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Measurements of atmospheric methane at the Japanese Antarctic Station, Syowa

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ABSTRACT

Precise and continuous measurements of the atmospheric CH_4 concentration were initiated at Syowa Station, Antarctica in February 1988, using a gas chromatograph equipped with a flame ionization detector. The measurement precision was typically $\pm 0.07\%$ in a concentration range of 0.5 to 2.5 ppmv. The standard gases were CH_4-in-air mixtures and their CH_4 concentrations were determined gravimetrically with uncertainties of $\pm 0.2\%$. The CH_4 concentrations measured at the station were extremely stable, and outliers due to local contamination such as station activities were not found. The diurnal CH_4 variation was hardly observable throughout the year. The average seasonal CH_4 variation showed minimum and maximum concentrations in early March and late September, respectively, and a peak-to-peak amplitude of 30 ppbv. Annual mean values of the CH_4 concentration were 1640 and 1651 ppbv in 1988 and 1989, respectively. A concentration difference of 11 ppbv between the two years may suggest that recent annual increase rate of the CH_4 concentration is smaller than previously reported values of about 1% year^{-1}.

1. Introduction

It is well-known that the concentration of atmospheric CH_4 has been increasing (Fraser et al., 1981; Khalil and Rasmussen, 1983; Ehhalt et al., 1983; Rasmussen and Khalil, 1984). Such an increase influences many facets of the atmospheric chemistry; depletion of the stratospheric ozone layer due to CFCs may be eased by removal of Cl by CH_4 (Molina and Rowland, 1974) and the concentration of the stratospheric H_2O will be increased by oxidation of CH_4 (Rasmussen and Khalil, 1981). The increase of CH_4 also leads to changes in radiation budget; increase of the globally-averaged surface temperature due to doubling of the atmospheric CH_4 concentration from 1.7 to 3.4 ppmv is estimated to be 0.44°C (Wang and Molnar, 1985).

In order to predict future levels of the atmospheric CH_4 concentration, causes of the observed CH_4 increase have to be elucidated. For this purpose, detailed knowledge of atmospheric CH_4 variations are indispensable.

It was expected from the results of CO_2 measurements (Tanaka et al., 1987; Nakazawa et al., 1991) that Japanese Antarctic Station "Syowa" is suitable for background monitoring of the atmospheric CH_4 concentration. Therefore, we initiated continuous CH_4 measurements at Syowa Station in February 1988. In this paper, we will report technical aspects of our new measurements and preliminary results obtained for the first 2 years of the program.

2. Sampling site and experimental procedures

2.1. Sampling site

Syowa Station (69°00′S, 39°35′E) is located on East Ongul Island in Lützow-Holm Bay, being separated from the Antarctic Continent by the Ongul Strait, as shown in Fig. 1. Lichened rock surface is exposed in summer and covered with snow in other seasons. Lützow-Holm Bay is usually frozen but open sea is seen between late summer and autumn.

Syowa Station was established in January 1957, and at present about 30 personnel are engaged in scientific research throughout the year. Almost all facilities of the station are powered by electric generators.

Annual mean value of air temperature is $-11°C$ and monthly mean temperature decreases down to $-20°C$ in August and increases up to $-1°C$ in January. Annual mean value of wind velocity is 6.2 m s^{-1}. Prevailing winds are north-north-easterly and easterly for almost 70% of windy conditions. Calm conditions with wind velocities of less than 0.3 m s^{-1} occur for about 4% of the year.

Measurement system of the CH_4 concentration was set in a laboratory building at the northeast coast of the island, away from main living quarters and generator hut by more than 100 m.

2.2. *Measurement system*

An automated measurement system of the atmospheric CH_4 concentration was developed for this study, using a gas chromatograph (GC) equipped with a flame ionization detector (FID) (Aoki and Kawaguchi, 1990). Fig. 2 shows a schematic diagram of the system. Almost all tubing was made of stainless steel, but copper was used for the tube between an air intake and a liquid water trap and glass for a water vapor trap. To achieve rapid gas exchange in the system, tubing was made as short as possible, and care was taken so that the tubes among the solenoid valves 1–5 can be purged by the gas of the channel to be measured.

