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GAS-CHROMATOGRAPHIC MEASUREMENTS OF ATMOSPHERIC METHANE AT SYOWA STATION IN 1983, AND BETWEEN TOKYO AND SYOWA STATION LATE IN 1984

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Abstract: Atmospheric methane was measured by a gas-chromatographic method. Air samples were collected at Syowa Station in 1983, and on board between Tokyo and Syowa Station late in 1984.

Mixing ratios at Syowa Station showed some seasonal variation and were in good agreement with those at Mawson Station.

Mixing ratio decreased gradually from 30 to 5°N, and steeply between 5°N and the equator. In the Southern Hemisphere, mixing ratios were almost constant between the equator and 66°S. The mean value was 1.577 ppm and the standard deviation was 0.008 ppm.

1. Introduction

Methane (CH_4) is an important trace gas in the atmosphere, because it contributes significantly to the atmospheric greenhouse effect, and to the chemistry of both the troposphere and the stratosphere. In the troposphere, it is a sink for OH and, therefore, a source of CO. In the stratosphere, it is a sink for Cl and a source of H_2O. Since the end of the 1970's, atmospheric CH_4 has been increasing by 1–2%/year (KHALIL and RASMUSSEN, 1983; BLAKE and ROWLAND, 1986). Such increase may significantly affect the earth's climate and the depletion of the stratospheric ozone.

In order to obtain the global distributions of minor constituents such as CF_2Cl_2, $CFCl_3$, N_2O and CH_4, air samples have been collected at Syowa Station and on board between Tokyo and Syowa Station since the 23rd Japanese Antarctic Research Expedition (JARE-23) (HIROTA *et al.*, 1984).

In this paper, preliminary results of CH_4 measurements for samples collected at Syowa Station in 1983 and on board of the icebreaker SHIRASE late in 1984 will be reported.

2. Experimental

2.1. *Sampling of air*

Air samples at Syowa Station were collected at 4 m above the ground surface on

the northeast side of a hut of the Upper Atmosphere Physics Laboratory. Air samples between Tokyo and Syowa Station were collected on the bridge of the icebreaker SHIRASE. Air was sucked through a copper tube into a stainless-steel cylinder (0.3 *l*) by an air pump (see Fig. 1 in HIROTA *et al.*, 1984).

2.2. *Gas-chromatographic analysis*

CH_4 in the sample air was analyzed using a Shimadzu Gas Chromatograph GC-MINI 2 equipped with dual flame ionization detectors (FID) and a Shimadzu Chromatopac C-R3A. The sample air in the cylinder was transferred to a gas sampler (Shimadzu MGS-4), which was evacuated beforehand, and then to the gas chromatograph.

Table 1. Gas-chromatographic conditions for CH_4 analysis.

Column	glass column 3 m×3 mm i.d.
packing	molecular sieve 5 A (30–60 mesh)
temperature	50°C
Carrier gas	ultra pure N_2 (>99.9995%)
flow rate	30 m*l*/min
Detector	dual FID
temperature	100°C
H_2	pure H_2 (>99.99%)
air	air passed through a drier tube filled with silica gel(6–10 mesh)
Sample size	6 m*l*

Gas-chromatographic conditions are summarized in Table 1. In the gas-chromatographic analysis, peak areas were used to calculate volume mixing ratios of CH_4. The peak area was proportional to the mixing ratio of CH_4 in the range between 0.2 and 3.0 ppm.

A mixed gas of 1.79 ppm CH_4 in pure air (Takachiho) was used as a reference gas. Accuracy of the reference gas was $\pm 1.5\%$, which was certified by Chemicals Inspection & Testing Institute.

The variation coefficient for repeated measurements of a reference gas was about 0.5%. Volume mixing ratio for dry air was obtained by using meteorological data on the hour nearest the sampling time.

Stability of CH_4 in the sampling cylinder was checked by measuring the reference gas filled in a sampling cylinder. For six measurements in one year and a half, the mean mixing ratio showed 99.6% for that of the reference gas and the variation coefficient was 0.4%.

3. Results and Discussion

3.1. *Time variation at Syowa Station*

CH_4 was analyzed for only 5 among 21 samples collected at Syowa Station in 1983, because CF_2Cl_2, $CFCl_3$ and N_2O were measured preferentially. Results are

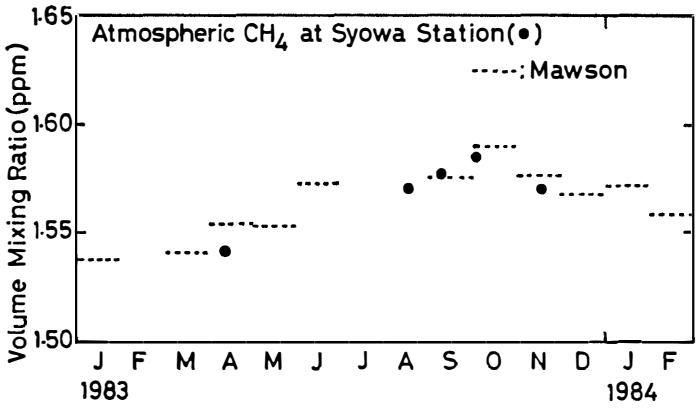

Fig. 1. Time variation of CH_4 at Syowa Station in 1983.
---: monthly mean value at Mawson Station (FRASER et al., 1986).

shown in Fig. 1. One sample on April 11 was collected at Tottuki Point, and one on October 2 at Lake Nurume in Langhovde. The locations are 15 km northeast and 25 km south from Syowa Station, respectively. Our results suggest some seasonal variation.

