Manuscript bg-2016-387

Replies to Referee #1

Comment 1:
Figure 1b is really a great figure and compelling for the point of the paper, but not discussed at all.

Reply:
Fig. 1b is mentioned on P6, L11 to pictorially describe the Capricorn Bunker Group of coral reefs to the SE of Heron Island. Fig. 1b was not discussed in the context of low-level cloud formation over these coral reefs because it is a contentious image among atmospheric scientists. While there may be broad agreement that convective processes have contributed to cloud alignment over the Capricorn Bunker Group of coral reefs shown in the MODIS image, we provide insufficient evidence to conclude that atmospheric DMS (DMS_a) derived from those reefs is the source of those clouds. In our manuscript we provide evidence that the Heron Island reef flat and the Capricorn Bunker Group of reefs can at times be significant sources of DMS_a. Those spikes of DMS_a can potentially contribute to development of clouds over the GBR; however, as stated in the final sentences of the conclusion "the extent to which DMS_a contributes to aerosol production and its role in CCN formation over the GBR is currently unknown. Aerosol formation and evolution studies are, therefore, required to determine if the GBR is a climatically important source of marine aerosol." This is the crux of the matter now requiring further investigation. After reading our manuscript we would like the reader to draw their own conclusion regarding the cloud cover over the reefs shown in Fig. 1b.

Another referee of the manuscript has recommended deleting Fig 1, stating the figure is not necessary to understand the information in the paper, and that it does not provide important new information. This contrasting comment possibly alludes to the contentious nature of the images shown in Fig 1. We wish to promote discussion by presenting this figure, but do not want to draw conclusions beyond what the data we collected allows. The conclusions we have made are in line with the objective of the study stated in the final sentence of the introduction.

Comment 2:
The wind compass in Figure 2 is a bit confusing. It would be easier to read and comprehend if it was in a wind rose format.

Reply:
The radar compass plot was used in Fig 2 because it provided the clearest representation of the frequency of wind directions for the two seasons when plotted together. When the wind direction data for both seasons is plotted on a wind rose style plot, it is difficult to distinguish the seasonal differences because they were minor. What we want to convey by including the compass plot in Fig 2 is to show that there was little difference in the directional frequency of the winds at Heron Island in both the wet and dry seasons.

Comment 3:
The description of the GC sampling could be more detailed. I see that the authors cited a previous methods paper, I would still like to know more about this particular experiment. What size tubing? How fast was the sample pumped? How was it pumped? Why was the air trapped 14 mins?

Reply:
In order to minimise the length of Section 2: 'Methods', a reference is provided to a 2015 publication that gives a complete description of the instrumentation and its measurement uncertainty. We appreciate that the referee would like more methodological information provided in this results focussed paper, so it will be included in the revision. Answers to the particular questions posed are as follows: Marine air was drawn through 6 mm internal diameter Teflon tubing via a high-capacity oxidant scrubber composed of 1% w/v sodium ascorbate and glycerol impregnated into a 47 mm diameter glass-fibre filter. Surface-level marine air was drawn through the sampling system at a flow rate of approximately 260 mL min^{-1} using a single-stage diaphragm vacuum pump (Vacuubrand, model ME2, Germany). The air was drawn into a cryogenically

cooled trap (cryotrap) that was constructed by passing 1.6 mm diameter Teflon tubing through ~50 cm of copper tubing of 2.0 mm internal diameter, and bending it into a loop. A sample collection time of 14.4 min was used to deliver 3.72 L of air into the cyrotrap. This volume of air was required to concentrate sufficient DMS_a for chromatographic analysis to provide a 0.1 nmol m^{-3} (2 ppt) reporting limit. Calibration was achieved using permeated ethyl methyl sulfide.

Comment 4:
I don't like the units of nmol/m3 and appreciate when ppt units also mentioned. Can this be done throughout?

Reply:
The photochemical ambient mass balance Eq. 1 used to determine seasonal DMS emission flux requires that DMS_a molar concentrations are entered to determine flux in the usual units of µmol m^{-2} d^{-1}. This is the main reason why DMS_a molar concentrations are reported throughout the manuscript. We are aware that DMS_a concentrations are dependent on pressure and temperature according to the ideal gas law, and that mixing ratios are more suitable than concentrations to describe the abundance of species in air, particularly when samples are collected in aircraft over various altitudes. All the DMS_a measurements we made were at sea level under relatively consistent temperature and pressure. Additionally, the DMS_a concentration of nmol m^{-3} used throughout the manuscript is a SI unit. In contrast, ppt is not an SI unit, and it is recommended by IUPAC that the SI unit of pmol mol^{-1} is used in place of ppt notation. However, we understand that it is customary for trace species in air to be reported in ppt because familiarity with this unit allows many readers to readily compare abundances of trace gaseous species. We would like to present SI concentrations throughout the manuscript by reporting our surface DMS_a measurements in nmol m^{-3} to maintain consistency with emission fluxes reported in µmol m^{-2} d^{-1}. Nevertheless, Table 1 will be edited to include the corresponding ppt mixing ratios for the DMS_a concentrations given in the table. The limit of reporting of 2 ppt will also be given in brackets next to the concentration in Section 2.1 (P3, L17); however, we think it will clutter the manuscript text to report ppt mixing ratios in brackets next to every concentration mentioned in Section 3: 'Results and Discussion'.