The intake for air samples was mounted atop an 8 m-high mast at the coast line of the island, away from the laboratory building by about 30 m, facing prevailing winds. Air samples were pressurized by a diaphragm pump and introduced into the sampling volume of the GC. Pressure pulsation of the sample air arisen from a vibrating diaphragm of the pump was absorbed by a buffering volume behind the pump. The pressure of air samples was adjusted by a pressure regulator to 1.22 hPa, and excess air was released at a rate of about 10 l min^{-1} from the system through a relief valve. Water vapor was removed from air samples by a glass trap cooled to $-60°C$ by an electric refrigerator. Measured values of the CH_4 concentration are therefore expressed in parts per billion by volume (ppbv) of dry air. Aerosol particles including in air samples were removed by glass and membrane filters. The solenoid valve 5 was attached to equalize respective quantities of air sample and standard gas in the sampling volume of which one end was opened to ambient atmosphere.

Gas chromatographic conditions employed in this measurement are shown in Table 1. The gas in the sampling volume was introduced into a main column by switching on a 10-port valve and CH_4 separated from other components was then led to the FID. A pre-cut column was used to prevent heavy hydrocarbons from intruding into the main column; such hydrocarbons were released to ambient atmosphere through a pre-cut vent by switching off the 10-port valve after introduction

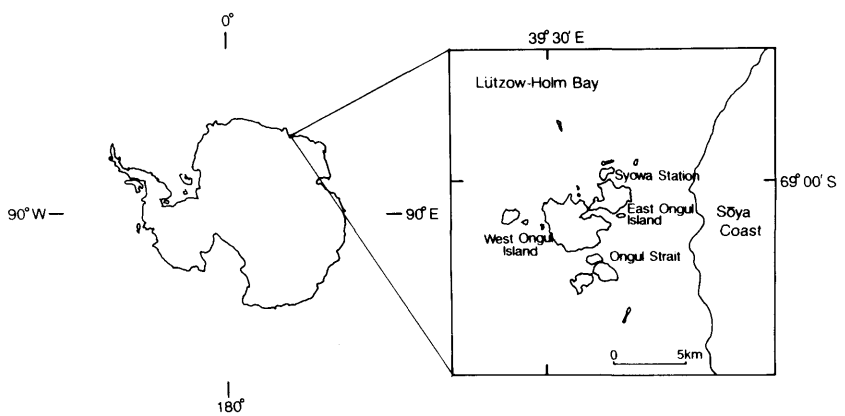

Fig. 1. Location of Syowa Station and its surrounding area.

