published by

EQA - International Journal of Environmental Quality
ISSN 2281-4485 - Vol. 42 (2021): 22-35
Journal homepage: https://eqa.unibo.it/

Variations of surface ozone levels in urban area of India: a focus on night-time residual concentrations

Rohit Sharma, Kamna Sachdeva*, Anu R. Sharma

Department of Energy and Environment, TERI School of Advanced Studies, Delhi, India

Corresponding author e-mail: kamna.sachdeva@terisas.ac.in

Article info
Received 14/4/2020; received in revised form 1/9/2020; accepted 20/12/2020.
DOI: 10.6092/issn.2281-4485/10809

Abstract

This study investigates the existing diurnal as well as night time surface ozone concentration trend over Delhi between 1990 and 2012. Secondary data obtained from the National Data Centre (NDC) of the India Meteorological Department (IMD) was analysed to assess the trend in the surface and night-time ozone concentration. This was further used to forecast the variation in the night-time ozone concentration over the city till 2025. A significantly increasing trend of the night-time ozone concentration was observed between 1990 and 2012 evidenced by a +0.158 value of the Mann Kendall test. Moreover, the forecasting of the variations conducted using the Autoregressive Integrated Moving Average (ARIMA) model revealed that the concentration of night-time ozone is expected to increase between the period of 2013 and 2025 if the current trend continues. This is the first study to conduct a trend analysis of night-time ozone concentration for a duration of three decades in the NCT of Delhi. Considering the negative impacts of elevated levels of ozone on the health status of individuals, agricultural productivity and air quality of the city, the present study highlights that it is imperative to take concentrated actions to curb the release of anthropogenic precursors of surface ozone.

Keywords
Mann-Kendall test, ARIMA forecasting, Night-time surface ozone, Residual ozone

Introduction

Tropospheric ozone has been regarded as a major global concern owing to its adverse effects on the environment, human health and vegetation when present at elevated levels in the atmosphere (Monks *et al.* 2015; Shukla *et al.* 2016; Cailleret *et al.*, 2018; Fleming *et al.*, 2018). It is a reactive oxidant gas present in trace amount in the earth's atmosphere (Crutzen, 1988; Kulkarni *et al.*, 2013; Akritidis *et al.*, 2016; Sicard *et al.*, 2016) and has been attributed as one of the major contributors to the global phenomenon of climate change (IPCC, 2007; Hayashida *et al.*, 2018). Even though the concentration of ozone in the troposphere is miniscule in comparison to that found in the stratosphere, yet it is an important greenhouse gas, a significant precursor of hydroxyl radical and a surface pollutant (Hu *et al.* 2017; Sharma and Khare 2017). The levels of tropospheric ozone in the atmosphere has witnessed a steady increase over the years which can be largely attributed to anthropogenic activities (Karthik L *et al.* 2017; Derwent *et al.* 2018; Díaz *et al.* 2018; Hayashida *et al.* 2018). For instance, in the post industrialised era, the average ozone mixing ratios has elevated from 20 ppb to 100 ppb in the lower atmosphere (Seinfeld and Pandis 2012). Moreover, it has been estimated that the global concentration of surface ozone is increasing at a rate of 0.32% per year which can be primarily ascribed to the increased

DOI: 10.6092/issn.2281-4485/10809

dependence on fossil fuels (Karthik L *et al.* 2017). It has also been observed that several countries across the world are experiencing elevated levels of surface ozone (Cooper *et al.* 2014; Derwent *et al.* 2018) which has gained attention of many researchers across the world. It has been well known that surface ozone shows a typical diurnal pattern in the urban and suburban settings with high concentration during the day, followed by a sharp decrease during the late afternoon and reaching to the lowest values at night (Jenkin and Clemitshaw 2000; Eliasson *et al.* 2003; Sousa *et al.* 2011).

Considering the erratic increase in the level of urbanisation and increased dependence on fossil fuels, the trend in the concentration of ozone has witnessed a variation from its usual diurnal pattern (Karthik L *et al.* 2017; Peshin *et al.* 2017). It has been reported by numerous studies that the concentration of night-time ozone has witnessed a steady rise in recent past in urban areas across the globe. For instance, (Awang *et al.* 2015) reported that night time concentration of ozone at Kemaman, Malaysia reveals an increasing trend over the years 1990 and 2010, which can be dominantly ascribed to the its precursors liberated due to anthropogenic activities and the meteorological conditions of the city during the time of examination. A similar trend of night-time enhancements of ozone has been observed majorly due to lowering of jet streams in Huntsville (Kuang *et al.* 2011). A recent study conducted by (Ghosh *et al.* 2013) examined the frequency of night-time ozone over a period of 6 months (October, 2010 – April, 2011) in Kolkata and observed that there was a steady rise in the concentrations which could be attributed to the horizontal long range transport system of the city. This ever increasing trend of night-time ozone concentrations in the atmosphere has become a cause of concern for many researchers and policy makers throughout the world (Mavrakis *et al.* 2010; Ghosh *et al.* 2013; Awang *et al.* 2015a).

In view of this, concerted efforts have been undertaken by many researchers in order to understand the reasons associated with this perplexing trend. It has been highlighted that anthropogenic emissions of night-time precursors of ozone is one of the major contributors of the increasing levels of night-time ozone in the atmosphere (Ghosh *et al.* 2013; Awang *et al.* 2015b). In addition to this, the generally stable nocturnal boundary layer and calm meteorological conditions at night have been acknowledged to facilitate the building up of night-time ozone as residual to the daytime formed ozone (Mavrakis *et al.*, 2010). In addition to this, there have been studies conducted in past that have reported that stratospheric ozone intrusion could be considered as one of the factors leading to an increase in the levels of surface ozone as well as night-time ozone in the atmosphere (Mavrakis *et al.*, 2010; Hayashida *et al.*, 2015). Even though numerous studies have attempted to understand this trend, yet there exists a lack in literature that provides consensus on the reasons associated with the increasing trend of night-time ozone in the atmosphere. (Sousa *et al.*, 2011; Awang *et al.*, 2015a; Sharma *et al.*, 2016a; Yadav *et al.*, 2016).

The present study aims to supplement the existing literature by assessing the trend of the night-time ozone levels in one of the biggest metropolitan cities of the developing world, i.e., Delhi. The city being the centre of socio-economic, cultural and political activities of India is in the phase of drastic transformation (Sharma *et al.*, 2016a). Owing to the rapid urbanisation and population explosion, the city has observed tremendous increase in the employment, housing and transportation demands. This has led to an increased dependence on fossil fuels which has further supplemented the ever increasing problem of air pollution in the city (Aggarwal and Jain, 2016). In addition to the primary pollutants, numerous studies have reported a steady increase in the levels of secondary air pollutants like ozone in the Delhi region (Kumar *et al.*, 2015; Peshin *et al.*, 2017). Thus, the current situation of the levels of surface ozone in Delhi renders it to be one of the important examples to evaluate the trend of night-time ozone concentrations. In view of this, the focus of the current study is to understand the night-time residual ozone variation over the period (1990 to 2012) in Delhi region and further understand the variations in the future concentrations using statistical analysis with an aim to enrich the exiting research gap in this regard.

Materials and Methods

The following section of the paper highlights the methodology adopted to conduct the present study. The study is primarily a comprehensive assessment of secondary data to assess the variation in the concentration of surface ozone and night-time ozone over a period of two decades. The study also forecasts the concentration levels of ozone over a period of 2013 to 2025 in order to demonstrate the probable change in the night-time concentration levels. An overview of the overall methodological approach adopted has been depicted in figure 1.

