

Long term trend in surface ozone over Indian stations

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सार – इस शोध पत्र में हमने तीन भिन्न महानगरों नामतः पुणे, नई दिल्ली और तिरुवनंतपुरम के लिए एक साथ दो दशकों से अधिक समयावधि (1990-2013) सतह ओजोन की दीर्घकालिक परिवर्तनशीलता को प्रस्तुत किया है। इन तीनों शहरों की सतह ओजोन सांद्रता को इलेक्ट्रोकेमिकल्स सेंसर का उपयोग करते हुए लगातार मापा गया है। ओजोन की वार्षिक प्रवृत्ति का विस्तृत विवरण प्रतिदिन दो बार व ऋतुनिष्ठ व्यवहार पर कार्य किया गया है। इस शोध पत्र में 1990-2000, 2000-2010 और 2010-2013 की तीन समयावधियों में परिवर्तन दिन में दो बार पाए गए और उनका विश्लेषण किया गया। प्रेक्षणाधीन समय के दौरान समय श्रृंखला विश्लेषण से सांद्रण इन तीनों स्टेशनों क्रमशः दिल्ली, पुणे और तिरुवनंतपुरम में बढ़ा है। दिल्ली, पुणे और तिरुवनंतपुरम में औसत दर में प्रतिवर्ष क्रमशः 0.05, 0.04, 0.04 PPB की वृद्धि हुई है। शहरी इलाकों में ओजोन की सांद्रता में दिन में दो बार परिवर्तनशीलता देखी गई है और दिन में दो बार परिवर्तन देखे गए, दिन के समय सांद्रता अधिक और रात के समय सांद्रता कम देखी गई है। ऊपर बताए गए विवरण के अनुसार दिन में दो बार परिवर्तन के अलावा दिन प्रतिदिन का रिकार्ड पूर्वाह्न में तेजी से बढ़ोतरी दिखाता है जो शहरी इलाकों में विशेष प्रकार से लक्षित होते हैं। इन तीनों स्थानों पर 1990-2000 से 2010-2013 तक सतह ओजोन सांद्रण में वृद्धि देखी गई है। 1990 से 2013 के दौरान सतह ओजोन सांद्रण में दिन में दो बार की बढ़ोतरी का एंप्लीच्यूड, जैसा कि प्राप्त हुआ, पुणे और तिरुवनंतपुरम की तुलना में दिल्ली का अर्थात् 0.5 ppb प्रतिवर्ष बहुत अधिक है।

ABSTRACT. In this paper we have presented long term variation of surface ozone over more than two decades (1990-2013) simultaneously for three different cities, viz., Pune, New Delhi and Thiruvananthapuram. Surface ozone concentration has been measured at these cities continuously with the help of a continuous recorder using electrochemical sensor. The detailed study of annual trend, diurnal as well as seasonal behaviour of ozone has been carried out. Diurnal changes seen over 3 time periods, i.e., 1990-2000, 2000-2010 and 2010-2013 have also been analyzed in this study. Time series analysis during the observational period indicates that annual average concentration of ozone is increasing at all the three stations, i.e., Delhi, Pune and Thiruvananthapuram respectively. Average rate of increase is estimated to be 0.05, 0.04, 0.04 ppb per year for Delhi, Pune and Thiruvananthapuram respectively. The diurnal variation in ozone concentration in urban areas exhibits marked diurnal variability, with high concentrations during the day and low concentrations at night. Apart from the above diurnal change, day to day record shows a forenoon sharp increase, a characteristic feature of an urban site. An increase in surface ozone concentration is also observed from (1990-2000) to (2010-2013) at all the three locations. The amplitude of diurnal increase in surface ozone concentration from 1990 to 2013 as obtained is more for Delhi, i.e., 0.5 ppb per year, as compared to Pune and Thiruvananthapuram.

Key words – Surface ozone, Electro-chemical sensor, Troposphere, Volatile organic compounds.

1. Introduction

Surface Ozone, one of the key trace gases in the atmosphere plays an important role in the complex oxidation chemistry of the carbon compounds in the lower troposphere, controlling the chemical composition and climate of the troposphere. For example, changes in ozone could affect the concentration of OH, which in turn could influence concentrations of many trace species removed from the atmosphere by reaction with OH (Fishman and Crutzen, 1978). Ozone, a dangerous air pollutant is of

immense societal concern over the globe in terms of damage to buildings, crop plants and human health. Ozone comes in contact with different life-forms of the earth and displays its destructive side mainly due to its toxicity. Several studies have documented the harmful effects of surface ozone on crop-production, forest and human health (Reich and Lassoie, 1985; Lipmann, 1991). Ozone in high concentration, is a toxic gas that can damage pulmonary tissue (Parmet *et al.*, 2003; Janneane *et al.*, 2003) and is thought to contribute to decay of urban buildings and other structures (Hisham and

Grosjean, 1991). Negative effects of ozone in plants and agriculture include reduced crop and grain yield (EPA, 1996; Finnan *et al.*, 1997; Agrawal *et al.*, 2003).

