J. Ind. Geophys. Union (January 2016)
v.20, no.1, pp: 101-111

Seasonal Variation of Daily Total Column Ozone (TCO), Its Depletion and Formation Role on Surface Temperature and Rainfall Over Chennai, India

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ABSTRACT

Various studies based on ground and satellite measurements have shown that overall ozone concentration is declining globally. The present manuscript contains results of study on the variation of total ozone concentration over Chennai, India during different seasons. It is concluded that the trend of ozone concentration during different seasons varies. After a critical analysis the following important results are obtained:

(i)The total ozone concentration increases during the pre-monsoon and winter periods; (ii) The Total Column Ozone (TCO) decreased during the monsoon and post-monsoon periods, throughout the extent of study; (iii) The rate of formation of ozone during monsoon is found to decrease in oscillatory manner, with the rise of surface temperature; (iv) The rate of depletion of ozone during monsoon is found to increase with the rise of surface temperature. However, a decreasing trend is noticed with the rise of surface temperature during post-monsoon period;(v) The overall ozone concentration over Chennai for the period of our study has shown slightly increasing trend;(vi) The variation of total rainfall with the rate of change of TCO (Total Column Ozone) is also presented for different seasons over Chennai and (v)Detailed chemical kinetics of ozone chemistry is presented along with possible explanation.

Keywords: Total Column Ozone (TCO), Gangetic West Bengal (GWB), Marine Boundary Layer (MBL), Monsoon, Pre-monsoon, Post-monsoon, Winter, Chemical Kinematics.

INTRODUCTION

Ozone is mainly found in two layers of the Earth's atmosphere. Significant quantity of ozone (about 90%) resides in a layer between approximately 10 and 50 km above the surface of Earth, the layer of the atmosphere called the stratosphere. The remaining ozone is in the lower layer of the atmosphere, called the troposphere. The total column ozone (TCO) indicates both the tropospheric as well as stratospheric ozone over a specified region. Ozone studies over India have already been done by different investigators (Chiplonkar 1939, Mani 1990, Karndikar et al. 1949 and Ramanathan et al. 1953). Various studies based on ground and satellite based measurements have shown that overall ozone concentration is declining globally (Stolarski et al. 1992). Seasonal variation of surface ozone over Athens, Greece was studied (Varotsos et al. 2000, 2001). It has been found that the trend of ozone concentration over Dumdum, India is declining (Jana et al. 2001). In a previous communication , it is shown that Indian summer monsoon rainfall over Gangetic West Bengal (GWB) depends on the rate of change of TCO (Total Column Ozone) during pre-monsoon period (Midya et al. 2011) and ozone formation depends on the cloud coverage over Kolkata (Jana et al. 2010). It is also shown that rate of change of TCO (Total Column Ozone) over Dumdum is different for different seasons and surface temperature of Dumdum depends on rate of depletion and formation rate of TCO (Total Column Ozone) (Midya et al. 2011). It is reported by Midya et al. (2011) that the rate of increase in surface relative humidity reaches maximum in the pre-monsoon season and decreases during other seasons. During the monsoon and post-monsoon seasons, the rate of depletion of TCO (Total Column Ozone) increases with the rate of decrease of surface relative humidity (Midya et al. 2011).It is reported (Midya et al. 2012) that TCO (Total Column Ozone) decreases steadily before and during the formation of cyclone and more or less an increasing trend is followed after dissipation of cyclone. It is also observed that when cyclone reaches its peak intensity with its maximum wind speed there is a sudden fall in ozone concentration over the regions, where the cyclones are intensified (Midya et al. 2012). Depletion of TCO (Total Column Ozone) in percentage increases with the increase of wind speed of cyclone (Midya et al. 2012). In the depletion mechanism of ozone, percentage contribution of nitrous oxide reaches maximum (Midya et al. 2000). Midya et al. (2011) have also shown that pre-monsoon rate of change of TCO (Total Column Ozone) plays a significant role on monsoon rainfall of that year and the ozone concentration lies between certain limits for sufficient rainfall over different stations of India (Midya et al. 2011). It is shown that average O_3

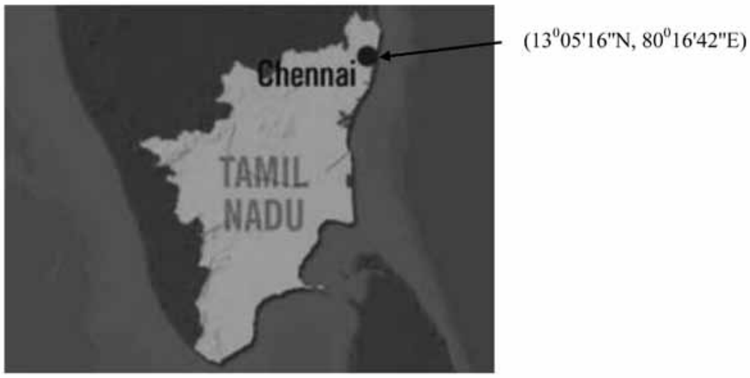

Figure 1. Map showing location of Chennai with Latitude and Longitude.

concentration is declining over Dumdum with smaller amount for short term ozone analysis (Ganda et al. 2010).

This paper presents variation of the rate of change of ozone concentration in different seasons, during 1997-2005 over Chennai. A detailed explanation of various causes has also been included; to cover results of different seasons during 1997 - 2005. Chennai is chosen as it is situated adjacent to the sea-shore, and its climate is expected to be different from rest of the India.

