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Continuous observations of surface air concentration of carbon dioxide and methane at Maitri, Antarctica

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A 23-month record of continuous hourly averaged carbon dioxide observations over the February 2002–January 2004 period and 16-month record of methane over the February 2003–June 2004 period for the Indian Research

Station, Maitri (Antarctica) have been examined to reveal baseline values in the atmosphere. During the observational period, CO₂ surface air concentration showed mean yearly value of 368.43 ppm in the year 2002 and 369.72 ppm in the year 2003, indicating an increase by 1.3 ppm. This corresponds to a growth rate of 0.35% per year. Mean CH₄ concentration for a 16-month period has been observed to be 1.699 ppm, with standard error of ± 0.0025 . Unlike CO₂, CH₄ does not show any evidence for an increase during the observation period. In the present communication, the experimental set-up and results obtained are discussed.

THE current important issues in atmospheric sciences which affect life on the earth are global greenhouse warming, global increase in carbon dioxide, regional increase in tropospheric ozone, urban and regional atmospheric pollution and decrease in stratospheric ozone and ozone hole over Antarctica^{1,2}. The distribution of greenhouse gases (GHGs) in the atmosphere, particularly those due to human and biosphere activities, is quite heterogeneous³. Increase in the atmospheric concentration of GHGs such as carbon dioxide, methane, nitrous oxide, halocarbons and tropospheric ozone since the industrial period (1750) has been identified as one of the major causes of the warming of the earth's surface^{4–6}. CO₂ has the largest radiative effect. Now it has been recognized that the global warming due to infrared active gases like O₃, CFCs, CH₄, N₂O, etc. is collectively as much as that due to CO₂ alone⁷, while it was only due to CO₂ during the pre-industrial era to 1950s. Recent studies have demonstrated that during 1999–2000, CO₂ alone had been responsible for about 60% of the increase in radiative forcing due to emissions from all GHGs⁸. Keeling and Whorf⁹ analysed that the average rate of increase in CO₂ since 1980 is 0.4% per year. Direct measurements of CO₂ concentrations made over 40 years show that year-to-year fluctuations in the rate of increase of atmospheric CO₂ are large⁹. In the 1990s, the annual rates of CO₂ increase in the atmosphere⁸ had fluctuated from 0.9 to 2.8 ppm/yr. Next to carbon dioxide, methane is the most abundant and important organic trace gas in the atmosphere. It absorbs infrared radiation¹⁰ and is also involved in tropospheric and stratospheric photochemical reactions¹¹. A downward trend was observed in the surface concentrations of methane in the northern and southern hemispheres between 1987 and 1992 and even larger downward trends were observed¹² for the period 1992–93. These trends have again reversed to the previous upward trend, almost 1% for methane. Dlugokencky *et al.*¹² reported that the global methane increase averaged 3.9 ppb per year during the three-year period 1995–97, but it was 12.7 ppb in 1998. In 1999 the increase was 2.6 ppb, suggesting that the large increase in 1998 was temporary¹². The large increase in global methane abundance during 1998 corresponds to an increase in methane emissions of about 5% of the total emissions. Dlugokencky *et al.*¹³ noted that the globally-averaged atmospheric methane abundance was constant at ~1751 ppb from 1999 through 2002, which suggests that

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during this four-year period the global methane budget has been at steady state.

Earlier, Francey *et al.*¹⁴ reported CO₂ measurement from air sample collected from the South Pole using Gas Chromatograph and Dlugokencky *et al.*¹⁵ reported methane measurement by gas chromatography with flame ionization detector. There is still considerable uncertainty associated with global methane budget due to the unavailability of methane distributions for many areas. Also, even if the main climatic effects of CO₂ are not local, it is important to measure baseline concentration of CO₂ at unpolluted sites like Antarctica, where human activities are mostly zero.

In view of the above, measurement of carbon dioxide and methane has begun during the 21 (2002) and 22 (2003) Indian Scientific Expedition at Maitri, Antarctica respectively. The continuous measurements will sequentially provide valuable data for modelling studies. Studies at Maitri station were aimed towards the estimation of baseline concentrations of CO₂ and CH₄, their annual trend and day-to-day variation in the near-surface air in Antarctica. In the present communication, continuous CO₂ and CH₄ observational records have been studied and results obtained are discussed.

