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**Dimethylsulfide, Climate and Coral Reef Ecosystems**

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**Abstract.** Dimethylsulfide (DMS) is the major biogenic source of atmospheric sulfur and is mainly derived from dimethylsulfiniopropionate (DMSP) produced by oceanic phytoplankton, marine algae and endosymbiont zooxanthellae in reef-building corals. Although coral reefs occupy <1% of the global oceans, the potential source strength of DMS from these areas was found to be significant in comparison to other oceanic areas. In this study, healthy nubbins of *Acropora valida* and *Acropora pulchra* collected at Heron Island were examined to assess the source strength of DMS from these common coral species. Total DMS (free DMS and DMSP-derived DMS) measured in these corals was on average 3.6 µmol cm$^{-2}$ surface area. Sediment from the coral reef flat was found to release ~1000 times less DMS than the *Acropora* corals when compared by weight. Megatonnes of DMS are released from the oceans to the atmosphere annually, where it is oxidised to contribute to new nanoparticles that can lead to cloud condensation nuclei (CCN). These affect cloud microphysical properties and consequently the Earth’s radiation budget and climate. The results suggest emissions of DMS from coral reefs are significant and may affect regional climate. Notably strong DMS plumes of up to 13 nmol m$^{-3}$ of air were detected above the coral reef flat during low tide when it was exposed at the end of the day under calm conditions. A seasonal comparison of atmospheric DMS concentrations determined at Heron Island with a temperate marine location showed the reef to be a greater source of DMS.

**Key words:** DMS, DMSP, Coral, Climate, Aerosol.

**Introduction**

DMS is the most abundant biogenic sulfur compound released from the oceans to the atmosphere (Andreae and Raemdonck, 1983) with recent global estimates at 28 Tg annually (Lana et al., 2011). The atmospheric lifetime of DMS is short (~1 day) because it is rapidly removed, mainly by hydroxyl radical, to form a variety of oxidized aerosol particles which affect solar radiation in the marine boundary layer (MBL) (Berresheim et al., 1990). Of particular importance is the oxidation product H$_2$SO$_4$ which can lead to the formation of new nanoparticles that may collectively affect the Earth’s radiation budget (Vallina and Simó, 2007). It is thought that a major source of CCN over the oceans is derived from DMS, and a link between phytoplankton, DMS and cloud albedo (reflectiveness) has been proposed (Charlson et al., 1987) which regulates temperature and climate.

Total aerosol particle concentrations over the Great Barrier Reef (GBR) were reported 34 years ago (Bigg and Turvey, 1978) to be on average 7 times higher than in typical maritime air. However, it was not until recently that Modini et al. (2009) reported what is believed to the first direct observation of particle formation over the GBR, and concluded this to be potentially climatically significant. Reports of high levels of DMS in and around coral reefs of the GBR (Broadbent and Jones, 2004; Jones et al., 2007) have led to the belief that emissions of DMS from coral reefs are locally significant and could affect cloud-cover and the amount of incident solar radiation that a reef receives (Fischer and Jones 2012). This is supported by recent research that suggests an ocean thermostat involving sea surface temperature (SST) and cloud cover operates in the Western Pacific Warm Pool to the north of Australia, where coral reefs in this region may influence cloud cover keeping sea surface temperatures below 30°C, limiting coral bleaching events (Kleypas et al., 2008).