Comment 5:
Style of the discussion sections seems a bit off - I miss a general description of the results. Instead, the manuscript seems to delve right into the spikes and the effect of tides.

Reply:
An introductory paragraph that provides a general description and summary of the results will be included at the beginning of Section 3: 'Results and Discussion' in the revised manuscript. This introductory paragraph will not repeat information given in Section 4: 'Conclusions'.

Comment 6:
How do the authors know that the large spike found during the dry season (shown in figure 6a) is not an instrumental problem? Why should there only be biological shock during the dry season (it seems that there are periods during the wet season also without rainfall and with low tide)?

Reply:
The intense DMS_a spike detected during the dry season campaign was not an instrumental problem. As stated in the manuscript, there was an intense odour of DMS at the time the spike was detected, which was evident to a number of people who remarked about the unusually strong "marine odour" coming from the platform reef surrounding the island. Although the DMS_a spike was relatively sharp it was not derived from a single measurement. The oceanic background DMS_a concentration on 25 July 2013 ranged from 1.0-1.8 nmol m^{-3} over the entire day prior to the intense DMS_a spike in the early evening at 17:50 when the DMS_a rapidly rose to 45.9 nmol m^{-3}. The following DMS_a measurement was 9.7 nmol m^{-3} at 18:14, which tapered off from 2.7 nmol m^{-3} at 18:38 to the preceding background concentration of 1.5 nmol m^{-3} by 21:24. As mentioned in the discussion, this DMS_a spike was brief due to rapid dilution by strong horizontal advection under a wind speed of 9.5 m s^{-1} at the time of the spike. These conditions require higher resolution sampling to adequately capture this sort

of DMS_a reef emission, which is one of the reasons why it is recommended in the conclusion that chemical ionisation mass spectrometry could assist further studies of DMS_a emissions from the GBR.

We are not saying in the manuscript that biological shock to the reef will only occur during the dry season. It just happened to be during the 2013 dry season campaign that we detected the particularly intense DMS emission that appeared to be brought about by coincidence of environmental conditions that were unfavourable to the coral reef. These conditions included *spring* low tides which aerially exposes more of the reef for longer periods than neap low tides, coinciding with a brief shower of rain onto the reef flat at the time when the reef was most exposed. Such conditions could occur at other times of the year. *Spring* low tides occur during December-January in the wet season, so it is possible that intense emissions of DMS could occur at that time if the exposed reef was showered by rainfall. In a previous study on the GBR in February (austral summer) elevated seawater DMS concentrations (54 nM) were measured during low tide when there was 20 minutes of rainfall, which reduced the seawater salinity by 0.75 PSU (Jones et al., 2007, Environmental Chemistry, doi:10.1071/EN06065). This situation is likely to have released a wet season DMS_a spike. As is evident from the entire winter dataset we show here, the intensity of the DMS_a spike detected in the early evening of 25 July 2013 was a unique event, and it was good fortune to be on-site at that time with equipment to detect and quantify it.

The referee comments that there are periods during the wet season also without rainfall and with low tide. Fig. 3a shows a period between 8 March and 17 March 2012 when there was only a few convective derived short showers. Low tide during periods of dry weather resulted in few detectable DMS_a spikes from the coral reef. In contrast, the convective shower that coincided with low tide in the evening of 14 March produced the second largest DMS_a spike (10.6 nmol m^{-3}) recorded during the late summer wet season campaign. This indicates that rain on the reef in the summer season can result in a DMS_a spike similar to the spike detected during the winter campaign. The reason that the DMS_a spike during the winter was much more intense than the one detected during the summer is not clear, but it may have to do with factors such as the level of the low tide, the time that the coral had been aerially exposed, the temperature of rain that fell on the reef and the resulting surface seawater temperature. It was apparent that it was not the amount of rainfall but *when* the rainfall occurred that led to detectable DMS_a spikes from the coral reef.

Comment 7:
Why didn't the authors play a bit with their results, for example looking at forward trajectories to see where the DMS ends or scaling up to the entire GBR?

Reply:
A few forward trajectories were made to observe air mass transport away from Heron Island. The reason these forward trajectories were prepared was to examine where Wedge-tailed Shearwaters (Mutton Birds) that nest on Heron Island might be going to find food. The forward trajectories indicated that if they flew with the wind they would often travel to the Swain Reefs, an extensive reef system to the north of Heron Island (seen in Fig. 2). If this forward trajectory analysis is extended to transport of DMS_a spikes from Heron reef it is possible that the DMS_a oxidation products might contribute to CCN formation over the Swain Reefs. We do not present evidence in the manuscript to support this possibility and the lead author is reluctant to extrapolate or scale up our results obtained at Heron Island on the southern GBR to the entire 2,300 km length of GBR. The GBR stretches 13 degrees of latitude along the Queensland coastline and it is risky to assume that processes operating in the northern GBR are the same as those on the southern GBR. The stark contrast in the extent of coral bleaching on the northern GBR compared to the minimal bleaching on the southern GBR during the summer of 2015-16 is a recent pertinent example of differences that can occur along the length of the GBR. Our manuscript was previously submitted to another journal and it was criticised by each referee for the suggestion that the coral reef DMS_a spikes observed at Heron Island on the southern GBR may occur over the entire GBR leading to formation of low-level marine clouds that possibly constitutes a regional climate feedback. At the present time that hypothesis remains speculative and much more research is required to determine if the GBR is a climatically influential source of marine aerosol, as stated in the last sentence of the conclusion.

