The Flux and Emission of Dimethylsulfide From the Great Barrier Reef Region and Potential Influence on the Climate of NE Australia

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Abstract
Concentrations of dimethylsulfoniopropionate (DMSP), dimethylsulfide (DMS), and DMS flux are reported for the Great Barrier Reef (GBR), Great Barrier Reef Lagoon (GBRL), and Coral Sea. Generally higher concentrations of dimethylsulfoniopropionate and DMS occurred in coral reef waters, compared with GBRL concentrations. DMS flux from GBR coral reefs in summer ranged from nondetectable to 153 μmol m⁻² d⁻¹ (mean 6.4), while winter fluxes ranged from 0.02 to 15 μmol m⁻² d⁻¹ (mean 2.4). No significant seasonal difference in DMS flux occurred for the GBRL. High DMSw concentrations and DMS fluxes periodically occur at coral reefs during very low tides and elevated sea surface temperatures (SSTs). For the GBR and GBRL coral reefs there was a significant correlation between seawater DMSw concentrations and SST (p < 0.001), up to temperatures of 30 °C. During coral bleaching DMS flux from reefs almost completely shuts down when SSTs are >30 °C. The GBRL and associated coral reefs emit 439 and 32 MmolS per year, respectively. Cyclones on average produce 170 MmolS to the GBR atmosphere in summer. This amount can markedly increase during severe cyclones such as severe tropical Cyclone Debbie in March 2017. Overall, the annual DMS emission estimate from the GBRL and coral reefs in the GBR is 0.64 GmolS, with cyclones contributing 27% or greater of the annual emission estimate, depending on the cyclone intensity. Oxidation of atmospheric DMS can potentially affect solar radiation, SSTs, low-level cloud cover, and rainfall causing cooling and warming of the climate in the GBR region as recent modelling predicts.

Plain Language Summary
This study reports the first detailed measurements of the flux and emission of dimethylsulfide (DMS, a trace sulfur gas thought to be involved in climate regulation), from the Great Barrier Reef Lagoon, Coral Sea, and coral reefs that form the Great Barrier Reef (GBR). Concentrations of DMS and its main precursor dimethylsulfoniopropionate are greatest at fringing and microatoll reefs, followed by midshelf and barrier reefs on the continental shelf. Seawater DMS and DMS flux are significantly correlated with SST up to temperatures of 30 °C, when production of DMS markedly decreases during coral bleaching. Very low tides increase seawater DMS and dimethylsulfoniopropionate concentrations and can significantly increase the flux of DMS to the atmosphere. There is now increasing evidence that coral reef production of DMS to the atmosphere of the GBR and its effect on the aerosol optical depth could have a significant effect on the climate of NE Australia.

1. Introduction
Benthic coral reefs produce appreciable quantities of dimethylsulfide (DMS), a trace sulfur gas that is thought to be involved in climate regulation of sea surface temperatures (SSTs) of coral reefs (Cropp et al., 2018; Fischer & Jones, 2012; Jones, 2015; Jones et al., 2017; Leahy et al., 2013). This potential coral reef-climate feedback is similar to the well-known global ocean-climate feedback that involves production of DMS from pelagic phytoplankton, oxidation in the atmosphere to sulfate aerosols, formation of cloud condensation nuclei (CCN), and low level clouds, which in turn lower solar radiation and SSTs, thereby keeping ocean temperatures stable (Charlson et al., 1987). High concentrations of the DMS precursor substance dimethylsulfoniopropionate (DMSP) have been measured in corals from the Great Barrier Reef (GBR,
Broadbent et al., 2002; Deschaseaux et al., 2014; Jones et al., 1994; Raina et al., 2013; Swan et al., 2016; Tapiolas et al., 2013). As the GBR consists of 3,200 coral reefs (Zann, 1996, 2000; Figure 1) this unique coral reef ecosystem contains a vast store of DMSP capable of emitting great quantities of DMS to the atmosphere (Jones et al., 2007; Swan et al., 2017).

Experiments with coral nubbins (small fragments of corals) have shown that hard corals such as Acropora spp. (a dominant coral in the Indo-Pacific) produce substantial amounts of seawater and atmospheric DMS (Deschaseaux et al., 2014; Fischer & Jones, 2012; Hopkins et al., 2016; Jones, 2015), as well as producing other volatile organic compounds (VOCs) such as isoprene and other sulfur compounds (Swan et al., 2016). Atmospheric DMS (DMS\textsubscript{a}) produced from coral reefs in the GBR can rapidly oxidize to climatically active sulfate aerosol particles (Bigg & Turvey, 1978; Modini et al., 2009; Swan et al., 2016) that could significantly affect the radiative climate of NE Australia (Fischer & Jones, 2012). Indeed DMS\textsubscript{a} can be oxidized to non–sea-salt sulfate (i.e., (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and (NH\textsubscript{4})HSO\textsubscript{4}) forming aerosol particles that reach concentrations as high as 3,200 to 40,000 particles/cm\textsuperscript{2} over the GBR (Leck & Bigg, 2008; Modini et al., 2009), with an emission estimate from the whole length of the GBR as high as 10\textsuperscript{19} aerosol particles/s, equivalent to emissions from forest fires (Bigg & Turvey, 1978). These non–sea-salt sulfate aerosol particles contribute to high concentrations of condensation nuclei (CN) over the GBR (Bigg & Turvey, 1978), which can then form CCN (Leck & Bigg, 2008), precursors of low level clouds (i.e., cumulus and stratocumulus), regulating SSTs and affecting solar radiation and the climate over the GBR (Cropp et al., 2018; Fischer & Jones, 2012; Jones, 2015; Jones et al., 2017; Leahy et al., 2013).

Periodic pulses of high concentrations of DMS\textsubscript{a} often occur over coral reefs in the GBR during very low tides and low wind speeds (Jones et al., 2007; Jones & Trevena, 2005; Swan et al., 2017). Studies by Hopkins et al. (2016) have shown that when the hard coral Acropora cf. horrida is exposed to air (simulating low tides) the coral-to-air emission (flux) of DMS\textsubscript{a} was 3–11 mmol-m\textsuperscript{2}-d\textsuperscript{-1}, suggesting short-term pulses of DMS\textsubscript{a} can be released from the coral. Upon resubmersion, an additional rapid rise in DMS\textsubscript{a} was observed, reflecting

Figure 1. Cruise track of the CSIRO RV Investigator during voyage 5 in October 2016. Intensive ocean and atmospheric studies were carried out at Heron Island reef, at station 1 (Hydrographers Passage), station 2 (Coral Sea), and station 3 (near PBR, Orpheus Island, and Kelso Reef). Land-based atmospheric measurements were also made at Mission Beach, in the northern GBR. CSIRO = Commonwealth Scientific and Industrial Research Organisation; GBR = Great Barrier Reef; PBR = Pioneer Bay Reef.
increased production by the coral and/or dissolution of DMS-rich mucus formed by the coral during air exposure (Broadbent & Jones, 2004). Swan et al. (2017) have reported that these spikes (pulses) of DMS\textsubscript{a} from coral reefs can last as long as eight and a half hours.

Natural stress events such as low tides, high SSTs, and high rainfall can cause the coral to up-regulate intracellular DMSP and DMS to cope with the resultant osmotic, solar radiation, and temperature stresses (Deschaseaux et al., 2014; Jones et al., 2014; Jones & King, 2015) and in the process produce enhanced concentrations of seawater and atmospheric DMS (Broadbent & Jones, 2004; Deschaseaux et al., 2014; Hopkins et al., 2016; Jones et al., 2007; Swan et al., 2017). These periodic pulses of DMS\textsubscript{a} at low tides (Swan et al., 2017) may be capable of increasing aerosol optical depth (AOD) and low level cloud cover over coral reefs in the GBR, keeping SSTs $\textless$30 °C (Jackson et al., 2018; Jones et al., 2017), thus decreasing the incidence of coral bleaching and significantly affecting regional climate of coral reefs in the western and central Pacific Ocean (Cropp et al., 2018; Fischer & Jones, 2012; Jones et al., 2017; Kleypas et al., 2008; Leahy et al., 2013; Mumby et al., 2011). However, the increased frequency of coral bleaching in the GBR in the last two decades (Berkelmans et al., 2004; Berkelmans & Oliver, 1999; Berkelmans & van Oppen, 2006; Hoegh-Guldberg, 1999; Oliver, 1985) and the back to back mass coral bleaching events in 2016 and 2017, where the top third of the GBR bleached (Hughes et al., 2018), could suggest that the strength of this feedback is decreasing and the GBR has reached a tipping point (Jackson et al., 2018). While the effect of mass coral bleaching on coral cover in the GBR is controversial (Osborne et al., 2011), increased aerosol production from coral reefs in summer could cause significant aerosol-cloud radiative effects that increase SSTs above the coral bleaching threshold of 30 °C (Jones et al., 2017). Rather than GHGs being the main driver of coral bleaching the increased frequency of these mass coral bleaching events could also be a function of reef produced aerosol-radiative effects. It is vital that further research is undertaken on this potential coral-derived climate feedback as recent research suggests that both cooling and warming in the GBR could occur from the variable emissions of DMS\textsubscript{a} from the actual coral reefs, with warming (i.e., SSTs $\textgreater$30 °C) a result of increased downwelling of solar radiation and marked decreases in AOD in summer over the GBR (Fischer & Jones, 2012; Jackson et al., 2018), enhancing coral bleaching (Jones et al., 2017; MacKellar et al., 2013).

