B-2.6 Study of Emission Estimate from Inland Water Surface

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Total Budget for FY 1990-1994 26,418,000 Yen (FY 1994; 5,263,000 Yen)

Abstract Dissolved methane and nitrous oxide concentrations in Japanese lakes and inland seas were measured. The results were analyzed with the environmental parameters to clarify the controlling factors making the seasonality of the concentration and the emission fluxes. The dissolved methane is monthly measured in an eutrophicated lake, Kasumigaura. The whole lake average was 157 nM, which was far higher than the atmospheric equilibrium concentration. There was a clear seasonality in the dissolved concentration. The average of the diffusive flux from the water surface was 3.1 mg CH_4/m^2/day. The bacterial oxidation of methane in the water was significant in late summer and autumn. Half of the dissolved methane diffused from the lake bottom sediment is oxidized within the water column. Dissolved nitrous oxide concentration was also measured. The concentration was higher in winter and lower in summer. The oversaturated concentration was around 20 % of the equilibrium concentration, showed no seasonality and had no relationship with the dissolved inorganic nitrogen. The dissolved methane concentration of Japanese various lakes, having different trophic levels, were measured. From the relationship between the measured dissolved methane and the trophic levels, a model calculation for the total methane emission was performed. The methane emission was estimated as 1.6 $GgCH_4$/year for the sum of all the Japanese natural lakes. Seasonal change in the methane concentration of seawater was measured in highly eutrophic Tokyo Bay. The sources of methane in these surface waters were attributed to lateral transport from the near shore zone. The calculated diffusive flux from the bay surface was 1.5 gCH_4/m^2/year, which was larger than that of Lake Kasumigaura. This indicates the possibility of large contribution of marginal sea to the global methane emission.

Key Words methane, nitrous oxide, lake, inland sea, flux

1. Introduction

Contribution of natural wetland methane emission is estimated to be 100 Tg/y that corresponds to 20 % of the global flux. Natural wetlands can be categorized into several types, i.e., bog, fen swamp, marsh, floodplain and freshwater lake. As the emission rate of methane per unit area, its seasonal variation and the mechanism of emission have large varieties, the emission rate estimate has a large uncertainty. Accumulation of observed flux data of various types of wetlands are needed for the improvement of flux estimates. The contribution of sea, especially eutrophicated continental shelves and inland seas, to the global methane and nitrous oxide is significant. Although the contribution of wetlands in Japan to the global methane and nitrous oxide is quite small, the precise study for the gas emission mechanism from the water is worthwhile for the verification of reported emission fluxes. In this study, mainly dissolved methane and nitrous oxide concentrations in Japanese lakes and inland seas was measured. The results were analyzed with the environmental parameters to clarify the controlling factors of making seasonality of the concentration change, and the emission fluxes.

2. Automated analytical system for dissolved methane and nitrous oxide

Water sample for dissolved methane and nitrous oxide is taken by Go-Flo type or Niskin designed water sampler. It is taken in a glass vial with rubber septum and aluminum seal. Sample is poisoned with HgCl2 solution and stored in refrigerator temperature. An automated analyzer for dissolved methane was developed including sample purging vessel, cryogenic trap with activated charcoal, FID-GC (gas chromatograph with flame ionization detector) and computer. The detection limit of dissolved methane is 10 times lower than the atmosphere equilibrium level of 2 nM. The precision of analysis is better than 1 % at 100 nM level, which is the typical concentration in fresh water sample.

System for nitrous oxide analysis is a modified one of that for methane. An ECD-GC (gas chromatograph with electron capture detector) is used for the detection. The precision of analysis is around 1% at the atmospheric equilibrium concentration, which is the typical concentration of dissolved nitrous oxide in fresh water sample.

3. Variation of concentration and flux of methane in an eutrophicated lake, Kasumigaura

Lake Kasumigaura is highly eutrophicated shallow lake, having surface area of 171 km2, volume of 948 x 109 m3 and the average depth of 4 m. As the shallow lake water is well mixed by the blowing wind, there rarely develops either vertical temperature gradient or bottom oxygen depleted layer.

