

Monitoring of Various Atmospheric Parameters over Maitri, Antarctica

S . L. JAIN

Radio and Atmospheric Sciences Division
National Physical Laboratory, New Delhi-110012
E-mail: sljain@cnspl.ren.nic.in

Abstract

The earth's environment is constantly changing. The scientific evidence indicates that these changes are result of a complex interplay among a number of natural and human related systems. Therefore in the recent times, concern has grown about global change which is related to natural and anthropogenic alteration of the Earth's environment. Among them the important issues which are dangerous for the survival of life on the earth are global green house warming, urban and regional atmospheric pollution, regional increases in tropospheric ozone and the decrease in stratospheric ozone in general and ozone hole over Antarctica in particular acid rain etc. The reporting of ozone depletion in general and ozone hole over Antarctica in particular witnessed a unprecedented surge of interest in the monitoring of various trace species and development of various models. The monitoring of green house gases also has an important role in the understanding of global change. In view of the above, various state of art systems have been set up at Maitri (70° 46'S, 110° 45'E), Antarctica for measurements of various atmospheric parameters such as green house gases, column ozone, water vapour UV-B radiation, aerosol optical depth, vertical profiles of ozone etc. The averaged CO₂ during the year 2002 was found out to be 368.32 ppm whereas during 2003 it was found out to be 369.51 ppm. The Annual average CH₄ from Feb 2003 to Feb 2004 was found out to be 17005 ppm. The daily average concentration of CO was found to vary in between 30 ppb to 60 ppb during the observational period of Jan to April 2004. The monthly mean concentration was observed 44 ppb, 38 ppb, 56 ppb and 58 ppb in January, February, March and April 2004 respectively. The minimum total ozone column of about 135 DU in 1997, 185 DU in 2002 and 126 DU in 2003 has been observed at Maitri. The ozone hole duration observed at Maitri during 2003 was 66.6%, 46.6% and 20.7% in the year 1997 and 2002 respectively. Our measurements were also compared with those obtained by satellite data and are in good agreements with our findings. However it will be too early to conclude about ozone hole recovery and to confirm it regular observations of column along with other parameters are being continued at Maitri. In the present communication the salient features of the highly sophisticated system such as laser heterodyne,

sun photometer, gas chromatogram etc. for atmospheric studies at Maitri and the results obtained will be discussed in detail.

Keywords

Tropical estuary, sediment budget, Turbidity Maximum Zone, India

Introduction

The earth's environment is constantly changing. The scientific evidence indicates that these changes are result of a complex interplay among a number of natural and human related systems. In 1995 the intergovernmental panel on climate change (IPCC, 1995) among other conclusions stated that the balance as evidence suggests that there is a discernible human influence on global climate. Therefore in the recent times, concern has grown about global change - which is related to natural and anthropogenic alteration of the Earth's environment. Among them the important issues, which are dangerous for the survival of life on the earth, are global green house warming, urban and regional atmospheric pollution, regional increases in tropospheric ozone, the decrease in stratospheric ozone in general and ozone hole (Johnston, 1971; Farman et al. 1985; Stolarski et al. 1986) over Antarctica in particular, acid rain etc. The atmospheric trace gases play an important role in many processes such as biosphere-troposphere interaction, the chemistry of troposphere, and the troposphere - stratosphere exchange. The monitoring of green house gases has an important role in the understanding of global change. The green house effect of CO₂ increase which has been the subject of scientific studies since later half of the nineteenth century (Tyndall, 1863; Arrhenus, 1896; Chamberlin, 1899) but the CO₂ problem gained tremendous momentum during last two decades. Now it has been recognized that the green house effect due to trace gases such as CFC's, CH₄, O₃, N₂O, H₂O etc. is as much as that due to CO₂ while it was only due to CO₂ during pre industrial era to 1950's. The greenhouse effects of many-polyatomic trace gases (eg. CFC's) is greater than that of CO₂ increase on a molecule-to-molecule basis. For example addition of one molecule of F-11 or F-12 to the atmosphere has the same warming effect as that due to addition of ten thousand molecule of CO₂. The list of the green house gases is growing day by day. The increase in these gases during the next several decades will lead to global warming and due to this the impact on coastal cities and low lying countries such as Bangladesh, Netherlands, Maldives islands etc. could be a catastrophic. The measurements of the various green house gases are being made at only few stations located at point Barrow (71.3°N, 156.6°W), Mauna Loa (19.5°N, 156.66°W), Cape Matatula, American Samoa (14.3°S, 170.66°W), & South pole, Alert North West Territories, Canada (82.5°N, 62.3°W), Tasmania (40.7°S, 144.8°E) etc. Various investigators (Tyndall 1863; Arrhenus, 1896; Chamberlin, 1899; Pearman et al 1984; Ayers et al. 1990; Nakazawa et al 1991;

Keeling et al. 1996; Matsudea et al. 1996; Notholt, 1997a, b; Reid et al. 1997; Francey et al. 1998; Stauffer et al. 1998; Taylor et al. 2000; Chedin et al. 2002, 2003; Cruber et al. 2002; Derwent et al. 2002; Idso et al. 2002; Nasrallah et al. 2003) have reported measurements as CO₂ in the upper troposphere as well as ground level. Methane (CH₄) is a biogenic gas produced from variety of anaerobic processes and the most abundant organic trace gas in the atmosphere. In addition, methane is currently the second most important greenhouse gas emitted from human activities, which have strong absorption bands and trap part of the thermal radiation from the earth's surface (Wang et al. 1976). On a per molecule basis, it is about 32 times effective greenhouse gas than additional CO₂. Therefore, it is of concern that increasing CH₄ may affect significantly on the global heat balance, causing a possible elevation of the global surface temperature. Carbon monoxide (CO) does not absorb terrestrial infrared radiation strongly enough to be counted as a direct greenhouse gas, but its role in determining tropospheric OH indirectly affects the atmospheric burden of CH₄ (Isaksen and Hov, 1987) and can lead to the formation of O₃. The most of the observations for green house gases are being made on western longitudes and almost no regular measurements in our region.