Comment 8:
How was H (or MLD??) actually determined? And why do the authors call it MLD? This is terminology used more for water mixed layers. Why not always say H? Or are these values somehow different?

Reply:
Atmospheric MLDs were obtained using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model developed by NOAA's Air Resources Laboratory, as stated in Section 2.2 of the manuscript. The model, which is described by Stein et al (2015), uses sophisticated computations of atmospheric transport and mixing.

The referee may be more familiar with the MLD when used in the marine context; however, meteorologists and atmospheric scientists also use this terminology to refer to the region of the lower troposphere immediately above the surface where there is nearly constant potential temperature and specific humidity with height. As in the ocean, this atmospheric zone is characterised by turbulence resulting in a stable vertical temperature profile. Given that the MLD terminology may present confusion for marine scientists, the atmospheric MLD will be referred to as the mixed layer height (MLH) in the revised manuscript, representing the height above the surface of the convective mixed layer or the convective boundary layer.

The MLH is the major part of the marine boundary layer (MBL), which is the height of the atmospheric mixed layer from the ocean surface to a capping inversion, referred to in the manuscript as the entrainment zone. The boundary between the convective mixed layer below and the warmer layer above is marked by the base of the clouds. In Eqn. 1, *H* describes the mean height of the MBL during each campaign, where as the MLH refers to the height of the MBL at noon for each day during each campaign. Thus, *H* and MLH are not interchangeable descriptors in the manuscript.

The authors thank the referee for commenting on the manuscript to improve its content.

Replies to Referee #2

Comments on Section 2: Method
The description of the measurement procedure is insufficient. More details are necessary to understand how atmospheric DMS was measured, e.g. what is the cryogenic trap consist of, is the DMS preconcentrated and trapped before analysis? Is it right that the inlet of the measurement device is around 100 m away from the coral reef? If is it so how you can be sure that the DMSa you measured is directly emitted by the reef.

Reply:
In order to minimise the length of Section 2: 'Methods', a reference is provided to a 2015 publication that gives a complete description of the instrumentation with a detailed analysis of its measurement uncertainty. We appreciate that the referee would like more methodological information provided in this results focussed paper, so it will be included in the revision. Answers to the particular questions posed are as follows: In order to obtain detectable quantities for chromatographic analysis it is necessary to pre-concentrate DMS_a onto a suitable adsorbent, or directly capture it in a cryogenically cooled trap (cryotrap). The cryotrap used with the automated GC-PFPD was constructed by passing 1.6 mm diameter Teflon tubing through ~50 cm of copper tubing of 2.0 mm internal diameter, and bending it into a loop. The cryotrap was immersed in liquid nitrogen during the sample loading period.

The inlet for the automated GC-PFPD was positioned at the highest point as close as possible to the coral reef, this being the roof-top of the station laboratory. This inlet was ~100 m from the reef flat on the southern side of the island. DMS was not liberated from the island; the DMS_a measured was derived from the marine environment because DMS is a marine-generated biogenic product. As explained in the manuscript, there was a continuous oceanic DMS_a signal derived from phytoplankton and other pelagic marine biota, while occasional DMS_a spikes were observed that were inconsistent with the usual wind speed driven physical processes that exchange DMS from the ocean surface. This is the objective of the manuscript, i.e. to explain at length why these spikes could be attributed to DMS emissions from the coral reef. In Section 3 of the manuscript we present a detailed analysis of the accompanying meteorological measurements, tidal information and air parcel back trajectories to provide compelling evidence that these DMS_a spikes came from the coral reef.

Comment:
Give more details about how you determined low and high tides. You give even a negative value (p6 line 18). Did you use the height of the reefs as a zero-point?

Reply:
As explained in Section 2.1, tidal information was sourced from predictions provided by the National Tidal Unit of the Australian Bureau of Meteorology (BoM). Australian tidal authorities have adopted a 20-year tidal datum epoch from 1992 to 2011 as the basis for calculating tidal planes. When the low water calculation falls below the datum it is given a minus value. Low tide heights given in the manuscript are reported as specified by the BoM. The time of the dry season campaign in 2013 was planned to coincide with the very low (*spring*) low tides that occur in July. It must be understood that tidal heights and times are predictions. The BoM clearly states that tidal predictions for Heron Island are based on limited observations and are, therefore, of secondary quality. The times predicted for high and low tides at this location are thus unlikely to be accurate because of the limited observations. As explained in Section 2.1, several site-specific observations of seawater drainage from the Heron Island reef flat showed that low tides consistently occurred +1.25 h after the predicted times, so tide times were adjusted accordingly. The observed delay from predicted low tide times might be due to the particular geomorphology of the reef flat in combination with possible drainage effects caused by the channel constructed to allow ship access to the island wharf. Accurate specification of the time of low tide was more important than the actual height of the low tide to temporally link our DMS_a measurements at Heron Island.

