

PRECISE MEASUREMENTS OF ATMOSPHERIC METHANE  
CONCENTRATION AT SYOWA STATION (69°00'S, 39°35'E),  
ANTARCTICA

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**Abstract:** Precise measurements of atmospheric CH<sub>4</sub> concentration was initiated at Syowa Station in February 1988. A regular diurnal variation is not observable but irregular variations are sometimes observed with extremely small amplitude of 5 ppbv at most. A seasonal variation is clearly seen with the amplitude of 30 ppbv. Annual mean values of CH<sub>4</sub> concentration are 1640 and 1651 ppbv for 1988 and 1989, respectively.

## 1. Introduction

It is well known that the concentration of atmospheric methane (CH<sub>4</sub>) has been increasing (FRASER *et al.*, 1981; KHALIL and RASMUSSEN, 1983; EHHALT *et al.*, 1983; RASMUSSEN and KHALIL, 1984). The increase of methane influences many facets of atmospheric chemistry. As CH<sub>4</sub> removes chlorine atoms from the stratosphere, increase in concentration may prevent some depletion of the stratospheric ozone layer (MOLINA and ROWLAND, 1974). Since oxidation of CH<sub>4</sub> produces water molecules, the concentration of stratospheric water vapor may increase in the future (RASMUSSEN and KHALIL, 1981). The increase of CH<sub>4</sub> also influences radiation budgets on the earth. The globally-averaged surface temperature increase for a doubling of atmospheric CH<sub>4</sub> from 1.7 to 3.4 ppmv has been estimated to be 0.44 K (WANG and MOLNAR, 1985).

In order to estimate the future level of atmospheric CH<sub>4</sub>, we must clarify the cause of observed increase of CH<sub>4</sub> concentration. This requires more data, especially from the southern hemisphere where a few data have been obtained in the past. Therefore, we initiated CH<sub>4</sub> measurements at Syowa Station operating a continuous measurement system since February 1988. In this paper, we reported a measurement system and preliminary results of our new measurements.

## 2. Experimental Procedure

We have developed an automated measurement system of atmospheric CH<sub>4</sub> concentration using a gas chromatograph (GC) equipped with a flame ionization

Table 1. Gas chromatographic conditions of automated CH<sub>4</sub> analysis system.

Column	Main column: SUS 3 mm i.d. × 1 m
Packing	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	Ultra pure N <sub>2</sub> (>99.9998%)
Flow rate	32 ml/min
Detector	FID
Temperature	80 ± 0.1 °C
H <sub>2</sub>	Ultra pure H <sub>2</sub> (>99.99999%)
Air	Water vapor, hydrocarbons and aerosols are removed
Sample size	10 ml

detector (FID). The precision of the GC was typically  $\pm 0.07\%$  in the range from 1000 to 2000 ppbv, which was attained by improving the gas flow lines and electric circuit of the commercially available GC. Details of the improvements have been described elsewhere (AOKI and KAWAGUCHI, 1990).

The gas chromatographic conditions are shown in Table 1. Activated charcoal (60–80 mesh) was packed in a main column of 3 mm i.d. × 1 m. In order to avoid deterioration of the main column, we adopted a pre-cut method to prevent heavy hydrocarbons from intruding into the main column. Ultra-high purity nitrogen (>99.9998%) was selected as the carrier gas. For the FID, ultra-high purity hydrogen and purified air were used as flame support gases. Water vapor and aerosols of the air were removed by silica gel (5–10 mesh) and filter, respectively. Hydrocarbons of the flame support air were decomposed by passing through the heated platinum catalyst. The sampling volume of the GC was 10 ml; it was housed in an oven of which temperature was controlled at  $60 \pm 0.1^\circ\text{C}$ .

Figure 1 shows a schematic diagram of the gas flow system for continuous measurements of atmospheric CH<sub>4</sub>. Tubing was made of stainless steel, copper and glass. Copper and glass were used only for tubing between the air intake and the liquid water trap and for the water vapor trap, respectively. To achieve rapid gas exchange in the system, the tubing was made as short as possible. The tubing was specially designed at the contact points of the standard gases and the sample air which allows clean sweeping of other residual gases by the flowing gas.

