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A Time Series Observation of DMSP Production in the Fast Ice Zone Near Barrow (Extended Abstract)

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1. Introduction

Dimethylsulfide (DMS) is the most abundant biogenic sulfur compound emitted from the ocean to the atmosphere (Kettle and Andreae, 2000). Subsequently, DMS is oxidized in the atmosphere and forms tropospheric aerosols, which affect the radiative balance of the Earth through the increase in both backscatter of solar radiation and number of cloud condensation nuclei (Charlson *et al.*, 1987). DMS is formed from its precursor dimethylsulfonio-propionate (DMSP), which is produced by marine phytoplankton (White, 1982). In the Arctic Ocean, primary production by ice algae significantly contributes to the carbon cycle (Legendre *et al.*, 1992; Gosselin *et al.*, 1997). In addition, ice algae are known to accumulate high amounts of intracellular DMSP for the purpose of cryoprotection in addition to osmoregulation (Kirst *et al.*, 1991). The Arctic Ocean has a vast continental shelf, which is covered with coastal sea-ice in the winter. Thereby, substantial amounts of DMSP produced by ice algae may be released to the water column resulting in high DMS emission to the atmosphere during the spring ice melt season (Levasseur *et al.*, 1994). However, DMSP production by Arctic ice algae is still unknown. This study was conducted to make clear the relation between the production of the sulfur compounds and biological activity in the sea-ice environment.

Methods

At a fixed sampling site in the land fast sea-ice zone in Barrow, Alaska (71°19.6′N, 156°42.2′W), a few hundred meters off the coast, 3-5 meters water depth, observations were conducted on six different days: March 4, April 3, April 17, May 1, May 22 and June 5, 2002.

Sea-ice cores were taken with a motorized corer (9 cm i.d.) and seawater was taken from a core hole with a plastic hand pump. Ice core and seawater samples for DMSP measurement were stored frozen until analysis. Each ice core was cut into short sections; 2, 3, 5 and 10 cm from the bottom of the lowermost part and 20 cm for the upper part. Concentrations of total DMSP (particulate+dissolved DMSP)+DMS in the sea-ice and seawater were determined after thawing frozen samples. DMSP in 5 to 0.05

ml (depending on concentration) of thawed sample was cleaved to DMS with 1 ml of 6 *M* sodium hydroxide, then measured as gaseous DMS with a gas chromatograph equipped with a flame photometric detector (Shimadzu GC-17A) and a GS-Q capillary column (J & W) following the gas stripping procedure with helium gas using a purge and trap gas concentrator (Tekmar 4000J). Analytical error was ±10%. All the samples were analyzed within three months after sampling. Concentrations of chlorophyll *a* were also determined as an indicator of algal biomass. Seawater samples were filtered with Whatman GF/F glass fiber filters within a few hours after samplings. Thawed sea-ice samples, that were cut into the same sections as DMSP samples, were filtered later. The algal pigments retained on the filters were extracted into 90% acetone for 24 hours and measured with the fluorescent method (Strickland and Parsons, 1972).

Results and discussion

In 2002, the ice thicknesses at the sampling site were 137, 139, 148, 156, 135 and 137 cm on Mar. 4, Apr. 3, Apr. 17, May 1, May 22 and June 5, respectively. In 2002, snow on the sea-ice began to melt in the middle of May, a few weeks earlier than usual, due to the unusually warm temperatures for that month.

Figure 1 shows vertical distributions of DMSP concentrations in sea-ice cores. Concentrations of DMSP in sea-ice revealed remarkable variability. A typical vertical

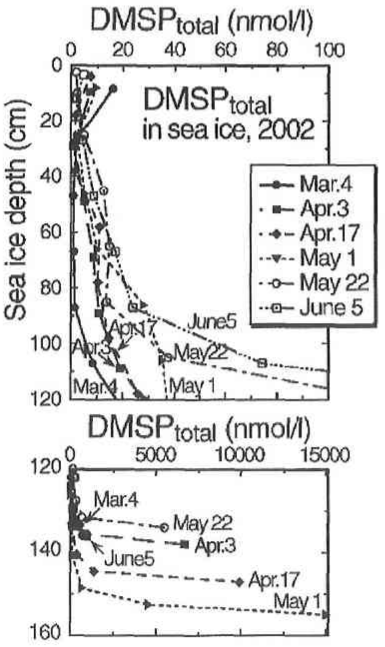

Figure 1. Vertical distributions of total DMSP in sea-ice cores.