Comment:
In section 2.2 "Flux calculation" you introduced the mass balance equation. Did you perform an error estimation of the different parameter of the equation? Did you estimate the variability of the parameter over time? A mass balance calculation can exhibit many errors due to uncertainties of the different parameter and their variability over time. You have to discuss in more detail that the different parameters you are used are reasonable.

Reply:
Section 2.2 introduces the photochemical ambient mass balance equation (Eq. 1) and the input variables used to calculate F_{DMS}. Eq. 1 is applied to estimate the long-term seasonal DMS emission fluxes during each campaign at Heron Island. The input values entered into Eq. 1 are, therefore, representative average values, which dampens out short-term variability. A large part of Section 3.3 in the 'Results and Discussion' is devoted to providing details of how these representative input values were obtained, to show that they are reasonable input values. A propagation of error analysis using the photochemical mass balance approach for DMS air-sea flux has shown that the overall uncertainty in flux estimates is in the range of 31-51% (Avg of 41%, Chen et al., 1999), which is said to compare favourably with other methods. Their sensitivity analysis indicated that F_{DMS} was mainly influenced by the DMS vertical profile and the diel profile for OH. Sensitivity analysis is the investigation of how the uncertainty in the output of a mathematical model or equation can be apportioned to different sources of uncertainty in its inputs. In other words, sensitivity analysis identifies which variables can cause the largest deviations in the outcome. Uncertainty estimations and sensitivity analyses are often run in tandem. In accordance with the uncertainty analysis of Chen et al., (1999) we have quoted an uncertainty of ~50% for the seasonal flux estimates at Heron Island. The following information is provided to satisfy the referee's concerns regarding the variability of each input value in Eq. 1, and will be incorporated into the revised manuscript.

1. [DMS_a]. It is stated in Section 3.3 that the number of DMS_a measurements is sufficiently large that the mean concentrations for each campaign are expected to be representative of DMS_a in the MBL over Heron Island during the wet and dry seasons. Table 1 shows that the mean and SD for DMS_a during the 2012 wet and 2013 dry seasons is 3.9 ± 1.5 ($n = 651$) and 1.3 ± 1.6 ($n = 923$) nmol m^{-3}, respectively.

2. [DMS_t]. This is reported to be typically 10% of MBL concentrations. The sensitivity of this variable in Eq. 1 is small. When values for [DMS_t] of 5% and 20% of MBL concentrations are entered into Eq. 1, F_{DMS} varies by only 1.4-2.6%.

3. *H*. The average midday mixed layer height (MLH) during the 2012 wet and 2013 dry seasons is 977 m (± 231m, range 680 to 1460 m, n = 15 days) and 786 m (± 290m, range 346 to 1312 m, n = 19 days), respectively. It is noted that these seasonal values determined using the HYSPLIT model are consistent with measurements made on-site at Heron Island during the June 2009 dry season and February 2010 wet season.

4. [*OH*]. Values of 1.8 x 10^6 (2012 wet season) and 1.6 x 10^6 molecules cm^{-3} (2013 dry season) were applied according to reported average values over the South Pacific Ocean, in conjunction with a comparison of average solar irradiance we measured at Heron Island in the different seasons.

5. *K*. A value of 6.5 x 10^{-12} cm molecule^{-1} s^{-1} was applied, this being the sum of the abstraction and addition rate reactions of OH with DMS at 25°C and 1 atmosphere pressure, which represents the temperature and pressure during both campaigns. This value for *K* is a well established value used in atmospheric models.

6. E_v. A value of 0.004 m s^{-1} was applied according to average data obtained from Lagrangian experiments in the southern hemisphere remote MBL. This entrainment rate from the lower troposphere into the MBL is typically very low, and when this E_v value is varied by ±100% in Eq. 1 it has a sensitivity effect of 12-19% on F_{DMS}.

Comments on Section 3: Results and Discussion:
An overall description of your data is missing. What are the general patterns of your data? Is there a general trend? Additionally, you start directly with the interpretation of the peaks without any introducing sentences. Say in the beginning shorty what you have done and why and what you found.

Reply:
An introductory paragraph that provides a general description and summary of the results will be included at the beginning of Section 3: 'Results and Discussion' in the revised manuscript. This introductory paragraph will not repeat information given in Section 4: 'Conclusions'.

Comment:
In the first paragraph (p5 l3-10) you mentioned many time points which is hard for the reader to follow. Additionally, the different time points are hard to see in fig. 3. Maybe show clearly in the fig the time steps you described in detail and maybe reword the text a little bit for a better understanding for the reader.

Reply:
The referee has previously asked how can we be sure that the DMS_a we measured is directly emitted from the reef? The information on P5, L3-10 is provided in sufficient detail to fully describe the circumstances leading to the DMS_a spike shown in Fig.3b, which provides compelling environmental evidence that the spike was derived from the platform reef surrounding Heron Island. This information is not hard to follow if carefully read while also carefully referring to Fig. 3b. When Fig. 3 is viewed at full screen width (e.g. 177% for PDF) the time points described can be clearly seen for reference to the textual description. The authors do not want to add any more detail to Fig. 3, such as notation points or description boxes, which will only serve to clutter the results presented. The information discussed in the manuscript on P5, L3-10 will be reviewed to see if it can be stated any more succinctly without removing any of the details required to fully describe the circumstances leading to the DMS_a spike.