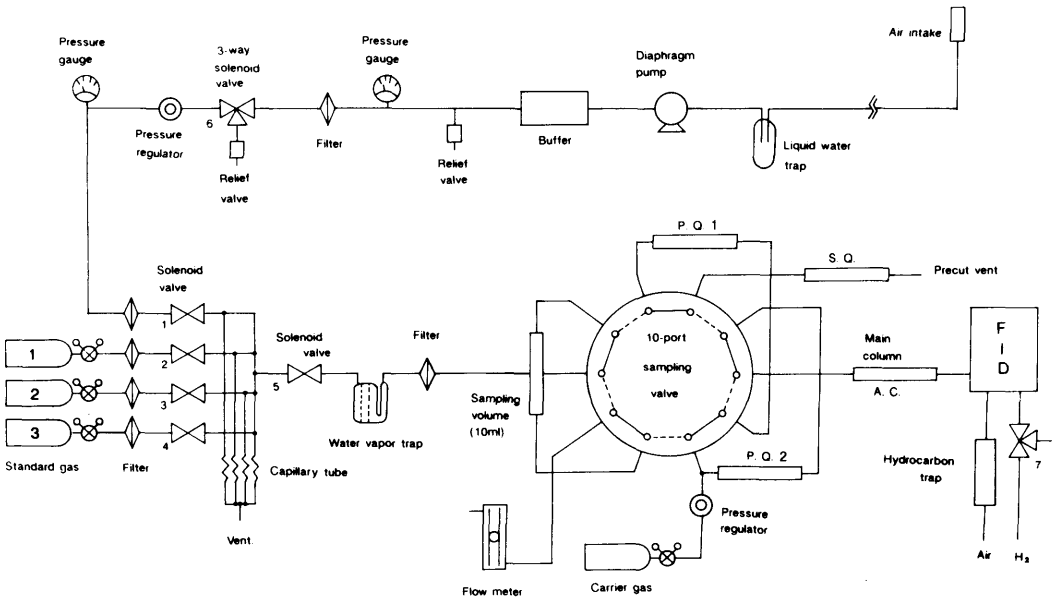

Fig. 2. Schematic diagram of the continuous measurement system of the atmospheric CH_4 concentration at Syowa Station.

of CH_4 into the main column. Ultra-high pure N_2 (>99.9998 %) was used as a carrier gas, and ultra-high pure H_2 (>99.99999 %) and purified and dried air as flame support gases for the FID. All columns and the sampling volume were housed in the thermostatic bath held at 60 ± 0.1 °C.

Gas chromatographic analyses were done 4 times every 1 h; 2 analyses are allocated for standard gases and the remainder for air samples. Therefore, the number of air samples analyzed for each year amounted to about 17,000. The CH_4 concentrations of respective standard gases were chosen to be higher and lower by about 400 ppbv than those of air samples. As shown in Fig. 3,

Table 1. *Gas chromatographic conditions of automated CH_4 measurement system at Syowa Station*

Column packing	Main column: SUS 3 mm i.d. × 1 m Activated charcoal (60–80 mesh) Precut column: SUS 3 mm i.d. × 1 m Porapak Q (80–100 mesh)
temperature	60 ± 0.1 °C
Carrier gas flow rate	Ultra pure N_2 (>99.9998 %) 32 ml/min
Detector	FID
temperature	80 ± 0.1 °C
H_2	Ultra pure H_2 (>99.99999 %)
air	Water vapor, hydrocarbons and aerosols are removed
Sample size	10 ml

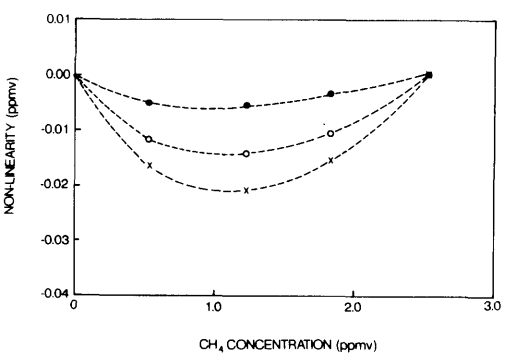

Fig. 3. Non-linear response of the gas chromatograph with FID to the CH_4 concentration for different flow rates of the flame support air. Solid circles, open circles and crosses represent the results for 200, 820 and 1000 ml min^{-1}, respectively.

we found that non-linear relationship between the CH_4 concentration and peak area of the chromatogram changes systematically depending on the flow rate of the flame support air. Similar phenomenon was also found for H_2. Non-linear relationship was therefore checked once every 15 days, using an additional standard gas with the CH_4 concentration nearly equal to air samples to be measured. All the CH_4 concentration data in this paper were corrected for these errors by interpolating respective results.

Operation of all solenoid valves and the 10-port valve was controlled by the main CPU. An analog output of the GC was digitized and then integrated by the CPU to obtain peak area of the CH_4 chromatogram. The integrated value was sent to a microcomputer which calculates and displays preliminary CH_4 concentrations of air samples and stored in a floppy disk, together with the channel number and time.

The precision of the GC used in this measurement was examined by determining the CH_4 concentrations of the standard gases ranging between 0.5 and 2.5 ppmv. The total number of gas samples was 143 and 6 to 14 measurements were made for individual gas. The results indicated that about 80% of all standard deviations fell within ± 1.5 ppbv. Relative values of the standard deviations to the CH_4 concentrations of the gas samples did not exceed $\pm 0.18\%$, their mean value being $\pm 0.07\%$.

