J Atmos Chem (2014) 71:95–112
DOI 10.1007/s10874-014-9284-y

Study of Ozone and NO_2 over Gadanki – a rural site in South India

K. Renuka · Harish Gadhavi · A. Jayaraman · Shyam Lal · M. Naja · S. V. Bhaskara Rao

Received: 1 November 2013 / Accepted: 17 June 2014 /
Published online: 8 July 2014

Abstract We have studied long-term changes in tropospheric NO_2 over South India using ground-based observations, and GOME and OMI satellite data. We have found that unlike urban regions, the region between Eastern and Western Ghat mountain ranges experiences statistically significant decreasing trend. There are few ground-based observatories to verify satellite based trends for rural regions. However, using a past study and recent measurements we show a statistically significant decrease in NO_X and O_3 mixing ratio over a rural location (Gadanki; 13.48° N, 79.18° E) in South India. In the ground-based records of surface NO_X, the concentration during 2010–11 is found to be lower by 0.9 ppbv which is nearly 60 % of the values observed during 1994–95. Small but statistically significant decrease in noon-time peak ozone concentration is also observed. Noon-time peak ozone concentration has decreased from 34±13 ppbv during 1993–96 to 30±15 ppbv during 2010–11. NO_X mixing ratios are very low over Gadanki. In spite of low NO_X values (0.5 to 2 ppbv during 2010–11), ozone mixing ratios are not significantly low compared to many cities with high NO_X. The monthly mean ozone mixing ratio varies from 9 ppbv to 37 ppbv with high values during Spring and low values during late Summer. Using a box-model, we show that presence of VOCs is also very important in addition to NO_X in determining ozone levels in rural environment and to explain its seasonal cycle.

Keywords Ozone · Trace-gases · NO_X · Atmospheric chemistry · Rural India · Oxides of nitrogen

K. Renuka (✉) · H. Gadhavi · A. Jayaraman
National Atmospheric Research Laboratory, Gadanki, Chittoor (dt), AP 517 112, India
e-mail: renuka.kavutharapu@gmail.com

K. Renuka
e-mail: renuka@narl.gov.in

S. Lal
Physical Research Laboratory, Ahmedabad, India

M. Naja
Aryabhatta Research Institute of Observational Sciences, Nainital, India

S. V. B. Rao
Department of Physics, Sri Venkateswara University, Tirupati, India

1 Introduction

Ozone plays an important role in the earth's atmosphere and has both good and bad effects on all lives on the earth either directly or indirectly. Some of the well known effects are: (1) its presence in the troposphere deteriorates air quality and thereby has harmful effects on health (National Research Council 1991; WHO 2003), while its presence in the stratosphere protects lives from harmful ultraviolet radiation (van der Leun et al. 1998); (2) it contributes to global warming by absorbing the terrestrial radiation in troposphere (Fishman et al. 1979; Forster et al. 2007); (3) High concentration of ozone in troposphere reduces crop yield and damages the natural ecosystems (Wang and Mauzerall 2004; Mohammed et al. 2012; Mohammed et al. 2013). Natural source of surface ozone is intrusion of stratospheric ozone (Ganguly and Tzanis 2011). However, large part of it is produced in-situ through complex photochemical reactions by oxides of nitrogen (NO_X), which are also responsible for forming secondary aerosols and acid deposition (Seinfeld and Pandis 1998; Varotsos et al. 2012). This in turn has many negative effects such as corrosion or soiling of cultural and historical heritage buildings/ structures (Tzanis et al. 2009; Tzanis et al. 2011).

Accordingly, the concentrations of ozone and NO_X have been considered important for monitoring and controlling directly (Holland et al. 2005; Foster and Kumar 2011; Berman et al. 2012; CAAC 2013) and for assessing indirectly through transport processes linked with global warming and climate change related dynamics (Price et al. 1997; Walter and Heimann 2000; Ganzeveld 2002; Sanderson et al. 2003; Wiedingmyer et al. 2006). Production, loss and transport of ozone and NO_X, however, are not homogeneous across the globe (Cartalis and Varotsos 1994; Chou et al. 2006; Jonson et al. 2006; Jaffe and Ray 2007; Tanimoto 2009; Tanimoto et al. 2009; Tripathi et al. 2012; Engardt 2008) and thus their monitoring from different parts of the globe, both urban and rural have assumed importance.

In the above context, several studies were initiated in India to study tropospheric ozone and its precursors (Naja and Lal 1996; Naja et al. 2003; Beig et al. 2007; Lal 2007; Ghude et al. 2008; Purkait et al. 2009; Kumar et al. 2010; David and Nair 2011; Ali et al. 2012; Ganguly 2012; Swamy et al. 2012; Ganguly and Tzanis 2013). However, very little has been done from rural India. One observational program, under the auspices of Indian Space Research Organisation's Geosphere-Biosphere Program (ISRO-GBP), to measure surface ozone, NO_X, CO and CH_4 was initiated from Gadanki (13.48° N, 79.18° E), a rural site in South India and observations were made during 1993–96 (Naja and Lal 2002). Realising the importance of these measurements, we have re-initiated a long-term observational program by setting up the first comprehensive observatory of the 'Indian Climate Observatory Network' (known as ICON) over Gadanki in 2010.

In this paper, we present new observations on ozone and NO_X concentrations, compare these with those observed in the past (1993–1996) and satellite based observations and discuss these results in the light of current understanding on the concentration of ozone from the rural environment of Gadanki. The paper is organised as follows. In section 2, we describe the rural site and the meteorological conditions prevailed during the observational period. In section 3, we describe instruments and data-sets used in this study. In section 4, we present the results and discuss the main findings in section 5.

2 Site description and meteorology

Observations presented in this work are from the National Atmospheric Research Laboratory (NARL) located at Gadanki (13.48° N, 79.18° E), a rural site in the Southern part of India.

NARL operates a large number of instruments, both ground-based remote sensing (viz. radio, optical, acoustic) and ground-based and balloon-borne sensors to measure atmospheric and ionospheric parameters. The laboratory is surrounded by hills having heights of ~750 m. Observations of trace-gases were carried out from Gadanki, the first climate observatory of ICON. The observatory is located on a hillock, a place whose altitude is the highest in the NARL campus. The analysers are kept on the top floor of the ICON building. There is no major industrial activity near the observational site except for the road connecting Tirupati and Bangalore, where the traffic is low. The aerial distance from the road to the observation site is 1.5 km and height difference between the road and the place of observation is about 50 m. The location is approximately 390 m above mean sea level.

Gadanki experiences tropical wet climate. Monthly mean relative humidity (RH), temperature, wind speed, wind direction and monthly total rainfall over Gadanki for 2010–11 are shown in Fig. 1. RH over Gadanki varies from 45 % in spring (pre-monsoon) to 90 % in winter (north-east monsoon period). Monthly mean temperature varies from 31ºC (from end of spring to beginning of summer) to 22ºC (in winter). Gadanki experiences two rainy seasons; one during south-west monsoon (June to September) and another during north-east monsoon (October to December). The period from January to May has minimum amount of rainfall. Total rainfall during 2010 and 2011 was 1,151 mm and 882 mm, respectively. The dominant wind directions close to surface are south-westerly during June to September, north-easterly during October to December and south-easterly during February to April. The wind speeds are generally higher during south-west monsoon with monthly mean values reaching as high as 2.3 m/s.