DOI: 10.6092/issn.2281-4485/10809

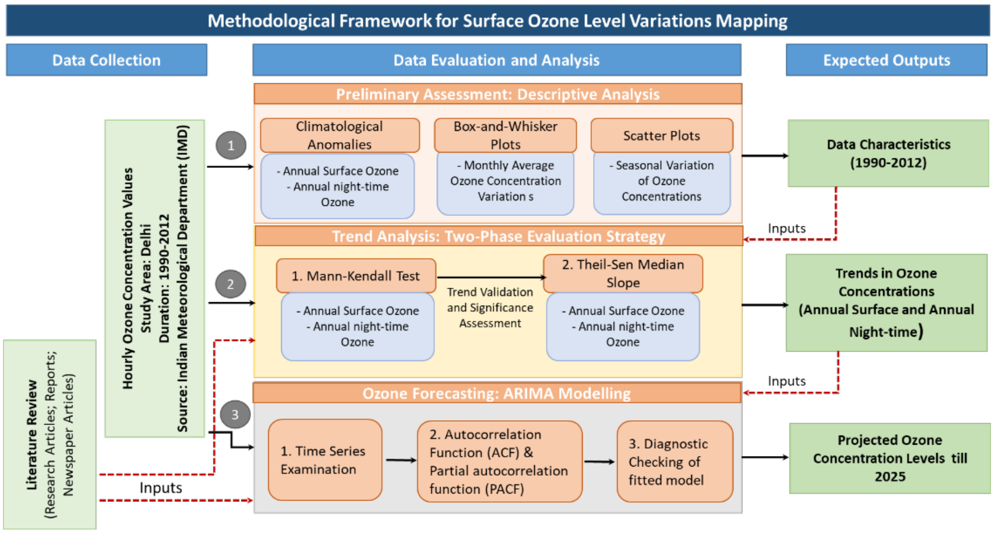

Figure 1. *Methodological framework for surface ozone mapping.*

Data Description and Data Collection

The study uses secondary data of ozone concentration monitored and recorded by the India Meteorological Department (IMD). Continuous hourly records of the surface ozone over Delhi were obtained from the National Data Centre (NDC) of IMD for the period of 1990 to 2012. The data has been obtained from IMD owing to the fact that it has been capturing the variations in the concentration of surface ozone since a very long time and hence could provide a dataset of past two decades. The quality of the dataset is pre-checked by IMD, however in order to validate the dataset pre-processing was carried out using linear interpolation method (Norazian *et al.* 2007).

Data Analysis and Forecasting

The secondary data gathered was first analysed using descriptive statistical techniques to understand the behaviour of data and the trends in the concentration of surface ozone. This understanding was further used to forecast the trend of ozone levels until the year 2025. Statistical analysis of the data was performed using Microsoft Excel 2016.

Descriptive Analysis. Climatological anomalies were generated for the data over the period of 1990 to 2012 in order to understand the overall deviation in the ozone concentration from the mean values. The anomalies were formulated for the annual average concentration of surface ozone over the entire time period and specifically for the night time, i.e., 20:00 to 06:00 hours for the same duration. The monthly average variation in the ozone concentration for the study period was also estimated and depicted using box-and-whisker plot. In addition to this, seasonal variation in the night-time ozone concentration levels was also mapped in order to get a better understanding about the influence of meteorological conditions in the accumulation of surface ozone during night time. The seasonal trend was depicted using scatter plot to highlight the observed variations in surface ozone concentrations.

Trend Analysis: Mann-Kendall (MK) Test and Theil-Sen Median Slope Evaluation. The study adopted a two-phase evaluation strategy to undertake the trend analysis of the data. The following section of the paper elaborates upon the statistical tools applied to evaluate and validate the trend in the surface ozone concentration levels over a period of 1990 to 2012.

Mann-Kendall (MK) Test. The first phase employed a non-parametric Mann-Kendall (MK) test in order to generate a trend in the observed data points. The MK test is a commonly employed technique to detect monotonic trends in series of environmental data and climate data (Chattopadhyay *et al.* 2012; Lefohn *et al.* 2018). The test follows the principle of hypothesis testing and proposes a null and alternate hypothesis which is tested on the basis of the MK test statistic S as defined in equation 1 (McBean and Motiee 2008; Narayanan *et al.* 2013). The null hypothesis H_0 states that the data series is independent and identically distributed whereas, alternative hypothesis H_a states existence of a trend. The values of the MK statistics can be either positive, negative or null which indicate the direction of the trend in the dataset.

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} (x_j - x_i) \qquad [1]$$

where *xj* is the sequential data series, *n* is the length of the data set and

$$\text{Sign } (x) = \begin{cases} 1 \text{ if } (x_j > x_i) \\ 0 \text{ if } (x_j = x_i) \\ -1 \text{ if } (x_j < x_i) \end{cases}$$

Mann Kendall test results are supposed to be normally distributed for n ≥ 8 with mean and variance described as:

$E(S) = 0$

$$V(S) = \frac{n(n-1)(2n+5) + \Sigma t_i (t_i-1)(2t_i+5)}{18} \qquad [2]$$

where t_i is the number of ties present with I as an extent. The standardised Z statistic is computed by:

$$Z = \begin{cases} S - 1/\sqrt{V(S)} & S > 0 \\ 0 & \\ S + 1/\sqrt{V(S)} & S < 0 \end{cases}$$

The standard MK statistic Z follows the standard normal distribution with zero mean and unit variance.

Theil and Sen's median slope estimator. The second phase of the analysis aimed at estimating the magnitude of the observed trend. Theil-Sen median slope estimator, which is considered to be one of the most popular non-parametric technique to estimate a linear trend (Lefohn *et al.* 2018) was used to calculate the magnitude of the trend obtained by the MK test. The fact that this test is not influenced by outliers renders it to be a robust estimate of the trend (Narayanan *et al.* 2013). It has been reported that the trends which have statistical significance might not have practical significance and vice versa (Yue and Hashino 2003), hence the practical significance of trend was assessed by estimating the Theil and Sen's median slope. Slope estimates of N pairs of data were first computed using equation [3].

$$Q_i = (x_j - x_k) / (j - k) \text{ for } i = 1, n \qquad [3]$$

Here, x_j and x_k are data values at time j and k $(j>k)$. The median of the N values of Q_i is the Sen's estimator of slope where:

$$N = n(n -) / 2 \qquad [4]$$

Ozone Forecasting: ARIMA Model. An autoregressive integrated moving average (ARIMA) model was used to forecast monthly mean ozone values for the years 2013 to 2025. ARIMA model approach consists of three steps, first being model identification which involves time series examination of the data, second is the model parameter estimation which examines the autocorrelation function (ACF) and partial autocorrelation function (PACF) of the time series, which is followed by diagnostic checking of the fitted model (Kumar *et al.* 2004). The time series method of Box and Jenkins ARIMA (1976) is a commonly used technique for forecasting ozone concentrations (Robeson and Steyn 1990). The model allows easier approach by predicting future values as a product of several past observations and random errors (Yurekli *et al.* 2007).

Mathematical expressions used for ARIMA forecast used as explained in (Robeson and Steyn 1990) are explained as follows;

Given w_t being differenced original series

$$w_t = ø_1 w_{t-1} + \cdots + ø_p w_{t-p} + a_t - \Theta_1 a_{t-1} - \cdots - \Theta_q a_{t-q} \qquad [5]$$

The autoregressive (*ø*) and moving average (*Θ*) model parameters are determined either by maximum likelihood or least squares estimation. The effects of all factors other than past time series values are incorporated into the 'random shock' term, (a_t). Proper model identification should result in an (a_t) series that is normally and independently distributed with a mean value of approximately zero.