METHODS AND ANALYSIS

Ozone data of Chennai for 1997-2005 are taken from internet website http:// jwocky.gsfc.nasa.gov/ozone/ozone.html .The total column ozone amount over any point on Earth for maximum days between November 1978 and December 1994 and from August 1996 till date can be obtained nowadays from website http://ozoneaq.gsfc.nasa.gov/tools/ozonemap, whereas surface parameter data are taken from www.weather.uwyo.edu/upperair/sounding.html by specifying the location in the Southeast Asia region.

The collected data were divided into the following four parts-

- Pre-monsoon period - March, April, May and up to 7th June
- Monsoon period - June (8th onwards), July, August, September and October (up to 10th).
- Post-monsoon period - October (11th onwards), November and December.
- Winter period – January and February.

RESULTS AND DISCUSSION

Location of Chennai, with Latitude and Longitude, is shown in map [Fig.1].

a) Daily variation of ozone:

Total ozone concentration is plotted against days, in a scatter diagram, for different time periods as mentioned above. The observed trends in different time periods are given below:

The trend during winter [Fig.2 (a)-(g)] and pre-monsoon [Fig. 4(a)-(i)] clearly shows an increasing tendency, i.e. the total column ozone concentration increases throughout the period of study. It is reported that (Zachariasse et al. 2000) the lifetime of O_3 is an important factor in transport studies. Photodissociation of O_3 occurs by short wave solar radiation (λ<340 nm) and electronically excited O (^{1}D) atoms are produced. They form OH radicals on reaction with water vapour. Thus the lifetime of O_3 is basically determined by the amount of water vapour and solar radiation (Zachariasse et al. 2000). The lifetime of O_3 can vary from 2 to 5 days to approximately 90 days in the moist tropical marine boundary layer (MBL) and free troposphere, respectively (Fishman et al. 1991). O_3 can be transported far away from its source regions when it is lifted from the boundary layer (Zachariasse et al. 2000). The decreasing trend of total column ozone concentration in winter season in the year 1997 and 1999 is probably due to the aforesaid fact, because in these two years no major meteorological events have occurred around Chennai (De et al. 2005). The two exceptional cases are shown in Fig. 3(a) and Fig. 3(b).

However, decreasing trend is observed for monsoon [Fig. 5(a)-(i)] and post-monsoon [Fig. 6 (a)-(i)].

b) Rate of change of TCO during different seasons:

The general trend clearly shows positive gradient values in the pre-monsoon and winter periods and negative gradient values in the monsoon and post-monsoon periods. This indicates that there is an increase in the ozone concentration during January to 7th June (i.e. the winter and pre-monsoon) and a decrease from 8th June to December (i.e. monsoon and post-monsoon). Within the period of study, in the pre-monsoon period, a maximum positive value of the rate of change of TCO (Total Column Ozone) is observed in the year 2004. However, in the winter period such a trend is observed in the year 2002. The magnitude of the highest positive gradient is much greater during