Measurements of carbon dioxide and methane were carried out at Maitri from February 2002 to January 2004 and February 2003 to June 2004 respectively. The station is located 120 m above sea level on Schimacher hill, ice-free area of Queen Maud Land of Antarctica. Figure 1 shows an aerial view of the experimental site. A gas chromatograph (GC) was installed in an Environmental Laboratory, which is situated around 100 m away from main station, as seen in Figure 1. The local minor sources of CO₂ near the experimental set-up are electrical generators at Maitri station as well as at the Russian station. The Generator Complex is situated behind the main station around 150 m away from sampling site. Most of the time the wind flows from east to west as shown in Figure 1, and does not carry air towards the sampling site, except during rare events when the wind direction changes. These events were associated with Antarctica blizzard, when no sampling was carried out at site. Thus, no serious contamination problem due to the main station existed. An automated on-line sampling technique was used for CO₂ and CH₄ measurements. Two separate columns, namely Molecular sieve 13X and Hyseape D have been used for detection of surface air concentrations of CH₄ and CO₂ respectively. Flame Ionization Detector (FID) has been used for measurement of the very low CH₄ concentrations in Antarctic air. CO₂ has also been measured using FID after methanization of CO₂ to CH₄. Air was sampled for a known interval of time by automated sampling pump and analysed by GC. The main air inlet was installed on top of the sidewall of the observatory around 3 m above the ground. The copper tube between the inlet and the instrument was around 3 m long, with an inner diameter of 2 mm. The inlet was protected against drifting snow with a specially designed tumbler

and sampling was avoided during heavy snowdrift and Antarctica blizzard.

Observations were made throughout the expedition every day on an hourly basis after suitably stabilizing the instrument. Low-level detection of surface air CO₂ and CH₄ concentration by GC (equipped with FID) requires periodic calibration of the system's sensitivity with calibration gases for data accuracy. CO₂ calibration by M/s Scotty standard of 303 ppm and Linde gas standard of 310 ppm were performed regularly. CH₄ calibration was done using M/s Scotty standard of 3.35 ppm and Linde gas standard of 5.0 ppm. FID cleaning was also done regularly to enhance the stability of the detector. A typical chromatogram of the air sample obtained on 8 February 2003 at Maitri, Antarctica is shown in Figure 2. The first methane peak corresponds to molecular sieve 13X column and second methane peak that appears along with CO₂ corresponds to Hyseape-D column. We have analysed the methane data which correspond to the first methane (methane) peak. Table 1 shows the sequence of results obtained from the chromatograms on 8 February 2003. Next, the variation of carbon dioxide and methane and results obtained are discussed.

A synopsis of the available daily mean CO₂ observations for a period of 23 months (February 2002–January 2004) is shown in Figure 3. Data have been collected regularly on an hourly basis and mean CO₂ concentration has been calculated for each day. The gap in Figure 3 is due to non-availability of data during blizzard days and when the GC malfunctioned. Sometimes due to instability in baseline of chromatographs and runaway from calibration, hourly values were observed below 300 ppm or above 400 ppm. Such values were carefully filtered out from the dataset.

As observed in Figure 3, the day-to-day CO₂ concentration was found to be variable. Periods of low variability were found to be interrupted by short-term increase or decrease in the mean CO₂ concentration. Daily average of near-surface atmospheric CO₂ concentration exhibited scatter throughout the observational period, yielding minimum and maximum values between 363 to 377 ppm. To find out the nature and distribution of near-surface atmospheric CO₂ concentration at the measurement site, frequency distribution analysis of the available daily mean CO₂ observations has been done against the concentration intervals (f_i) of 1 ppm. Although CO₂ concentration is found to be distributed between 363 and 377 ppm, most of the values have been observed in the range between 367 and 373 ppm, as seen in Figure 4.

