

Tropical tropospheric chemistry and climate change

B.H. SUBBARAYA*, SHYAM LAL** and M. NAJA**

* ISRO Headquarters, Bangalore - 560094, India

**Physical Research Laboratory, Ahmedabad - 380009, India

सार - इसरो के भूमंडल जीवमंडल कार्यक्रम - 1991 के अंतर्गत भारत में कुछ चुने हुए स्थानों पर सतह ओजोन और उसकी CH_4 , CO और NO_x ($\text{NO} + \text{NO}_2$) पूर्वगामी गैसों के मॉनीटरिंग का एक व्यवस्थित कार्यक्रम शुरू किया गया। एक शहरी प्रदूषित स्थान - अहमदाबाद, एक अपेक्षाकृत स्वच्छ ग्रामीण स्थान-गंडकी, मुक्त क्षोभमंडल वाला ऊँचाई पर स्थित स्थान - गुरुसिखर और समुद्री हवा से प्रभावित एक तटीय (अपेक्षाकृत स्वच्छ) स्थान - त्रिवेन्द्रम में मान लिए गए। उष्णकटिबंध में क्षोभमंडलीय रसायन के विभिन्न लक्षणों का अध्ययन करने के लिए इन ऑक्सीडों का उपयोग किया गया। इस कार्यक्रम के जलवायु परिवर्तन की समस्या से संबंधित कुछ परिणामों को इस शोध - पत्र में प्रस्तुत किया गया है।

ABSTRACT. A systematic programme of monitoring surface ozone and its precursor gases CH_4 , CO and NO_x ($\text{NO} + \text{NO}_2$) at some selected sites in the Indian region was started under ISRO's geosphere biosphere programme in 1991. Measurements have been made at Ahmedabad an urban polluted site, Gadanki a rural relatively clean site, Gurusikhar a high altitude site representative of the free troposphere and Trivandrum a coastal (relatively clean) site influenced by marine air. The data has been used to study different features of troposphere chemistry in the tropics. Some of the results from this programme relevant to the climate change problem are presented in this paper.

Key words - Tropics, Tropospheric, Chemistry, Climate change.

1. Introduction

Atmospheric chemistry plays the key role in determining the earth's climate. Several constituents of the atmosphere are radiatively active, *i.e.*, they absorb and re-emit both solar (UV) and terrestrial (long wave) radiation, determine the temperature structure of the atmosphere, provide the energy for the large scale atmospheric dynamics and regulate the radiation regime as well as the environmental conditions in the biosphere which control the sustenance and evolution of the life forms on earth as we know them today. Many of the gases, important in chemistry and radiation, are minor constituents in the atmosphere, *i.e.*, their abundances are in parts per million by volume or less, some of them exist as traces, with abundances in parts per billion (10^{-9}) or even parts per trillion (10^{-12}) by volume. Further, the abundances of most of these gases are determined either by emissions from the biosphere below (the earth's surface and the oceans), *e.g.*, CO_2 , CH_4 , CFCs, or by photochemistry involving the biospherically emitted gases and solar radiation, *e.g.* O_3 , O , NO_2 . The sources of these gases include both natural as well as anthropogenic processes, the later forming a substantial part. Due to the ever increasing population, increased industrialization,

changing life styles *etc.* the atmospheric composition is changing, the abundances of some of these trace gases have been increasing with time, *e.g.*, CO_2 , CH_4 . In recent years several new chemicals have been introduced in the atmosphere, *e.g.*, CFCs, HCFCs. There is growing concern that as a result of these, the earth's climate is changing, the most significant feature being increased surface temperature - Global Warming. There is now observational evidence that the global mean surface temperature has been increasing over the past hundred years or so at the rate of 0.02 to 0.04° K per decade (Fig. 1) and that this increase in temperature is correlated with increasing abundances of greenhouse gases, such as CO_2 and CH_4 .

The tropical regions are of special significance in atmospheric chemistry and climate change studies (Naza, 1997) because (i) the tropics contribute almost half of the biogenic input of trace gases, (ii) abundant solar radiation throughout the year and a higher level of solar UV penetration into the tropical troposphere (due to lower total ozone content) gives rise to a higher level of photochemical activity, increased production of trace gases of photochemical origin, in the tropics when compared to middle and higher latitude regions,

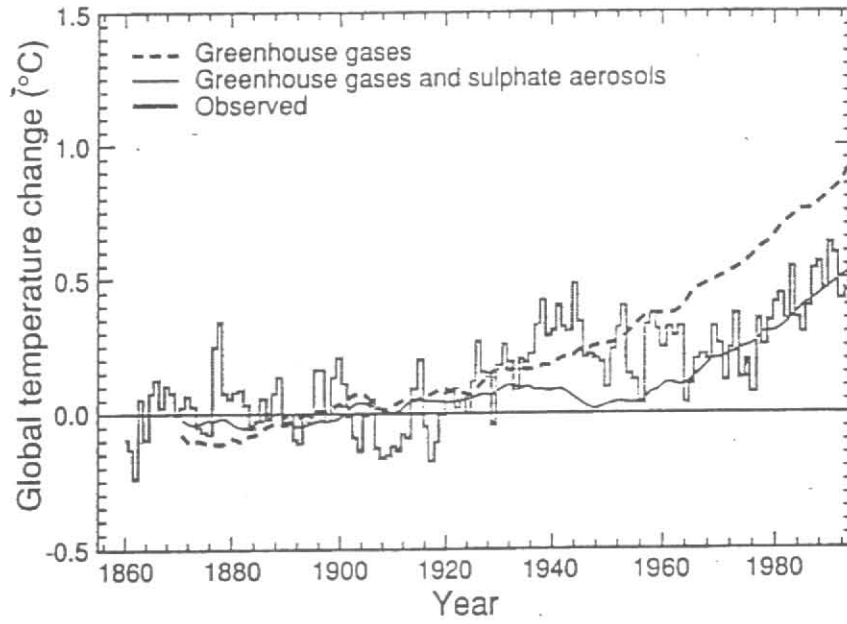


Fig. 1. Observed global mean surface temperatures for the period 1860 to 1980 compared with model simulations (IPCC 1994)

