Atmospheric methane over the western Pacific and the Antarctic Ocean from 1978 to 1986

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Methane concentrations were determined for air samples collected over the western Pacific and the Antarctic Ocean in the years from 1978 to 1986. The latitudinal distribution from 35°N to 65°S revealed a decrease in methane concentration towards south, with two sharp gradients around 20°N and the inter-tropical convergence zone (ITCZ). The methane concentrations south of ITCZ were much lower than those in the Northern Hemisphere. The average concentrations of methane in samples collected over the western North Pacific (9°N–24°N) indicate an almost linear increase from 1978 to 1986 with no significant fluctuation of the annual rate of methane increase. The average rate of the increase from 1978 to 1986 was calculated to be 17 ± 2 ppb/yr over the western North Pacific, and that over the Antarctic Ocean was estimated to be 16–17 ppb/yr from 1978 to 1984.

INTRODUCTION

Atmospheric methane is recognized as one of the most important trace gases that participates in the greenhouse effect and causes global warming (Wang *et al.*, 1976; Lacis *et al.*, 1981; Ramanathan *et al.*, 1985). Several workers have pointed out that change in methane concentrations might ultimately influence the tropospheric cycle of carbon monoxide and hydroxyl radicals (Logan *et al.*, 1981; Levine *et al.*, 1985), and the stratospheric cycle of ozone and water vapor (Owens *et al.*, 1982; Blake and Rowland, 1986; Ramanathan, 1988). Thus, it is important to clarify the recent trend of changes in methane concentrations for the prediction of global changes in the atmospheric environment in the future.

From the late 1970's, accurate measurements of atmospheric methane have been carried out using a gas chromatograph with a flame ionization detector (GC/FID). Three research groups

began systematic recording of methane concentrations in clean air in 1978 (Blake and Rowland, 1986; Fraser *et al.*, 1986; Khalil and Rasmussen, 1986). Subsequently, the other two groups also started to take frequent measurements at the background stations from 1982 (Steele *et al.*, 1987; Brunke *et al.*, 1990). These studies indicate that levels of atmospheric methane are rapidly increasing in both hemispheres. However, there have been some uncertainties on the rate of methane increase over a decade (Blake and Rowland, 1986), because the accurate measurements of tropospheric methane before 1982 are limited.

We collected air samples over the western Pacific Ocean and the Antarctic Ocean from 1978 to 1986. Methane in these samples was analyzed recently by GC/FID to determine the past concentrations of atmospheric methane. In this report, we describe the latitudinal distribution and temporal rate of increase in levels of methane over nearly a decade. We discuss our

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results in comparison with those of the previous studies.

EXPERIMENTAL

Samples

Locations for air sampling are shown in Fig. 1. Air samples at 137°E were collected in January–February from 1978 to 1986 except for 1980 and 1981 during a cruise of R/V Ryōfū Maru, Japan Meteorological Agency (JMA). Sampling over the western South Pacific and the Antarctic Ocean was performed during cruises of R/V Umitaka Maru (Tokyo University of Fisheries) in 1978 and R/V Hakuho Maru (Ocean Research Institute, the University of Tokyo) in 1983. Air samples were collected occasionally at sea off the coast of Japan during

cruises of the Ryōfū Maru and R/V Kōfū Maru (JMA). Detailed information about sampling sites and dates for 60 samples is listed in Table 1.

Sample air was sucked from the bow to avoid contamination from the ship by using a diaphragm pump with a flow rate of 5–10 l/min. Air was passed through an HA filter (0.45 μm) to remove aerosols and then cooled in an alcohol bath maintained at -60°C to remove water vapor. Several air samples were not passed through the cold trap after filtration, but these samples were completely dried before analysis. A cylindrical glass bottle (100 ml) fitted with ground-glass stopcocks lubricated with Apiezon-H grease or Dow Corning high vacuum grease (Toray Silicon Co. LTD) at both ends was flushed with the filtrated air. After flushing, air sample was sealed in the bottle at positive pressure, attained by first closing the outlet and then the inlet after confirming of increased inside pressure. All of the samples, with a pressure slightly greater than ambient, were kept at room temperature in the dark until analysis.

Analysis

Methane in air samples was analyzed on a gas chromatograph (GC-5A; Shimadzu Japan) with a flame ionization detector. A stainless-steel column (2 m long $\times$ 3 mm i.d.) packed with Molecular Sieve 5A (60/80 mesh) was operated at 50°C . Nitrogen was used as carrier gas at a flow rate of 40 ml/min. The peak area of methane was integrated by a chromatographic data processor (Chromatopak C-R4A; Shimadzu Japan). The analysis was repeated four times for each sample so that the analytical variation by GC could be estimated. All measurements by our procedure showed analytical reproducibility with a standard deviation of less than $\pm 0.3\%$.