In view of the above, various state of art systems have been set up at Maitri (70° 46'S, 110 45'E), Antarctica for measurements of various green house gases, column ozone, water vapour, UV-B radiation, aerosol optical depth and vertical profiles of ozone which in turn will go a long way to fill in the gaps and provide valuable data for modeling studies. The observations, made at high latitude like Antarctica will also help to understand photochemical, heterogeneous and dynamical processes that control the distribution of atmospheric trace gases. In the present communication the salient features of the highly sophisticated system such as laser heterodyne, sun photometer, gas chromatogram, CO analyzer setup for atmospheric studies at Maitri and the results obtained will be discussed in detail.

Greenhouse Gases

The "greenhouse effect" is a naturally occurring phenomenon that results from the ability of certain gases, such as water vapor and carbon dioxide, to change the radiant energy balance of the Earth. These greenhouse gases keep the planet habitable. They absorb the infrared wavelengths of radiant energy more efficiently than they absorb the radiant energy at solar wavelengths. Thus, greenhouse gases allow solar radiant energy to pass through the atmosphere to be absorbed at the Earth's surface, but they trap most of the radiant heat emitted from the Earth's surface in the lower atmosphere, not allowing it to escape to space. Greenhouse gases influence the Earth's temperature by allowing solar radiant energy to pass through the atmosphere, where it is absorbed at the surface, and subsequently trapping most of the radiant heat that is re-emitted

into the atmosphere. In the absence of this green-house effect, the Earth's surface should have become 33°C colder than it is today. The human activity on the planet has increased the green house gases in the atmosphere and has the potential of global warming.

Experimental Setups

1. Laser Heterodyne System (LHS)

In the infrared region of the spectrum where the fundamental vibrational-rotational absorption bands of most of the atmospheric molecules are located and a study of window region (8- 14 μm) with high resolution instruments give quantitative information and their concentrations at various altitude. Infrared laser heterodyne spectroscopy provides a powerful tool for identification of weak molecular and atomic species (Menzies, 1976).

The advantages of the laser heterodyne system over other techniques are its ultra high spectral resolution, high spatial resolution, high quantum detection efficiency and very good signal to noise ratio. The high resolution makes the system very selective as the interference problem due to overlapping lines or bands are minimized and the lines can be resolved completely. The laser heterodyne system with one GHz acousto-optic spectrometer (AOS) as backend, was set up at Maitri an Indian Antarctic station (70° 46' S, 11° 44' E) during 1993-94 and 1994-95 Antarctic summer to obtain ozone profiles and is first of its kind over Antarctic region. However the system was brought back that time due to non-availability of liquid nitrogen during winter, as liquid nitrogen plant could not be operationalised during summer of 1997. Again in the sixteenth expedition the system has been setup at Maitri and made operational in summer as well as winter. The liquid nitrogen plant, which was brought during 1993-94 Indian Scientific Antarctic Expedition for producing liquid nitrogen for the laser heterodyne system was also made operational during 1997.

The block diagram of the laser heterodyne system designed, developed and set up at NPL is depicted in Fig.1. In this the CO₂ laser used as a local oscillator is tuned on a line corresponding to the absorption line of the minor constituent of the interest. The solar tracker (heliostat) follows the sun and brings in the solar radiation. The incoming chopped solar radiation is filtered out and IR radiation (8-12 μm) and CO₂ laser beam of moderately low power are combined via a Zinc Selenide beam splitter. The solar radiation and CO₂ laser beam are co-aligned and focused on the high speed liquid nitrogen cooled Hg-Cd-Te detector which acts as a mixer as well as narrow band filter. The detected signal is nothing but the difference frequency (IF) The IF signal is further amplified in low noise wide band (5-1200 MHz) RF amplifiers and passed through various RF filter channels (25-1200) MHz. The signal from various channels is square law detected and is fed to lock-in amplifier where

synchronous detection takes place. The signal can be read directly from the lock-in-amplifier or recorded on a strip chart recorder. The observations taken at different frequency channels in the wings of the absorption line of the minor constituents of interest would resolve the line completely and vertical profile can be obtained with these data using inversion technique. The number of points in the wing of the line would decide the height resolution. This system was being manually operated by tuning various RF filters (25-1200 MHz) and was time consuming and subjected to errors in the measurement. In view of the above to make this system semi-automatic one, a wide band acousto-optic spectrometer has been developed.

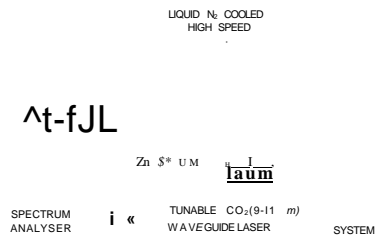


Fig. 1. Block diagram of laser heterodyne system.

2. Acousto-Optic Spectrometer (AOS)

The Acousto-Optic technique for power spectral measurement have been exploited for a variety of signal analysis applications (Turpin,1981). The Bragg cell converts RF signal to ultrasonic traveling waves modulating the optical index of the cell. The cell is illuminated across its aperture by a laser beam. A fraction of light is diffracted by acoustic waves, the angle of diffraction is determined by the frequency while the intensity of the diffracted light is proportional to the power of the input RF signal. The intensity distribution can be detected by linear array of photo-detectors which in turn represent the required RF power spectrum. An AOS with one GHz bandwidth was designed

and developed in collaboration with Meudon observatory, France and integrated with the LHS developed at NPL, New Delhi. The block diagram of the AOS is shown in Fig. 2. The acousto optic spectrometer consists of 1 GHz Bragg cell (Li Nb O₃), diode laser at 784 nm, Fourier lens, 1050 pixel CCD array and PC based data acquisition system. A proper software and hard ware had to be developed to digitize the frequency power spectrum and stored for further analysis to get height profiles of various minor constituents.

