

A prominent maximum in surface ozone concentration during winter months at Pune (India)

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सार — विद्युत-रासायनिक संवेदक के उपयोग से, निरन्तर चलने वाले सतही ओजोन रिकार्डर द्वारा, पुणे (भारत) में 1972 से घरातल के निकट ओजोन की मात्रा को रिकार्ड किया जा रहा है। शीत ऋतु के रिकार्ड के विश्लेषण से यह ज्ञात हुआ कि स्थानीय मानक समय के अनुसार, लगभग 1000 से 1200 बजे के बीच, ओजोन की मात्रा में अप्रत्याशित वृद्धि हुई। 1985 से पहले, पूर्वाह्न में सतही ओजोन की मात्रा में इस प्रकार की उच्च वृद्धि के बाद अपराह्न में अधिकतम मान और उस दिन के अधिकतम तापमान की समयावधि एक ही साथ पाए गए। 1985 के बाद सतही ओजोन रिकार्डों से ज्ञात हुआ कि पूर्वाह्न का अधिकतम मान अपराह्न के मान की तुलना में नियत रूप से बढ़ गया। वायुमंडल में मानवोद्भव (एंथ्रोपोजेनिक) गैसों की बढ़ती हुई मात्रा के कारण क्षेपणमंडल में ओजोन की प्रकाश संश्लेषण उत्पत्ति की संभावना है। अतः जब मौसमी अवस्थाएं ओजोन के उत्पादन में सहायक इस प्रकार की गैसों से संचयन के अनुकूल होंगी, तब इसके कारण सतही ओजोन के उच्च मानों में वृद्धि हो सकती है।

ABSTRACT. Concentration of ozone near the ground has been recorded at Pune (India) since 1972 with the help of a continuous surface ozone recorder using electro-chemical sensor. The analysis of the records of winter season indicates a sharp rise in ozone amount in the forenoon around 1000 to 1200 LST. Prior to 1985 this forenoon higher value in surface ozone concentration was followed by another maximum in the afternoon hours coinciding with the maximum temperature epoch of the day. After 1985 the surface ozone data indicates that the forenoon peak value has become invariably higher than the afternoon value. Due to increasing concentration of anthropogenic gases in the atmosphere there is a possibility of photochemical production of ozone in the troposphere, which may give rise to higher surface ozone values, when the meteorological conditions are favourable for the accumulation of such gases which are involved in ozone production.

Key words — Surface ozone, Diurnal variation, Temperature, Concentration, Anthropogenic gases, Troposphere, Photochemical production, In situ, Tropospheric sources, Forenoon peak value.

1. Introduction

Concentration of tropospheric ozone has been monitored at various stations in the northern and southern hemisphere from ground-based and balloon-borne instruments (Oltmans and Komhyr 1986, Fabian and Pruchniewicz 1977) and also the rate of destruction (flux measurement) near the ground has been computed. Till 1970, it was generally agreed that the middle and the upper stratosphere is the only source region for ozone production by the photochemical reaction of the sunlight on oxygen molecules. The ozone was assumed to be photochemically inert in the lower stratosphere and the upper troposphere till it reached the ground where it was destroyed due to chemical reaction with organic matter in the biosphere. The rate of production of ozone in the stratosphere and the flux (rate of destruction at the surface) calculated by various workers (Galbally 1968, Tiwari 1973) was found to be in equilibrium. Increased interest in tropospheric ozone in recent years has resulted from the modelling of the chemistry of the

troposphere. The traditional view that ozone originates in the stratosphere, becomes nearly a conservative property of the lower stratosphere and the troposphere where it is chemically inert and is finally destroyed at the earth's surface, is no more valid. Recently, many research studies have reported a systematic increase in the tropospheric ozone, particularly in the Northern Hemisphere. In fact, a rising trend in the tropospheric ozone, especially in the Northern Hemisphere, is not unexpected. Ozone is produced photochemically in the troposphere and its precursors, carbon monoxide, methane and non-methane hydrocarbons as well as nitrogen oxides, are known to have increased mainly due to anthropogenic emissions.