The intake for air samples was mounted atop an 8 m-high mast at the coast line of East Ongul Island, about 30 m away from the laboratory building, facing the prevailing wind. Air samples were pressurized by a diaphragm pump and were introduced in the sampling volume *via* a 10-port valve. Liquid water and water vapor were removed from air samples by a stainless steel trap maintained at room temperature and a glass trap cooled to  $-60^\circ\text{C}$  by an electric refrigerator, respectively. The concentration of CH<sub>4</sub> is therefore measured in parts per billion by volume (ppbv) for dry air. Aerosol particles are removed from the sample air by a glass filter and a membrane filter inserted into the tubing system.

Gas chromatographic analyses were done successively every 15 min and 4 analyses

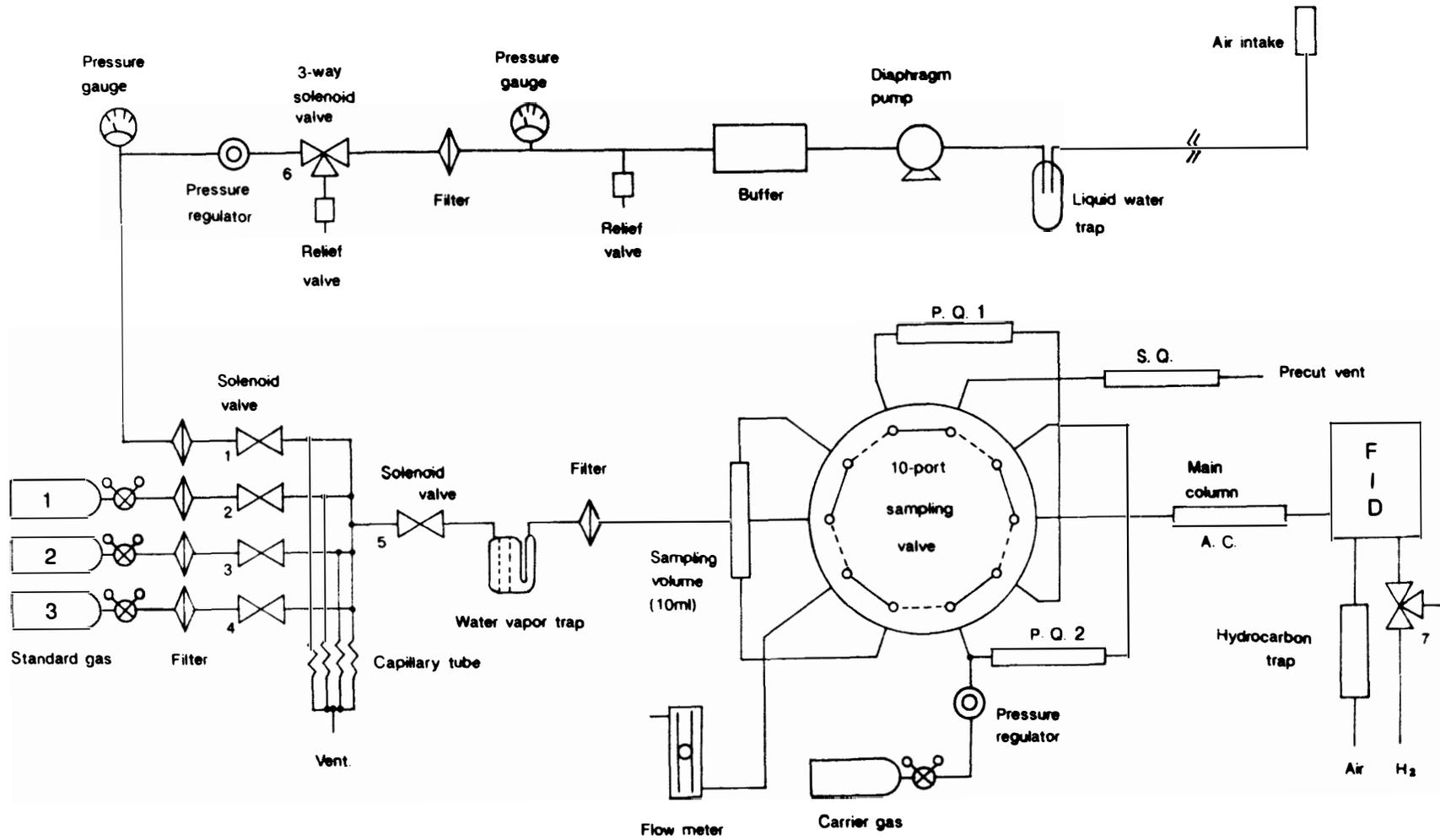


Fig. 1. The schematic diagram of the gas flow system for continuous measurements of atmospheric  $\text{CH}_4$ .