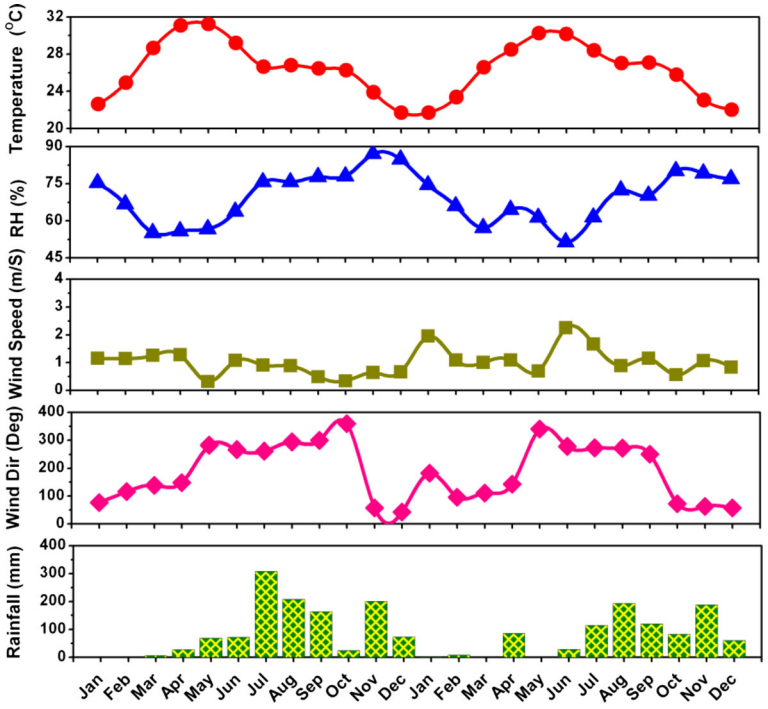

Fig. 1 Monthly mean temperature, relative humidity, wind speed, wind direction and monthly total rainfall over Gadanki for 2010–2011

3 Instruments and data

Surface concentrations of O_3 and NO_X were measured continuously using on-line analysers (Model: 49i for O_3, and 42i for NO_X, Thermo Scientific, USA) since January 2010. Ambient air is drawn through a 293 cm long inlet running from the top of the building to a glass manifold located inside a room. The ozone analyser has in-built calibration unit for the span and zero checks. Ozone analyser works on the principle of Beer-Lambert-Baugher's law, which relates absorption of light to the concentration of species. UV light of wavelength 254 nm is used as light source where ozone has strong absorption. Zero check for the ozone analyser is done once in a week. The span checks were done four times during the study period (2010–11). The changes in the consecutive calibrations have been very small. The zero offset reduced by 0.1 ppbv and span constant reduced by 2 % during the study period. The lowest detection limit of the analyser is 1 ppbv and the response time is 20 s. The accuracy of the ozone analyser is ± 5 % for an ozone concentration of 60 ppbv.

The NO_X analyser works on the principle of chemiluminescence. The analyser uses molybdenum converter to convert NO_2 into NO and the intensity of light emitted in the reaction of NO with O_3 is related to total amount of NO_X. The response time is 60 s and the lowest detection limit is 0.4 ppbv for one minute time resolution. Molybdenum converter can also convert other nitrogen containing substances to NO and hence NO_2 measurement by this analyser should be regarded as upper limit. The analyser is equipped with facilities of zero and span calibrations. The zero calibration checks are done on weekly basis. Span calibration checks were done three times during the study period. Here too there has been very small differences in consecutive calibrations. Average differences of consecutive calibrations have been zero for NO_X analyser and variabilities of calibration constants have been of the order of 7 %.

To a small extent we have used total irradiance data from Pyranometer operated from ICON terrace. In addition to our own data, GOME (Global Ozone Monintoring Experiment) and OMI (Ozone Monitoring Instrument) satellites' tropospheric NO_2 data (Boersma et al. 2004; Boersma et al. 2007) have also been used to study NO_2 trend over South India. GOME instrument was launched onboard ERS-2 satellite of European Space Agency in 1995. It was in operation from 1996 to 2003. The tropospheric NO2 retrieval from GOME has precision of the order of 35 to 60 % depending upon location. OMI instrument was launched in 2004 on board of NASA's Aura satellite. The OMI data are available globally at 0.125° X 0.125° grid resolution. OMI data has error of the order of 0.7 x 10^{15} molec/cm^2 which is about 40 % over Southern India.

4 Results and observations

4.1 Ozone variability

Figure 2a shows diurnal variations of surface ozone for four seasons: spring (March-May), summer (June-August), autumn (September-November) and winter (December-February). The peak concentration is found to be in the afternoon and low concentration just before the sunrise. The time of peak concentration changes from 16:00 h in spring to 14:00 h in autumn. Observations also suggest that ozone mixing ratio builds up (at the rate 1 to 3.5 ppbv per hour on average depending on season) during 7-14/16 LT and decreases rather slowly during 14/16-7 LT. The diurnal range of mixing ratio is found to be in the range of 15–47 ppbv in spring, 14–31.5 ppbv in winter, 11.5 - 22.8 ppbv in summer and 11.4 - 20.8 ppbv in autumn. These results suggest that the ozone mixing ratio maximises in spring followed by winter, summer and autumn.

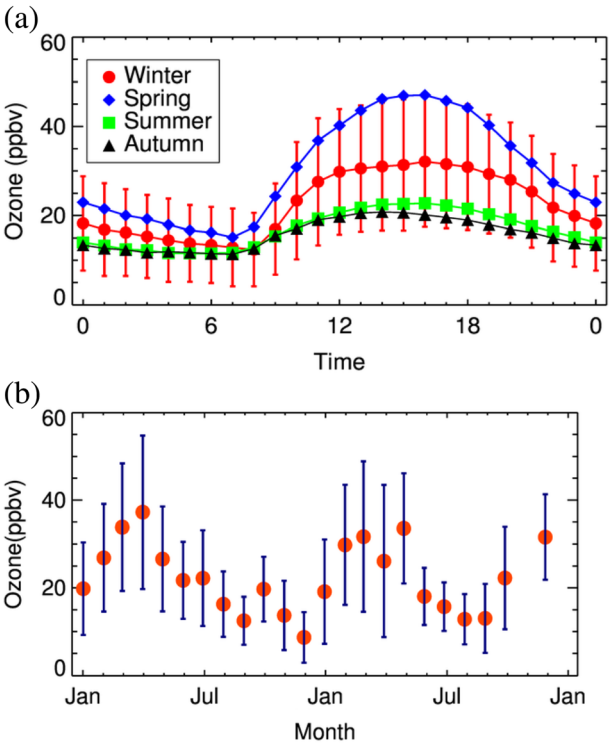

Fig. 2 (**a**) Diurnal variation of ozone over Gadanki for the period 2010–2011 for four seasons. For the sake of clarity, standard deviation is shown only for winter. (**b**) Monthly mean variation of ozone over Gadanki from January 2010 to December 2011. Filled circles are monthly mean ozone concentration whereas vertical bars are 1σ standard deviation

Figure 2b shows monthly mean ozone mixing ratios for the period January 2010-December 2011. Monthly mean mixing ratios varies from 9 ppbv to 37 ppbv and follows a clear seasonal cycle. It is generally higher during March-May and low during August-September. Variability of ozone mixing ratio represented by standard deviation is also found to be high during March-May and low during August-September.

