Annual Variation of Methane in Seawater in Funka Bay, Japan

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The concentration of methane in seawater was determined approximately once a month for one year from August 1990 to July 1991 at a station close to the center of Funka bay (92 m depth) and some supplementary observations were also carried out. The concentration of methane was usually increased with increasing depth, suggesting that methane was emitted from the bottom of the bay. While highly variable both spatially and temporally, the emission was intense in March and April, a period immediately after the spring bloom of phytoplankton. The maximum of methane found in the intermediate water suggests its source from the slope of the bay. The concentration of methane in the surface water changed seasonally and also interannually. The annually averaged flux of methane transferred to the atmosphere in the bay was estimated to be $6 \times 10^{-3}$ gCH$_4$/m$^2$/day. The coastal zone in the world may be a significant source of the atmospheric methane, although its source strength has yet to be accurately estimated from more data in different coastal seas.

1. Introduction

Methane, one of greenhouse gases, has been drawn much attention especially to the global atmospheric chemists (e.g., IGBP Report No. 12, 1990). They, however, have considered methane derived from the marine environment to be of minor importance to the atmosphere in the global warming issues. According to the IPCC report (Houghton et al., 1990), the contribution of the marine source to the atmospheric methane is only about 2%. This value has been first calculated by Ehhalt (1974) and cited by Cicerone and Oremland (1988), based on the fact that the pelagic water is oversaturated by 30% with respect to the air. The situation in coastal seas, however, was not specially considered in their estimate of methane of marine origin. Although the area shallower than 200 m is less than 10% of the entire ocean, the coastal seas cannot be ignored as the excess concentration of methane, relative to the solubility (2–3 n mol/l) in the coastal water is more than one order of magnitude larger than that in the pelagic water. The methane concentrations are 16.7–27.4 n mol/l in Chesapeake Bay (Lamontagne et al., 1973) and 107–366 n mol/l in the mouth of Mississippi river (Swinnerton and Lamontagne, 1974), while those in the pelagic water are 1.83–2.81 n mol/l (Burke et al., 1983). Since the methane concentrations in the coastal seas are locally and temporally highly variable, it is important to determine extensively the methane concentration in various coastal seas as well as its temporal variation.

Even if the present source strength of the coastal region is not large for the atmospheric methane, the future marine source is not necessarily ignored for the increased flux of methane to the atmosphere due to the rapid change in the region by the recent human activities. The eutrophication increases the organic carbon flux to the bottom and the organic carbon enlarges the anoxic zones of sediments producing methane. Not only the flux itself, but the processes,
especially the feedback processes between the methane formation and the climate change in the changing coastal seas are also necessary to be clarified, if they are quantitatively significant. The extensive and intensive studies on methane in coastal seas may reveal those processes. In this study, we describe spatial and temporal variation of methane in Funka Bay, of which hydrography is well known, and discuss the factors controlling its concentration.

2. Study Site

The hydrographic oceanography of Funka Bay has been fairly well studied (e.g., Ohtani and Kido, 1980; Kido and Ohtani, 1981; Watanabe and Tsunogai, 1984). Funka Bay has a round plan and fairly flat bottom with an area of 2270 km² and its maximum and mean depths are 102 and 59 m, respectively (Fig. 1). The volume of water is about 10 times larger than that of Tokyo Bay. The major turnover of the bay water occurs twice a year in early spring and early autumn, although the turnover is not complete and its small scale exchange by the tidal and local currents is continuously occurring.

The main sampling station (Sta. 30) located 42°15' N, 140°36' E (92 m depth) close to the center of the bay and some other stations for the supplementary observation are shown in Fig. 1.

![Fig. 1. Map showing sampling stations with contour depths in meters in Funka Bay. The station numbers are underlined, which are commonly used by the Funka Bay study scientists.](image-url)

3. Sampling and Analytical Methods

Seawater collected in a 51 Niskin bottle was sucked into a glass syringe of 100 ml and added 2 ml of 10 mM mercuric chloride from another syringe, avoiding contact with the air. The solution was mechanically mixed. The samples were stored at 5°C or lower and analyzed within 24 hours.
Table 1. Conditions for the gas chromatographic analysis of methane in seawater.