Surface ozone concentration has been measured at Pune (Lat. 18° 32' N, Long. 73° 51' E) with a continuous recorder using an electrochemical ozone sensor (Sreedharan and Tiwari 1971). The diurnal and seasonal variation of surface ozone at Pune using data obtained during 1972-73 (Tiwari and Sreedharan 1973) could be explained on the basis of

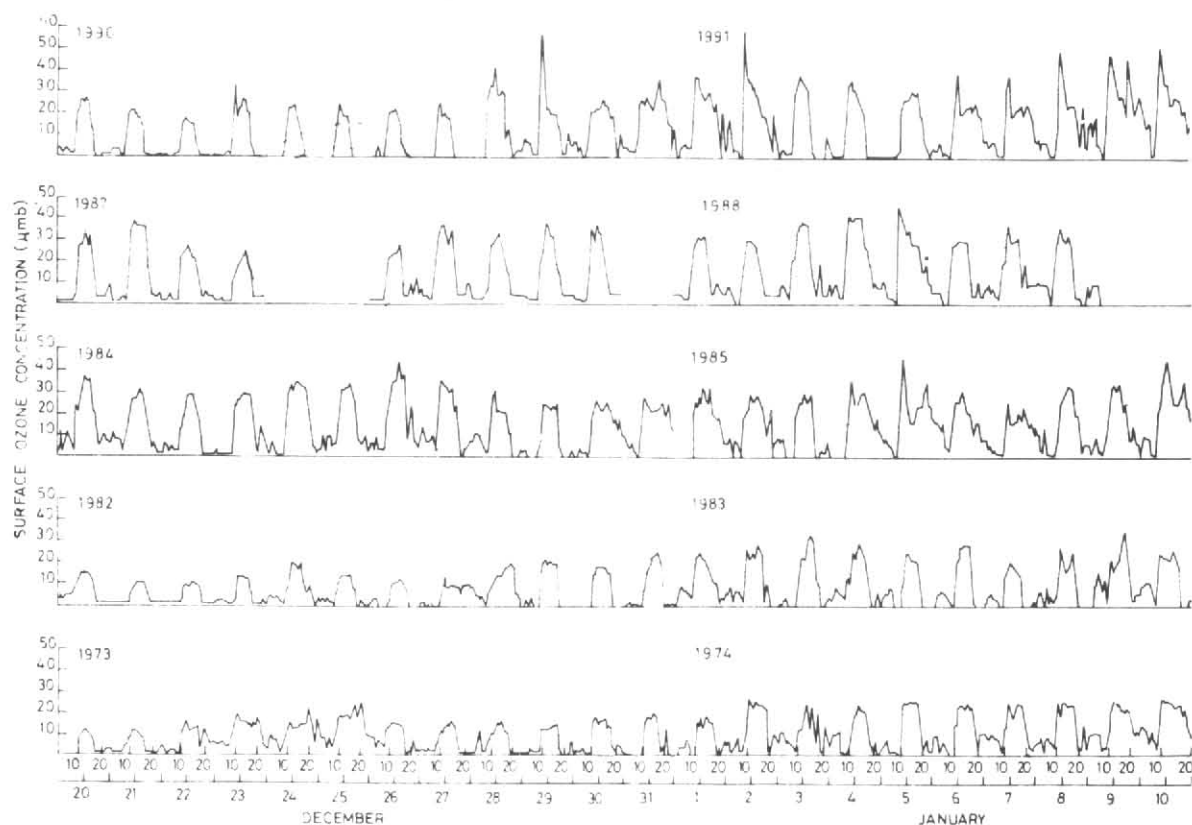


Fig. 1. Hourly surface ozone variation at Pune (20 December to 10 January)

vertical mixing and the stability conditions in the boundary layer. The ozone concentration near the ground is governed by factors which transfer the gas from the stratosphere to the ground. The records of surface ozone at Pune since 1972 emphasize the predominant role of mixing processes in the transport of ozone in the lower troposphere. This supported the view that in an atmosphere, free from anthropogenic emissions, the dominant source and sink regions of ozone are the stratosphere and the ground respectively.