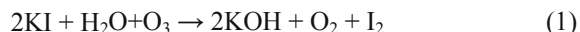
In the lower troposphere, *in-situ* production of ozone is mainly done via photo-chemical oxidation of carbon linked compounds such as CO, CH₄, VOC's in presence of NO_x (Zhang *et al.*, 2008) and as well as from natural sources such as lightning, wildfires, soils and vegetation. In the presence of strong solar radiation ($\lambda < 424$ nm) and volatile organic compounds (VOCs) and nitrogen dioxides (NO + NO₂ → NO_x), ozone is photo-chemically produced and can accumulate to hazardous levels during certain meteorological conditions (Fishman and Crutzen, 1978). Photochemical oxidation processes that produce O₃ depend on precursor gas concentration such as (CO, CH₄, NO_x, VOC's) and as well as on meteorological conditions such as wind-speed, temperature, solar-radiation and pressure. The distribution of surface ozone mainly produced from anthropogenic sources is highly localized and time-variant. The formation of ground level ozone depends on the intensity of solar radiation, the absolute concentrations of NO_x and VOCs and the ratio of NO_x and VOCs (Mauzerall *et al.*, 1998). In the case of NO_x rich air, the production of NO₂ takes place by reaction of NO with HO₂ or RO₂ (peroxy radicals) which ultimately helps ozone production (Crutzen, 1988; Sillman and Samson, 1995). But during night-time and in the case of NO_x poor air like rural air, these peroxy radicals react with ozone (O₃ + NO → NO₂ + O₂) and can lead to ozone loss (Liu *et al.*, 1987). It is well documented from the studies that basically higher temperature increases the emission rate of surface ozone precursors (Valente and Thorton, 1993) which in turn enhances the production rate of surface ozone. The most remarkable day-to-day variations of ground level ozone occur during spring and summer than in winter season, when intense sunshine hours are stagnant for a longer duration of time, providing favorable temperature conditions for photochemical production of ozone. The characteristics of these temporal patterns of ozone are determined by the complex interaction between precursor emissions, chemistry, depositional processes and meteorological controls on dispersion (Lelieveld *et al.*, 2001). Brasseur *et al.* (1998 a&b) also showed that the change in tropical ozone is very sensitive to climate forcing. Estimations made by a chemical transport model showed that on increasing the anthropogenic emissions, ozone production efficiency is maximized over the Indian region, which is explained on the basis of an increase in NO_x emissions from anthropogenic emissions in the last decade, leading to production of OH and peroxy radicals, the highly reactive radicals of the atmosphere that can initiate almost all the oxidation processes in the atmosphere. (Berntsen *et al.*, 1997). Therefore, detailed study of ozone behaviour

that includes its origin and trends associated with meteorological conditions has become an important priority in atmospheric chemistry research.

In this paper we have presented long term variation of surface ozone for over more than two decades simultaneously for three different Indian cities, *viz.*, Delhi, Pune and Thiruvananthapuram. Surface ozone concentration has been measured at these cities with the help of a continuous recorder using an electrochemical ozone sensor (Sreedharan and Tiwari, 1971). In this paper, detailed study of diurnal as well as seasonal behaviour of ozone over three different cities of India has been carried out.

2. Methodology and data used

The data of surface ozone of three stations namely Pune, Delhi, Thiruvananthapuram measured continuously with a continuous recorder using electrochemical sensor (Sreedharan and Tiwari, 1971) for the period 1990-2013 have been used in this study. Measurement of surface ozone is done by using Potassium Iodide (KI) technique (IMD Publication, 1995). The technique involves forceful drawing of ozone present in the sampled ambient air into the sensing solution in the electrochemical cell (bubbler) with the help of a suction pump. Two electrodes (a cathode of Platinum and an anode of Silver) connected with an external circuit are dipped in an alkaline potassium iodide solution. A polarizing potential of 0.42 V is applied between the electrodes such that no current will flow unless iodine is present. When air enters the solution, the ozone present in the air reacts with KI liberating free Iodine at the cathode according to the following reaction:



The free Iodine (I₂) liberated at the cathode is reduced to Iodide by the uptake of two electrons per molecule of I₂ as:



At the anode, the Iodine is reformed (through ionization by release of two electrons) and combines with Silver (Ag) to form Silver Iodide (AgI).



The AgI precipitates out of the solution and thereby prevents the reformed Iodine from recirculation. As reaction (1) indicates, every molecule of ozone liberates