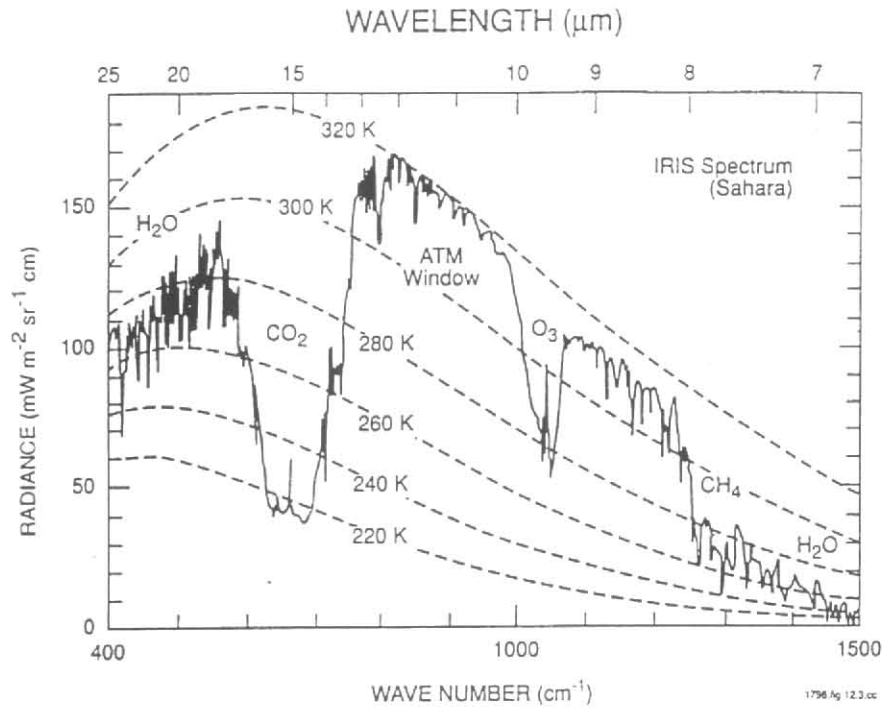


Fig. 2. Satellite measurements of terrestrial radiation showing significant absorption by H₂O, CO₂, O₃ and CH₄ contributing to the greenhouse effect

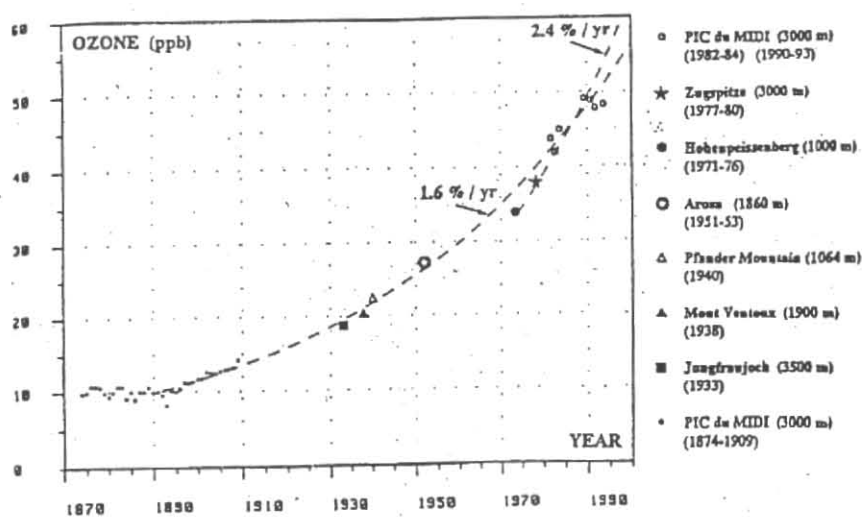


Fig. 3. Long-term trend in surface ozone at different locations (after Marengo *et al.* 1994)