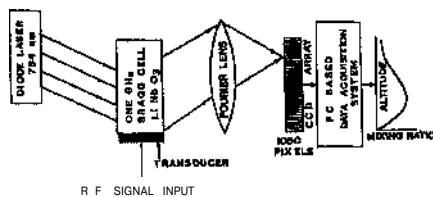


Fig 2 Block diagram of Acoustic Optic Spectrometer (AOS)

The acousto-optic spectrometer developed was tested using the laser heterodyne system of Reims University, France. The frequency power spectra obtained using an empty cell of 200 cm length and 600 milli torr ozone in the cell are as expected. The P(24) CO₂ laser line in 9.6 μ m band was used. The spectra thus obtained show very well defined ozone absorption lines. A spectral resolution better than 5 MHz has been obtained. A typical ozone line spectra obtained over Maitri, Antarctica during February 1994 is shown in Fig. 3. The use of AOS as back end of laser heterodyne system is timely and well suited to detection of weak signal buried in noise. The main advantages of the AOS are wide bandwidth, high resolution, large number of channels, high detection sensitivity and compactness, light weight and high energy efficiency.

3. MICROTOP II- Ozonometer

A highly sophisticated and hand held microprocessor based sun photometer (MICROTOP-II, Solar Light Company Make) has been used to measure the solar radiation at 300, 305, 312, 940 and 1020 nm. The block diagram of the sun photometer is shown in Fig. 4. The optical block is shaping the field of view of the instrument, filtering the incoming solar radiation, detecting it and

facilitating targeting at the sun. The electrical signals from the photodetectors are amplified, converted to digital form and numerically processed in the signal-processing block. The sun photometer used in the present case is slightly different from the conventional wheel filter type where the individual filters are rotated with the help of wheel and filtered signal is detected by the common detector and electronics. In the present case all the five filters are exposed to solar radiation simultaneously and the signal is detected using separate detectors and electronics for each channel. The first three exceptionally narrow bandwidth (2.5 nm FWHM, Full Width At Half Maximum) filter channels are used to derive atmospheric total ozone while later two channels having bandwidth of 10 nm FWHM are used for water vapour and aerosol optical depth. The FWHM i.e. full width at half maximum of first filters is 2.5 nm while that of the other two filters is 10 nm. The field of view of each optical channel is 2.5° . The system needs input parameters such as latitude, longitude and altitude of the place of observation, which were obtained from GPS receiver of the ship. On board clock and calendar keeps track of the time necessary for astronomical calculations. A built in barometer provides atmospheric pressure for the Rayleigh scattering correction and best of all, both raw data and calculated results from upto 800 measurements are stored in an on-board non volatile memory and can be both viewed on the instrument's LCD and transferred to a PC. All the data are arranged in a tabular form convenient for processing and interpretation. The instrument was used successfully at Goa, on board ship, Mauritius on the way to Antarctica and finally at Maitri. The system is presently being used to measure ozone and several other parameters at Maitri, Antarctica and it will provide first hand information to us for the study of "Ozone hole" phenomenon.

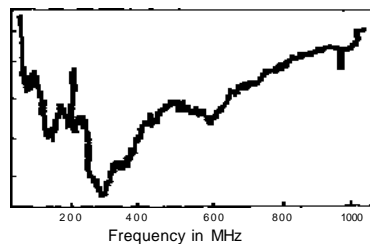


Fig.3. Observed ozone absorption line spectra near p(24) CO₂ laser Line on February 10, 1994.

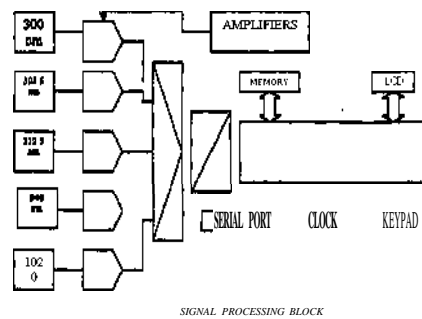


Fig. 4. Block Diagram of MICROTOP II Spectrophotometer

4. Gas Chromatograph

During 21st Indian Scientific Antarctic Expedition, the experimental facility to monitor green house gases at Maitri Antarctica was established in January 2002 and since then, the measurements of atmospheric CO₂ are being made continuously by online gas chromatography, using flame ionization detector. The GC systems are very reliable and technically less difficult to operate and maintain. In gas chromatography, chromatograms are recorded using physical method of separation of the components of a mixture by distribution between two phases and by an integrator or computer, which processes the output of detector electronically and analytically and further determines peaks height and area. Mixing ratios for the samples are determined relative to the standard calibration technique. The gas chromatograph established at Maitri during this expedition is a state of art technology consisting of an independent nitrogen generator producing nitrogen as carrier gas at site and directly connected to the system. It also has in built hydrogen generator and air compressor for hydrogen and air needed to ignite the flame ionization detector. The sample from ambient air is injected in the column by a computer controlled sampling pump for known interval of time. The appropriate software is being used to estimate CO₂ ambient

concentration. The system is being calibrated on regular basis using standard calibration gases of interest. The Gas chromatograph system block diagram is depicted in Fig.5.