In order to estimate the overall precision of our measurement system, we introduced the standard gas from the inlet of the diaphragm pump and measured its CH_4 concentration. Mean value of the measured concentrations was 1.8336 ± 0.0008 ppmv, which is just equal to the calibrated value of the standard gas (1.8336 ± 0.0007 ppmv). Taking account of the above results, we conclude that the overall precision of our measurements is equal to that of the GC itself, i.e., $\pm 0.07\%$.

2.3. *Standard gases*

To maintain the consistency of measurements for a long time, our standard gases were classified into 3 categories, i.e., primary, secondary and working. CH_4-in-air mixtures were chosen for our standard gases to equalize analytical conditions of the air samples and the standard gases, since O_2 affects the sensitivity of the FID (King, 1971). The primary standard gases were stored in 91 aluminum cylinders and the secondary and working standard gases in 471 aluminum cylinders.

The primary standard gases were prepared gravimetrically using an extremely precise balance with a standard deviation of 1.5 mg in a wide range of 1 mg to 100 kg and 4-stage dilution in August 1986 and in April 1991. The procedures were almost the same as those in Tanaka et al. (1983, 1987). Purity of CH_4 gas was better than 99.99%. Impurities of the purified air such as CO_2, CH_4 and CO were less than 0.1 ppmv and its dew point temperature was lower than $-70°C$. Since CH_4 in the air yields substantial errors in the gravimetric method, we first determined the CH_4 concentration in the air using our GC. The mean concentration was 21.8 ppbv for 1986 standards and 20.0 ppbv for 1991 standards. These values were corrected in calculation of the CH_4 concentrations of the standard gases.

Approximate CH_4 concentrations of the gases in the first, the second and the third dilution stages

Table 2. *CH_4 concentrations of the primary standard gases prepared gravimetrically in 1986 and 1991*

1986			1991	
Cylinder	CH_4 (ppbv)	Calibrated by the 1991 standards	Cylinder	CH_4 (ppbv)
DC9246	1030	1030	CPB00729	521
DC9251	1528	1531	CPB00730	1021
DC9247	2028	2030	DC5182	1520
DC9245	3003	3006	CPB00731	2021
			DC7212	2521
			CPB00728	3021

Table 3. *Stability of the CH_4 concentrations of the secondary standard gases*

Cylinder	CH_4 concentration (ppbv)			
	July 1987	March 1988	July 1989	March 1990
HA7431	2527.6 ± 1.7	2526.4 ± 0.7	2527.8 ± 1.0	2527.3 ± 1.3
HA7430	1830.9 ± 1.3	1832.1 ± 0.8	1830.4 ± 0.7	1831.1 ± 0.8
HA7429	1228.3 ± 0.7	1228.0 ± 0.9	1228.9 ± 0.6	1228.0 ± 1.1
HA3178			1103.5 ± 0.3	1103.8 ± 0.6
HA7428	527.8 ± 1.6	528.0 ± 1.0	527.9 ± 0.2	528.3 ± 0.6

were 16,000, 700 and 30 ppmv, respectively, and the primary standard gases ranging from 0.5 to 3 ppmv were finally prepared in the fourth stage. Molecular weights of the purified air and CH_4, which were necessary to calculate the CH_4 concentration of each standard gas, were determined to be 28.960 and 16.043, respectively, assuming natural abundances of air components and isotopes (Wedepohl et al., 1978). Uncertainties in the CH_4 concentration of the primary standard gases were estimated to be about ±0.2%.

The concentration scale of the standard gases employed in this measurement was based on the primary standard gas system prepared in 1986. As shown in Table 2, the CH_4 concentrations of the primary standard gases prepared in 1986 and 1991 agree well with each other, differences in the CH_4 concentration between both gas systems being within the estimated uncertainties of ±0.2%.