We report here the first DMS\textsubscript{w} concentrations and flux estimates for the Coral Sea and Great Barrier Reef Lagoon (GBRL) during voyage 5 of the Commonwealth Scientific and Industrial Research Organisation’s (CSIRO) new research ship RV Investigator from 30 September to 23 October 2016. This voyage was an initiative to obtain natural background information on the atmosphere over the GBR. The large international field project entitled The Great Barrier Reef as a significant source of climatically relevant aerosol particles and known as the Reef-to-Rainforest (R2R) campaign was led by Professor Zoran Ristovski (Chief Scientist) of the Queensland University of Technology and nine other chief investigators (Ristovski et al., 2017). The overall scientific objective of this project is to gain an improved understanding of the natural processes that regulate CCN, cloud cover, solar radiation, and SSTs over the GBR. Four key questions to be addressed by this study are the following: (1) Does marine aerosol along the north Queensland coast have a significant signature that is coral derived?; (2) How does this aerosol change its physicochemical properties, especially its capacity to act as CCN, as winds carry it from the reefs to the north Queensland rainforests?; (3) What is the significance of this ecosystem as a source of aerosol particles, and will potential degradation of the reef cause significant variations in particle number being generated over the reef?; (4) Should changes in this aerosol, associated with reef degradation, be taken into account when modeling the radiative climate and rainfall? This was the first comprehensive measurement campaign of the atmospheric composition over the GBR ever undertaken. Ship-based measurements aboard the CSIRO ship RV Investigator were made inside and outside the GBR between Heron Island and Cairns (Figure 1). Two of the sampling sites at sea were inside the reef and upwind of a land-based sampling station at Garners Beach (17.82°S, 146.10°E) near Mission Beach (Figure 1) on the far north Queensland coast. In this communication we compare DMS\textsubscript{w} and DMSP concentrations and DMS flux estimates made on the Investigator voyage with those made on the CSIRO RV Franklin in 1992 (GBRL) and 1995 (GBRL, Coral Sea, Gulf of Papua, Bismarck Sea, and Solomon Sea). In addition, these DMS\textsubscript{w} concentrations and DMS flux estimates are compared with measurements made previously at five coral reefs in the GBR, since no measurements were made at coral reefs in October 2016 from RV Investigator. These coral reef DMS flux estimates are also compared with recent flux estimates made at Heron Island coral cay using atmospheric DMS concentrations (Swan et al., 2017). Seasonal, tidal, and SST effects on DMS\textsubscript{w} and DMS flux were also investigated, as well as assessing the influence of cyclone activity on DMS flux to the atmosphere over
the GBR. Finally, a DMS emission estimate has been calculated for the GBRL and the 3,200 coral reefs that make up the GBR, and assessments made of potential cooling and warming effects from DMS aerosols released from the coral reefs, and the potential effect on the climate of NE Australia.

1.1. Region of Study

The Great Barrier Reef (GBR) extends over 14.8° of latitude between the NE Torres Strait (9°30′S) and Lady Elliot Island (24°20′S), in the southern GBR (Figure 1). The GBR is 2,300 km in length and 347,000 km² in area (Furnas & Mitchell, 1996, 1997; Zann, 1996, 2000). The continental shelf of this GBR World Heritage Area contains approximately 3,200 identified coral reefs and 918 islands (Furnas et al., 2005). Overall, reefs occupy ~9% of the total continental shelf area (224,000 km²) within the GBR World Heritage Area (i.e., ~20,000 km²) (Hopley et al., 1989). The GBR region may therefore be considered a shallow coastal sea, bounded by and encompassing to varying degrees a porous matrix of coral reefs (Furnas & Mitchell, 1997). Between the reef matrix and the coastline (Figure 1) lies a contiguous N-S body of open water commonly referred to as the GBR Lagoon or GBRL (Pickard et al., 1977). Reef area as a proportion of shelf area is highest in the far northern GBR (36.7%) between 12°S and 13°S, where the continental shelf is also narrowest (22 km at 14°S) and lowest (1.1%) in the southern GBR (22–23°S) where the outermost reefs lie >250 km offshore. The reef matrix, to varying degrees, isolates the GBRL from the adjacent Coral Sea. However, the Australian Current pumps cold, saline, nutrient-rich water up the slope to the shelf break (Andrews, 1983; Andrews & Gentian, 1982). These intrusions tend to be confined near the bottom, and phytoplankton development quickly takes place inshore of the shelf break.

2. Methods

2.1. Investigator Studies

During October 2016 regular surface seawater samples (0–5 m) were taken from the GBRL and the Coral Sea using the CSIRO research vessel RV *Investigator* (Figure 1). Initially, surface seawater samples were taken close to 08.00, 12.00, 16.00, and 22:00 hr every day from 29 September to 14 October. Thereafter, hourly surface samples were analyzed at stations 1 (near Slasher Reefs, NE of Townsville) and 3 (close to Penrith Island reefs) in Hydrographers Passage, opposite Mackay (Figure 1). These samples were processed for seawater DMS$_w$ and total DMSP (DMSP$_t$).

2.2. Seawater Sampling and Analysis

Seawater samples from the Coral Sea and GBRL were collected from *Investigator*’s underway system (0- to 5-m depth) with seawater pumped to the wet chemistry laboratory. Seawater DMS$_w$ was determined by purge and trap gas chromatography using a Shimadzu gas chromatograph (GC-2010) coupled with a flame photometric detector. In the *Investigator* study this detection system was used up to the 14 October, when the GC was needed for more intensive Conductivity-Temperature-Depth (CTD) studies. DMS$_w$ was then determined by an Equilibrator Inlet-Proton Transfer Reaction Mass Spectrometry system (Kameyama et al., 2009; Omori et al., 2013, 2017). An intercalibration of the two techniques for DMS$_w$ on *Investigator* gave excellent agreement ($r^2 = 0.999, p < 0.001$).

For total DMSP (= DMSP$_t$) concentrations seawater (100 mL) was collected in an amber glass bottle, and the seawater acidified to pH < 2 using 10% hydrochloric acid. Storage tests have shown that DMSP$_t$ concentrations do not change over 6 months when samples are acidified to pH < 2 (Curran et al., 1998). DMSP$_t$ analysis was by GC-mass spectrometry with a GC-mass selective detector (MSD) operated in Single Ion Monitoring (SIM) mode as described in Deschaseaux et al. (2018).

2.3. DMS Flux

One of the most widely used methods for calculating DMS flux across the air-sea interface is described by the following relationship:

\[ F = K(T) \Delta C \]  

where $F$ is the flux of gas; $K(T)$ is the overall gas transfer velocity; $\Delta C = (C_a H^{-1}) - C_w$ is the air-water gas concentration difference; $C_a$ is the concentration of gas in air; $C_w$ is the concentration of gas in water; and $H$ is the Henry’s law constant of gas, when ($C_a$ and $C_w$) are at equilibrium (Liss et al., 1993; Liss & Slater, 1974). The
atmospheric concentration of DMS is several orders of magnitude lower than the concentration in the water phase \( (C_w) \) and is usually ignored for flux calculations (Andreae, 1990). Equation (1) simplifies to

\[
F = K_w C_w
\]

The gas transfer velocity \( (K_w) \), for a Schmidt number of 600, was calculated based on the wind speed \( (u) \) using three equations put forward by Liss and Merlivat (1986) that describe the transfer velocity as a function of wind speed. The Schmidt number for DMS was then calculated, based on the SST \( (T) \) using equation 1.4 from Saltzman et al. (1993). An adjustment factor \( (r) \) was then used to correct the transfer velocity for a Schmidt number \( (Sc) \) deviating from 600.

\[
r = 600^{2/3} Sc^{-2/3} \text{ for } u < 3.6 \text{ m/s}
\]

\[
r = 600^{5/2} Sc^{-1/2} \text{ for } u > 3.6 \text{ m/s}
\]

The calculated flux, with an uncertainty factor of 2 (Andreae, 1990; Bates et al., 1987; Erickson et al., 1990) was then calculated using the following formula.

\[
F = 0.24 r K_w C_w
\]

Table 1: DMS Flux Estimates \( (\mu mol \cdot m^{-2} \cdot d^{-1}) \) From PBR (Orpheus Island) in the Central GBR, Using Various Wind Speed Data Sets

<table>
<thead>
<tr>
<th>Season</th>
<th>nDMS(_w) ( (nM) )</th>
<th>Est wind ( (m/s) )</th>
<th>nBoM</th>
<th>mdBoM</th>
<th>mmBoM</th>
<th>mm 53y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>30</td>
<td>5.6</td>
<td>7.8</td>
<td>5.1</td>
<td>6.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Winter</td>
<td>41</td>
<td>0.7</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Note: DMS = dimethylsulfide; BoM = Bureau of Meteorology; PBR = Pioneer Bay Reef; GBR = Great Barrier Reef.

As wind speed is such an important driver of air-sea flux we estimated DMS flux from PBR (Orpheus Island) using various wind speed data sets such as estimated wind speed at site \( (Est \text{ wind}) \), nearest Bureau of Meteorology \( \text{BoM} \) wind speed to time of collection \( (nBoM) \), mean daily BoM wind speed \( (mdBoM) \), mean monthly wind speed \( (mmBoM) \), and mean monthly wind speed from the National Oceanic and Atmospheric Administration archives \( (mm 53y) \). As we can see from Table 1, DMS flux estimated in summer from wind speed made at the time of collection \( (our \text{ treatment}) \) is very close to the DMS flux estimated when using the mean monthly 53y mean wind speed from the National Oceanic and Atmospheric Administration archives, while other treatments are underestimated in summer. There is a slight overestimate for winter flux estimates, but the fluxes only range from 0.2 to 1.0 \( \mu mol \cdot m^{-2} \cdot d^{-1} \) as reefs do not produce much DMS when SSTs are much lower in winter. As flux estimates are accurate to ±50% we believe our calculations of flux are reasonably accurate. This paper gives a first estimate of DMS flux from the GBRL and associated coral reefs, and as such we hope that further research from others will improve the flux estimate for the GBR region.