Surface ozone measurements at Pune have been made since 1972 using an electrochemical continuous ozone sensor (Sreedharan and Tiwari 1971) and this measurement has also been started at Thiruvananthapuram and New Delhi. The sensor part of the equipment has been exposed on the top of the sixth floor of the main Meteorological Office building at New Delhi at a height of 35m above ground. Examination of continuous record of surface ozone shows that the minimum value occurs in the morning around sunrise (coinciding with minimum temperature) and maximum in the afternoon. This could be explained on the basis of

vertical mixing depth which is minimum in the morning due to formation of stable cool layer near the ground. The depth of vertical mixing is highest in the afternoon due to maximum temperature of the day and the maximum surface ozone values are nearly representative of the free tropospheric ozone amount.

Apart from the above diurnal change, day-to-day record shows a forenoon higher value in surface ozone during winter months, followed by the maximum value in the afternoon. During 1972-73 this variation was thought to be the result of formation of stable layers with or without temperature inversion during winter months (Tiwari and Sreedharan 1973). The analysis of subsequent data after 1980 shows that the peak value of forenoon maximum during winter months has been steadily increasing and on many days it becomes the highest value of the day. Authors found it difficult to explain the occurrence of maximum value in the surface ozone in the forenoon on the basis of mixing in the lower troposphere. In this paper, this aspect of forenoon higher value has been explained and a possible explanation for the steady increasing trend is discussed.

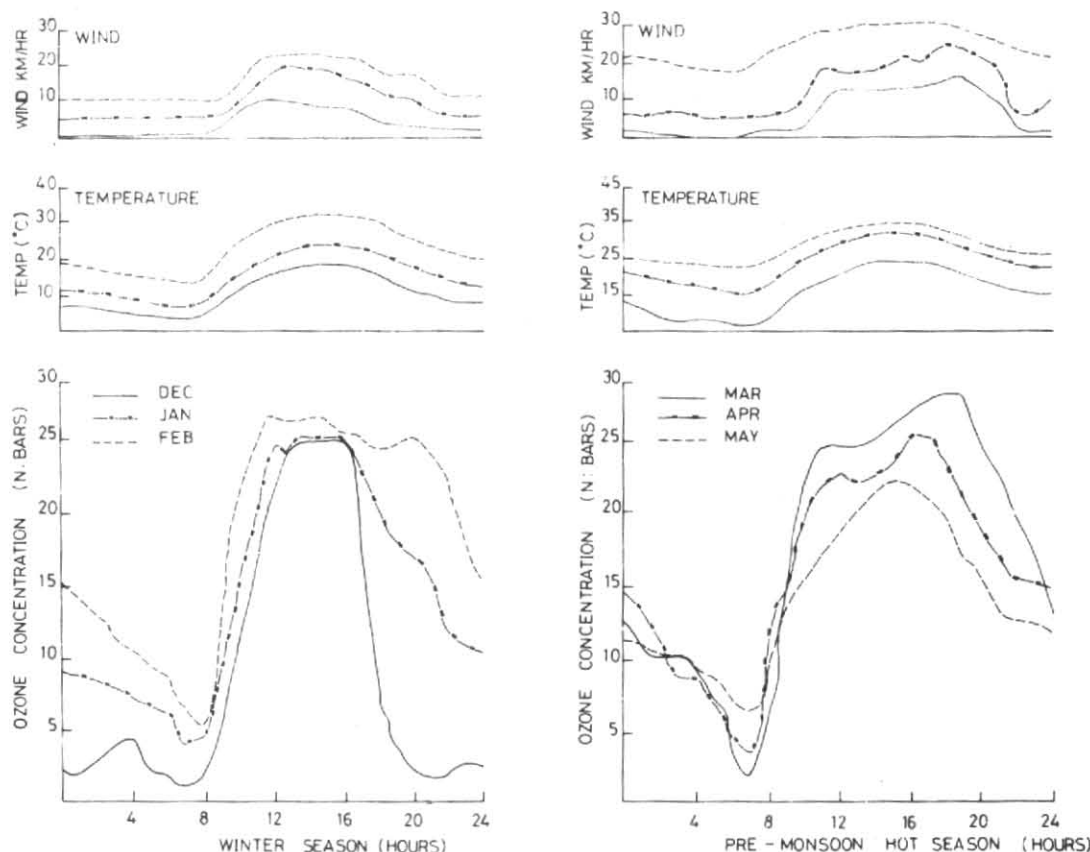
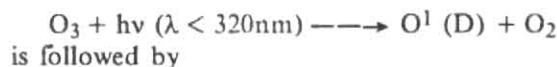


