Dissolved methane distribution in the South Pacific and the Southern Ocean in austral summer

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[1] Oceanic methane (CH_4) was examined in the South Pacific and the Southern Ocean from December 2001 to February 2002. From the oligotrophic South Pacific (10°S) to the Subtropical Front (STF), we observed the maximum concentrations of CH_4 in the subsurface layer which ranged from 2.7 to 3.9 nmol kg^{-1}. South of the STF, higher levels of CH_4 were often detected in both the surface and the subsurface layers. Elevated surface CH_4 concentrations (3.4–6.1 nmol kg^{-1}) south of the STF tended to be higher than those north of the STF. Higher CH_4 were often concomitant with an increase in chlorophyll a levels in the Seasonal Ice Zone (SIZ). Considering that phytoplankton does not generate methane directly, the high CH_4 production probably resulted from the grazing processes of Antarctic krill and/or zooplankton fed on phytoplankton and the subsequent microbial methanogenesis in addition to the aerobic CH_4 production in the water column. Present results showed a good relation between surface CH_4 data (<50 m) and σ_θ between 10°S and the Polar Front (PF), which allow us to provide interpolation/extrapolation schemes for CH_4 concentration and sea-air CH_4 flux in the wide area ($[CH_4] = 0.15 \, \sigma_\theta - 0.98$ (RMS = 0.21 nmol kg^{-1}, $r = 0.68$, $n = 49$, $p < 0.001$). The sea-air fluxes estimated during our survey were from 2.4 to 4.9 mol CH_4 km^{-2} d^{-1} between 10°S and the PF (54°S), and from 0.8 to 2.3 mol CH_4 km^{-2} d^{-1} south of the PF, where the sea-air CH_4 flux was largely affected by the wind speed.

1. Introduction

[2] Methane (CH_4) is both a chemically and radiatively active gas in the atmosphere, and its concentration has more than doubled during the last 150 years [*Intergovernmental Panel on Climate Change (IPCC)*, 2007]. In 2008 the atmospheric CH_4 exceeds the highest annual mean abundance recorded so far and represents the growth rate of 7 ppb y^{-1} [*World Meteorological Organization*, 2009]. The probable major source/sink terms for atmospheric CH_4 have been identified [*IPCC*, 2007]. However, there remain great uncertainties in the estimation of the source/sink magnitude, which makes it difficult to understand variations in the CH_4 cycle on time scales from years to decades.

[3] The surface ocean has been reported to act as a source of atmospheric CH_4, though its release could be minor compared with cumulative natural and anthropogenic sources on land [*Cicerone and Oremland*, 1988; *Lambert and Schmidt*, 1993]. The estimation of CH_4 flux from the ocean to the atmosphere has varied greatly, from 0.4 [*Bates et al.*, 1996] to 11–18 Tg-C y^{-1} [*Bange et al.*, 1994]. Coastal areas cover only a small portion of the world's oceans but appear to be a significant source of atmospheric CH_4 due to high biological productivity. *Bange et al.* [1994] reported that coastal areas released 75% of the total flux from the oceans to the atmosphere.

[4] The subsurface maximum of CH_4 often occurs in the open ocean, and its concentration reaches a few nanomolars [e.g., *Watanabe et al.*, 1995; *Kelley and Jeffrey*, 2002; *Oudot et al.*, 2002]. In the water column, only methanogenic bacteria can produce CH_4 for a while, but they cannot survive in conditions with any traces of oxygen. Therefore methanogenic bacteria were considered to be present in an anaerobic microenvironment in organic particles or the guts of zooplankton [*Alldredge and Cohen*, 1987; *Karl and Tilbrook*, 1994; *Reeburgh*, 2007]. Recently, *Karl et al.* [2008] reported aerobic methane production as a byproduct of methylphosphonate decomposition. On the basis of measurements of the concentration and $\delta^{13}C$ of dissolved CH_4 in the western North Pacific, *Sasakawa et al.* [2008] recently observed a release of CH_4 from sinking particles into the water column. In a laboratory experiment, *de Angelis and Lee*

