Twenty Second Indian Expedition to Antarctica, Scientific Report, 2008
Ministry of Earth Sciences, Technical Publication No. 20, pp 117-124

Online Measurement of Surface Air Concentration of CH_4 and $C0_2$ at Maitri, Antarctica

S. L. Jain, B. C. Arya, Ashok Kumar, V. B. Gupta* and Sachin D. Ghude

Radio and Atmospheric Sciences Division
National Physical Laboratory
New Delhi-110012

*School of Future Studies and Planning, Devi Ahilya University,
Indore-452017 (India)

ABSTRACT

Measurement of surface air concentration of methane and carbon dioxide has been carried out using Automated Gas Chromatograph at Indian research Station, Maitri (70°.44'S, 11°.45'E), Antarctica during 21^{s1} and 22nd Indian Scientific Expedition to Antarctica. Very small day-to-day variation of surface CH_4 concentration was observed during observational period. The mean CH_4 concentration for sixteen-month period (February 2003 to June 2004) was found out to be 1.70 ppm. The averaged $C0_2$ concentrations were found out to be 368.32 ppm and 369.51 ppm in the year 2002 and 2003 respectively. The values of CO, observed over Maitri are comparable to present Global CO, values. In present communication experimental setup and results obtained are discussed in detail.

Key Words: Gas Chromatograph (GC), Methane, Carbon dioxide, Antarctica

INTRODUCTION

The current important issues, which are dangerous for the survival of life on the earth, are global greenhouse warming, global increase in carbon dioxide, regional increase in tropospheric ozone, urban and regional atmospheric pollution and the decrease in stratospheric ozone and ozone hole over Antarctica[12]. The distribution of greenhouse gases in the atmosphere, particularly those due to human and biosphere activities, is quite heterogeneous[3]. The growth of the atmospheric concentration levels of greenhouse gases since the industrial period (1750) such as carbon dioxide, methane, nitrous oxide, halocarbons and tropospheric ozone has been identified as one of the major causes of the warming of the Earth's surface[4,,6]. In polluted environment the concentration of greenhouse gases fluctuate widely from place to place, and even from day to day. However, in

Antarctica contaminations sources are distant, the air is very well mixed and extremely clean. It is truly the background air of the planet when compared to measurements made elsewhere around the glob. Therefore, special conditions at Antarctica makes it an ideal site for the baseline monitoring of atmospheric composition.

Measurement of surface concentration of greenhouse gases like $C0_2$, CH_4, CO, CFC's etc. is continued since long. Various techniques have been used for the continuous in situ measurement of atmospheric greenhouse gases at various places over globe. Bacastow (1981)[7] reported gas flasks sampling technique for continuous measurement of $C0_2$ using non-dispersive infrared gas analyzer at South Pole, Antarctica. Langenfelds (2001)[8] reported analysis of air sample collected from the South Pole using Gas Chromatograph (GC). For a continuous monitoring of greenhouse gases at Maitri Antarctica, automated Gas Chromatograph Instrument using flame ionization detector was setup during 21^{s1} Indian scientific Expedition to Antarctica (2002-03) for the measurements of atmospheric $C0_2$ and CH_4. In the present communication detailed synopsis of experimental setup and results obtained are discussed.

EXPERIMENTAL SETUP

The gas chromatograph established at Maitri during the measurement period 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 which provide fuel (Hydrogen + Air) to the flame ionization detector. The samples from ambient air are injected into the column by a computer controlled sampling pump for known interval of time. The appropriate software is being used to estimate CO,, CH_4 ambient concentration. To achieve optimum separation, good accuracy and precision, good regulation of pressure and flow rate of carrier gas and temperature programming of the column is done using dedicated computer controlled software.

The complete block diagram of experimental setup for the online measurement of near surface air concentration of CO, and CH_4 using gas chromatograph at Maitri, Antarctica is as shown in Fig. 1. The complete system incorporates Nitrogen Generator, Hydrogen Generator, computer controlled sampling pump, Gas Chromatograph and Data Processing unit.

The system has an independent nitrogen generator which supplies ultra high pure nitrogen as carrier gas to GC at site. Carrier gas separates the components of a mixture using physical method of separation while transporting the sample components through the column to the detector.