4.1.1 Comparison of Ozone levels with other places

In order to compare these results with those observed from other locations in India, we show monthly average surface ozone for few places in Fig. 3. Inset figure depicts the map of locations from where observations were made. Sources of data for other stations are as follows: Nainital (Kumar et al. 2010), Ahmedabad (Lal 2007), Pune (Beig et al. 2007), Hyderabad (Swamy et al. 2012) and Thiruvananthapuram (also known as Trivendrum) (David and Nair 2011). Trivandrum has very different seasonal variation in ozone compared to Gadanki and other stations shown in the figure. Trivandrum experiences maximum ozone mixing ratio during winter whereas Gadanki and other stations are experiencing maximum [O_3] during spring. Trivandrum is located on west coast of India. Because of its geographic location, Trivandrum experiences minimum RH and rain-fall during February and soon after that RH starts building up due to air-masses coming from

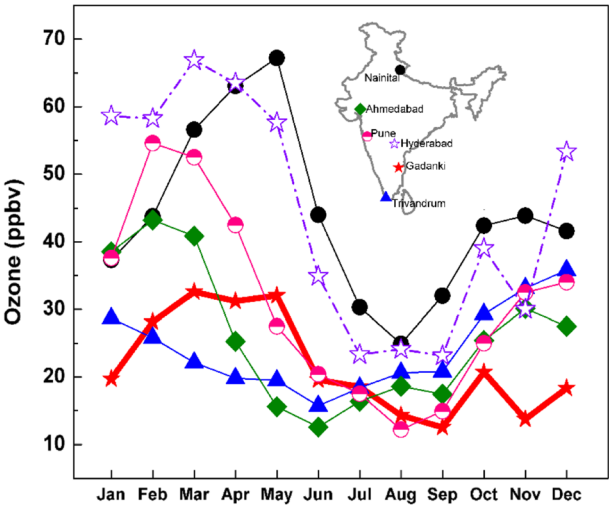

Fig. 3 Comparison of monthly mean ozone concentration during 2010–11 over Gadanki with other places in India

Indian Ocean and Arabian Sea. Whereas, in-land stations including Gadanki experience minimum RH during spring. RH and ozone are known to be negatively correlated (Camalier et al. 2007). There is steep rise in ozone concentration soon after the minimum during monsoon season over most of the stations whereas in case of Gadanki, ozone concentration during monsoon and winter is more or less same. This is again could be linked to rain-fall and RH variation. Whereas other stations do not get rain-fall in winter, Gadanki receives large fraction of annual rain-fall during winter. Ozone mixing ratio over Gadanki is higher or comparable to some of the major cities of India for e.g. Kolkata (Purkait et al. 2009), Ahmedabad, Delhi (Lal 2007) and Thiruvanthpuram (David and Nair 2011). However, these cities have 3 to 10 times higher [NO_X] compared to Gadanki. The cities which have ozone mixing ratio higher than Gadanki are Hyderabad (Swamy et al. 2012) and Pune (Beig et al. 2007; Lal 2007; Londhe et al. 2008). High altitude remote sites like Mt. Abu (Naja et al. 2003) and Nainital (Kumar et al. 2010) have higher ozone mixing ratio compared to Gadanki. However, the diurnal variation of ozone over Gadanki is quite different from Nainital and Mt. Abu where noon-time peak is not very prominent. This is indicative of in-situ ozone production through photochemical reactions rather than being a place of high background ozone level.

4.2 NO_X variability

NO_X ($NO+NO_2$) mixing ratio over Gadanki is relatively low. To have better insights in observational skewness and variance, we have plotted median values of [NO_X] (circles) and its inter-quartile range (vertical bars). Diurnal variation with hourly median values is shown in Fig. 4a. NO_X has high mixing ratio in morning and evening and low mixing ratio in afternoon. The morning peak mixing ratio is higher than evening peak mixing ratio. Monthly median variation of [NO_X] is shown in Fig. 4b. It varies from 0.5 ppbv to 2 ppbv. Being very low values, it is not possible to see seasonal variation as clearly as for ozone nevertheless increase during winter and decrease during summer is discernible.

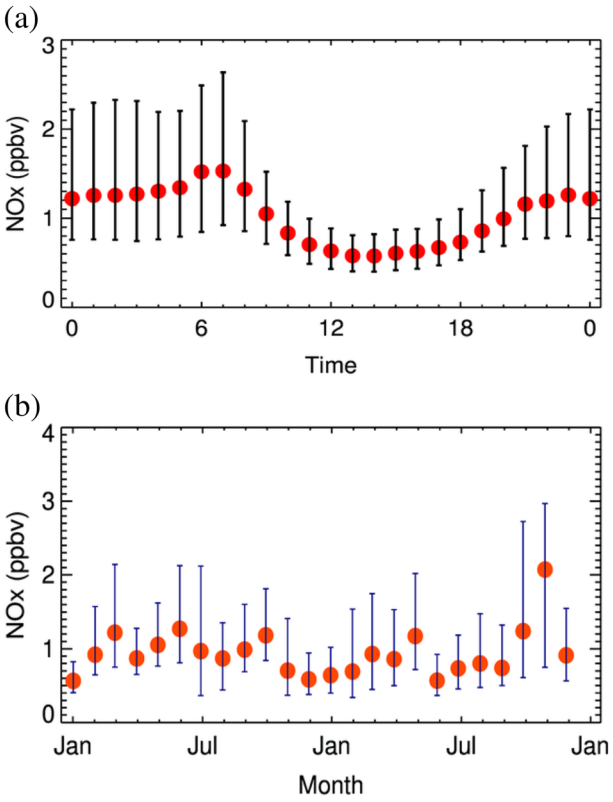

Fig. 4 (**a**) Diurnal variation of NO_X over Gadanki for 2010–2011. The filled circles are median values and vertical bars represent inter-quartile range. (**b**) Monthly median concentration of NO_X over Gadanki for 2010–2011. Vertical bars are inter-quartile range

5 Results and discussion

5.1 Comparison between past and present observations

As noted earlier, (Naja and Lal 2002) have carried out observations of O_3, NO_X, CO and CH_4 over Gadanki between 1993 and 1996. The observations of $[O_3]$ were made from November 1993 to December 1996 while observations of $[NO_X]$ were made from January 1994 to December 1995. For the sake of brevity, observations reported in (Naja and Lal 2002) are referred as past observations and the observations reported in preceding section are referred as present observations.

Average noon time maximum $[O_3]$ is 30±15 ppbv for the period 2010–11 and it is 34±13 ppbv for the period 1993–96. The difference is significant at confidence level of 99.9 % though the satellite based tropospheric $[O_3]$ trend is insignificant. The comparison of monthly mean $[O_3]$ for 2010–11 and 1993–96 is shown in Fig. 5. The difference between monthly mean of all data as well as monthly mean of noon-time peak concentration is statistically significant at confidence level of 99 % except for the March. Overall, the present $[O_3]$ is less than the past and the difference between two periods is not uniform across all the months. Winter months are having bigger differences than spring and summer months. April and May have present $[O_3]$ higher than the past $[O_3]$. The high values of present $[O_3]$ during April and May are mainly due to night-time high $[O_3]$ during these months as can be seen in the Fig. 6b.

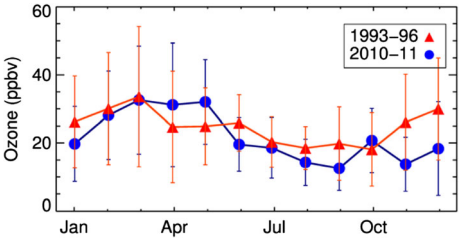

Fig. 5 Comparison of monthly mean ozone mixing ratios between past (1993–1996) and present (2010–2011) observations

A comparison of diurnal variations of [O_3] for the past and present is shown in Fig. 6 for different seasons. Night-time [O_3] have relatively less seasonal variation and small differences between past and present values. In case of day-time mixing ratios, past [O_3] values are significanlty higher than the present [O_3] for Winter and Autumn. The amplitude of diurnal cycles for all the seasons are more in past observations compared to present observations. Winter season has highest amplitude difference of 13.4 ppbv between past and present followed by autumn (12.7 ppbv), spring (6.6 ppbv) and summer (0.33 ppbv). This indicates there is a decrease in photochemically produced ozone during recent years. The morning rate of change of ozone is high (7 ppbv per hour) during 1993–96 compared to 2010–11 (4 ppbv per hour) as shown in Fig. 7. Asymmetry between morning and evening rate of change of ozone is characteristics of rural environment (Naja and Lal 2002).