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>FID Gas chromatograph, type GC-8A (Shimadzu Co. Ltd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation column</td>
<td>3 m × 3 mm i.d. stainless steel column packed with charcoal (0.25-0.50 mm, grain size)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Temperatures</td>
<td>Separation column, 50°C; Vaporization chamber, 70°C; Detector, 70°C</td>
</tr>
<tr>
<td>Concentration columns</td>
<td>1 m × 3 mm i.d. and 0.3 m × 3 mm i.d. stainless steel columns packed with charcoal (0.5–1.0 mm, grain size)</td>
</tr>
<tr>
<td>Desiccant</td>
<td>Magnesium perchlorate (GFS Chemicals Co. Inc.)</td>
</tr>
<tr>
<td>Standard gases</td>
<td>2.41 and 5.01 ppm of methane in nitrogen (Takachiho Trading Co. Ltd.)</td>
</tr>
</tbody>
</table>

after the sampling. The analytical method was after that of Weiss (1981) with slight modification: Two concentration columns rather than one column in the original method were used. The gas chromatographic analytical conditions are summarized in Table 1. The precision (1 sigma value for 10 determinations) was 5.2% at the concentration level of 60 n mol/l and the detection limit was 0.02 n mol/l. The standard gases used were those containing 2.41 and 5.01 ppm methane in nitrogen gas that were calibrated by Takachiho Trading Co. Ltd.

4. Results and Discussion

Figure 2 shows that the water column distributions of methane that were determined 13 times approximately once a month from 27 August 1990 to 29 July 1991 at the main station in Funka Bay. The depth interval was about 10 m at each observation. Generally, the concentration of methane was increased with increasing depth. The highest concentration of methane was observed in the bottom layer in the period of just or post spring bloom of phytoplankton in March and April. These results suggest that the source of methane in the water column is located in or on the bottom. However, its release to the bottom water is apparently not continuous, probably due to changes in the redox condition of the thin surface layer of bottom sediments and in the bacterial activities producing and decomposing methane. This suggestion is supported by the finding that the anoxic interstitial water approaches the seawater-bottom interface in late spring just after the spring bloom and in summer when the bottom is covered by the stagnant water (Watanabe and Tsunoai, 1984).

The source of methane in the water column, however, not necessarily the bottom beneath the water followed by transported upward one dimensionally. There was a marked maximum of methane concentration in the intermediate water at 50 m depth on 3 June 1991. The salinity of the water was 33.313 PSU, which was significantly smaller than those of the bottom waters having the maxima in March (33.619 PSU) or in April (33.577 PSU). This means that the maximum of methane in intermediate water in June was not originated in the bottom water around 90 m depth in March or April. The distribution of methane also means that the lifetime of methane in seawater for consumption due to oxidation was not so short as compared to the replacement
Fig. 2. Depth profile of concentration of methane observed at Sta. 30 in Funka Bay during the period from 27 August 1990 to 29 July 1991. The unit of the concentration of methane in this figure is n mol/l.

Fig. 3. Isopleths of the concentration of methane (n mol/l) at Stas. 55, 29 and 30 in Funka Bay on 2 July 1991. These stations on the horizontal axis represent the relative distance from the coast.
of water inside the bay or the time necessary for the transport of the intermediate water containing much methane from the source region.

To corroborate the above view, we occupied two more stations (Stas. 29 and 55 in Fig. 1) in July 1991. The results illustrated in Fig. 3 clearly show the existence of a large source of methane at the slope in July rather than the basin of the bay where a marked source was found in March and April. Figure 3 also shows that methane emitted from the active source flowed out isopycnally and mixed slowly. These results suggest the following for the behavior of methane in the coastal sea. The intermittent emission of methane from the bottom may be due to highly accidental factors, which are the production in the anoxic sediments and the decomposition in the oxic thin surface sediment. The methane escaped from the oxidation at the bottom and diffused into seawater may be fairly stable for the oxidation in the water column as found by Ward and Kilpatrick (1993). The highly variable concentration of methane in the surface may be due to its intermittent release at the bottom, and the fairly stable nature of methane makes its transfer to the atmosphere across the air-sea interface possible.