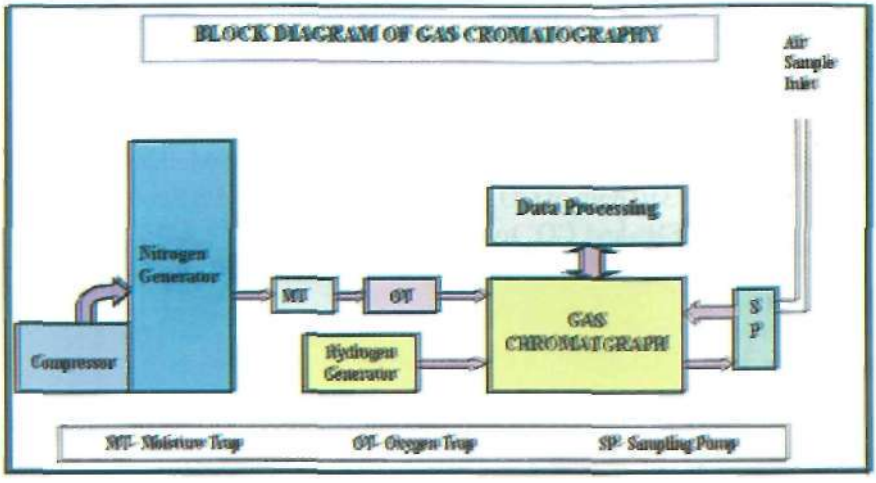

Fig. 1: Block Diagram of Gas Chromatograph setup at Maitri, Antarctica

The samples from ambient air are injected into the column by an online sampling pump for known interval of time.

The switching of carrier gas is achieved using ten port switching valve already integrated in GC. Column switching is used to switch the carrier gas through sample loop, which injects sample into the column at different interval of time, and also for venting, back-flushing, dual column operation. Two separate columns namely Molecular sieve 13X and Hyseape D are incorporated to determine surface concentration of $CH_4$and $C0_2$ respectively. The detector system incorporates Flame Ionization Detector, amplifier and processing unit. Due to its high sensitivity to virtually all-organic compound no response to water and $C0_2$, good linearity over a wide sample concentration range FID detector makes it Ideal GC detector. As FID is less sensitive to $C0_2$, methanizer is included which converts $C0_2$ into methane. The FID detector consists of a small hydrogen-air flame at a small metal jet. Organic compounds eluted from the column bum and form ions in the flame. The ions travel to the collector electrode, which is maintained at a negative potential with respect to flame jet and produces the electrical signals. The signal is amplified and conditioned by a high input impedance amplifier needed for computer interface. Further, computer analytically to determine surface concentration of the interested species processes it.

The observations were made throughout the expedition every day on hourly basis after befittingly stabilizing the instrument. Once a week 24 hourly

data were also taken. For data accuracy and to enhance stability for low-level detection of CH_4 concentration in Antarctic air, $C0_2$ and CH_4 measurements by GC equipped with FED require a periodic calibration of the systems sensitivity by using calibration gases. The system is being calibrated on regular basis using 3.35 ppm and 5 ppm of Methane standard and 303 ppm and 310 ppm of $C0_2$ standard supplied by M/S Scotty standard respectively for CH_4 and $C0_2$ to obtain error free data.

RESULTS

Methane :

Methane (CH_4) is a biogenic gas produced from variety of anaerobic processes and the most abundant organic trace gas in the atmosphere. It is an important greenhouse gas because it absorbs the Infrared radiation and is also involved in tropospheric and stratospheric photochemical reactions. The major sources of Methane are agriculture, natural wetlands, rice paddies and enteric fermentation. Biomass burning and animal waste treatment facilities are other source of methane.

The daily mean atmospheric methane measured at Maitri from February 2003 to June 2004 is depicted in Fig. 2. The day-to-day variation of surface CH_4 concentration was observed vary 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 CH_4 was found out to be 1.70 ppm. The CH_4 measurements using GC are very consistent and the small variation observed may be attributed to meteorological parameters and wind. Air 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 CH_4 observed at Maitri are comparable to present global CH_4 values.

Database of monthly mean CH_4 concentration for the observational period of February 2003 to June 2004 is depicted in Table 1. Because of technical fault in the instrument, measurement could not be carried out in January 2003 and October 2003. Daily mean CH_4 concentrations have been averaged to derive monthly mean CH_4 concentration. Monthly mean CH_4 concentration has been observed to vary from 1.695 ppm to 1.704 ppm.