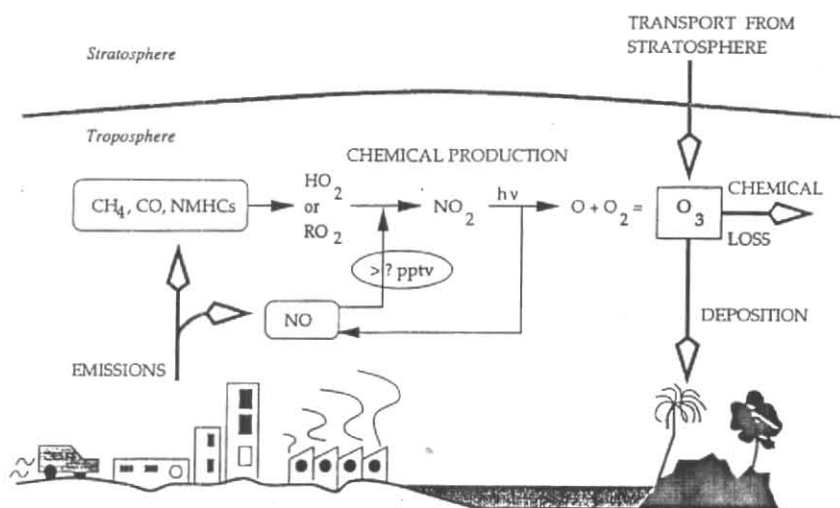


Fig. 4. Sources and sinks of tropospheric ozone

(iii) Higher tropopause level (16-18 km) over the tropics when compared to mid-latitudes (12-14 km) and high latitude regions (10-12 km) gives rise to a situation in which most of the biogenic air in the middle and high latitude regions originate in the tropics and (iv) higher water vapour content and lower tropopause temperatures gives rise to a special features of the chemistry in the tropical troposphere. Another special feature of the tropics is the frequent occurrence of convective storms which transport large quantities of biospheric air across

the boundary layer into the free troposphere where the life times of the trace gases are large and they can have a longer term impact on atmospheric physicochemical processes.

In the tropics the Asian region has features which make it special significant for climate change studies. It is a densely populated/inhabited region, currently experiencing a rapidly expanding economy with concomitant growth in industrial and human activity such

as intense land use change. All this makes this region highly prone to human induced perturbation in atmospheric composition relevant for climate change.

2. Greenhouse effect in the earth's atmosphere

Greenhouse effect is largely due to trapping of the terrestrial long wave radiation by the atmosphere and results in raising the mean surface temperature by about 33°K. The contribution of different atmospheric constituents is as follows :

H ₂ O	CO ₂	N ₂ O	CH ₄	O ₃	Others (CFCs, CCl ₄ , NH ₃ , NO ₂ , O ₂ etc.
20.6°K	7.2°K	1.4°K	0.8°K	2.3°K	0.8°K

Water vapour is seen to be the largest contributor, contributing about 60% to the total. This is also seen in Fig. 2, which shows a spectrum of the terrestrial long wave radiation as seen from space (Hanel *et al.*, 1972). Water vapour and carbon dioxide have a large number of absorption bands in the 4 µm to 100 µm region and their role in atmospheric radiation budget has been known for a long time. The wavelength region 8 µm to 12 µm is free from CO₂ and H₂O absorption and is known as the atmospheric window. Methane and nitrous oxide have absorption features in the window region. Ozone has a strong absorption band around 9.6 µ. Hence even though their relative concentrations are small, they become important greenhouse gases.

Even though water vapour in the atmosphere is the major contributor to greenhouse effect in the earth's atmosphere, it is not affected by human activities and its abundances have been relatively constant with time (changes have taken place only in the early stages of atmospheric evolution). The concentration of most of the other radiatively active gases, except O₂, have been increasing with time largely due to anthropogenic activities and contribute to enhanced greenhouse effect - Global Warming and Climate Change. CO₂ is the main contributor, contributes about 55% in global warming (IPCC, 1990). Next in importance is the fluorocarbon family of CFCs and HCFCs, 24% followed by methane 15% and nitrous oxide 6%.

Even though ozone is a major greenhouse gas next only to carbon dioxide from the mean greenhouse effect point of view, it does not figure in most climate change estimates because of lack of adequate reliable information on tropospheric ozone trends. In recent years there have

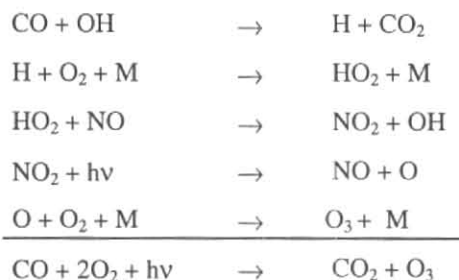
been several studies that show that tropospheric ozone as well as ozone near the surface (in the biosphere) has been on the increase in several regions of the globe. Wege *et al.* (1989) analyzed a twenty-year record (1967 to 1987) of balloon ozonesonde observations at Hohenpeisenberg and found a roughly 1 ppbv per year, which amounts to 2 to 2.5% per year increase at all heights in the 2-8 km region. Similarly Staehlein *et al.* (1994) observed a 1.5% per year increase of all altitudes in the troposphere during the period 1975 - 1985. Bojkov (1988) estimated that on the average tropospheric ozone has been on the increase at the rate of 1% to 2% per year over the past few decades even though there are stations, which do not show any increase or even show a negative trend. Surface ozone has been on the increase at almost all sites where there has been a systematic record of observation. Marengo *et al.* (1994) suggest an increase of 1.6% to 2.4% per year over the last forty years (Fig. 3). Tropospheric ozone exhibits large spatial and temporal variations, spatial features include regional and local effects which need to be delineated from the large scale features, which are of interest to climate change. However, several recent studies indicate that tropospheric ozone is indeed an important contributor to global warming and climate change, may even be the second most important candidate for climate change studies.

3. Tropospheric ozone and its chemistry

Ramanathan and Dickinson (1979) were the first to point out the importance of ozone in greenhouse effect and global warming studies. On a per molecule basis the importance of tropospheric ozone is 1600 times more than that of CO₂. Most of the ozone in the atmosphere is in the stratosphere in the altitude region of 20 to 35 km. Troposphere contains only 10 to 14% of the total ozone. Nevertheless this is more important for climate change problem since most of the greenhouse warming of the earth's atmosphere takes place in the altitude region of 8 to 16 km. Further, since the half-width of the rotational lines is proportional to atmospheric pressure, IR absorption by ozone is more dominant at these altitudes inspite of the low ozone mixing ratios in the region.