Results and Discussions

Descriptive Analysis

Overview of the trends of surface ozone concentrations over Delhi between 1990 and 2012.

Climatological Anomalies. The annual climatological anomalies generated for the period of 1990 and 2012 revealed that there has been a gradual increase in the overall concentration levels of surface ozone over the years as depicted in figure 2.

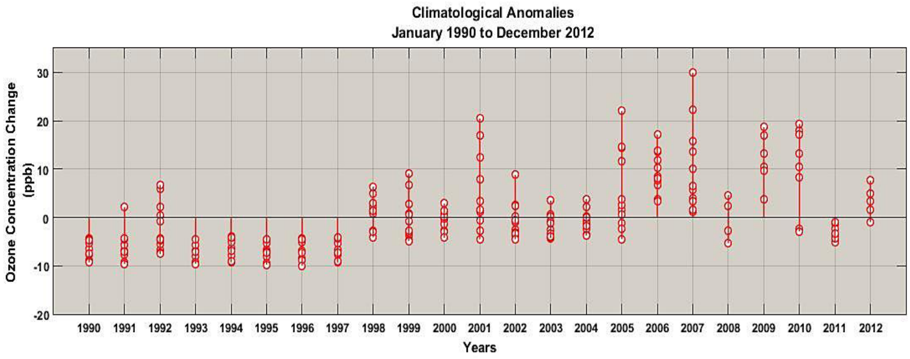

Figure 2. *Climatological anomalies for the duration 1990 to 2012.*

It was observed that ozone concentration values had a positive deviation for sixteen out of the twenty-three years ranging from +2.12 ppb in the year 1991 to +29.91 ppb in the year 2007. Moreover, a dramatic increase in the ozone concentrations was observed after the year 1998 and most of the values witnessed a positive deviation thereafter as evident from the figure.

A comparison between the climatological anomalies for the years 1994 to 1997 and the values after the year 1998 verified that there has been a sudden jump in the surface ozone concentration values post 1998.

Further, in the years 2007 and 2012, the values were found to be much higher than the averaged normal, thus indicating an incremental trend in the surface ozone levels in Delhi. A similar incremental trend in the surface ozone concentration levels over Delhi has been reported by (Peshin *et al.* 2017). The study conducted a continuous real time monitoring of surface ozone and other gaseous air pollutants for the period October 2010 to December 2014 within a network of eight air quality monitoring stations covering an area of 2000 km^2. The study highlighted that there has been a considerable increase in the surface ozone concentration levels in the city over this period which can be attributed to large scale anthropogenic emissions in the surrounding regions of study site. In addition to this, there exists a quantum of literature that supplements the fact that there has been a dramatic increase in the levels of surface ozone over Delhi region which can be attributed to anthropogenic activities (Tiwari *et al.* 2015; Sharma *et al.* 2016a, b; Supriya and Madhoolika 2018). Moreover, Delhi being at the cusp of drastic transformation has witnessed dramatic increase in its mobility demands which has increased the dependence on private modes of transportation as evident from the fact that the number of registered vehicles in the city increase at a rate of 10 percent per year (Mohan *et al.* 2009). This ever increasing private vehicle dependence has become the urban emission hotspots and can be considered as a major cause of the increased levels of ozone precursors in the atmosphere (Peshin *et al.* 2017). Furthermore, the implementation of CNG scheme in Delhi aggravated the concentration of ozone precursors like NO_x in the atmosphere (Goyal and Sidhartha 2003), which could be considered as one of the explanatory reasons for the increasing trend of surface ozone concentrations in the city (Saxena and Ghosh 2010).

In addition to this, annual climatological anomalies were also generated to observe a trend in the night-time surface ozone concentration for the study region. The results of the analysis revealed a similar increasing trend in the night-time ozone concentration levels as evident from figure 3.

A prominent incremental increase ranging from 5 ppb to 13 ppb were found during 2001-2010, indicating a 160 % increase in night-time surface ozone concentration during this period. It is relevant to point out that most of the existing studies predict the variations in the day time surface ozone concentration, however not much attention has been paid on the variations in the night-time ozone levels. Most of the studies focus on estimating the day time ozone concentration levels owing to the fact that the conducive environment for the formation of ozone is not available during night (Sharma *et al.* 2016a, c; Yadav *et al.* 2016). However, a few studies have reported that the concentration of night-time ozone levels has witnessed an increase in urban areas across the world which could be attributed to numerous meteorological factors (Li *et al.* 2016; Sicard *et al.* 2016). This incremental change of observed night-time ozone could be linked to various factors like temperature inversions allowing the Residual Ozone (RO) to build up amidst the already increased day time ozone concentration (Brandvold et al. 1996).

Additionally, synoptic meteorological phenomenon, such as height of nocturnal boundary layer which changes with respect to time further allows deposition of surface ozone at night (Mavrakis *et al.* 2010). Within this boundary layer, ozone remains high resulting in formation of the ozone reservoir at a constant level throughout the night near the ground surface (Neu *et al.* 1994; Mavrakis *et al.* 2010). Also, the temperature inversions isolate the surface ozone level with that of the upper levels allowing no or very less mixing resulting in dry deposition of night-time ozone (Aneja *et al.* 2000b).

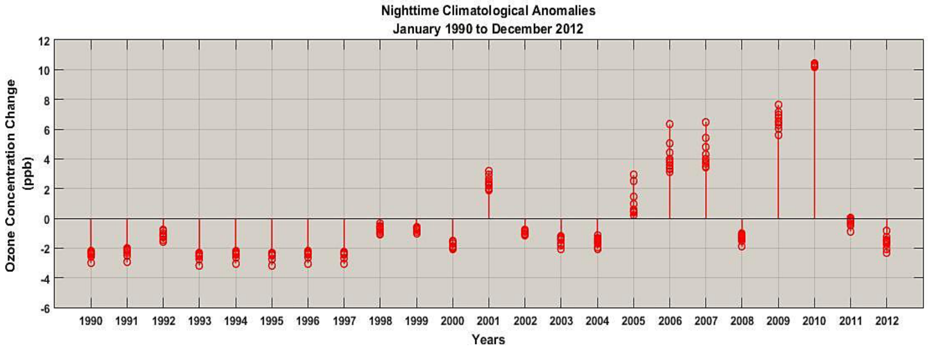

Figure 3. *Night time (20:00 to 06:00 hours) climatological anomalies for the duration 1990 to 2012.*

Monthly average variation of tropospheric ozone. The monthly variations of the average concentration of surface ozone over Delhi region for the period of 1990 to 2012 have been depicted in figure 4.

