma *et al.* (2013b) have also observed that 24 hour average PM_{10} concentrations follow lognormal distribution at three different locations in Delhi city. However, the topographical and geographical characteristics of the site may affect the particle distribution (Taylor *et al.*, 1986; Sansuddin *et al.*, 2011).

PARAMETER ESTIMATION

The *location* and *scale* parameters of the best fitted distribution model were estimated using MLE techniques at 95% confidence level, i.e., 5% significance level. The *location* and *scale* parameter represents the mean and standard deviations of the data, respectively (Table 7). It was observed that values of scale parameter were found higher during winter compared to summer season at APH-1. This high value of scale parameter indicates high extreme events of pollutant in winter. Further, $PM_{2.5}$ and NO_2 concentrations were predicted using estimated *location* and *scale* parameters and later compared with observed concentrations in form of probability distribution plots (Figs. 8 and 9). These plots describe the relatively higher values of *scale* parameter which represented by adequate dispersion of NO_2 and $PM_{2.5}$ concentration. However, relatively higher values of *location* parameter imply the high pollutant concentrations. The predicted concentrations of $PM_{2.5}$ and NO_2 concentration were further used to evaluate the regulatory compliance in next section.

REGULATORY COMPLIANCE

The *pdf* plots were used to find out the regulatory compliance for air quality management plan (Sharma *et al.*,

Table 7. Estimated *location* and *scale* parameters of best fitted SDM.

Study Sites	Pollutant	Season	Identified fitted distribution	Parameters	
				Location	Scale
APH-1	NO_2	Winter	Lognormal	4.055	0.929
		Summer	Log-logistic	3.907	0.520
	$PM_{2.5}$	Winter	Lognormal	5.048	0.473
		Summer	Lognormal	4.708	0.546
APH-2	$PM_{2.5}$	Winter	Lognormal	4.117	0.432
		Summer	Lognormal	3.638	0.465

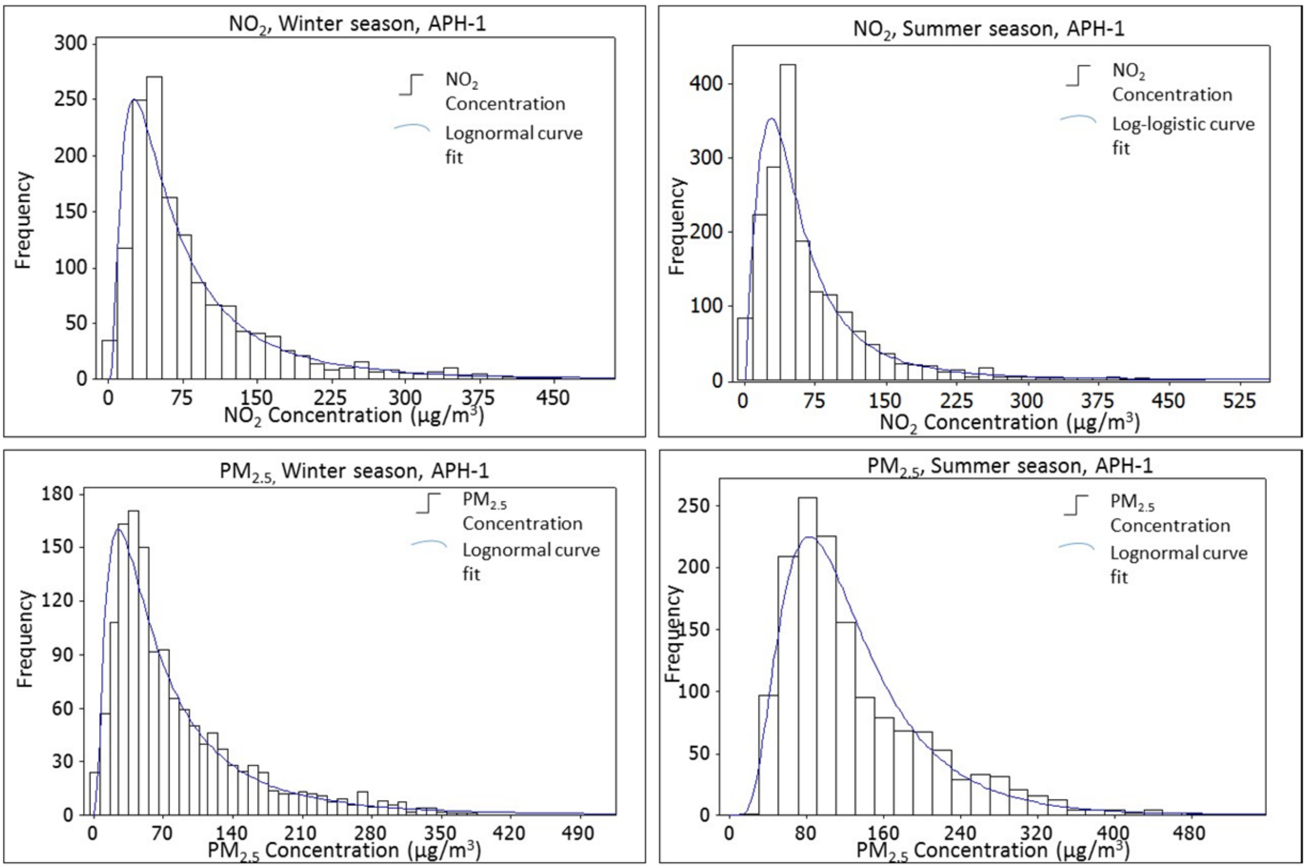

Fig. 8. Curve fitting of best fit distribution model on histogram by using estimated parameters at APH-1.