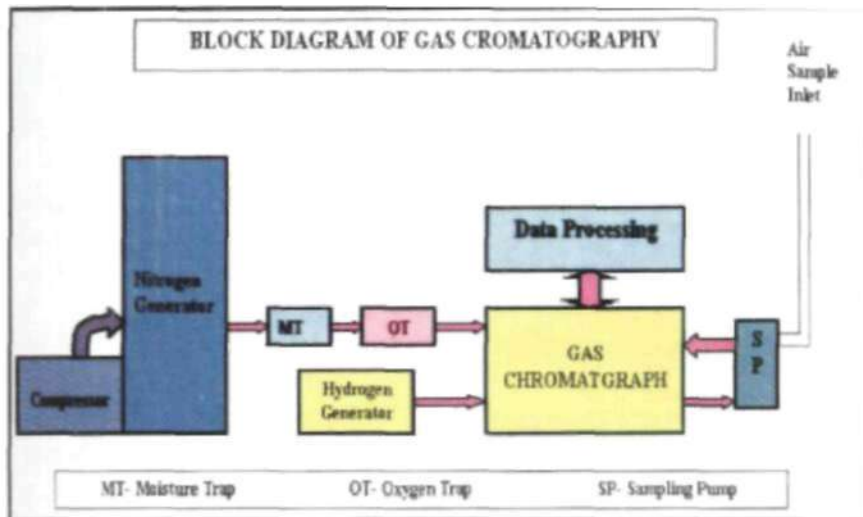


Fig.5. The Gas chromatograph system block diagram.

Inversion Technique

The composition profile or temperature profile can be obtained by analysis of individual spectral line measured at ultra high resolution through inverse solution of radiatives transfer equation(Kaplan, 1959). A Software program has been developed and tested to obtain the height profiles for ozone using inversion technique, (Jain, 1987). It is found that the retrieved profiles match well with the model profiles and are independent of initial guess (Jain, 1987). The inversion technique was also tested using actual profiles during normal and ozone hole

Results and Discussions

1. Vertical profiles of ozone

The pressure broadened absorption line width varies with altitude, which in turn used to get height profile of ozone. The absorption at the line center is strongly influenced by the upper altitude molecules while absorption at the wing of the line will be influenced by the lower altitude molecules. The absorption line profile of ozone at 1043.1775 cm^{-1} has been obtained with high resolution by laser heterodyne system using a one GHz acousto-optic spectrometer. A Typical ozone line spectrums acquired over Maitri, Antarctica during February 1994 is depicted in Fig.3. The ozone line spectra obtained on clear sunny days have been used to get ozone vertical profile using inversion technique. A guess profile of uniform mixing ratio of 3 ppm has been used for the retrieval. The system was operated during normal as well as ozone hole period. The typical retrieved ozone profiles during normal period on February 6, 1998 and during ozone hole period on October 14, 1997 are shown in Figs. 6 and Fig 7 respectively. The ozone was found to be depleted during ozone hole period from 3 percent to 68 percent in the height range 13 to 40 km.

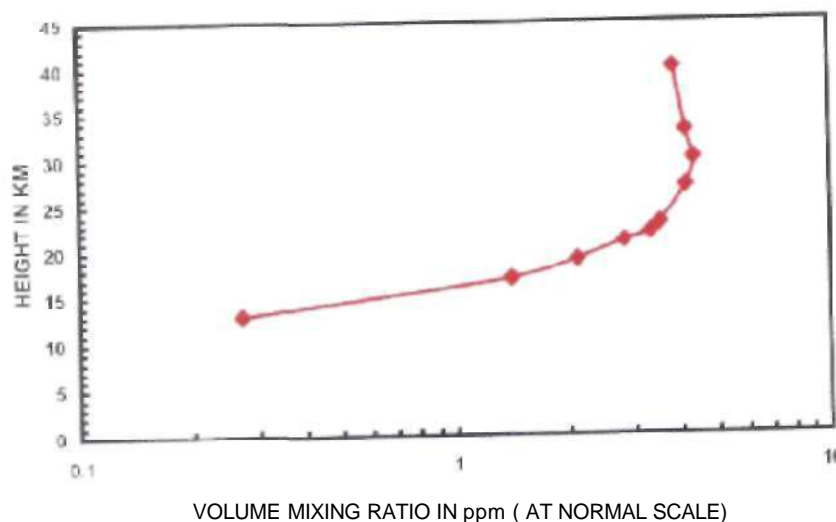


Fig .6. Vertical profile of ozone at Maitri on February 6, 1998.

The laser heterodyne system has thus demonstrated successfully its capability to monitor ozone height profiles in the atmosphere in the harsh environmental conditions like that of Antarctica during both normal and ozone hole period. However the system has some limitations as it can be operated only

during clear sky and sunny days. Also it needs liquid nitrogen for cooling the detector and therefore generation of liquid nitrogen is required which is a very difficult task at Antarctica. The monitoring of ozone along with other constituents in the atmosphere is of great importance to understand the complex interaction between atmospheric dynamics, chemistry and radiation budget which in turn requires a large data base on regular basis at tropical as well as at Antarctic latitudes. In order to extend the wavelength coverage of the CO₂ laser the other carbon isotopes such as C-14 or C-13 are to be used which in turn needs some R and D work.

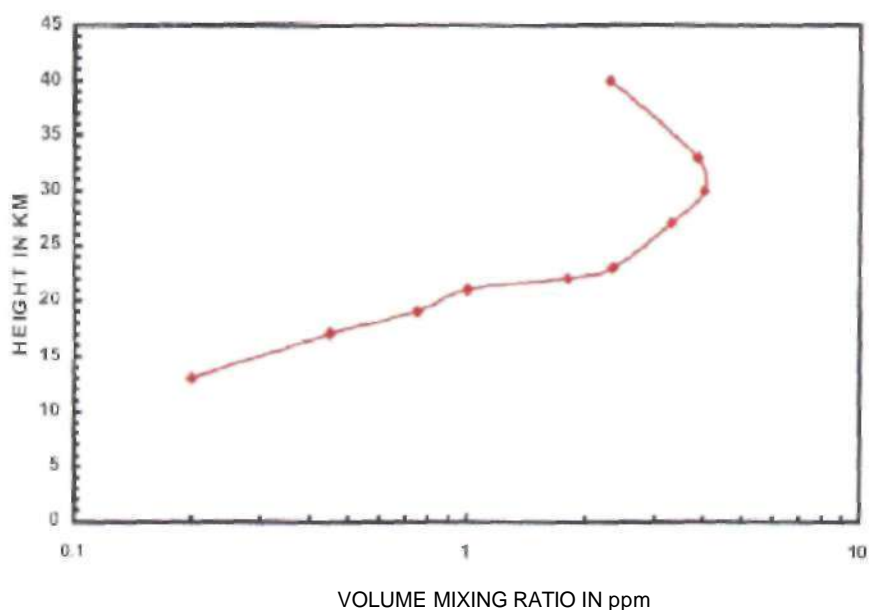


Fig .7. Vertical profile of ozone at Maitri during ozone hole on October 14, 1997.