It has been shown that coral reefs are a source of DMS that is subsequently transferred to the atmosphere, and then oxidised to aerosol precursors of CCN such as non-sea-salt-sulfate, potentially forming cloud over reefs (Modini et al., 2009, Fischer and Jones, 2012). However, it has also been reported that corals may shut down DMS production when stressed by elevated SST and light levels, thus possibly reducing DMS derived aerosols and cloud cover in the marine boundary layer, increasing solar radiation levels over reefs and exacerbating coral bleaching (Fischer and Jones, 2012). The cause of this shut down in DMS emission could be linked to the use of these sulfur substances as antioxidants within stressed corals (Jones et al., 2007).
In marine ecosystems DMS and DMSP may also provide a mechanism to assist the flow of nutrients and energy via an infochemical role. It has been demonstrated that organisms as small as copepods will react to plumes of DMS injected into their surroundings (Steinke et al., 2006) and that DMS and DMSP increase the foraging success of zooplankton predators to find and capture prey (Seymour et al., 2010). Planktivorous reef fish will aggregate to DMSP experimentally deployed at biogenic concentrations (10^{-7} M) along a fringing coral reef (De Bose et al., 2008), while herbivorous reef fish can be agents of DMSP decomposition and DMS distribution (Dacey et al., 1994). Apex predators such as procellariform seabirds can detect localised elevation in atmospheric DMS as an ocean surface foraging cue (Nevitt, 2011). DMS and DMSP thus appear to assist the process of predation, which is a dominant driving force on coral reefs required for the rapid and efficient recycling of nutrients and energy through these unique ecosystems (Hoegh-Guldberg and Dove, 2008). The abilities of reef fish to detect infochemical cues could however be affected by increased ocean acidification, which will apparently impair their olfactory discrimination and disrupt the predatory process (Dixon et al., 2010). This could greatly impact the biodiversity of coral reefs, and possibly lead to adverse climatic implications by affecting emissions of DMS to the atmosphere. The atmospheric and trophic processes outlined indicate that biogeochemical cycling, ecosystem health and climate are not mutually exclusive (Nevitt, 2011).

Material and Methods
This study was conducted at the Heron Island Research Station (23°26’34”S, 151°54’48”E) in the Capricornia Cays on the southern end of the GBR during May/June 2011. It formed part of the first Coral Reef Aerosol Characterisation Experiment (CORACE-1) with the aim to better characterize reef aerosol emissions and gauge their importance to regional climate (Deschaseaux et al., 2012, this issue).

Sampling and Analysis of Atmospheric DMS
Atmospheric DMS (DMS_a) was sampled through a 12.5 mm diameter tube using a low flow vacuum pump (~330 mL min^{-1}). The sample intake was above roof height at ~15 m ASL in a direct line of sight to the ocean. Each air sample was drawn through a high-capacity oxidant scrubbing filter and then through a Pyrex tube containing gold-coated glass wool, according to a previously reported procedure (Kittler et al., 1992). The air volumes sampled were measured using a high-precision gas meter (Toyo ML2500, Japan). These gold-wool chemisorption traps were sealed and stored for later analysis at SCU using the valving and cryotrap configuration shown in Fig. 1. DMS was released from the gold-wool by thermal desorption at 350°C for 25 mins and sent to a cryotrap prior to analysis with a Varian CP3800 gas chromatograph equipped with a pulsed flame photometric detector (GC/PFPD). An internal standard of methylethylsulfide (MES) was added to each sample, via a certified permeation tube, and calibration was achieved using a certified DMS permeation tube (Dynacal, Vici Metronics, USA). Further details of this analysis procedure are described elsewhere (Swan and Ivey, 1994).

It has been shown that S-gases can be quantitatively adsorbed onto and thermally desorbed from metal surfaces such as Pd, Pt and Au (Kagel and Farwell, 1986), and this chemisorption technique using Au is a convenient means for the sampling of atmospheric DMS (Kittler et al., 1992). The recovery of DMS from the gold-wool traps has previously been found to be 97.0 ± 2.8 % (n = 49) provided their breakthrough volume of ~120 L of air is not exceeded (Swan and Ivey, 1994).

Sampling and Analysis of DMS from Coral Nubbins and Sediment
Small nubbin tips (~0.5-1 g) were removed from healthy colonies of Acropora valida and Acropora pulchra (clade C2). Without delay, each nubbin was placed on paper to drain, weighed, and then transferred into a 20 mL capacity headspace (HS) vial containing 5 mL of 20% sodium sulfate acidified with 0.1% HCl, then crimp capped. Other samples were prepared in HS vials containing 5 mL of 20% sodium sulfate with the addition of one pellet of NaOH (~0.2 g = ~1M) to each vial. The samples treated with HCl were used to measure free DMS, while those treated with NaOH gave a measure of
total DMS (i.e., free DMS and DMSP-derived DMS via alkaline hydrolysis). Total DMSP (DMSP$_{\text{t}}$) was obtained from the difference of the NaOH and HCl treated samples. The surface areas of the nubbins were determined by hot wax displacement (Chancerelle, 2000) after analysis for DMS. Sediment, largely comprised of granular coral fragments, was also collected from below the live coral colonies. Approximately 5 g of this wet sediment was weighed into HS vials and prepared as described for nubbins.