2.4. Previous DMS\(_w\) Measurements in the GBRL

Seawater DMS measurements have been made in the northern and southern GBRL on two previous voyages of the CSIRO RV Franklin in September/October 1992 \( (19-25°S) \) and July 1997 \( (13°55'-10°52'S) \) and have been reported previously (Jones et al., 1994; Jones & Trevena, 2005). DMS flux estimates have now been calculated for these voyages using the Liss et al. (1993) method and are now reported here for comparison with the Investigator DMS fluxes. Underway wind speed and SST measurements were made by CSIRO staff throughout all three voyages.
2.5. Previous Measurements at GBR Coral Reefs

Concentrations of DMS\textsubscript{w}, SSTs, and wind speed measurements were made at the following coral reefs, which were then used to calculate DMS flux using equation (5) above.

2.5.1. Pioneer Bay Reef

A major seasonal study of seawater DMS\textsubscript{w} and DMSP\textsubscript{t} was conducted at Pioneer Bay Reef (PBR) over 19 months from 7 December 1992 to 19 July 1994. PBR at Orpheus Island (18°35' S – 146°29' E) is an inshore fringing reef ~70 km NE of Townsville (Figure 1). Sample collections, analysis, and concentrations of DMS\textsubscript{w}, DMSP\textsubscript{t}, and SST have already been reported (Curran, 1996; Jones et al., 2007). Wind speed was obtained from the BoM (Curran, 1996) and DMS flux calculated (see above).

2.5.2. Nelly Bay Reef and Geoffrey Bay Reef

The most extensive and accessible fringing coral reefs around Magnetic Island (19°0.9' S, 146°50' E) are those of Nelly Bay Reef (NBR) and Geoffrey Bay Reef (GeofBR). NBR is a fringing reef (19°10.5' S, 146°51' E) 7 km offshore from Townsville (Figure 1) and 43 ha in size. Seawater samples from NBR were collected at 0.5-m depth from 6 November 1993 to 2 May 1994 and processed for DMS\textsubscript{w}, DMSP\textsubscript{t}, and SST. Wind speed was obtained from the BoM (Curran, 1996).

Daily SST measurements were made by Australian Institute of Marine Science (AIMS) at GeofBR at 18°92', 147°S from 1993 to 1994, close to NBR (Jones, 1995; Jones et al., 2017, 1997). These SST measurements were used to calculate DMS\textsubscript{w} at GeofBR using a statistically significant correlation between DMS\textsubscript{w} and SST (Jones et al., 2017), and equation (5) to determine DMS flux.

2.5.3. Kelso Reef

Kelso Reef (KR) is a midshelf patch reef located in the central section of the GBR (18°28, 147°S, Figure 1) and is largely protected from the prevailing SE swells and wave action by adjacent reefs (Broadbent, 1997; Jones & Broadbent, 1996). The windward margin is well defined, dropping rapidly to a depth of 40 m, with a reef flat of about 150-m width. The shallow (5–27 m) lagoon is only semi-enclosed, with a diffuse matrix composed of patch reefs ranging from 5 to 100 m in diameter. The lagoon floor is composed of fine carbonate sediment. Like most of the midshelf reefs at this latitude, large macroalgae are rare on KR. Surface seawater samples (~ 0.5 m) were collected from January–May 1994 to July 1995–December 1996 and analyzed for seawater DMS\textsubscript{w} with DMS flux reported here.

2.5.4. One Tree Reef

One Tree Reef (OTR) is located in the Capricorn-Bunker group at the southern end of the GBR (23°30', 152°06' E) near Heron Island (Figure 1). The reef structure is typical of this area, built on a Pleistocene platform and with geomorphology determined by the consistent prevailing SE winds and swell and a large tidal range (Kinsey & Davies, 1979). The resultant structure is a coral reef with an emergent rim and large lagoon, which is isolated (moated) from inter-reefal water at tide heights less than 2.5 m. A distinguishing feature of One Tree Island is the presence within the lagoon of small (usually <30 m) circular patch reefs, described locally as microatolls. The enclosed structure of the microatolls means that during each low tide period (usually 3–4 hr) water exchange between the microatoll and the main reef lagoon is limited, allowing for the interchange of material between the microatoll and the lagoon. The microatolls therefore represent a shallow reef site to examine a build-up of DMS\textsubscript{w} and DMSP concentrations within the microatolls (Broadbent & Jones, 2006), with potentially greater atmospheric DMS fluxes. Water samples were collected from February to March 1993 and thereafter every 3 months from October 1994 to March 1996. All samples for DMS flux measurements were collected from within the microatolls in the lagoon at OTR, and wind speed measurements were made at the University of Sydney’s marine station on OTR.

2.5.5. Heron Island Reef studies

Heron Island Research Station (23.44°S, 151.91°E) is situated 80 km off the east Australian coastline, in the Capricorn-Bunker Group of southern GBR reefs (Figure 1). Heron Island lies at the western end of a surrounding 27 km\textsuperscript{2} lagoonal platform reef. The reef lagoon has a cover of 15% coral and 85% permeable carbonate sands (Cyrnak et al., 2013). Seawater samples were collected from the wharf at Heron Island when seawater was ebbing from the reef flat (low tide) and close to high tide during November and December 2015.

2.6. Seawater Sampling and DMS\textsubscript{w} and DMSP\textsubscript{t} Analysis at the GBR Reef Sites

Surface seawater samples were collected from the fringing reef at PBR (Orpheus Island) near the marine station and at a marked buoy over NBR at Magnetic Island in the central GBR (Jones et al., 2007). KR
and OTR samples were collected from a pontoon (Broadbent & Jones, 2006). A 2- to 2.5-L amber glass silanized glass bottle was used at a depth of approximately 0.5 m to collect all samples. At KR seawater samples were collected inside the lagoon at about 100 m from the mooring pontoon (Broadbent, 1997; Jones & Broadbent, 1996). Seawater samples taken at the coral reef sites in this study were typically conducted on day trips or short (1 week) field trips. This ruled out transporting the GC to several of the field sites. Seawater samples were 0.45 μm filtered using a Sartorius filter and a peristaltic pump at a low flow rate that transferred 25 mL of sample directly into a glass purge chamber with glass frit that had been silanized.

A gold tube was attached to the outlet of the purge vessel and the sample purged of dissolved DMS for 20 min at a flow rate of 60 mL/min (Curran, 1996; Jones et al., 2007; Kittler et al., 1992). The dissolved DMS was then chemisorbed onto the gold contained in the quartz tube and analyzed for DMS using either a Varian 3700 fitted with a sulfur specific flame photometric detector (or a 3800 GC fitted with a pulsed flame photometric detector; Curran et al., 1998; Jones et al., 2007; Jones & Trevena, 2005). Comparison of samples collected using the gold tube method at the same time as immediate analysis of seawater DMS gave results of 1.4 ± 0.15 (immediate analysis) and 1.2 ± 0.3 nM (gold tube analysis, n = 30) after storage for 6 months (Curran et al., 1998). Recoveries using this method averaged 85%, with an Relative Standard Deviation (RSD) of 11%. The detection limit was typically 0.1 pmol.

Samples from Heron Island reef flat were immediately acidified to pH < 2 with HCl analyzed for total DMSPt (dissolved + particulate DMSP) using GC-mass spectrometry (Deschaseaux et al., 2018) and are reported here against tidal variation.

2.7. DMS Flux Measurements at the Reef Sites

Measurements of seawater DMS concentrations, together with wind speed, transfer velocity, and SST were used to calculate DMS flux for all reef sites using the Liss et al. (1993) wind speed parameterization method (see above).

2.8. Statistical Analysis

Statistical Package for the Social Sciences (SPSS) 11 was used for the statistical analysis of the data sets. For the seawater data statistically significant differences between treatments were tested using a Pearson’s Product Linear Correlation analysis (parametric, normally distributed) with significance determined at the 0.01 to 0.001 level.

3. Results and Discussion

3.1. DMSPt Concentrations

To enable comparison of the seasonal trends, the data were pooled into summer (October–March) and winter (April–September) periods. These seasonal definitions were chosen by examination of recent temperature records for inshore waters, with the major increase or decrease in SST being defined by these months. Mean concentrations of DMSPt in seawater, collected from the GBRL in early summer on Investigator ranged from 1 to 23 nM (mean 8 nM) (Table 2). Although these concentrations were higher than concentrations determined in GBRL waters from Franklin in 1992 for the same season (range 0.2–12 nM, mean 4.5 nM, n = 12) there is little difference in the average summer-winter comparison (Table 2). Although these concentrations were higher than concentrations determined in GBRL waters from Franklin in 1992 for the same season (range 0.2–12 nM, mean 4.5 nM, n = 12) there is little difference in the average summer-winter comparison (Table 2), although there is much lower sampling for the winter Franklin voyage (n = 3). Inshore fringing reefs generally had higher DMSPt concentrations than midshelf reefs such as KR. No seasonal difference was apparent for DMSPt concentrations in Coral Sea seawater (mean summer = 8.4 nM, n = 30; mean winter = 8 nM, n = 10), again with reservations of sampling frequency for these earlier voyages. In contrast, the overall mean DMSPt concentrations in the GBR coral reef waters indicated increased concentrations in summer, compared with winter concentrations (summer = 10.8 nM, n = 85; winter = 4.4 nM, n = 117). No significant seasonal differences occurred for the midshelf coral reef KR, which had a mean summer DMSPt concentration of 4.2 nM and a mean winter concentration of 5 nM (Table 2). Highest DMSPt concentrations occurred in summer GBR coral reefs > Coral Sea > GBRL. In the GB the highest mean DMSPt concentrations in summer (mean = 14 nM, n = 6) occurred in Palm Passage (near Kelso Reef, Figure 1), perhaps reflecting intrusions of nutrient and phytoplankton-rich Coral Sea water (Table 2). In winter DMSPt concentrations in Solomon Sea waters were closely similar to GBRL and Coral Sea waters, while GBR reef waters were the lowest in DMSPt concentrations (Table 2). The coastal
waters of the Gulf of Papua and the Bismarck Sea-Sepik River displayed a higher mean and range of winter DMSP<sub>t</sub> concentrations, compared to the Coral Sea and GBRL waters (Table 2).