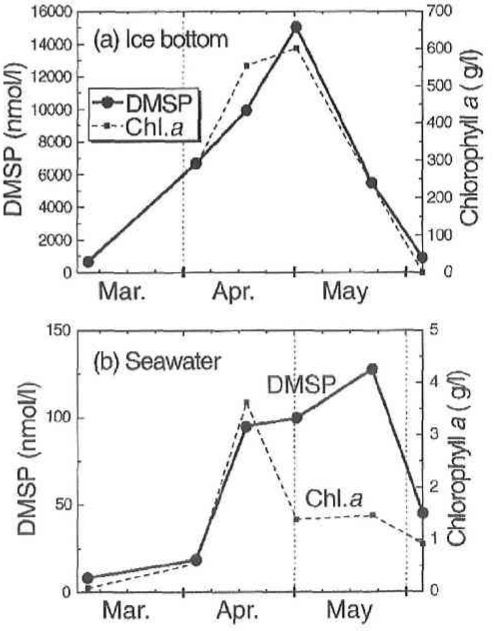

Figure 2. Temporal variations of total DMSP and chlorophyll *a* in (a) sea-ice bottom and (b) seawater.

profile of DMSP from the bottom to the top shows highest concentrations at the bottom decreasing exponentially toward the top, a minimum at around the depth of 20 cm, and a slight increase at the top. In the lowermost part, where ice algae actively developed, extremely high amounts of DMSP were observed with a maximum of 15 μmol/l coinciding with high chlorophyll *a* concentrations with a maximum of 0.6 mg/l in early May. As time went on, the ice became softer and more fragile, especially in the last two periods, when concentrations of DMSP in the lower interior part of ice cores increased gradually, reflecting the seawater penetration from the bottom through channels in the ice. Small amounts of DMSP found in the top portion may come from phytoplankton residue kept frozen since the sea-ice formed.

Figure 2 shows temporal variation of concentration of DMSP with chlorophyll *a* in the bottom 2 cm layer of the sea-ice and seawater samples. Concentrations of DMSP and chlorophyll a at the ice bottom (Fig. 2a) increased from March to early May. The highest amounts of DMSP were obtained in early May, followed by rapid decreases as ice thinned. In sea-ice, the DMSP/chlorophyll *a* ratio was relatively low and consistent during the observed period with a value about 20 nmol/μg (range: 18-25 nmol/μg), except for in June (880 nmol/μg) when chlorophyll *a* concentration declined to the seawater level. This is reasonable because ice algae are usually dominated by diatoms (Kirst *et al.*, 1991; Levasseur *et al.*, 1994; Turner *et al.*, 1995), a low DMSP producer (Keller *et al.*, 1989). Although DMSP concentrations in this study contain the dissolved fraction of DMSP and DMS, the ratio obtained appears to be still higher than the typical value for diatoms in seawater in temperate regions (generally less than 10 nmol/μg, Liss *et al.*, 1994; Turner *et al.*, 1995), confirming the higher DMSP production by polar diatoms (Levasseur *et al.*, 1994; Matrai and Vernet, 1997).

Concentrations of DMSP and chlorophyll *a* in seawater (Fig. 2b) increased dramatically in April. By May, the concentration of chlorophyll *a* in seawater decreased rapidly, although DMSP concentration remained high. Consequently, DMSP/chlorophyll a ratio increased from 26 to 72 nmol/μg, suggesting the succession in the major algal composition from low DMSP producer to higher one. In late May, when sea-ice was melting, concentrations of DMSP and chlorophyll a in sea-ice dropped to two thirds of those in early May. Meanwhile in seawater, significant increase in DMSP was observed with the highest value of 130 nmol/l. This may be caused by the mass release of DMSP from detached ice algae to the water column under sea-ice. DMSP concentration in seawater decreased rapidly by June, suggesting that active microbial removal is enhanced possibly by the increase of organic materials in water column as a consequence of the release of ice algae and warmer water temperature.

These results confirm that ice algae in the fast sea-ice produce DMSP efficiently and may contribute to the subsequent DMS sea-to-air flux in the Arctic.

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