From April 1990, the dissolved methane concentration is monthly measured at the 7 stations in the lake. Vertical sampling is performed at 4 stations. The whole lake averaged concentration is obtained from a box model of the lake and the analytical results. In Fig. 1, the whole lake averaged concentration are shown. The average for April 1990 to March 1994 was 175 nM. The 1991 summer gave an extraordinary high concentration. The average excluded 1991 data was 157 nM. As the atmospheric equilibrium concentration of dissolved methane is 2-5 nM, depending on water temperature, an efflux of methane from the water surface exists every time. December to March and September are the periods of high concentration and April to July is that of low concentration. Every November the minimum in the year was recorded.

A thin layer model was applied to calculate the diffusive flux from the water surface of the lake, using the data for the dissolved concentration, the water temperature and the wind velocity. Maximum efflux is recorded in summer and low efflux is in winter to spring. Flux in 1991 summer was highest, because of the highest dissolved concentration. The average of the ordinary years was 3.1 mg $CH_4/m^2/day$.

The oxidation rate of dissolved methane in the lake water was measured since 1991 summer. The dissolved methane is decomposed by bacteria during the incubation experiment. The oxidation rate is proportional to the concentration of methane, which indicates the reaction is described as a 1st order reaction scheme. From late summer to autumn, the reaction rate was maximum. The half life of dissolved methane in the water was 6 hours at the maximum decomposition period. The reaction rate drastically decreased in winter and spring. The half life of methane in the low oxidation period was longer than 1 week. Using the dissolved concentration and the oxidation rate, the oxidative loss in the water column can be calculated. The average of the ordinary year was 3.0 $mgCH_4/m^2/day$. Then the total amount of methane generation can be given by the sum of the diffusive flux and the oxidative loss as 6.1 $mgCH_4/m^2/day$.

The seasonality of the dissolved concentration was interpreted by the seasonality of the diffusive flux and the oxidation. The methane generation in the bottom sediment is 10 times higher in summer than in winter. However, the diffusive flux and oxidation are higher in summer. The dissolved concentration in summer is not highest in the year. The methane generation rapidly decreases in autumn when the active bacterial oxidation remains. It makes the clear minimum in November. In winter, both of the low diffusive flux and oxidation loss make the dissolved concentration highest in a year.