### 3.2. DMS<sub>w</sub> Concentrations

Concentrations of DMS<sub>w</sub> in GBRL waters collected from Investigator in early summer 2016 ranged from 0.1 to 2.7 nM (mean 1.5 nM, n = 212), which was lower than concentrations determined from Franklin in summer 1992 (range 1.1–3.4, mean 2.2, n = 12), and much higher than DMS<sub>w</sub> concentrations determined from Franklin in winter 1997 (range 0.6–1 nM, mean = 0.8 nM, n = 4) (Table 3), although coverage in 1997 is very low. Summer-winter comparisons of DMS<sub>w</sub> in GBRL waters suggested 138% more DMS<sub>w</sub> was produced in summer compared to winter (Table 3). Much higher concentrations of DMS<sub>w</sub> occurred in seawater at most coral reefs in summer, compared with winter (Table 3). The exception was KR where there was no significant difference in mean summer and winter concentrations of DMS<sub>w</sub> at this reef. However, the small database may have masked any seasonal variation at this reef. The more sheltered reef locations where ocean mixing would be low (i.e., NBR, OTR) generally showed a much higher range of DMS<sub>w</sub> concentrations in summer than in winter (Table 3), with a distinct seasonal cycle apparent for NBR and PBR (Jones et al., 2007). In the microatolls at OTR DMS<sub>w</sub> concentrations in summer ranged from 0.4 to 25 nM (mean 5.1 nM); and for the sheltered PBR DMS<sub>w</sub> concentrations ranged from nd-54 nM (mean 3.8 nM), much higher than concentrations found in winter at these reefs (e.g., PBR and NBR, Table 3). The overall average DMS<sub>w</sub> concentrations for all five reefs (Table 3) indicated that about 82% more DMS<sub>w</sub> occurred in coral reef waters in summer (3.1 nM), than in winter (1.7 nM), and coincided with increases in SSTs in the summer monsoonal months. The average winter DMS<sub>w</sub> concentrations for all five coral reefs were closely similar to the average Coral Sea winter DMS<sub>w</sub> concentration. DMS<sub>w</sub> in Coral Sea waters in summer averaged 1.6 nM, similar to mean concentrations in Palm Passage, although a higher range of DMS<sub>w</sub> concentrations occurred in Palm Passage (Table 3). Overall, DMS<sub>w</sub> concentrations in summer in GBRL coral reefs > Gulf of Papua > Coral Sea, while in winter Bismarck Sea-Sepik River waters were > Gulf of Papua and GBR reef waters > Solomon Sea and GBRL waters (Table 3).
Table 3
Mean Summer and Winter Dissolved DMS Concentrations (nM) in Seawater From the GBRL and Coral Reefs in the GBR, Coral Sea, Gulf of Papua, Solomon Sea, and the Bismarck Sea-Sepik Estuary

<table>
<thead>
<tr>
<th>Location</th>
<th>Reef site/type</th>
<th>Summer&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Winter&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Great Barrier Reef Lagoon</td>
<td>0.1–2.7</td>
<td>1.5 (212)</td>
<td>-</td>
</tr>
<tr>
<td>RV Investigator (18.14–22.5°S)</td>
<td>-</td>
<td>-</td>
<td>0.6–1.0</td>
</tr>
<tr>
<td>RV Franklin (18°32′–14°45′S)</td>
<td>1.1–3.4</td>
<td>2.2 (12)</td>
<td>-</td>
</tr>
<tr>
<td>Average GBRL</td>
<td>0.1–3.4</td>
<td>1.9 (224)</td>
<td>0.6–1.0</td>
</tr>
<tr>
<td>Great Barrier Reef (coral reefs)</td>
<td>nd–54</td>
<td>3.8 (30)</td>
<td>nd–3.9</td>
</tr>
<tr>
<td>GeoBR (fringing)</td>
<td>0.1–4.6</td>
<td>3.1 (151)</td>
<td>1.5–2.8</td>
</tr>
<tr>
<td>NBR (fringing)</td>
<td>0.1–4.3</td>
<td>1.8 (13)</td>
<td>0.3–7.7</td>
</tr>
<tr>
<td>KR (midshelf)</td>
<td>0.8–3.4</td>
<td>1.8 (13)</td>
<td>0.4–4</td>
</tr>
<tr>
<td>OTR (microatoll)</td>
<td>0.4–255.1 (19)</td>
<td>0.6–6.1</td>
<td>2.6 (23)</td>
</tr>
<tr>
<td>Average GBR Coral Reefs</td>
<td>nd–54</td>
<td>3.1 (226)</td>
<td>nd–7.7</td>
</tr>
<tr>
<td>Coral Sea</td>
<td>0.8–2.1</td>
<td>1.5 (22)</td>
<td>-</td>
</tr>
<tr>
<td>RV Investigator (18.6–23°S)</td>
<td>0.3–2.7</td>
<td>1.5 (19)</td>
<td>-</td>
</tr>
<tr>
<td>Palm Passage (near Kelso Reef)</td>
<td>(10°53′S–146°00′E–10°52′S–149°52′E)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average Coral Sea</td>
<td>0.8–2.1</td>
<td>1.6 (18)</td>
<td>0.38–2.8</td>
</tr>
<tr>
<td>Gulf of Papua</td>
<td>nd–54</td>
<td>3.1 (226)</td>
<td>nd–7.7</td>
</tr>
<tr>
<td>RV Franklin (8°54′S–144°29′E–9°11′S–143°12′E)</td>
<td>-</td>
<td>-</td>
<td>0.41–3.29</td>
</tr>
<tr>
<td>Solomon Sea</td>
<td>nd–54</td>
<td>3.1 (226)</td>
<td>nd–7.7</td>
</tr>
<tr>
<td>RV Franklin (10°43′S–150°28′E–6°50′S–147°59′E)</td>
<td>-</td>
<td>-</td>
<td>0.56–1.46</td>
</tr>
<tr>
<td>Bismarck Sea-Sepik River Estuary</td>
<td>nd–54</td>
<td>-</td>
<td>0.34–5.67</td>
</tr>
<tr>
<td>RV Franklin (3°47′S–144°37′E–3°49′S–144°33′E)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Note. PBR = Pioneer Bay Reef (Orpheus Island); NBR = Nelly Bay Reef (Magnetic Island); KR = Kelso Reef; OTR = One Tree Reef; GeoBR = Geoffrey Bay Reef; DMS = dimethylsulfide; GBRL = Great Barrier Reef Lagoon; GBR = Great Barrier Reef.
<sup>a</sup>Summer from October to March. <sup>b</sup>Winter from April to September. <sup>c</sup>Sampled October 2016. <sup>d</sup>Sampled July 1997. <sup>e</sup>Sampled September/October 1992.

3.3. Effect of Tides on DMSP<sub>f</sub> and DMS<sub>sw</sub> Concentrations in the GBRL

At stations 1 and 3 close to reefs in the Investigator study there was no correlation of hourly DMSP<sub>f</sub> concentrations with tidal height (data not plotted). However, when only low tide-high tide DMSP<sub>f</sub> concentrations were considered there was a significant correlation ($r^2 = 0.40, p < 0.05, n = 24$) between DMSP<sub>f</sub> concentrations and tidal height (Figure 2s). The correlation highlights that at low tide and high tide slack water DMSP<sub>f</sub> concentrations increase. When tidal data from 2 to 4 m (midtides) was considered (data not plotted) no correlation occurred between DMSP<sub>f</sub> and tides, possibly reflecting more influence from phytoplankton-generated DMSP than from benthic coral reef production of DMSP<sub>f</sub>. At the Heron Island reef flat (Figure 2b) a quadratic fit was not as significant ($p < 0.05$) as the fourth-order polynomial fit that is highly significant ($p < 0.001$). Figures 2a and 2b provide evidence that coral reefs produce enhanced DMSP<sub>f</sub> concentrations as a function of low and high tide slack water irrespective of the type of mathematical fit. The steep increase in DMSP<sub>f</sub> at low and high tide slack water (Figures 2a and 2b) could reflect enhanced production of DMSP from the benthic coral reefs as a consequence of expelled coral zooxanthellae and coral mucus, which are highly concentrated in DMSP (Broadbent et al., 2002; Broadbent & Jones, 2004). In the Great Barrier Reef, the dominant genus of hard corals, Acropora, exudes up to 4.8 L of mucus per square meter of reef area per day. Between 56% and 80% of this mucus dissolves in the reef water (Wild et al., 2004). For Heron Island reef flat the increase in DMSP<sub>f</sub> concentrations at 1- to 2-m tides could reflect incoming seawater breaking over the reef crest (which was close to the sampling site) causing corals to release coral mucus that is enriched in DMSP (Broadbent & Jones, 2004; Hopkins et al., 2016). Further studies may confirm this effect as seawater floods over the reef crest. Measurements of DMS<sub>sw</sub> made on the Investigator voyage were also correlated with tide. At station 3 close to Slashers Reefs in the GBRL (Figure 1) from 7.00 a.m. on 15 October to 7.00 a.m. on 18 October 2016 some of...
the lowest and highest tides were experienced (Figure 3a), with low tides ranging from 0.1 to 0.5 m (mean = 0.27 m). The relationship between DMSw and tide at station 3 is shown in Figure 3b ($r^2 = 0.54$, $p < 0.001$, $n = 49$) and comprised three significant ($p < 0.05$ to $< 0.001$) linear correlations over the 3-day (low tide-high tide) tidal cycles (Figures 3c–3e), strongly suggesting that increased DMSw concentrations, at very low and high tides, possibly reflect an increase in coral mucus from the reefs enriched in DMSw (Broadbent & Jones, 2004). Slicks of surfactant material were observed on the surface at station 3 during our time there. Low tides can stress corals causing the release of coral mucus high in DMS, and as tidal mixing is low at these times (low tide slack water) an increase in DMSw concentrations could occur. As tidal mixing increases DMSw concentrations would decrease, until high tide slack water when concentrations of DMSw could also increase again.

