Variation of dimethylsulfide mixing ratio over the Southern Ocean from 36°S to 70°S

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Abstract

Atmospheric dimethylsulfide (DMS) was measured to investigate the variation in its concentration over sea ice free oceans and sea ice regions of the Southern Ocean, using a proton transfer reaction-mass spectrometer (PTR-MS) on board the icebreaker *Shirase* from 1 December 2009 to 16 March 2010. In general, DMS concentrations over sea ice regions were very low compared with those over the sea ice free ocean. However, abrupt increases in DMS concentrations occurred over sea ice regions while the ship was moving and crushing the sea ice. Undoubtedly, the elevated DMS concentrations were caused by large DMS emissions from gaps in the ice made by the ship. During the period when *Shirase* had anchored off Syowa Station (69°00.4′S, 39°35.3′E), Antarctica, DMS concentrations were not detected. At this time, the surrounding sea of East Ongul island, on which Syowa Station is located, was completely covered with multi-year fast ice. Sea ice probably inhibits DMS emission from the ocean to the atmosphere. In addition, there was no evidence that chlorophyll *a* concentration in the sea water or wind speed above the sea surface affect atmospheric DMS concentrations over the sea ice free ocean regions.

1. Introduction

Dimethylsulfide (DMS) is the most important gaseous precursor to sulfur containing aerosols in the remote marine atmosphere (Andreae and Crutzen, 1997). The biochemical precursor of DMS is dimethylsulfonioproprionate (DMSP), which is produced by several classes of phytoplankton in the ocean. DMSP in algal cells serves as an osmolyte, a cryoprotectant (Thomas and Dieckmann, 2002; Bentley and Chasteen, 2004), and an antioxidant (Sunda et al., 2002). DMS in seawater is produced by the enzymatic cleavage of DMSP. Complex biotic and abiotic processes in seawater affect the yield of DMS from DMSP (Stefels et al., 2007).

Although only a small fraction of DMS in seawater is released to the atmosphere (Simó, 2001), the DMS emission is a dominant natural source of reduced sulfur compounds in the troposphere. Lana et al. (2011) estimated that $17.6-34.4$ TgS yr^{-1} in the form of DMS are transferred from the ocean to the atmosphere

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with a best estimate of 28.1 TgS yr^{-1}. According to Lana et al. (2011), the annual DMS emission from the ocean in the Southern Hemisphere accounts for 61—62% of the global annual emission.

Generally, it is known that the primary production of phytoplankton is quite large in the Southern Ocean. This gives rise to high DMS concentrations in the atmosphere over the Southern Ocean. Koga et al. (1993) measured atmospheric DMS concentrations using gas chromatography with a flame photometric detector on board the icebreaker *Shirase* in the Indian sector of the Southern Ocean in December 1990 during the 32nd Japanese Antarctic Research Expedition (JARE32). They reported that DMS concentrations south of 50°S increased substantially poleward. DMS concentrations exceeding 400 pptv were observed at around 61°S. Colomb et al. (2009) measured selected volatile organic compounds (VOCs) including DMS using a proton transfer reaction-mass spectrometer (PTR-MS) during December 2004, in order to better understand their potential sources and sinks over the Southern Indian Ocean from 24°S to 49°S. They found that DMS was the most abundant VOC and was highly variable within the range of 50—885 pptv. The areas of elevated DMS values corresponded to those of high chlorophyll *a*.

Atmospheric DMS is oxidized to dimethyl sulfoxide, dimethyl sulfone, methansulfonate, and SO_2. These sulfur compounds are finally converted to non-sea salt sulfate (Barnes et al., 2006). Sulfate derived from DMS contributes substantially to sulfate masses in aerosols in the remote marine atmosphere (Koga and Tanaka, 1999). Sulfate particles act as cloud condensation nuclei, and also affect the radiative properties of clouds and the direct scattering of solar radiation. Meskhidze and Nenes (2006) explored the effect of ocean biological productivity on marine clouds over a phytoplankton bloom in the Southern Ocean using remote sensing data. They found that water clouds near the bloom region have effective droplet radii 30% smaller than those of background clouds over the Southern Ocean. Changes in Chl *a* and aerosol optical depth over the melting sea ice zone during the spring-early summer period suggest that the release of DMS and/or volatile organic compounds from melting sea ice may be significant (Gabric et al., 2005). An abundance of ice algae exists in the bottom of sea ice. High concentrations of DMSP were found in the ice algae (Thomas and Dieckmann, 2002). DMS concentrations were much higher at the bottom of sea ice than in under-ice water (Delille et al., 2007; Nomura et al., 2011). Lana et al. (2011) asserted that further work is

required to better quantify the effect of sea ice on the sea to air flux of DMS.