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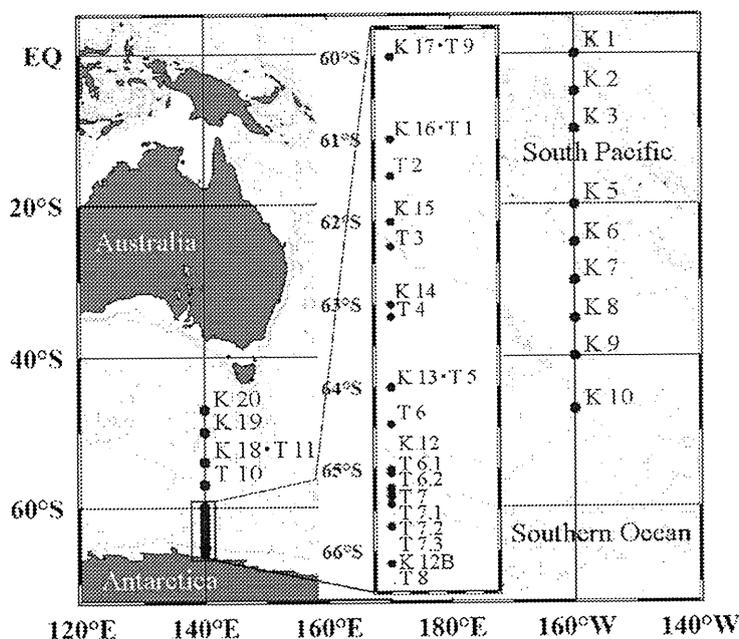
Figure 1. Cruise tracks and locations (solid circles) of water samplings during the cruises of the R/V *Hakuho-maru* (KH01–3 cruise) and the R/V *Tangaroa* (JARE43 cruise) in the South Pacific (140°E and 160°W) and Southern Ocean (140°E) from December 2001 to February 2002. The hydrographic station starting with K is the site observed by the R/V *Hakuho-maru* and that starting with T is the site observed by the R/V *Tangaroa*.

[1994] reported that a significant amount of CH$_4$ was released from the mixed cultures of phytoplankton and zooplankton. Below the CH$_4$ maximum, the concentration decreased gradually, which was interpreted as a residual effect of CH$_4$ input from surface waters [*Scranton and Brewer*, 1977] and/or CH$_4$ oxidation [*Oudot et al.*, 2002]. The diffusive flux away from the subsurface maximum to the surface is generally smaller than the net flux between the sea and the air [*Ward et al.*, 1987; *Oudot et al.*, 2002]. Therefore it has been considered that the vertical transport from the maximum concentration layer and CH$_4$ production in the mixed layer are balanced by the microbial oxidation and sea-air CH$_4$ flux [*Bates et al.*, 1996].

[5] There are only a few works that have measured CH$_4$ concentration in the Southern Ocean [*Lamontag et al.*, 1973; *Tilbrook and Karl*, 1994; *Heeschen et al.*, 2004]. The surface waters of the Southern Ocean have been reported to be generally undersaturated with respect to atmospheric CH$_4$ and are a small sink to the atmosphere. *Tilbrook and Karl* [1994] suggested that undersaturation result from the entrainment of CH$_4$ depleted warm deep water in the surface layer and from seasonal ice cover acting as a barrier for gas exchange. *Heeschen et al.* [2004] reported that air-sea CH$_4$ exchange is the major source of CH$_4$ to the Weddell Sea, and the distribution of CH$_4$ is controlled mainly by the mixing between surface seawater and warm deep water.

[6] The Southern Ocean, one of the most biologically productive regions among the world's oceans, is characterized by high biomass of zooplankton, Antarctic krill, and salps [*Knox*, 2007], from which the CH$_4$ production could

be expected. In this work, we measured oceanic CH$_4$ in the South Pacific and Southern Ocean from December 2001 to February 2002 and examined relationship between CH$_4$ and oceanographic parameters to discuss factors controlling CH$_4$ distributions and air-sea CH$_4$ flux in these two regions.

2. Material and Methods

2.1. Sampling and Measurements

[7] About 1000 seawater samples were obtained from the South Pacific and the Southern Ocean (Figure 1) from December 2001 to February 2002 during the KH01–3 cruise of the R/V *Hakuho-maru* (Ocean Research Institute, University of Tokyo, Japan) and during the JARE-43 cruise of the R/V *Tangaroa* (National Institute of Water and Atmospheric Research, New Zealand).

[8] The seawater was collected with 1 L buckets for surface samples and 12 L Niskin bottles mounted on a Seabird CTD rosette sampler for samples below the surface to the bottom. After sampling for oxygen and salinity measurements, seawater samples were immediately taken and placed in 30 mL glass vials. The seawater samples were poisoned with 20 μL of saturated HgCl$_2$ solution [*Watanabe et al.*, 1995; *Yoshida et al.*, 2004], and then the vials were closed with rubber and aluminum caps and stored in a cool, dark place until gas chromatographic analysis was conducted on board or in our laboratory on land.