2. Signature of recovery ozone hole

The reporting of ozone hole in particular by Farman et al. (1985) and further confirmation of the decrease in total ozone during Antarctica spring by Stolarsky et al.(1986) using Total Ozone Mapping Spectrometer (TOMS) aboard Nimbus-7 satellite data and the catalytic destruction ozone by ClO_x and NO_x in general by Johnston et al. (1971) has generated an unprecedented surge of interest in the scientific community in monitoring of ozone in the atmosphere. It has now been established that the cause of very low ozone during Antarctic spring is due to the presence of chloro-fluoro carbons, polar stratospheric clouds (PSCs) formation at very cold temperature and the formation of polar vortex.

The planetary wave phenomenon plays an important role in breaking down of polar vortex and the distribution of the springtime ozone in the Antarctica (Newmann, 1986; Chandra and R.D. McPeters, 1986). In Polar Regions high-speed wind jet circulates around the poles and serves as a barrier to air exchange between Polar Regions and mid latitudes which forms polar vortex. Very low temperature during winter leads to the formation of polar stratospheric clouds (PSCs). Temperatures colder than -78°C produce PSCs consisting of water and nitric acid trihydrate (Crutzen and Arnold 1986) whereas temperatures lower than -85°C produce PSCs of nearly pure water-crystals (Molina *et al.* 1978). Both types of PSCs provide surfaces where in the presence of ice particles and sunlight it enhance the production and lifetime of reactive chlorine and heterogeneous reactions (Cadle *et al.* 1975) occur that convert less reactive molecules into much more reactive forms that readily destroy ozone (WMO, 1999). The heterogeneous chemical reactions take place on the surface of PSCs, which are responsible for the ozone hole phenomenon (Manney *et al.*, 1996). Ozone have been found to be strongly affected by the dynamical behavior of the polar vortex (Carswell *et al.* 1998). In view of the above a highly sophisticated and hand held microprocessor based sun photometer, MICROTOP-II, has been used to measure the solar radiation at 300, 305, 312, 940 and 1020 nm to which in turn was used to obtain total ozone, water vapour, optical depth etc. The MICROTOP-II was also used on shipboard during the voyage to study the latitudinal distribution of total ozone, water vapour etc. (Jain 2001). The ozone measured by this system has been compared with those obtained by Brewer spectrometers at Maitri and found to be with in 2-3 %. The observations were carried out during 1996-1998 and again during 2002-2003 at Maitri Antarctica on all clear days. Variation of TOC over Maitri during 1997, 2002 and 2003 is shown in Fig. 8. MICROTOP-II instrument can produce data only for daylight-viewing conditions of solar zenith angle (SZA) less than 67 degrees, so total ozone data are not available at polar latitudes during winter darkness. Total ozone measurement at Maitri is available from September onward, which showed the prevalence of annual ozone hole during all the observational years, as seen in fig 8. At Maitri, maximum TOC up to 320 DU has been recorded in the months of January and February during all the observational years. The minimum TOC of about 135 DU on 25 September 1997, 185 DU on 20 September 2002 and 126 DU on 3 October 2003 has been observed at Maitri, Comparison of TOC frequency distribution during ozone hole period (August to December) is depicted in Table 1. Ozone values less than 135 DU were observed 0.7% in the year 1997, 0% in 2002 and 15% in 2003. TOC values less than 150 DU were observed 0% in 2002, whereas, 8.1% in 1997 and 15% in 2003, which showed that Ozone hole in 2003 was much deeper as compared to 1997 and 2002. The ozone hole values (values below 220

DU) during ozone hole period were found out to be 63.7 % in the year 2003, 45.1 % in 1997 and 20.7% in 2002. These observation reveals that the estimated chemical loss of ozone over Maitri in 2003 was increased by 18.6% and 43% as compared to 1997 and 2002 respectively. The observation also showed that the chemical ozone depletion inside the vortex over Maitri during winter and spring 2002 was significantly very less of about 20% and terminated earlier than in normal ozone hole in winter 2003 and 1997.

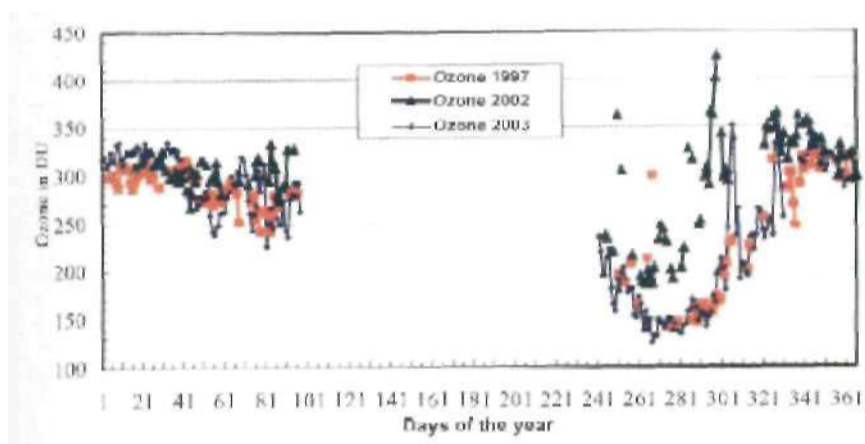


Fig.8. Variation of TOC during 1997, 2002 and 2003 at Maitri, Antarctica.