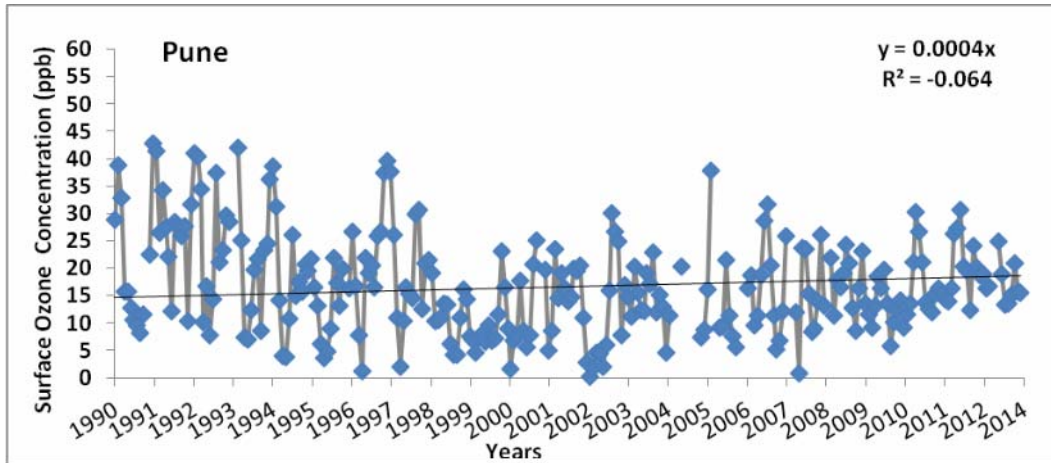


Fig. 1. Surface ozone time series for Pune during 1990-2013

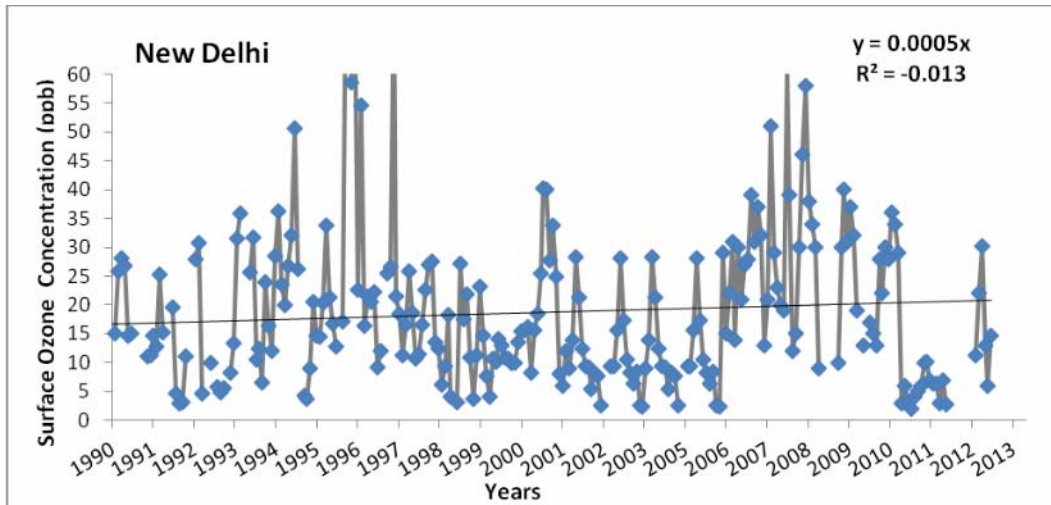


Fig. 2. Surface ozone time series for New Delhi during 1990-2013

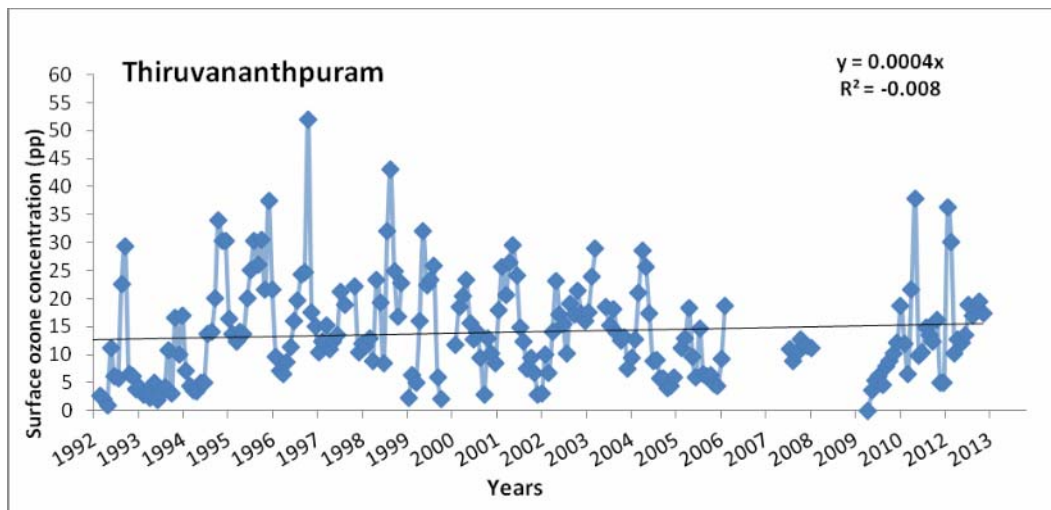


Fig. 3. Surface ozone time series for Thiruvananthapuram during 1992-2013

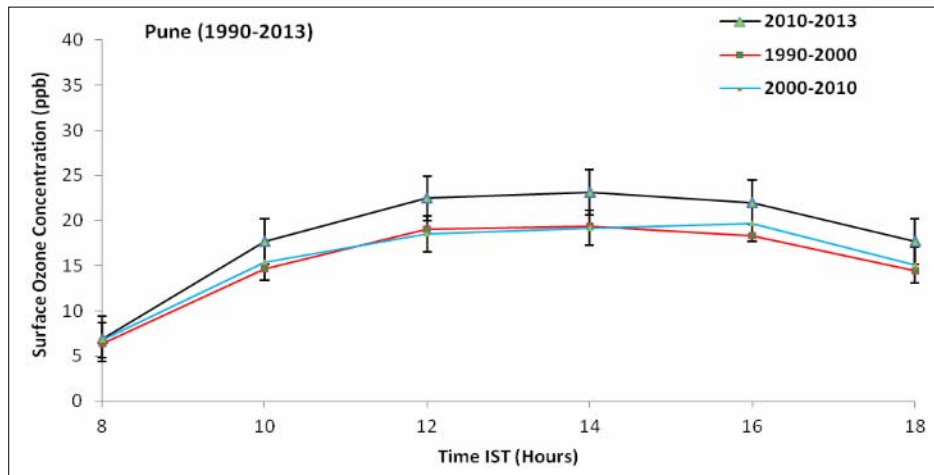


Fig. 4. Diurnal increase observed in surface ozone at Pune (0800 hrs IST to 1800 hrs IST) during three time scales - (1990-2000), (2000-2010) and (2010-2013)