Comment:
P6 L3-15: Why you talked in this paragraph about the measurements on 16 March and before about data from 17 March. Why it is not in chronological order?

Reply:

The manuscript will be revised so that each DMS_a spike detected during the wet season campaign is discussed in chronological order in separate paragraphs to assist reader interpretation.

Comment:

The mixed layer depth (MLD) you mentioned in the text (p7 line 28) is it in the water or in the atmosphere. Is it the same like the MBL? The MLD is generally used for the water. Please clarify.

Reply:

The referee may be more familiar with the MLD when used in the marine context; however, meteorologists and atmospheric scientists also use this terminology to refer to the region of the lower troposphere immediately above the surface where there is nearly constant potential temperature and specific humidity with height. As in the ocean, this atmospheric zone is characterised by turbulence resulting in a stable vertical temperature profile. Given that the MLD terminology may present confusion for marine scientists, the atmospheric MLD will be referred to as the mixed layer height (MLH) in the revised manuscript, representing the height above the surface of the convective mixed layer or the convective boundary layer. The MLH is the major part of the marine boundary layer (MBL), which is the height of the atmospheric mixed layer from the ocean surface to a capping inversion, referred to in the manuscript as the entrainment zone. The boundary between the convective mixed layer below and the warmer layer above is marked by the base of the clouds.

Comment:

Can you discuss in the results and discussion section the stress level and health conditions of the coral reef you investigated? Is the reef already affected by global change (temperature, pH), has it a high biodiversity, was coral bleaching observed? Can these factors affect the DMSP and DMS production? Are the events observed during the measurements (very low tides, reef exposure to the air, rainfall on the corals) normal events which occurred on a regular base or were these extreme and seldom events?

Reply:

Complementary measurements of the store of DMSP in *Acropora aspera* branching coral during the campaigns in 2012 and 2013 indicated that this coral growing on the platform reef surrounding Heron Island was not temperature stressed and appeared to be in good health. This supporting information will soon be reported in Analytical and Bioanalytical Chemistry (doi:10.1007/s00216-016-0141-5). There was no evidence of coral bleaching in the 2012 late summer wet season to affect the usually high biodiversity. A note about this supporting information relating to the health of *Acropora aspera* growing on the Heron Island reef flat will be incorporated into the revised manuscript. The southern GBR has been less affected by warming sea surface temperatures than the northern GBR. This was dramatically shown in the previous 2015-16 summer when a strong *El Niño* Southern Oscillation event enhanced abnormally warm sea surface temperatures, resulting in extensive bleaching to the northern third of the GBR. There was a gradation of coral bleaching mortality, ranging from high in the northern GBR to virtually none on the southern GBR where the Capricorn Bunker Group of coral reefs is situated. We observed a few instances of coral colony bleaching on the Heron Island reef flat in February 2016, which was not observed in March 2012. The GBR Marine Park Authority provides further information about this north to south gradation of coral bleaching during the 2015-16 summer at this web link http://www.gbrmpa.gov.au/media-room/coral-bleaching

Coral reefs are regularly aerially exposed; the extent of that exposure depends on the tidal phase. Very low *spring* tides are experienced in the middle (austral winter) and end of the year around Christmas (austral summer) along the Australian east coast. The very low *spring* tides in July during the 2013 dry season campaign were not unexpected for that time of the year. Rainfall on an aerially exposed coral reef is an unpredictable and irregular event. This is expected to be one of the factors leading to the intermittent nature of the DMS_a spikes detected at Heron Island. As is evident from the entire winter dataset, the intensity of the DMS_a spike detected in the early evening of 25 July 2013 was a unique event, and it was good fortune to be on-site at that time with equipment to detect and quantify it.

Comment:

It would be also interesting to measure directly DMS emissions by the corals in incubation experiments under different environmental conditions to have the direct evidence that the DMSa is coming from the corals directly. It is clear that this cannot be part of this study but is interesting to investigate in future studies.

Reply:

Previously, a number of coral chamber studies have been conducted to investigate the release of DMS from coral into the chamber headspace under varying conditions. The following publications describe laboratory studies where coral (or its endosymbiotic algae) were placed into chambers and DMS emission from the coral was measured:

Fisher and Jones (2012), *Biogeochemistry*, doi:10.1007/s10533-012-9719-y

Deschaseaux et al., (2014), *Journal of Experimental Marine Biology and Ecology*, doi:10.1016/j.jembe.2014.05.018

Deschaseaux et al., (2014), *Limnology and Oceanography*, doi:10.4319/lo.2014.59.3.0758

Swan et al., (2016), *Journal of Atmospheric Chemistry*, doi:10.1007/s10874-016-9327-7

Hopkins et al., (2016), *Scientific Reports*, doi:10.1038/srep36031

In each of these laboratory chamber studies it is apparent that the coral or its algal symbionts were the source of the DMS measured. What is unique about the manuscript we present here for publication in Biogeosciences is that it is the first study conducted on-site at the GBR with sufficient sampling frequency to environmentally characterize coral reef DMS emissions providing convincing evidence that the coral reef is a source of DMS to the natural atmospheric environment. As stated in the conclusion, what is now required is further on-site continuous sampling of DMS_a at the GBR to more closely examine factors that cause coral reefs to emit DMS to the atmosphere. Chemical ionisation mass spectrometry is recommended because it provides higher temporal resolution than the automated GC we used for the 2012 and 2013 campaigns at Heron Island.