Table 1 Frequency distribution of ozone values during ozone hole period (August to December) observed over the Maitri by TOMS.

Year	Days of observation	Values less than 135DU	Values less than 150DU	Values between 150-220DU	Above 220DU	Days of ozone hole in %
1997	135	1 (0.74%)	11 (8.1%)	50 (37%)	73	46.6%
2002	140	0	0	29 (20.7%)	111	20.7%
2003	138	4 (2.8%)	22 (15%)	66 (47.8%)	66	66.6%

3. Water Vapour

Water in its various phases constitutes the critical link between the chemical component of global change and the dynamics, radiation and climate components. In the upper troposphere and lower stratosphere the radiative¹ and

chemical² effects of water vapor are large and atmospheric concentration varies considerably with the temperature and relative humidity (Shine et al 1990, Brasseur et al, 1986). In global climate models, almost half of the projected increase in temperature due to a doubling of carbon dioxide in the atmosphere results from the effects of increased water vapor (Hansen et al 1989). Effect of increasing water vapor in the stratosphere on stratospheric temperature has considerable cooling effect similar to that due to ozone depletion. Recent studies by Smith (2001) have shown a stratospheric cooling in regions of H₂O increases, of magnitude similar to that due to stratospheric ozone loss indicating a significant additional cause of observed stratospheric temperature decrease. However, doubling of water vapor in the stratosphere could lead to a 1°C raise in surface temperature (Wang et al. 1976) Total water vapour column amounts very low in Antarctica, however plays a significant role in ozone depletion (Rodríguez et al 1988, Hofmann et al. 1992). A recent study has shown that water vapor concentration determines the effectiveness of the heterogeneous reaction and under stratospheric conditions affects the ozone chemistry and plays significant role in the Antarctic ozone depletion by providing reaction site as polar stratospheric clouds in the form of H₂O ice (Kondratyev, 2000).

Scatter plots of daily averaged total water vapor column during 1997²⁰, 2002-03 and summer 2004 are depicted in Fig. 9. Total water vapour column data are not available at polar latitudes during polar night as MICROTOP-II instrument can produce data only for daylight-viewing conditions. Therefore, Measurements are not available for the months of May, June and July. Day-to-day water vapor at Maitri was found to be highly variable in both the years however, general trend showed maximum during polar summer and minimum during polar winter. During polar winter, minimum recorded water vapour was observed to be of the order less than 0.1 cm. However, Maximum daily averaged total water vapour column was observed 0.51 cm, 0.96 cm, 0.90 cm and 0.95 cm in the month January 1997, 2002, 2003 and 2004 respectively. This observation showed that maximum total water vapour column was increased by 88.2%, 76.4% and 86.2% in January 2002, 2003 and 2004 respectively as compared to maximum daily averaged total water vapour column observed in Jan 1997. In 1997, the annual averaged water vapour was found out to be 0.24 cm while 0.42 cm in 2002 and 0.45 cm in 2003.

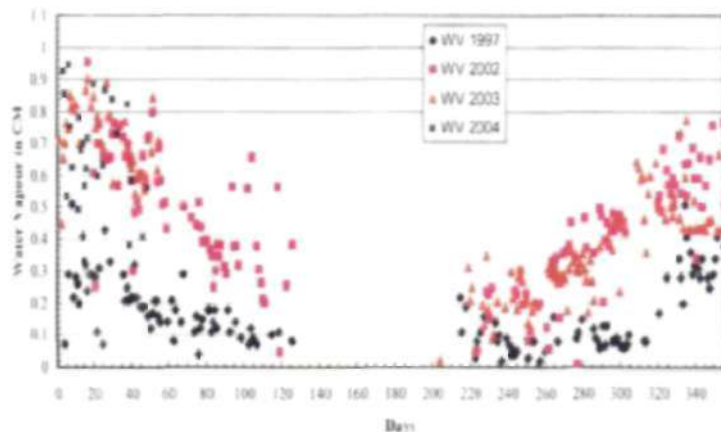


Fig.9. Water vapor variation at Maitri, Antarctica during 1997 and 2002 and 2003.

4. Green house gases

Under the present investigations the measurements for CO_2 was carried out using a state of art technology GC at Maitri, Antarctica. The GC based system was set up in last week of January 2002 and data was collected cyclically every day on half hourly basis during daytime and occasionally night times after befitting stabilization of the system that takes nearly three hours to stabilize. Once a week 24 hourly data were also taken. The GC was calibrated using the peaknet software on regular basis with CO_2 (303 & 320 ppm) standards to obtain an error free data.

Atmospheric carbon dioxide was analyzed by gas chromatography with flame ionization detection. The monthly averaged variation of atmospheric CO_2 measured at Maitri during Feb 2002 - Jan 2004 is depicted in Fig.10. The gaps in data are due to the inability to conduct measurements during Antarctica blizzards. The carbon dioxide was found to vary in the range around 360 to 377ppm. The averaged CO_2 during the year 2002 was found out to be 368.32 ppm whereas; during 2003 it was found out to be 369.51 ppm. The values of CO_2 observed over Maitri are comparable to present Global CO_2 values. No seasonal variation of carbon dioxide has been observed at Maitri. The CO_2 measurements using the GC are very consistent and the variation observed may be attributed to Meteorological parameters and wind.

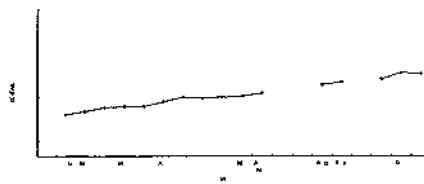


Fig.10 . Monthly averaged CO₂ from 2002 - Jan 2004 at Maitri Antarctica

Methane

Methane is a most abundant hydrocarbon in the atmosphere. Its troposphere chemistry affects hydroxyl (OH) radical and CO concentration. In stratosphere the oxidation of methane by OH radical is a major source of water vapour and its reaction with chlorine atom and its reaction with chlorine atom terminate the chlorine catalyzed destruction of ozone.