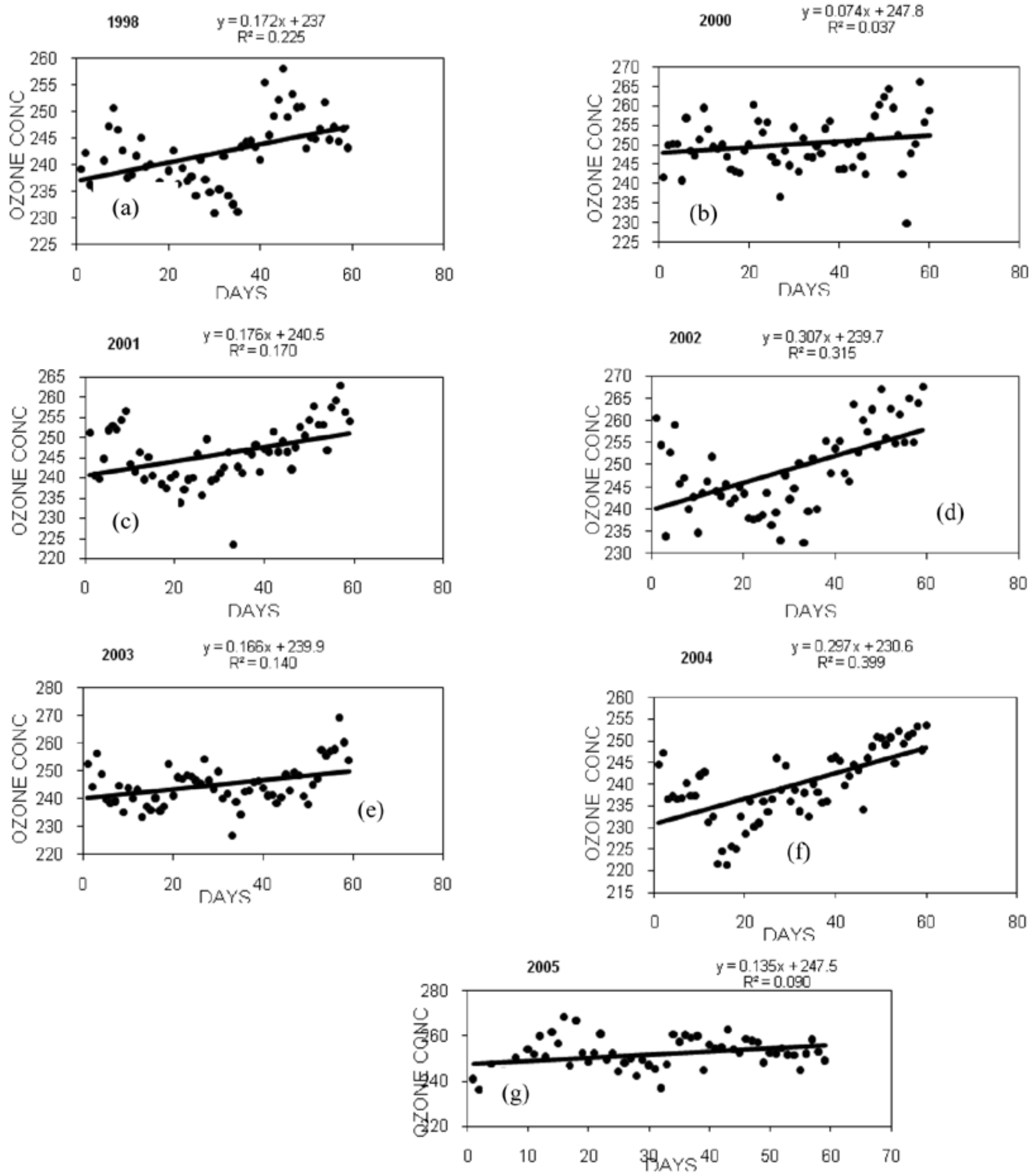

Figure 2. Daily variation of ozone in Dobson unit during winter in Chennai showing increasing trend during the period (a)1998, (b) 2000, (c) 2001, (d) 2002, (e) 2003, (f) 2004 and (g) 2005.

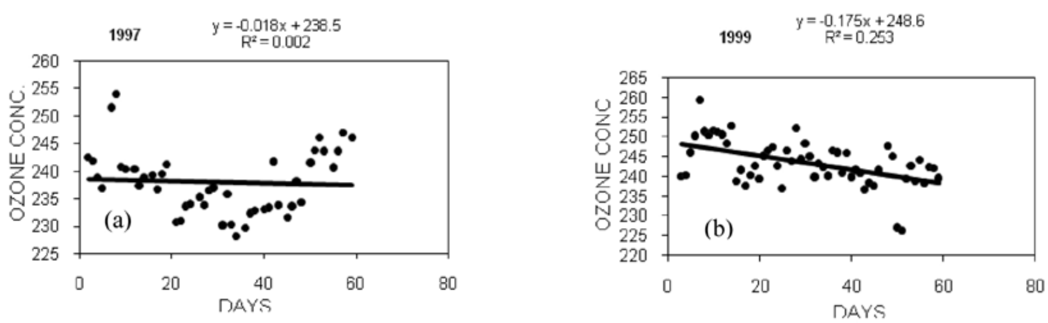

Figure 3. Daily variation of ozone in Dobson unit during winter in Chennai showing decreasing trend during the period (a)1997, (b) 1999.