Dotted lines show monthly mean values at Mawson Station, location of which is about 1000 km east from Syowa Station and where a few samples per month were collected in 0.5 *l* glass flasks in 1983. Observations at two stations show good agreement with each other. FRASER *et al.* (1986) have reported similar seasonal variations of CH_4 at Cape Grim (41°S, 145°E) and at Mawson Station (68°S, 63°E) with a broad maximum in austral spring and a narrow minimum in late summer since 1980. Therefore, this agreement indicates that a similar seasonal variation can be observed at Syowa Station. At Palmer Station (66°S, 64°W) also, a similar seasonal variation was observed in 1983, though the mean value was rather low (ROBINSON *et al.*, 1984).

In July 1983, an unusually high value was observed at Cape Grim. A similar phenomenon was not observed at Palmer Station. Unfortunately there was no data at Mawson and Syowa Stations in the same period.

3.2. Latitudinal variation

Samples were collected at intervals of about 5° in latitude. Results are shown in Fig. 2. Mixing ratios decreased gradually from 30 to 5°N, and steeply between 5°N and the equator. The sample air at the equator was collected at 19 GMT on November 20. It is known that the intertropical convergence zone (ITCZ) moves into the summer hemisphere between the Central Pacific Ocean and the Indian Ocean. Corresponding to our results, it seems, however, that from cloud images of the GMS, the ITCZ drifted north on November 20 just like it was dragged by the typhoon T8426. In the Southern Hemisphere, mixing ratios were almost constant between the equator and 66°S. The mean value (---) was 1.577 ppm and the standard deviation was 0.008 ppm.

BLAKE and ROWLAND (1986) have reported a similar pattern for the latitudinal distribution of CH_4 between March and May 1983. A different pattern, however, was observed in August 1983, when CH_4 decreased steadily from north to south. According to them, the latter pattern has been observed in the latter part of other

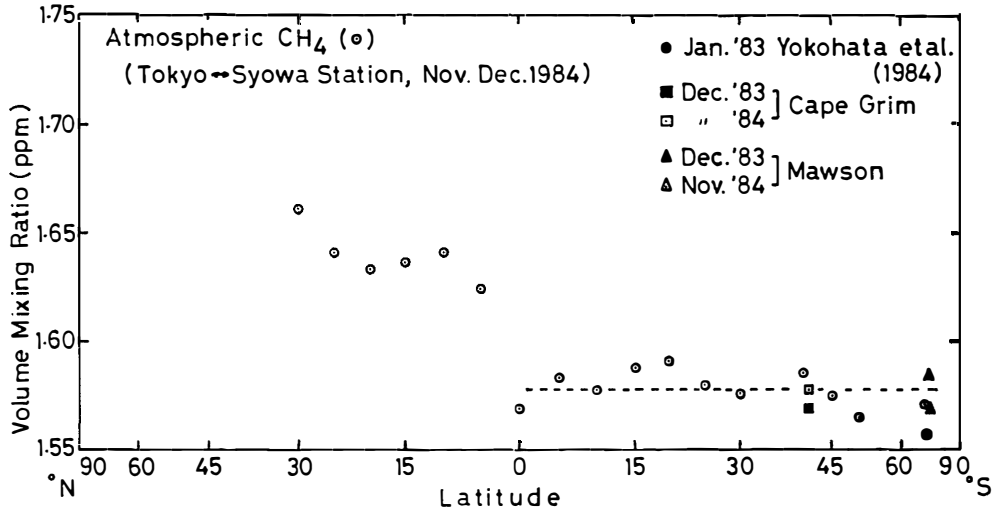

Fig. 2. Latitudinal variation of CH_4 between Tokyo and Syowa Station late in 1984.
---: mean value between the equator and 66°S.
●: mean value in January 1983 at Syowa Station (YOKOHATA et al., 1984).
■ and □: monthly mean value in December 1983 and 1984 at Cape Grim (FRASER et al., 1986).
▲ and △: monthly mean value in December 1983 and November 1984 at Mawson Station (FRASER et al., 1986).

calendar years, which is not consistent with our results obtained late in 1984. As for the variability in latitudinal gradient of CH_4, more observations are needed.

In Fig. 2, a solid circle is the mean value observed at Syowa Station in January 1983 by YOKOHATA *et al.* (1984). Solid and open squares are the monthly mean values observed at Cape Grim in December 1983 and 1984 respectively (FRASER *et al.*, 1986). Solid and open triangles are those observed at Mawson Station in December 1983 and November 1984 respectively (FRASER *et al.*, 1986). If a regular seasonal variation would be expected at Mawson Station in 1984, the value in December would be about 5 ppb lower than that in November. These values including our results show good agreement with one another taking the increase of 7–8 ppb/year into consideration.

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