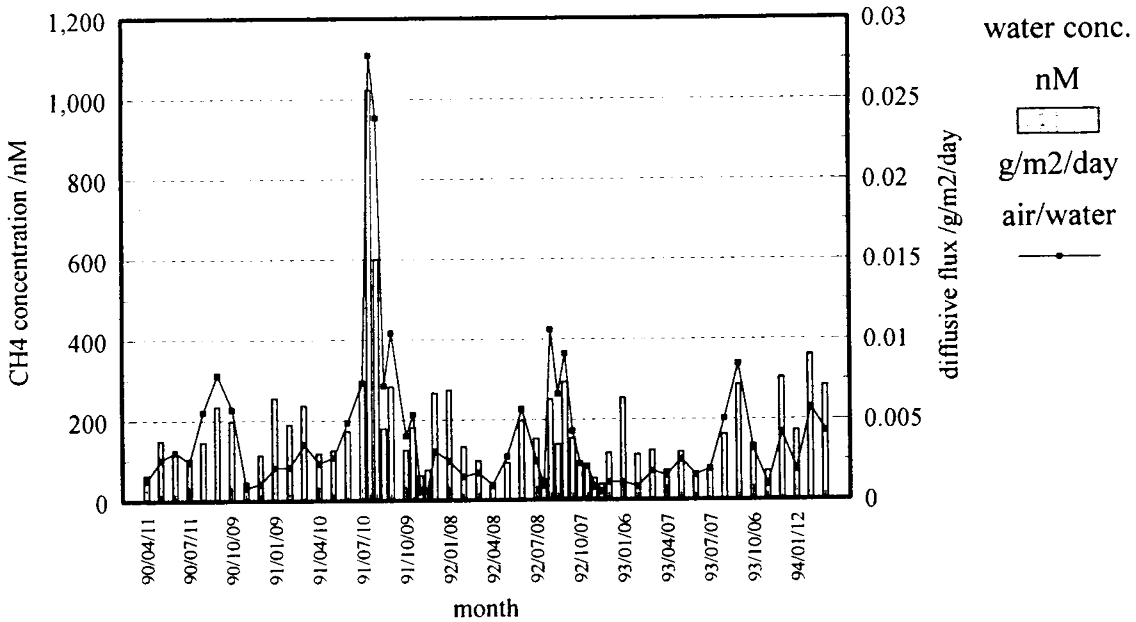


Fig. 1 Variation of dissolved methane concentration and diffusive flux of methane in lake Kasumigaura water

4. Methane concentration in deep lakes

To estimate the methane emission flux from inland water surface, the dissolved methane concentration in the water column of various Japanese lakes of different trophic levels was analyzed. Methane concentration levels in oligotrophic deep lakes was around 10 nM in the surface mixing layer. The vertical dissolved methane profile showed a sub-surface maximum just below the surface mixing layer in these deep lakes. We found methane accumulation due to the volcanism in some deep caldera lakes. The bottom methane accumulation is good indicator of the lake water circulation, because the methane oxidation in the bottom layer is a slow process.

The seasonal change of dissolved methane was observed in mesotrophic Lake Nojiri, having 34 m of the maximum depth. The surface methane concentration increased from 50 nM in the spring toward the summer season, and then turned to decrease. The maximum was 170 nM in

August. The accumulation methane in the bottom layer was established in the autumn. In December, the bottom accumulated methane was release by the whole lake overturn. The precise measurement of the holizontal distribution of dissokved methane revealed that the sub-surface maximum is built with the horizontal migration of methane from the shallower basin of the lake.

In 1993/1994 winter, the dissolved methane concentration variation was precisely measured in lake Nojiri. The winter concentration maximum of 350 nM is caused by the overturn of lake water in the late December. The methane oxidation rate increased with the circulation, then the concentration decreased rapidly to 120 nM. The dissolved methane concentration in March was 250-300 nM. In this period, the lake water is in a reverse stratification. As the vertical density gradient is quite small, the vertical diffusion of the lake water is large. These data indicate the dissolved methane concentration after the lake water overturn is generally higher than that in summer season. In the deep lakes like lake Nojiri, methane generation in the bottom sediment occurs with nearly same rate during the whole season as the temperature is nearly constant. The methane generated in the deep bottom sediment are accumulated in the period of stratification, then released in the winter season because of the larger diffusion in the lake water.

5. Emission estimate of methane from Japanese freshwater lakes

The surface methane concentration of lake generally increases with its trophic level. The relationship between the trophic level and dissolved methane concentration in surface water is shown in Fig. 2. The lake trophic level generally represented with its total phosphorous concentration in the water. A log-log regression line of surface water methane against total phosphorous was given from the measured 8 lakes. A data base of Japanese lakes including the