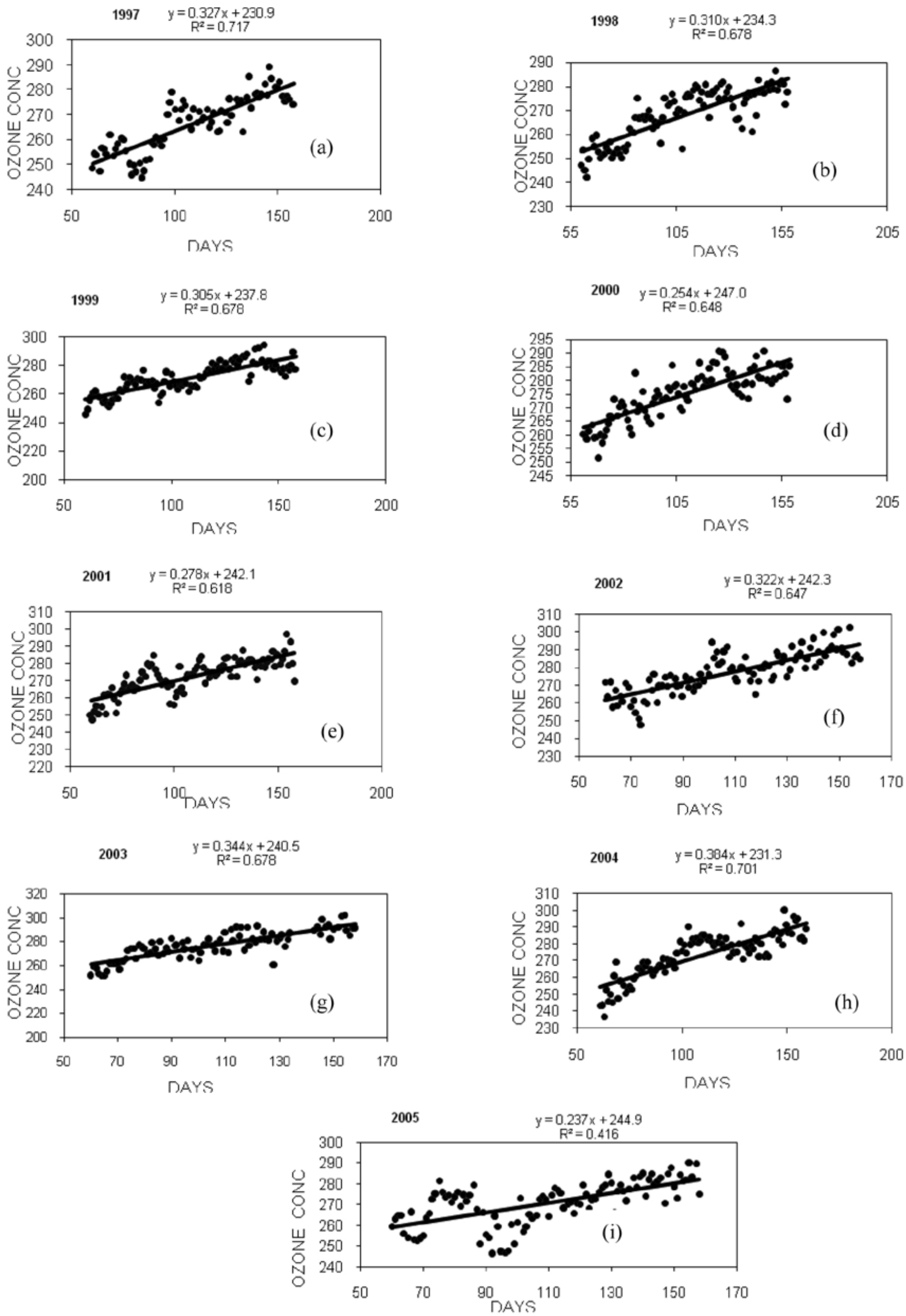

Figure 4. Daily variation of ozone in Dobson unit during pre-monsoon in Chennai showing increasing trend during the period (a)1997, (b) 1998, (c) 1999, (d) 2000, (e) 2001, (f) 2002, (g) 2003, (h) 2004 and (i) 2005.

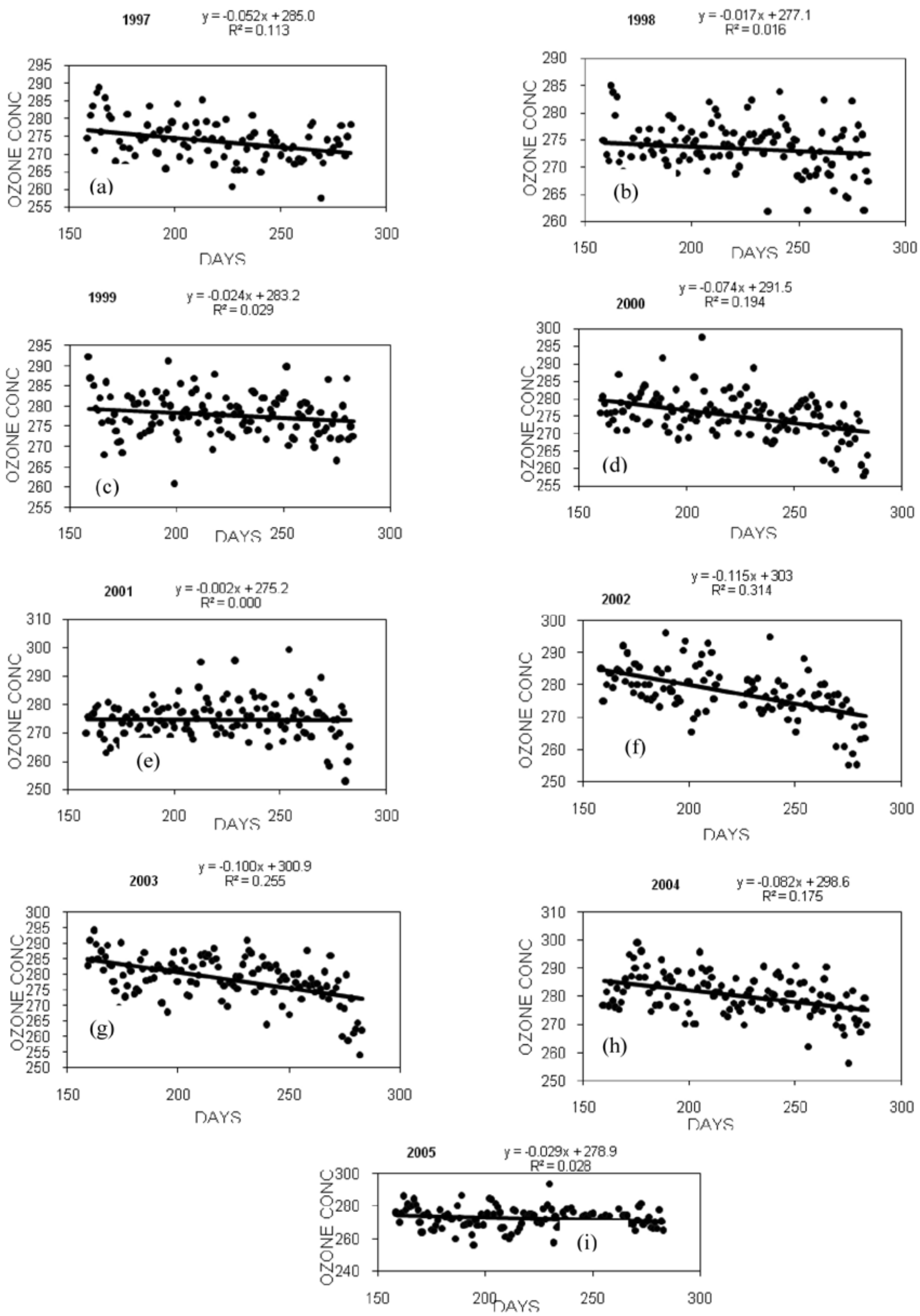

Figure 5. Daily variation of ozone in Dobson unit during monsoon in Chennai showing decreasing trend during the period (a) 1997, (b) 1998, (c) 1999, (d) 2000, (e) 2001, (f) 2002, (g) 2003, (h) 2004 and (i) 2005.