At station 1 in Hydrographers Passage (data not plotted) there was also a significant polynomial correlation between DMSw and tide (not shown) ($r^2 = 0.32$, $p < 0.01$, $n = 78$) from 7.30 a.m. on 18 October to 7.00 a.m. on 22 October, but this correlation was not as strong as that found at station 3. During this period the lowest tides at station 1 were higher ranging from 0.21 m to 1.58 m (mean = 0.84 m, Figure 3a) and may not have been low enough to cause significant coral reef stress and enhanced release of coral zooxanthellae and mucus high in DMSw and DMSP (Broadbent & Jones, 2004). The highly significant polynomial correlation between DMSw and tide at station 3 close to Slashers Reefs is in agreement with the significant polynomial correlation of atmospheric DMS and tides recorded for a large area of the western Pacific (GBRL, Coral Sea, Gulf of Papua, Solomon, and Bismarck Seas) when reefs in these regions were exposed at very low tides and samples were taken close to the reefs (Jones et al., 2007).

The effect of very low tides on DMSw concentrations has been further examined at the PBR fringing reef (Orpheus Island, Figure 4) over four low tides from 6 to 8 February 1993, which varied from 0.59 to –0.04 m over the 3 days, followed by flooding tides. At 15:00 on 6 February DMSw concentrations reached 2.3 nM on a tide of 0.59 m, increasing to 3.1 nM at 19:30 and a tide of 2.35 m. At 03:00 on 7 February a low tide of –0.04 m DMSw reached 3.6 nM, increasing to 5.6 nM at 13:00 on a 1.97 m tide, and reached 5 nM at 13:30 on a tide of 0.53 m. The very high concentration of 54 nM at 03:30 on the 8 February occurred during a very low tide (−0.24 m) that exposed the reef. During exposure the reef was affected by a 20-min rainfall event that further stressed the corals from a drop in salinity of 0.7 psu, which increased the DMSw concentration to 54 nM. During this period there was an obvious odor of DMS above the exposed reef. When no rain fell on the reef the increase in DMSw seemed to lag the low tide (e.g., 03.00 to 15:30 on 7 February), while rainfall on the exposed coral reef caused an almost instantaneous increase in DMSw, reaching 54 nM, the highest concentration measured (Figure 4). When plotting atmospheric DMS versus tide for PBR and the wider western Pacific studies, a distinct polynomial correlation was apparent with a peak at very low tides and a peak during the rising tides over the reefs (Jones & Trevena, 2005). We believe the elevated seawater DMSw concentrations observed at PBR (Figure 4), and also recorded during the _Investigator_ 2016 voyage...
are the result of very low and high tides that can lead to pulses or spikes in DMS\textsubscript{a} over coral reefs in this region (Swan et al., 2017). These tidal pulses of DMS\textsubscript{a} can last for significant amounts of time and could cause the high aerosol particle and CN concentrations that have been observed over the GBR (Bigg & Turvey, 1978; Modini et al., 2009).

3.4. Effect of SST on DMS\textsubscript{w}

A significant correlation occurred between DMS\textsubscript{w} concentrations and SST measured in GBRL waters at stations 1 and 3 from *Investigator* ($r^2 = 0.23$, $p < 0.02$, $n = 133$; Figure 5a); however, the correlation only explains 23% of the variation, leading us to conclude that in the GBRL waters other factors affect DMS\textsubscript{w} (e.g., tidal variation as we have indicated, plus other factors). For the PBR and NBR coral reefs the DMS\textsubscript{w}-SST correlation was also significant ($r^2 = 0.22$, $p < 0.05$, $n = 84$; Figure 5b). However, the correlation highlighted five DMS\textsubscript{w} outliers from 26 to 29 °C (>6 nM), which we believe reflect the influence of tidal stress on the coral reefs. When we

![Figure 3](image-url)
removed these outliers the correlation between DMS\textsubscript{w} and SST markedly improved for the coral reefs ($r^2 = 0.54$, $p < 0.001$, $n = 75$; Figure 5c). The equations for Figures 5a–5c have very similar slopes (0.3–0.4) indicating that DMS\textsubscript{w} increases at a very similar rate in the GBRL and in the GBR coral reefs for every 1\textdegree centigrade increase in SST. If we included DMS\textsubscript{w} concentrations at SSTs >30 °C in summer at NBR there was no significant correlation between DMS\textsubscript{w} and SST as DMS\textsubscript{w} ranged from nd-2.2 nM (mean 1.1 nM, $n = 4$) at these higher SSTs. These low DMS\textsubscript{w} concentrations occurred during coral bleaching and significant loss of coral zooxanthellae (Jones, 1995; Jones et al., 2017). We have found that when corals are stressed in chamber experiments with higher light levels and seawater temperatures, DMSP production, an indicator of zooxanthellae expulsion from coral, increased markedly, while DMS production almost completely shut down. These results suggest that when seawater temperatures in the GBR are >30 °C corals shut down DMS production (Deschaseaux et al., 2014; Fischer & Jones, 2012). In contrast to Figures 5a–5c when combining the GBRL and coral reef data the DMS\textsubscript{w}-SST correlation is exponential and also highly significant ($r^2 = 0.45$, $p < 0.001$), possibly reflecting increased biological production of DMS\textsubscript{w} in or near coral reefs, especially in summer (Figure 5d).

### 3.5. DMS Flux

Despite the low coverage of data points in winter 1997 there was higher DMS flux in the GBRL in winter than summer (mean summer = 2.9 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}, $n = 166$; mean winter = 4 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}, $n = 4$; Table 4). In contrast a distinct seasonal difference in DMS flux occurred for most coral reefs (reef summer flux estimates ranged from nd-153 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}, mean 6.4, $n = 237$; winter fluxes ranged from 0.02 to 15, mean = 2.4, $n = 156$). The reef summer flux was similar to the global flux of 6.7 μmol·m\textsuperscript{-2}·d\textsuperscript{-1} (Lana et al., 2011) and suggests that coral reefs in the western Pacific Ocean contribute significant amounts of DMS to the atmosphere of this region (Jones, 2015). In summer the range and mean DMS flux from the coral reefs of the GBR was often greater than summer DMS fluxes from the GBRL and adjacent Coral Sea (Table 4). The inshore fringing coral reefs (PBR, NBR, and GeoBFR), and the microatoll environment of OTR, all showed clearly defined seasonal cycles of high fluxes in the summer season (October–March) and much lower DMS fluxes from these reefs in winter (April–September, Table 4). During the diurnal study at PBR when DMS concentrations reached as high as 54 nM (Figure 4), wind speed was 7.8 m/s and SST was 27.7 °C giving a huge flux of 153 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}, over twice the highest flux measured at the microatoll reef site of One Tree Reef (74 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}) in the southern GBR, and orders of magnitude higher than the mean DMS fluxes from the coral reefs reported in Table 4. The mean flux of DMS in summer and winter at the midshelf KR was similar in summer and winter suggesting there is no seasonal variation of DMS flux from the bulk of the coral reefs that make up the GBR on the continental shelf (Table 4), suggesting perhaps greater phytoplankton production of DMS\textsubscript{w} in both seasons (Andrews & Gentian, 1982; Furnas & Mitchell, 1986, 1996). The overall
mean summer flux for the GBRL is lower than the mean summer flux for the Coral Sea (2.9 and 3.4 $\mu$mol·m$^{-2}$·d$^{-1}$), with a higher mean winter flux for the Coral Sea than in summer (7.4 and 4 $\mu$mol·m$^{-2}$·d$^{-1}$) (Table 4). Although the low sampling frequency precludes any definitive conclusions the difference perhaps reflects greater phytoplankton productivity and wind speeds in winter in the Coral Sea (Table 4, Muslim & Jones, 2003). The Australian Current may be a factor in the different summer-winter fluxes of DMS as it pumps cold, saline, nutrient-rich water up the slope to the shelf break (Andrews, 1983; Andrews & Gentian, 1982). These intrusions tend to be confined near the bottom, and phytoplankton development quickly takes place inshore of the shelf break. These intrusions are thought to be wind driven and often lead to increased phytoplankton activity, such as *Trichodesmium* blooms during spring, and affect large areas of the GBRL and coral reefs (Furnas & Mitchell, 1996, 1997), significantly affecting nutrient and trace metal concentrations (Jones et al., 1982; Jones et al., 1986; Muslim & Jones, 2003), and likely DMS$_w$ concentrations. This may explain the higher mean flux in Palm Passage in summer (Table 4). The effect of these wind-driven intrusions on DMS$_w$ and DMS flux at the shelf break needs to be investigated in more detail in summer and winter.