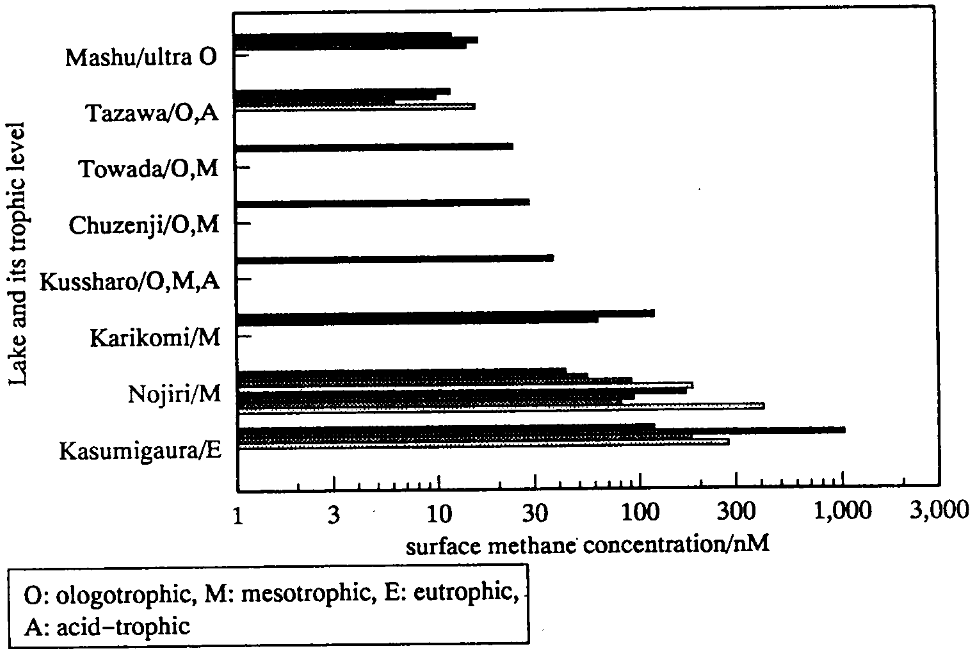
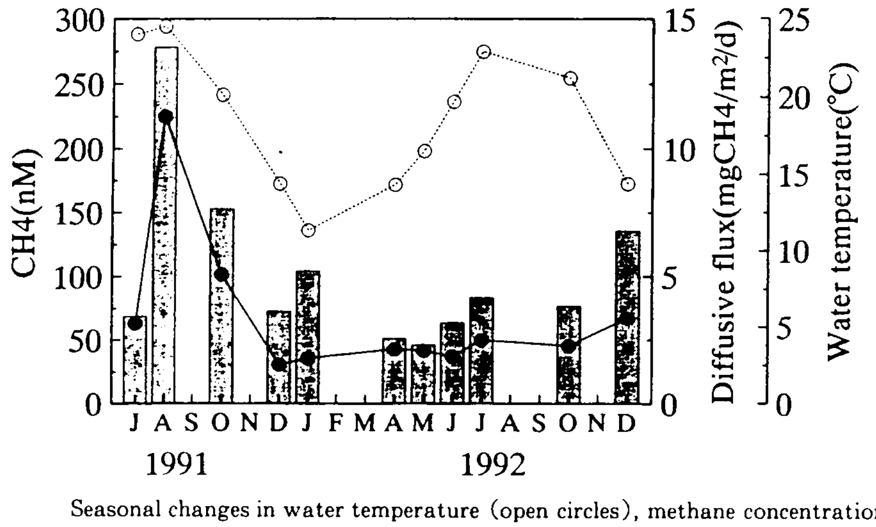


Fig. 2 Relationship between surface water dissolved methane and lake trophic level in Japanese lakes

lake parameters as its area, depth, freezing period, climate and phosphorous level were used for the emission model. An adequate wind velocity was applied according to the size of the lakes, which gives the appropriate gas exchange coefficient already reported. Temperature variation was also applied according to the climate of the region of each lake. Then the total methane flux from all Japanese natural lakes was summarized by the model calculation. The total flux of methane from the Japanese natural lakes was estimated as 1.6 Gg CH_4/year. It shares only 0.1 % of the national methane emission of Japan. The contribution of large shallow eutrophicated lakes is large for the methane emission.

6. Methane emission from Tokyo Bay

Seasonal change in the methane concentration of seawater were measured in highly eutrophic Tokyo Bay. Methane concentration varied from 27.8 to 1850 nM during May 1991 to December 1992 and were always supersaturated with the atmospheric methane. During the spring and summer seasons, when bottom water became anoxic, dissolved methane was observed to accumulate. There was inverse correlation between oxygen and dissolved methane in bottom water, when dissolved oxygen concentrations in the bottom water fluctuated. Throughout the experimental period, fluctuations of methane concentrations at mid-depth were relatively small. Particularly during summer, methane concentrations in surface water frequently increased to the same levels, or became higher than concentrations in bottom water. The source of methane in these surface waters were attributed to lateral transport from the near shore zone. From fall throughout winter, methane concentrations decreased and resulted in uniform distribution through the water column. Methane oxidation activities measured in June and August 1991 in surface and bottom waters were extremely low. In Fig. 3, the calculated diffusive flux from the bay surface is shown. The average was 1.5 gCH_4/m^2/year, which was 40 % larger than that from eutrophicated lake Kasumigaura.