The secondary standards consisted of 5 gases with different CH_4 concentrations ranging from 0.5 to 2.5 ppmv, and their concentrations were calibrated against the primary standary gas system almost once every year. In this calibration procedure, 4 primary standard gases were used and the concentrations were determined by a least-square-fit technique, assuming a quadratic relation between the CH_4 concentration and the chromatogram area. As shown in Table 3, concentration drifts of the secondary standard gases over the last 3 years do not exceed ±1 ppbv. The cylinder of HA3178 was newly prepared in May 1989 and its concentration was stable for 1 year. These results could suggest that the CH_4 concentrations of the primary standard gases prepared in 1986 were also stable.

Table 4. *CH_4 concentrations of the working standard gases used at Syowa Station for the periods February 1988–January 1989 and February 1989–January 1990*

Cylinder	Before use (ppbv)	After use (ppbv)	Difference (ppbv)
February 1988–January 1989			
HA7406	1224.9	1225.2	+0.3
HA7407	1236.4	1237.3	+0.9
HA7408	1231.9	1232.2	+0.3
HA7410	1637.0	1637.2	+0.2
HA7411	2039.8	2039.5	−0.3
HA7412	2040.4	2040.8	+0.4
HA7413	2039.2	2039.6	+0.4
February 1989–January 1990			
HA3185	1204.2	1204.6	+0.4
HA3190	1205.3	1205.6	+0.3
HA3188	1205.5	1206.1	+0.6
HA3180	1603.8	1604.4	+0.6
HA3187	2006.5	2007.1	+0.6
HA3189	2007.1	2006.9	−0.2
HA3181	2005.6	2005.6	0.0

The working standard gases were used for the measurements of the atmospheric CH_4 concentration at Syowa Station. These standards were calibrated 4 or 5 and 1 or 2 times before and after their use, respectively, against the secondary standard gas system. As seen from the results given in Table 4, our working standard gases showed no appreciable drifts in concentration. Therefore, the results of both calibrations were simply averaged to calculate the CH_4 concentrations of air samples.

The working standard gases were aged for more than 1 month before their first calibration, to minimize possible initial drifts of the CH_4 concentration. The usage of all working gases was terminated at a pressure of about 30 kg cm^{-2} because the drift in concentration may occur with further decrease of the pressure in the cylinders.

3. Results and discussion

In order to examine variabilities of the CH_4 concentration at Syowa Station, we first calculated daily standard deviations of CH_4 concentration for the period of 17 February 1988 to 31 January 1990. 48 data were usually used for the calculation of each standard deviation. Only 5 data of abnormal values due to system errors were selected out from this analysis. The standard deviations thus obtained are shown in Fig. 4. As seen in this figure, the distribution of the standard deviation is extremely sharp; center of the peak is 1.1 ppbv and more than 90% of the data fall between 0.6 and 1.4 ppbv. The distribution is almost the same as that of the precision of our measurement system. We therefore conclude that the CH_4 concentrations at the station were extremely stable and that outliers due to local contamination were hardly observable throughout the whole period of the measurements. Visual inspection of the observed data of the CH_4 concentration also supported this conclusion.

The diurnal CH_4 variation was clearly observed in the Venezuelan savanna (Scharffe et al., 1990) and the Amazon River floodplain (Bartlett et al., 1990) where soil acts as a CH_4 source. Bartlett et al. (1990) also mention in their paper that diurnal changes in CH_4 sink characteristics also cause the diurnal variation of the atmospheric CH_4 concentration. To clarify whether or not the diurnal CH_4 variation is seen at Syowa Station, monthly averaged deviations of hourly mean CH_4 concentrations from daily means were calculated for each month between February 1988 and January 1989. The results for June and December 1988 are shown in Fig. 5 as examples of winter and summer months, respectively. As seen in this figure, the diurnal CH_4 variation was not observed throughout the year. Our results therefore suggest that there are no strong CH_4 sources and diurnal changes in CH_4 sink characteristics around the station. This is a great advantage for background monitoring of the atmospheric CH_4 concentration.

