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CHANGES IN SURFACE OZONE AMOUNT AND ITS DIURNAL AND SEASONAL PATTERNS, FROM 1990-95 TO 1996-2000, MEASURED AT NEW DELHI (28° N)

1. Tropospheric ozone is the precursor of OH radical and contributes to the greenhouse effect. Photodissociation of ozone molecules by the solar UV-radiation (< 320nm) produces O¹D radicals which in turn, through its reaction with water vapour, give rise to OH radical which are the main oxidizing agents. These radicals react with CO, CH₄, light non-methane hydrocarbons, NO₂, HCFC s etc and control their flux into the stratosphere. Ozone absorbs the earth's infrared radiation at 9.6 μm and contributes to the greenhouse effect.

Free tropospheric ozone is controlled by changes in the levels of ozone in the planetary boundary level as well as transport from the stratosphere. Photochemical processes play major role in controlling the tropospheric ozone concentration (Chameides and Walker, 1976; Crutzen, 1988). Surface ozone as well as free lower tropospheric ozone have been observed to be increasing specially in the northern hemisphere (Schmidt, 1994; Logan, 1994; Oltmans and Lavy, 1994; Staehelin *et al.*,

1994; Cartalis and Varotsos, 1994). In spite of the fact that ozone plays a crucial role in greenhouse induced global warming and in the production of OH radicals, there are not many systematic long-term measurements in the tropical region, the region of most intensive photochemical activity.

Increase in surface ozone are of concern, in part because of the important role ozone plays in controlling the chemical composition and climate of the troposphere and in part because of the deleterious effects of the gas on vegetation and human health. For example, changes in ozone could affect the concentration of OH, which in turn could influence concentration of the many trace species removed from the atmosphere by reaction with OH. A doubling of tropospheric ozone could increase surface temperature by 0.9 K, according to model results of Fishman *et al.* (1979). Ozone is thought to be responsible most of the crop damage caused by air pollution in the United States.

In the atmosphere containing CO, CH₄, NO_x and non methane hydrocarbons, *in situ* production of ozone can become very large. In general, the presence of OH radicals give rise to a sink for tropospheric odd oxygen (ozone). In this case.



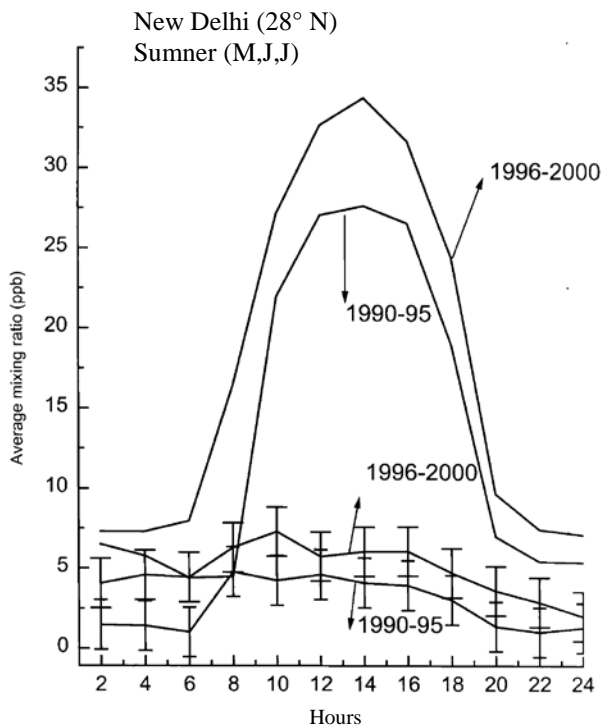
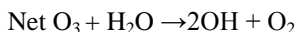
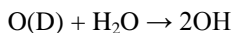
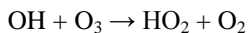


Fig. 1. Average diurnal variation of surface ozone at New Delhi for summer season (May, June, July) 1990-95 and 1996-2000. The vertical line shows the standard deviations

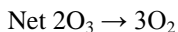
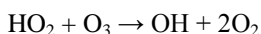
Is followed by



Further, OH can react with O_3 to set up a catalytic destruction sequence as indicated below :



and



Fishman and Crutzen (1977) estimated that approximately one half of the ozone entering the troposphere from the stratosphere would be destroyed by the above photochemical reactions before reaching the ground. However in an atmosphere containing CO or CH_4 , it is more probable that OH radicals once formed will react with CO or CH_4 rather than with ozone in the troposphere (Logan *et al.* 1981) leading to *in situ* photochemical generation of tropospheric ozone.