Comment:

Figures: Fig 1 is not necessary to understand the paper and is not discussed in detail in the paper. It has not important new information. I recommend to delete it.

Reply:

The conceptual model shown in Fig.1a concisely describes the factors and processes controlling DMS_a derived sulfate aerosol production over the GBR. In particular, it shows the oceanic DMS_a source that provided the baseline DMS_a signal shown in Figs 3&6, and how rainfall can induce emissions of DMS from the coral reef at low tide. Fig. 1a also depicts the atmospheric processes leading to formation of CCN, providing scattering of solar radiation back into space. Fig. 1b is referred to on P6, L11 to pictorially describe the Capricorn Bunker Group of coral reefs to the SE of Heron Island, which is important to assist the discussion about the indicated reason for the largest DMS_a spike detected during the 2012 wet season campaign. Another referee of our manuscript has commented that Fig. 1b is a ‘great’ figure that provides a compelling picture of cloud formation processes in operation over the southern GBR. The authors would like to retain Fig. 1 in the manuscript because we consider that it provides a useful pictorial to support information provided in the introduction and the discussion of results.

Comment: Figures 3 and 6 are hard to read. The grey, green and blue colors are hard to distinguish and there are too many parameters in one graph. Additionally, you discussed a lot time points but they are hard to see in the sub-panels. See comment above.

Reply:

As previously explained to the referee, the time points shown in Figs 3&6 can be clearly seen for reference to the textual description when viewed at full screen width (e.g. 177% for PDF). The four colours chosen for DMS_a, WS, tide height and rainfall were selected to provide good contrast between each parameter. Figs 3&6 may appear to be “loaded” with data but each of the parameters shown are key to understanding the evolution of the DMS_a spikes and the background DMS_a signal. For example, the alignment of WS with the background DMS_a signal shown in Fig 3a provides a convincing picture that it is the oceanic-derived DMS_a signal because WS is the major factor associated with mass transfer of DMS from the ocean surface to the atmosphere. If any of the four parameters shown in Figs 3&6 were to be removed from the time plots it would be impossible to adequately explain the reasons for the DMS_a spikes detected from the coral reef. This complexity of interacting processes leading to the DMS_a spikes from the coral reef demands that Figs 3&6 highlight these four parameters even if they appear “busy”. With this in mind, the extracted time series shown in Figs 3b&c and 6b&c were generated to provide additional clarity of the particular events discussed in the manuscript.

The authors thank the referee for commenting on the manuscript to improve its content.

<u>List of relevant changes made to revised manuscript</u>

P11, L10: New reference included

P11, L28: New reference included

P12, L18-29: Additional information about of DMS_a sampling methodology included as requested by both referees

P13, L22: The word ‘atmospheric’ included to emphasise that Eq. 1 relates to the atmospheric environment rather than the marine environment

P13, L31: ‘depth’ changed to ‘height’ to respond to comment 8 by Ref#1 and similar comment by Ref#2

P14, L9-26: Introductory paragraph added to respond to comment 5 by Ref#1 and similar comment by Ref#2. New reference included at the end of this paragraph to provide information about the state of health of coral growing on the Heron Island reef flat in the late summer wet season of 2012, as requested by Ref#2

P16, L8-13: Rearrangement of section 3.1 to put all information in chronological order as requested by Ref#2

P17, L21-33: Rearrangement of section 3.3 to improve reader interpretation with inclusion of sensitivity analysis information for input variables in Eq. 1

P18, L3-4: Inclusion of sensitivity analysis information for input variable E_v in Eq. 1

P18, L6: Clarification of input variable K in Eq. 1

P19, L34: Inclusion of additional funding information

P20-23: References. EndNote X3 was used to insert and format references. The reference listing was moved from the end of the manuscript to P20, so the entire reference listing is marked-up in red in the revised manuscript.