Maximum density of CO₂ values was found to be in the concentration range between 369 and 371 ppm. CO₂ values between 363 and 366 ppm and between 374 and 377 ppm were observed to be 25%. About 75% values were observed in the range between 367 and 373 ppm. These results show that the day-to-day variability in near-surface CO₂ concentration over the measurement site is nearly invariant compared to the regions where anthropogenic activities are highly concentrated. This indicates that the air over Maitri station is almost well mixed. The observed scattering

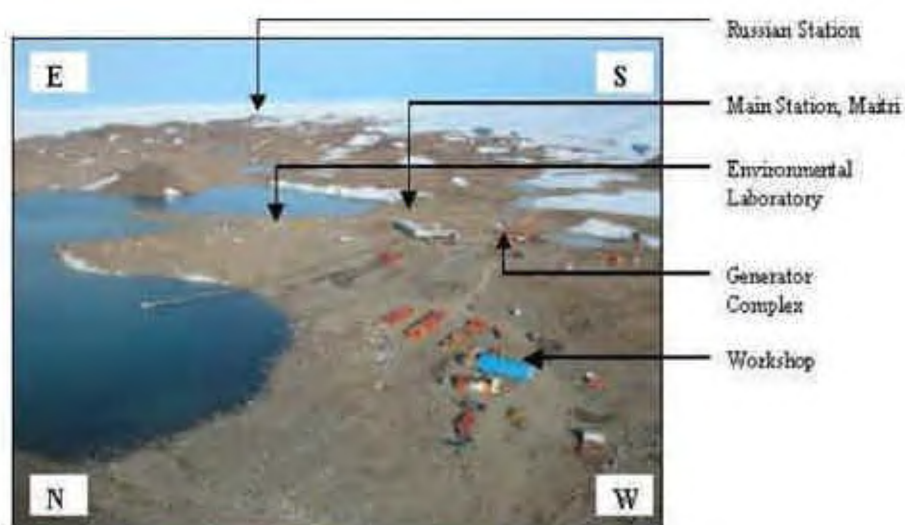


Figure 1. Aerial view of experimental site at Maitri, Antarctica.

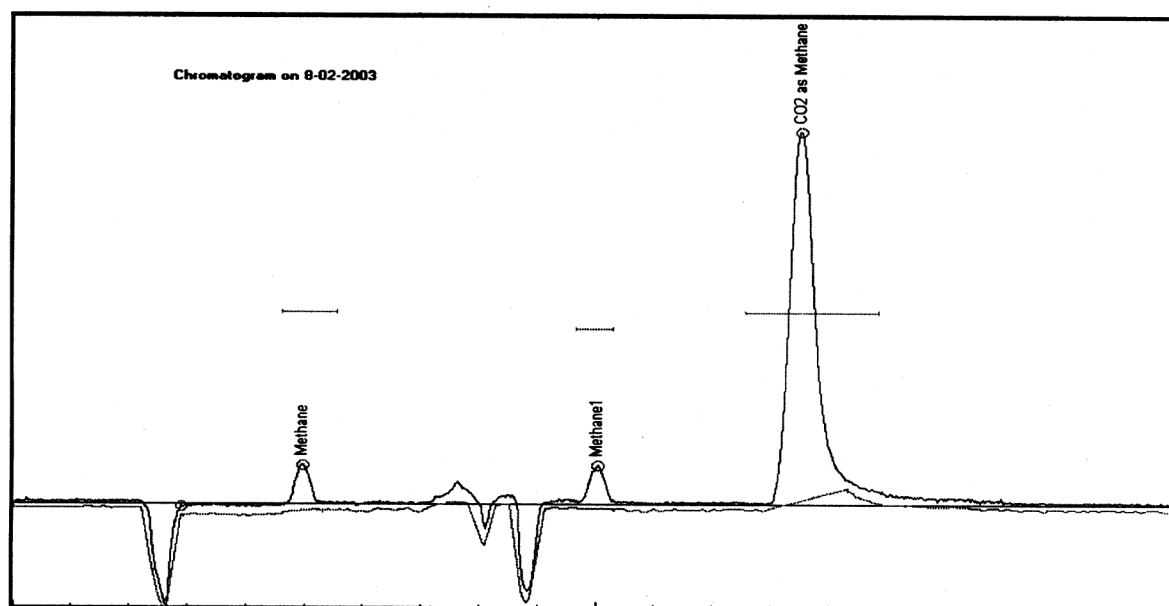


Figure 2. Typical chromatogram of air samples obtained on 8 February 2003 at Maitri, Antarctica.

of the CO_2 values at this site may be due to the impact of outflow air masses that arise from man-made fuel combustion and short-range transport of air parcels from nearby Russian station, Novolazarevskaya (situated ~ 4 km east of Maitri station (see Figure 1) to the measuring site and local meteorological conditions. The local sources of CO_2 at Novolazarevskaya station are electrical generators, which continuously supply the required electrical power to the station and run on Aviation Turbine Fluid.