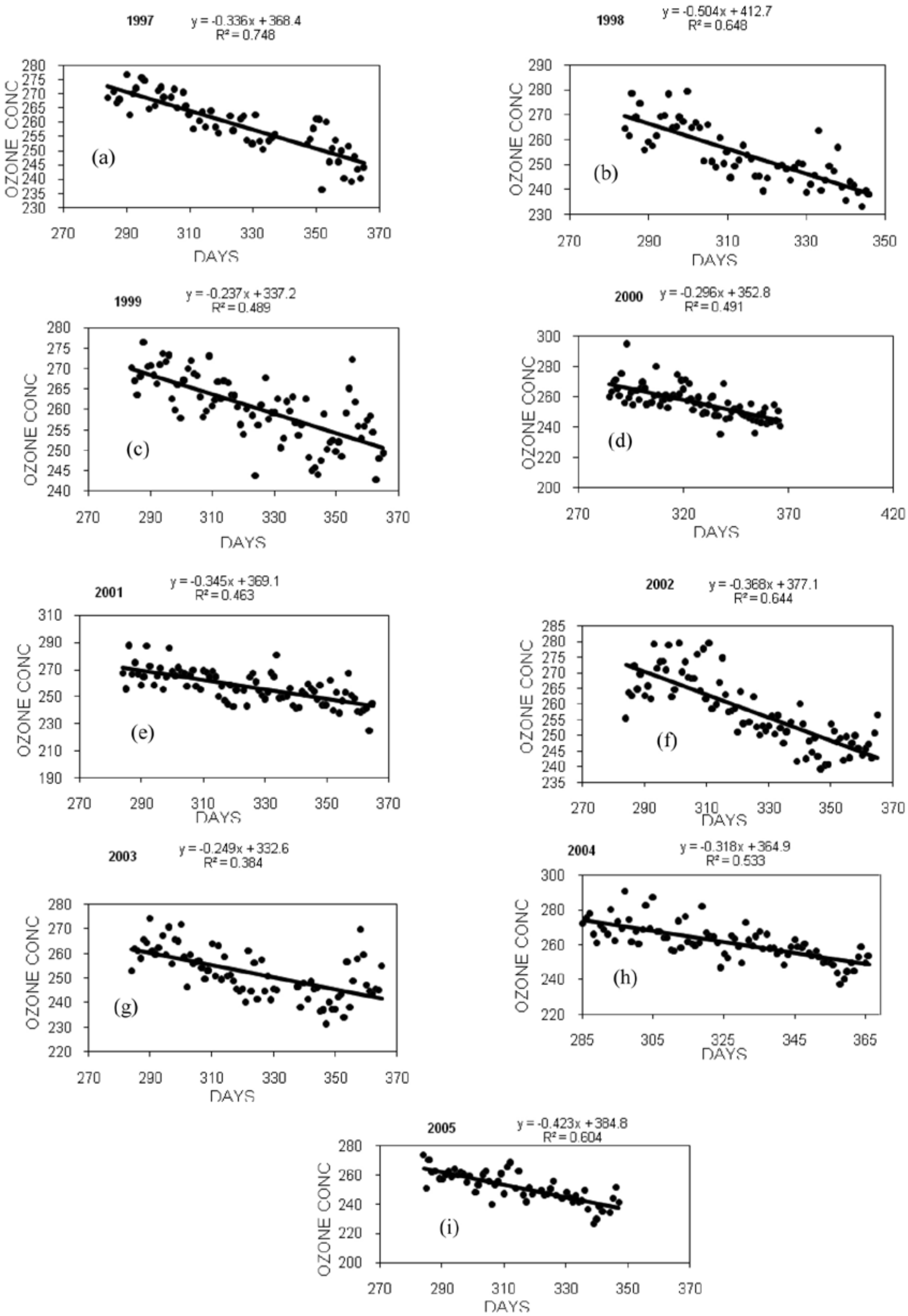

Figure 6. Daily variation of ozone in Dobson unit during post-monsoon in Chennai showing decreasing trend during the period (a) 1997, (b) 1998, (c) 1999, (d) 2000, (e) 2001,(f) 2002, (g) 2003, (h) 2004 and (i) 2005.

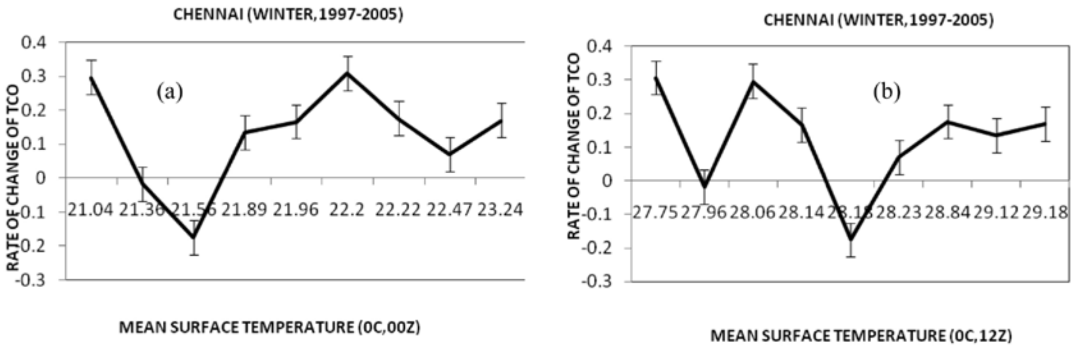

Figure 7. Variation of rate of change of TCO in Chennai with mean surface temperature, (a) (°C, 00Z) and (b) (°C, 12Z) during winter period.