Daily mean values of the CH_4 concentration are shown in Fig. 6. The annual increase and the seasonal variation of the CH_4 concentration are clearly seen in this figure. Day-to-day variations of the CH_4 concentration are extremely small. These small variations relate probably to the exchange of different air masses in association with synoptic

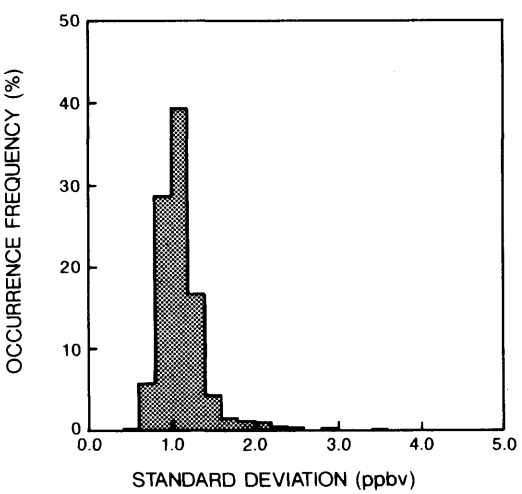

Fig. 4. Distribution of daily standard deviations of the CH_4 concentration at Syowa Station for the period 17 February 1988–31 January 1990.

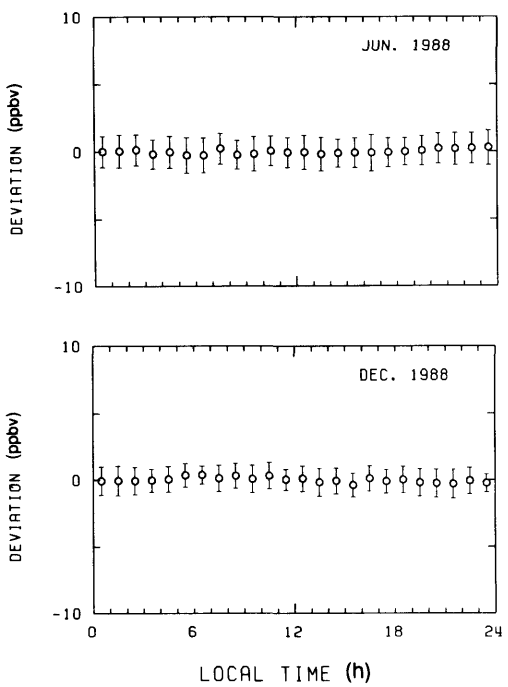

Fig. 5. Monthly averaged deviations of hourly mean CH_4 concentrations from daily means at Syowa Station in December and June 1988. Vertical bars represent the standard deviations.

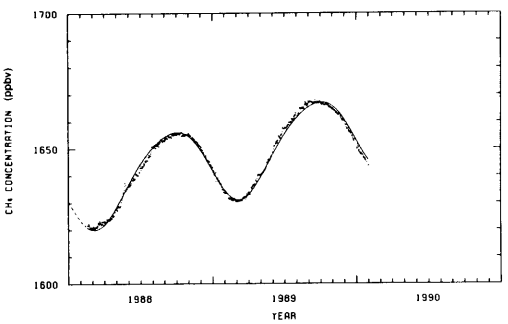

Fig. 6. Daily mean CH_4 concentrations calculated from all available data at Syowa Station. Solid curve shows the best fit of a time-dependent function (cf. text) to the data.

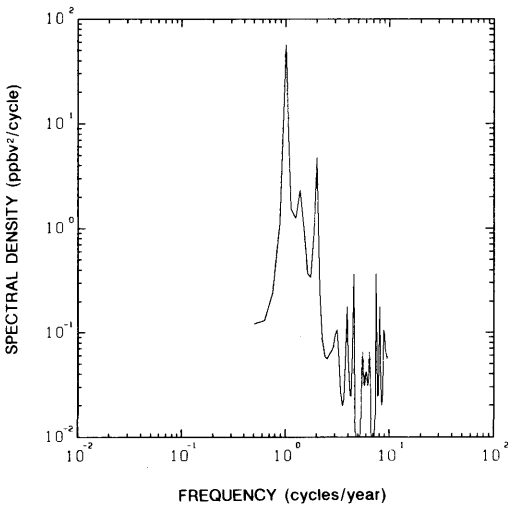

Fig. 7. Power spectrum of the CH_4 concentrations observed at Syowa Station for the period February 1988–January 1990.

scale weather disturbances. Similar phenomenon has been found by Nakazawa et al. (1991) for the CO_2 concentration at Syowa Station.