Fig. 2. Mean hourly surface ozone concentration at Pune. Temperature and wind are presented by shifting the grid by 5 units (From Tiwari, V.S. 1973)

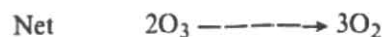
In the atmosphere containing CO, CH₄, NO_x and non-methane hydrocarbons, *in situ* production of ozone can become very large. In general, the presence of OH radicals gives rise to a sink for tropospheric odd oxygen (ozone). In this case,



Further, OH can react with O₃ 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 CH₄, it is more probable that OH radicals once formed will react with CO or CH₄ rather than with ozone in the troposphere (Logan *et al.* 1981) leading to *in situ* photochemical generation of tropospheric ozone.

The two most important reaction sequences leading to photochemical generation of O₃ in the free atmosphere are the oxidation of CO and CH₄ as follows :



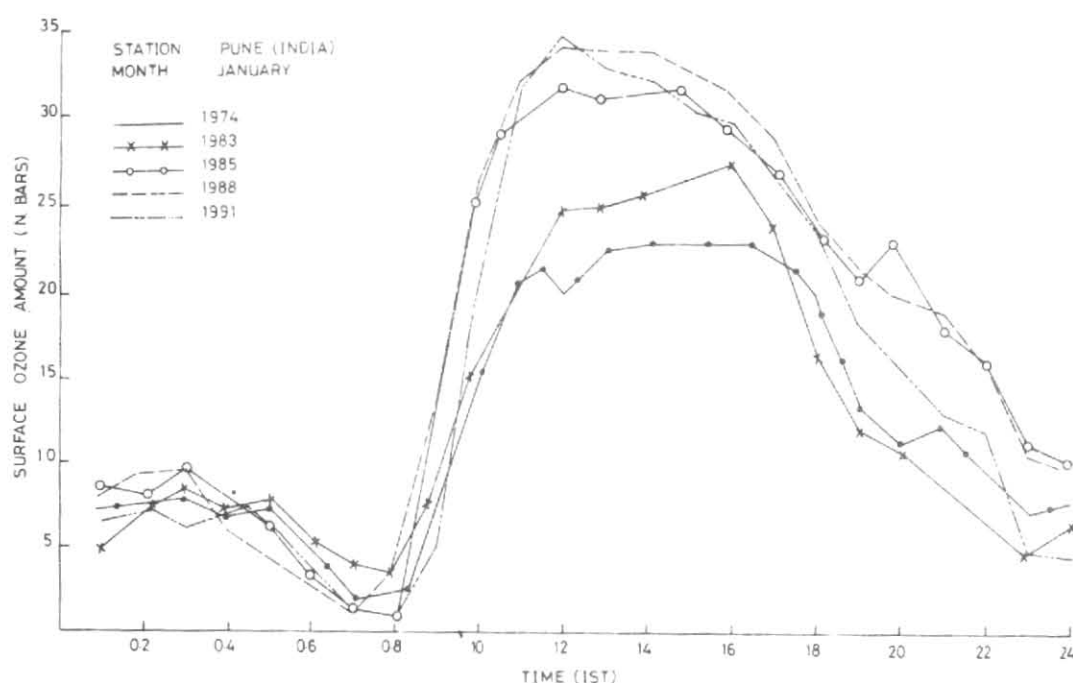
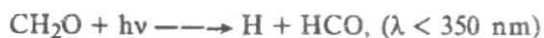


