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Air-Sea Exchange of Methane in the Sea of Okhotsk

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1. Introduction

Anomalies of dissolved methane concentration (DM) at sea surface were often observed off east shore of Sakhalin Island [1]. Observations of DM have been carried out near Japan (Hokkaido) coast facing to the Sea of Okhotsk off shore and on the coast stations since 2000 and in the cruises of the icebreaker "Soya" of the Japan Coast Guard since 2002. These observations strongly suggest that the drift ice from Sakhalin Island brings DM anomalies to Japan [2] [3]. As the result, the Sea of Okhotsk near Japan acts as the methane source to the atmosphere when the drift ice rushed to Japan. In the previous report [4], mass flux between air and sea surface was estimated for each "Soya"'s cruise in 2002-2005.

On the other hand, on the coastal stations, richer DMs were observed in the year when the drift ice rushed to Japan coast and many ice blocks grounded on the beach [3]. This paper describes the results of monitoring of the dissolved methane anomalies and their annual differences among 2002-2007. The methane mass flux of air-sea exchange including coastal affects is also estimated for each year.

2. Sampling and Measurement Procedures

Seawater samples were obtained with a stainless steel pail from sea surface among drift ice blocks and 500 ml glass vials were filled with the water and sealed after overflow. A headspace technique was applied to measure dissolved methane concentrations (DM) in seawater. Headspace gases of heated 27 ml vials were injected with a syringe to a gas chromatograph / FID (GC-FID). Air was also sampled at each station with Tedlar bag and the sampled air was directly injected with a gas sampler (2ml) to the same GC-FID at the measurements of the methane concentrations in the air. No significant anomaly was found in the atmospheric methane concentration. So no further description is in this report.

3. Dissolved Methane Concentrations in Sea water

The results of the surveys of dissolved methane concentration in February 2006 and 2007 cruises of icebreaker Soya were shown in Fig.1 and Fig.2, respectively with the visible images of the channel 1 from artificial satellites NOAA on the nearest clear day to each period of the cruises. The results and the similar figures for 2002-2005 were shown in the previous report [4]. White images of sea ice were observed in Fig.1 and Fig.2 on the visible images of channel 1 from NOAA. Because both sea ice and clouds are shown in white images, they were distinguished with the differences of temperature with the infrared images of the channel 4 or 5 on NOAA. The values of the dissolved methane concentrations are indicated in n moles per litter of water [n mol/L] in the same Fig.1 and 2. 'UD' shows undetectable level. Mild DM anomalies of 20-30 n mol/L were regularly found in wide area of the Sea of Okhotsk in February 2002, 2003 and 2005 [4]. On the contrary, in the case of 2004, 2006 and 2007 cruises, dissolved methane anomaly was seldom observed near Japan coast. Such remarkable annual changes in DM can be obviously explained by ice concentrations. As shown in Fig.1, for example, DM anomalies were generally observed at only stations which were covered with drift ice. The result suggests two facts; the first, DM at the sea surface in the observed area is normally in near equilibrium before drift ice comes. Another on is that the DM anomalies at the sea surface in the sea of Okhotsk near Japan is transported with the drift ice from off shore of Sakhalin Island.

The relation between ice concentrations (covering area fraction) and average dissolved methane concentrations in the survey area for 2002-2007 was shown in Fig.3. The average DM increases with an increase in ice concentration almost proportionally. The result can be expressed approximately with the equilibrium DM as follows,

$$\overline{C}_{DM} = 35.97 \times C_{ICE} + 3.7 \qquad (1)$$

$\overline{C}_{DM}$ is the average dissolved methane concentration in n mol/L, and C_{ICE} is the ice concentration.