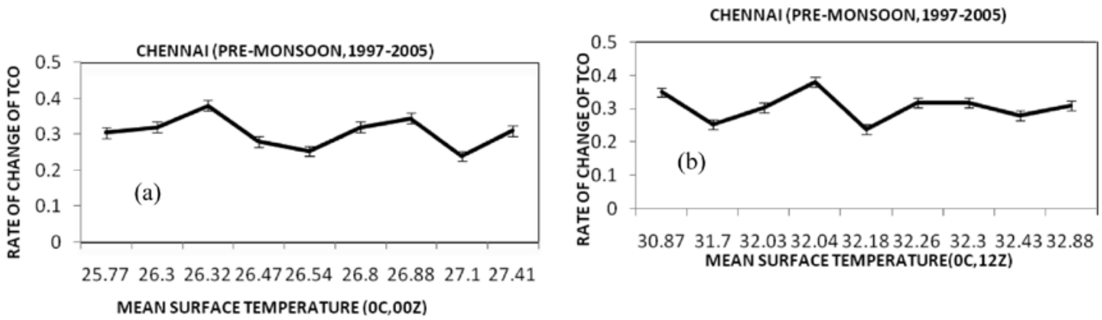

Figure 8. Variation of rate of change of TCO in Chennai with mean surface temperature, (a) (°C, 00Z) and (b) (°C,12Z) during pre-monsoon period.

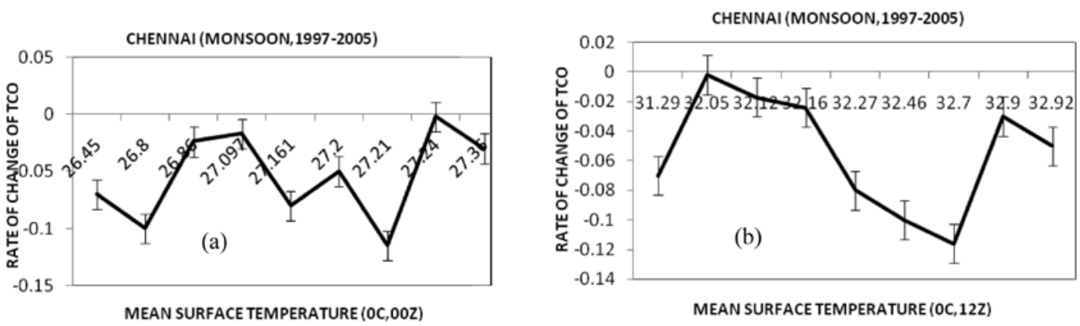

Figure 9. Variation of rate of change of TCO in Chennai with mean surface temperature, (a) (^{0}C, 00Z) and (b) (^{0}C,12Z) during monsoon period.

the pre-monsoon period (0.384) than in winter (0.307). Both in the monsoon and post-monsoon period negative gradient values are observed, with more negative values in the post-monsoon period as compared to the monsoon period. The highest negative value (-0.115) in monsoon is found in the year 2002 and in the post-monsoon period (-0.504) in the year 1998.

c) Variation of depletion and formation rate of O_3 concentration with surface temperature:

The variation of formation and depletion of O_3 concentration with surface temperature over Chennai during different seasons are shown in Figs. 7-10, both at 00Z and 12Z. Figs.7 and 8 confirm that during winter and pre-monsoon period O_3 trend is positive and the rate of formation of ozone increases with the rise of surface temperature.

During monsoon period rate of depletion of ozone shows an increasing trend with increase of surface temperature (Fig.9).

It is found that a uniform presentation of mean surface temperature values is maintained in Figs 9 (a) and 9 (b).

During post-monsoon period rate of depletion of ozone shows a decreasing trend with increase of surface temperature (Fig. 10).

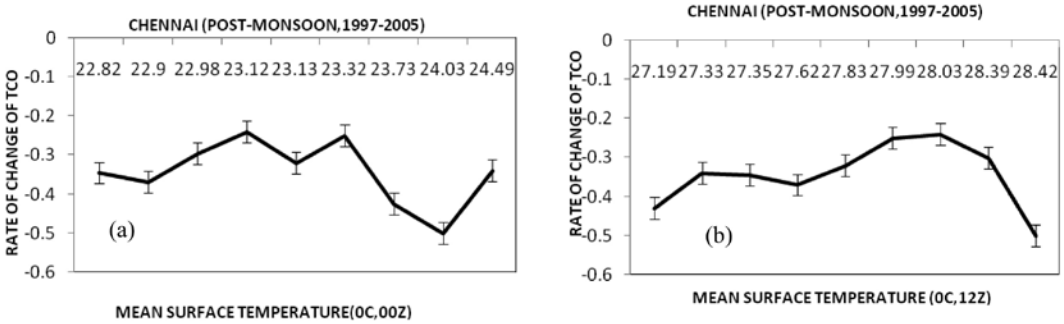

Figure 10. Variation of rate of change of TCO in Chennai with mean surface temperature, (a) (0C, 00Z) and (b) (0C, 12Z) during post-monsoon period.

d) Variation of rainfall with depletion and formation rate of O_3 concentration:

Analysis shows that rainfall rate increases with the increase of rate of formation of TCO (Total Column Ozone) for winter and pre-monsoon seasons. For the post-monsoon period rate of rainfall shows a decreasing trend, with the decrease of depletion rate of TCO (Total Column Ozone). However, rainfall rate shows, during monsoon period, a slightly increasing trend with the decrease of depletion rate of TCO (Fig.11).