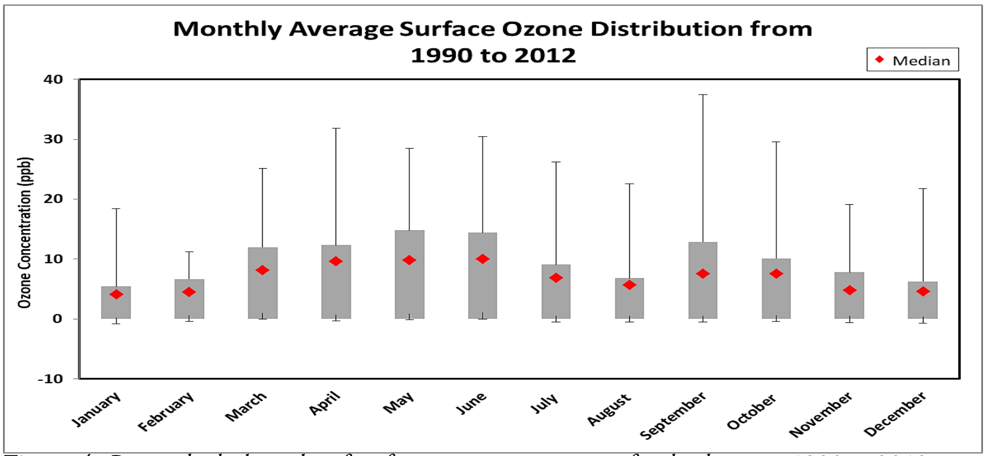

Figure 4. *Box and whiskers plot of surface ozone concentration for the duration 1990 to 2012.*

The results of the analysis revealed that the variation in the surface ozone levels followed the anticipated trend of high accumulation during summer months in comparison to that of winter months, as reported by numerous studies conducted in past (Aneja *et al.* 2000a; Bloomer *et al.* 2009; Reddy 2012; Peshin *et al.* 2017). The trend highlighted that monthly maximum was observed during the months of May and June which could be attributed to the relatively high temperatures reported in these months due to longer sunlight hours. It was also observed that the ozone levels in the months of July and August observed the minimum values which can be related to the increased levels of humidity in the atmosphere. In addition to this, rain washouts of pollutants and insufficient sunshine for the photochemical production of surface ozone during these months caused the monthly average surface ozone concentration to decline and reach as low as 5 ppb. However, in the post monsoon months the levels of surface ozone doubled and reached 10 ppb demonstrating the effect of meteorological conditions on the accumulation of ozone in the atmosphere. This anticipated increase in ozone levels could be primarily associated with the less cloud interference and longer duration of sunlight reaching the ground surface. Similar trends of the monthly variation of surface ozone concentrations in Delhi have been reported by Sharma *et al.* (2016) and (Ali *et al.* 2012) wherein the maximum average mixing ratios of surface O_3 were reported in the summer months while minimum values were observed in winter months.

Seasonal Variation of night time ozone concentration. Figure 5 represents the annual average variability of night-time ozone in Delhi for the period of 1990 to 2012. The overall concentration of night-time ozone in the atmosphere has witnessed a steady increase over the years. For instance, the mean summer night-time surface ozone concentration exceeded 18 ppb in 2010, which is almost twice to the levels of 2007, whereas constant mean concentration varied between 3 to 4 ppb throughout the duration as evident from the above figure. The results also revealed that the pre-monsoon and summer months represented by March, April and May (MAM) had the highest accumulation of night-time ozone. Moreover, an orderly positive incremental change in the ozone concentrations was observed during post monsoon months (September, October and November). This reversal of trend could be primarily attributed to calm wind and low moisture conditions along with anthropogenic precursors allowing day time ozone to accumulate as RO during the night-time.

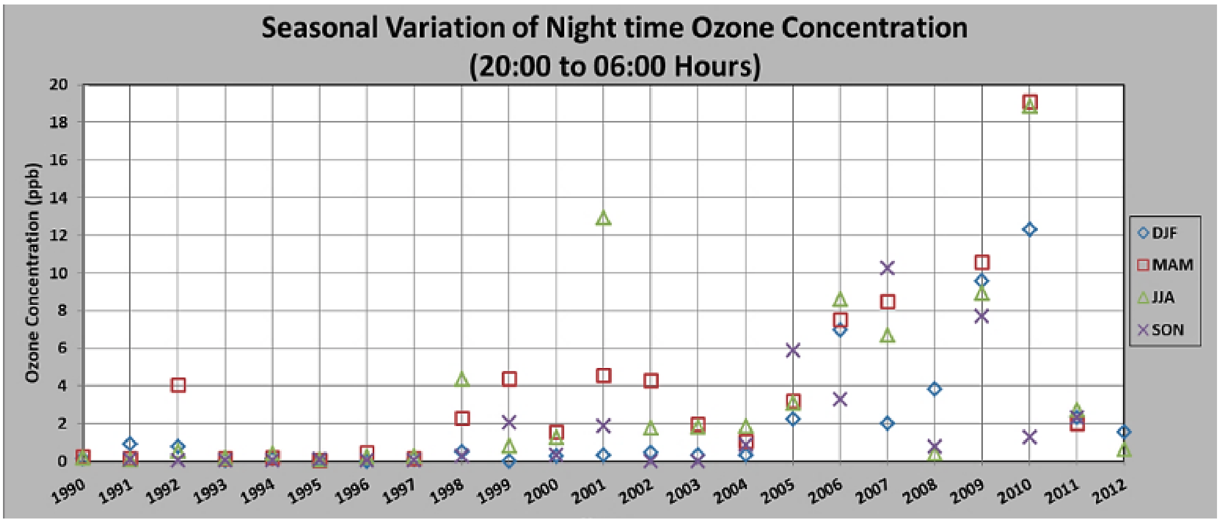

Figure 5. *Seasonal Variation of Night Time Ozone concentration (ppb) for the duration 1990 to 2012.*

Trend Analysis

Trends in the concentration of day time surface ozone over Delhi region between 1990 and 2012. The results of the statistical validation of the trend of surface ozone concentrations over Delhi between 1990 and 2012 conducted using the MK test revealed that a statistically significant trend was observed in the variation of ozone levels for all the months except for February (α=5%). Kendall's tau (τ), i.e., coefficient of variation for the average monthly concentration of surface ozone levels over this period is represented in figure 6(a). The values of the Kendall's tau coefficient and Sen's slope have been elaborately presented in table 1.

The results of the analysis highlighted a positive increase of ~211% in the ozone concentration levels between 1991 and 2001 while a ~79% increase over the next decade i.e., from 2001 to 2010 over Delhi region. The overall results of the MK test have been summarized in table 1 highlighting a positive trend in the variation of ozone concentration over Delhi during the study period. In order to gaze the magnitude of variation in the observed trend, Sen's slope was estimated for all the months during the study period, i.e., between 1990 and 2012. The results of the Sen's slope have been represented in figure 6(b) to provide a pictorial representation of the observed positive trend of ozone concentration levels.

As evident from the figure, magnitude of the obtained trend was maximum for the summer months (April and June), while minimum values of Sen's slope were reported in the winter months (December and January) for the duration of analysis between 1990 and 2012.

Month	Standard Deviation	Kendall's tau	S	Sen's Slope	Trend Significance
January	5.568	0.427	89	0.388	Significant
February	3.403	0.338	46	0.357	Not Significant
March	7.113	0.427	73	0.708	Significant
April	9.099	0.505	96	1.077	Significant
May	8.653	0.400	76	0.901	Significant
June	9.366	0.532	91	1.041	Significant
July	7.593	0.467	56	0.799	Significant
August	6.431	0.359	55	0.403	Significant
September	9.327	0.484	92	0.613	Significant
October	8.799	0.532	91	0.733	Significant
November	5.529	0.600	114	0.419	Significant
December	6.399	0.543	114	0.298	Significant

Table 1 *The values of the Kendall's tau coefficient and Sen's slope.*

Similar results have been reported by (Lefohn *et al.* 2018) in which the authors have applied MK test and Theil and Sen's Slope methods to estimate the trend in the global surface ozone concentration. The study also reports that the concentration of surface ozone is relatively high in the summer months in comparison to that of winter months.