**Figure 5.** (a) DMS$_w$-SST correlation for the GBRL, and (b) PBR + NBR coral reefs, (c) for PBR coral reef, and (d) for the GBRL and GBR coral reefs. DMS = dimethylsulfide; SST = sea surface temperature; GBRL = Great Barrier Reef Lagoon; GBR = Great Barrier Reef; PBR = Pioneer Bay Reef.
3.6. DMS Flux and SST

DMS flux calculated from the DMSw measurements made on Investigator was significantly correlated with SST for GBRL waters (p < 0.001, r² = 0.56, n = 49; Figure 6a). For the two coral reefs (PBR + NBR) DMS flux often significantly increased at SSTs of 26–29 °C (Figure 6b), and for the GBRL flux also markedly increased at SSTs >26 °C (Figure 6a). In the summer of 1994 pulses of DMS flux at PBR reached as high as 18–21 and 14–20 μmol·m⁻²·d⁻¹ (Figure 6b), well above the mean flux for this reef (Table 4). The high DMS fluxes from PBR in summer often occurred during low tides, above average wind speeds (7–8 m/s), and when significant rainfall occurred over the reef (Jones et al., 2017). In contrast to these fluxes very low DMS fluxes occurred at NBR in August in the winter of 1995 ranging from 0.02 to 0.44 μmol·m⁻²·d⁻¹ (mean 0.10, n = 28) when SSTs and coral reef production of DMSw were at their lowest (Table 4 and Figure 6b). This was also the case for PBR in winter 1993 (Table 4, Jones et al., 2007). When SSTs over 30 °C occurred at NBR and caused coral bleaching DMS flux markedly decreased (range 0.02–3.6, mean 1.15 μmol·m⁻²·d⁻¹, n = 5; Figure 6c). In summer 1994 in early January when corals bleached at NBR SSTs ranged from 30.5 to 33.5 °C and there was almost no low level cloud cover in the Townsville region, the low DMS fluxes occurred during low tides, high SSTs and solar radiation, and when short intense bursts of tropical rainfall periodically fell on the reefs at low tide (Jones et al., 2017). Several weeks after the coral bleaching at NBR increasing pulses of low level cloud cover occurred over coral reefs in the Townsville region as corals increased their zooxanthellae concentrations (Jones et al., 2017).

3.7. Comparison With Other Flux Measurements

DMS fluxes from the GBRL and Coral Sea determined on Investigator were compared with previous flux measurements made in the GBRL, Coral Sea, Gulf of Papua, Solomon, and Bismarck Seas (Jones & Trevena, 2005, Table 5). Also included was the comprehensive study of mean summer and winter DMS fluxes at Heron Island coral cay 70-km offshore from Gladstone in the southern GBR produced by Swan et al. (2017, Table 5). These

### Table 4: Mean Summer and Winter DMS Flux Estimates (μmol·m⁻²·d⁻¹) From the GBRL, Coral Reefs in the GBR, Coral Sea, and Tropical Cyclones

<table>
<thead>
<tr>
<th>Location/voyage</th>
<th>Reef site/type</th>
<th>Summerᵃ</th>
<th>Winterᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Barrier Reef Lagoon</td>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>c RV Investigator (18°06′−23°S)</td>
<td></td>
<td>0.1−10.4</td>
<td>2.9 (166)</td>
</tr>
<tr>
<td>d RV Franklin (18°32′−14°45′S)</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>e RV Franklin (19−25°S)</td>
<td></td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Average GBRL</td>
<td></td>
<td>0.1−10.4</td>
<td>2.9 (166)</td>
</tr>
<tr>
<td>Great Barrier Reef (coral reefs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBR (fringing)</td>
<td></td>
<td>0.4−153</td>
<td>5.0 (24)</td>
</tr>
<tr>
<td>GeoFBR (fringing)</td>
<td></td>
<td>nd-8.6</td>
<td>5.4 (151)</td>
</tr>
<tr>
<td>NBR (fringing)</td>
<td></td>
<td>0.02−20</td>
<td>3.3 (30)</td>
</tr>
<tr>
<td>KR (midshelf)</td>
<td></td>
<td>2.4−10</td>
<td>5.4 (13)</td>
</tr>
<tr>
<td>OTR (microatoll)</td>
<td></td>
<td>3−74</td>
<td>12.8 (19)</td>
</tr>
<tr>
<td>Average GBR Coral Reefs</td>
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<td>6.4 (237)</td>
<td>0.02−15</td>
</tr>
<tr>
<td>Coral Sea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c RV Investigator (22°2′−18°52′S)</td>
<td></td>
<td>0.1−8</td>
<td>3.6 (21)</td>
</tr>
<tr>
<td>d PBR (fringing)</td>
<td></td>
<td>0.1−12</td>
<td>3.2 (17)</td>
</tr>
<tr>
<td>Palm Passage (near Kelso Reef)</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d RF Franklin (13°55′−10°52′S)</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average Coral Sea</td>
<td></td>
<td>0.1−8</td>
<td>3.4 (38)</td>
</tr>
<tr>
<td>Cyclones 1958–2015</td>
<td></td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

Note: The average number of tropical cyclone days along the GBR, between 1958 and 2015, with wind speeds that average at least 32 m/s, was 5 per year (Lough, 1994; Puotinen et al., 2016). Also, 75% of cyclones in the GBR are reported to occur between January and March, which often coincide with the highest seawater DMS and DMSP production. Taking the mean January to March DMSw concentration (3.1 nM; n = 31) and seawater temperature (29 °C; n = 31) from the Orpheus Island (PBR) and Magnetic Island data (NBR, GeoFBR), and a wind speed of 32 m/s (lowest mean cyclone wind speed), a flux of 100 μmol·m⁻²·d⁻¹ was calculated. PBR = Pioneer Bay Reef (Orpheus Island); NBR = Nelly Bay Reef (Magnetic Island); KR = Kelso Reef; OTR = One Tree Reef; GeoFBR = Geoffrey Bay Reef; GBR = Great Barrier Reef; DMS = dimethylsulfide.

Fluxes were determined from atmospheric DMS concentrations and a photochemical box model and are slightly lower than our coral reef fluxes. Compared with the Swan et al. data, our slightly higher fluxes both in summer and winter most probably reflect the greater number of coral reefs sampled, some of which were shallow and partially enclosed (NBR, OTI), thus minimizing dilution effects on DMS\textsubscript{w} with adjacent GBRL seawater.

The average summer flux for the six coral reefs studied to date was a factor of 3 more than the winter flux from these reefs (Table 5). Flux measurements from the Gulf of Papua in winter are much higher than winter fluxes from the GBRL and Coral Sea (Table 5), with lower fluxes from the Solomon and Bismarck Seas at 2.8 and 2.1 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}, respectively. The overall mean summer DMS flux of for coral reefs of the GBR is 5.7 μmol·m\textsuperscript{-2}·d\textsuperscript{-1} (n = 888), slightly lower than the global flux figure of Lana et al. (2011; Table 5), and

**Figure 6.** DMS flux versus SST correlations for the GBRL waters from (a) 07:00 on 15 October to 07:00 on 18 October 2016, (b) for PBR and NBR coral reefs for the SST range 22–30 °C, and (c) for PBR and NBR coral reefs for the SST range 22–33.5 °C. DMS = dimethylsulfide; SST = sea surface temperature; GBRL = Great Barrier Reef Lagoon; PBR = Pioneer Bay Reef; NBR = Nelly Bay Reef.

Fluxes were determined from atmospheric DMS concentrations and a photochemical box model and are slightly lower than our coral reef fluxes. Compared with the Swan et al. data, our slightly higher fluxes both in summer and winter most probably reflect the greater number of coral reefs sampled, some of which were shallow and partially enclosed (NBR, OTI), thus minimizing dilution effects on DMS\textsubscript{w} with adjacent GBRL seawater.

The average summer flux for the six coral reefs studied to date was a factor of 3 more than the winter flux from these reefs (Table 5). Flux measurements from the Gulf of Papua in winter are much higher than winter fluxes from the GBRL and Coral Sea (Table 5), with lower fluxes from the Solomon and Bismarck Seas at 2.8 and 2.1 μmol·m\textsuperscript{-2}·d\textsuperscript{-1}, respectively. The overall mean summer DMS flux of for coral reefs of the GBR is 5.7 μmol·m\textsuperscript{-2}·d\textsuperscript{-1} (n = 888), slightly lower than the global flux figure of Lana et al. (2011; Table 5), and
indicates that the flux of DMS from coral reefs in the western Pacific is significant sources of DMS to the atmosphere of this region.

### 3.8. Effect of Cyclones on DMS Flux

The average number of tropical cyclone days along the GBR between 1958 and 2015, with wind speeds that average at least 32 m/s, is 5 days per year (Lough, 1994; Puotinen et al., 2016). About 75% of cyclones in the GBR are reported to occur between January and March, which coincides with the highest SSTs and DMS and DMSP production rates from coral reefs in the GBR (Fischer & Jones, 2012; Jones et al., 2007, 2014). Taking the mean January to March DMSw concentrations of 3 nM for PBR and NBR (\(n = 31\)), and a seawater temperature of 29 °C, with a mean wind speed of 32 m/s (the mean cyclone wind speed), a flux estimate of 100 \(\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}\) was calculated (Table 4). We have assumed in this calculation that a linear relationship between transfer velocity of DMS (\(k_{\text{dms}}\)) and wind speed is valid up to 32 m/s.