Fig. 3. Hourly surface ozone concentration



and



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

2. Data used

Hourly values of surface ozone have been extracted from the continuous record for the period from January 1974 to December 1991. Monthly average values have been computed from daily hourly values (after rejecting days of any doubtful record or malfunctioning of the sensor). Similarly, from the monthly average values, seasonal means have been computed. Twenty two days' continuous record of hourly surface ozone values has been selected, to be representative of winter months, from 20 December to 10 January and are presented in the paper for the sake of clarity and feasibility. The monthly mean and seasonal mean values computed from daily data have also been discussed in the text.

3. Results and discussion

3.1. Diurnal variation of surface ozone

The diurnal variation of surface ozone closely follows the diurnal variation of surface temperature. Also, a close correlation is observed between wind and ozone concentration, particularly at night (Fig. 2). The minimum surface ozone concentration occurs at the time of minimum temperature at about 0700 to 0800 LST and maximum in the afternoon between 1400 and 1600 LST coinciding with the maximum temperature epoch of the day. Fig. 1

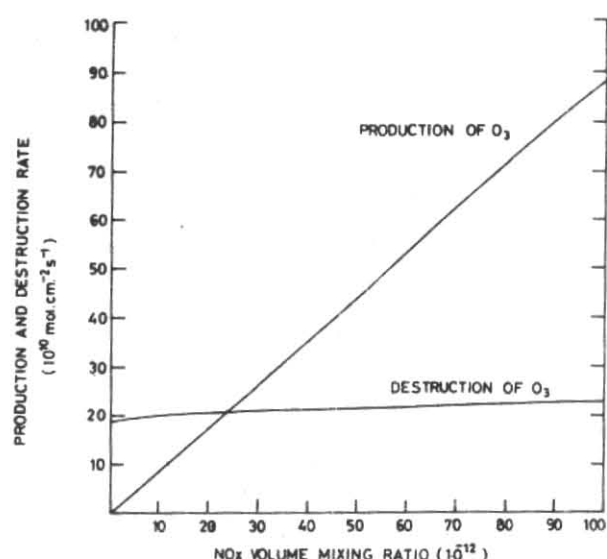


Fig. 4. Model-derived, annual mean, photochemical production and destruction rates of tropospheric ozone in Northern Hemisphere as a function of the prescribed NO_x concentration (after Fishman, J. S., 1979)

depicts the hourly values of ozone from 0000 hrs of December 20 to 2400 hrs of 10 January, the period which is representative of coldest spell during each year. Fig. 1 depicts broadly the diurnal variation described above. However, on many days, a sharp rise in ozone value can be seen around 1000 hr. Such sharp fluctuations have been observed since 1974 and could be broadly explained on the basis of the formation of stable layers accompanied with or without temperature inversion on cold winter morning and the resulting reduction of vertical mixing in the layers near the ground. The sharp increase in surface ozone amount appears to coincide with the breaking of stable layer and role of *in situ* photochemistry with availability of plenty of sunlight and ozone precursors. Examination of year-to-year variation reveals that the average ozone concentration as well as the peak values have been gradually increasing. The highest morning value observed during January 1974 was about 20-25 nanobar, while in January 1991 this value has increased to about 33-40 nanobar (Fig. 3). This means that precursors have increased from 1971 to 1991.

With the increasing concentration of CO , CH_4 , NO_x and non-methane hydrocarbons due to anthropogenic sources, the tropospheric generation of O_3 may dominate over the normal stratospheric source. Fishman *et al.* (1979) have shown that due to increasing concentration of NO_x in the tropospheric layers near the ground, the production rate of ozone becomes much higher, whereas destruction is constant (Fig. 4). This probably explains

the dominance of photochemical production of ozone near the earth's surface in recent years.