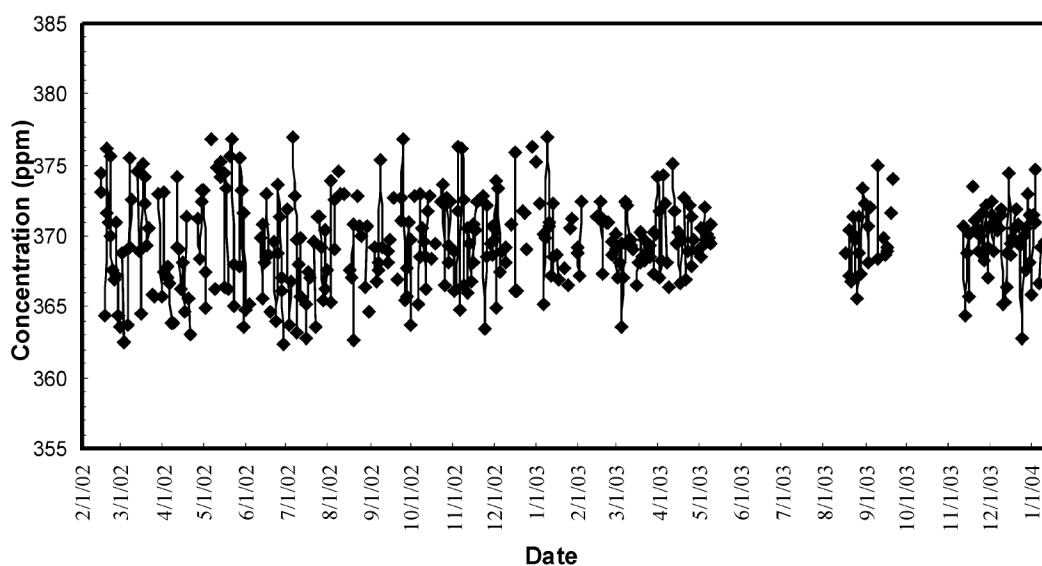
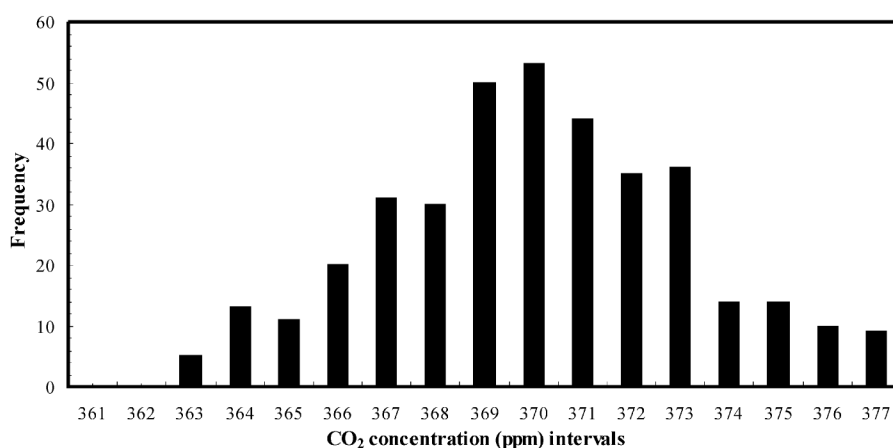
To illustrate the nature of the annual trend of CO_2 concentration irrespective of small day-to-day variations at the measurement site, monthly mean has been calculated from daily mean CO_2 observations, as depicted in Table 2. Due to

frequent occurrence of blizzards and also due to malfunctioning of the instrument, few daily CO_2 observations were possible during June, October and November 2002 and May 2003. Therefore, smoothing of monthly mean CO_2 values with the adjacent months has been done, as depicted in Table 2. The monthly mean CO_2 concentration is found to have increased from 367.8 to 370.6 ppm as seen in Figure 5. The observed trend of CO_2 concentration in near-surface air illustrates linear increase.