Spatial distributions of DMS concentrations in the atmosphere, however, are not well known over the sea ice free ocean area in the Southern Ocean and over sea ice near coastal regions of Antarctica. Therefore, atmospheric DMS concentrations were investigated using PTR-MS on board the icebreaker *Shirase* in the Southern Ocean during the JARE51 from 1 December 2009 to 16 March 2010. This paper reports the spatial distribution of atmospheric DMS concentrations measured during the JARE51 voyage.

2. Materials and methods

Fig. 1 shows the whole voyage track of *Shirase* from Fremantle to Syowa Station (69°00.4′S, 39°35.3′E) and from Syowa Station to Sydney. The voyage tracks of *Shirase* in the vicinity of Syowa Station are shown in Fig. 2.

PTR-MS (Ionicon Analytik GmbH, Innsbruck, Austria) and a gas calibration unit (GCU-s: Ionimed Analytik GmbH, Innsbruck, Austria) were installed in a container placed on the right side of the deck for marine observation on *Shirase*. Air samples were drawn from about 8 m above sea level through a Teflon tubing of 4 mm ID and about 7 m in length.

PTR-MS enables the simultaneous real-time monitoring of VOCs in ambient air. A major advantage of PTR-MS is that it does not require pre-concentration or chemical separation procedures. Thus air samples can be introduced directly into the drift tube. The PTR-MS technique is based on the chemical ionization of VOCs through the proton transfer reaction between hydronium ions (H_3O^+) and VOCs. The proton transfer reaction is possible for VOCs with a proton affinity higher than that of water. This reaction produces an ionized molecule (VOCsH$^+$) and a neutral water molecule (H_2O). Therefore, a mass (*m/z*) of 63 amu was employed to estimate DMS concentrations.

PTR-MS calibrations were performed using GCU-s. The standard gas was 1 ppmv of DMS included in an internal SilcoCan canister (Apel-Riemer Env. Inc., Broomfield, CO, USA). Ambient air, drawn into the GCU-s via an internal pump, was used as the GCU-s carrier gas without changing the humidity. Most VOCs in the carrier gas flow were destroyed through the catalytic converter. To produce a carrier gas stream containing known DMS mixing ratios, a steady flow of standard gas was mixed with a steady flow of VOC-free air. The standard gas flow rates ranged from 0.3 to 8 ml min^{-1}. Although the optimum VOC-free air
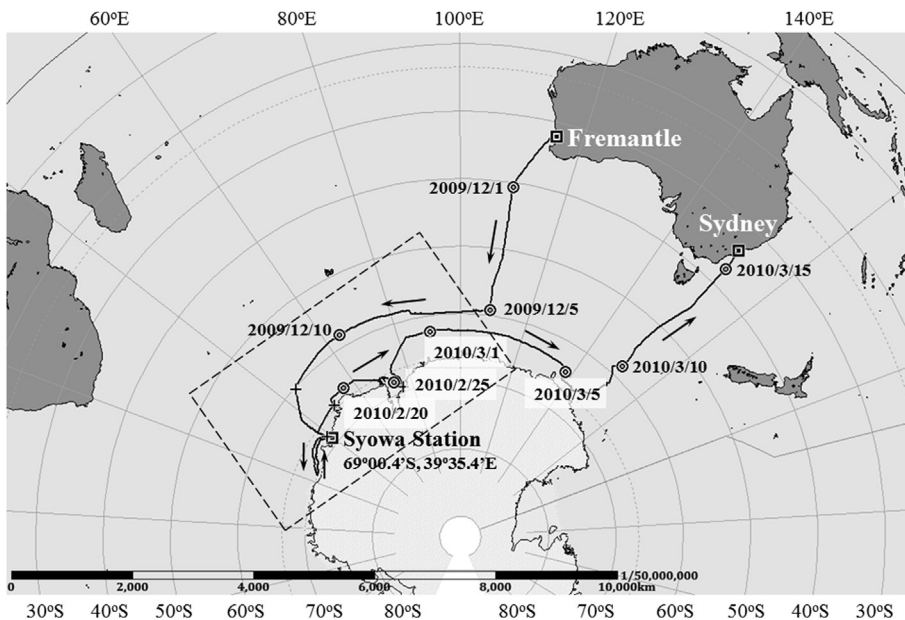
Fig. 1. Voyage track of the icebreaker *Shirase*. The period of the voyage was from 29 December 2009 to 17 March 2010. Dual circles indicate the ship's positions at 0:00 UTC on the annotated dates. The inside area of the broken line is shown with plus symbols in detail in Fig. 2.