Figure 2 also shows the uniform vertical distribution of methane during the period of winter months due to the active vertical mixing. For example, a mean concentration with a standard deviation was $62 \pm 5 \text{ n mol/l} (n = 10)$ in the water column on 14 February 1991, while that was $77 \pm 67 \text{ n mol/l} (n = 10)$ on 18 April 1991, showing a large difference in the deviation values. This indicates a possibility that methane in water may be used as a tracer of water mixing and movement, although the use is confined to somewhat limited area and time scales. For example, a sectional distribution of methane (Fig. 4) along a line between Muroran and Sawara (at Stas. 9, 10, 15 and 16 in Fig. 1) indicates a maximum of methane concentration at the southern part of the border in the intermediate water. This result may be due to the anticlockwise flow in the bay deduced by physical oceanographers (Ohtani and Kido, 1980), but further observations are necessary to depict it in detail.

The concentration of methane in the surface water (Fig. 2) was decreased with time from the first determination on 27 August 1990 (103 n mol/l) to that on 29 July 1991 (8 n mol/l), while

![Fig. 4. Isopleths of the concentration of methane (n mol/l) at Stas. 8, 10, 16 and 15 locating along a line from Muroran to Sawara. The data were obtained from the cruise on 28 June 1993.](image-url)
the tendency was not observed for the subsurface water. The methane concentration determined supplementarily at Sta. 30 in summer of 1993 (Fig. 5) was somewhat similar to that observed in 1991 for the surface water, but not for the subsurface water. The cause of the large interannual variation cannot be fully explained. However, it may be due to the fact that the water containing much methane does not necessarily exist only in the bottom layer and the water is sometimes brought to the surface by the vertical advection and diffusion especially when the warm Kuroshio water flows into the deep of the bay in August. The statement that methane once emitted to seawater from sediments is considerably stable, has been discussed above.

Using the observed concentrations of methane, the gas transfer velocities obtained in Funka bay (Tsunogai and Tanaka, 1980) and the surface film model for the gas transfer (Liss and Slater, 1974), we have derived the transfer rate of $6 \times 10^{-3} \text{gCH}_4/\text{m}^2/\text{day}$ as a mean for the period from August 1990 to July 1991 in Funka Bay. The following values are used for the calculation. The mean concentrations of methane in the surface water are 30 and 46 n mol/l in, respectively, summer (April–September) and winter (October–March). The gas transfer velocities for methane are 20 and 61 cm/hr in, respectively, summer and winter. The transfer rate obtained in Funka Bay is two or three orders of magnitude larger than those estimated in the open ocean (Sheppard et al., 1982; Khalil and Rasmussen, 1983; Cicerone and Oremland, 1988). We can realize this large transfer rate obtained here if it is applied to the world continental shelf zone comprising 7.6% of the entire ocean (Sverdrup et al., 1942). The annual transfer rate turns out to be 60 Tg methane. This is extremely larger than the oceanic source of methane of 10 Tg with a range of 5–20 Tg presently accepted in the IPCC report (Houghton et al., 1990). Admittedly the annual emission rate in Funka Bay cannot be regarded as a mean of all the coastal seas, although the eutrophication of Funka Bay due to the recent human activities has not been observed and the bay is an ordinal coastal sea in the northern Japan. It is extremely difficult to derive a reliable estimate for the
methane flux from the coastal seas, since the concentration of methane in the coastal zone is 
highly variable both areally and temporally even interannually. However, there remains a 
possibility that the coastal zone is a significant source region for the atmospheric methane.

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