P24, Table 1: ppt mixing ratios have been included with DMS_a molar concentrations to partly respond to comment 4 by Ref#1

Coral reef origins of atmospheric dimethylsulfide at Heron Island, southern Great Barrier Reef, Australia

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Abstract Atmospheric dimethylsulfide (DMS_a), continually derived from the world's oceans, is a feed gas for the tropospheric production of new sulfate particles, leading to cloud condensation nuclei that influence the formation and properties of marine clouds, and ultimately the Earth's radiation budget. Previous studies on the Great Barrier Reef (GBR), Australia, have indicated coral reefs are significant sessile sources of DMS_a capable of enhancing the tropospheric DMS_a burden mainly derived from phytoplankton in the surface ocean; however, specific environmental evidence of coral reef DMS emissions and their characteristics is lacking. By using on-site automated continuous analysis of DMS_a and meteorological parameters at Heron Island in the southern GBR, we show that the coral reef was the source of occasional spikes of DMS_a identified above the oceanic DMS_a background signal. In most instances, these DMS_a spikes were detected at low tide under low wind speeds, indicating they originated from the lagoonal platform reef surrounding the island, although evidence of longer range transport of DMS_a from a 70 km stretch of coral reefs in the southern GBR was also observed. The most intense DMS_a spike occurred in the winter dry season at low tide when convective precipitation fell onto the aerially exposed platform reef. This co-occurrence of events appeared to biologically shock the coral resulting in a seasonally aberrant extreme DMS_a spike concentration of 45.9 nmol m^{-3} (1122 ppt). Seasonal DMS emission fluxes for the 2012 wet season and 2013 dry season campaigns at Heron Island were 5.0 and 1.4 µmol m^{-2} d^{-1}, respectively, of which the coral reef was estimated to contribute 4 % during the wet season and 14 % during the dry season to the dominant oceanic flux.

1 Introduction

Dimethylsulfide (DMS) is the major volatile sulfur compound released from the global oceans (Andreae and Raemdonck, 1983). The primary source of DMS is dimethylsulfoniopropionate (DMSP) which is a metabolite of many marine phytoplankton (Stefels, 2000). DMSP is also present in coral tissue, its symbiotic microalgae, and coral mucus (Broadbent and Jones, 2004). When DMS diffuses from the coral biomass to the water column it is then available for exchange across the air-sea interface which is mostly driven by wind (Ho and Wanninkhof, 2016). The shallow water column over a coral reef has a lower thermal capacity than the open ocean so it is subject to enhanced heating by incident solar radiation (McGowan et al., 2010). This will lower the diffusivity resistance for mass transfer of DMS through the seawater surface film, as described by the Schmidt number, which is temperature dependent (Saltzman et al., 1993). This thermal effect, which can enhance the air-sea exchange of DMS (Yang et al., 2011), is expected to be pronounced during daytime low tides over coral reefs when elevated atmospheric DMS (DMS_a) concentrations have been observed (Jones and Trevena, 2005). Additionally, DMS may be directly exchanged to the atmosphere from the coral surface if aerially exposed at low tide (Hopkins et al., 2016). These particular characteristics of coral reefs suggest that they could be 'hotspots' for production of DMS_a oxidation products contributing to the sulfate component of new aerosol particles measured from the Great Barrier Reef (GBR) (Modini et al., 2009; Vaattovaara et al., 2013). These new sulfate particles typically have hygroscopic properties that allow them to grow to a critical threshold diameter capable of acting as cloud condensation nuclei (CCN, D_p ~100 nm), which can produce high-albedo low-level marine clouds with numerous small droplets that efficiently scatter sunlight and reflect it back to space (Ayers and Gillett, 2000) (Fig. 1a). Since these high-albedo clouds are capable of altering incident solar radiation, it was hypothesized almost thirty years ago that biological DMS production and its subsequent air-sea exchange leading to sulfate aerosol and CCN might generate a climate feedback loop (Charlson et al., 1987); however, two decades of intensive Earth Systems research has provided a lack of evidence for DMS dominated control of CCN leading to global climate regulation (Quinn and Bates, 2011). Nevertheless, since DMS is an important trace gas that has the potential to play a significant role in the Earth's radiation budget, there is continuing interest in measuring DMS in the biosphere for the estimation of sea-to-air emission fluxes to assist climate and Earth System modeling (Lana et al., 2011).

Even though the total area of the world's coral reefs amount to ~0.2 % of the entire marine environment, the GBR is classed as the single largest living organism on Earth that stretches ~2,300 km along the NE coast of Australia, and covers an area of ~344,400 km^2 that can be seen from space (Hutchings et al., 2008). Considering these dimensions, the GBR is clearly a significant marine ecosystem that has been under-studied in comparison to the surface ocean for DMS production. Chamber experiments have provided evidence that *Acropora* spp. of branching coral can be a source of DMS_a in the natural reef environment. This genus of reef-building coral, which is dominant throughout the GBR (Wild et al., 2004), has been found to liberate DMS to the headspace of sealed chambers when submersed in seawater and bubbled with air (Deschaseaux et al., 2014; Fischer and Jones, 2012). A more recent chamber study that examined *Acropora* coral in filtered seawater detected DMS in the chamber headspace only when the coral was visibly coated in mucus or releasing mucus strands (Swan et al., 2016a), which indicates that coral reefs are likely to be intermittent sources of DMS_a. There is currently insufficient data available from previous GBR DMS_a field studies to environmentally assess that recent chamber observation. The few previous field studies that have measured DMS_a over the GBR (Broadbent and Jones, 2006; Jones and Trevena, 2005) employed gold-wool chemi-adsorption (Barnard et al., 1982; Kittler et al., 1992), a low-frequency grab-sampling technique.