flow of the GCU-s is in the range of 250–1500 ml min^{-1}, 2000 ml min^{-1} was used as well as 1000 ml min^{-1} in this study. Therefore, the dilution ratio ranged from 1.5×10^{-4} to 8×10^{-3}.

Calibrations were conducted 11 times during this expedition. The correlations between PTR-MS output and known DMS mixing ratio were very close to 1 (Coefficients of determination $r^2 = 0.99944–0.99998$. The number of data $n = 3–13$), without any blank

values X_B of PTR-MS outputs in zero gas. When the vertical axis is PTR-MS output, the y-intercept values of regression lines are always higher than detection limits X_D (=$X_B + 3.29 \sigma$, σ is the standard deviation of X_B) derived from Currie (1968). Consequently, DMS concentrations in the real atmosphere can be calculated from PTR-MS output values higher than the y-intercept values using the equations of the regression lines. If PTR-MS outputs are lower than the y-intercept, DMS
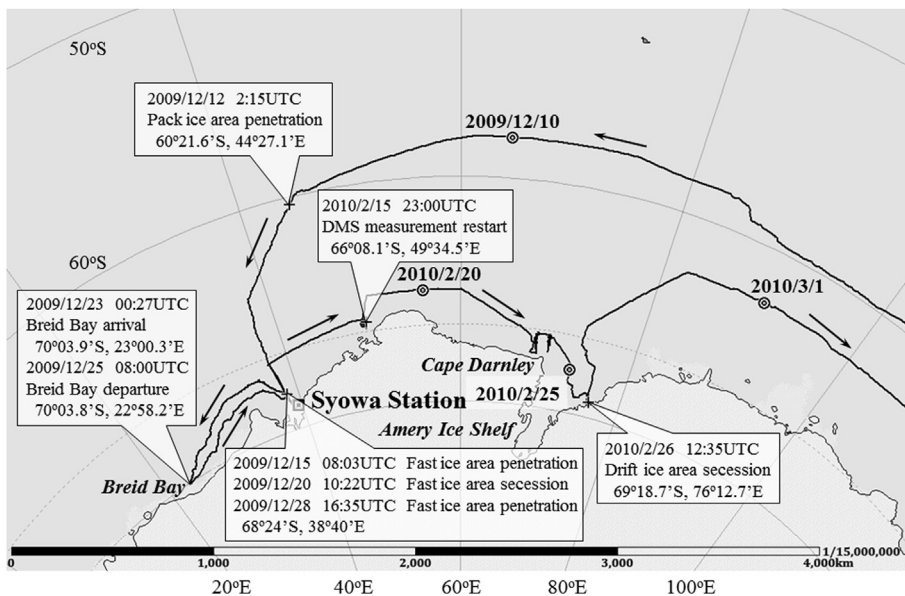

Fig. 2. Voyage track of the ice breaker *Shirase* in the vicinity of Antarctica.

concentrations in the real atmosphere are considered to be zero.

3. Results

Atmospheric DMS concentrations during the voyage from 1 December 2009 to 10 January 2010 are displayed in Fig. 3, together with wind speed, air temperature, and water temperature. Most of the atmospheric DMS concentrations ranged from 50 pptv to 700 pptv over the sea ice free ocean. Values at the higher end of this range, from 400 to 700 pptv, were observed near the edge of the pack ice region from 11 December to 13 December. The highest value in this period, 1410 pptv, was observed at the point of 62°35.4'S and 40°33.8E. From measurements of atmospheric DMS concentrations in the period of the JARE34 voyage, Koga et al. (1993) reported a maximum DMS concentration of 461 pptv around 61°S. Kiene et al. (2007) observed high DMS emissions to the atmosphere in the Southern Ocean, near the northern edge of the sea ice and in the Ross Sea. These results are associated with very high DMS concentrations in the seawater released from melting sea ice.