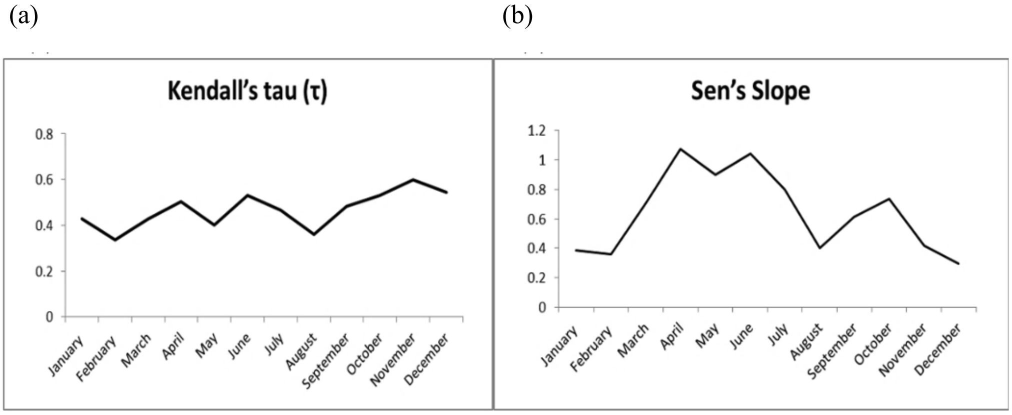

Figure 6. (a) *Kendall coefficient of correlation (τ) and Sen's slope* (b) *obtained for each month.*

Trends in the concentration of night time surface ozone over Delhi region between 1990 and 2012. The analysis of the trend for the night-time surface ozone concentration over Delhi region for the study period also revealed an increasing trend as highlighted in the previous section of the paper. The MK test generated a value of 0.503 of the Kendall's tau coefficient, which depicted a statistically significant increasing trend in the concentration of night-time ozone over the study region between 1990 and 2012. Furthermore, a positive value of 0.158 of the Sen's slope validated a positive trend observed in the analysis. The results of the current study highlight a key point that even though ozone is photolytic in nature, yet its concentration is increasing in the atmosphere even in the absence of sunlight in the study area. This perplexing trend of surface ozone presents an arena of further research in this regard. It is relevant to point out that since this increasing trend of the night-time ozone concentration levels cannot be explained by trend statistics, hence further investigation considering the tropospheric and stratospheric chemistry, synoptic behaviour of atmosphere, meteorological parameters and availability of day time precursors and residual concentrations including novel night-time ozone formation process, need to be considered in order to explain incremental increase of night-time surface ozone (Banta *et al.* 1998).

Ozone Forecasting: Predicted future trend of the annual surface ozone concentration over Delhi till 2025

The forecast by the ARIMA model highlighted an increasing trend in the concentration of surface ozone over Delhi between 2013 and 2025. The quantitative results of ARIMA model have been elaborately presented in table 2, while a diagrammatic representation of the variation in the average monthly ozone concentration levels till the year 2025 have been depicted in figure 7.

Table 2. *ARIMA model parameters and RMSE values for 1990 to 2025*

Fit Statistic	Mean	SE	Min	Max	Percentile						
					5	10	25	50	75	90	95
Stationary R-squared	0.497	0.335	-0.034	0.844	-0.034	-0.005	0.136	0.632	0.783	0.844	0.844
R- squared	0.247	0.11	-0.028	0.394	-0.028	0.024	0.189	0.281	0.315	0.372	0.394
RMSE	6.349	1.54	3.086	8.445	3.08	3.57	5.083	6.489	7.487	8.294	8.445
MAPE	284.58	152.44	53.74	645.36	53.74	62.73	208.5	269.7	354.2	562.63	645.36
Max APE	2376.73	2036.99	273.81	7655.72	273.82	279.98	1083.5	1707	3586	6499.6	7655.7
MAE	4.217	1.045	2.367	5.527	2.36	2.56	3.222	4.266	5.332	5.504	5.52
Max AE	16.237	5.748	6.233	25.752	6.23	7.69	12.06	15.96	20.81	25.40	25.75
Normalized BIC	3.87	0.602	2.42	4.567	2.42	2.68	3.465	4.006	4.271	4.53	4.56

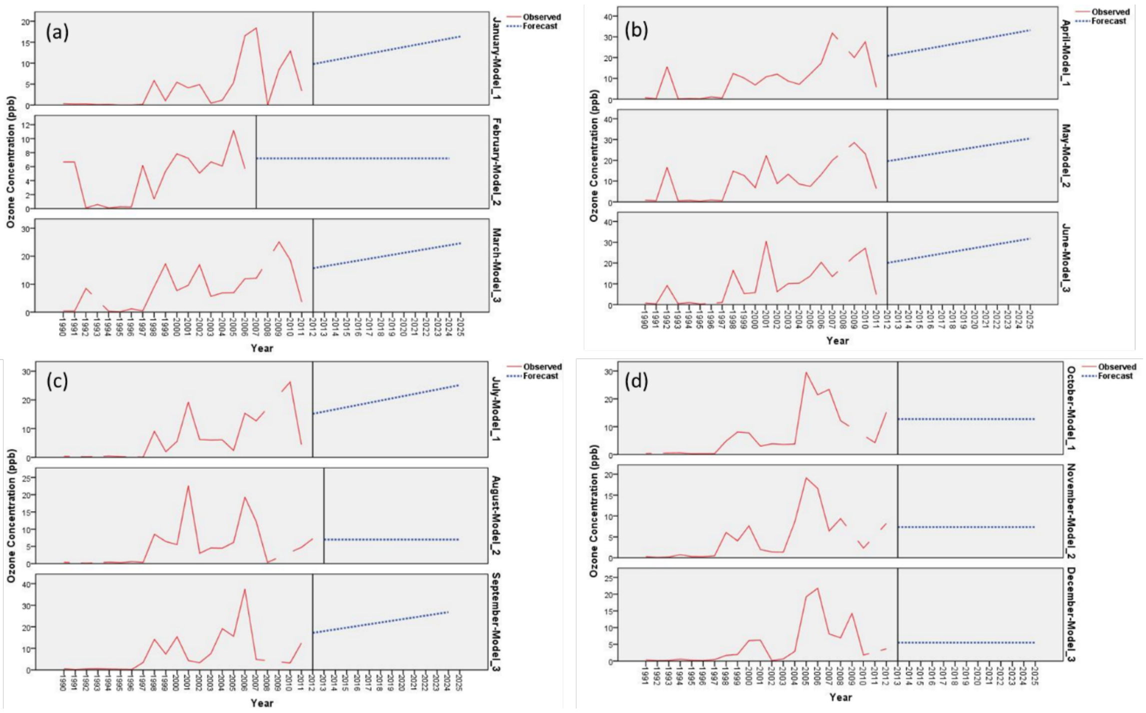

Figure 7. *ARIMA Modelling forecast for the duration of 1990 to 2025.*

The annual forecast revealed an increase in the surface ozone concentration over the succeeding years (2013 to 2025) reaching more than 30 ppb by the year 2025 for the summer months. The visual interpretation of the results of ARIMA model depict a good fit to the tropospheric ozone in all the seasons as evident from the figure. The forecast results of the variation in the night-time ozone (20:00 hours to 06:00 hours) also revealed an increasing trend for the succeeding years, i.e., between 2013 and 2025 as represented in figure 8.