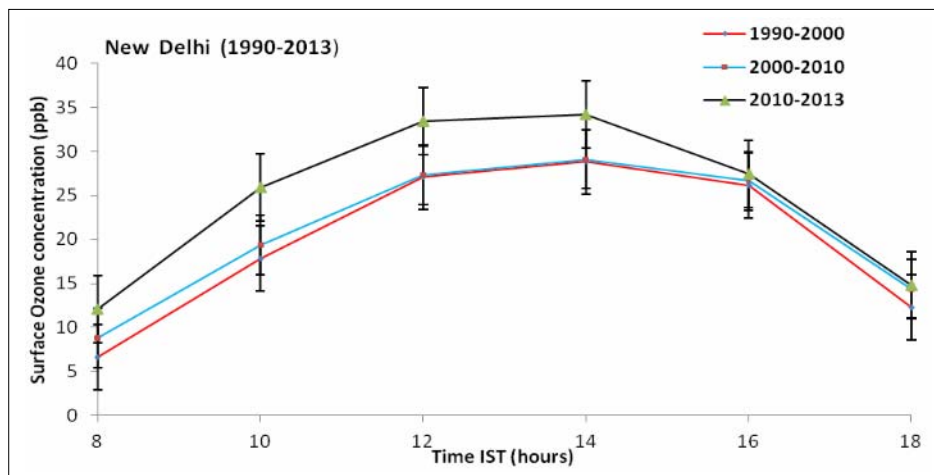


Fig. 5. Diurnal increase observed in surface ozone at New Delhi (0800 hrs IST to 1800 hrs IST) during three time scales - (1990-2000), (2000-2010) and (2010-2013)

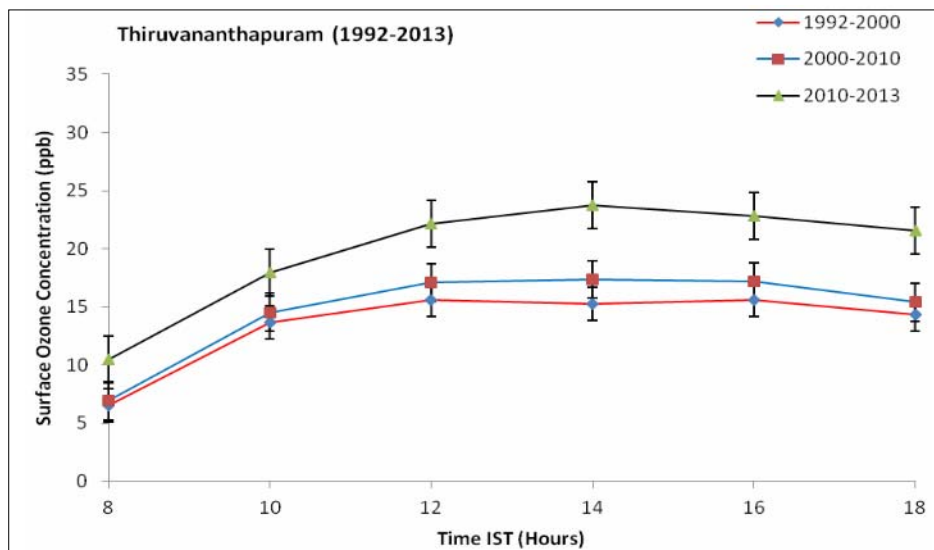


Fig. 6. Diurnal increase observed in surface ozone at Thiruvananthapuram (0800 hrs IST to 1800 hrs IST) during three time scales - (1992-2000), (2000-2010) and (2010-2013)

two Iodine atoms after reaction with the solution which in turn results in a flow of two electrons in the external circuit. These two electrons form the ozone current and absolute value of ozone is recorded by a 0 - 1 μ A strip chart recorder. The accuracy of the ozone measurements by this technique has been estimated to be $\pm 10\%$ (Sreedharan and Tiwari, 1971).

Two hourly surface ozone concentrations have been extracted from the continuous record for the observational period that is, 1990-2013 for three stations, *viz.*, Delhi, Pune and Thiruvananthapuram. The ozone data so obtained are averaged for individual months of each year (after rejecting days of any doubtful record or malfunctioning of the sensor) and are then used for various statistical analysis. Diurnal increase in ozone has also been studied using the data for three different time periods, *viz.*, 1990-2000, 2000-2010 and 2010-2013. It may be noted that for the seasonal analysis of surface ozone, a year has been divided, as per India Meteorological department (IMD) into four different seasons, *i.e.*, Winter (December-February), Summer or Pre-Monsoon (March-May), Monsoon (June-September) and Post-monsoon (October-December) seasons .