In general, DMS concentrations over the sea ice regions were very low compared with those over the sea ice free ocean. Abrupt increases in DMS concentration, however, were very often observed over the pack and fast ice regions during ice breaking. This suggests high DMS emissions being released through sea ice cracks formed during ice breaking, due to high DMS concentrations in the seawater near the bottom of sea ice (Delille et al., 2007; Nomura et al., 2011). The maximum DMS concentration of 3280 pptv during this voyage was observed just before the *Shirase* landed at Syowa Station. At this time, large amount of brownish seawater including many ice algae came out of cracks formed during ice breaking.

Curran et al. (1998) observed atmospheric DMS concentrations over the Australian sector of the Southern Ocean (60°E to 165°E) and found that atmospheric DMS concentrations in the seasonal ice zone ranged from non-detectable to 70 pptv with an average of 18 pptv during the austral summer (December to February). Over the perennial ice zone of the western Weddell Sea in December 2004, Zemmelink et al. (2008) found that the atmospheric DMS concentration remained relatively low at around 5 to 120 pptv and remained at around 17 pptv toward the end of December. In the present study, atmospheric DMS concentrations over the pack and fast ice regions, except for high values under ice breaking, were appreciably lower than those over the sea ice free ocean. These values are identical to the results of Curran et al. (1998) and Zemmelink et al. (2008).

Fig. 4 shows atmospheric DMS concentrations over the multi-year fast ice (69°00'S, 39°37'E) off Syowa
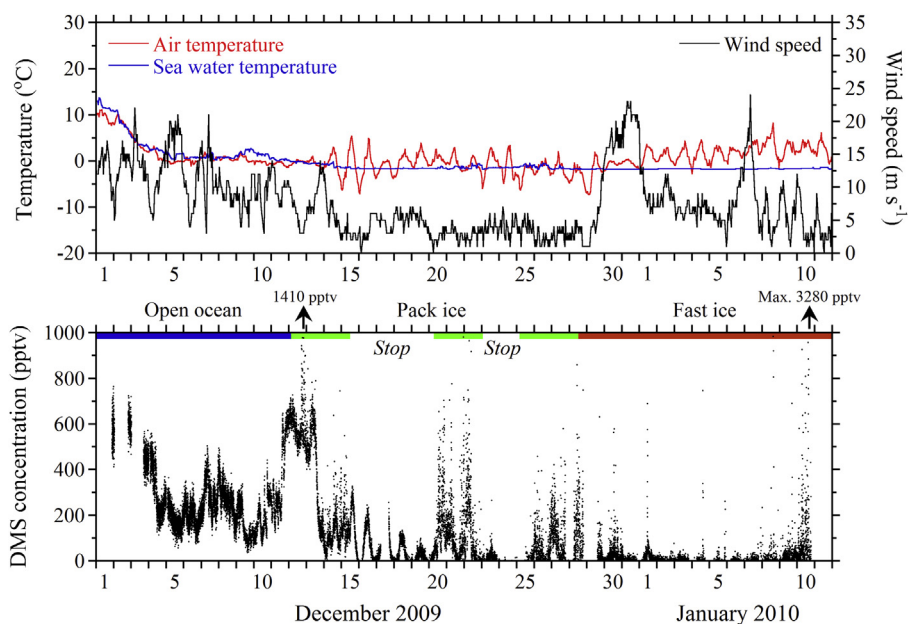

Fig. 3. Air temperature, sea water temperature, wind speed (top panel), and atmospheric DMS concentrations (bottom panel) during the voyage from 1 December, 2009 to 10 January, 2010.

Station from 11 January to 3 February 2010. The *Shirase* was anchored during this period. There were strong winds from 15 to 18 January during a blizzard with a wind direction of northeast. High DMS concentrations were observed only during this period. The source of these high DMS concentrations appears to be from air masses that previously passed over the open ocean. Except during this blizzard, atmospheric DMS concentrations were below the detectable level over the fast ice off Syowa Station, although high diatom and phytoflagellate blooms have been found under the fast ice in summer (Satoh et al., 1991; Ishikawa et al., 2001). This suggests that DMS emissions from the fast ice surface are negligible.