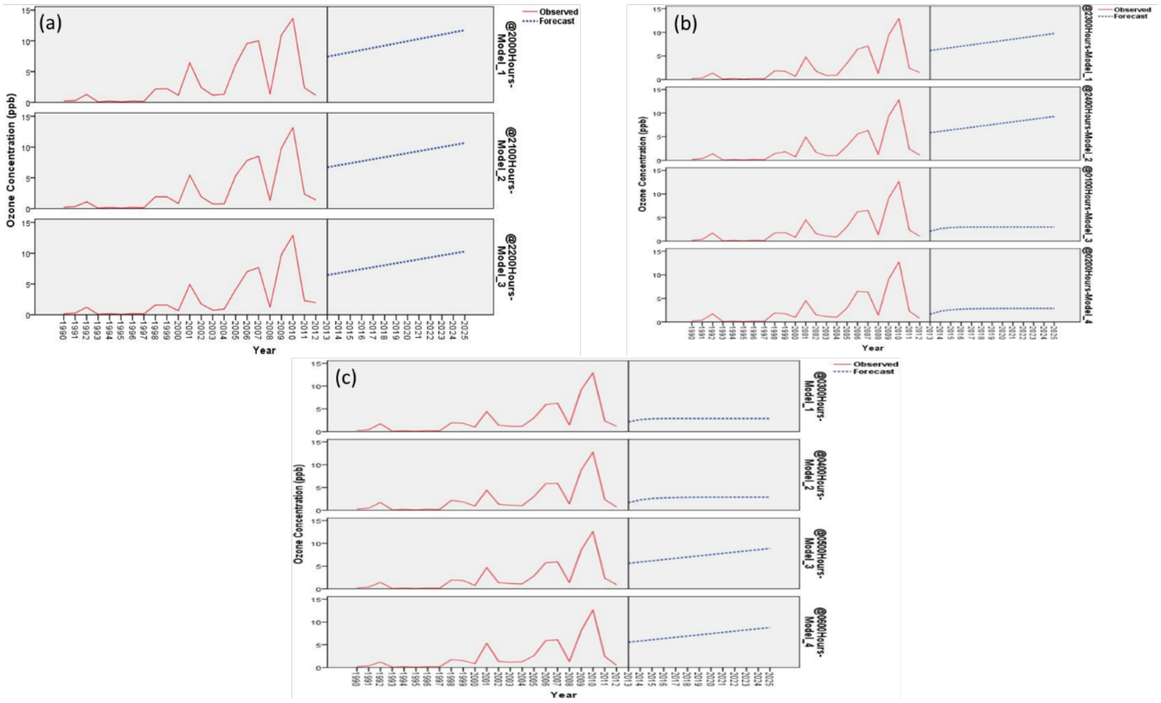

Figure 8. *ARIMA Modelling forecast for the Night time (20:00 hours to 06:00 hours) ozone concentration for the duration of 1990 to 2025.*

The figure clearly depicts that the concentration of night-time ozone will increase between these years and might reach up to 10 ppb by the year 2025. The predicted increase in the night-time ozone concentration levels over Delhi has become a cause of concern for the researchers and policy makers owing to the fact that there are numerous negative externalities associated with the increased levels of surface ozone concentrations. The increased levels of night-time ozone is sure to impact the overall agricultural productivity as well the health of the residents of the city (Singh *et al.* 2009) thus, making it imperative to understand the reasons associated with this increasing trend in order to curb the problem.

Summary and Conclusions

The tremendous increase in the levels of population and urbanisation coupled with the increased dependence on fossil fuels over the last two decades has deteriorated the air quality of Delhi. The city has witnessed a tremendous increase in the concentrations of both primary as well as secondary pollutants in the atmosphere. The present study evaluated the trends of ozone concentration over a period of three decades in Delhi. Of late surface ozone has become a cause of concern for researchers all across the world owing to its ill effects on human health and agricultural productivity. Thus, an effort was made to evaluate the trend of surface ozone concentrations over Delhi in order to identify the various sources of the pollutants in the city. The results of the long-term analysis of surface ozone revealed an increasing trend in the day time as well as night time ozone concentration over Delhi region. Moreover, anomaly variation suggested that post 1998 there has been a significant positive increase in the day time and night-time surface ozone concentration where deviation from the mean reached 29.91 ppb for 2007 (day time) and 10ppb for 2010 (night-time).

The annual average distribution of data for the period of 1990 to 2012 highlighted a gradual increase in ozone concentration over the study area. An increasing trend was also observed for the mean night-time ozone concentration which exceeded 18 ppb in 2010, while the mean concentration varied between 3 to 4 ppb throughout the period of analysis. The observed trends suggest that there exists a direct relationship between the day time concentrations and the increased night-time surface ozone levels. The increasing trend observed was verified by the Mann Kendall test, which revealed a statistically significant trend at 95% significance level with +0.158 value of the Sen's slope. Considering the implications of elevated levels of surface ozone in the atmosphere, the present study forecasted the trend of both surface as well as night-time ozone concentration levels over Delhi till the year 2025 using the ARIMA model. The results of the model revealed an increasing trend of the of both surface and night-time ozone concentration levels between 2013 and 2025. The trend analysis and literature review conducted in this study suggest that numerous factors could be attributed to the increased and increasing levels of night-time ozone levels in the city. Therefore, the emphasis of the current study is to understand the importance of identifying various sources and limiting the increasing concentration of surface ozone in the city. Moreover, it is relevant to point out that there exists significant amount of literature that explains the variation of day-time surface ozone, but the night-time variations and chemistry of ozone formation are often neglected. Hence, the current study is an attempt to understand this variation and demonstrate the factors attributable to the increased trend of surface ozone concentration in Delhi city. Moreover, this study is one of the important contribution which will pave the path for the discussions on the role of residual ozone accumulation and role of night-time chemistry and meteorology in understanding the impact of surface ozone on agriculture, climate and human health.

Acknowledgment

The authors would like to acknowledge the contribution of National Data Centre (NDC), India Meteorological Department (IMD) for providing the requested ozone dataset. The author is also thankful to HSBC foundation and internal grant committee of TERI School of Advanced Studies for providing scholarship during the period of study.

References

AGGARWAL P., JAIN S. (2016) Energy demand and CO_2 emissions from urban on-road transport in Delhi: current and future projections under various policy measures. J Clean Prod, 128:48–61. Doi: http://doi.org/10.1016/j.jclepro.2014.12.012

AKRITIDIS D., POZZER A., ZANIS P., TYRLIS, E., ŠKERLAK, B. (2016) On the role of tropopause folds in summertime tropospheric ozone over the eastern Mediterranean and the Middle East. Atmos Chem Phys Discuss, 0:1–24. Doi: http://doi.org/10.5194/acp-2016-547

ALI K., INAMDAR S.R., BEIG G., GHUDE, S. AND PESHIN, S. (2012) Surface ozone scenario at Pune and Delhi during the decade of 1990s. J Earth Syst Sci, 121:373–383. Doi: http://doi.org/10.1007/s12040-012-0170-1

ANEJA V.P., ADAMS A.A., ARYA S.P. (2000a) An observational based analysis of ozone trends and production for urban areas in North Carolina. Chemosph - Glob Chang Sci, 2:157–165. Doi: http://doi.org/10.1016/S1465-9972(00)00007-6

ANEJA V.P., ARYA S.P., LI Y., MURRAY JR, G.C. AND MANUSZAK, T.L. (2000b) Climatology of diurnal trends and vertical distribution of ozone in the atmospheric boundary layer in urban North Carolina. J Air Waste Manag Assoc, 50:54–64. Doi: http://doi.org/10.1080/10473289.2000.10463984