To separate the annual increase and the average seasonal variation of the CH_4 concentration, we fitted daily mean values to a time-dependent function including a linear and Fourier harmonic terms:

$$Y(t) = C_1 \sin 2\pi t + C_2 \cos 2\pi t + C_3 \sin 4\pi t + C_4 \cos 4\pi t + C_5 + C_6 t, \quad (1)$$

where Y denotes the CH_4 concentration and t is the elapsed time (years) relative to 1 January 1988. The harmonics in this equation were determined by applying a maximum entropy method (Burg, 1967) to daily mean CH_4 concentrations. As seen in Fig. 7, the harmonics contributing significantly to the seasonal CH_4 variation are only fundamental annual cycle and its first harmonics. The least-square fit of eq. (1) to daily mean values of the CH_4 concentration yielded the coefficients: $C_1 = -14.3$, $C_2 = -4.0$, $C_3 = -1.4$, $C_4 = 0.7$, $C_5 = 1634.1$ ppbv and $C_6 = 11.1$ ppbv year^{-1}, with the standard deviation of 1.2 ppbv. The best fit curve obtained by this procedure is also shown in Fig. 6. Differences between the curve and daily mean values are found in this figure. Its cause is attributed to the fact that the increase trend of the CH_4 concentration is not approximated well by a linear equation and/or the seasonal CH_4 variation contains small irregular components which change year by year.

The average seasonal CH_4 variation, representing by the fundamental annual cycle and its first harmonics, showed minimum and maximum concentrations in early March and late September, respectively and peak-to-peak amplitude of 30 ppbv. Measurements of the atmospheric CH_4 concentration have been made at several stations in the Antarctic region; in situ continuous measurements at Palmer Station (Robinson et al., 1984) in 1982 and 1983 and discrete air sampling with subsequent laboratory analysis at the South Pole and Palmer Station since 1983 (Steele et al., 1989) and at Mawson since 1980 (Fraser et al., 1986). The seasonal CH_4 variations at all these stations reach the minimum between late February and March and the maximum between September and October. These variations are in good agreement with ours. Amplitudes of the average seasonal CH_4 variation at the South Pole and Palmer Station for the period of 1983 to 1988 were 29.2 ± 1.6 and 32.1 ± 4.0 ppbv, respectively (Steele et al., 1989), which also agree quite well with our value. However, these values are larger than 23 ppbv observed at Mawson for the period of 1980 to 1984 and smaller than about 40 ppbv at Palmer Station by continuous measurements in 1983.

Annual mean values of the CH_4 concentration were 1640 and 1651 ppbv in 1988 and 1989, respectively, showing an increase of 11 ppbv between the two years. This difference is in excellent agreement

with the increase rate of 11.1 ppbv year^{-1} obtained by fitting eq. (1) to daily mean CH_4 concentrations. Almost the same increase rates of 11.0 and 12.1 ppbv year^{-1} were also observed by NOAA/CMDL at Syowa Station and the South Pole, respectively for the same period using the grab sampling method (E. Dlugokencky, personal communication). Higher rate of about 18 ppbv year^{-1} was reported by Blake and Rowland (1986) for the world-wide tropospheric CH_4 concentration between 1978 and 1983 and by Fraser et al. (1986) from measurements at Cape Grim, Australia between 1978 and 1984. Steele et al. (1987) reported that the increase rate at the South Pole from 1983 to 1984 was 15.6 ± 0.5 ppbv year^{-1}, but they suggested that the recent increase rate of the atmospheric CH_4 concentration is reduced as compared with previously reported values. Our results support their suggestion.

Precise and continuous measurements of the atmospheric CH_4 concentration have been initiated at Syowa Station, Antarctica. Since the CH_4 concentrations observed for the first 2 years of the program were extremely stable, it is expected that not only the mean rate of annual increase of the concentration but also its small year-to-year fluctuations will be detected precisely from longer data record, both quantities being very important for elucidating the global budget of the atmospheric CH_4.

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