However, it is interesting to consider a severe tropical cyclone such as Severe Tropical Cyclone Debbie in recent times that has affected the GBR, where wind strength reached 54 m/s, well above 32 m/s. In March 2016 this cyclone caused extensive flooding in Australia and New Zealand and billions of dollars in damages. During the cyclones transit to the Queensland coast is intensified, both in category of cyclone and wind strength, as it traveled over coral reefs in the Coral Sea Islands (off the GBR) and coral reefs in the GBR. A highly significant correlation occurred between low tide and cyclone category as the cyclone traveled toward the Queensland coast (\(r^2 = 0.88, p < 0.001\)). At present we do not have direct measurements for DMS flux that extend to severe tropical cyclone conditions. There are theoretical reasons and some experimental evidence to think that the drag coefficient and whitecap fraction will level off or even decline as wind speeds increase above a certain threshold or that the interfacial component of the transfer coefficient most relevant to DMS flux will level off and decline as wind speed decreases and sea state develops (Smith et al., 2011), but the issue is far from settled. However, certain assumptions could be applied as a first estimate and this will form a later

### Table 5

**Comparison of DMS Flux \((\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1})\) From Coral Reef Regions of the Western Pacific Ocean**

<table>
<thead>
<tr>
<th>Location/reef site/type</th>
<th>Summer(^a)</th>
<th>Winter(^b)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Barrier Reef Lagoon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c RV Investigator (18.6–23°S)</td>
<td>0.1–10</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>d RV Franklin (18°32'–14° 45'S)</td>
<td>-</td>
<td>2–6.8</td>
<td>Jones &amp; Trevena (2005)</td>
</tr>
<tr>
<td>e RV Franklin (19–25°S)</td>
<td>NR</td>
<td>4 (4)</td>
<td>Jones et al. (1994)</td>
</tr>
<tr>
<td>Average GBRL</td>
<td>0.04–10</td>
<td>2.9(^f) (166)</td>
<td>This work</td>
</tr>
<tr>
<td>Great Barrier Reef (coral reefs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBR, NBR, GBR, KR, OTR</td>
<td>nd-153</td>
<td>6.4 (237)</td>
<td>This work</td>
</tr>
<tr>
<td>Heron Island (coral cay)</td>
<td>-</td>
<td>5 (651)</td>
<td>Swan et al. (2017)</td>
</tr>
<tr>
<td>Average coral reefs</td>
<td>nd-153</td>
<td>5.7 (888)</td>
<td>This work</td>
</tr>
<tr>
<td>Coral Sea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c RV Investigator (18.6–23°S)</td>
<td>0.1–8</td>
<td>3.4 (38)</td>
<td>This work</td>
</tr>
<tr>
<td>d RV Franklin (13°55’–10°52’S)</td>
<td>-</td>
<td>3.2–14.4</td>
<td>Jones and Trevena (2005)</td>
</tr>
<tr>
<td>Average Coral Sea</td>
<td>0.1–8</td>
<td>3.4 (38)</td>
<td>This work</td>
</tr>
<tr>
<td>Gulf of Papua</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d RV Franklin (8°54'S–144°29'E–9°11'S–143°12'E)</td>
<td>-</td>
<td>1.4–12</td>
<td>Jones and Trevena (2005)</td>
</tr>
<tr>
<td>Solomon Sea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d RV Franklin (10°43'S–150°28'E–6°50'S–147°59'E)</td>
<td>-</td>
<td>1.9–4.3</td>
<td>**</td>
</tr>
<tr>
<td>Bismarck Sea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d RV Franklin (3°47'S–144°37'E–3°49'S–144°33'E)</td>
<td>-</td>
<td>0.13–8.6</td>
<td>**</td>
</tr>
<tr>
<td>GBR cyclones 1958–2015</td>
<td>-</td>
<td>100</td>
<td>This work</td>
</tr>
<tr>
<td>Global ocean flux</td>
<td>-</td>
<td>6.7</td>
<td>Lana et al. (2011)</td>
</tr>
</tbody>
</table>

Note. GBR = Great Barrier Reef; PBR = Pioneer Bay Reef (Orpheus Island); NBR = Nelly Bay Reef (Magnetic Island); KR = Kelso Reef; OTR = One Tree Reef; DMS = dimethylsulfide; GBRL = Great Barrier Reef Lagoon.

\(^a\) Summer from October to March. \(^b\) Winter from April to September. \(^c\) Sampled October 2016 (summer from October to March). \(^d\) Sampled July 1997 (winter from April to September). \(^e\) Sampled September/October 1992. \(^f\) Mean GBRL flux taken as 2.9 as so few samples collected in the Franklin summer voyage.
Table 6
Summer and Winter Emission Estimates of DMS-S From the Great Barrier Reef Region

<table>
<thead>
<tr>
<th>Season</th>
<th>GBR emission (MmolS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBR coral reefs(^a)</td>
<td></td>
</tr>
<tr>
<td>Summer (November–April)</td>
<td>23</td>
</tr>
<tr>
<td>Winter (May–October)</td>
<td>9</td>
</tr>
<tr>
<td>Great Barrier Reef Lagoon(^b)</td>
<td>183</td>
</tr>
<tr>
<td>Winter (May–October)</td>
<td>256</td>
</tr>
<tr>
<td>GBR cyclones(^c)</td>
<td></td>
</tr>
<tr>
<td>Cyclones 1958–2015</td>
<td>170</td>
</tr>
<tr>
<td>Total annual reef and GBRL emissions</td>
<td>0.64 Gmol</td>
</tr>
</tbody>
</table>

Note. DMS = dimethylsulfide; GBRL = Great Barrier Reef Lagoon; GBR = Great Barrier Reef.
\(^a\)The mean DMS flux from the GBRL in summer (2.9) and winter (4) is given in Table 4. The area of the GBRL is 347,800 km
\(^2\). \(^b\)Over an average of 5 days per year, throughout the GBR (347,800 km
\(^2\)), this equated to an estimated emission of 0.17 Gmol/S-year\(^{-1}\) due to cyclone events during 1958–2015. \(^c\)GBR emissions estimated from coral reefs in the GBR calculated from DMS fluxes in summer (6.4) and winter (2.4, Table 4). The area of coral reefs in the GBR taken was 20,000 km
\(^2\) (Hopley et al., 1989).

The increase from winter to summer, and about one fourteenth of the emission in summer, compared with 9 MmolS in winter, about 2.5 times the increase from winter to summer, and about one fourteenth of the emission from the GBRL. Considering cyclone influence on DMS flux from 1958 to 2015, we compute that on average 170 MmolS are emitted into the atmosphere in 4-5 days from cyclones that are directed toward the coast of Queensland. We calculate that the total annual emission estimate of DMS-S to the atmosphere over the GBR, from both coral reefs and GBRL waters, including emissions from average cyclone activity in summer during the period 1958–2015, is 0.64 Gmol/S per annum. Clearly, the greatest emission of DMS-S to the atmosphere of the GBR is from the GBRL, being a much greater area than the coral reefs. However, tidal pulses of atmospheric DMS (DMS
\(_{a}\)) from coral reefs can be greater periodically than from the surrounding GBRL (Swan et al., 2017), and it is these tidal pulses of DMS that are not included in this first emission estimate. This will form the basis of another publication.

3.10. Potential Influence of DMS on the Climate of NE Australia

Studies have shown that coral in chamber experiments are a source of DMS and isoprene when the coral is stressed and release mucus, but these VOCs are not emitted from mucus-free coral (Swan et al., 2016). Seven minor reduced sulfur compounds including dimethyl disulfide, methyl mercaptan, and carbon disulfide were identified, while coral reef seawater was a source of methylene chloride, acetone, and methyl ethyl ketone. Swan et al. (2016) believe that the VOCs emitted by coral and reef seawater are capable of producing new atmospheric particles <15 nm diameter as observed at Heron Island reef. DMS and isoprene are known to play a role in low-level cloud formation (cumulus and stratocumulus), which can reduce solar radiation over the GBR, thus reducing SSTs (Fischer & Jones, 2012; Jones et al., 2017; Leahy et al., 2013; Swan et al., 2016). We believe a localized climate feedback involving DMS and other VOCs originating from GBR corals could occur for the following reasons. The GBR is 2,300 km long and contains 3,200 coral reefs such that climatically active aerosol particles would be generated every day from the benthic coral reefs. These aerosols would be concentrated in the northern GBR by the SE Trade Winds where they would be available for secondary organic aerosol (SOA) formation, particularly in the hot summer monsoonal months, when solar radiation levels can be extreme. Swan et al. (2016) state that the conditions required to observe precursor-to-particle formation over coral reefs in the GBR appear to be sunlight, low tide, low relative humidity, and lack of wind. This could suggest that pulses or plumes of precursor VOCs (including DMS
\(_{a}\)) aerosols could be produced at the coral reef point source and spread to adjacent areas. This would occur over the 3,200 coral reefs that make up the GBR and could affect cloud cover and rainfall along the north Queensland coast. Each cm
\(^2\) of coral surface area contains the equivalent of a phytoplankton bloom (~2 × 10
\(^{6}\) cells/cm
\(^3\)) that acts as a point source of DMS to the atmosphere of the GBR (Broadbent et al., 2002; Deschaseaux et al., 2014; Jones, 2015; Hopkins et al., 2016), potentially available for SOA formation.