Fig. 5 shows the variation of DMS concentration measured during the voyage from 15 February to 15 March 2010. The *Shirase* made a voyage through a drift ice region from 19 to 26 February 2010. The sea surface during this period was not completely covered with sea ice. Hence, there was a possibility of DMS emissions from the sea surface, but atmospheric DMS concentrations were nevertheless still very low. The cause of these low values is not known. After 27 February 2010, atmospheric DMS concentrations over the open ocean ranged substantially, from 100 to 300 pptv, and were appreciably higher than those over drift ice regions.
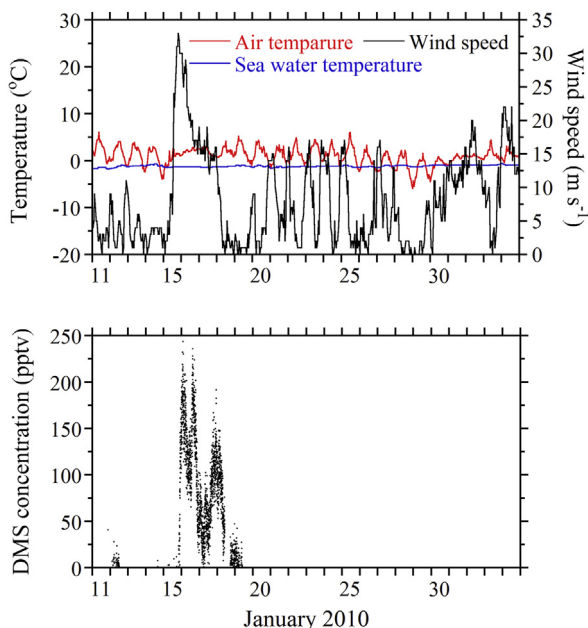

Fig. 4. Air temperature, sea water temperature, wind speed (top panel), and atmospheric DMS concentrations (bottom panel) off Syowa Station from 11 January to 3 February, 2010.
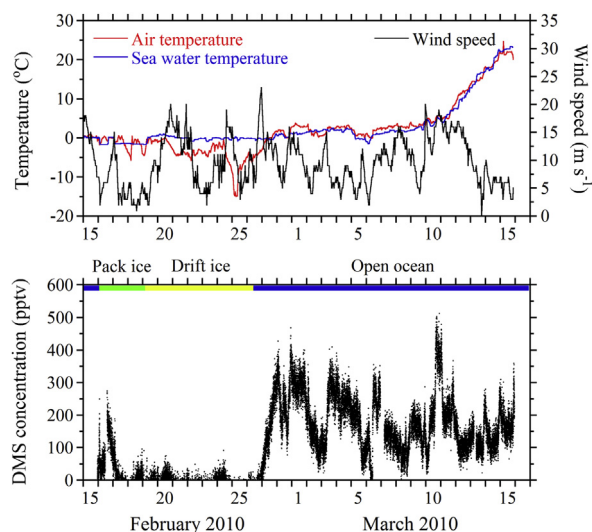

Fig. 5. Air temperature, sea water temperature, wind speed (top panel), and atmospheric DMS concentrations (bottom panel) during the voyage from 15 February to 15 March 2010.

4. Discussion

DMS oxidation is regulated by the reactions with OH, NO_3, halogen atoms, and halogen oxides (Barnes et al., 2006). These oxidant concentrations depend strongly on ultraviolet radiation intensity. There is no information about these oxidant concentrations during the voyage. Nevertheless, the atmospheric DMS concentration is expected to increase with increasing latitude, because of the gradual decrease in ultraviolet radiation intensity. The observed variations of DMS concentrations, however, were completely unrelated to the estimated change of radiation intensity (Figs. 3 and 5) and so must be related to other factors.