3. Results and discussion

3.1. Time series analysis

Time series analysis of surface ozone concentration at Pune, Delhi and Thiruvananthapuram is done from 1990-2013 and is plotted in Figs. 1, 2 and 3 respectively. It may be seen in the figures that, during the observational period, ozone concentration at all the three locations is less during cold months and high during hot months when solar radiation reaching the ground surface is also high. This implies, in general, that the dominant factor controlling the concentration of ozone at both the locations is photochemistry and the major factor controlling it is temperature. Trend analysis during the observational period indicates that annual average concentration of ozone is increasing at all the three stations, *i.e.*, Delhi, Pune and Thiruvananthapuram respectively ($m = 0.0005$, $m = 0.0004$, $m = 0.0004$). However, the increase observed is less significant (it is higher for Delhi as compared to other two stations). Average rate of increase is estimated to be 0.05, 0.04, 0.04 ppb per year for Delhi, Pune and Thiruvananthapuram respectively.

3.2. Diurnal variation of surface ozone at Pune, Delhi and Thiruvananthapuram

Figs. 4, 5 and 6 depicts average increase in diurnal variation of surface ozone observed at Pune, Delhi and

Thiruvananthapuram observed across three data sets, *i.e.*, (1990-2000), (2000-2010), (2010-2013) during a 23-year period from 1990 to 2013 (0800 hrs IST in the morning to 1800 hrs IST in the evening). Vertical bars shown at every two hours of the day along the diurnal curve indicate standard deviation values of surface ozone concentration at those hours. The surface ozone concentration showed a slowly increasing trend but the basic general feature of forenoon sharp increase in diurnal variation of surface ozone is seen at all the three locations. The concentration of surface ozone is less during the evening hours and more during day hours. The noon sharp increase in surface ozone concentration is a characteristic feature of an urban site and occurs because of favorable temperature conditions required for photochemical production of ozone due to precursors (Peshin *et al.*, 2003). At all the locations concentration is minimum at 0800 hrs IST, *i.e.*, 6.67 ppb for Pune, 7.74 ppb at New Delhi and 7.3 ppb at Thiruvananthapuram respectively. As the sun rises, a sharp increase in ozone concentration is observed at all the three locations reaching its maximum value at afternoon hours (around 1400 hrs IST) that is 21.05 ppb for Pune, 11.45 ppb for Delhi and 17.6 ppb for Thiruvananthapuram. These changes could be explained on account of breaking down of stable layer may or may not be accompanied by temperature inversion, which is formed during night time. After sun rises, when the inversion layer breaks down, it suddenly brings a surge of ozone rich air near the ground surface causing a forenoon sharp increase. The afternoon increase is due to strong mixing in the lower troposphere coinciding with the maximum temperature of the day (Tiwari and Peshin, 1995). Afterwards, surface ozone concentration starts decreasing at all the three locations. However, the rate of decrease observed is different for the three cities. Surface ozone decreases at a slower rate for Pune and Thiruvananthapuram, *i.e.*, 1.23 ppb/2 hr and 0.25 ppb/2 hr respectively as compared to Delhi which is 4.57 ppb/2 hr. This can be due to different meteorological conditions such as temperature, humidity and amount of rainfall of the three cities. An increase in surface ozone concentration is observed from (1990-2000) to (2010-2013) at all the three locations. The surface ozone concentration increased from 6.57 ppb to 12.07 ppb, 6.35 to 6.91 ppb and 6.51 ppb to 10.05 ppb from 1990 to 2013 at 0800 hrs IST in the morning in New Delhi, Pune and Thiruvananthapuram respectively. The increase in ozone levels (at 1400 hrs IST) during the afternoon hours is also observed at all the three locations. It increased from 28.81 ppb to 34.2 ppb, 19.39 ppb to 22.04 ppb, 15.2 ppb to 24 ppb in New Delhi, Pune and Thiruvananthapuram respectively. The diurnal change in three periods shows very clearly the enhanced photochemical production of ozone at noon hours during 1990- 2000 to 2010-2013. This is attributed to increase in levels of precursors such

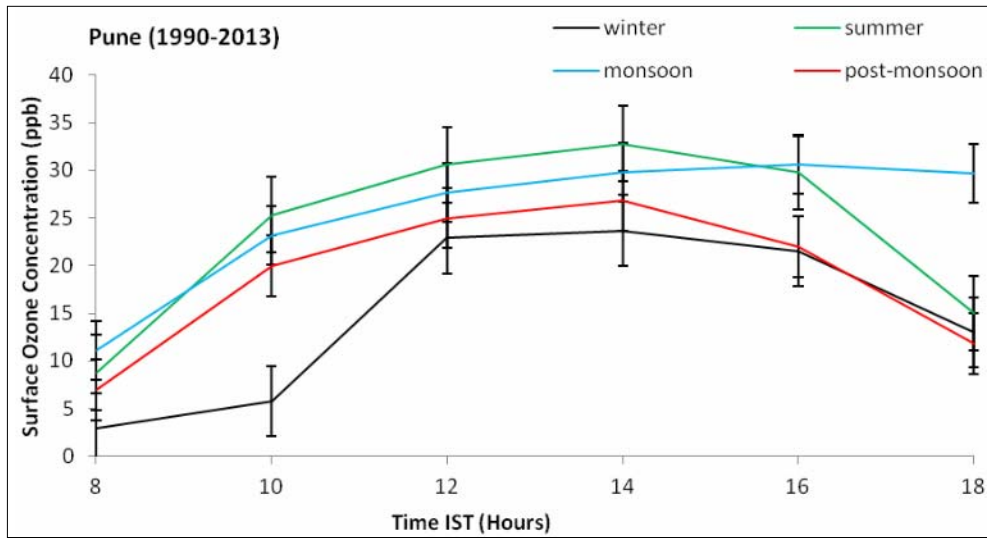


Fig. 7. Diurnal variation of surface ozone over four different seasons at Pune (0800 hrs IST to 1800 hrs IST) based on the data for the period from 1990-2013