AWANG N.R., RAMLI N.A., YAHAYA A.S., ELBAYOUMI M. (2015a) High Nighttime Ground-Level Ozone Concentrations in Kemaman: NO and NO2 Concentrations Attributions. Aerosol Air Qual Res 15:1357–1366. Doi: http://doi.org/10.4209/aaqr.2015.01.0031

AWANG N.R., RAMLI N.A., YAHAYA A.S., ELBAYOUMI M. (2015b) Multivariate methods to predict ground level ozone during daytime, nighttime, and critical conversion time in urban areas. Atmos Pollut Res, 6:726–734. Doi: http://doi.org/10.5094/APR.2015.081

BANTA R.M., SENFF C.J., WHITE A.B, TRAINER, M., MCNIDER, R.T., VALENTE, R.J., MAYOR, S.D., ALVAREZ, R.J., HARDESTY, R.M., PARRISH, D. AND FEHSENFELD, F.C. (1998) Daytime buildup and nighttime transport of urban ozone in the boundary layer during a stagnation episode. J Geophys Res, 103:22519. Doi: http://doi.org/10.1029/98JD01020

DOI: 10.6092/issn.2281-4485/10809

BLOOMER B.J., STEHR J.W., PIETY C.A., SALAWITCH, R.J. AND DICKERSON, R.R. (2009) Observed relationships of ozone air pollution with temperature and emissions. Geophys Res Lett, 36:1–5. Doi: http://doi.org/10.1029/2009GL037308

BRANDVOLD D.K., MARTINEZ P., HIPSH R. (1996) Field measurements of O_3 and N_2O produced from corona discharge. Atmos Environ, 30:973–976. Doi: http://doi.org/10.1016/1352-2310(95)00234-0

CAILLERET M., FERRETTI M,. GESSLER A., RIGLING, A. AND SCHAUB, M. (2018) Ozone effects on European forest growth-Towards an integrative approach. J Ecol, 1377–1389. Doi: http://doi.org/10.1111/1365-2745.12941

CHATTOPADHYAY G., CHAKRABORTHY P., CHATTOPADHYAY S. (2012) Mann-Kendall trend analysis of tropospheric ozone and its modeling using ARIMA. Theor Appl Climatol, 110:321–328. Doi: http://doi.org/10.1007/s00704-012-0617-y

COOPER O.R., PARRISH D.D., ZIEMKE J., BALASHOV, N.V., CUPEIRO, M., GALBALLY, I.E., GILGE, S., HOROWITZ, L., JENSEN, N.R., LAMARQUE, J.F. AND NAIK, V. (2014) Global distribution and trends of tropospheric ozone: An observation-based review. Elem Sci Anthr 2:000029. Doi: http://doi.org/10.12952/journal.elementa.000029

CRUTZEN P.J. (1988) Tropospheric Ozone : An Overview, 3–32. Doi: http://doi.org/10.1007/978-94-009-2913-5_1

DERWENT RG, MANNING AJ, SIMMONDS PG, SPAIN, T.G. AND O'DOHERTY, S. (2018) Long-term trends in ozone in baseline and European regionally-polluted air at Mace Head, Ireland over a 30-year period. Atmos Environ 179:279–287. Doi: http://doi.org/10.1016/j.atmosenv.2018.02.024

DÍAZ J, ORTIZ C, FALCÓN I, SALVADOR, C. AND LINARES, C. (2018) Short-term effect of tropospheric ozone on daily mortality in Spain. Atmos Environ 187:107–116. Doi: http://doi.org/10.1016/j.atmosenv.2018.05.059

ELIASSON I., THORSSON S., ANDERSSON-SKÖLD Y. (2003) Summer nocturnal ozone maxima in Göteborg, Sweden. Atmos Environ, 37:2615–2627. Doi: http://doi.org/10.1016/S1352-2310(03)00205-X

FLEMING Z.L., DOHERTY R.M., SCHNEIDEMESSER E. VON, MALLEY, C., COOPER, O.R., PINTO, J.P., COLETTE, A., XU, X., SIMPSON, D., SCHULTZ, M.G. AND LEFOHN, A.S. (2018) Tropospheric Ozone Assessment Report : Present-day ozone distribution and trends relevant to human health.

GHOSH D., LAL S., SARKAR U. (2013) High nocturnal ozone levels at a surface site in Kolkata, India: Trade-off between meteorology and specific nocturnal chemistry. Urban Clim, 5:82–103. Doi: http://doi.org/10.1016/j.uclim.2013.07.002

GOYAL P., SIDHARTHA (2003) Present scenario of air quality in Delhi: A case study of CNG implementation. Atmos Environ 37:5423–5431. Doi: http://doi.org/10.1016/j.atmosenv.2003.09.005

HAYASHIDA S, KAJINO M., DEUSHI M., ET AL (2018) Seasonality of the lower tropospheric ozone over China observed by the Ozone Monitoring Instrument. Atmos Environ, 184:244–253. Doi: http://doi.org/10.1016/j.atmosenv.2018.04.014

HAYASHIDA S., LIU X., ONO A., YANG, K. AND CHANCE, K. (2015) Observation of ozone enhancement in the lower troposphere over East Asia from a space-borne ultraviolet spectrometer. Atmos Chem Phys, 15:9865–9881. Doi: http://doi.org/10.5194/acp-15-9865-2015

HU L., JACOB D.J., LIU X., ZHANG, Y., ZHANG, L., KIM, P.S., SULPRIZIO, M.P. AND YANTOSCA, R.M. (2017) Global budget of tropospheric ozone: Evaluating recent model advances with satellite (OMI), aircraft (IAGOS), and ozonesonde observations. Atmos Environ, 167:323–334. Doi: http://doi.org/10.1016/j.atmosenv. 2017.08.036

IPCC (2007) Summary for Policymakers. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

JENKIN M.E., CLEMITSHAW K.C. (2000) Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer. Atmos Environ, 34:2499–2527. Doi: http://doi.org/10.1016/S1474-8177(02)80014-6

KARTHIK L.B., SUJITH B., RIZWAN A.S., SEHGAL M. (2017) Characteristics of the Ozone Pollution and its Health Effects in India. Int J Med Public Heal, 7:56–60. Doi:http://doi.org/10.5530/ijmedph.2017.1.10

KUANG S., NEWCHURCH M.J., BURRIS J., WANG, L., BUCKLEY, P.I., JOHNSON, S., KNUPP, K., HUANG, G., PHILLIPS, D. AND CANTRELL, W. (2011) Nocturnal ozone enhancement in the lower troposphere observed by lidar. Atmos Environ, 45:6078–6084. Doi: http://doi.org/10.1016/j.atmosenv.2011.07.038

KULKARNI P,S,, BORTOLI D,, SILVA A,M, (2013) Nocturnal surface ozone enhancement and trend over urban and suburban sites in Portugal. Atmos Environ, 71:251–259. Doi: http://doi.org/10.1016/j.atmosenv.2013.01.051

KUMAR A., SINGH D., SINGH B.P., SINGH, M., ANANDAM, K., KUMAR, K. AND JAIN, V.K. (2015) Spatial and temporal variability of surface ozone and nitrogen oxides in urban and rural ambient air of Delhi-NCR, India. Air Qual Atmos Heal, 8:391–399. Doi: http://doi.org/10.1007/s11869-014-0309-0

KUMAR K., YADAV A.K., SINGH M.P., HASSAN, H. AND JAIN, V.K. (2004) Forecasting daily maximum surface ozone concentrations in Brunei Darussalam--an ARIMA modeling approach. J Air Waste Manag Assoc, 54:809–814. Doi: http://doi.org/10.1080/10473289.2004.10470949