During the voyage from Fremantle to Syowa Station, high concentrations of Chl a, from 0.9 to 1.9 µg L^{-1}, were observed at around 58°S, 81°E in the sea ice free ocean on 8 December 2009 (Iida and Shinagawa, 2011) (Fig. 6). The fluorescence maximum measured with a fluorometer (Model 10AU, Turner Designs, Inc., USA) also occurred on 8 December 2009. High Chl a concentrations suggest that there would be high DMS emission to the atmosphere due to high DMS concentrations in the surface seawater. However, the atmospheric DMS concentrations were relatively moderate during this period. High concentrations of atmospheric DMS were observed at the edge of the pack ice region on 11, 12, and 13 December 2009 (Fig. 3), while fluorescence was generally low. During the voyage from Syowa Station to Sydney, the maximum Chl a value of 8.0 µg L^{-1} was observed at 69°13'S, 76°05'E in the drift
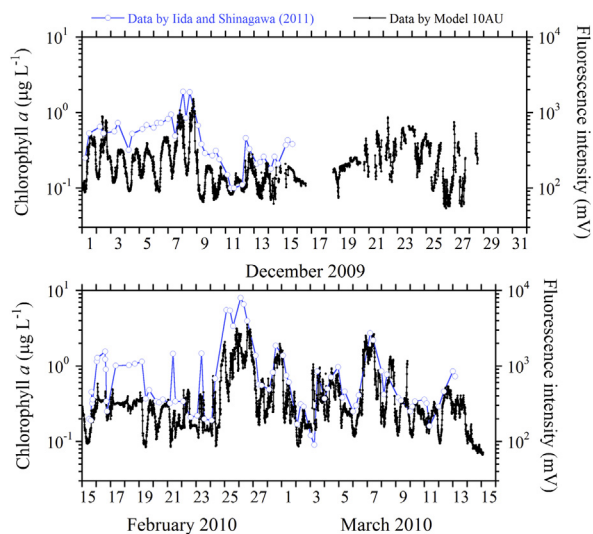
Fig. 6. Fluorescence intensity data measured with a fluorometer and Chl *a* concentrations by Iida and Shinagawa (2011).

ice region on 26 February 2010 (Iida and Shinagawa, 2011), coinciding with the fluorescence maximum (Fig. 6). However, atmospheric DMS concentrations were very low (Fig. 5). Unfortunately, no estimation of DMS emission rate could be made for the period of the JARE51 voyage, because no seawater DMS concentration data was collected.

The DMS emission rate to the atmosphere can be estimated as a product of the DMS transfer velocity, k_{DMS}, in the liquid phase and the DMS concentration, [DMS]w, in the surface seawater (Liss and Merlivat, 1986; Nightingale et al., 2000). On the whole, [DMS]w is related to the Chl *a* concentration in the sea water. A good correlation, however, is not necessarily found between [DMS]w and Chl *a* or phytoplankton cell number, because the major producers of DMSP as the precursor of DMS are a limited number of species that belong to the classes of Haptophyceae, Dinophyceae, and Chrysophyceae. Variations in abiotic factors, i.e., light, nutrients, seawater temperature, and salinity, also strongly affect ratios of DMSP to Chl *a* (Stefels et al., 2007). In addition, local wind speed is an important factor that affects the DMS emission rate, because k_{DMS} depends strongly on local wind speed (Liss and Merlivat, 1986; Nightingale et al., 2000). However, in the present study, there was apparently no correlation between atmospheric DMS concentrations and wind speed data over the sea ice free ocean (Figs. 3 and 5).

The results of the present study show that atmospheric DMS concentrations were not affected by the Chl *a* concentration or by the wind speed. Trevena and Jones (2006, 2012) concluded that large amounts of seawater

DMS are released from melting sea ice and are not from *in situ* production by an ice edge bloom. Therefore, a relationship between DMS emission to the atmosphere and the sea ice condition will be discussed below.

To make direct measurements of DMS emission rates from the sea ice surface to the atmosphere under different sea ice interface conditions, Nomura et al. (2012) set up three sampling stations off Syowa Station during the ice melt season, a station on level ice for time series analyses, a station near an ice crack, and a station on a melt pond. They determined DMS emission rates based changes in DMS concentrations in air within Teflon-coated chambers on these sea ice interfaces, from 12 January to 2 February 2010. The DMS emission rates over the slush (slurry of seawater and sea ice) layer were in the range of 0.1–5.3 $\mu mol\ m^{-2}\ d^{-1}$. The DMS concentrations in the slush water ranged from 1.0 to 103.7 nM and are identical with the values from <1 to 92 nM in the slush layer in the western Weddell Sea reported by Zemmelink et al. (2008). Nomura et al. (2012) also showed a very good positive correlation between the DMS emission rate over the slush layer and the DMS concentration in the slush water. DMS emission rates over snow and superimposed ice, however, were constant at 0.09 ± 0.02 $\mu mol\ m^{-2}\ d^{-1}$ and were independent of the DMS concentration in the slush water beneath snow and superimposed ice (an ice layer formed by the freezing of snow meltwater). Therefore, it appears that the snow accumulation and the formation of an ice layer over the slush layer impede DMS emissions from the slush water. Very low DMS concentrations over pack and fast ice regions are most likely caused by very low DMS emission rates from the sea ice surface (Figs. 3–5). Nomura et al. (2011) measured DMSP + DMS concentrations in the fast ice off Syowa Station from 28 December 2006 to 29 January 2007. The DMSP + DMS concentrations were higher in the bottom layer of sea ice than in the water under the ice. The DMSP + DMS concentrations in the sea ice were higher in the bottom layer than in the upper layer. These high values in the bottom layer of sea ice are most likely caused by the presence of algae assemblages within the sea ice. The bottom layer of sea ice would be a source of DMSP + DMS. Diffusion rates of dissolved gases and exchange of inorganic nutrients, however, are retarded because of the closed pore spaces within the ice (Gleitz et al., 1995). The fact that snow and superimposed ice impede DMS emissions explains why atmospheric DMS was undetectable over the fast ice off Syowa Station (Fig. 4).