The daily average atmospheric methane measured at Maitri from February 2003 to February 2004 is depicted in Fig. 11. The day to day variation of surface CH₄ concentration was observed very small during observational period. The daily average surface methane concentration was found to vary in between 1.64 to 1.73 ppm. The Annual average CH₄ from Feb. 2003 to Feb 2004 was found out to be 1.7005 ppm. No seasonal variation of methane has been observed at Maitri. The CH₄ measurement using GC are very consistent and the small variation observed may be attributed to Metrological parameters and wind. An arriving at Maitri is well mixed traveled over the Southern Ocean and is far removed from spatial and seasonal variations in source strength characteristic of land areas. The values of CH₄ observed at Maitri are comparable to present global CH₄ values.



Fig.11. Daily averaged CH_4 at Maitri Antarctica from Feb 2003 to Feb 2004.

Carbon Monoxide

During 22nd Indian Scientific Antarctica expedition a new system has been deployed at Maitri, Antarctica to monitor Carbon-mono-oxide on round the clock basis. The variability in CO concentration has been observed, with hourly mean mixing ratios ranging from 30 ppb to 65 ppb. Diurnal changes in CO concentrations were systematically observed in Antarctic Atmosphere showing higher CO during daytime. Due to some technical problem in the instrument we could not get data for CO from May 2003 to December 2003. However, the problem was successfully rectified in the summer phase of 23rd ISAE and since the continuous measurement of surface concentration of CO is going on at Maitri, Antarctica. The daily average concentration of CO was found to vary in between 30 ppb to 60 ppb during the observational period of Jan to April 2004 as shown in Fig.4. Some time values shows as high as 150 ppb and low up to 70 ppb, which depends upon the local meteorological conditions. The monthly mean concentration was observed 44 ppb, 38 ppb, 56 ppb and 58 ppb in January, February, March and April 2004 respectively. Diurnal variation of CO has also been observed at Maitri showing higher concentration during the daytime and relatively low concentration in nighttime. The daytime increase of carbon-monooxide is attributed to the photolysis of formaldehyde in Antarctic atmosphere. Recent studies have reported production of formaldehyde in the snow pack. Formaldehyde is rapidly destroyed by sunlight to produce HO_2 and carbon-mono-oxide. The average diurnal variation of CO observed over Maitri is depicted in Fig. 12.

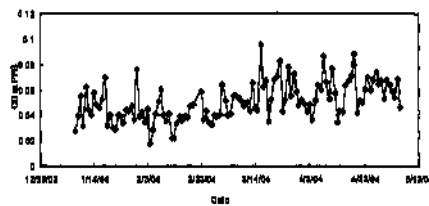


Fig. 12. Daily Averaged CO at Maitri Antarctica from Jan 2004 to April 2004

The issues of global change are complex and the systematic observations of green house gases (CO_2 , CH_4 , N_2O , CFC's, tropospheric ozone), reactive gases (CO, NOx, SO_2 , VOCs), will aid in understanding the changing chemical composition of the atmosphere and related physical characteristics and will be useful in framing national and international policy decisions affecting the environment. The measurements of water vapour and ozone are also being carried out at Maitri along with the CO_2 , while the measurements of carbon monoxide and CH₄ will be commenced during January 2003. The observations, made at high latitude like Antarctica will help to understand photochemical, heterogeneous and dynamical processes that control the distribution of atmospheric trace gases and hence the climate change.

Acknowledgement

The author is grateful to Directors, NPL (former and present i.e. Dr. S. K. Joshi, Dr. ESR Raj Gopal, Dr. Roy Chudhan, Dr. K. Lal, Dr. Vikram Kumar), Heads RASD, NPL (former and present i.e. Dr. B. M. Reddy, Dr. K. K. Mahajan, Dr. S. C. Garg, Dr. M. K. Tiwari) for their keen interest and encouragement during the progress of the work. I also express my thanks to CSIR and National Centre for Antarctica and ocean Research, Goa, Department of Ocean Development, Govt. of India, New Delhi for financial and logistic support. Thanks are also due to Shri G. Sudhakar Rao, Dr. S. D. Sharma, Sri Arun Chaturvedi, Dr. A. L. Koppa, Mr. R. P. Lal and Dr. Hanchinal the leaders of 13th, 14th, 15th, 16th, 21st and 22nd Antarctic expeditions respectively. Thanks are also due to Dr. B. C. Arya, Mr. Sachin Ghude and Mr. Arun Kumar for their help.