[9] The analytical method was reported earlier [*Tsurushima et al.*, 1996; *Yoshida et al.*, 2004]; therefore only a short description is given here. The analytical system
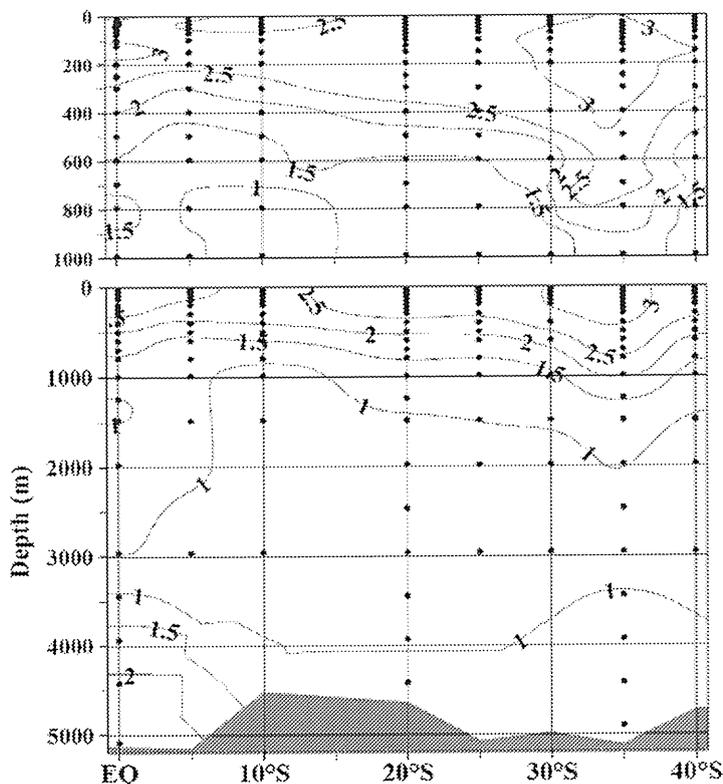
Figure 2. Vertical sections of CH_4 concentrations (nmol kg^{-1}) along 160°W in December 2001.

consists of a unit for CH_4 extraction from seawater and a trap unit immersed in a dry ice-ethanol mixture, a chemical desiccant column, rotary valves, a gas chromatograph (Shimadzu GC-8A) equipped with a flame ionization detector, and a data acquisition unit. The whole volume of seawater in each 30 mL glass vial was moved to the CH_4 extraction unit and weighed before and after analysis. The precision obtained from replicate determinations of CH_4 concentration (n = 70) was estimated to be better than 5%. The standard gas used contained 2.02, 19.6, and 38.4 ppmv of CH_4 in pure nitrogen (Nippon Sanso Co., Ltd.).

2.2. Oceanographic Settings

[10] In the Southern Ocean, there are four major fronts, the Sub-Tropical Front (STF), the Sub-Antarctic Front (SAF), the Polar Front (PF), and the Southern Antarctic Circumpolar Current Front (SACCF), which are characterized by physical and chemical properties of seawater [*Rintoul et al.*, 1997; *Rintoul and Bullister*, 1999]. Along 140°E, the STF, which is the boundary between warm, salty subtropical water and cool, fresh sub-Antarctic water, is located at 47°S. A steep horizontal gradient of sea surface temperature (SST) occurred around 49°S (SAF), which was the northern edge of the eastward flowing Antarctic Circumpolar Current. The PF, characterized by a steep tem-

perature gradient of surface seawater and the northern limit of minimum-temperature water with temperatures of less than 2°C near a depth of 200 m, was 54°S. The SACCF, which coincides with the southern limit of a temperature maximum water over 1.8°C [*Orsi et al.*, 1995], was located around 63°S in January 2002 and 65°S in February 2002. The Sub-Antarctic Zone (SAZ) is the region between the STF and SAF, the Polar Frontal Zone (PFZ) is between the SAF and PF, the Permanently Open Ocean Zone (POOZ) is between the PF and SACCF, and the Seasonal Sea Ice Zone (SSIZ) is south of the SACCF. We determined their locations using continuous SST and SSS (sea surface salinity) and hydrographic data (Preliminary Report of the Hakuho-maru Cruise KH01–3; Preliminary Report on the 43rd Japanese Antarctic Research Expedition Marine Science Cruise by R/V *Tangaroa*).

