



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.

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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 dimethylsulfoniopropionate (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 sulfide, dimethyl sulfone, methanesulfonate, and SO₂. 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 (H₃O⁺) 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 (H₂O). 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

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