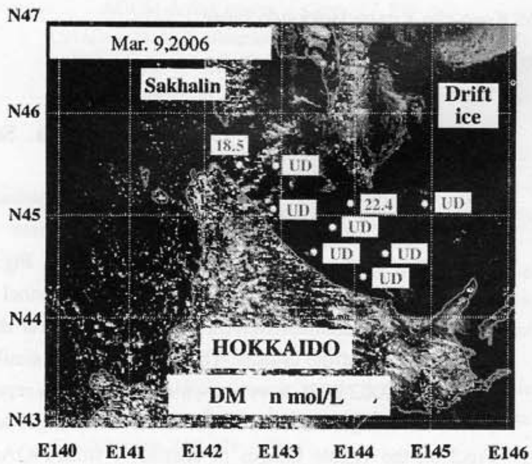

Fig.1 DM distribution and drift ice distribution in 2006

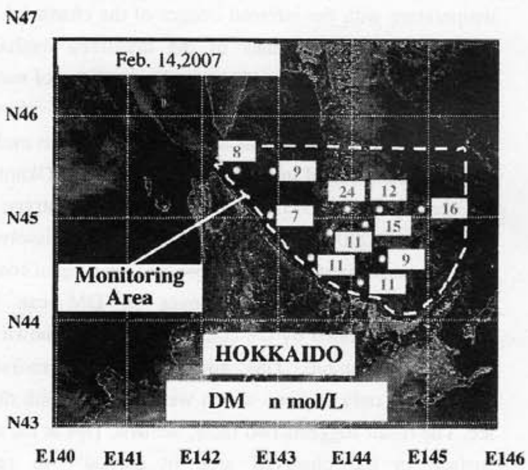

Fig.2 DM distribution and drift ice distribution in 2007

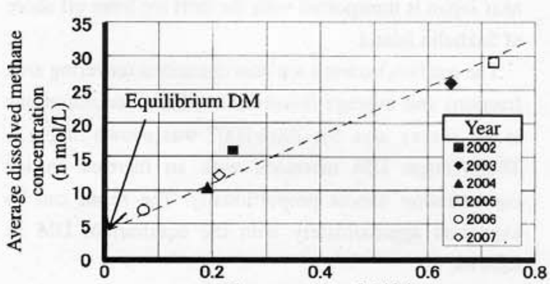

Fig.3 Relation between Concentration of drift ice and average dissolved methane concentration in the survey area in 2002-2007

4. Air-Sea exchange of methane

When the atmospheric concentration of methane is generally about 1.8 parts per million in February, equilibrium dissolved methane concentration is about 3.7 n mol/L [5]. Therefore, the Sea of Okhotsk acts as the methane gas source to atmosphere near Japan during drift ice season.

Mass flux is proportional to the fugacity difference of methane between air and sea. Mol flux of air-sea exchange was estimated by following equation, actually.

$$F = k_l \times \Delta C_{g-l} \qquad (2)$$

F is the mol flux in n mol/(m_2 · hr), k_l is the exchange coefficient of liquid in m/hr, and ΔC_{g-l} is air-sea difference of mol concentration in solution. Equilibrium dissolved methane concentrations were calculated from the data by Wiesenburg [5]. The following assumptions were made in order to estimate the mass flux of methane from sea to air and total mass of methane released into the atmosphere from the observed area. Though the exchange coefficient depends on the wind velocity generally, it is assumed that the constant value of 0.2 m/hr might be available because the water among drift ice blocks is very calm even under high wind velocity condition. And it is also assumed that no exchange occurs between air and the surface of drift ice, i.e. the methane exchange occurs only from open sea area among drift ice blocks.

Since the surface DMs on the coastal stations were often greater than the DMs observed at stations off shore as described below, it was desired that the coastal effect on the mass flux of methane was taken into account to estimate the mass exchange in the Sea of Okhotsk near Japan coast. Total annual mass of methane exchange in the target area m_{total} was obtained by following equation;

$$m_{total} = m_{off} + m_{coast} \qquad (3)$$

where, suffices $_{off}$ and $_{coast}$ denote off shore and on the coast, respectively. Average mass flux was defined as follows,

$$f_{av} = m_{total} / A \qquad (4)$$

where, A is the observed area [m^2] (not open water area) shown in Fig.2.

4.1 Methane exchanges off shore

In the previous report [4], an average surface DM from Eq.(1) was used to obtain ΔC_l in Eq.(2). This procedure felt inadequate in the year when the ice concentration was extremely low, e.g. 2004 and 2006, and many undetectable (UD) stations were observed. In the present report, Soya's observation area was divided into n (= station number) segments centering on each stations and mol flux of each stations (F_i) was calculated by Eq.(2) for each segment. Total mass of methane released from the observation area to the atmosphere m_{off} in Gg-CH_4/yr was integrated by following equations.

$$m_{off} = M_{CH4} \times \Delta t_{loff} \times \sum_{i}^{n} (F_i \times A_i)(1-\phi_i) \qquad (5)$$

where, M_{CH4} is molecular weight of methane, Ai is the area of i segment in m^2, and ϕ_i is the ice concentration of i segment. The period of drift ice season Δt_{off} was three month here because it is assumed that DM were maintained during three month (drift ice season), and remaining dissolved methane after melting of the drift ice could be disregarded.

4.2 Methane exchanges along the coast

Back ground DMs were observed just before drift ice grounding on the coastal stations every year. Usually, the background DM was undetectable or extremely low except the 2002 observation. The change in DM under the grounding ice blocks on Abashiri and Tokoro beaches in 2002 and 2003 are shown in Fig.5 and 6, respectively. After DM jumped sharply to the peak just after grounding, the concentration decreased gradually. The phenomena might be caused by drainage of brines from the grounding drift ice blocks. Exchange period was divided into several intervals as shown in each figure. Time series integrations were conducted under following assumption; DM maintains each observed level during each interval as shown in the figures. As the result, the exchange period Δt is not three month, but is actually observed period from the first grounding until equilibrium DM.