The average hourly variation for the month of January for selected five years *i.e.*, 1974, 1983, 1985, 1988 and 1991 is shown in Fig. 8. Some of the main features of the hourly changes which are inferred from Fig. 3 are listed below:

- (a) The minimum value occurs just after the sunrise between 0700 and 0800 LST. There is no change in the time of occurrence of minimum surface ozone since 1972 as reported earlier (Tiwari and Sreedharan 1973).
- (b) The concentration from the midnight to 0800 hr (period of low surface ozone values) has also not shown any significant change.
- (c) The sharp rise after 8 a.m. shows similar trend since 1974. However, the peak value observed during 1974 was about 20-21 nanobar, while during 1985 to 1991, the observed peak value has become 32 to 33 nanobar. The graph shows that hourly ozone amount during day time has shown a steady increase since 1974. The diurnal variation during 1974 and 1983 does exhibit a forenoon peak followed by a slight decrease and the occurrence of maximum ozone amount in the afternoon around 1600 IST. During 1985 the forenoon and afternoon peak values are nearly same, while during 1988 and 1991 the forenoon peak has become higher than afternoon value. The value has started decreasing thereafter (after 1200 noon). The hourly ozone amount during January 1985 appears to represent a transition phase between the natural atmosphere free from anthropogenic gases in early seventies from the atmosphere containing anthropogenic gases in late eighties & nineties.
- (d) During winter night a cool and stable layer is invariably formed in the boundary layer near the ground. After the day break the ground is heated up slowly initiating mixing in the lowest layers. The mixing depth keeps on increasing with more solar radiation and as soon as the stable layer breaks down, ozone-rich air gushes to the ground and a forenoon peak in surface