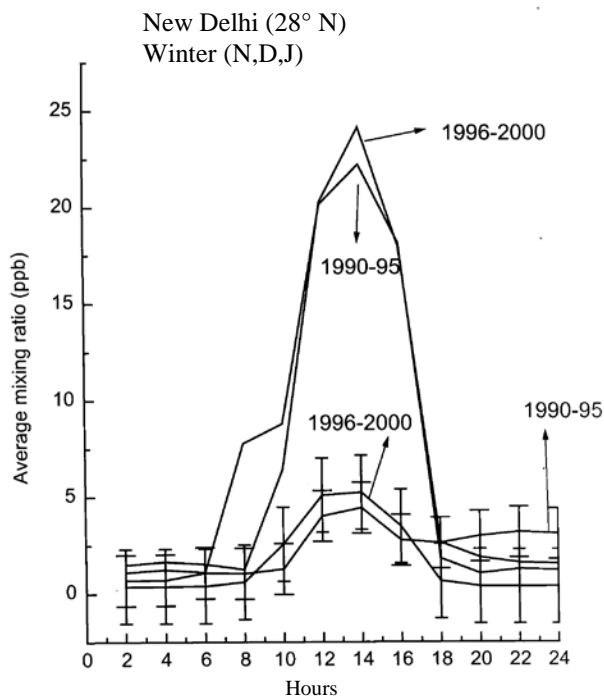
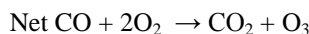
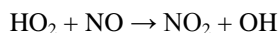
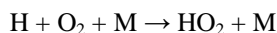
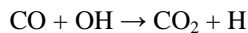
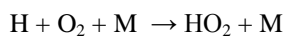
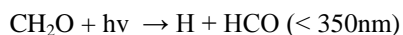
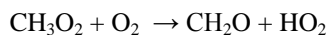
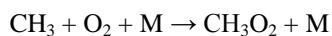
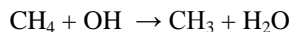


Fig. 2. Average diurnal variation of surface ozone at New Delhi for winter season (Nov, Dec, Jan) 1990-95 and 1996-2000. The vertical line shows the standard deviations

The two most important reaction sequences leading to photochemical generation of O_3 in the free atmosphere are the oxidation of CO and CH_4 as follows



and



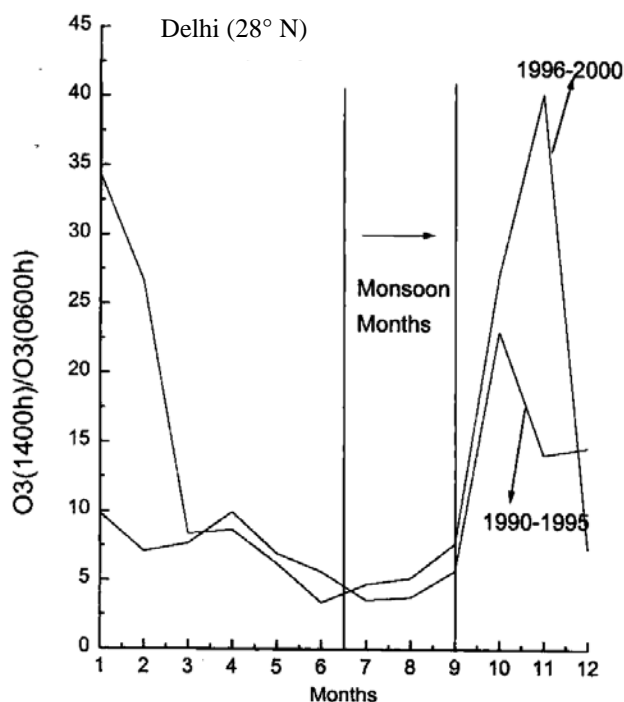
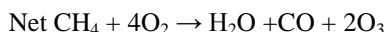
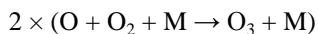
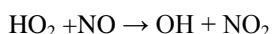
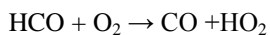