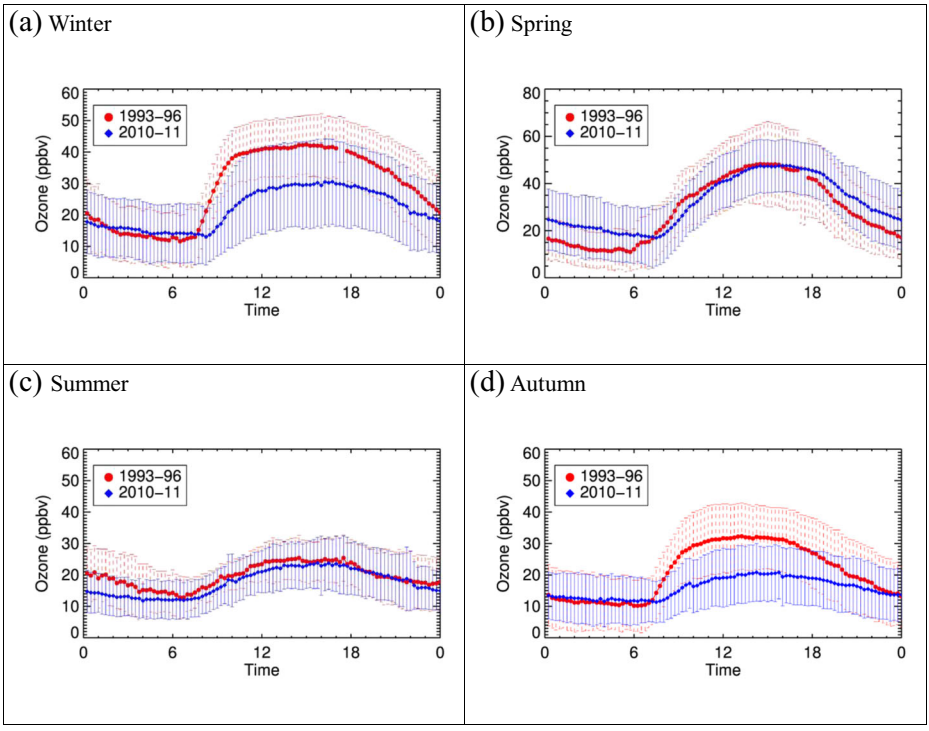

Fig. 6 Comparison of seasonal diurnal patterns of surface ozone over Gadanki for the past and present observations

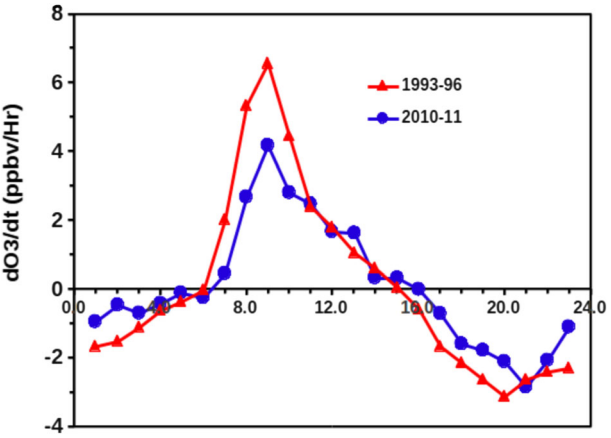

Fig. 7 Comparison of rate of change of ozone between past and present observations

There has been very few studies that report ozone trend over regions of India. Naja and Lal (1996) have reported a significant increase in [O_3] over Ahmedabad – a major city in western part of India. Ali et al. (2012) have reported increase in [O_3] over Delhi but decrease over Pune for the period between 1990 and 1999. As noted earlier, ozone trends are not uniform over globe. Cartalis and Varotsos (1994) have reported increasing trend of ozone over Athens, Greece during last century. Chou et al. (2006) have reported increasing trend of ozone over Taipei, Taiwan during 1994 to 2003 in spite of decrease in volatile organic compounds, NO_X and non-methane hydrocarbon. They attribute increase in ozone to reduced titration of ozone by NO. Jaffe and Ray (2007) have studied ozone trends for period from 1987 to 2004 over 11 rural and remote sites in north and western US including Alaska. They have found increasing trend over seven out of eleven sites. (Tanimoto 2009; Tanimoto et al. 2009) have studied ozone trends over several remote sites in Japan. They have found overall increasing trend over all the sites with mountain sites having higher increasing trends. They attribute increasing trend to increase in atmospheric pollution in Asian countries and their long-range transport to Japan. Fiore et al. (1998) studied ozone trends over 549 sites across contiguous United States and found no significant increase in ozone during 1980 to 1995 period. Decreasing trends are predominantly observed over urban regions attributable to decrease in NO_X and VOCs. Jonson et al. (2006) have studied trends of ozone and its precursor gases using observations and model. They have found significant decrease in summer time ozone over Europe during 1990–2002, however, the decrease in annual averages is less than expected from reduction in precursor gases. Tripathi et al. (2012) have studied ozone trends over eight sites across Ireland from 1994 to 2009. They have found either negative trend in peak ozone concentration or no increasing trend. In majority of cases ozone trends when decreasing attributed to new pollution control norms to reduce precursors like NO_X and when increasing attributed to increase in precursor gases or long-range transport of pollutants. In one instance increase in [O_3] is linked to decrease in [NO] (Chou et al. 2006) .

The comparison of monthly median [NO_X] for the two periods is shown in Fig. 8. The present [NO_X] are nearly half of the past values. Statistical significance was determined using *t*-test and it is found that the difference is statistically significant at the level higher than 99.9 % for all the months. Absolute value of difference is of the order of 0.9 ppbv except for October, November, December and February. The difference during October, November, December and February is 0.5, 0.5, 0.6 and 0.6 ppbv respectively. No comparison could be made for

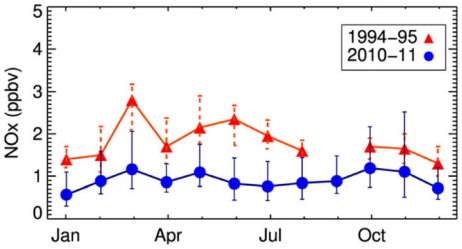

Fig. 8 Comparison of monthly median of NO_X mixing ratios during 1994–95 with that observed during 2010–11. Vertical bars represent inter-quartile range

September. There are several places around the world e.g. the USA, Europe, etc. where a decreasing trend in NO_X is observed (Akimoto 2003). However, these changes are mostly in the western world. In Asia, mostly increasing trends in NO_X or NO_2 are reported (Akimoto, 2003; Sheel et al. 2010; Hilboll et al. 2013). Main reason for increase in NO_X or NO_2 mixing ratios over Asian region is increase in industrial and vehicular emissions. However, rural regions have different economic activities compared to urban regions and far less industrialization and vehicular emissions. Over a rural location, the major sources of NO_X are soil emission, lightning activity, nitrogen-based fertilizer and biomass-burning. It is difficult to say at this stage whether the decrease in concentration is part of continuous decreasing trend or a difference between anomalous years. Nevertheless, one can conclude with great degree of confidence that NO_X mixing ratio is not increased over this region in contrast to the trends observed over urban regions of Asia.

To look into the aspect whether the 'decrease' in NO_X is a localized phenomenon or a phenomenon applicable to a larger region, we have used GOME and OMI satellite data (Boersma et al. 2004; Boersma et al. 2007). GOME and OMI are two different sets of satellite sensors and there is a difference in spatial resolution of two data-sets as well. This requires special care in calculating trends from combined data set. Different sensor characteristics and spatial resolution can produce differences in mean and variability. We have followed the method described in (Mieruch et al. 2008) and (Hilboll et al. 2013) to calculate bias and trends. While the decrease in NO_2 values is not seen over Gadanki as one might have expected from ground-based data of NO_X, satellite data show statistically significant decreasing trend in west of Gadanki and increasing trend in East and South of Gadanki with Gadanki in transition zone (Fig. 9).