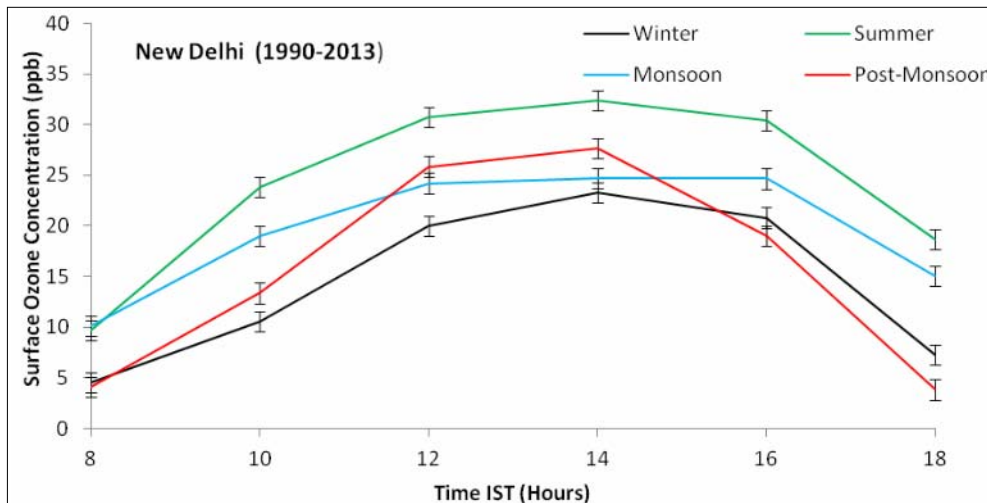


Fig. 8. Diurnal variation of surface ozone over four different seasons at New Delhi (0800 hrs IST to 1800 hrs IST) based on the data for the period from 1990-2013

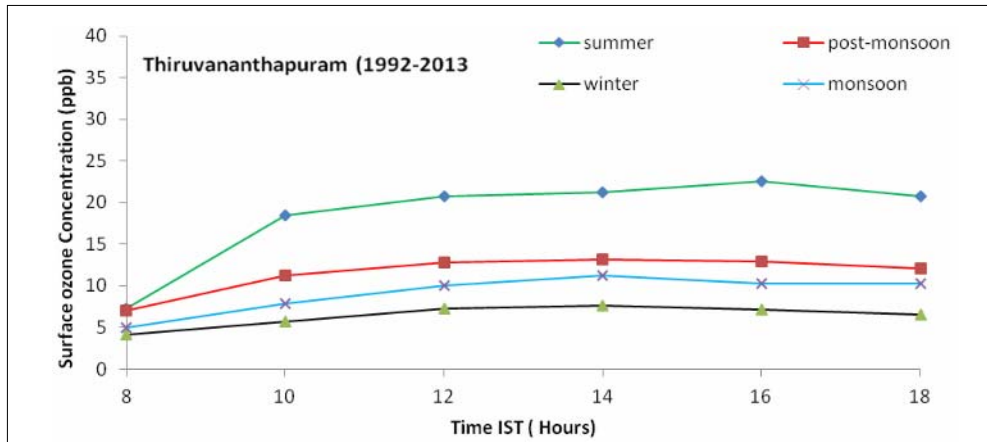


Fig. 9. Diurnal variation of surface ozone over four different seasons at Thiruvananthapuram (0800 hrs IST to 1800 hrs IST) based on the data for the period from 1992-2013

as NO_x, CH₄, CO and NMHCs from 1990-2000 to 2010-2013. The amplitude of diurnal increase in surface ozone concentration from 1990 to 2013 is more for Delhi, *i.e.*, 0.5 ppb per year, as compared to Pune and Thiruvananthapuram. This may be due to increase in number of vehicles in Delhi from 1990 to 2013. Crutzen (1988) estimates, suggests that 80% of surface ozone is produced by photochemical oxidation of precursors in presence of NO_x. Since, vehicular combustion is the major source of CO and NO_x, it is more likely the levels of these gases have increased due to the increase in number of vehicles in the city.