were repeated cyclically; two analyses were allocated for working standard gases and the remainder were for air samples. Therefore, the number of air samples analyzed by this measurement system amounts to about 17000 for each year. The pressure of the sample air or the standard gas in the sampling volume is equilibrated with atmospheric pressure for 12 s by closing solenoid valve 5; then the gas is introduced in the pre-cut column (P. Q. 1) with the carrier gas after the 10-port valve is switched on. Only methane is introduced in the FID *via* the main column while other hydrocarbons remain in the pre-cut column. After obtaining a methane chromatogram, the 10-port valve is again switched off, and then hydrocarbons are released to the ambient air from a pre-cut ventilator. Columns of P. Q. 2 and S. Q. were inserted in the flow line in order to maintain equal conductance of flow lines before and after the 10-port valve is switched on or off.

All solenoid valves and the 10-port valve are controlled by the main controller CPU. An analog output of the GC is digitized at the main controller, and then the CH<sub>4</sub> chromatogram is integrated. The integrated value with the channel number and the time is sent to a personal computer which calculates preliminary CH<sub>4</sub> concentrations of air samples; those original data are stored into a floppy disk. A security program is also contained in the main controller against a leakage of hydrogen; in case of hydrogen flaming off, the CPU will de-activate solenoid valve 7 and hydrogen will be released to the outside of the laboratory building.

To maintain the consistency of measurements for a long time, our standard gases were classified into three categories: primary, secondary and working. CH<sub>4</sub>-in-air mixtures are used for our standard gases to equalize analytical conditions of the air sample with those of standard gases, since oxygen changes the sensitivity of the FID (KING, 1971). In normal operation, two working standard gases were used for calibration of air samples. Concentrations of these standard gases were selected so as to be about 400 ppbv higher and lower than those of air samples. The non-linear relation between chromatogram areas and methane concentrations was checked once every 15 days by using an additional working standard gas with CH<sub>4</sub> concentration nearly equal to the air samples to be measured. These results were used for data correction. The working standard gases were calibrated 4 or 5 times before use and 1 or 2 times after use against our secondary standard gases at National Institute of

*Table 2. CH<sub>4</sub> concentrations of the working standard gases used at Syowa Station for the period February 1988–January 1989. Concentrations of lower and higher standard gases were about 1200 and 2000 ppbv, respectively. The concentration of an additional working standard gas (cf. text) was about 1600 ppbv.*

Cylinder	Before use (ppbv)	After use (ppbv)	Difference (ppbv)
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

Polar Research. An example of the concentrations of working standard gases used is given in Table 2. The drift in concentration was within 1 ppbv. Therefore, the results of both calibrations were simply averaged to calculate the CH<sub>4</sub> concentration in air samples. The secondary standard gases have been calibrated by the primary standard gases once per year. The primary standard gases were made by gravimetric method using an extremely precise balance, and the accuracy of their CH<sub>4</sub> concentrations was estimated to be  $\pm 0.2\%$  (AOKI and KAWAGUCHI, 1990).

In order to obtain overall precision of this system, we measured the concentration of a working standard gas connected at the inlet of the diaphragm pump. The mean concentration ( $1.8336 \pm 0.0008$  ppmv) was just equal to the calibrated value of the standard gas ( $1.8336 \pm 0.0007$  ppmv), and standard deviation was 0.04%. Therefore we conclude that the overall precision of this system is equal to that of GC itself, *i. e.* 0.07%.

### 3. Results and Discussion

Figure 2 shows all data obtained at Syowa Station for the period of June 1–10, 1988. As shown in this figure, the CH<sub>4</sub> concentration measured at the station were extremely stable. The standard deviations of daily mean CH<sub>4</sub> concentrations for these days were between 1.4 and 1.0 ppbv. A slight increase in CH<sub>4</sub> concentration, which was part of the seasonal cycle of CH<sub>4</sub> concentration, was also seen in this figure. Outliers due to local contamination such as station activity were not observed. So, all data can be used for a data analysis.