The trend analysis for entire South India is shown in Fig. 9b. Grid-boxes having a trend, which is statistically significant at confidence level 95 % or more are shown with black dots. There are few hotspots with very high increasing trends viz: Chennai, Vizag, Bellari, Madurai. This may be due to recent industrialisation of these places. Besides hot-spots, there are regions of increasing trend. The spatial pattern of increasing trends follows geographical pattern of river basins in South India known for intense agricultural activities. Increase in use of fertilizers can be one of the reasons for increasing trend over these regions. However, more interesting is the decreasing trends observed between mountain ranges known as Eastern and Western Ghats. The decrease in tropospheric NO_2 over this region is found in-spite of increase in population and vehicular traffic. Possibly the decrease over this region is linked with changes in land-use pattern since soil emissions are one of the major source of NO_2 in the atmosphere. Sheel et al. (2010) and Hilboll et al. (2013) have reported increasing trend over urban centres in India. Ghude et al. (2008) studied NO_2 hotspots and trends over five regions of India using GOME and SCIAMACHY data between year 1996 to 2006 and have reported increasing trends. They attribute increase in NO_2 to rapid industrialisation and vehicular traffic

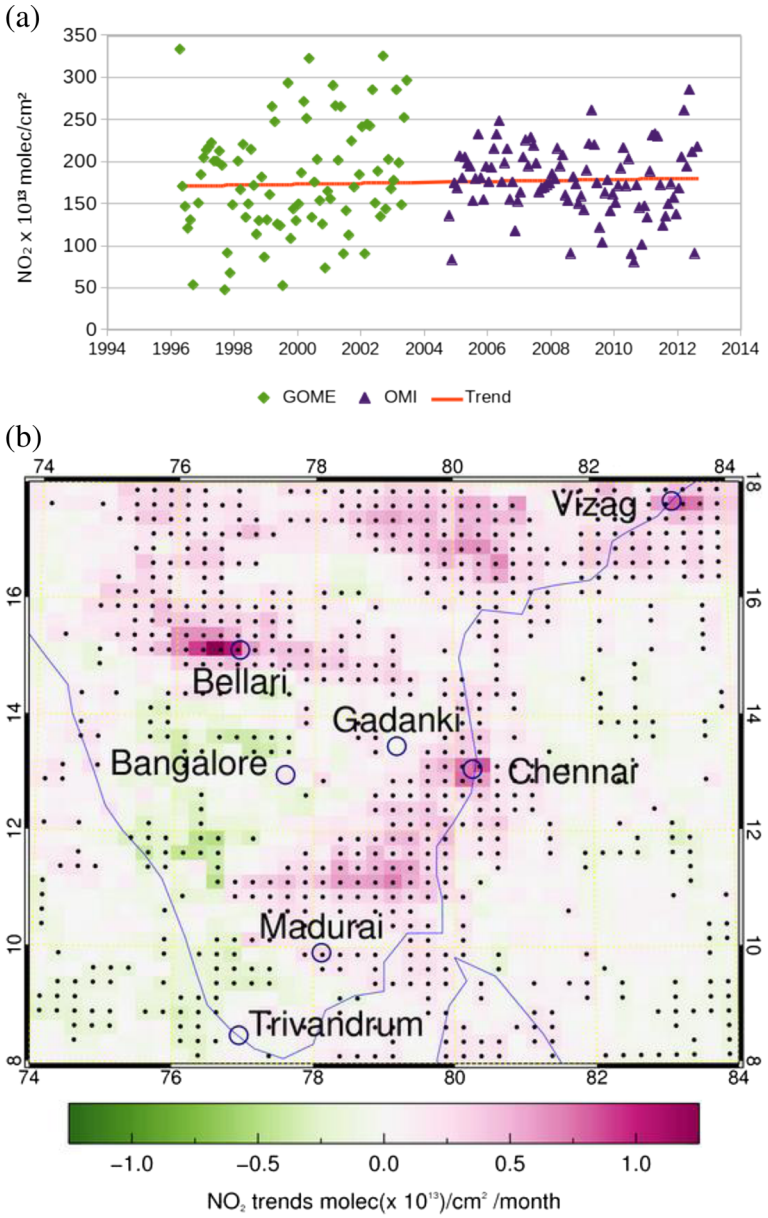

Fig. 9 (**a**) Monthly mean tropospheric column NO_2 concentration observed over Gadanki using GOME (1996–2003) and OMI (2005–2011). (**b**) Trends in tropospheric NO_2 over South India calculated for the period between 1996 to 2011 after combining GOME and OMI data. Grid-boxes with black dots show statistically significant trend at confidence level 95 % or more. Trends are calculated using method described in (Hilboll et al. 2013) and (Mieruch et al. 2008)

growth. However, there exist high degree of heteorogeneity in NO_2 trends over sub-regional scale. Out of all the regions studied by Ghude et al. (2008), the minimum trend was found over South India, 1.38±0.12 % per year. They have also found far less number of hot-spot over

South India compared to other parts of India. Since regulations and population dynamics are not significantly different from one region to other region in India such heteroroogeity in trends, we believe is driven by geographic condition of the place and factors such as land-use change.

Though there is a significant decrease in surface [NO_X], decrease is less for surface [O_3]. Photochemical production of ozone depends on [NO] and [NO_2] in complex manner. In such a low [NO_X] environment, other factors such as presence of VOCs play very important role in determining ozone-production-efficiency of NO_X molecules. Using numerical simulations, we try to understand seasonal variation of [O_3], its high mixing-ratio in-spite of low [NO_X] and level of decrease in [O_3] expected based on [NO_X] decrease.

5.2 Numerical simulation of Ozone at Gadanki

Our objective in carrying out the numerical simulations is to understand seasonal variation of [O_3], the high ozone values over rural areas of India in-spite of low [NO_X] in comparison to big cities and the role of [NO_X] decrease on [O_3] with respect to past values. It is not expected that the numerical simulation will exactly reproduce observed [O_3] since VOC values are not based on observations over the place, cloudiness is over simplified, the [NO] are near detection limit of the instrument and hence not constrained for diurnal variation, and transport processes are not considered. Nevertheless the simulations are helpful in understanding the role of NO_X in diagnostic manner and to identify gaps in observational strategy to better understand the trends. Numerical simulation of ozone concentration over Gadanki are carried out using NCAR Master Mechanism (NCAR-MM) Box (0D) model (Madronich and Calvert 1990; Aumont et al. 2000; Stroud et al. 2003; Madronich 2006). The model consists explicit and detailed gas phase chemistry combined with box model solver. Photolysis rates are calculated using TUV (Tropospheric Ultraviolet and Visible) radiation model included with NCAR-MM. The model has ability to simulate 5,000 reactions among 2,000 species (Madronich 2006). The model is developed at National Center for Atmospheric Research (NCAR), USA and can be downloaded from NCAR/UCAR Community data portal [http://cdp.ucar.edu/].

We have run the model for various sets of inputs and simulated the [O_3] and [NO] on diurnal cycle. Each simulation is done for 48 h and the values from the second cycle of 24 h are reported in this study. In Fig. 10, noon-time peak ozone mixing ratios from various model-runs are compared with observations made during (a) 2010–11 and (b) 1993–96. Inputs for various model runs are described in Table 1. The model run M-01 has set of inputs which are very close to observed values during 2010–11 or climatological values over Gadanki and assuming zero VOCs. [NO_2] for M-01 is fixed to monthly mean diurnal variation during 2010–11. Initial [O_3] is set to 21 ppbv which is close to observed night time [O_3] over Gadanki. Diurnal variation of boundary layer height (BLH) over Gadanki is taken from (Basha and Ratnam 2009). Four different sets of BLH variations are used for the four seasons. In order to simulate effect of cloudiness, we have used pyranometer data but in indirect way. Clouds affect surface [O_3] because of their ability to control amount of surface reaching solar radiation. The daily mean surface reaching solar energy is maximum in April with value 6.6 $kWhr/m^2$. Simulations are carried out assuming clear sky fraction equal to ratio of daily mean solar energy for a given month to daily mean solar energy received in April. This approach makes April month simulations as fully clear sky day simulation and for other months the simulations are for partially cloudy sky in relation to April simulation. To understand the role of VOCs for tropical climate, in the model run M-02, ozone simulations are carried out keeping all the inputs same as M-01 except for VOCs. Since no observations of VOCs are available for this region, we have used diurnally varying isoprene values reported in (Karl et al. 2007). Karl et al. (2007) have studied diurnal variation of isoprene and monoterpene over