We have investigated the variability in a satellite decadal time series of fine-mode AOD over the GBR (Cropp et al., 2018). A coral stress metric was formulated as a function of irradiance (photosynthetically active radiation), water clarity, and low tide, at Heron Island in the southern GBR over the period 2000–2015. We found that AOD (to which DMS and other VOCs contribute) was correlated with the coral stress metric, and the correlation increased at low wind speeds, when horizontal advection of air masses was low and the production of nonbiogenic aerosols (e.g., sea salt) was minimal. We suggested that coral reefs may be able to protect
themselves from irradiance stress during calm weather by affecting the optical properties of the atmosphere and local incident solar radiation over the GBR. The AOD cycle is similar to the only seasonal DMS data for the GBR measured at a fringing coral reef at Orpheus Island (PBR) in the central GBR (Jones et al., 2007). The timing of AOD peaks is consistent with reports of increased coral reef DMS (P) production in early summer in the GBR (Fischer & Jones, 2012; Jones et al., 2014) and increased DMS flux to the GBR atmosphere (Swan et al., 2017; this research). The lack of synchronicity between AOD and CHL annual cycles at Heron Island argued against a simple relationship between ocean phytoplankton-generated DMS-derived aerosols (Cropp et al., 2018).

It is interesting to note that the combination of low tides and high noon irradiances does have the potential to cause widespread (mass) coral bleaching in the GBR (Anthony & Kerswell, 2007). Visual surveys of coral mortality and bleaching status of more than 13,000 corals at 14 reef sites around Orpheus and Pelorous Islands (18.38°S, 146.30°E) in the central GBR during September 2005 indicated that most coral taxa at sheltered sites were severely affected by the extreme low tides (40–75%). In contrast, corals at wave exposed sites were largely unaffected (>1%), as periodic washing by waves prevented desiccation. During the period 12–18 September maximum irradiances on the reef crest increased from ~1,000 to 1,800 μmol·m⁻²·s⁻¹, with low tides of 0.1–0.2 m in the early afternoon. Despite significant cloud cover on 15 September, the integrated amount of irradiance impinging on the air-exposed corals in September was twice or 3 times greater than at any other time of the year. SSTs increased from 22 to 26 °C during the spring study period and were well below the coral bleaching threshold, indicating that bleaching was predominantly from enhanced solar radiation and the low tides. Analyses of an 8-year data set of tidal records for the area suggested that the combination of extended periods of aerial exposure and high irradiances can cause widespread coral bleaching in the GBR (Anthony & Kerswell, 2007).

Sulfate aerosols derived from the oxidation of DMS have a range of compositions from H₂SO₄ to (NH₄)₂SO₄, which can enhance solar radiation levels by up to 10 million (Charlson et al., 1987). Variations in optically thin and thick clouds are known to enhance downwelling of IR radiation over coral reefs in the GBR (Barton & Paltridge, 1979; Elvidge et al., 2004; Jones, 1995; Jones et al., 2017; MacKellar et al., 2013) and may explain enhanced solar radiation levels over the GBR from 2000 to 2010 (Masiri et al., 2008). The aerosol-cloud radiative effects on solar radiation could explain the results of Masiri et al. (2008) over the GBR and may be responsible for mass coral bleaching episodes in the GBR. Further research on this aspect is clearly needed and is of utmost importance. Under light winds and low tides in summer at the Heron Island reef flat, daily net downwelling shortwave solar radiation can exceed +800 W/m², with up to 95% of the net radiation during the morning heating the water column and benthic coral cover (MacKellar et al., 2013). These extreme solar radiation levels caused heating of Heron Island reef flat that were exacerbated by a midafternoon low tide when the shallow reef water reached 34 °C, and near-bottom water temperatures reached 33 °C, exceeding the thermal tolerance of corals at Heron Island, causing coral bleaching (MacKellar et al., 2013).

The atmospheric lifetime of DMSa in the MBL is in the order of 1 day. If we assume that the atmospheric lifetime of DMSa is 6 hr in the tropics under a high actinic flux, the DMSa source gas can still be horizontally transported far from its source by the time it nucleates and grows to CCN size (50–100 μm). Assuming a typical WS of 4.5 m/s and a 6-hr DMS tropical atmospheric lifetime, a DMSa molecule will be transported ~100 km from its source by the time it undergoes nucleation. If we add another day or two for it to grow to CCN size, the DMSa molecule will be transported ~100 km from its DMSa source region (Quinn & Bates, 2011).

DMSa will also be vertically transported aloft from its seawater source point. We know that nucleation leading to new particle formation in the mixed layer of the MBL is not a common occurrence there due to the presence of preexisting particles that scavenge any new particles as they form. Conditions must be very clean (i.e., low preexisting particle number concentrations) for homogeneous nucleation of DMSa to occur in the MBL. Such clean conditions are more common in the free troposphere (FT). DMSa transported aloft to the FT will more readily undergo nucleation there, and new particles formed will be transported away in the FT from their source region until they are transferred from the lower FT into the MBL under convective downdraughts, which do occur during the sea breeze effect over the GBR and adjacent land.

Such disconnects between the region of DMS emission and the region of new particle formation can prevent a local climate feedback regulation as proposed here. However, it is known that the shallow seawater over
coral reef platforms has a lower thermal capacity than the deeper water of the GBRL; hence, the seawater over the shallow coral reef heats up more during the day than the deeper GBRL seawater. Consequently, there is more convective atmospheric uplift over the GBR than the deeper GBRL seawater, with this process generating convective uplift for cloud formation over coral reef platforms. This phenomenon was observed at Heron Island where a convective internal boundary layer similar to that over the land was reported over the reef (MacKellar et al., 2013). Therefore, given that cloud formation is assisted by the convective uplift that exists over a reef platform, it is possible that cloud formation over a coral reef is predominantly sourced from the reef beneath the clouds. However, whether reef-derived DMS and other reef-derived VOCs are the major driver of cloud formation over the reef is still to be determined.

4. Conclusions

Our research has highlighted the GBRL and coral reefs within the GBRL as significant sources of DMS flux to the atmosphere over the GBR. Low tides and elevated SSTs increase DMS_\text{w} concentrations and DMS flux and are in agreement with previous studies on coral reefs (Hopkins et al., 2016; Jones et al., 2007; Jones & Trevena, 2005; Swan et al., 2017). Further research is needed to investigate whether aerosol substances generated from the 3,200 coral reefs in the GBR, together with aerosol substances generated from the GBRL, could produce SOA and CCN, leading to the production of low level cloud cover over the GBR, which could participate in a regulation of SSTs to <30 °C (Jones et al., 2017). However, it has now become apparent that the enhanced scattering of solar radiation from nss-sulfate aerosols derived from oxidation of DMS_\text{s} produced from coral reefs in the GBR could have a warming effect from the associated cloud-aerosol radiative effects (Fischer & Jones, 2012; Jones et al., 2017). Our research has highlighted that when SSTs are >30 °C, corals shut down production of atmospheric DMS and DMS flux, and this could decrease AOD and low level cloud over the GBR causing SSTs to increase to 33–34 °C when mass coral bleaching can occur (Fischer & Jones, 2012; Jackson et al., 2018; Jones, 2015; Jones et al., 2017). The increased radiative forcing from clouds and aerosols can be as high as 4 times as large as the radiative forcing from a doubling of CO2 levels in the atmosphere (Ramanathan et al., 1989) and needs to be taken into account when ascribing coral bleaching events in the GBR solely to GHG warming (Jones et al., 2017).

Australian and UK climate models have recently quantified the role of DMS in the climate system in terms of cloud fraction, solar radiation, and precipitation (Fiddes et al., 2018). The authors have found that by removing all DMS, or alternatively significantly enhancing marine DMS, they find a top of the atmosphere radiative effect of +1.7 W/m^2 (a climate warming effect) and −1.4 W/m^2 (a climate cooling effect), respectively. The largest responses to these DMS perturbations (removal/enhancement) are in stratiform cloud decks in the Southern Hemisphere. These regions show significant differences in low cloud (<9+6%), surface incoming shortwave radiation (+7–5 W/m^2) and large-scale rainfall (+15–10%). The authors demonstrate a precipitation suppression effect of DMS-derived aerosol in stratiform cloud deck regions, coupled with an increase in low cloud fraction. The difference in low cloud fraction is an example of the aerosol lifetime effect. Globally, the authors find a sensitivity of temperature to annual DMS flux of 0.027 and 0.019 K per Tg/year of sulfur, respectively.

Although DMS liberated from the reef (and the GBRL) has the potential to alter cloud microphysical properties to generate more numerous small droplets leading to increased cloud albedo for planetary cooling, the climate feedback mechanism driven by coral produced DMS may be more complex than first thought (Quinn & Bates, 2011), although more compelling evidence has been recently published in support of it (Jackson et al., 2018). However, hard evidence to support the climate feedback mechanism requires a quantitative demonstration of the relationship between the mass air-sea flux of coral reef-generated DMS-derived sulfate and the number concentration of CCN in the air over the reef. Clearly, more focused and intensive research needs to be carried out on the cloud-radiative effects of DMS_\text{s} and other VOCs released from coral reefs in the GBR (Swan et al., 2016), and assessments made on the cooling and warming effect of coral-derived aerosols produced by coral reefs in the GBR, and the effect on the climate of the NE coast of Australia. In addition anthropogenic aerosols from increased shipping in the GBR, biomass burning, and land-based pollution sources to the GBR may seriously compromise any natural reef-aerosol feedback described above. Only detailed research on the atmosphere over the GBR such as the R2R project during summer and winter will resolve these issues.
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