On the basis of monthly mean CO_2 concentration, annual mean CO_2 concentration was found out to be 368.52 ppm in the year 2002 and 369.61 ppm in the year 2003. On the other hand, after smoothing the monthly mean CO_2 data as

Table 1. Sequence of air samples collected on 8 February 2003 at Maitri, Antarctica

Date	Time	CH ₄			CO ₂		
		Retention time of CH ₄ peak	Area of peak	CH ₄ in ppm	Retention time of CO ₂ peak	Area of peak	CO ₂ in ppm
2/08/03	10 : 08	4.888	11.76849	1.7171	13.365	809.1175	371.2059
2/08/03	11 : 08	4.905	11.59783	1.6922	13.333	798.4283	366.3019
2/08/03	12 : 08	4.909	11.87746	1.7330	13.354	805.2352	369.4248
2/08/03	13 : 08	4.901	11.55739	1.6863	13.375	797.9138	366.0659
2/08/03	14 : 08	4.905	11.74656	1.7139	13.377	804.3041	368.9976
2/08/03	15 : 08	4.915	11.60263	1.6929	13.372	805.6967	369.6365
Standard error			± 0.051	± 0.0074		± 1.79	± 0.824

**Figure 3.** Daily mean CO₂ variation at Maitri, Antarctica from February 2002 to January 2004.**Figure 4.** Frequency distribution of measured CO₂ concentration from February 2002 to January 2004 for f_i (frequency interval) = 1 ppm and $\sum f = 375$, ($\sum f = N$ = Total number of measurements).

mentioned above, annual mean CO₂ concentration was found out to be 368.43 ppm in the year 2002 and 369.72 ppm in the year 2003. These results showed that CO₂ concentration

has increased by 1.1 ppm in the year 2003 and after smoothing the monthly mean CO₂ data, it was found to be increased by 1.3 ppm in the year 2003. No seasonal variations

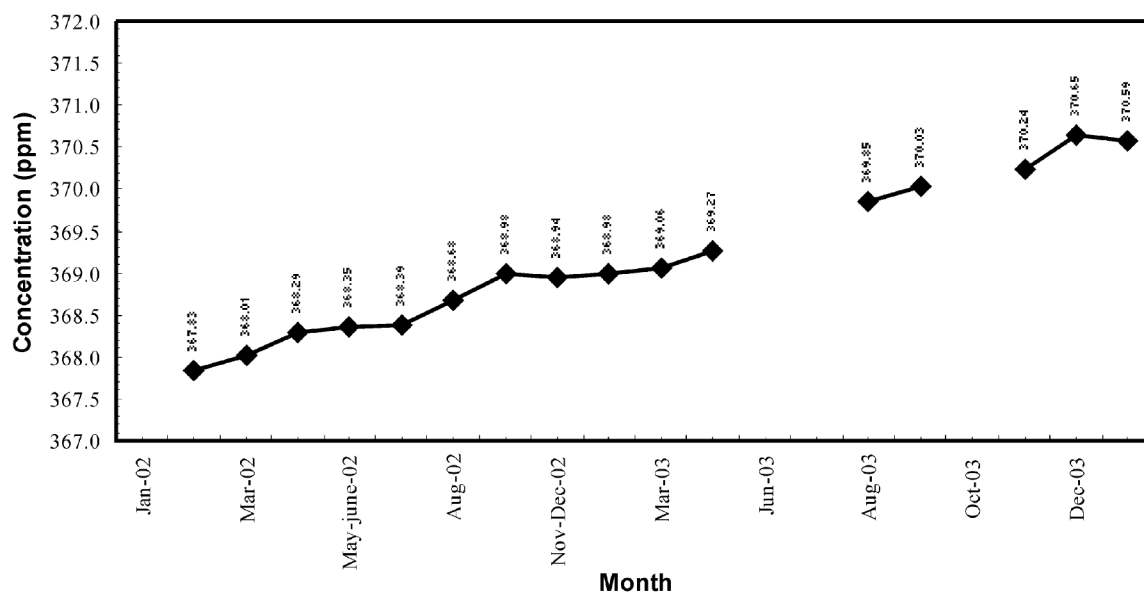


Figure 5. Monthly mean (smoothed) CO₂ concentration from February 2002 to January 2004 at Maitri, Antarctica.