To clarify whether or not a systematic diurnal variation of CH<sub>4</sub> concentration can be seen at Syowa Station, monthly means of diurnal CH<sub>4</sub> variations were examined for each month between February 1988 and January 1989. The results are shown in

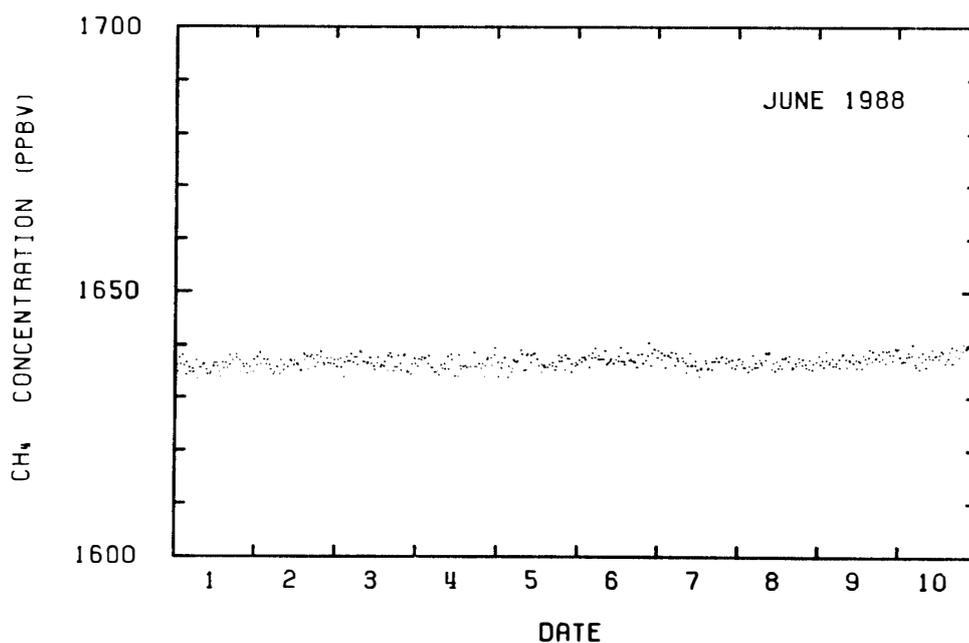


Fig. 2. All CH<sub>4</sub> concentrations obtained at Syowa Station for the period June 1–10, 1988.

Fig. 3 for June and December 1988 as examples of winter and summer, respectively. A systematic diurnal variation of  $\text{CH}_4$  concentration was not seen throughout the year. On the other hand diurnal variations of  $\text{CH}_4$  concentration were clearly seen in the Venezuelan savanna (SCHARFFE *et al.*, 1990) and in the Amazon river flood plain (BARTLETT *et al.*, 1990) where soil acts as a  $\text{CH}_4$  source. BARTLETT *et al.* (1990) mentioned that diurnal changes in sink characteristics will also cause diurnal changes in  $\text{CH}_4$  concentration. Our results suggest that there is no source of  $\text{CH}_4$  and no diurnal change in sink characteristics of  $\text{CH}_4$  around Syowa Station throughout the year.

Daily mean values of the  $\text{CH}_4$  concentration are shown in Fig. 4. The secular increase and seasonal cycle of  $\text{CH}_4$  concentration are clearly seen in this figure. The day-to-day variations of  $\text{CH}_4$  concentration are extremely small, except that irregular variations with amplitude of a few ppbv and periods of 1–2 weeks are observed. Such irregular  $\text{CH}_4$  variations are probably attributed to the transport of different air masses from other latitudes in association with synoptic scale weather disturbances.