Fig. 3. Average increase in ozone concentration from 0600h to 1400h in different months during 1990-95 and 1996-2000



The availability of adequate amount of NO is a must for the above oxidation sequences of CO and CH₄.

2. *Measurement technique and data used* - Surface ozone concentration has been measured at Delhi (Lat. 28° 35' N and Long. 77° 12' E) with a continuous recorder using electrochemical sensor (Sreedhran and Tiwari 1971). The sensor part of the equipment has been exposed on the roof of the "National Ozone Centre" building at a height of 10 m above ground.

Two hourly values of surface ozone have been extracted from the continuous record for the period 1990-2000. Monthly average values have been computed from daily hourly values (after rejecting days of any doubtful record or malfunctioning of the sensor).

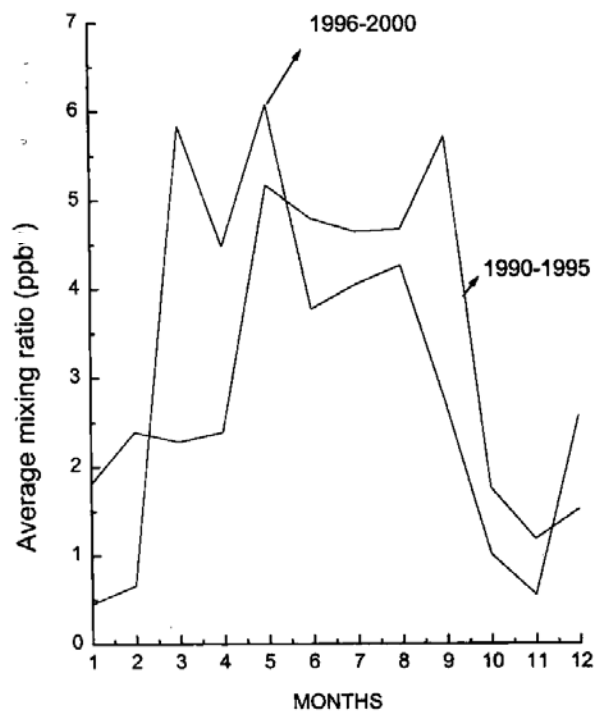


Fig. 4. Monthly average surface ozone concentration measured at Delhi at 0600h during 1990-95 and 1996-2000

3. *Results - Changes in diurnal pattern* - Figs. 1 & 2 show average diurnal variation of surface ozone for the summer months (May, June and July) and for the winter months (November, December and January) respectively for the 1990-95 and 1996-2000 periods. The basic feature of diurnal variation such as low levels during early morning and night hours and high values during noon hours are seen in both the data sets during all the months. The noon time higher ozone concentration has a characteristic of an urban site and occurs because of its photochemical production due to precursors. However, the amplitude of diurnal variations are different during different periods.

The surface ozone concentration showed a slowly increasing trend but the nature of diurnal variation was identical with a forenoon sharp increase followed by the main maximum which occurred in the afternoon. These changes could be explained on account of breaking down of stable layer, which formed during winter night, often accompanied by temperature inversion or otherwise near the ground. After sunrise, when the inversion breaks down, a sudden surge of ozone rich air is brought down causing the forenoon increase. The afternoon increase is due to strong mixing in the lower tropospheric coinciding with the maximum temperature of the day (Tiwari and Peshin, 1995).