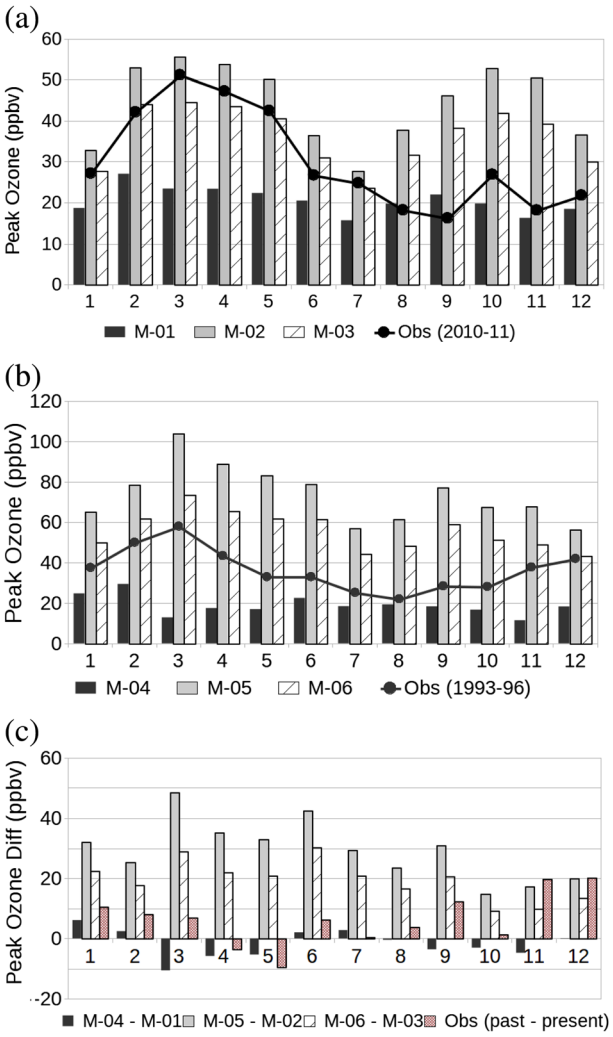

Fig. 10 Comparison of monthly mean noon-time peak ozone mixing ratios between box-model (NCAR-MM) and observations for year (**a**) 2010–11 and (**b**) 1993–96. For all the model runs NO_2 concentration is constrained to monthly mean observations. Model run M-01 and M-04 are without any VOCs. M-02 and M-05 are with Isoprene values based on (Karl et al. 2007) M-03 and M-06 are with Isoprene values equal to 1/10 of the values used in M-02 and M-05. (**c**) Difference between past and present noon-time peak ozone mixing ratios for observations and models

Central Amazonian which has the tropical climate. Model run M-03 is similar to M-02 but the Isoprene values are reduced by factor 10. Model runs M-04 to M-06 are similar to the model runs M-01 to M-03 but the [NO] and [NO_2] are scaled by factors such that [NO_X] matches with values reported in (Naja and Lal 2002) for year 1994 to 1995. The multipliers are of the order of 2. Besides these model runs, we have done several runs to study sensitivity to various input parameters. It is found that the noon-time peak [O_3] is highly sensitive to [NO], [NO_2], isoprene and cloudiness. It is moderately sensitive to CO, aerosol properties, boundary layer height and columnar ozone concentration.

Table 1 Inputs for numerical simulations of ozone concentration over Gadanki

Model Runs	Inputs	Input Sr. No.	Values or basis of values
M-01	Ozone (Initial conc.)	1	4.9628 x 10^11 molec./cm^3 (21 ppbv)
	Ozone columnar	2	247 DU
	Ozone background	3	Zero
	CO	4	8.2115 x 10^12 molec./cm^3 (352 ppbv)
	CH_4	5	4.0473 x 10^13 molec./cm^3 (1,736 ppbv)
	Temperature	6	Obs. mean diurnal variation for given month
	H_2O	7	Obs. mean diurnal variation for given month
	N_2	8	1.8415 x 10^19 molec./cm^3
	O_2	9	4.8951 x 10^18 molec./cm^3
	Aerosol Optical Depth	10	0.3
	Single scattering albedo	11	0.92
	Angstrom Exponent	12	1.13
	Surface albedo	13	0.08
	NO (initial conc.)	14	Zeroth hour value from obs. monthly mean diurnal variation during 2010–11 in their respective months.
	NO_2 (diurnally constrained)	15	Obs. monthly mean diurnal variation during 2010–11 in their respective months.
	Boundary Layer Height (BLH)	16	Diurnally varying and season dependent. Based on (Basha and Ratnam 2009) .
	Clear Sky Fraction	17	Diurnally fixed but varies monthly based on Fig. 12.
	Isoprene (diurnally constrained)	18	Zero
M-02	Inputs 1 to 17		Same as in M-01
	Isoprene (diurnally constrained)		Diurnally fixed to the values reported in (Karl et al. 2007); Same for all months
M-03	Inputs 1 to 17		Same as in M-01
	Isoprene		One tenth of the values used in M-02
M-04	Inputs 1 to 13 and 16 to 18		Same as in M-01
	NO (initial conc.)		M-01 NO input value being scaled such that ($NO+NO_2$) will match (Naja and Lal 2002) .
	NO_2		- as above -
M-05	Inputs 1 to 17		Same as in M-04
	Isoprene		Same as in M-02
M-06	Inputs 1 to 17		Same as in M-04
	Isoprene		One tenth of the values used in M-05

Presence of isoprene in the atmosphere is very important in determining peak [O_3]. In the absence of isoprene, simulated peak [O_3] is significantly smaller than the observed peak [O_3] for both the present and the past [NO_2] scenarios. In the absence of isoprene, it is also not reproducing the observed seasonal cycle of [O_3]. When the diurnally varying but seasonally fixed isoprene concentration as reported in Karl et al. (2007) is included, the simulated peak [O_3] is moderately higher than the observed peak [O_3] for the first half of year but significantly higher than the observed peak [O_3] for second half of the year in case of present day scenario (M-02 in Fig. 10a). This is because inclusion of isoprene in simulations leads to seasonal cycle

with two maxima in simulated values, one during spring and another during autumn. However, in-case of observations, only spring-time maxima is observed. This could be because of seasonally fixed isoprene but seasonally varying [NO_2] and solar radiation. It is worth noting that spring is the season of biomass burning (agricultural waste burning in open and forest fires) in South India which can be a potential source of various VOCs that may participate in ozone production but in winter there is very little biomass burning activity. Hence, one can expect a seasonally varying VOC concentration over South India.

The simulated peak [O_3] is very high in comparison to observed values for the past [NO_2] when isoprene concentration at the same level as in reported in Karl et al. (2007) are used (M-05 in Fig. 10b). When isoprene concentration is scaled down to 1/10 of values being used in the run M-02 and M-05, the simulated peak [O_3] is also reduced but still higher than the past observations.

The differences in simulation output, which include isoprene are considerably greater than observed differences (Fig. 10c). At the same time, absence of isoprene in simulation inputs (model runs M-01 and M-04) is also not able to explain differences as they are found to be reverse way that is past low and present high [O_3]. There exists a possibility that isoprene or VOC concentrations may not have been same in past and present. In absence of observations of VOC it will be difficult to quantify role of [NO_X] and effect of its decrease on ozone concentrations, nevertheless the simulations bring-out the importance of VOCs in rural atmospheric chemistry and their role in high ozone level in spite of low [NO_X]

6 Summary

Surface level NO_X and O_3 observations are carried out over a rural location in Southern India. Though the [O_3] is not very low compared to major cities of India, concentration of NO_X is quite low and typical of a rural background site. The ground-based measurements of [NO_X] from period 2010–11 are nearly half of the past values (1994–95) in relative terms and about 0.9 ppbv low in absolute terms. A statistically significant decreasing trend in tropospheric columnar [NO_2] is also found in GOME and OMI satellite data over several parts of the South India. This is in contrast to urban places and fertile river basins where these satellite sensors have detected increasing trend. A small but statistically significant decrease is also observed in [O_3] compared to past. The decrease is observed mostly in day-time ozone concentration indicative of decrease in photochemically produced ozone. The decrease is high during winter. A likely cause of decrease of [O_3] is a decrease of [NO_X], however magnitude of decrease of [O_3] is less than expected from decrease in [NO_X].