Fig. 4 illustrates the sources and sinks of tropospheric ozone. The sources are transport from the stratosphere and *in situ* photochemical production. The sink is mostly due to deposition to the ground and subsequent destruction at the surface, even though there is some chemical destruction. It was earlier believed that most of the ozone in the troposphere is due to downward transport from the stratosphere. However, in recent decades it has become clear that there is significant *in situ* production of ozone in the troposphere (Chameides and Walker, 1973, Crutzen, 1984) and on a global average,

in situ production is as important as transport from stratosphere (Levy *et al.*, 1985). *In situ* production involves photooxidation of several pollutants, such as CH₄, CO and non-methane hydrocarbons (NMHCs) released into the atmosphere from the surface (Fig. 4). The oxidation involves the peroxy radical HO₂ and requires a certain amount of background nitric oxide levels. A typical reaction scheme for CO is as follows :

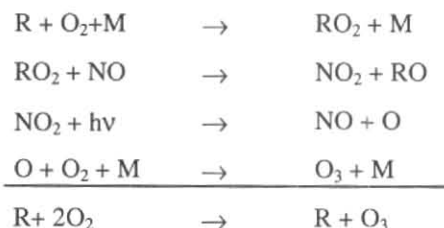


The OH radical comes from photodissociation of O₃



The OH and the NO_x radicals are recovered in the tact after the reaction cycle.

Similar, but somewhat more involved reaction cycles can be written for CH₄ and several other organic compounds (both industrial and vegetation emissions).



Where R can be any organic molecule like CH₃, C₂H₅ or more complex hydrocarbons. In the absence of sufficient NO, instead of



and reaction cycle ends up in destruction of O₃ rather than production.

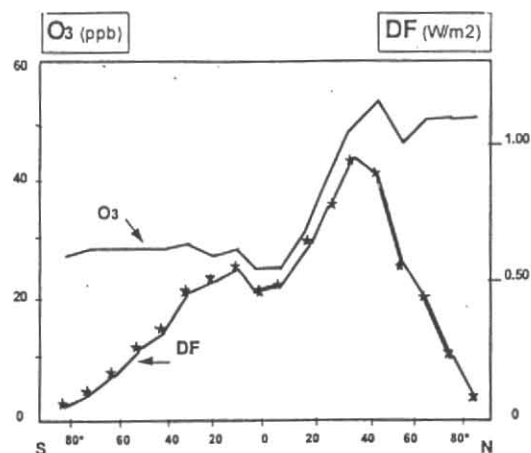


Fig. 5. Global distribution of radiative forcing of tropospheric ozone (after Marengo *et al.* 1995)

Hence the key to *in situ* production of tropospheric ozone is in addition to solar radiation availability of pollutants and sufficient NO-NO_x. These are called ozone precursors. Sources of these precursors for the production of tropospheric ozone are mainly three (i) anthropogenic origin, (ii) lightning and (iii) supersonic aircrafts. In addition to this downward transport from stratosphere to troposphere should also be considered. However, most of the sources for these precursor gases are believed to be of anthropogenic origin. Hence, tropospheric production of ozone exhibits large spatial variability. More production is expected in the northern hemisphere than in southern hemisphere. This is illustrated by Fig. 5 which shows the global distribution of radiative forcing by tropospheric ozone based on observations (Marengo *et al.*, 1995; Lelieveld and Dorland, 1995). It shows a distinct asymmetry between northern and southern hemispheres and a maximum in 40°-60°N region. A model study by Lelieveld and Van Dortland shows that global tropospheric ozone content has increased by a factor of 1.7 since pre-industrialization times (1850-1990) as a result of anthropogenic CO +CH₄ emissions.

4. ISRO-GBP programme of monitoring of ozone and its precursor gases in the Indian region

India has a long history of atmospheric ozone studies. G.M.B. Dobson made some pioneering measurements with his spectrophotometer at Kodaikanal in 1945 as part of a global observation campaign. Systematic observations of ozone in India were initiated somewhat later under the leadership of K.R. Ramanathan who set up a network of ozone spectrophotometer stations in India. Both total ozone as well as Umkehr observations are being made from a network of stations, which include Kodaikanal, Pune, Mt. Abu, Ahmedabad, Varanasi, New

Delhi and Srinagar. Recently, this network has been augmented by the installation of Brewer spectrophotometer, which can measure in addition to ozone, NO_2 as well as ground reaching UV radiation in six selected wavelengths. Some of these stations have now a data base extending 30 years or more and this data has been used to study several features relating to the behaviour of ozone in the tropics as well as its short term and long term variations. Balloon ozonesonde ascents for measuring the ozone vertical distribution are being made from three stations, viz. Trivandrum (8°N), Pune (18°N) and New Delhi (28°N) since the early seventies. Surface ozone is being monitored by the bubbler instrument at a number of sites. However, there has been no measurement of the ozone precursors, CH_4 , CO , NMHCs and NO_x in the Indian region, which is needed for assessing the contribution of *in situ* production of ozone at the surface and in the free troposphere. Recognizing this, a systematic programme of monitoring ozone and its precursor gases in the Indian region was mounted in the early nineties under ISRO's Geosphere Biosphere Programme. The programme consists of systematic (routine) monitoring of ozone and regular measurements of its precursor gases CH_4 , CO and NO_x at a number of sites selected to represent different types of environments, viz. Ahmedabad (urban polluted), Gadanki (relatively clean rural), Mt. Abu (high altitude free troposphere) and Trivandrum (coastal/marine environment). Even though these measurements are made within the boundary layer (with the exception of Mt. Abu), it is expected that the measurements are representative of the free troposphere in these regions in so far as the large scale features and long term trends are concerned.