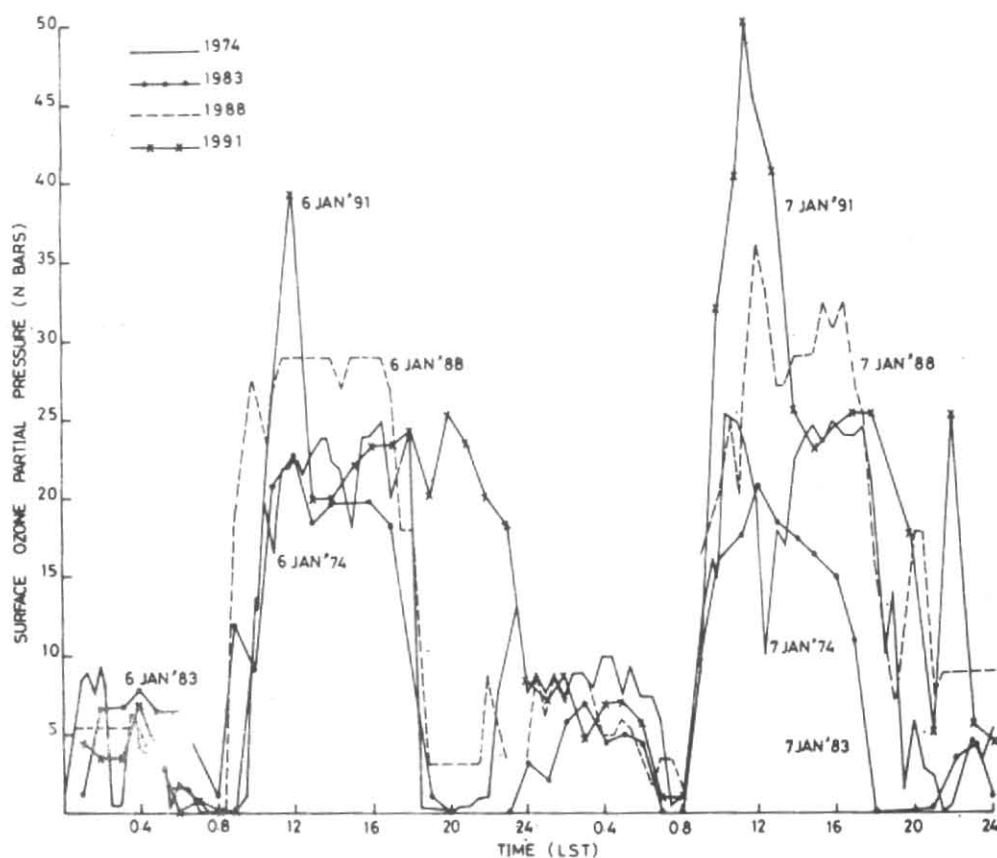


Fig. 5. Sample surface ozone record showing the forenoon maximum

ozone is registered. The tropospheric mixing is highest in the afternoon due to deep convection and shows a maximum value of surface ozone in the afternoon. From above discussion authors feel that January 1974 shows hourly variation in surface ozone due to natural mixing processes in an unpolluted atmosphere where the maximum occurs in the afternoon coinciding with maximum convection and mixing processes. While the diurnal variation after 1985 exhibits the affect of anthropogenic gases in photochemical production of ozone in the lower troposphere superimposed over the natural atmospheric processes. The accumulation of anthropogenic gases and automobile exhaust trapped in the stable layers near the ground becomes a source of ozone when sun's radiation falls on them. On account of some *in situ* production in the lower troposphere the forenoon peak attains the maximum value of the day. The peak value slowly starts decreasing when the dispersion of pollutant begins and

destruction of ozone dominates at the ground.

- (e) Another hump in ozone distribution is sometimes observed after sunset around 8 to 9 p.m. This is prominently shown during 1974 and 1985. It may appear due to advection of ozone-rich air, but its precise reason needs further investigation.

3.2. Observed diurnal changes: Tropospheric mixing versus photochemical production

The surface ozone variation in 1972-74 was explained assuming that ozone production occurred in the stratosphere, the destruction takes place near the ground and the concentration of ozone near the earth's surface was governed by tropospheric exchange mechanism. The minimum value occurred in the morning when the tropospheric layers near the ground were stable and there was no replenishment from the free troposphere. The forenoon maxima might occur if there is an inversion layer during night and the forenoon