2.3. Calculations of the CH_4 Saturation Ratio and Sea-Air CH_4 Flux

[11] The degree of saturation of dissolved CH_4 (R) was calculated from the observed concentrations of CH_4 (C_w) and the concentrations of CH_4 in water equilibrated with ambient air (C_a). We interpolated the monthly means of atmospheric CH_4 at the South Pole (90°S), Cape Grim (41°S), American Samoa (14°S), and Christmas Island (2°N) from
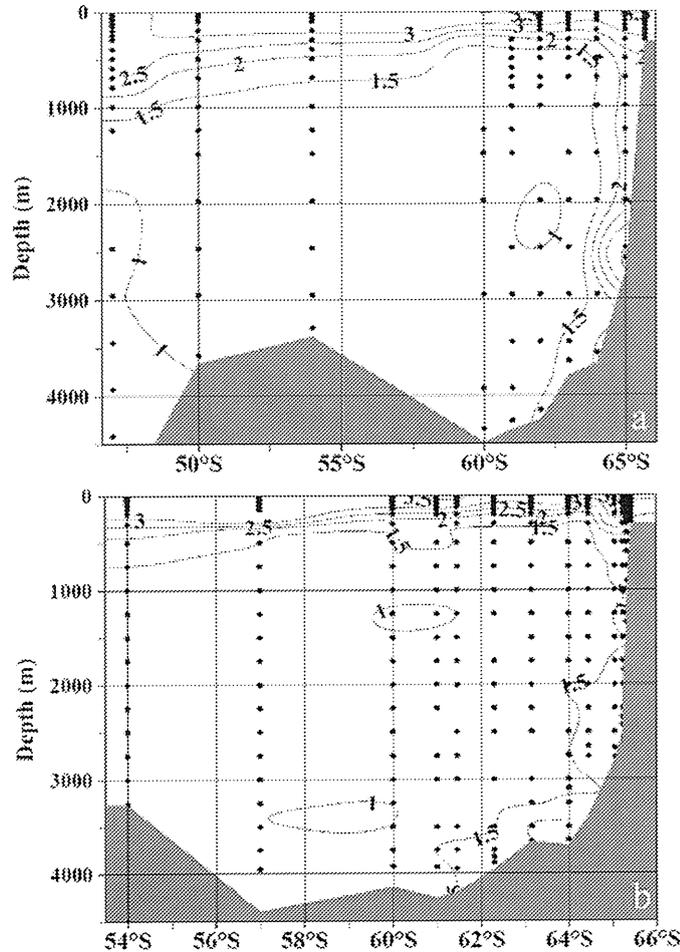
Figure 3. Vertical sections of CH$_4$ concentrations (nmol kg^{-1}) along 140°E in (a) January and (b) February 2002.

December 2001 to February 2002 [*Tans et al.*, 2002] and used the solubility equation given by *Wiesenburg and Guinasso* [1979]:

$$R(\%) = \left(\frac{C_w}{C_a}\right) \times 100. \tag{1}$$

[12] The sea-air CH$_4$ flux (F) was calculated from

$$F = k_w \times (C_w - C_a), \tag{2}$$

where k_w is the gas transfer coefficient conventionally expressed as a function of wind speed at 10 m height (v_{10}). In order to compute k_w, we used the quadratic k_w-v_{10} relationship reported by *Sweeney et al.* [2007]:

$$k_w = 0.27 v_{10}^2 (Sc/660)^{-1/2}, \tag{3}$$

where Sc is the Schmidt number for CH$_4$ in seawater. The wind speed used in this work was the daily mean from December 2001 to February 2002 prepared by the NCEP/NCAR [*Kalnay et al.*, 1996].