Injection of the air sample into the GC column was performed using a gas sampler with a six-way valve and a sample loop of 5 ml volume. The sample loop was evacuated by a vacuum pump and then the sample air was expanded to the sample loop. The air sample was completely dried before transfer into the sample loop by passage through a coil of stainless-steel tubing

Fig. 1. Map showing locations where air samples were collected.

immersed in an alcohol bath maintained at -80°C . The air pressure in the sample loop was determined with a vacuum gauge (Digital Vacuum Gauge VD-76A; Okano Works, LTD, Japan) with a precision of less than $\pm 0.1\%$. Methane concentrations in this paper are expressed in the unit of parts per million by mole fraction (ppm) or parts per billion by mole fraction (ppb) in dry air.

The sample air and standard gas were analyzed by turns for more accurate determination of the concentration of methane. All measurements of air samples were calibrated by using two working standards of methane in air with the concentrations of about 1.40 ppm and 1.80 ppm. The linearity of the GC response was checked with several primary standard gases with levels of methane from 1.40 ppm to 1.80 ppm, which had been prepared by the gravimetric method (Nippon Sanso Co. Ltd., Japan). The absolute concentrations of working standard gases were routinely determined by comparison with primary standard gases. The absence of any change in levels of methane in the working standard gases was confirmed before and after analysis of samples.

RESULTS AND DISCUSSION

Storage effect for the samples

The air samples collected from 1978 to 1986 were stored in glass bottles with greased stopcocks over a long period till the analysis in 1986. It has been reported that air samples can be contaminated with methane that emanates from the vacuum grease used on the stopcocks (Craig and Chou, 1982). Therefore, we carried out a storage test under the same conditions as used for the storage of the air samples. Glass bottles with greased stopcocks were filled with the standard gas and dry natural air, and kept in the dark at room temperature for 8–11 months. The air samples before and after storage were analyzed for the concentration of methane by an automatic injection system with an analytical reproducibility of less than $\pm 0.2\%$ (Matsueda *et al.*, in preparation). The six-way valve and stop-

Fig. 2. Methane concentrations of standard gas (a) and dry natural air (b) before and after storage in the glass bottles with greased stopcocks. The straight lines and dashed lines denote the mean values of all measurements and analytical errors of $\pm 0.2\%$, respectively. The procedure for the storage test is described in the text.

cocks of this system were electrically controlled by the chromatographic data processor to apply the repetitive analysis of 8 samples.

The results of our storage test clearly indicated no significant change in the measured concentration of methane in both the standard gas and natural air over the course of about one year (Fig. 2). Steele *et al.* (1987) also reported that the methane content of air samples in glass flasks with Apieson-N greased stopcocks was not affected during storage for more than one year. A further test of long-term storage could not be performed using glass bottles, but the standard gas in the aluminum cylinder showed no change in methane concentration over the course of four years.

To check for any leakage of the air samples, the pressure of such samples was determined for all sample bottles before methane analysis. We confirmed that in most of the samples the pressure was maintained slightly above the ambient pressure. However, several samples of air at ambient pressure had high concentrations of methane, above 1.8 ppm, indicating air exchange between the inside and outside of the bottles. Since air samples with unusual concen-

trations of methane or no excess pressure above ambient were excluded from our data, all of the samples listed in Table 1 had been preserved without any abrupt change in the methane concentration until analysis.

Latitudinal distribution of methane

The concentrations of methane in all samples of air collected from 1978 to 1986 are listed in Table 1. Figure 3 shows the latitudinal distributions of methane concentrations in winter since a large number of samples has been collected from January to February. The distribution curve between 35°N and equator illustrated in Fig. 3 was obtained by fitting a cubic spline function (Greville, 1967) under the following data selection. First, the measurements of samples collected between January and May were used since no seasonal variation during this period was observed in the Northern Hemisphere (Steele *et al.*, 1987). Second, average values of more than two measurements within a latitudinal difference of 2 degrees were used in the spline analysis.