We assume that the variations of  $\text{CH}_4$  concentration consist of a linear trend, a mean seasonal cycle and irregular variations. In order to separate the mean seasonal

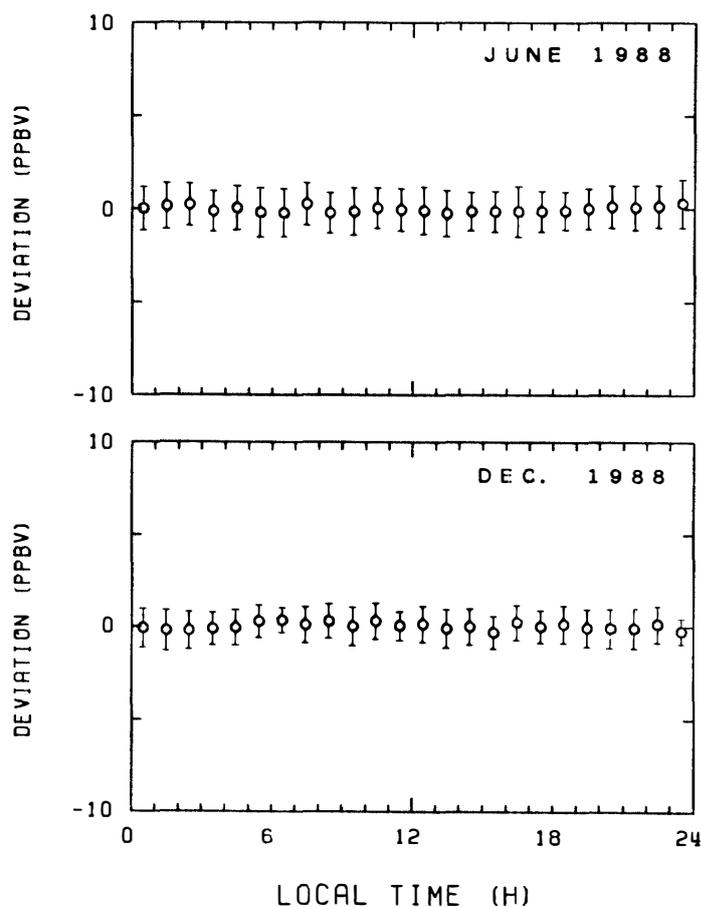


Fig. 3. Monthly means of hourly  $\text{CH}_4$  deviations obtained at Syowa Station for December and June 1988. The hourly  $\text{CH}_4$  deviations of each day were calculated by hourly mean  $\text{CH}_4$  concentrations minus the daily mean  $\text{CH}_4$  concentration. Vertical bars represent standard deviations.