Table 2. Monthly mean CO₂ concentration from February 2002 to January 2004 at Maitri, Antarctica

Month	Monthly mean					
	2002 CO ₂ in ppm	Standard error	2003 CO ₂ in ppm	Standard error	2004 CO ₂ in ppm	Standard error
January	—		368.96	± 0.706	370.6	± 1.130
February	367.83	± 1.120	369.00	± 0.477	—	
March	368.01	± 0.984	369.06	± 0.386	—	
April	368.29	± 0.752	369.52	± 0.548	—	
May	368.86	± 0.982	369.02	± 0.365	—	
June	367.84	± 0.793	—		—	
July	368.39	± 0.732	—		—	
August	368.68	± 0.857	369.85	± 0.635	—	
September	368.73	± 0.763	370.28	± 0.649	—	
October	369.23	± 0.548	—		—	
November	368.62	± 0.672	370.24	± 0.566	—	
December	369.27	± 0.854	370.65	± 0.464	—	
AVG	368.52	± 0.823	369.61	± 0.533	—	

Month	Monthly mean (smoothed)				
	2002 CO ₂ in ppm	Standard error	Month	2003 CO ₂ in ppm	Standard error
January	—		January–February	368.98	± 0.450
February	367.83	± 1.120	March	369.06	± 0.385
March	368.01	± 0.984	April–May	369.27	± 0.406
April	368.29	± 0.752	June	—	
May–June	368.35	± 0.690	July	—	
July	368.39	± 0.732	August	369.85	± 0.634
August	368.68	± 0.857	September	370.03	± 0.648
September–October	368.98	± 0.462	October	—	
November–December	368.94	± 0.524	November	370.24	± 0.566
			December	370.65	± 0.464
AVG	368.43	± 0.765		369.72	± 0.508

AVG, Annual average.

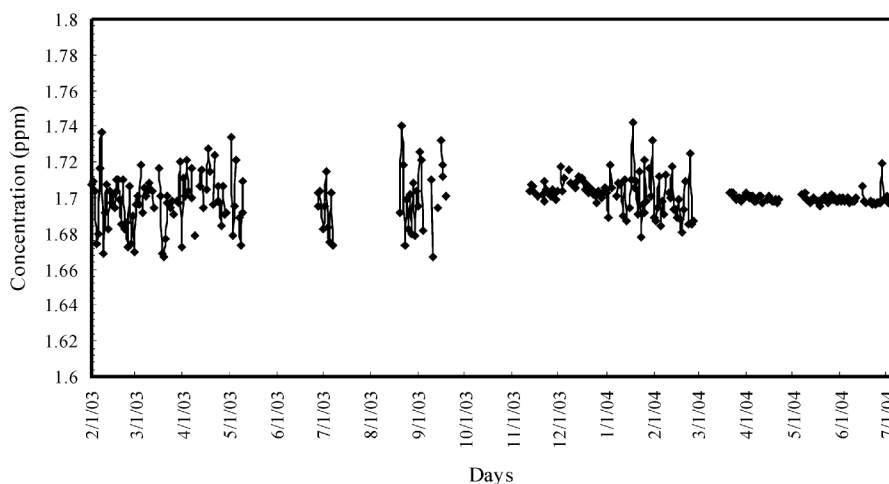


Figure 6. Daily mean CH₄ variation at Maitri, Antarctica from February 2003 to July 2004.

Table 3. Monthly mean CH₄ concentration from February 2003 to June 2004

Month	2003 CH ₄ in ppm	Standard error	2004 CH ₄ in ppm	Standard error
January	—	—	1.704	± 0.0028
February	1.695	± 0.0025	1.696	± 0.0021
March	1.697	± 0.0028	1.701	± 0.0005
April	1.704	± 0.0028	1.7	± 0.0004
May	1.699	± 0.0052	1.699	± 0.0003
June	1.701	± 0.0068	1.699	± 0.0002
July	1.692	± 0.0052	—	—
August	1.697	± 0.0035	—	—
September	1.704	± 0.0046	—	—
October	—	—	—	—
November	1.703	± 0.0005	—	—
December	1.706	± 0.0006	—	—
Annual average	1.699	± 0.0034	1.699 (6 months)	± 0.0010

were observed at Maitri, Antarctica during the observational period. This may be due to the fact that air arriving at the site after travelling over an uninterrupted fetch of several thousand kilometres of ocean is well mixed and far removed from variation in source strength characteristic of land areas.

These results indicate that monthly and thereby yearly CO₂ concentration in the air is almost steadily increasing at a rate of approximately 1.3 ppm/yr. However, due to scarcity of yearly data, it is difficult to estimate the exact trend and rate of increase in CO₂ concentration at the site. Secondly, absence of seasonal variation illustrates that the air arriving at the site (Maitri) after travelling over an uninterrupted fetch of several thousand kilometres of ocean is well mixed and far removed from variation in source strength characteristic of land areas. Another notable feature is that impact of local sources on CO₂ measurements at the measurement site is not significant and therefore provides an ideal site for baseline measurements of trace gases.