References

- ARRHENIUS, S (1896) *Philos Mag*, v 14, pp 237
- AYCRS, G P and GELLERT, RW (1990) Tropospheric chemical composition Overview of experimental methods in incubation *Rev Geophys*, v 28, pp 297
- BORSUK, G M (1981) A review of Acousto-optical Deflection and Modulation devices *Proc IEEE*, v 69, pp 100
- BRASSEUR, G and SOLOMON, S (1986) (In) *Aeronomy of the Middle Atmosphere* D Reidel Publishing Company, Norwell, Mass, 2nd ed
- CADLH, R D, CRUZILN, P J and EHHALI, D H (1975) Heterogeneous chemical reactions in the stratosphere *J Geophys Res*, v 80 pp 3381-3385
- CARSWELL, A I et al (1998) Lidar Measurements of Stratospheric Ozone at the Eureka NDSC station 1993 - 1998 19th ILRC, NASA, July, pp 327-330
- CHAMBERLIN, I C (1899) An attempt to frame a working hypothesis of the cause of glacial periods on an atmospheric basis *J Geol* v 7, pp 545
- CHANDRA, S and McPEIERS, R D (1986) Some observations on the role of planetary waves in determining the spring time ozone distribution in the Antarctic *Geophys Res Lett* v 13(12), pp 1224-1227
- CLIFORD, A, SERRAR, S, ARMANTE, R, SCOTT, N A and HOLLINGSWORTH, A (2002) Signatures of annual and seasonal variations of CO₂ and other greenhouse gases from comparison between NOAA/NOV observations and radiation model simulations *J Climate* v 15, pp 95-116
- CLIFORD, A, SERRAR, S, HOLLINGSWORTH, A, ARMANTE, R and SCOTT, N A (2003) Detecting annual and seasonal variations of CO₂, CO and N₂O from a multi-year collocated satellite-radiosonde data-set using the new Rapid Radiance Reconstruction (RR-N) model, *Journal of Quantitative Spectroscopy & Radiative Transfer*, v 77, pp 285
- CLIFORD, A, KEELING, C D AND BATES, N R (2002) Ups and Downs of CO₂ uptake, *Science*, v 298, pp 2374
- CRUTZEN, P J and ARNOLD, F (1986) Nitric acid cloud formation in the winter Antarctic stratosphere a major cause for the springtime ozone hole *Nature*, v 324, pp 651-655
- DIERWENT, R G, RYALL, D B, MANNING, A J, SIMMONDS, P G, DOHERTY, S O, BIRAUD, S, CIAIS, P, RAMONET, M and JENNINGS, S G (2002) Continuous observations of carbon dioxide at Mace Head, Ireland from 1995 to 1999 and its net European ecosystem exchange *Atmospheric Environment*, v 36, pp 2799-2807
- ELMAN, J C, GARDINER, B G and SHANKLIN, J D (1985) Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction *Nature*, v 315, pp 207
- FRANCEY, R J, STEELE, L P, LANGENFELDS, R L, ALLISON, C E, COOPER, L N, DUNSE, B L, BELL, B G, MURRAY, T D, TAIT, H S, THOMPSON, L and MASARIE, K A (1998) Atmospheric carbon dioxide and its stable isotope ratios, methane, carbon monoxide, nitrous oxide and hydrogen from Shetland isles *Atmospheric Environment*, v 32, No 19, pp 3331
- HANSEN, I, LACIS, A and PRATHER, M (1989) Greenhouse effect of chlorofluorocarbons and other trace gases *J Geophys Res*, v 94, pp 16417-16421
- HOMVIANN, D J and OLTMANS, S J (1992) *Geophys Res Lett*, v 19, pp 2211-2214

- HOUGHTON JT JENKINS GJ and EPHRAUMS JJ (Eds) (1994) *Climate Change The IPCC Scientific Assessment* Cambridge University Press pp 1 339
- IDSO S B IDSO C D and BALLING R C (2002) Seasonal and diurnal variations of near surface atmospheric CO₂ concentration within a residential sector of the urban CO₂ dome of Phoenix AZ USA *Atmospheric Environment* v 36 pp 1655 1660
- ISAISEN I S A and HOV O (1987) Calculation of trends in the tropospheric concentration of O₃ OH CO CH and NO_x *Tellus* v 39B pp 271 283
- JAIN S L AND ARYA B C (1988) Laser heterodyne system for atmospheric studies ozone *J of Opt cs* pp 108
- JAIN S L (2001) Monitoring of ozone water vapour etc during the voyage to Antarctica *Asian J of Phys* v 10 pp 315 321
- JAIN S L (1987) Inverse techniques to get vertical profiles of ozone in atmosphere using laser heterodyne system *Indian J Radio & Space Phys* v 16 pp 324
- JOHNSTON H S (1971) Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust *Science* v 173 pp 517
- KAPLAN L D (1959) Inference of atmospheric structure from remote radiation measurements *J Opt Soc Am* v 49 pp 1004
- KEELING C D CHIN J F S and WHORF T P (1996) Increased activity of northern vegetation inferred from atmospheric CO₂ measurements *Nature* v 382 pp 146 149
- KONDRATYEV K Ya and VAROTSOS C (2000) *Atmospheric Ozone Variability Implications for Climate Change Human Health and Ecosystems* Springer Praxis Crchester UK pp 617
- Matsuda H and Inoue H Y (1996) Measurements of atmospheric CO₂ and CH₄ using a commercial airliner from 1993 to 1994 *Atmospheric Environment* Vol 30 Nos 10U pp 1647 1655
- MOLINA M J TSO T L MONILA L T and WANG F C Y (1987) Antarctic stratospheric chemistry of chlorine nitrate hydrogen chloride and ice *Science* v 238 pp 1253 1257
- NASRALLAH H A BALLING R C MADI S M and ANSARI L A (2003) Temporal variations in atmospheric CO₂ concentrations in Kuwait City Kuwait with comparisons to Phoenix Arizona USA *Environmental Pollution* v 121 pp 301305
- NAKAZAWA T MIYASHITA K AOKI K S and TANAKA M (1991) Temporal and spatial variations of upper tropospheric and lower stratospheric carbon dioxide *Tellus* v 43 pp 106 117
- NEWMANN P A (1986) The final warming and polar vortex disappearance during the southern hemisphere spring *Geophys Res Lett* November v 13(12) pp 1228 1231
- NOTHOLT J (1997a) Comparison of Arctic and Antarctic trace gas column abundances from ground based Fourier transform infrared spectrometry *J of Geophys Res* v 102 D11 pp 12863 12869
- NOTHOLT J (1997b) Seasonal variations of atmospheric trace gases in the High Arctic at 79°N *J of Geophys Res* v 102 011 12 pp 855 12 861
- PEARMAN G I and BEARDMORE D J (1984) Atmospheric carbon dioxide measurements in the Austral an region in years of aircraft data *Tellus* v 36 B pp 1 24