[13] *Wanninkhof et al.* [2004] determined gas transfer velocities in the Southern Ocean during the Southern Ocean Iron Fertilization experiment using the dual deliberate tracer technique. They reported that the concentration decrease of tracers could be predicted slightly better with established relationships if gas transfer was modeled as a function of the cube rather than the square of the wind speed, particularly over a time interval with high and variable winds. However, both fits can model the concentration decrease within the uncertainty of the observations. *Sweeney et al.* [2007] also mentioned that their equation yielded piston velocity values consistent with those obtained from some small-scale deliberate tracer studies and with the total bomb-produced ^{14}C inventory obtained for the stratosphere and troposphere.
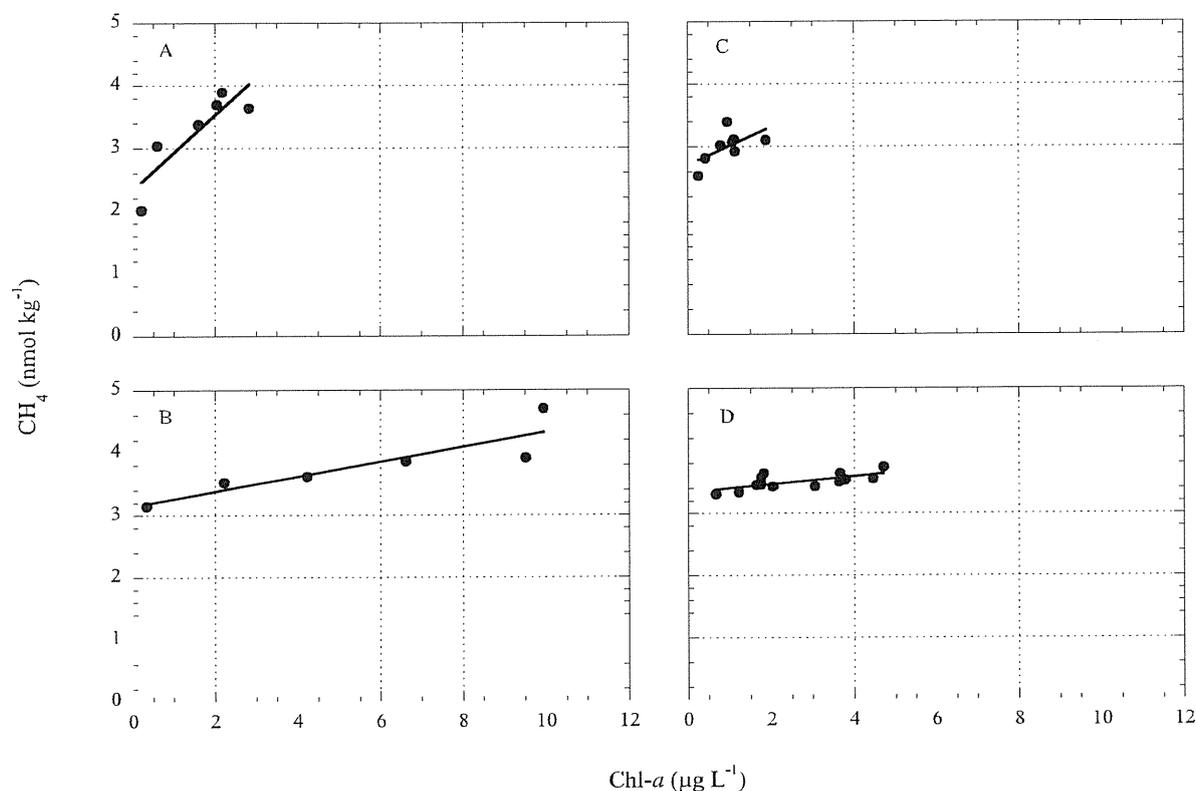
Figure 4. Examples of relationships between chlorophyll a and CH$_4$ concentrations in January and February 2002. Data (a) at 64°S, 140°E in January 2002 (K13); (b) at 65°S, 140°E in January 2002 (K12); (c) at 64.45°S (T6), 140°E in February 2002; and (d) at 65.15°S, 140°E in February 2002 (T8).

Therefore in this study we use a quadratic gas transfer relationship.

3. Results and Discussion

3.1. CH$_4$ Distribution

[14] Figures 2 and 3 show the vertical sections of CH$_4$ concentration in the South Pacific along 160°W and the South Pacific and Southern Ocean along 140°E. In the surface and subsurface layers, the CH$_4$ concentrations were relatively high (>2.0 nmol kg^{-1}). The CH$_4$ levels became low in deeper waters except at high latitudes of the Southern Ocean. A relatively high CH$_4$ concentration was found along the continental slope and in the bottom water extending to 60°S. Along the WOCE SR3 section of 145°E, *Sabine et al.* [2002] showed the distribution of anthropogenic CO$_2$ as well as relatively high concentrations of CFCs. The distributional patterns were similar to our oceanic CH$_4$ distributions near the coast at the southern end of the SR3 section. *Rehder et al.* [1999] reported that spatial distribution patterns of methane and CFC-11 in the water column were remarkably similar in the Atlantic between 50°N and 60°N. We speculate that the bottom water, possibly formed at the Adelie Land coast [*Rintoul and Bullister*, 1999], might transport water with high CH$_4$ concentrations in the abyssal depths. Above the continental slope, high CH$_4$ concentra-

tions occurred at a depth of 2500 m, and that differed from the vertical profiles of anthropogenic CO$_2$ and CFCs. High CH$_4$ concentrations at 2500 m could be caused by the seepage of CH$_4$ from the seafloor. Although the measurements of δ^{13}C of dissolved CH$_4$ are useful to infer the CH$_4$ sources [e.g., *Whiticar*, 1996, 1999], they are beyond the scope of this paper.