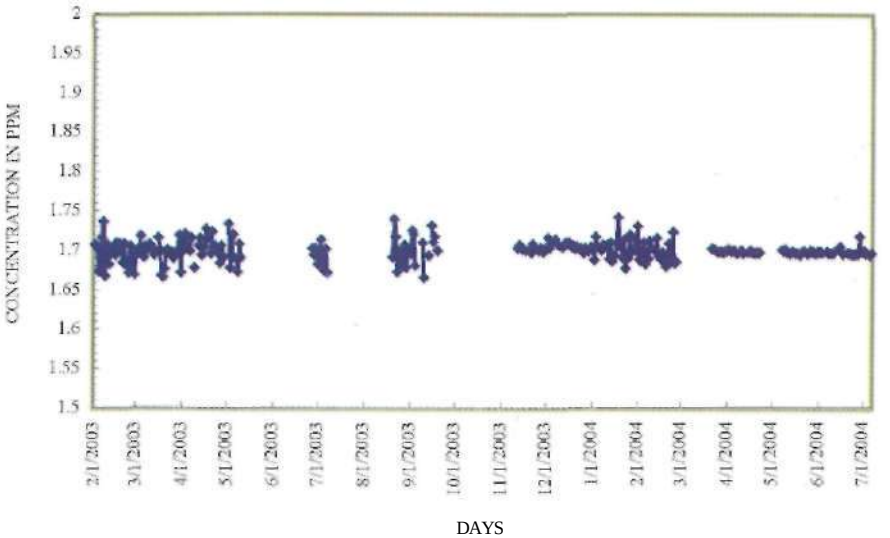

Fig. 2: Daily mean CH_4 variation at Maitri, Antarctica from February 2003 to June 2004

Table 1 Monthly mean CH_4 concentration from February 2003 to June 2004

Months	2003	2004
	CH_4 in ppm	CH_4 in ppm
January	—	1.704
February	1.695	1.696
March	1.697	1.701
April	1.704	1.700
May	1.699	1.699
June	1.701	1.699
July	1.692	—
August	1.697	—
September	1.704	—
October	—	—
November	1.703	—
December	1.706	—
AVG	**1.699**	**1.699 (6 months)**

AVG: Annual Average.

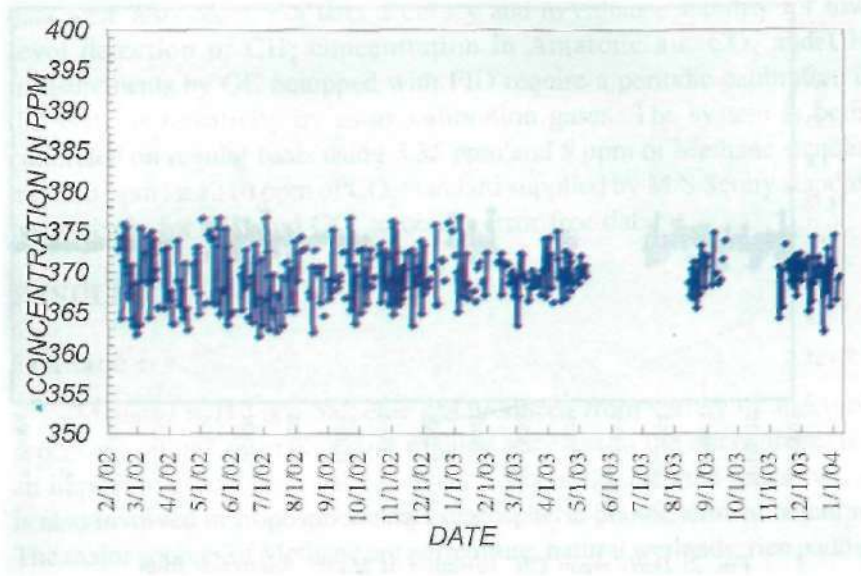

Fig. 3: Daily mean CO_2 variation at Maitri, Antarctica from Feb. 2002 to Jan. 2004

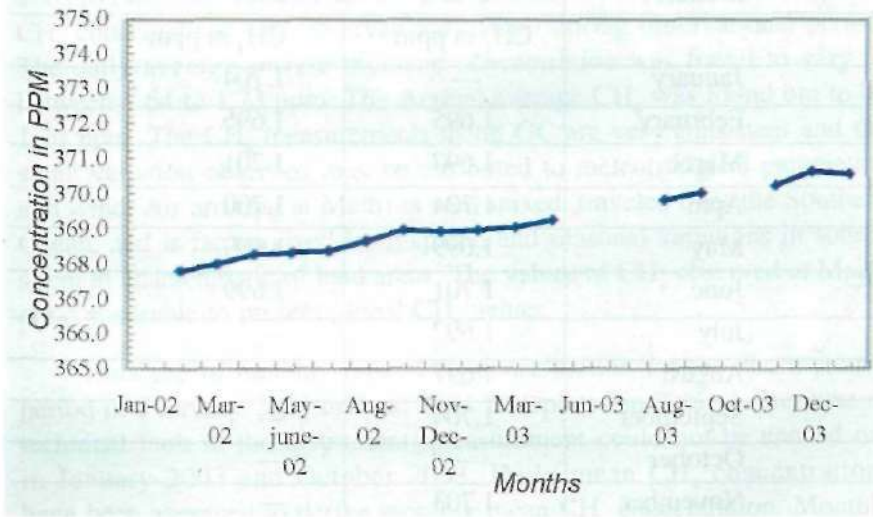

Fig. 4: Monthly mean CO_2 variation at Maitri, Antarctica from Feb. 2002 to Jan. 2004