3.3. Diurnal season-wise variation of surface ozone at Pune, Delhi and Thiruvananthapuram

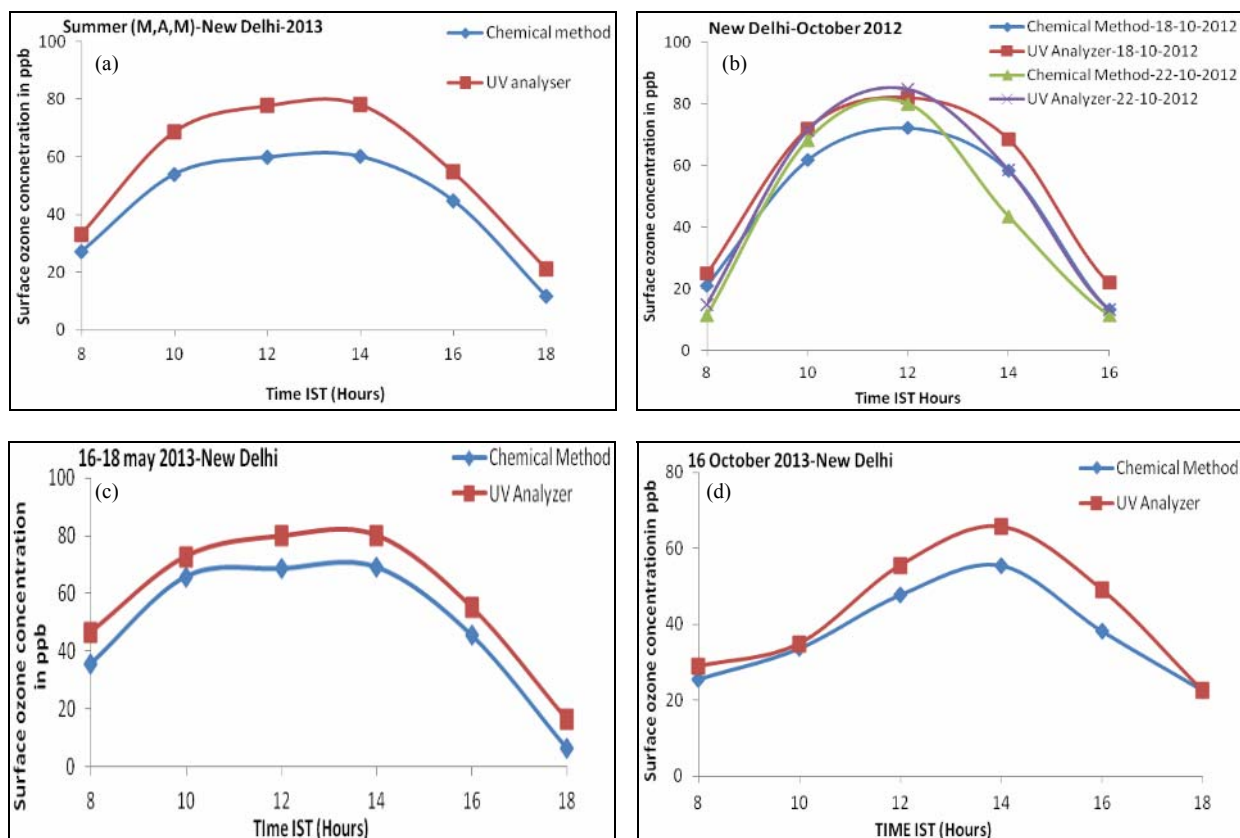
Figs. 7, 8 and 9 show diurnal variation of surface ozone from 0800 hrs to 1800 hrs over four different seasons for Pune, Delhi and Thiruvananthapuram.

It is observed from the Fig. 7 that average minimum surface ozone concentration at Pune is found during winter season, *i.e.*, 2.91 ppb at 0800 hrs IST. The minimum surface ozone concentration of Pune for winter, summer, monsoon and post-monsoon season are 0.05 ppb, 0.95 ppb, 0.04 ppb and 0.12 ppb respectively. It is seen that rise from minimum to maximum surface ozone concentration is sharp and curves are more peaked for winter season than for the other three seasons, *viz.*, summer, monsoon and post-monsoon season. This is because of nighttime depletion of surface ozone concentration due to NO_x titration process is more and amount and intensity of sunshine hours is less during winter season, thus providing less favorable temperature condition required for photochemical production of surface ozone. It can be also due to low boundary layer height that may or may not be accompanied by temperature inversion that prevails during night of winter season, thus decreasing convective mixing of ozone near the ground surface, causing a sharp increase in surface ozone when this boundary layer breaks as the sun-rises. The curve for summer season is comparatively flat because the duration and intensity of sunshine hours is more and is stagnant for a longer duration of time in the afternoon hours, favoring photochemical production of surface ozone. The amplitude of diurnal increase of surface ozone is less during monsoon season because of minimum amount of solar radiation reaching the ground causing minimum photochemical production of surface ozone. During the monsoon season, when overcast condition prevails and the levels of precursors are low due to washout by rain and removal by wet deposition, the local photochemical production of surface ozone during day time is minimum. Hence, changes in surface ozone concentrations during night and early morning hours

during monsoon months can be taken as representative of background meteorological conditions.

It is observed from the Fig. 8 that average minimum surface ozone concentration at New Delhi is found during winter season, *i.e.*, 4.57 ppb at 0800 hrs IST. The average minimum surface ozone concentration of New Delhi for winter, summer, monsoon and post-monsoon season are 0.45 ppb, 3.36 ppb, 1.96 ppb and 2.05 ppb respectively. It is seen that rise from minimum to maximum surface ozone concentration is sharp and curves are more peaked for winter season and post-monsoon season. This is similar to that as seen in case of season wise diurnal variation at Pune and hence explanation for this is also based on the distribution of incoming solar radiation and temperature over the total length of the sunshine hours. In summer season, average maximum concentration is found to be highest (32.4 ppb) that is observed at 1400 hrs IST and its duration is also longer. The curve for summer season is comparatively flat because the duration and intensity of sunshine hours is more and is stagnant for a longer duration of time in the afternoon hours, favoring photochemical production of surface ozone. The amplitude of diurnal increase of surface ozone is less during monsoon season because of minimum amount of solar radiation reaching the ground causing minimum photochemical production of surface ozone. During the monsoon season, when overcast condition prevails and the levels of precursors are low due to washout by rain and removal by wet deposition, the local photochemical production of surface ozone during day time is minimum. Hence changes in surface ozone concentrations during night and early morning hours during monsoon months can be taken as representative of background concentration. The diurnal and diurnal season-wise variation of ozone at all the three locations clearly indicates the role of amount and intensity of sunshine hours on the photochemical production of surface ozone.