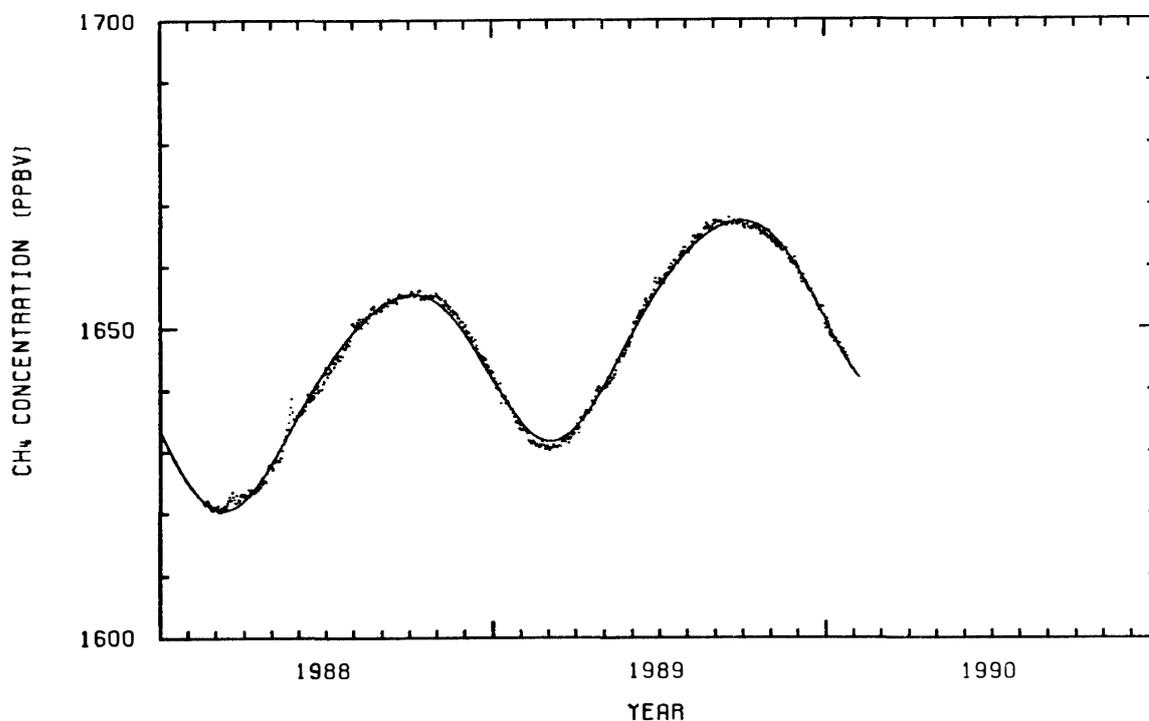


Fig. 4. Daily mean  $\text{CH}_4$  concentrations at Syowa Station obtained from all available data. The solid curve shows the best fit of a time-dependent function (cf. text) to the data.

cycle and the annual increase of  $\text{CH}_4$  concentration, we fitted the daily mean values with a time-dependent function including a linear and Fourier harmonic terms:

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

where  $Y$  denotes the  $\text{CH}_4$  concentration in ppbv and  $t$  is the elapsed time (in years) relative to January 1, 1988. The harmonic frequencies in the above equation were estimated from a spectral analysis of monthly mean  $\text{CH}_4$  concentrations for the period February 1988–January 1990 by the maximum entropy method (BURG, 1967). In order to raise spectral resolution, time series of 8-year-long data were made artificially; we first calculated a de-trended time series of monthly mean  $\text{CH}_4$  concentrations for 2 years and then added the time series 3 times one after another. As shown in Fig. 5, the harmonics significantly contributing to the seasonal  $\text{CH}_4$  variation were only the fundamental annual cycle and its first harmonics. A least-square fit of the eq. (1) to the daily mean values yielded the coefficients:  $C_1 = -14.1$ ,  $C_2 = -4.1$ ,  $C_3 = -1.4$ ,  $C_4 = 0.5$ ,  $C_5 = 1633.7$  ppbv and  $C_6 = 11.4$  ppbv  $\text{yr}^{-1}$ , with the standard deviation of 1.2 ppbv. Figure 4 also shows that the eq. (1) was not a perfect fitting function. This fact suggests that the secular trend of  $\text{CH}_4$  concentration was not linear and the seasonal cycle of  $\text{CH}_4$  concentration might contain small components which change year by year.

The average seasonal cycle of  $\text{CH}_4$ , represented by the fundamental annual cycle and its first harmonics, showed minimum and maximum concentrations early in March and late in September, respectively, with a peak-to-peak amplitude of 30 ppbv. Measurements of atmospheric  $\text{CH}_4$  concentration have been made at several stations in