Seasonal changes in water temperature (open circles), methane concentration in surface water (bar), and estimated methane diffusive flux from the bay to the atmosphere (solid circles) at Sta. A 2 in Tokyo Bay.

Fig. 3 Methane concentration and diffusive flux in Tokyo Bay

7. Nitrous oxide concentration in highly eutrophicated Lake Kasumigaura

Both the anaerobic and aerobic environments can be the source of nitrous oxide. In the freshwater environment, nitrous oxide is generated in both the nitrification and denitrification. Thus the emission may have relationship between the nitrogen cycling in the system. In this study, dissolved nitrous oxide concentration in the eutrophicated lake Kasumigaura around 3 years were analyzed with the nitrogen cycling in the lake.

Dissolved nitrous oxide concentration was measured using the similar system with some modification as the dissolved methane analysis (section 2). The change of nitrous oxide concentration from April 1994-January 1995 for the lake center sampling point is shown in Fig. 4. The nitrous oxide concentration was higher in winter and lower in summer. The atmospheric equilibrium concentration changes with the water temperature. The oversaturated concentration relates to the nitrous oxide emission. The oversaturated portion showed no seasonality, shown in the lower figure. In lake Kasumigaura, nitrate concentration shows higher in winter but nearly zero in summer. Ammonium shows irregular concentration variation. The oversaturated nitrous oxide concentration showed no relationship with the inorganic nitrogen compounds. The ratio of the nitrous oxide to the total nitrogen in the water was around 0.01% at the lake center sampling point. The oversaturated concentration was higher in the shallower bay area in the lake and decreased toward the lake center and the outlet.

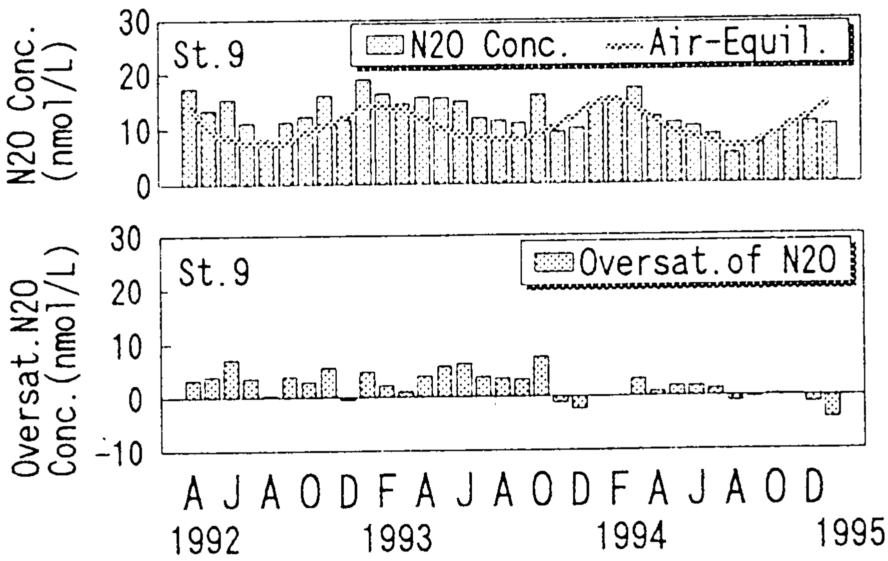


Fig. 4 Nitrous oxide concentration in Lake Kasumigaura
Oversaturated nitrous oxide is the concentration subtracted the air-equilibrium portion.