In order to compare our measurements with those in the NOAA/Geophysical Monitoring for Climatic Change (GMCC) program (Steele *et al.*, 1987), monthly mean concentrations in January at the three Pacific stations of NOAA/GMCC program are shown in Fig. 3. The distribution patterns of methane found in the NOAA/GMCC study and in ours were very similar, but the absolute values were differed systematically by about 10 ppb. The difference seems to be caused by a difference in standard

Table 1. Sampling date, time, and location, and concentration of methane for individual air samples collected from 1978 to 1986

	Date and time (JST)*	Latitude	Longitude	Concentration of methane (ppm)
1978	1/22 10:00	8°00'N	137°00'E	1.535
1978	1/26 12:00	0°07'S	137°03'E	1.532
1978	1/28 9:00	64°42'S	150°54'E	1.456
1978	1/31 15:00	49°12'S	150°36'E	1.454
1978	2/03 6:00	38°16'S	151°18'E	1.463
1978	2/05 9:00	29°57'S	153°32'E	1.453

Table 1. (Continued)

	Date and time (JST)*	Latitude	Longitude	Concentration of methane (ppm)
1978	2/14 15:00	19°54'S	154°42'E	1.475
1978	2/16 9:00	9°59'S	154°17'E	1.487
1978	2/18 3:00	0°04'S	154°24'E	1.541
1978	2/20 3:00	10°18'N	149°54'E	1.538
1978	4/21 18:00	34°58'N	139°45'E	1.623
1978	4/22 6:00	33°33'N	141°50'E	1.617
1978	4/22 12:00	32°56'N	142°49'E	1.599
1978	4/27 12:00	30°28'N	142°19'E	1.592
1978	4/28 12:00	29°48'N	136°42'E	1.607
1978	5/04 16:00	31°29'N	130°31'E	1.595
1978	5/04 18:00	31°09'N	130°42'E	1.590
1978	5/05 12:00	30°58'N	132°00'E	1.579
1978	5/07 10:00	31°18'N	131°52'E	1.568
1978	11/02 6:30	45°32'N	147°06'E	1.624
1978	11/04 8:00	48°00'N	145°14'E	1.664
1978	11/11 0:00	44°51'N	152°47'E	1.611
1979	1/20 12:00	30°55'N	137°00'E	1.609
1979	1/22 15:00	23°33'N	137°01'E	1.602
1979	1/24 15:00	15°36'N	137°01'E	1.593
1979	1/26 15:00	8°19'N	137°02'E	1.556
1979	2/16 12:00	31°20'N	130°42'E	1.649
1982	1/20 12:00	34°00'N	137°00'E	1.663
1982	1/21 0:00	25°00'N	137°00'E	1.657
1982	1/24 15:00	19°54'N	137°00'E	1.639
1982	1/27 12:00	9°12'N	137°00'E	1.614
1982	1/29 0:00	5°00'N	137°00'E	1.608
1982	2/01 0:00	0°52'S	137°02'E	1.590
1983	1/22 15:00	23°00'N	137°00'E	1.658
1983	1/27 0:00	6°17'N	137°00'E	1.600
1983	1/30 15:30	0°00'	137°00'E	1.590
1983	2/15 15:00	29°51'N	133°13'E	1.652
1983	12/03 9:30	16°22'S	154°40'E	1.563
1983	12/19 12:00	61°35'S	150°24'E	1.563
1984	1/24 12:30	24°41'N	136°57'E	1.670
1984	1/30 18:30	4°59'N	136°49'E	1.626
1984	11/13 12:00	31°03'N	145°49'E	1.702
1984	11/14 0:00	31°00'N	145°42'E	1.716
1985	1/20 0:00	30°00'N	137°00'E	1.734
1985	1/22 12:00	25°11'N	137°00'E	1.686
1985	1/24 6:00	19°50'N	137°00'E	1.686
1985	1/24 6:00	19°50'N	137°00'E	1.680
1985	1/25 13:00	14°59'N	137°00'E	1.675
1985	1/26 15:00	11°02'N	137°00'E	1.640
1985	1/26 15:00	11°02'N	137°00'E	1.638
1985	1/28 18:20	5°02'N	137°00'E	1.633
1985	1/31 18:30	0°18'S	137°00'E	1.641
1985	4/20 10:30	33°16'N	142°46'E	1.734
1985	4/24 15:00	31°11'N	145°47'E	1.721
1986	1/23 17:00	25°04'N	136°56'E	1.733
1986	1/25 12:00	18°13'N	137°00'E	1.714
1986	1/26 14:00	14°11'N	137°00'E	1.670
1986	1/28 10:00	7°37'N	136°59'E	1.659
1986	1/29 12:30	5°01'N	137°03'E	1.648
1986	1/31 14:00	0°37'N	137°00'E	1.665

*JST, Japan Standard Time.