Carbon dioxide: [1]

The greenhouse effect of $C0_2$ increase, which has been the subject of scientific studies since later half of the nineteenth century, has gained tremendous momentum during last two decades. CO, is the critical element in the greenhouse effect and has the largest radiative effect. The atmospheric carbon dioxide was analyzed by gas chromatography with flame ionization detection. The variation of daily mean and monthly mean of $C0_2$ concentration measured at Maitri during Feb 2002 - Jan 2004 is depicted in Figs 3 and 4 respectively. The gaps in data are due to the inability to conduct measurements during blizzards. The carbon dioxide was found to vary in the range around 360 to 377 ppm, most of the values have been observed in the range of 367 to 373 ppm. The averaged $C0_2$ during the year 2002 was found out to be 368.32 ppm and during 2003 it was found out to be 369.51 ppm. The values of CO, observed over Maitri are comparable to present Global CO, values (World Data Center for Greenhouse Gases (WDCGG), "http://gaw.kishou.go.jp/wdcgg.html, IPCC 2001). The CO, measurements using the GC are very consistent and the variation observed may be attributed to meteorological parameters and wind.

CONCLUSION

Thus, the aforesaid analysis indicates that baseline level of carbon dioxide is increasing in the atmosphere. Nearly invariant daily mean concentration of CH, and CO, illustrates that the air at Maitri is well mixed and far removed from the source strength characteristics of land area and hence ideal site for the baseline measurements of trace gases in the atmosphere. Finally, the observation made in extreme cold conditions of Antarctica has proved the Gas Chromatograph to be an important tool to measure low-level surface air concentration of CH_4 and CO, in Antarctic air.

ACKNOWLEDGEMENTS

We thank to the Director, NPL and Head, RASD, for their encouragement during the progress of the work. Thanks are also due to the National Centre For Antarctic and Ocean Research (NCAOR), Department of Ocean Development and CSIR (Council of Scientific and Industrial Research) for logistic and financial assistance. A line of appreciation is for the cooperation and help of leaders and every member of 21st and 22nd ISEA team.

REFERENCES

1. Farman J.C, Gardiner B.G. and Shankiin J.D, "Large losses of total ozone in Antarctica reveal seasonal CIOxNOx interaction." Nature 315, 207-210, (1985).

2. Solomon, S., "Progress towards a quantitative understanding of Antarctic ozone depletion." Nature, 347, 347-354, (1990).

3. S. K. Mukhopadhyay, H. Biswas, T. K. De, B. K. Sen, S. Sen and T. K. Jana, "Impact of Sundarban mangrove biosphere on the carbon dioxide and methane mixing ratios at the NE Coast of Bay of Bengal, India." 36(4), 629-638, (2002).

4. Hansen, J. E., M. Sato, A. Lacis, R. Ruedy, I. Gegen, and E. Matthews, "Climate forcing in the industrial era." Proceedings of the National Academy of Sciences, 95, 12,753-12,758, (1998).

5. Lacis, A., J. Hansen, P. Lee, T. Mitchell, and S. Lebedeff, "Greenhouse effect of trace gases 1970-1980." Geophys. Res. Lett. 8, 1035-1038, (1981).

6. Wang, W.-C, Y.L. Yung, A.A. Lacis, T. Mo, and J.E. Hansen., "Greenhouse effects due to man-made perturbation of trace gases." Science, 194, 685-690, (1976).

7. Bacastow, R.B., and CD. Keeling. "Atmospheric carbon dioxide concentration and the observed airborne fraction." In B. Bolin (Eds.), Carbon Cycle Modelling, SCOPE 16. John Wiley and Sons, New York. (1981).

8. Langenfelds, R.L., L.P. Steele, C.E. Allison, and R.J. Francey.. GASLAB Calibration Information, Internal Report, CSIRO Atmospheric Research, Aspendale, Australia (2001).

9. Houghton, J. T., Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell, and C A. Johnson (Eds.) (2001), Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, 881 pp., Cambridge Univ. Press, New York.