

# Dimethylsulphide and dimethylsulphonioacetate in Antarctic sea ice and their release during sea ice melting

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## Abstract

This study presents concentrations of dimethylsulphide (DMS) and its precursor compound dimethylsulphonioacetate (DMSP) in a variety of sea ice and seawater habitats in the Antarctic Sea Ice Zone (ASIZ) during spring and summer. Sixty-two sea ice cores of pack and fast ice were collected from twenty-seven sites across an area of the eastern ASIZ (64°E to 110°E; and the Antarctic coastline north to 62°S). Concentrations of DMS in 81 sections of sea ice ranged from <0.3 to 75 nM, with an average of 12 nM. DMSP in 60 whole sea ice cores ranged from 25 to 796 nM and showed a negative relationship with ice thickness ( $y = 125x^{-0.8}$ ). Extremely high DMSP concentrations were found in 2 cores of rafted sea ice (2910 and 1110 nM). The relationship of DMSP with ice thickness (excluding rafted ice) suggests that the release of large amounts of DMSP during sea ice melting may occur in discrete areas defined by ice thickness distribution, and may produce 'hot spots' of elevated seawater DMS concentration of the order of 100 nM. During early summer across a 500 km transect through melting pack ice, elevated DMS concentrations (range 21–37 nM, mean 31 nM,  $n = 15$ ) were found in surface seawater. This band of elevated DMS concentration appeared to have been associated with the release of sea ice DMS and DMSP rather than in situ production by an ice edge algal bloom, as chlorophyll *a* concentrations were relatively low (0.09–0.42  $\mu\text{g l}^{-1}$ ). During fast ice melting in the area of Davis station, Prydz Bay, sea ice DMSP was released mostly as extracellular DMSP, since intracellular DMSP was negligible in both hyposaline brine (5 ppt) and in a melt water lens (4–5 ppt), while extracellular DMSP concentrations were as high as 149 and 54 nM, respectively in these habitats. DMS in a melt water lens was relatively high at 11 nM. During the ice-free summer in the coastal Davis area, DMS concentrations in surface seawater were highest immediately following breakout of the fast ice cover in late December (range 5–14 nM), and then remained at relatively low concentrations through to late February (<0.3–6 nM). These measurements support the view that the melting of Antarctic sea ice produces elevated seawater DMS due to release of sea ice DMS and DMSP.

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## 1. Introduction

Dimethylsulphide (DMS) is the major volatile sulphur compound in the oceans and is climatically important since it affects the radiative properties of clouds

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through its atmospheric oxidation products. Its biochemical precursor is dimethylsulphoniopropionate (DMSP), which is ubiquitous in the oceans where it is produced by several classes of phytoplankton (see Malin et al., 1994). DMS production from DMSP occurs predominantly via enzymatic cleavage in surface waters (e.g., Malin and Kirst, 1997; Stefels, 2000). Production and accumulation of DMS is intricately linked with food-web dynamics (e.g., Ledyard and Dacey, 1996; Archer et al., 2002). The true function of DMS is uncertain (Stefels, 2000). It may simply be a physiological waste product associated with DMSP (Malin and Kirst, 1997) or a key component in the altruistic behaviour of marine algal communities that acts, via ocean–atmosphere feedback (see Malin et al., 1994) to maintain the radiative balance of the earth and create conditions optimal for photosynthetic life (Simó, 2001). DMS may also function as an antioxidant, which protects cells during conditions of oxidative stress (i.e., increased UV radiation, CO<sub>2</sub> and/or Fe limitation; Sunda et al., 2002).

The function of DMSP in algal cells is reported to include a compatible solute, which contributes to protection against high salinity (e.g., Dickson and Kirst, 1986) and freezing (Karsten et al., 1996), a multifunctional defence precursor for the production of acrylic acid (produced by DMSP cleavage) (Wolfe et al., 1997), a regulatory coupling mechanism between assimilatory sulphate and nitrate reduction (Stefels, 2000), and as an antioxidant (Sunda et al., 2002).

The relative ratios of intracellular DMSP (DMSPp), extracellular DMSP (DMSPd) and dissolved DMS in surface waters are influenced by the life stages of an algal community and the composition of the microbial food web. DMSPp generally dominates during exponential and stationary growth phases while DMSPd and DMS concentrations typically increase during senescence, increased grazing pressure (e.g., Wolfe et al., 1997; Archer et al., 2002), bacterial activity (Visscher et al., 1992; Ledyard and Dacey, 1996), and the presence of viruses (Malin et al., 1994). The release of DMSPd by healthy algal cells may occur in response to decreasing salinity (Stefels and Dijkhuizen, 1996). DMS production occurs via enzymatic cleavage of DMSP by either algal or bacterial DMSP-lyase enzymes (Visscher et al., 1992; Stefels and Dijkhuizen, 1996). Bacterial activity accounts for the majority of DMSPd and DMS turnover, with consumption being the major process (Visscher et al., 1992; Archer et al., 2002). DMS production is generally a small component of DMSP turnover (<20%, e.g., Ledyard and Dacey, 1996; Kiene and

Linn, 2000; Archer et al., 2002), though the yield of DMS may vary seasonally (Ledyard and Dacey, 1996; Archer et al., 2002) or with mixed layer depth (Simó and Pedrós-Alió, 1999).

Antarctic sea ice contains very large but variable concentrations of DMSP (Kirst et al., 1991; Turner et al., 1995; Curran et al., 1998; DiTullio et al., 1998; Trevena et al., 2000, 2003; Gambaro et al., 2004). Concentrations from across seven sea ice studies, summarised by Trevena et al. (2003), ranged from less than 5 to around 1660 nM, with averages for each study of the order of 100 to 300 nM. The large variability in sea ice DMSP has been attributed mostly to the patchy distribution of ice algal biomass and its variable taxonomic composition (Kirst et al., 1991; Turner et al., 1995; Curran et al., 1998; DiTullio et al., 1998; Trevena et al., 2000, 2003). Considering that the development of sea ice algal assemblages is intrinsically linked with ice growth and history (Ackley and Sullivan, 1994), it is plausible that DMSP concentrations thus may vary characteristically between sea ice of different thicknesses (see Trevena et al., 2000, 2003). It is thought the release of sea ice DMSP during annual ice melting is, in part, responsible for elevated concentrations of DMSP and DMS in seawater (Fogelqvist, 1991; Kirst et al., 1991; Curran et al., 1998; DiTullio et al., 1998; Curran and Jones, 2000). Kirst et al. (1991) suggested that the release of large amounts of DMSP during Antarctic sea ice melting could produce high concentrations of seawater DMS with the potential to effect local climate. In Arctic sea ice, Levasseur et al. (1994) reported extremely high DMSP (up to 90 µM) and suggested its release following ice melting could produce a one day pulse of DMS flux ten times higher than the average summer flux. However, we have little knowledge of the release and transformation processes affecting the fate of sea ice DMS and DMSP during sea ice melting (Levasseur et al., 1994; Trevena et al., 2003).

In this study we report the first DMS concentrations in Antarctic sea ice and relate these to concentrations of total DMSP (DMSPt=dissolved DMSP+particulate DMSP) and chlorophyll *a* (Chl *a*). We make a preliminary characterisation of sea ice DMSP concentration as a function of ice thickness and report DMSP and DMS concentrations during sea ice melting from different pack and fast ice habitats along with seawater concentrations at a coastal site during the ice-free summer. We investigate the dynamics of DMSP and DMS in sea ice and surface seawater during sea ice

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