5. Measurement programme

Ozone is being continuously monitored (normally at fifteen minute intervals and more frequently during special observation periods/campaigns) using a standard dual beam UV analyzer based on ozone absorption at the mercury line 253.7 nm. Total NO_x ($\text{NO} + \text{NO}_2$) is also being continuously monitored with a standard chemiluminescent analyzer based on measurement of the luminescence produced by the reaction of NO with O_3 . There is also provision for separating the NO and NO_2 components in the NO_x data. CO and CH_4 are being monitored by a programme of regular gas sampling and subsequent gas chromatographic analysis of the samples the following table gives the details of data collection and availability from the programme.

Ahmedabad	O_3	Nov. 1991 till Dec 1995
	NO_x	Nov 1993 till Dec 1995

Gadanki	CH_4 , CO	Jan 1993 onwards
	O_3	Nov 1993-1996 with some breaks
	NO_x	Nov 1993-1996 with some breaks
Mt. Abu / Gurushikar	CH_4 , CO	1994-96
	O_3	1995 onwards
	NO_x	1995 onwards
	CH_4 , CO	1995 onwards

Some sporadic measurements were also made during 1993-94.

Trivandrum	O_3	1997 onwards
	NO_x ,	(to be initiated)
	CH_4 , CO	
Remote marine Observations	O_3 , NO ,	Several ocean cruises in the Arabian Sea and Indian Ocean during 1996, 1997, 1998 and 1999 including INDOEX
	CH_4 , CO	

In the following, we will present a few results from the programme that are relevant to the climate change problem.

6. Results

Diurnal variations of surface ozone are shown in Fig. 6 for Ahmedabad, Gadanki, Mt. Abu and Indian Ocean. Both Ahmedabad and Gadanki show day time buildup of ozone during the morning hours and decreasing mixing ratio in the evening and night hours. Ozone production is basically due to photochemical oxidation of CO , CH_4 and NMHCs in the presence of higher levels of NO_x . Even though both these stations show increase in the concentration of ozone during forenoon hours and decreases during the afternoon hours, the rate of decrease is slower for Gadanki than for Ahmedabad. Since loss of ozone is basically due to reaction with NO , low levels of NO_x (NO and NO_2) at Gadanki cause this slow decrease.

Mt. Abu shows a decrease during the day time in surface ozone. This is attributed to two factors, (i) due to very low levels of NO_x (the detection limit of the instrument is about 350 pptv), there may be some net loss of ozone and (ii) some loss of ozone could be due to surface loss along the mountain slopes when the wind is upward during daytime. It is important to note that the overall level of surface ozone at Mt. Abu is about 40-45 ppbv, which is higher than sometimes the peak values at

Ahmedabad and Gadanki. This is due to the elevation of Mt. Abu. The laboratory is situated at around 1700 m height.

Surface ozone variation in the Indian Ocean region (Lal *et al.*, 1988) is different from that seen at all the three land sites. It shows a slight decrease in the mixing ratio in the afternoon hours. Boundary layer mixing and photochemical loss of ozone are the two main processes responsible for this decrease. The overall low level, about 20 ppbv of ozone, is representative of cleaner marine environment. Ozone mixing ratios as low as 5-10 ppbv have been observed in pristine marine environment.

The diurnal variations of NO_x and that of CO (Fig. 7) are totally different from that of ozone. Both NO_x and CO show higher values in the morning around 8 am and in the evening /night around 8-10 pm and lowest values in the afternoon around 4 pm. The morning and nighttime higher concentrations may be due to anthropogenic emissions and boundary layer processes. However, the noontime low values are due to their consumption in producing higher levels of ozone. Both CO and NO_x are used in the production of ozone. So, while ozone is maximum during noon hours, these two ozone producing gases are lowest.

However, if we see the seasonal variation of ozone together with NO_x and CO and other ozone precursors like CH_4 we find that higher levels of precursor gases lead to higher levels of ozone and *vice versa* (Fig. 8). Precursor gases as well as ozone are higher in winter season at Ahmedabad and lower in the monsoon season. Average daytime (1000 - 1600 hr) ozone increases from low values (15-20 ppbv) in monsoon period to as high as 60 ppbv in winter. CO and NO_x vary from 200 ppbv and 5 ppbv respectively in monsoon period to about 800 ppbv and 15-20 ppbv respectively in winter. This clearly indicates the role of precursors in changing the levels of ozone. The precursors are lowest in the monsoon season due to the wind pattern, which brings the cleaner marine air from the Indian ocean and the Arabian Sea and washout of pollutants (Lal *et al.*, 1988). The wind patterns in the winter is reversed and it is from the north-east direction, which brings the continental polluted air.