Fig. 3. Latitudinal distribution of concentrations of methane over the western North Pacific and the Antarctic Ocean from 1978 to 1986. The closed circles, open circles and open squares represent measurements in January–February, in April–May and in November–December, respectively. The distribution curves north of equator are obtained by fitting a cubic spline function, which is described in the text. The triangles represent the monthly mean concentrations in January at Christmas Island (2°N), Marianas Island ($13^{\circ}26'\text{N}$) and Cape Kumukahi, Hawaii ($19^{\circ}31'\text{N}$), as reported by Steele *et al.* (1987).

gas scales between the NOAA/GMCC study and ours.

As shown in Fig. 3, the concentrations of methane over the western North Pacific were the highest near Japan and decreased toward the equator every winter. A similar distribution with a north-to-south decrease was also observed from mid-latitudes to the equator in several meridional studies (Ehhalt, 1978; Heidt *et al.*, 1980; Cofer, 1982; Singh and Salas, 1982), although the north-south gradient depends on the study region and the season. It is well known that the

main source of atmospheric methane is biological production under anaerobic conditions on land, such as rice paddies and wetlands, and enteric fermentation (Cicerone and Oremland, 1988). Thus, the north-south gradient of tropospheric methane is largely maintained by major sources located in the middle and higher latitudes of the Northern Hemisphere.

In the western North Pacific, a sharp concentration gradient seems to appear at around 20°N every winter season, but the exact latitude is unclear because of the limited number of measurements from 1978 to 1986 (Fig. 3). Thus, a detailed examination of the latitudinal distribution of methane was performed from 35°N and 3°N along 137°E from January to February in 1987 (Fig. 4a). A rapid decrease in the concentration of methane was observed from 21°N to 18°N in 1987. The surface wind direction north of 20°N was predominantly composed of NE or NW components that originated from the winter monsoon, while the easterly component of the trade wind dominated south of 20°N (JMA, 1989). Such a weather condition along the 137°E line in the western North Pacific was maintained throughout the winter season for the years of 1978 to 1986, as reported in the JMA cruise reports. These results suggest that the sharp gradient around 20°N in winter was formed by the development of the winter monsoon.

The concentrations of methane between 35°N and 11°N are closely related to those of carbon dioxide observed at the same time in 1987 (Fig. 4b). A linear fit of the data, if we omit the data south of 11°N , gives a slope of 19 ppb CH_4 per ppm CO_2 . Inoue *et al.* (1991) reported that such a slope was suggestive of averaged ratio between CH_4 and CO_2 fluxes to the atmosphere, although only limited information was available on the relationship between atmospheric CH_4 and CO_2 at that time. Such a good correlation between levels of CH_4 and CO_2 in this region was also found for every winter season from 1988 to 1990 (Matsueda *et al.*, in preparation). Considering the latitudinal range of the air samples collected from 35°N to 11°N , the correlation be-

Fig. 4. a. Latitudinal distribution of concentrations of methane over the western North Pacific observed from January to February in 1987. The closed and open circles represent the data north of 11°N and south of 11°N , respectively. b. Relationship between concentrations of methane and carbon dioxide in 1987. The regression line north of 11°N is given by $\text{CH}_4 (\text{ppm}) = 0.019 \times \text{CO}_2 (\text{ppm}) - 4.95$.

tween CH_4 and CO_2 in winter is representative of fairly large-scale phenomena. These results suggest that there is no direct effect from local emissions on the distribution of methane from 35°N to 11°N . However, the measurements of levels of methane and carbon dioxide south of 11°N deviated from the correlation obtained with data from north of 11°N . It is possible that an air mass with different ratio of methane to carbon dioxide intruded near the equator in 1987, but such an intrusion was not clearly indicated by the data on surface wind vectors during the same period.

The level of methane over the South Pacific and the Antarctic Ocean in 1978 and 1983 was much lower than that in the Northern Hemisphere (Fig. 3). In 1978, an abrupt reduction in the concentration of methane was observed between the equator and 10°S , where the intertropical convergence zone (ITCZ) is generally located in the western Pacific during the winter seasons of the Northern Hemisphere. A large latitudinal gradient in the concentration of tropospheric methane across the ITCZ was also found in several sets of interhemispheric observations (Heidt *et al.*, 1980; Cofer, 1982; Blake and Rowland, 1986).