The coastal area is defined as area whose depth is within 20 m, in which the surface characteristics are maintained. The Sea of Okhotsk coast was classified into the east area and the west area which were characterized by Abashiri stations and Tokoro stations, respectively, as shown in Fig.4.

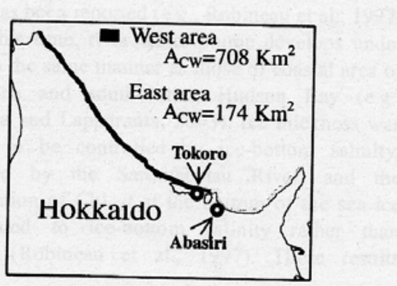

Fig.4 Coastal area within the depth of 20m

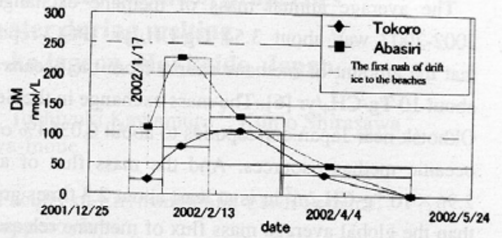

Fig.5 DM changes after the first grounding of drift ice on the beaches in 2002

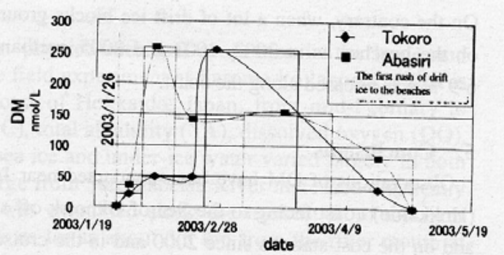

Fig.6 DM changes after the first grounding of drift ice on the beaches in 2003

The coastal area corresponds to only 1.6 % of observed area. Methane flux along coastal area was estimated by following equations;

$$m_{coast} = M_{CH_4} \times \begin{Bmatrix} (1-\phi_{CW}) \cdot \Delta t_{CW} \cdot F_{CW} \cdot A_{CW} \\ +(1-\phi_{CE}) \cdot \Delta t_{CE} \cdot F_{CE} \cdot A_{CE} \end{Bmatrix} \qquad (6)$$

where, suffices CE and CW denote the east and west coastal areas, respectively.

Results of the estimations of mass flux of air-sea exchange and the annual mass of methane released into the atmosphere in the Sea of Okhotsk near Japan coast during drift ice season were shown in Fig.7.

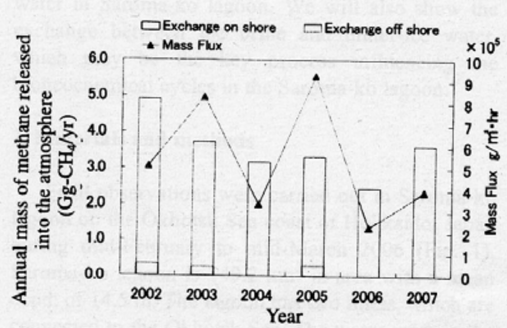

Fig.7 Results of the estimations of mass flux of methane and the annual total mass of methane released into the atmosphere in the Sea of Okhotsk near Japan coast during drift ice season

The average annual mass of methane exchange in 2002-2007 was about 3.54 Gg-CH_4/yr. IPCC reported that the amount of methane source from the oceans was about 10 Tg-CH_4/yr [6]. The mass exchange in the Sea of Okhotsk near Japan corresponds to about 0.0354% of the oceanic methane sources. And the mass flux of about 2.96×10^{-5} g-CH_4/m^2 hr is at least about 2.3 times greater than the global average mass flux of methane released to the air from the oceans. Almost no coastal affect was observed when no grounding drift ice block was found as in 2004, 2006 and 2007 as shown in Fig.7 (no white bar). On the contrary, when a lot of drift ice blocks grounded on the beaches as in 2002, 2003 and 2005, methane of 6-9 % was released along the coast.

5. Conclusions

Observations of DM have been conducted near Japan (Hokkaido) coast facing to the Sea of Okhotsk off shore and on the cost stations since 2000 and in the cruises of the icebreaker "Soya" of the Japan Coast Guard since 2002. The results of investigations were summarized briefly as follows,

1. Dissolved methane anomalies at the sea surface in the sea of Okhotsk near Japan coast in winter occurred as the rush of the drift ice from off Sakhalin shore. Such methane anomalies were seldom found during open water season.
2. The average dissolved methane concentrations at the sea surface increased almost proportionally with an increase in ice concentrations.
3. Annual total mass of methane released into the atmosphere in the Soya's cruising area and coastal area was about 3.54 Gg-CH_4/yr. The area average mass flux is at least 2.3 times greater than the global annual average flux.

Acknowledgement

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