7. Long-term changes

Surface ozone has been measured at the same location at Ahmedabad during 1954-55 and also from 1991 onwards (Naja and Lal, 1996). Measurements during 1954-55 were made using an electrochemical titration instrument acquired through the International Ozone Commission. Surface ozone measurements were

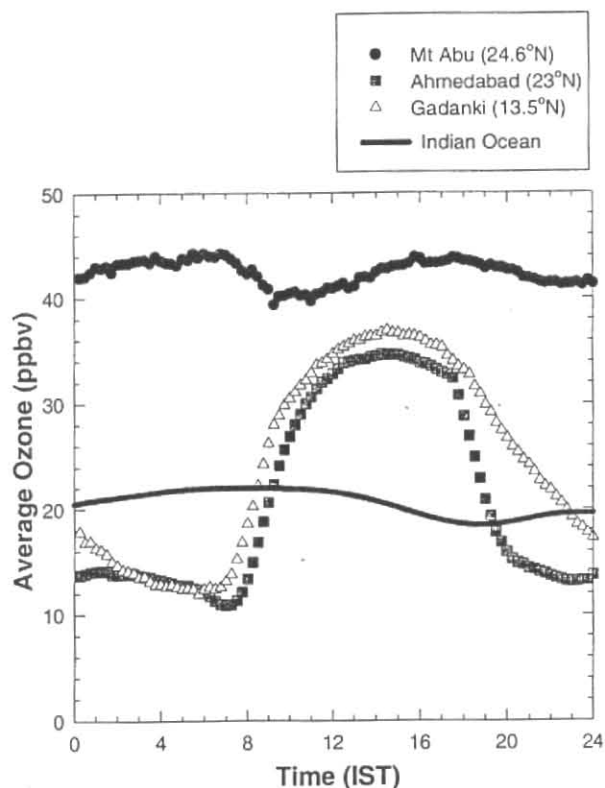


Fig. 6. Average diurnal variation of surface ozone at different sites in the Indian region

made five times a day for one year. Present measurements are made very 15 minutes using an automatic analyser based on absorption of UV radiation at 253.7 nm. Fig. 9 shows diurnal variations in ozone during 1954-55 and 1991-93. It shows clearly, larger diurnal buildup of ozone during the day in 1991-93 period than in 1954-55. While in 1954-55, the maximum daytime ozone was about 25 ppbv, the present values go as high as 55 ppbv for the same period. Even the monthly average values also show this difference clearly. Both the data sets show low values during monsoon period but the annual maxima are in different seasons. During 1954-55, the maximum ozone mixing ratios were observed in spring, while the present measurements show maximum in winter season (Fig. 10). This is an important feature. Many locations worldwide show maxima in spring, winter maxima is a typical feature of Ahmedabad. This is mainly due to the location of Ahmedabad and the large scale wind patterns in different seasons. The wind pattern has not changed over this period, but the north-easterly wind is bringing more polluted air to this site. The spring maximum is caused by relatively higher levels of pollutants together with higher levels of solar flux giving rise to higher photochemical production of ozone.

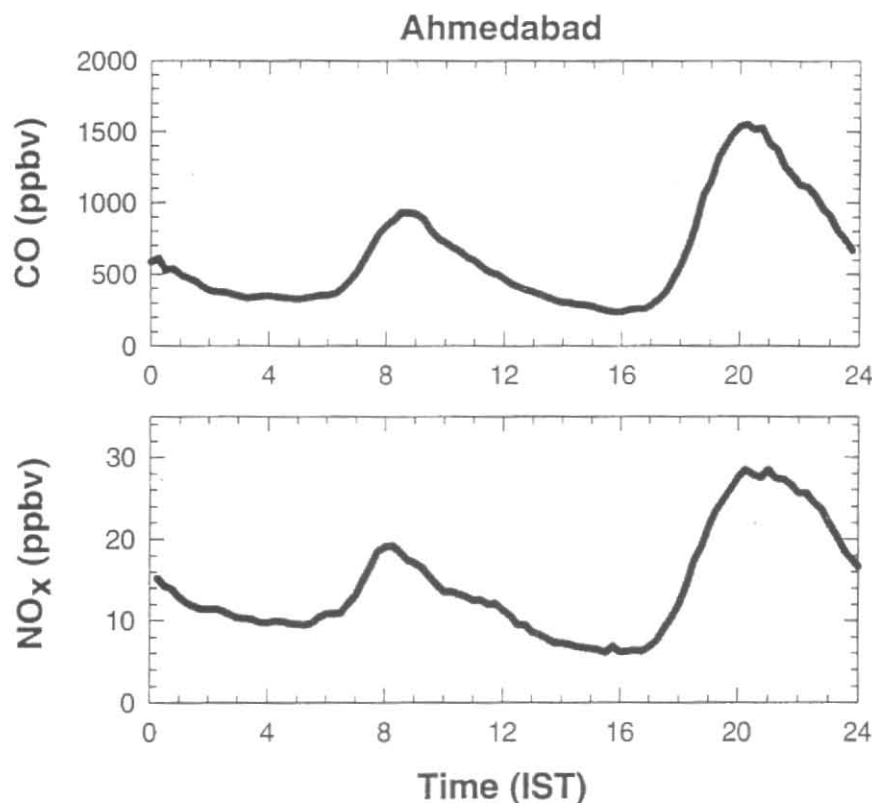


Fig. 7. Typical diurnal variation of CO_2 and NO_x at Ahmedabad

The present measurements show higher levels of precursors during winter than in spring offsetting the effect of increase in solar flux during spring/summer season. No data is available for the precursor gases during 1954-55 period. However their levels are likely to be much lower than the present levels.