Presence of VOCs is very important to explain not only the high [O_3] in spite of low [NO_X] but also the observed seasonal cycle to some extent. Though we have used only isoprene, it fairly outlines the importance of VOCs for rural atmospheric chemistry. Overall our results indicate that the atmospheric chemistry and trends of trace-gases such as O_3 and NO_X in rural India where a major bulk of population lives are distinctly different from urban India.

Acknowledgments Authors gratefully acknowledges the financial support provided by Indian Space Research Organization's Geosphere-Biosphere Program through its sub-program Atmospheric Chemistry and Transport (ISRO-GBP – ATCTM). Authors acknowledge the free use of tropospheric NO_2 column data from the GOME and OMI sensors from www.temis.nl. Authors acknowledge T. N. Rao and his team members for maintaining weather station and providing meteorological data used in this study. Authors acknowledge help of V. Ravi Kiran for maintaining gas-analysers. Authors are grateful to Atmospheric Chemistry Research Division at NCAR for providing NCAR Master Mechanism model used in this study through NCAR Community Data Portal. Authors thank Amit Kumar Patra for his help in grammatical and linguistic editing of the manuscript.

References

Akimoto, H.: Global Air Quality and Pollution. Science **302**, 1716–1719 (2003). doi:10.1126/science.1092666

Ali, K., Inamdar, S.R., Beig, G., Ghude, S., Sunil, P.: Surface ozone scenario at Pune and Delhi during the decade of 1990s. J. Earth Syst. Sci. **121**, 373–383 (2012)

Aumont, B.: Madronich, S.: Bey, I.: and Tyndall, G.: Contribution of secondary VOC to the composition of aqueous atmospheric particles: A modeling approach. J. Atmos. Chem., 59–75 (2000)

Basha, G. and Ratnam, M.V.: Identification of atmospheric boundary layer height over a tropical station using high-resolution radiosonde refractivity profiles: Comparison with GPS radio occultation measurements. J. Geophys. Res. 114, D16101+ (2009). doi:10.1029/2008jd011692

Beig, G., Gunthe, S., Jadhav, D.B.: Simultaneous measurements of ozone and its precursors on a diurnal scale at a semi urban site in India. J. Atmos. Chem. **57**, 239–253 (2007). doi:10.1007/s10874-007-9068-8

Berman, J.D., Fann, N., Hollingsworth, J.W., Pinkerton, K.E., Rom, W.N., Szema, A.M., Breysse, P.N., White, R.H. and Curriero, F.C.: Health Benefits from Large Scale Ozone Reduction in the United States. Environ. Health Perspect., 1404–1410 doi:10.1289/ehp.1104851. (2012)

Boersma, K., Eskes, H. and Brinksma, E.: Error analysis for tropospheric NO2 retrieval from space. J. Geophys. Res. 109, D04311+. doi:10.1029/2003JD003962 (2004)

Boersma, K.F., Eskes, H.J., Veefkind, J.P., Brinksma, E.J.: van Der, Sneep, M., van den Oord, G.H.J., Levelt, P.F., Stammes, P., Gleason, J.F. and Bucsela, E.J.: Near-real time retrieval of tropospheric NO2 from OMI. Atmos. Chem. Phys. **7**, 2103–2118 (2007). doi:10.5194/acp-7-2103-2007

CAAC: Twelfth five-year plan on air pollution prevention and control in key regions (China clean air policy briefing no. 1) (English Translation), Clean Air Alliance of China, Secretariat for Clean Air Alliance of China, suit 1705, Building 1, Park Avenue, 16 Jianguomenwai Street, Beijing 100022 (2013)

Camalier, L., Cox, W., Dolwick, P.: The effects of meteorology on ozone in urban areas and their use in assessing ozone trends. Atmos. Environ. **41**, 7127–7137 (2007). doi:10.1016/j.atmosenv.2007.04.061

Cartalis, C., Varotsos, C.: Surface ozone in Athens, Greece, at the beginning and at the end of the twentieth century. Atmos. Environ. **28**, 3–8 (1994). doi:10.1016/1352-2310(94)90018-3

Chou, C.C.K., Liu, S.C., Lin, C.-Y., Shiu, C.-J., Chang, K.-H.: The trend of surface ozone in Taipei, Taiwan, and its causes: Implications for ozone control strategies. Atmos. Environ. **40**, 3898–3908 (2006). doi:10.1016/j.atmosenv.2006.02.018

David, L.M. and Nair, P.R.: Diurnal and seasonal variability of surface ozone and NOx at a tropical coastal site: Association with mesoscale and synoptic meteorological conditions. J. Geophys. Res. 116, D10303+. doi:10.1029/2010jd015076 (2011)

Engardt, M.: Modelling of near-surface ozone over South Asia. J. Atmos. Chem. **59**, 61–80 (2008). doi:10.1007/s10874-008-9096-z

Fiore, A.M., Jacob, D.J., Logan, J.A. and Yin, J.H.: Long-term trends in ground level ozone over the contiguous United States, 1980–1995. J. Geophys. Res. 103, 1471+. doi:10.1029/97jd03036 (1998)

Fishman, J., Ramanathan, V., Crutzen, P.J., Liu, S.C.: Troposheric Ozone and Climate. Nature **282**, 818–820 (1979)

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D., Haywood, J., Lean, J., Lowe, D., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Dorland, R.: Chapter 2, In : Changes in atmospheric constituents and in radiative forcing. In: Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M., Henry LeRoy Miller, J., Chen, Z. (eds.) In Climate Change 2007: The Physical Science Basis (4th Assessment report of the Intergovernmental Panel on Climate Change), pp. 129–235. Cambridge University Press, Cambridge (2007)

Foster, A., Kumar, N.: Health effects of air quality regulations in Delhi. India. Atmos. Environ. **45**, 1675–1683 (2011). doi:10.1016/j.atmosenv.2011.01.005

Ganguly, N.D., Tzanis, C.: Study of Stratosphere-troposphere exchange events of ozone in India and Greece using ozonesonde ascents. Met. Apps **18**, 467–474 (2011). doi:10.1002/met.241

Ganguly, N.: Influence of Stratospheric Intrusion on the Surface Ozone Levels in India. ISRN Meteorology, 1–7 . doi:10.5402/2012/625318 (2012)

Ganguly, N. and Tzanis, C.: High Surface Ozone Episodes at New Delhi, India, In on a sustainable future of the earth's natural resources., Springer Berlin Heidelberg (2013)

Ganzeveld, L.N.: Global soil-biogenic NO x emissions and the role of canopy processes. J. Geophys. Res. 107. doi:10.1029/2001jd001289 (2002)

Ghude, S.D., Fadnavis, S., Beig, G., Polade, S.D. and van Der: Detection of surface emission hot spots, trends, and seasonal cycle from satellite-retrieved NO2 over India. J. Geophys. Res. 113, D20305+ (2008) doi:10.1029/2007jd009615

Hilboll, A., Richter, A., Burrows, J.P.: Long-term changes of tropospheric NO2 over mega cities derived from multiple satellite instruments. Atmos. Chem. Phys. **13**, 4145–4169 (2013). doi:10.5194/acp-13-4145-2013

Holland, M., Watkiss, P. and Pye, S.: Cost-benefit analysis of the Thematic strategy on air pollution for service contract for carrying out cost-benefit analysis of air quality related issues, in particular in the Clean Air for Europe (CAFE) programme, European Commission DG Environment (2005)