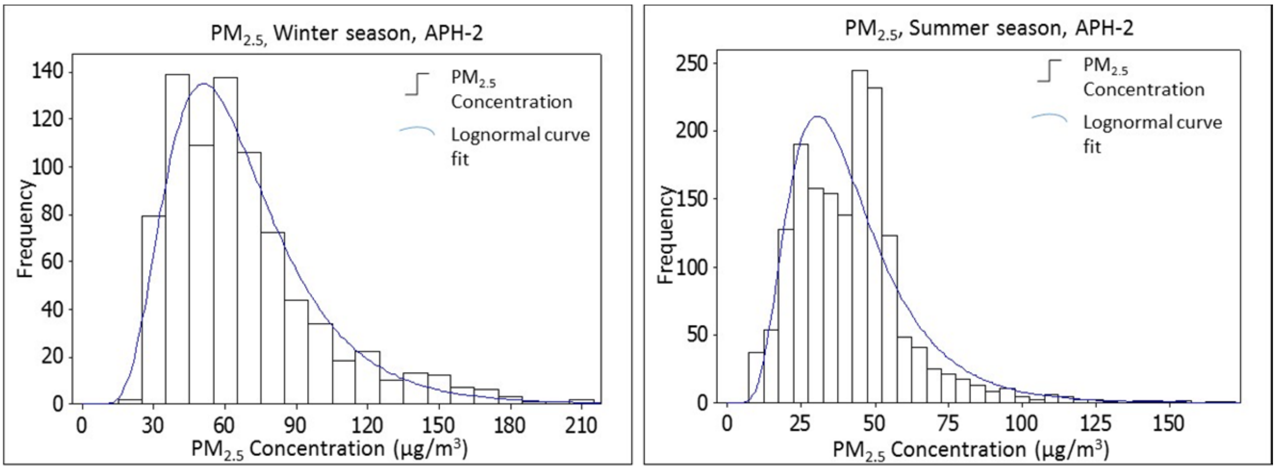

Fig. 9. Curve fitting of best fit distribution model on histogram by using estimated parameters at APH-2.

2013b). It allows calculation of *exact* or *expected* number of violations of a specified air quality standards. The probability that a particular concentration level 'x' exceeding a single observation value were estimated by the complementary *cdf* (Eq. (1)).

$$\bar{F}(x) = Pr\{C > x\} = 1 - F(x) \quad (1)$$

where:
$F(x) = Pr(C \leq x)$.
$\bar{F}(x)$ = complementary *cdf.*
$F(x)$ = *cdf.*
C = pollutant concentration as a random variable.
x = Pollutant concentration values.

At APH-1, the exceedences of hourly average NO_2 concentrations were predicted to be 9% and 6.4% during winter and summer seasons, respectively. Similarly, exceedences of hourly average $PM_{2.5}$ concentrations over specified standard were predicted to be 93.1% and 72.8%, respectively. On the other hand, the exceedences of hourly average $PM_{2.5}$ concentration over standard were predicted to be 26.98% and 5.48% during winter and summer seasons, respectively. The exceedances of predicted and monitored pollutant concentration were observed to be in agreement (Section 4.2).

CONCLUSIONS

This study evaluated the distribution patterns of $PM_{2.5}$ and NO_2 and their frequency of exceedances over specified standards/guidelines at two urban air pollution hotspots in Delhi and Chennai cities. The hourly concentration data for $PM_{2.5}$ and NO_2 were analysed with the aim to quantify the seasonal variability of their concentrations, their correlations with meteorological parameters and their best fit statistical distribution model.

The following conclusions were drawn:

- High variability in both NO_2 and $PM_{2.5}$ concentrations were found in winter and summer seasons at APH-1. At APH-2, the hourly $PM_{2.5}$ concentrations were found to be high during winter (66.90 ± 31.98 µg m^{-3}) compared to summer (39.28 ± 20.94 µg m^{-3}) at APH-2.
- Hourly average NO_2 and $PM_{2.5}$ concentrations were exceeded upto 3 and 5 times, respectively over the specified NAAQS standards/WHO guidelines in both winter and summer seasons at AHP-1. However, at AHP-2, $PM_{2.5}$ was exceeded by 8% and 4% of the times during winter and summer seasons, respectively.
- At APH-1, the NO_2 concentrations were fitted with lognormal and log-logistic model for winter and summer seasons, respectively. It implies that the distribution pattern of NO_2 show significant influence of meteorology and their reactive nature in two different climatic conditions. On the contrary, $PM_{2.5}$ concentrations of both winter and summer seasons at APH-1 and APH-2 were fitted with the lognormal model. This might be due to its less reactivity and particle nature compared to NO_2, which is gaseous.
- The frequency of exceedances of predicted and monitored concentrations of NO_2 and $PM_{2.5}$ were found in agreement. Therefore, statistical distribution model are efficient to satisfactorily predict the extreme range of air pollutants concentration.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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