In the Ahmedabad region most of the contribution to the precursor gases comes from vehicular pollution. The number of vehicles in the city during 1954-55 was only a few hundreds. The two wheeler industry picked up dramatically in sixties and presently their numbers have exceeded one million. Automobiles and the two wheelers are the major sources of NO_x and CO. The annual average ozone concentration at 1400 hr increased from a value of 26 (± 6) ppbv during 1954-55 to a value of 41 (± 12) ppbv during 1991-93 registering a linear increase of 1.91 (± 0.04)% per year. Even in the night (at 2100 hr) and in the early morning (at 0600 hr) during monsoon months, the average ozone concentration has increased from a value of 8.9 (± 4) ppbv in 1954-55 to a value of 10.7 (± 3.3) ppbv in 1991-93 showing an increase of 0.49 (± 0.37)% per year. This can be ascribed to the change in the background ozone levels in

this region. There are many locations in the world where such surface ozone increases have been observed. At Mauna Loa (19°N) the annual growth rate of ozone is found to be 0.37% per year (Oltmans and Levy, 1994). Arkona (54.7°N) also shows a significant linear increase from 1956 - 79 by 2.4% per year, but subsequently a linear decrease during 1980s (Low *et al.* 1990) has been reported. However, in cleaner sites in Canada and at South Pole a declining trend in surface ozone has been observed (Logan 1994, Tarasick *et al.*, 1995, Oltmans and Levy, 1994). Chakrabarty (1999) observed similar increasing trend in the Umkehr layer I representing troposphere at other stations in India also [Delhi (28°N), Ahmedabad (24°N) and Trivandrum (8°N)].

Marenco *et al.* (1994) have studied ozone time series data at several elevated sites for the period (1974 - 93). They conclude that surface ozone has been increasing in the Western Europe over the period at a rate of 1.6% per year. Many sites in the southern hemisphere [American Samoa (14°S), South Africa (34°S), Cape Grim (41°S)] also show increasing surface ozone in the last two decades.

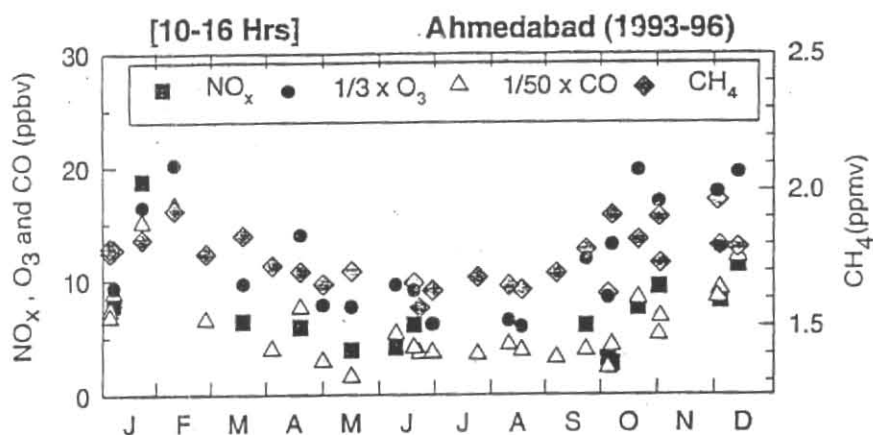


Fig. 8. Seasonal variation of surface ozone and its precursor gases CH_4 , CO_2 and NO_x .

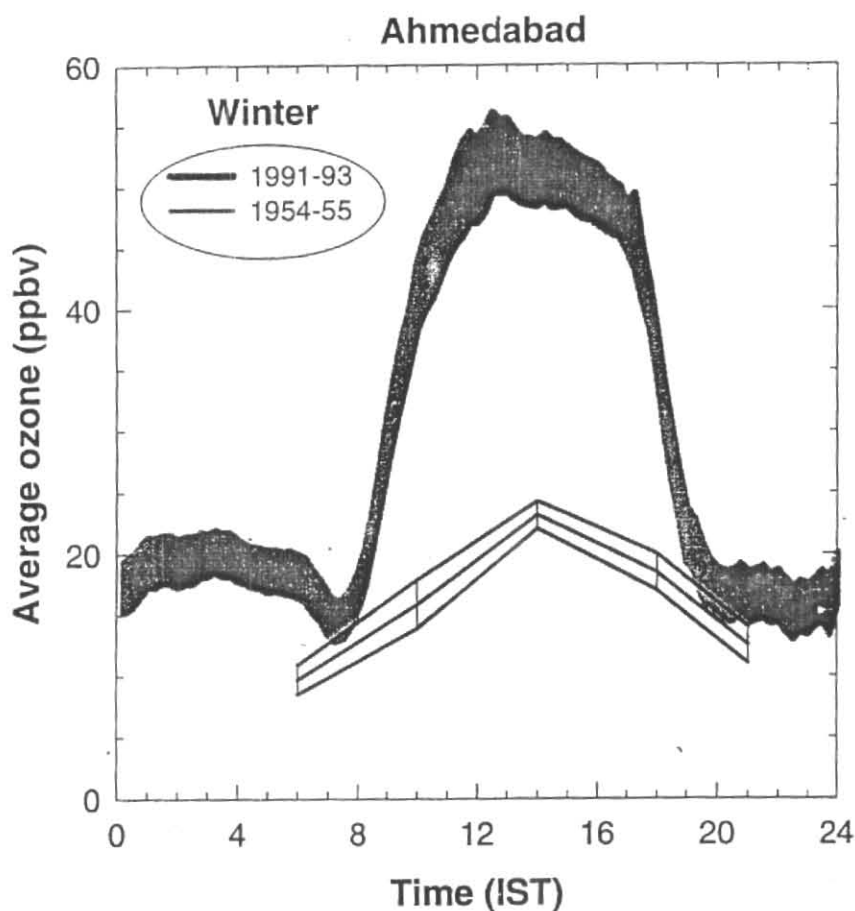


Fig. 9. Long-term changes in surface ozone at Ahmedabad

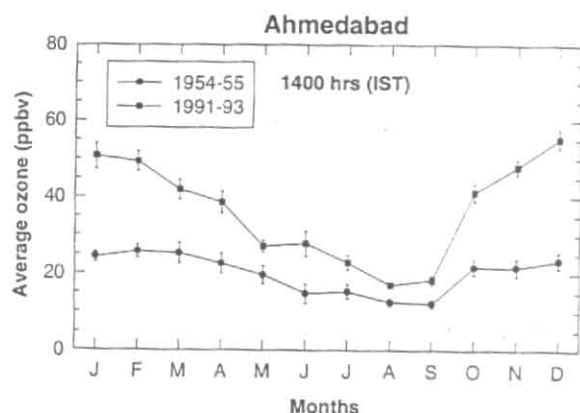


Fig. 10. Seasonal variation of noontime average surface ozone during 1991-93 compared with that during 1954-55