It is observed from the Fig. 9 that average minimum surface ozone concentration at Thiruvananthapuram is found during winter season, *i.e.*, 4.86 ppb at 0800 hrs IST and it remains low throughout the day. This is because of nighttime depletion of surface ozone concentration due to NO_x titration process is more and amount and intensity of sunshine hours is less even in noon hours during winter season, thus providing less favorable temperature condition required for photochemical production of surface ozone. The average minimum surface ozone concentration of Thiruvananthapuram for winter, summer, monsoon and post-monsoon season are 0.6 ppb, 1.36 ppb, 0.03 ppb and 1 ppb respectively. It is seen that the seasonal curves obtained for Thiruvananthapuram is comparatively flat for all the four seasons with respect to our other two locations. The amplitude of increase in



Figs. 10 (a-d). Comparison of surface ozone values obtained from Chemical method with values obtained from UV analyzer during (a) summer season of 2013, (b) October 2012, (c) May 2013 and (d) October 2013

diurnal concentration of ozone from minimum to maximum is also less for Thiruvananthapuram. This can be due to uniform sunshine hours for a long duration of time and low precursor concentration. This can also be due to less data points available for this city during our period of study. However, there is a need for extensive measurement of meteorological parameters at Thiruvananthapuram to further verify and study this feature in more detail. This will be carried out in our next study. In summer season, average maximum concentration is found to be highest (20.51 ppb) that is observed at 1400 hrs IST. Thus we can say that, the diurnal and diurnal season-wise variation of ozone at all the three locations clearly indicates the role of amount and intensity of sunshine hours on the photochemical production of surface ozone.

4. Inter-comparison of surface ozone from chemical method with UV surface ozone analyzer

Inter-comparison of data of surface ozone obtained from Chemical method with surface ozone obtained from UV analyzer was done for summer season (March, April

and May) of 2013 and for some days of May and October 2012-2013 to study the reliability of data source. It was found that a good agreement exists between the two data sets {however, the values of surface ozone concentration found from Chemical method were lower as compared to values obtained from UV surface ozone analyzer as can be seen from [Figs. 10(a-d)]}. During summer season of 2013 [Fig. 10 (a)] the correlation coefficient was calculated to be 0.993 which is very near to +1 and r squared value (coefficient of determination) was 0.9867 which means that 98.67% of data points are correlated to each other. It can be concluded that both the data sets during this time period are strongly correlated to each other.

On 18th and 22nd October, 2012 [Fig. 10 (b)] the correlation factor between the datasets was found to be 0.997 and 0.989 (very near to +1) respectively which says that 99.54% and 97.86% of data points are correlated to each other on the mentioned days respectively. From 16th to 18th May, 2013 [Fig. 10 (c)] the correlation factor was found to be 0.997 and coefficient of determination was 0.9959 which says that 99.59% data points are correlated

to each other. Also on 16th October, 2013 [Fig. 10 (d)] the correlation factor was found to be 0.985 and coefficient of determination, *i.e.*, r^2 value was found to be 0.97 which says that 97.1% data points are perfectly correlated to each other. The above comparison during summer period and certain specific days of 2012 and 2013 holds a fairly good agreement between each other which indicates that both the methods are reliable.

5. Conclusion

Surface ozone concentration data is compiled for three locations, New Delhi, Pune and Thiruvananthapuram for a period of 23 years and is analyzed in terms of its annual long term trend, diurnal changes seen over 3 time periods, *i.e.*, 1990-2000, 2000-2010 and 2010-2013 and diurnal season-wise variation of surface ozone. Following broad conclusions can be drawn from the analysis:

(i) Time series analysis during the observational period indicates that annual average concentration of ozone is increasing at all the three stations, *i.e.*, Delhi, Pune and Thiruvananthapuram respectively ($m = 0.0005$, $m = 0.0004$, $m = 0.0004$). However, the increase observed is less significant (it is higher for Delhi as compared to other two stations). Average rate of increase is estimated to be 0.05, 0.04, 0.04 ppb per year for Delhi, Pune and Thiruvananthapuram respectively.

(ii) The surface ozone concentration showed a slowly increasing trend but the basic general feature of forenoon sharp increase in diurnal variation of surface ozone is seen at all the three locations. The concentration of surface ozone is less during the evening hours and more during day hours.

(iii) An increase in surface ozone concentration is observed from (1990-2000) to (2010-2013) at all the three locations. The diurnal change in three periods shows very clearly the enhanced photochemical production of ozone at noon hours during 1990- 2000 to 2010-2013. This is attributed to increase in levels of precursors such as NO_x, CH₄, CO and NMHCs from 1990-2000 to 2010-2013.

(iv) The inter-comparison between chemical surface ozone and UV-surface ozone shows a good agreement with each other.

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