The average trend of O_3 concentration over Chennai for the period 1997-2005 is shown in Fig.12. It is clear that overall O_3 concentration shows slightly increasing trend for the period of our study over Chennai.

Different formation and destruction processes of ozone are given below:

Reactions	Rate constants
1. $O_3 + h\nu \xrightarrow{I_{abs}} O_3^*$	I_{abs}
2. $O_3^* \xrightarrow{K_1} O_2 + O$	K_1
3. $O + O_3 \xrightarrow{K_2} 2O_2$	K_2
4. $O + O_3^* \xrightarrow{K_3} 2O_2$	K_3
5. $O + O \xrightarrow{K_4} O_2$	K_4
6. $O + O_2 \xrightarrow{K_5} O_3$	K_5

[1]

An empirical equation of O_3 concentration with the concentrations of other atmospheric constituents is established (Midya et al. 1995).

The rate of change of $[O_3]$ with respect to time is given by :

$d[O_3]/dt = -I_{abs} - K_2[O][O_3] + K_5[O][O_2]$

For small variation of time, I_{abs}, [O] and $[O_2]$ do not change their values so much. So we may consider

$I_{abs} = K_6$, $K_2[O] = K_7$ and $K_5[O][O_2] = K_8$

$d[O_3]/dt = -K_6 - K_7[O_3] + K_8 = K_9 - K_7[O_3]$

[Where $K_9 = K_8 - K_6 = K_5[O][O_2] - I_{abs}$]

Or $\int d[O_3]/(K_9 - K_7[O_3]) = \int dt$

Or $-\ln(K_9 - K_7[O_3])/K_7 = t + K_{10}$

Where K_{10} is integration constant

Or $[O_3] = K_9/K_7 - (1/K_7)\exp[-K_7(K_{10}+t)]$,

putting the values of K_9 and K_7 ,

$$[O_3] = \{K_5[O_2]/K_2\} - \{I_{abs}/K_2[O]\} - \{1/K_2[O]\}\exp[-K_2[O](K_{10}+t)] \qquad [2]$$

$[O_3]$, $[O_2]$, and [O] are the concentrations of ozone, molecular oxygen and atomic oxygen respectively. I_{abs} and all K values are the rate constants of different reactions and these values can be determined from chemical kinetics (Midya et al.1995). The net reaction for the formation of ozone in stratosphere is given below:

$$\begin{array}{lcl} O_2 + O_2 & \longrightarrow & O_2 + O + O = O_3 + O \\ O + O_2 + M & \longrightarrow & O_3 + M \\ \hline 3O_2 & \longrightarrow & 2O_3 \end{array} \qquad [3]$$

Ozone formation reaction is endothermic. So, higher temperature will favour higher equilibrium concentration of O_3. Again if temperature decreases rate of formation of O_3 will also decrease. Thus, it is expected that concentration of ozone decreases with the decrease of temperature. During pre-monsoon period, temperature of surface is higher. So, in order to obtain higher concentration of ozone, rate of formation of ozone will be higher during pre-monsoon period and increases with the increase of surface temperature. So, the nature of variation as shown in Fig. 8 is as expected.

Depletion mechanism of O_3 as given by Bates et al. (1950) is given below:

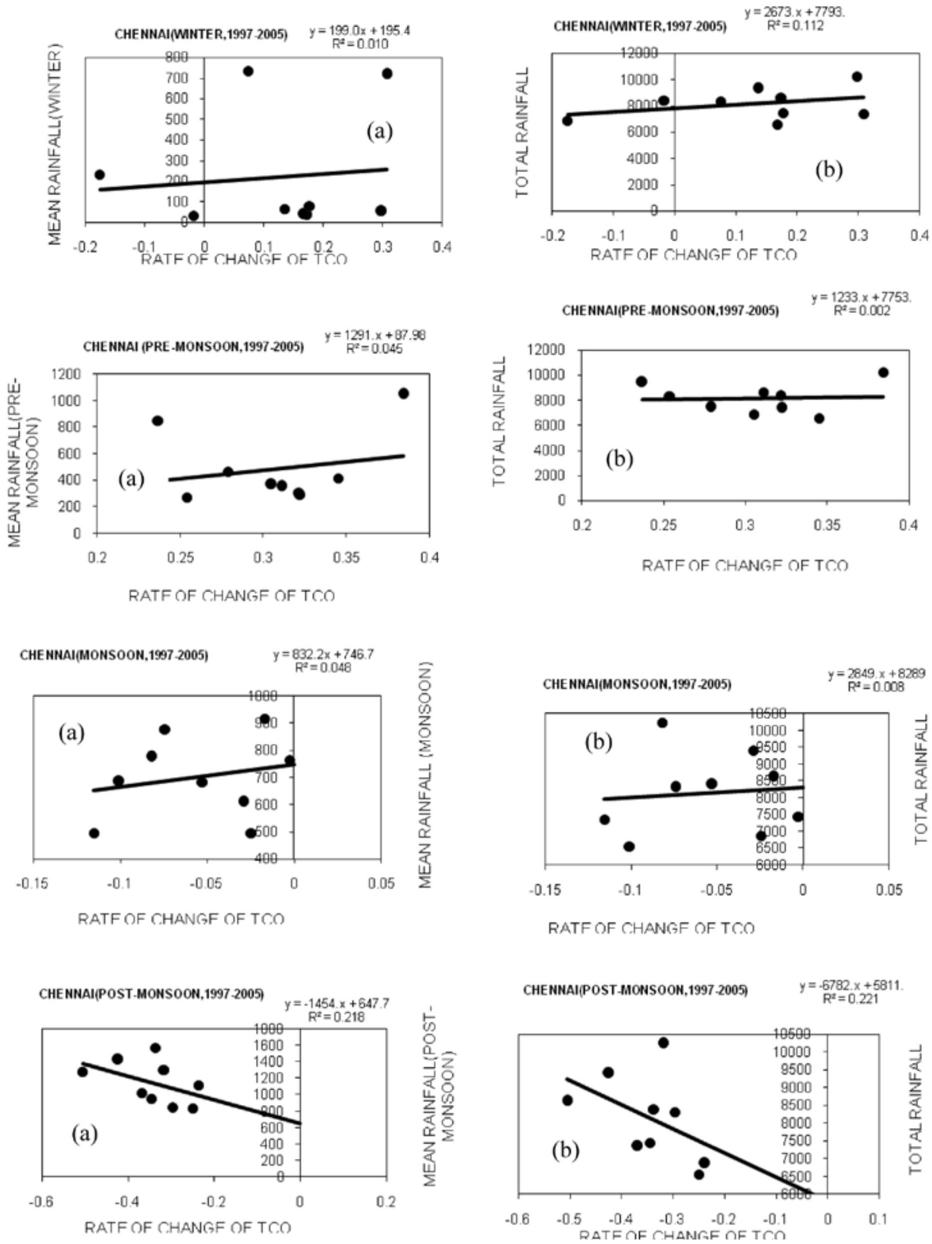

Figure 11. Variation of rate of change of TCO in Chennai with (a) mean rainfall and (b) total rainfall during winter, pre-monsoon, monsoon and post-monsoon period.

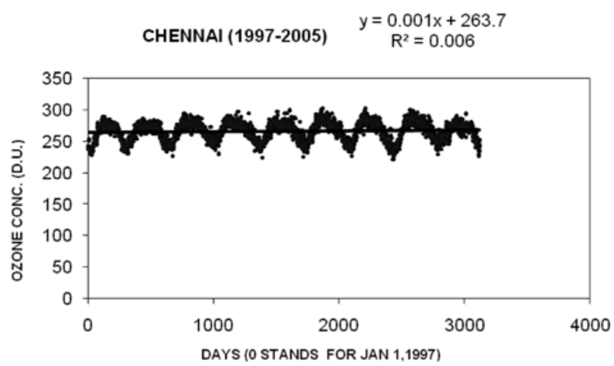

Figure 12. Variation of Ozone trend over Chennai for the period 1997-2005.

$$OH+O_3 \longrightarrow HO_2+O_2$$
$$HO_2+O \longrightarrow OH+O_2$$
$$O_3+O \longrightarrow 2O_2 \quad [4]$$

This mechanism is used earlier to explain ozone chemistry (Midya et al. 2011).

Atomic and molecular oxygen are produced due to photo-dissociation of H_2O molecule in the troposphere (Ghosh et al. 1994).

$$H_2O+h\nu \longrightarrow H+OH$$
$$OH+ h\nu \longrightarrow O+H$$
$$O+O+M \longrightarrow O_2+M \quad [5]$$

M is the third body, which conserves energy and momentum of the reaction.

During monsoon period, probability of OH radicals' presence increases in the atmosphere. As a result depletion rate increases with the rise of temperature, as probability of H_2O molecules in vapour state increases with the rise of temperature (Fig 9).

During post-monsoon period probability of H_2O molecules in vapour state decreases and as a result depleting rate of ozone gradually decreases during post-monsoon period (Fig. 10). Again rainfall rate depends on presence of water molecules in vapour state. Ozone is also formed due to the decomposition of water molecules in vapour state. Thus the trend of rainfall rate with rate of change of TCO (Total Column Ozone) is as expected (Fig.11). Monsoon rainfall depends on different factors such as monsoon trough, cyclonic system, El Nino etc. Slight change of trend of rainfall rate with the TCO (Total Column Ozone) during monsoon depends on these factors.

CONCLUSIONS

It is concluded that the rate of change of total ozone concentration over Chennai is not same for all seasons. It depends on the change of surface temperature for different seasons. It is also concluded that ozone concentration over Chennai shows slightly increasing trend for the total period of our study. Rainfall rate is also influenced by rate of change of TCO (Total Column Ozone) during different seasons. This type of variation is explained considering ozone destruction mechanism (Bates et al.1950).

The schematic representation of the variation of rate of change of the daily changes in the total ozone from 1997-2005 is presented in Fig. 12, which confirms that ozone trend is slightly increasing over Chennai. Variation of surface temperature with rate of change of TCO (Total Colum Ozone) over Chennai is different from Gangetic West Bengal (GWB), which may be due to slight increase of ozone concentration over Chennai. This agrees fairly well with previous observation over GWB (Gangetic West Bengal) by Midya et al. (2011). Marginal variation from Midya et al. (2011) findings is due to some special meteorological events. These events caused marginal temperature variations from normal trend in Chennai and Gangetic West Bengal.

ACKNOWLEDGEMENTS

We acknowledge with thanks the authority of ozone data source and surface parameter data source. The references of all the data sources are mentioned in methods and analysis portion of the article. Thanks are due to anonymous reviewer and Editor of the journal, for useful suggestions.

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