These samples were analysed at the National Measurement Institute (NMI), Sydney, using static headspace gas chromatography with a mass spectral detector (HS/GC/MS). This equipment (Agilent G1888HS, 6890GC, 5973MSD) was operated in scan mode (range m/z 25-150) using multiple headspace extraction (Kolb and Ettre, 2006). DMS was confirmed by its characteristic 70 eV mass spectrum at the expected GC retention time, and it was quantified by the sum of the responses from extracted ions m/z 62, 63, 64. A DMSP.HCl reference material (170.7 g mol$^{-1}$) of 90.3 ± 1.8% purity was prepared at the NMI from the reaction of excess DMS with acrylic acid in dry toluene followed by the addition of ethereal HCl to precipitate the product (Howard and Chancerelle, 2000) after analysis for DMS.

The chemical reaction that generates DMS is:

$$\text{DMSP.HCl + NaOH} \rightarrow \text{DMS} + \text{A} + \text{H}_2\text{O} + \text{NaCl},$$

where A is acrylate.

Results

Free DMS and total DMS released from coral nubbins was 9.6 ± 2.5 and 17.4 ± 3.8 µmol g$^{-1}$, respectively (n = 7). When related to coral surface area these concentrations are 1.5 ± 0.5 and 3.6 ± 1.7 µmol cm$^{-2}$, respectively. The increased relative standard deviation for these figures reflects the difficulty of determining the surface areas of small nubbins. *A. valida* and *A. pulchra* contained similar concentrations of DMS. Free DMS and total DMS measured in the sediment was 9.0 and 19.5 nmol g$^{-1}$, respectively.

The concentrations of DMS$_{\text{t}}$ from gold-wool samples taken between 30th May – 8th June 2011 were found to range from none detected to 13.1 nmol m$^{-3}$ (mean 2.3 nmol m$^{-3}$, n = 43, Fig. 2). The maximum DMS$_{\text{t}}$ was detected on the 6th of June around sunset under still conditions. This sample of 67.9 L of air was collected on a rising tide just after a low tide of 0.6 m when the coral reef platform was exposed. Another high DMS$_{\text{t}}$ of 12.8 nmol m$^{-3}$ was detected on the 3rd of June from a 47.0 L air sample, under similar calm conditions around sunset after a low tide of 0.4 m. The air temperature was 23°C when both these samples were collected.

Discussion

**DMS and DMSP production from Coral Reefs**

The analysis of small coral nubbins by static HS/GC/MS is a non-disruptive means to measure *in-situ* DMS in coral biomass. The procedures allowed determination of free DMS and DMSP, from the zooxanthellae and host cells. This study was used to assess methodology and gauge the level of DMS present in coral for further analysis by isotope dilution with deuterated internal standards (Smith et al., 1999). The results indicated that free DMS is a significant fraction of the potential DMS present in coral biomass in the form of DMSP, and may be generated enzymatically from the DMSP precursor as part of the symbiotic process. Coralline DMS appears to originate from the zooxanthellae symbionts rather than the invertebrate host (van Alstyne et al., 2008) where it may accumulate before release to the water column. The concentrations of free DMS and total DMS released from coral nubbins were approximately 10$^3$ times higher than in the sediment, which indicates that actively growing coral biomass is a far richer source of DMS than the benthos in the sediment.

On a cellular basis, *Symbiodinium* sp are a very rich source of DMS to coral reef ecosystems. By applying a winter mean *Acropora* sp zooxanthellae density of 3 x 10$^6$ cells cm$^{-2}$ (Moothien-Pillay et al., 2005) and a *Symbiodinium* (Clade C) cell diameter of 8.5 µm (spherical cell volume of 322 fL), the mean free DMS and DMSP, measured in this study is 0.5 and 0.7 pmol cell$^{-1}$, respectively. This equates to 1675 and 2299 mmol L$^{-1}$ (cell volume), respectively. These concentrations are within the broad range of 36 to 7590 mmol L$^{-1}$ (cell volume) reported by Broadbent et al (2002). It has been found that the concentrations of DMS and DMSP, and the production of DMS are strain-specific in cultures of *Symbiodinium* sp (Steinke et al., 2011), which provides one reason for the broad range of observed cellular concentrations.
Mucus exuded from *Acropora formosa* has been reported to contain 25.4 µM DMS, while mucus ropes contained 18.7 µM DMS and 54.4 µM DMSP (Broadbent and Jones, 2004). This data, along with measurements of coral nubbins from this study, are some of the highest concentrations of DMS and DMSP measured in any natural marine system. Coral reefs are therefore marine ‘power-houses’ for DMS and DMSP production, which are important components of the biogeochemical cycling of sulfur and carbon within these ecosystems.