Variation of daily mean CH₄ concentration for the observational period of February 2003 to June 2004 is depicted in

Figure 6. Hourly sampled data were averaged and mean CH₄ concentration has been calculated for each day. Like in the case of CO₂, due to baseline drift in the chromatogram (due to malfunctioning of the instrument) and runaway from calibration, incorrect CH₄ values were carefully filtered out from the dataset. Measurements made over the period of 16 months showed day-to-day variation of a few ppb in surface air CH₄ concentration at the site. As low as 1.67 ppm and as high as 1.73 ppm of daily mean CH₄ concentration has been observed. In general, hourly values were observed between 1.66 and 1.77 ppm. To derive the nature of scatter in daily mean CH₄ concentration, frequency histogram against the concentration intervals (f_i) of 0.010 ppm has been plotted as illustrated in Figure 7.

Although the day-to-day variation of CH₄ has been observed from 1.67 to 1.73 ppm, most values (about 86.5%) have been observed in the range from 1.685 to 1.715 ppm. About 71% CH₄ concentration has been observed between 1.695 and 1.705 ppm. The exhibited small scatter of a few ppb in daily averages of near-surface atmospheric CH₄

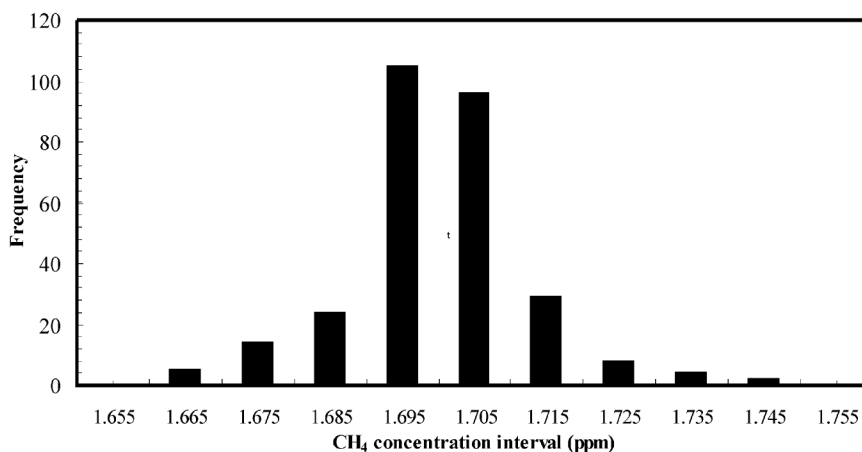


Figure 7. Frequency distribution of measured CH₄ concentration from February 2003 to June 2004 for f_i (frequency interval) = 0.010 ppm and $\sum f = 278$, ($\sum f = N$ = Total number of measurements).

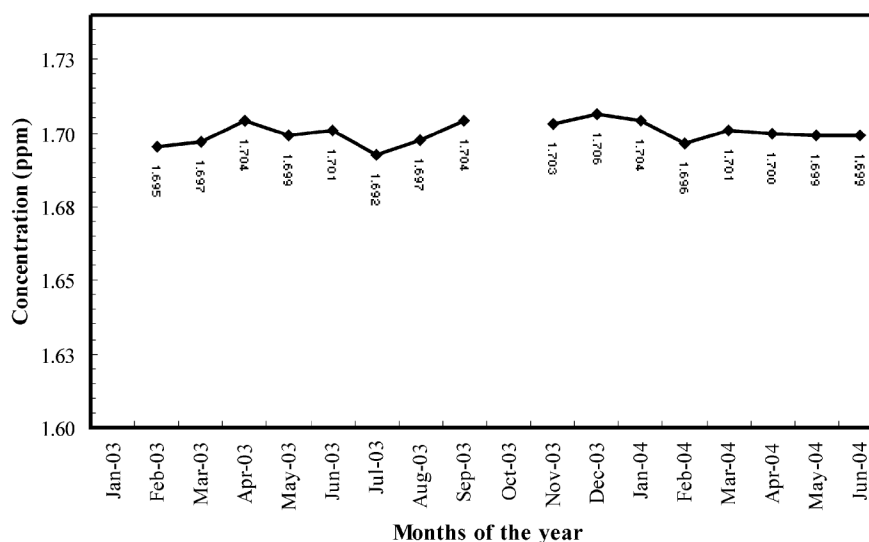


Figure 8. Monthly mean CH₄ concentration from February 2003 to June 2004 at Maitri, Antarctica.