[15] Maximum concentrations of CH$_4$ ranging from 2.7 to 3.9 nmol kg^{-1} occurred in the subsurface layers between 10°S and 47°S (STF). South of STF, the maximum concentration often occurred in the surface layer as well as the subsurface layer. At high latitudes, the maximum CH$_4$ concentration in the surface layer tended to be high, suggesting the enhancement of biological CH$_4$ production and/or air-sea CH$_4$ flux [*Heeschen et al.*, 2004]. *Nicol et al.* [2000] showed that salps were mainly found in less productive areas with warm water and low chlorophyll a, whereas Antarctic krill were more abundant in productive regions. Antarctic krill has been reported in the cool surface waters south of the Antarctic Circumpolar Current, which is a region showing high concentrations of CH$_4$. In this study, higher CH$_4$ concentrations were often concomitant with an increase in chlorophyll a (a marker for phytoplankton abundance) levels in January and February 2002 (Figure 4). Considering that phytoplankton does not generate methane directly, the high CH$_4$ production probably resulted from the grazing processes of
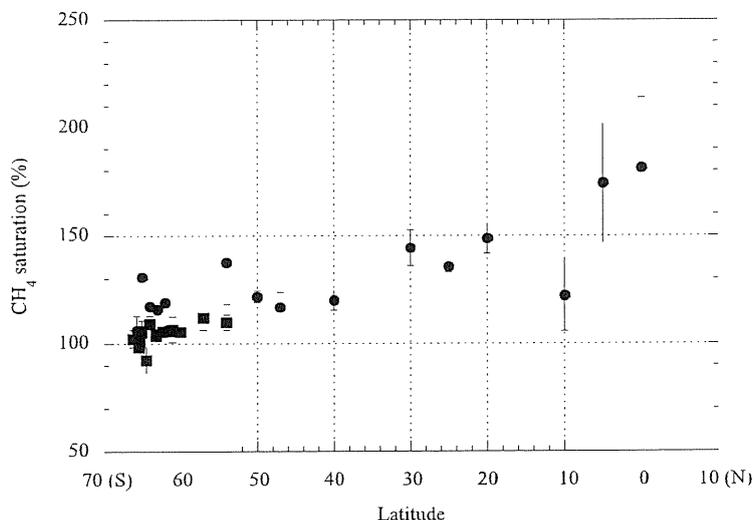
Figure 5. Latitudinal distribution of degree of CH$_4$ saturation in the South Pacific and Southern Ocean in December 2001 (solid circles) and January and February 2002 (solid squares).

Antarctic krill and/or zooplankton fed on phytoplankton and the subsequent microbial methanogenesis. *Damm et al.* [2008] showed a relationship between chlorophyll *a* and CH$_4$ concentrations ranging from 9 to 25 nM in Arctic shelf water. They concluded that the CH$_4$ production-consumption cycle was related to phytoplankton blooms and the CH$_4$ production was derived from dimethlysulfoniopropionate (DMSP), a potential substrate for methyltrophic methanogenesis and produced by several groups of phytoplankton. In the Southern Ocean, the prymnesiophyte *Phaeocystis*, which regularly forms massive blooms in seasonal ice zones and coastal Antarctic waters, is considered to be a major producer of DMSP [*DiTullio et al.*, 2000]. During the same cruise of the R/V *Hakuho-maru* and R/V *Tangaroa*, *Kasamatsu et al.* [2004] reported that the concentration of dissolved DMSP (DMSP$_d$) + DMS increased after incubations with krill (65°S, 140°E). On the other hand, the addition of salps to natural seawater did not change the DMSP$_d$ + DMS concentration. These results also suggest the surplus addition of CH$_4$ via DMSP from Antarctic krill. Earlier studies suggest major role of air-sea CH$_4$ flux and vertical mixing of subsurface water with low concentrations of CH$_4$ [*Tilbrook and Karl*, 1994; *Heeschen et al.*, 2004]. We found relatively high CH$_4$ concentration (3.4–6.1 nmol kg^{-1}) in surface water of Seasonal Ice Zone as compared with those of previous studies (~3 nM) [*Tilbrook and Karl*, 1994]. The degree of CH$_4$ saturation, however, is low due to low water temperature. If sea surface temperature rises with global warming, the Southern Ocean might change to a large CH$_4$ discharge region. More data are needed in order to evaluate factors controlling surface CH$_4$ concentration in the Southern Ocean.

3.2. Sea-Air CH$_4$ Flux

[16] We calculated the degree of CH$_4$ saturation in the South Pacific and the Southern Ocean from December 2001 to February 2002 and plotted the average degree of satura-

tion (Figure 5). The degree of saturation varied within the range from 87% to 210%. The surface CH$_4$ concentration was sometimes undersaturated with respect to the atmospheric CH$_4$ in the Southern Ocean [*Tilbrook and Karl*, 1994; *Heeschen et al.*, 2004] and largely supersaturated in the central equatorial Pacific. As mentioned above, the CH$_4$ concentration was high in higher latitudes, but the degree of saturation decreased toward the south due to the temperature dependence of CH$_4$ solubility.

[17] In the South Pacific, we have derived an empirical CH$_4$-σ_θ relationship in the South Pacific, which allows us to evaluate monthly mean of sea-air CH$_4$ flux. Figure 6 shows the relationship between surface CH$_4$ concentration and σ_θ in the South Pacific and the Southern Ocean. The CH$_4$ concentration ([CH$_4$]) in surface seawater (shallower than 50 m) increased with water density between 10°S and the PF, [CH$_4$] = 0.15 σ_θ − 0.98 (RMS = 0.21 nmol kg^{-1}, r = 0.68, n = 49, p < 0.001). A good CH$_4$ relationship seems to suggest an important role of the difference in density between particles having anaerobic microenvironment and seawater. On the other hand, the anticorrelation in the high latitudes south of the PF was found.