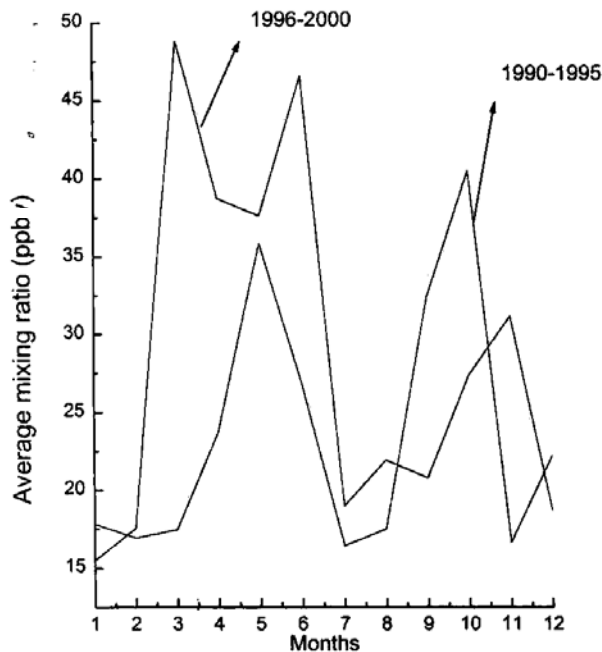


Fig. 5. Monthly average surface ozone concentration measured at Delhi at 1400h during 1990-95 and 1996-2000

Fig. 3 shows the increase in ozone concentration from 0600h to 1400h during different months of 1990-95 and 1996-2000. It is observed that during both these periods, the increase is less in July, August and September (monsoon months). Lowest increase in ozone concentration from 0600 to 1400 is found to be in the month of July, when the rainfall is highest with minimum amount of solar radiation reaching the ground causing minimum photochemical production of ozone. Less ozone is also found in summer months in both the data sets. This may be due to hazy conditions prevailing over Delhi. Higher increase in ozone is observed during October and November months.

3.1. *Changes in seasonal pattern* - The seasonal variation in surface ozone shows increase in the concentrations during all the months of 1996-2000 as compared in concentrations in 1990-95. The 1990-95 data shows less seasonal variation compared to that observed during 1996-2000. Figs. 4 & 5 show seasonal variability in monthly average surface ozone during these periods at 0600h and at 1400h. The increase in ozone levels at 0600h in different seasons from 1990-95 and 1996-2000 is higher during summer seasons. There is increase in ozone concentration from 1990-95 to 1996-2000 at 1400h as compared to 0600h.

4. *Discussion and conclusion* - The diurnal change during the two periods show very clearly the enhanced

photochemical production of ozone at noon hours during 1996-2000 when compared to 1990-95. This is attributed to increase levels of precursors such as NO_x , CH_4 , CO, NMHCs etc from 1990-95 to 1996-2000. Crutzen (1988) estimates, suggest that 80% of the tropospheric ozone is produced *via* photochemistry of precursors in the presence of NO_x . Since combustion is the major source of CO and NO_x , it is more likely that levels of these gases have increased due to the number of vehicles present in the city. In Figs. 4 & 5 there have been anomalies during June-November at 0600h, in 1990-95 where it is showing more ozone as compared with 1996-2000. Similarly in Fig. 5 at 1400h, between August to November the ozone concentration is more in 1990-95 against 1996-2000. The question is why surface ozone has decreased during these months in 1996-2000, when large number of pollutants are released in the atmosphere. These anomalies are to be investigated thoroughly which will be done in the next study.

The seasonal patterns also show higher ozone concentrations during 1996-2000 than that during 1990-95. During the monsoon period, when the sky is generally overcast and the levels of precursors are low, the local photochemical production of ozone during day time is minimum. Hence changes in average ozone concentrations during night and early morning hours during monsoon months can be taken as representative of background changes.

There is no sign of increased ozone production in the stratosphere or in total amount of ozone during last decade as evident from observations over Indian stations. Hence any perceptible increase in surface ozone must be thought of due to tropospheric sources. The measurement indicate that the amount of anthropogenic gases in the atmosphere over Delhi has been increasing during the last decade and *in situ* production of tropospheric ozone is important.

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