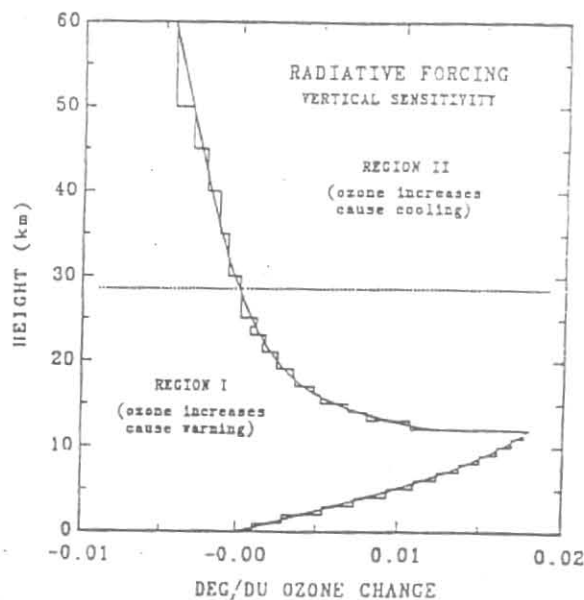


Fig. 11. Height profile of the radiative forcing of ozone (Lacis *et al.* 1990)

8. Conclusions

Realizing the importance of tropospheric ozone in the absorption of the earth's infrared radiation and its increasing trend, estimates have been made for its contribution to the change in the radiative forcing from the pre-industrial times to the present. Marengo *et al.* (1994) have found that the relative contribution of ozone to the change in the radiative forcing is about 18% which is next to CO₂ only. Contributions by CH₄, N₂O and CFCs are lower than that of ozone. This is reflected in the 1994 revision of IPCC report.

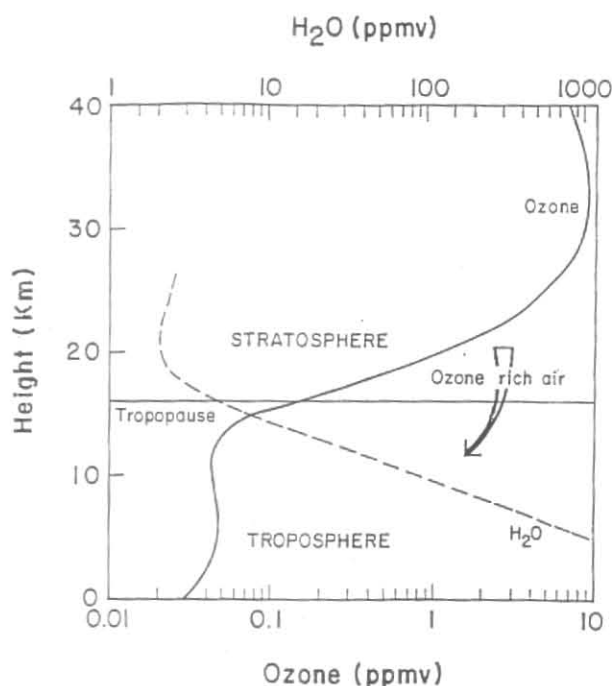


Fig. 12. Characteristics of stratosphere-troposphere transport of ozone

Based on the population growth and energy consumption, the 3D IMAGES model of NCAR suggests that future changes in tropospheric ozone should be largest in the tropics, especially in Asia (Brasseur *et al.* 1998). This will enhance the contribution of tropospheric ozone to climate change.

It is observed that the maximum effect of ozone on radiative forcing is around the tropopause region as shown in Fig. 11 (Lacis *et al.* 1990). In order to understand the effect of ozone on climate, there is a need to study the variability, sources, sinks *etc.* of ozone in this crucial altitude region. This needs measurements of vertical profiles of ozone. The extent of the downward transport of ozone from the ozone rich stratosphere into the troposphere is highly uncertain. As shown in Fig. 12, if there is a transport of ozone from the stratosphere into the troposphere, it will be possible to differentiate the stratospheric source if vertical distribution of ozone and water vapour are made simultaneously. Very high levels of ozone upto 500 ppbv have been observed in the tropical troposphere from the aircraft measurements. The authors link these high ozone levels to the transport from the stratosphere. Almost zero level of ozone has been observed on some occasions in the upper troposphere. They suggest that these could be due to convective activities. Thus in the tropical upper troposphere widely varying levels of ozone from near zero to as high as 500 ppbv has been observed. A study of the vertical distribution will also provide insight on the transport from

the stratosphere, effects of convection, biomass burning *etc.* on ozone. While IMD is regularly making measurements of vertical distribution of ozone at three sites in India (Delhi, Pune and Trivandrum), there is a need for more extensive measurement so, ozone preferably with simultaneously water vapour measurements of ozone and related gases in the troposphere and lower stratosphere are ideal due to their global coverage and long-term measurements.

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