[18] Between 10°S and the PF, we calculated the σ_θ field from the monthly mean SST [*Reynolds et al.*, 2002] and climatological SSS data [*Antonov et al.*, 2006], and we estimated the surface CH$_4$ concentrations from the CH$_4$-σ_θ relationship. South of the PF, we used an average surface CH$_4$ concentration (3.57 ± 0.26 nmol kg^{-1}, n = 117). C_w-C_a tended to increase from December to February in each latitudinal zone (Table 1), and that is probably due to relatively large decreases in CH$_4$ concentrations equilibrated with the atmosphere.

[19] We calculated the sea-air CH$_4$ flux south of 10°S from December 2001 to February 2002 (Table 1). It has been reported that sea-air CH$_4$ fluxes in the Southern Ocean are less commonly observed in the open ocean [*Tilbrook and Karl*, 1994; *Heeschen et al.*, 2004]. Those earlier
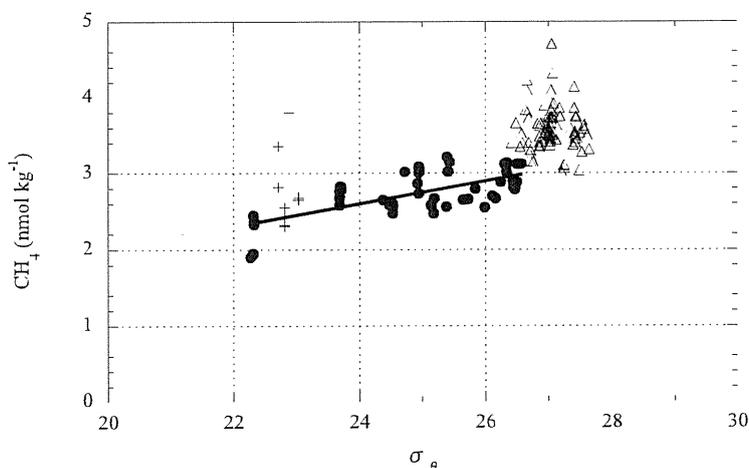
Figure 6. CH$_4$-σ_θ relationship in the surface layer (<50 m) in the South Pacific and Southern Ocean in December 2001 and January 2002. Solid circles represent the data between 10°S and the PF, open triangles represent the data in the Southern Ocean south of the PF, and plusses represent the data in the equatorial Pacific (160°W). The solid line shows a CH$_4$-σ_θ relationship, [CH$_4$] = 0.15 σ_θ − 0.98 (RMS = 0.21 nmol kg^{-1}, r = 0.68, n = 49, p < 0.001).

studies have reported a negative CH$_4$ flux in the Drake Passage and Weddell Sea, which means the sink for atmospheric CH$_4$. However, our results show that the sea-air CH$_4$ flux south of the PF remained at nearly the same level as those of lower latitudes, suggesting a significant effect of wind speed because the degrees of supersaturation were the lowest in high latitudes (Figure 5). It seems to suggest that the high winds here tear down the concentration gradient of CH$_4$ but increase the gas transfer velocity. If we could use a

cubic gas transfer coefficient of k_w instead of a quadratic, there is little latitudinal difference of the flux. The latitudinal distribution of wind speed tended to have opposite effects on sea-air CH$_4$ flux, as compared with those of Cw-Ca. In December 2001 and January 2002 sea-air CH$_4$ flux was fairly constant in each latitudinal zone and increased in February 2002 due to high wind speed.

[20] *Kelley and Jeffrey* [2002] reported a CH$_4$ flux ranging from −0.74 to 4.13 mol km^{-2} d^{-1}, with a mean value of

Table 1. Sea-Air CH$_4$ Flux F and Cw-Ca in the South Pacific and the Southern Oceans Estimated Based on the CH$_4$-σ_θ Relationship[a]