Jaffe, D., Ray, J.: Increase in surface ozone at rural sites in the western US. Atmos. Environ. **41**, 5452–5463 (2007). doi:10.1016/j.atmosenv.2007.02.034

Jonson, J., Simpson, D., Fagerli, H., Solberg, S.: Can we explain the trends in European ozone levels? Atmos. Chem. Phys. **6**, 51–66 (2006)

Karl, T., Guenther, A., Yokelson, R.J., Greenberg, J., Potosnak, M., Blake, D.R. and Artaxo, P.: The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia. J. Geophys. Res. 112, D18302+. doi:10.1029/2007jd008539 (2007)

Kumar, R., Naja, M., Venkataramani, S. and Wild, O.: Variations in surface ozone at Nainital: A high-altitude site in the central Himalayas. J. Geophys. Res. 115, D16302+. doi:10.1029/2009jd013715 (2010)

Lal, S.: Trace gases over the Indian region. Indian. J. Radio. Space. **36**, 556–570 (2007)

van der Leun, J., Tang, H.H., Tevinil, M.: Environmental effects of ozone depletion: 1998 Assessment. United Nations Environment Programme (UNEP), Nairobi (1998)

Londhe, A., Jadhav, D., Buchunde, P., Kartha, M.: Surface ozone variability in the urban and nearby rural locations of tropical India. Curr. Sci. **95**(12), 1724–1729 (2008)

Madronich, S.: Chemical evolution of gaseous air pollutants down-wind of tropical mega cities: Mexico City case study. Atmos. Environ. **40**, 6012–6018 (2006). doi:10.1016/j.atmosenv.2005.08.047

Madronich, S., Calvert, J.: Permutation reactions of organic peroxy radicals in the troposphere. J. Geophys. Res. **95**, 5697–5715 (1990)

Mieruch, S., Noel, S., Bovensmann, H., Burrows, J.P.: Analysis of global water vapour trends from satellite measurements in the visible spectral range. Atmos. Chem. Phys. **8**, 491–504 (2008)

Mohammed, N., Ramli, N., Yahya, A.: Paddy Response to Ozone: A Comparison between an Industrial and Residential Area in Malaysia. Environ. and Poll. **1**, 169–175 (2012). doi:10.5539/ep.v1n2p169

Mohammed, N., Ramli, N., Yahya, A.: Ozone phytotoxicity evaluation and prediction of crops production in tropical regions. Atmos. Environ. **68**, 343–349 (2013). doi:10.1016/j.atmosenv.2012.09.010

Naja, M., Lal, S.: Changes in surface ozone amount and its diurnal and seasonal patterns, from 1954–55 to 1991–93, measured at Ahmedabad (23 N). India. Geophys. Res. Lett. **23**(1), 81–84 (1996)

Naja, M. and Lal, S.: Surface ozone and precursor gases at Gadanki (13.5Â°N, 79.2Â°E), a tropical rural site in India. J. Geophys. Res. 107, 4197+. doi:10.1029/2001jd000357 (2002)

Naja, M., Lal, S., Chand, D.: Diurnal and seasonal variabilities in surface ozone at a high altitude site Mt Abu (24.6°N, 72.7°E, 1680m asl) in India. Atmos. Environ. **37**, 4205–4215 (2003). doi:10.1016/s1352-2310(03)00565-x

National Research Council, U., Rethinking the ozone problem in urban and regional air pollution, (1991)

Price, C., Penner, J. and Prather, M.: NO x from lightning: 1. Global distribution based on lightning physics. J. Geophys. Res. 102, 5929+. doi:10.1029/96jd03504 (1997)

Purkait, N., De, S., Sen, S., Chakrabarty, D.: Surface ozone and its precursors at two sites in the northeast coast of India. Indian. J. Radio. Space. **38**, 86–97 (2009)

Sanderson, M.G., Jones, C.D., Collins, W.J., Johnson, C.E., Derwent, R.G.: Effect of Climate Change on Isoprene Emissions and Surface Ozone Levels. Geophys. Res. Lett. **30**, 1–4 (2003). doi:10.1029/2003gl017642

Seinfeld, J.H., Pandis, S.N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley, New York (1998)

Sheel, V., Lal, S., Richter, A., Burrows, J.P.: Comparison of satellite observed tropospheric NO2 over India with model simulations. Atmos. Environ. **44**, 3314–3321 (2010). doi:10.1016/j.atmosenv.2010.05.043

Stroud, C., Madronich, S., Atlas, E.R.B., Flocke, F., Weinheimer, A., Talbot, R., Fried, A., Wert, B., Shetter, R., Lefer, B., Coffey, M., Heickes, B., Blake, D.: Photochemistry in the Arctic free troposphere: NOX budget and the role of odd nitrogen reservoir recycling. Atmos. Environ. **37**, 3351–3364 (2003). doi:10.1016/S1352-2310(03)00353-4

Swamy, Y.V., Venkanna, R., Nikhil, G.N., Chitanya, D.N.S.K., Sinha, P.R., Ramakrishna, M., Rao, A.G.: Impact of Nitrogen Oxides, Volatile Organic Compounds and Black Carbon on Atmospheric Ozone Levels at a Semi Arid Urban Site in Hyderabad. Aerosol. Air. Qual. Res. **12**, 662–671 (2012). doi:10.4209/aaqr.2012.01.0019

Tanimoto, H.: Increase in springtime tropospheric ozone at a mountainous site in Japan for the period 1998–2006. Atmos. Environ. **43**, 1358–1363 (2009). doi:10.1016/j.atmosenv.2008.12.006

Tanimoto, H., Ohara, T. and Uno, I.: Asian anthropogenic emissions and decadal trends in springtime tropospheric ozone over Japan: 1998–2007. Geophys. Res. Lett. 36, L23802+. doi:10.1029/2009gl041382 (2009)

Tripathi, O.P., Stephen, G.J., O'Dowd, C., O'Leary, B., Lambkin, K., Moran, E., O'Doherty, S.J., Spain, T.G.: An assessment of the surface ozone trend in Ireland relevant to air pollution and environmental protection. Atmos. Poll. Res. **3**, 341–351 (2012)

Tzanis, C., Varotsos, C., Ferm, M., Christodoulakis, J., Assimakopoulos, M.N., Efthymiou, C.: Nitric acid and particulate matter measurements at Athens, Greece, in connection with corrosion studies. Atmos. Chem. Phys. **9**, 8309–8316 (2009). doi:10.5194/acp-9-8309-2009

Tzanis, C., Varotsos, C., Christodoulakis, J., Tidblad, J., Ferm, M., Ionescu, A., Lefevre, R.A., Theodorakopoulou, K., Kreislova, K.: On the corrosion and soiling effects on materials by air pollution in Athens, Greece. Atmos. Chem. Phys. **11**, 12039–12048 (2011). doi:10.5194/acp-11-12039-2011

Varotsos, C., Ondov, J., Tzanis, C., Öztürk, F., Nelson, M., Ke, H., Christodoulakis, J.: An observational study of the atmospheric ultra-fine particle dynamics. Atmos. Environ. **59**, 312–319 (2012). doi:10.1016/j.atmosenv.2012.05.015

Walter, B.P., Heimann, M.: A process-based, climate-sensitive model to derive methane emissions from natural wetlands: Application to five wetland sites, sensitivity to model parameters, and climate. Global Biogeochem. Cy. **14**, 745–765 (2000). doi:10.1029/1999gb001204

Wang, X., Mauzerall, D.L.: Characterizing distributions of surface ozone and its impact on grain production in China, Japan and South Korea: 1990 and 2020. Atmos. Environ. **38**, 4383–4402 (2004). doi:10.1016/j.atmosenv.2004.03.067

WHO. Health aspects of air pollution with particulate matter ozone and nitrogen dioxide, WHO, (2003)

Wiedingmyer, C., Tie, X., Guenther, A.: Future changes in biogenic isoprene emissions: How might they affect regional and global chemistry. Earth. Interact. **10**, 1–19 (2006). doi:10.1175/EI174.1