throughout the observational period may be attributed to day-to-day variation in local meteorological conditions at the site. In order to study the growth of CH₄ in the atmosphere, daily mean values have been averaged to derive monthly mean CH₄ concentration, as depicted in Table 3. Monthly mean CH₄ concentration has been observed to vary from 1.695 to 1.704 ppm. As observed in Figure 8, the mean yearly values of near-surface CH₄ concentration during the observational period are nearly stable, exhibiting mean yearly value of 1.699 ppm in 2003 with standard error of ± 0.0034 and 1.699 ppm in 2004 (six months) with standard error of ± 0.0010 .

Mean CH₄ concentration for the 16-month period was found to be 1.699 ppm with standard error of ± 0.0025 . Similarly, no seasonal variations were observed at Maitri, Antarctica. The present data available for a limited period of 16 months does not show any evidence for increase in CH₄

concentration during that period. This is in agreement with observations by Dlugokencky *et al.*¹³, who noted that the globally-averaged atmospheric methane abundance was constant at ~ 1751 ppb from 1999 through 2002, suggesting that during this four-year period the global methane budget has been at a steady state. However, our understanding is still not sufficient to examine whether the prolonged pause in CH₄ increase is temporary or permanent.

Thus, the aforementioned measurements and analysis at the Indian Antarctic station, Maitri reveal that carbon dioxide concentration is increasing in the atmosphere. On the other hand, the atmospheric concentration of CH₄ is not increasing. Nearly invariant daily mean concentration of CO₂ and CH₄ observed at Maitri, illustrates that the air at Maitri is well mixed and far removed from the source strength characteristics of land area and hence is an ideal site for baseline measurements of trace gases in the atmosphere. The linearly

increasing CO₂ concentration indicates that the global abundance of CO₂ in the atmosphere is increasing either due to increase in CO₂ emission or imbalance between sources and sinks of CO₂. On the other hand, the observed stable CH₄ concentration indicates a decrease in emissions, which may have accelerated the global methane budget towards a steady state. The reason for the change is unclear. Dlugokencky *et al.*¹³ believe that a major contributing factor was the break-up of the Soviet Union in 1991. Oil and gas production fell, and the industry became more efficient at plugging gas leaks from pipes and wells. They also noted that the methane emissions from the former Soviet Union dropped significantly throughout the 1990s due to lower fossil-fuel production. Based on current knowledge of the observed data, it is not possible to tell whether we are only observing a persistent but temporary pause in its increase or global levels of methane are likely to stabilize in the near future. However, to derive acceleration and deceleration of global budget of these trace gasses, it is necessary to have continuous measurements for prolonged duration.

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Nondestructive evaluation of the Delhi iron pillar

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We discuss results obtained on nondestructive evaluation of the Delhi iron pillar using various non-destructive techniques such as ultrasonics, impact echo, radiography, radiation gauging, X-ray fluorescence, *in situ* metallography and electrochemical analysis. The microstructural analysis of the ornamental portion of the pillar indicated the presence of forged structure in the main body of the pillar, whereas the top platform consists of microstructure similar to 'as cast structure'. Further, the radiation gauging, radiography, ultrasonics and impact echo testing indicated the presence of voids at different locations in the pillar. The large aspect ratio (axial to radial) of the voids indicated that the pillar could have been forged in the radial direction rather than in the axial direction. The passivation current density for the 'passive' rust scales of the pillar formed on the surface clearly indicated the protective nature of the oxide structure developed and its stability against corrosion.

ANCIENT and medieval India did its countrymen proud and made tremendous impact on the world scene through many spectacular achievements in iron and steel technology. The technology of iron in India culminated in major achievements during the period 2nd–6th century AD. An exemplary monument of the time is the Delhi iron pillar (late fourth to early fifth century AD) standing at Mehrauli village, near Qutab Minar, on the outskirts of Delhi. It is a wrought iron product about 7.375 m high, 41.6 cm in diameter at the bottom and 34 cm at the top. The top has an aesthetic ornamental struc-

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