	North of STF (10°S–47°S)	SAZ (47°S–49°S)	PFZ (49°S–54°S)	South of PF (54°S–65°S)
December 2001				
140°E				
F	3.7 ± 0.1	3.7 ± 0.1	2.4 ± 0.6	0.8 ± 0.6
Cw-Ca	0.82 ± 0.04	0.73 ± 0.03	0.50 ± 0.12	0.15 ± 0.11
160°W[b]				
F	3.4 ± 0.6 (2.9 ± 0.3)	4.1 ± 0.3	4.0 ± 0.5	2.3 ± 1.3
Cw-Ca	0.81 ± 0.07 (0.79 ± 0.01)	0.78 ± 0.01	0.69 ± 0.06	0.45 ± 0.23
January 2002				
140°E				
F	2.7 ± 0.1	3.1 ± 0.1	2.6 ± 0.4	1.3 ± 0.7
Cw-Ca	0.82 ± 0.03	0.75 ± 0.03	0.56 ± 0.09	0.24 ± 0.12
160°W[b]				
F	2.7 ± 0.8 (3.4 ± 0.1)	3.9 ± 0.2	3.9 ± 0.3	1.6 ± 1.0
Cw-Ca	0.77 ± 0.06 (0.79 ± 0.01)	0.80 ± 0.01	0.73 ± 0.05	0.32 ± 0.18
February 2002				
140°E				
F	4.2 ± 0.3	4.9 ± 0.1	4.2 ± 0.5	2.0 ± 1.1
Cw-Ca	0.83 ± 0.04	0.74 ± 0.03	0.54 ± 0.09	0.26 ± 0.10
160°W[b]				
F	2.9 ± 1.1 (4.6 ± 0.2)	4.5 ± 0.1	4.2 ± 0.2	2.1 ± 1.0
Cw-Ca	0.75 ± 0.08 (0.79 ± 0.01)	0.82 ± 0.01	0.75 ± 0.06	0.34 ± 0.16

[a]Sea-air CH$_4$ flux F uses the unit of measure mol CH$_4$ km^{-2} d^{-1} and Cw-Ca uses the unit of measure nmol kg^{-1}. Values after the plus/minus symbol mean the natural variability estimated from σ_θ, barometric pressure, and atmospheric/oceanic CH$_4$ concentrations.
[b]Values in parentheses mean the averages between 40°S and 47°S.

0.38 µmol m^{-2} d^{-1} along the transect from southern Chile through the Panama Canal to the Gulf of Mexico. *Bates et al.* [1996] also reported an average CH$_4$ flux of 0.20 mol km^{-2} d^{-1} from the five meridional cruises in the Pacific. The sea-air CH$_4$ fluxes obtained in this work are generally higher than the sea-air CH$_4$ fluxes given by *Bates et al.* [1996] and *Kelley and Jeffrey* [2002]. Because our data are rather limited in both time and space, further data are needed to better characterize oceanic CH$_4$ distribution and sea-air CH$_4$ exchange in the South Pacific and Southern Ocean.

4. Summary

[21] Measurements of oceanic CH$_4$ were made during the KH01–3 cruise of the R/V *Hakuho-maru* (Ocean Research Institute, University of Tokyo, Japan) and the JARE-43 cruise of the R/V *Tangaroa* (National Institute of Water and Atmospheric Research, New Zealand) in the South Pacific (140°E and 160°W) and Southern Ocean (140°E) from December 2001 to February 2002. Between 10°S and 54°S (Polar Front, PF), the maximum concentrations of CH$_4$ occurred in the subsurface layers, and the CH$_4$ concentrations were considerably dependent on the density (σ_θ). Between 10°S and the PF, the surface CH$_4$ concentration can be expressed as [CH$_4$] = 0.15 σ_θ − 0.98 (RMS = 0.21 nmol kg^{-1}, $r = 0.68$, $n = 49$, $p < 0.001$) for a surface layer shallower than 50 m. In the biologically productive region, south of the PF, the CH$_4$ concentrations in the surface seawater varied greatly (2.9–4.7 nmol kg^{-1}) and were usually higher than those of the South Pacific. In high latitudes of SSIZ, we often found a relationship between chlorophyll *a* and CH$_4$ in the surface layer. Considering that phytoplankton and CH$_4$ production occur in sunlit aerobic and anaerobic conditions, respectively, the high CH$_4$ production probably resulted from the grazing processes of krill and/or zooplankton fed on phytoplankton and the subsequent microbial methanogenesis. Close to the continent, a relatively high concentration of CH$_4$ (~2.0 nmol kg^{-1}) was found in the middle/deep layers and extended to the north (~60°S) in the bottom water. The CH$_4$ distribution showed a pattern similar to those of anthropogenic CO$_2$ and CFCs caused by the transport of surface CH$_4$ in bottom water and possibly formed at the Adelie Land coast [*Rintoul and Bullister*, 1999].

[22] From December 2001 to February 2002, the sea-air CH$_4$ flux estimated based on [CH$_4$]-σ_θ relationship and wind data prepared by NCEP/NCAR ranged from 2.4 to 4.9 mol km^{-2} d^{-1} between 10°S and the PF and from 0.8 to 2.3 mol km^{-2} d^{-1} south of the PF. The sea-air CH$_4$ flux south of the PF was nearly the same as those at lower latitudes, though the degree of supersaturation was low. This flux was caused by the effect of high wind speeds at high latitudes. The South Pacific/Southern Ocean seems to have a minor impact on the global sea-air flux of CH$_4$. However, the sea-air CH$_4$ flux estimated in the Southern Ocean is based on limited time/space data. More data including winter data are needed to accurately determine sea-air CH$_4$ flux in the Southern Ocean.

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