It is of interest that the methane concentration in the Southern Hemisphere in 1978 showed no geographical variation between 30°S and

65°S . Steele *et al.* (1987) also reported that the level of tropospheric methane in the Southern Hemisphere was quite uniform. These results strongly suggest that there was no major source of atmospheric methane in the Southern Hemisphere in contrast with the Northern Hemisphere.

Temporal increases

The distributions of methane over the western North Pacific from 1978 to 1987 clearly showed increases in concentrations year by year (Figs. 3, 4). An elevation of the level of atmospheric methane was also found over the Antarctic Ocean between 1978 and 1983. Such gradual increases since 1978 have also been observed by other long-term observations in both hemispheres (Khalil and Rasmussen, 1986; Blake and Rowland, 1988). This study confirmed that the concentration of atmospheric methane has been increasing globally since 1978.

Figure 5 shows average concentrations of methane over the western North Pacific in the latitudinal range from 9°N to 24°N in the winter seasons from 1978 to 1986. The average concentration for each year was obtained by taking the mean of the values for every one degree of latitude that was interpolated from the spline fit curve. Since the interpolated values between 9°N and 24°N could be calculated by every spline fit

Fig. 5. Average concentrations of atmospheric methane between 9°N and 24°N in the western North Pacific from 1978 to 1986. The rate of increase in concentration, estimated by least squares fit, was 17 ppb per year as shown by a straight line.

curve, this latitudinal range was taken for the estimation of average concentration.

The average data indicate a small interannual fluctuation in the rate of increase in methane concentration during the years 1978–1986. Khalil and Rasmussen (1986) reported that the rate of increase at Cape Meares (45°N, 124°W), Oregon, fell significantly with a substantial decrease in methane concentration during the 82/83 ENSO event. Although our data from 1982 and 1983 show a slight reduction of the rate of increase, no decrease in the concentration of methane was observed. Our results compare well with that by Blake and Rowland (1988), suggesting that the ENSO event had no major effect on the rate of increase in levels of methane. No abrupt change in rate of methane increase from 1982 to 1983 was also observed at Cape Grim (41°S, 145°E) in the Southern Hemisphere (Fraser *et al.*, 1986).

The rate of methane increase from 1983 to 1985 in the western North Pacific tended to be lower than that before 1982 as shown in Fig. 5. Several workers have also pointed out that the rate of increase in levels of methane from 1983 to

1985 has fallen from the preceding several years (Steele *et al.*, 1987; Blake and Rowland, 1988; Brunke *et al.*, 1990). From these results, it is apparent that the rate of methane increase in the troposphere exhibited slight interannual fluctuations for the past decade, although the cause for the fluctuation can not be deduced from the limited data at present stage.

Since the interannual variability in the rate of increase is relatively small in the western North Pacific, the annual increase in levels of methane can be approximated by a straight line to allow estimation of the average rate over nearly a decade (Fig. 5). The rate of increase in tropospheric methane in the western North Pacific was calculated to be 17 ± 2 ppb per year for 1978–1986 by the least squares fit. Blake and Rowland (1988) reported that the best linear fit of averaged global data gave a rate of 16 ± 1 ppb per year for 1978 to 1987, while the rate at Cape Meares, Oregon, was calculated to be 16 ppb per year for 1979 to 1985 from continuous measurements (Khalil and Rasmussen, 1986). Thus, the rate in the western North Pacific determined here was nearly consistent with those from the two previous studies. Although the number of measurements in our study was much smaller than those in the previous studies, the close agreement with the other studies on the average rate of methane increase is thought to be due to the fact that the estimate is based on long-term observations over about ten years.

In the Southern Hemisphere, we have only two data for 1978 and 1983. The methane concentration in the Antarctic Ocean increased from 1.455 ppm in January 1978 to 1.563 ppm in December 1983. Steele *et al.* (1987) reported that the concentration of methane in the Southern Hemisphere showed a clear seasonal variation and decreased by about 5–10 ppb from December to January. Taking such seasonal variation into account, we estimated a rate of increase in the Antarctic Ocean from January in 1978 to January in 1984 to be 16–17 ppb per year. This value is nearly consistent with 18 ppb/yr (1978–1984) observed at Cape Grim in the Southern Hemisphere (Fraser *et al.*, 1986).

Recent increases in methane concentrations are thought to be due to increase in emission from human activities and decrease in oxidation associated with depletion of atmospheric OH radicals, but these causes cannot be quantitatively identified at the present stage (Khalil and Rasmussen, 1985; Blake and Rowland, 1986). Thus, further long-term observations of levels of tropospheric methane are necessary for a better understanding of trends in the near future as well as their source functions.

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