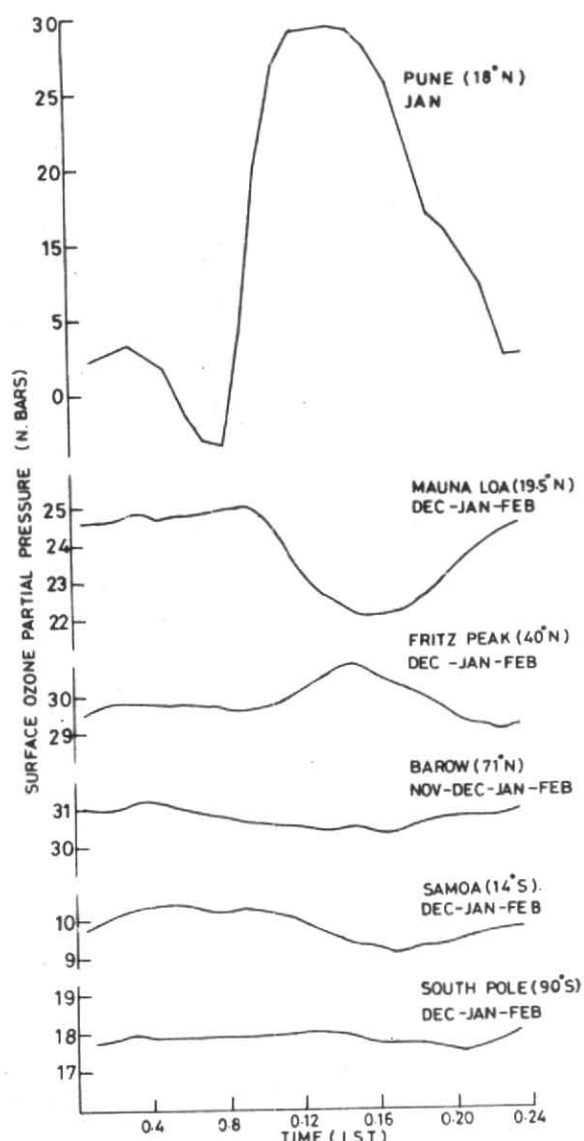


Fig. 6. Diurnal variation of surface ozone for the winter season

maxima coincide with the breaking of inversion or stable layer. But the main maximum occurred only in the afternoon in all seasons when the mixing and the exchange in the tropospheric layer was maximum. But the occurrence of a single pronounced maximum around local noon and the highest concentration of surface ozone in recent years (1985 to 1991) leads one to think of *in situ* source due to photochemical production. The increasing amount of anthropogenic gases in the troposphere (described in preceding section) suggest the possibility of higher *in situ* production of ozone in the troposphere. The graphs for 1988 and 1991 in Figs. 3 & 5 represent the natural variation superimposed by *in situ* production. The occurrence of maximum value near local noon and a decreasing trend

thereafter suggests that the natural concentration in forenoon hours combined with the *in situ* production makes the forenoon peak value higher than the free tropospheric ozone concentration. Hourly surface ozone values for 6 and 7 January for 1974, 1983, 1988 and 1991 are shown in Fig. 5 which clearly bring out the differences in daily hourly variation from 1974 to 1991.

3.3. Comparison of diurnal variation at Pune with other stations

The diurnal hourly variation of surface ozone during the month of December and January at Mauna Loa (Lat. 19° 32' N, Long. 155° 35' W), Pune (Lat. 18° 32' N, Long. 73° 51' E), Fritzpeak (along Lat. 40°N), Barow (Lat. 71° 19' N, Long. 156° 36' W), Samoa (Lat. 14° 15' S, Long. 170° 34' W) and south Pole (Lat. 90°S) are shown in Fig. 6. Variation at Fritzpeak along (Lat. 40°N) is similar to that of Pune but variation at Mauna Loa (Lat. 19° 32' N, Long. 155° 35' W) is opposite to Pune since Mauna Loa is situated at a height of 3500 m above sea level and the diurnal changes at this station are governed by mountain ascending and descending winds rather than photochemical induced changes. Near poles, there is hardly any diurnal variation. At Samoa (Lat. 14° 15' S, Long. 170° 34' W), the diurnal variation shows a reversal of phase due to its location in the Southern Hemisphere and the magnitude is also low.

4. Conclusions

From the examination of surface ozone data recorded at Pune (Lat. 18° 32' N, Long. 73° 51' E) during winter months, December and January, a pronounced ozone increase in the forenoon between 10 a.m. to 12 noon has been invariably observed since 1974. The minimum value occurs in the morning hours immediately after the sunrise and the ozone partial pressure recorded is about 2 to 5 nanobar. The diurnal variation during winter season seen in earlier years could be explained due to variation in vertical mixing and stability conditions in the tropospheric layers near the ground. The surface ozone data from 1974 to 1983 support the traditional view that ozone is produced in the stratosphere and remains nearly a conservative property in the lower stratosphere and the upper troposphere and is finally destroyed at the earth's surface. But the surface ozone data after 1983 though emphasizing the important role of mixing processes in the lower troposphere, does indicate dominance of *in situ* source of ozone in the troposphere. When the stability conditions are

favourable for the accumulation of anthropogenic gases near the ground. Some evidence supporting the *in situ* tropospheric source is given below:

(a) From 1974 to 1983, 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 layers, 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 maximum is due to strong mixing in the lower troposphere coinciding with the maximum temperature of the day. After 1985 there appears to be an increase of about 10-12 nanobar in the forenoon peak and as a result this forenoon peak becomes the main maximum of the day. This is reflected in the average January surface ozone concentration (Fig. 3) as well as the individual days (Figs. 1 & 5). On individual days the forenoon value may be higher depending upon the local stability conditions favouring the accumulation of anthropogenic gases during night and a bright sunlight on following morning. In recent years it is being noticed that the tendency of highest value in the forenoon in surface ozone is even seen during the month of February and sometimes in March also.

(b) 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 measurements indicate

that the amount of anthropogenic gases in the atmosphere over Pune has been increasing during the last decade and an *in situ* production of tropospheric ozone is important.

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