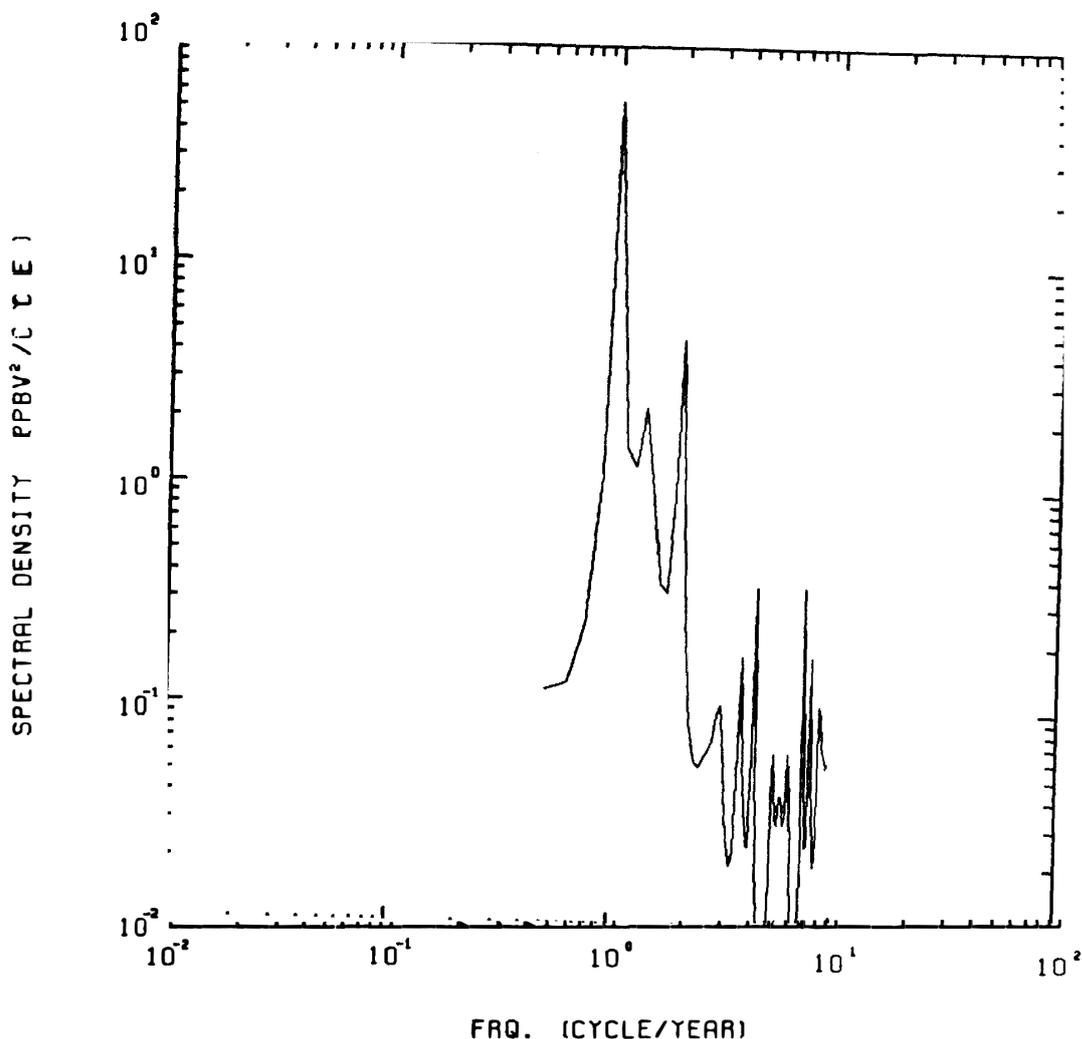


Fig. 5. Power spectrum of monthly mean  $\text{CH}_4$  concentrations observed at Syowa Station for the period February 1988–January 1990.

the Antarctic region. *In situ* continuous measurement have been made at Palmer Station (ROBINSON *et al.*, 1984) for 1982 and 1983, and discrete measurements using the grab sampling method have been made at South Pole, Palmer Station and Halley Bay since 1983 (STEELE *et al.*, 1987) and at Mawson since 1980 (FRASER *et al.*, 1986). The phases of the seasonal  $\text{CH}_4$  cycle for all these stations were in good agreement with our results; minimum and maximum concentrations appeared in March and from September to October, respectively. The mean amplitudes of seasonal  $\text{CH}_4$  cycle at South Pole, Palmer Station and Halley Bay for the period of 1983–1984 obtained by STEELE *et al.* (1987) were 29, 31 and 32 ppbv, respectively; and these amplitudes also agree quite well with our result. A smaller amplitude of 23 ppbv was obtained at Mawson for 1980–1984 and larger amplitude of about 40 ppbv at Palmer Station in 1983 by continuous measurement.

The annual mean values of  $\text{CH}_4$  concentration were 1640 and 1651 ppbv for 1988 and 1989, respectively, yielding an increase of 11 ppbv  $\text{yr}^{-1}$  for the two years. The same increase rate of 11.4 ppbv  $\text{yr}^{-1}$  was obtained by the fitting function (1). STEELE

*et al.* (1987) reported a growth rate of  $15.6 \pm 0.5$  ppbv yr<sup>-1</sup> at South Pole for 1983–1984. A higher growth rate of about 18 ppbv yr<sup>-1</sup> was reported by BLAKE and ROWLAND (1986) for world-wide tropospheric concentration of CH<sub>4</sub> during 1978–1983, and by FRASER *et al.* (1986) at Cape Grim, Australia during 1978–1984. STEELE *et al.* (1987) suggested that the CH<sub>4</sub> growth rate might be slowing down. We conclude from those results that the increase rate of the secular trend of CH<sub>4</sub> concentration has been decreasing.

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