LEFOHN A.S., MALLEY C.S., SMITH L., WELLS, B., HAZUCHA, M., SIMON, H., NAIK, V., MILLS, G., SCHULTZ, M.G., PAOLETTI, E. AND DE MARCO, A. (2018) Tropospheric ozone assessment report: Global ozone metrics for climate change, human health, and crop/ecosystem research. Elem Sci Anth, 6:28. Doi: http://doi.org/10.1525/elementa.279

LI J., YANG W., WANG Z., CHEN, H., HU, B., LI, J., SUN, Y., FU, P. AND ZHANG, Y. (2016) Modeling study of surface ozone source-receptor relationships in East Asia. Atmos Res, 167:77–88. Doi: http://doi.org/10.1016/j.atmosres.2015.07.010

MAVRAKIS A., FLOCAS H.A., MAVROMATIDIS E., KALLOS, G., THEOHARATOS, G. AND CHRISTIDES, A. (2010) A case of nighttime high ozone concentration over the greater Athens area. Meteorol Zeitschrift, 19:35–45. Doi: http://doi.org/10.1127/0941-2948/2010/0428

MCBEAN E., MOTIEE H. (2008) Assessment of impact of climate change on water resources: a long term analysis of the Great Lakes of North America. Hydrol Earth Syst Sci, 12:239–255. Doi: http://doi.org/10.5194/hess-12-239-2008

MOHAN D., TSIMHONI O., SIVAK M., FLANNAGAN M.J. (2009) Road Safety in India: Challenges and Opportunities.

MONKS P.S., ARCHIBALD A.T., COLETTE A., COOPER, O., COYLE, M., DERWENT, R., FOWLER, D., GRANIER, C., LAW, K.S., MILLS, G.E. AND STEVENSON, D.S. (2015) Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer. Atmos Chem Phys, 15:8889–8973. Doi: http://doi.org/10.5194/acp-15-8889-2015

NARAYANAN P., BASISTHA A., SARKAR S., KAMNA S. (2013) Trend analysis and ARIMA modelling of pre-monsoon rainfall data for western India. Comptes Rendus - Geosci, 345:22–27. Doi: http://doi.org/10.1016/j.crte.2012.12.001

NEU U., KÜNZLE T., WANNER H. (1994) On the relation between ozone storage in the residual layer and daily variation in near-surface ozone concentration-A case study. Boundary-Layer Meteorol, 69:221–247. Doi: http://doi.org/10.1007/BF00708857

NORAZIAN M.N., MUSTAFA A.M., BAKRI A., A.M.M., SHUKRI, Y.A. AND AZAM, R.N. (2007) Estimating Missing Data Using Interpolation Technique : Effects on Fitting Distribution. 3rd IMT-GT 2007 Reg Conf Math Stat Appl, 0–5.

PESHIN S,K,, SHARMA A,, SHARMA S,K, NAJA, M. AND MANDAL, T.K., (2017) Spatio-temporal variation of air pollutants and the impact of anthropogenic effects on the photochemical buildup of ozone across Delhi-NCR. Sustain Cities Soc, 35:740–751. Doi: http://doi.org/10.1016/j.scs.2017.09.024

REDDY B.S.K. (2012) Analysis of Diurnal and Seasonal Behavior of Surface Ozone and Its Precursors (NOx) at a Semi-Arid Rural Site in Southern India. Aerosol Air Qual Res, 1081–1094. Doi: http://doi.org/10.4209/aaqr.2012.03.0055

ROBESON S.M., STEYN D.G. (1990) Evaluation and comparison of statistical forecast models for daily maximum ozone concentrations. Atmos Environ Part B, Urban Atmos, 24:303–312. Doi: http://doi.org/10.1016/0957-1272(90)90036-T

SAXENA P., GHOSH C. (2010) Status of Tropospheric Ozone and other primary air pollutants after the implementation of CNG in Delhi. Asian J Chem, 22:7498–7506.

SEINFELD J.H., PANDIS S.N. (2012) Atmospheric From Air Pollution to Climate Change Second Edition.

SHARMA A., SHARMA S.K., PATHAK U, GUPTA, N.C. AND MANDAL, T.K. (2016a) Study on surface ozone and its precursors at an urban site of Delhi , India. Indian J Radio Sp Phys 45:95–100.

DOI: 10.6092/issn.2281-4485/10809

SHARMA S., SHARMA P., KHARE M., KWATRA S. (2016b) Statistical behavior of ozone in urban environment. Sustain Environ Res 26:142–148. doi: http://doi.org/10.1016/j.serj.2016.04.006

SHARMA S.K., ROHTA.S.H., MANDAL T.K., DEB, N.C. AND PAL, S (2016c) Measurement of Ambient NH3, NO and NO2 at an Urban Area of Kolkata, India. Mapan - J Metrol Soc India 31:75–80. Doi: http://doi.org/10.1007/s12647-015-0147-z

SHARMA S., KHARE M. (2017) Simulating ozone concentrations using precursor emission inventories in Delhi – National Capital Region of India. Atmos Environ, 151:117–132. Doi: 10.1016/j.atmosenv.2016.12.009

SHUKLA K., SRIVASTAVA P.K., BANERJEE T., ANEJA V.P. (2016) Trend and variability of atmospheric ozone over middle Indo-Gangetic Plain: impacts of seasonality and precursor gases. Environ Sci Pollut Res, 24 (1):164-179. Doi: http://doi.org/10.1007/s11356-016-7738-2

SICARD P., SERRA R., ROSSELLO P. (2016) Spatiotemporal trends in ground-level ozone concentrations and metrics in France over the time period 1999-2012. Environ Res, 149:122–144. Doi: http://doi.org/10.1016/j.envres.2016.05.014

SINGH S., AGRAWAL S.B.., AGRAWAL M. (2009) Differential protection of ethylenediurea (EDU) against ambient ozone for five cultivars of tropical wheat. Environ Pollut, 157:2359–2367. Doi: http://doi.org/10.1016/j.envpol.2009.03.029

SOUSA S.I.V., ALVIM-FERRAZ M.C.M., MARTINS F.G. (2011) Identification and origin of nocturnal ozone maxima at urban and rural areas of Northern Portugal - Influence of horizontal transport. Atmos Environ, 45:942–956. Doi: http://doi.org/10.1016/j.atmosenv.2010.11.008

SUPRIYA T., MADHOOLIKA A. (2018) Ozone Concentrations in Troposphere : Historical and Current Perspectives. In: Tropospheric Ozone and its Impacts on Crop Plants A Threat to Future Global Food Security. Springer, Cham, pp 2–21.

TIWARI S., DAHIYA A., KUMAR N. (2015) Investigation into relationships among NO, NO2, NOx, O3, and CO at an urban background site in Delhi, India. Atmos Res, 157:119–126. Doi: http://doi.org/10.1016/j.atmosres.2015.01.008

YADAV R., SAHU L.K., BEIG G., JAAFFREY S.N.A. (2016) Role of long-range transport and local meteorology in seasonal variation of surface ozone and its precursors at an urban site in India. Atmos Res. 176–177:96–107. Doi: http://doi.org/10.1016/j.atmosres.2016.02.018

YUE S., HASHINO M. (2003) Long-term trends of annual and monthly precipitation in Japan. Am Water Resouces Assoc. 39:587–596. Doi: http://doi.org/10.1111/j.1752-1688.2003.tb03677.x

YUREKLI K., SIMSEK H., CEMEK B., KARAMAN S. (2007) Simulating climatic variables by using stochastic approach. Build Environ, 42:3493–3499. Doi: http://doi.org/10.1016/j.buildenv.2006.10.046