Bates et al. (1992) estimated 2.1 $\mu mol\ m^{-2}\ d^{-1}$ of DMS emission rate in summer (November to April) from

65°S to 80°S. This estimate was obtained only from extrapolation of regional and seasonal emission rates for the North Pacific Ocean. On the basis of measurements of DMS concentrations in the sea water, the first estimate of DMS emission rates from the Australian sector of the Southern Ocean (63°E to 162°E) was made by Curran and Jones (2000). In spring, from September to November, there is no estimate of DMS emission rates for the seasonal ice zone because the seawater surface was covered with ice. During this period, atmospheric DMS concentrations ranged from non-detectable to 34 pptv with an average of 5 pptv (Curran et al., 1998). In summer, from December to February, the average DMS emission rate for the seasonal ice zone was estimated to be 49 μmol m^{-2} d^{-1}, although the emissions were only calculated for the ice-free ocean areas (Curran and Jones, 2000). This value is higher than the values measured by Nomura et al. (2012). As mentioned above, the averaged atmospheric DMS concentration in summer of 18 pptv was measured by Curran et al. (1998). Despite the large increase of DMS emission rate from spring to summer, the increase of atmospheric DMS concentration during this period was quite small. This shows the inflow of air masses passed through regions of low DMS emissions compared with the seasonal ice zone. Zemmelink et al. (2008) measured high DMS emission rates with an average of 11 μmol m^{-2} d^{-1} which is also higher than the values measured by Nomura et al. (2012). Nomura et al. (2012) discussed a discrepancy in DMS emission rates between their study and Zemmelink et al. (2008) and noted that the each method is aimed at very different spatial scales. This may be one reason for this discrepancy.

During the period of the present study, the maxima of the DMS concentration in slush water and of DMS emission rate were observed at the ice-crack station (Nomura et al., 2012). Ice-cracks may play a role in venting DMS directly to the atmosphere, as well as it being released from sea ice melting (Trevena and Jones, 2006, 2012). DMS may be released as a result of melting and breakup of the sea ice. The release of large amounts of DMSP during sea ice melting may occur in discrete areas and may produce "hot spots" of elevated seawater DMS concentration. Hot spot areas may be important sources of high DMS emission (Trevena and Jones, 2006, 2012). The overlying granular snow might also allow more active emission of DMS to the atmosphere (Zemmelink et al., 2008). However, it seems to be unsuitable to use the high DMS emission rates at hot spots as the estimation of DMS emission from the whole sea ice region. There were no prominent ice-cracks in the vicinity of *Shirase*. In addition, snow and superimposed

ice most likely impeded DMS emissions. The very low DMS concentrations shown in Fig. 4 can be attributed to negligible DMS emissions from the surface of multi-year fast ice. There is room for further investigation on DMS emissions in sea ice regions to better quantify the global annual sulfur emission.

5. Summary

The following results were obtained on the spatial distribution of atmospheric DMS concentrations measured during the JARE51 voyage.

(1) Atmospheric DMS concentrations were appreciably lower over sea ice regions than over sea ice free ocean.
(2) Abrupt increases of DMS concentration were very often observed during ice breaking. These were most likely caused by large DMS emissions through sea ice cracks.
(3) Atmospheric DMS concentrations over fast ice off Syowa Station were almost zero.
(4) Judging from (1), (2), and (3) above, the DMS emission from the sea ice surface to the atmosphere appears to be impeded by snow and superimposed ice over the slush layer. However, ice-cracks are likely to play an important role in DMS emission to the atmosphere.
(5) The atmospheric DMS concentrations over the sea-ice free ocean were unrelated to the Chl *a* concentration in the seawater or to the wind speed above the sea surface.

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