**Atmospheric DMS: Comparisons and Patterns**

Significant emission of DMS to the atmosphere from coral reefs is expected to occur based on the concentrations of DMS released from the coral nubbins examined in this study. The two highest DMS concentrations at Heron Island of 12.8 and 13.1 nmol m\(^{-3}\) measured at the start of winter are similar to maximum summer DMS (13-14 nmol m\(^{-3}\)) at the temperate location of Cape Grim in NW Tasmania (40°41’S, 144°41’E) during 1991 and 1992 using this technique (Gillett *et al.*, 1993; Swan and Ivey, 1994). At Cape Grim, maximum DMS is associated with seasonal summer phytoplankton blooms, while DMS typically does not exceed 1 nmol m\(^{-3}\) during the dormant austral winter. At One Tree Reef (23°30’S, 152°06’E) DMS was found to range from 0.12 to a summer maximum of 23 nmol m\(^{-3}\) (mean 6.5 nmol m\(^{-3}\)) in a seasonal study reported by Broadbent and Jones (2006). These seasonal and latitudinal comparisons indicate that more DMS originates from coral reefs than other temperate marine ecosystems.

It has been noted that DMS over coral reefs in the northern GBR, and the wider Coral, Solomon and Bismarck Seas to the northeast of Australia often increased after low tide which exposed the reefs to the atmosphere (Jones and Trevena, 2005). The tendency for elevated DMS at low tide or on the rising tide after low water was also observed from the coral reef flat at Heron Island (Fig. 2), which indicates that it is a point source for the emission of DMS. When the reef flat is exposed direct release of DMS to the atmosphere can occur and there is no need for wind to act as a sea-to-air transfer mechanism (Liss and Merlivat, 1986). A rising tide over the surface of the reef could also provide sufficient agitation to release DMS to the air without the need for wind to break the surface water film barrier. Consequently maximum DMS is expected to occur around low tide during still conditions when mixing and dilution of the coral reef point source emission with maritime air is least.

The observation of enhanced biogenic emissions associated with low tides is however not peculiar to coral reefs. It has been reported that an algal field on the Atlantic coast of Western Brittany (France) when uncovered at low tide was a notably more active source of DMS than when covered at high tide (Luce *et al.*, 1993). At the Mace Head Atmospheric Research Station in western Ireland, elevated emissions of organo-iodine compounds from brown kelp have been found to coincide with low tides when the kelp is exposed (Carpenter *et al.*, 2001). Like DMS, these halogenated organic emissions from kelp can lead to the formation of climatically relevant aerosol via photochemically produced oxidation products such as iodine monoxide (O’Dowd and Hoffman, 2005).

Factors such as surface seawater DMS concentrations, wind speed and direction, solar radiation intensity, atmospheric oxidant levels, conditions in the MBL, tides and SST all influence the observed DMS concentrations and thus its variability. Increased wind speed enhances emission of dissolved DMS to the atmosphere via wave and bubble-mediated action (Wanninkhof, 1992); air that has travelled over the oceans and particularly coral reefs will contain more DMS than air that has a back trajectory from the continent; high actinic flux leads to increased production of hydroxyl radical from O\(_3\) photolysis and thus daytime destruction of DMS (Ayers *et al.*, 1995); the DMS sea-to-air transfer velocity is dependent on SST (Yang *et al.*, 2011). Fig. 2 shows the high variability of DMS which may occur, where tide height is just one of many physical processes that can influence observed concentrations. The processes controlling short-term fluctuations in DMS cannot be completely assessed using gold-wool chemisorption because it is a low frequency sampling technique. Therefore, as part of future CORACE studies, high time-resolved on-line DMS sampling coupled with continuous light, wind, DMS in seawater and tidal monitoring is planned to further understand the processes that control short-term variability in DMS. These measurements will also allow the sea-to-air flux of DMS from the Heron Island coral reef to be determined.

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