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While the investigators of those previous field studies reported that the GBR appears to be a significant source of DMS_a, their low frequency sampling technique did not provide sufficient data to characterize coral reef DMS emissions. In this study we used an automated gas chromatograph (GC) with a higher sampling frequency to examine short-term variations in DMS_a over 2-3 week periods at a coral cay in the southern GBR. The objective of this study was to gather specific environmental evidence of coral-derived DMS emissions from the GBR, and to determine the intensity, frequency and significance of those reef emissions in the wet and dry seasons at the Tropic of Capricorn.

2 Methods

2.1 Location and sampling procedures

The automated GC was used to continuously measure DMS_a at the Heron Island Research Station (23.44°S, 151.91°E), situated ~80 km off the east Australian coastline, in the Capricorn-Bunker Group of southern GBR reefs (Fig. 2). Heron Island lies at the western end of a surrounding 27 km^2 lagoonal platform reef. The reef lagoon has a cover of ~15 % coral and 85 % permeable carbonate sands (Eyre et al., 2013). Two campaigns were conducted: 6-20 March 2012, and 18 July to 5 August 2013, providing a comparison of DMS_a in the austral warmer wet (November to March) and cooler dry (April to October) seasons that are recognised at the Tropic of Capricorn.

DMS_a was sampled through Teflon™ tubing via a high-capacity oxidant scrubber composed of 1 % w/v sodium ascorbate and glycerol impregnated into a glass-fibre filter. The sample line intake was fixed to the roof of the Research Station laboratory; the intake was shielded from rain and had a clear line of sight to the reef flat ~100 m away. Surface-level marine air was drawn through the sampling system at a flow rate of ~260 mL min^{-1} using a single-stage diaphragm vacuum pump. The air was drawn into a cryogenically cooled trap (cryotrap) that was constructed by passing 1.6 mm diameter Teflon tubing through ~50 cm of copper tubing of 2.0 mm internal diameter, and bending it into a loop. A sample collection time of 14.4 min was used to deliver 3.72 L of air into the cyrotrap. This volume of air was required to concentrate sufficient DMS_a for chromatographic analysis, providing a 0.1 nmol m^{-3} (2 ppt) limit of reporting. A custom-built autosampler controlled the movement of the cryotrap, actuation of two gas valves, and started the GC. This automated GC was fitted with a pulsed flame photometric detector (Cheskis et al., 1993), and had a cycle time of 26 min. Specified DMS_a concentrations are reported at the mid-time of the 14.4 min collection period. The relative expanded measurement uncertainty was 13 % (k = 2 for a 95% confidence level). Calibration was achieved using permeated ethyl methyl sulfide. A complete description of the configuration, operation, calibration and measurement uncertainty of the automated GC DMS_a sampling system is reported elsewhere (Swan et al., 2015).

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A wireless automatic weather station (AWS, model XC0348, Electus Distribution, Rydalmere NSW, Australia) was mounted above the roof-line of the research station laboratory within 1 m of the air intake used to sample DMS_a. This AWS provided data for wind speed (WS), wind direction (WD), rainfall, indoor and outdoor air temperature, humidity and barometric pressure, which were logged at 15 minute intervals. The accuracy of the AWS was specified as: WS ± 1 m s^{-1} (WS < 10 m s^{-1}) and ± 10 % (WS > 10 m s^{-1}), relative humidity ± 5 %, temperature ± 1°C and pressure ± 3hPa. Water vapour mixing ratios were calculated from the AWS data using reported formulas (Vaisala, 2013). A pyranometer was placed on the laboratory roof next to the AWS (HOBO pendant sensor, Onset Computer Corp., Bourne, MA, USA). It logged solar irradiance (spectral range 300 - 1100 nm) every 15 min and was specified by the manufacturer to have an upper light intensity limit of 323,000 lumens m^{-2} (Lux), which is equivalent to ~6000 µmol m^{-2} s^{-1} or 3.613 x 10^{21} photons m^{-2} s^{-1}. The photon flux (µmol m^{-2} s^{-1}) measured with this sensor was converted to radiometric energy (J m^{-2} s^{-1} or W m^{-2}) using a 0.342 J μmol^{-1} multiplication factor (Thimijan and Royal, 1982). To complement the AWS data, daily backward trajectory air parcel information was obtained using the NOAA Air Resources Laboratory HYSPLIT transport and dispersion model (Stein et al., 2015). Mean surface layer pressure synoptic charts at 00:00 UTC and 12:00 UTC were also obtained from the Australian Bureau of Meteorology (BoM). Tidal information was sourced from predictions provided by the National Tidal Unit of the Australian Bureau of Meteorology. Several site-specific observations of seawater drainage from the Heron Island reef flat showed that low tides consistently occurred +1.25 h after the predicted times; tide times were adjusted accordingly. All specified dates and times are Australian Eastern Standard Time.

2.2 Flux calculations

Seasonal DMS emission fluxes for the wet season (14 day) and dry season (18 day) campaigns at Heron Island were calculated using the atmospheric photochemical ambient mass balance equation applied by *Ayers et al*., (1995) under clean marine conditions:

$$\frac{d[DMS]}{dt} = \frac{F_{DMS}}{H} - K[OH][DMS] + \frac{E_v([DMS_t]-[DMS])}{H} \quad (1)$$

where F_{DMS} is the flux of DMS; [DMS] is the mean concentration of DMS_a in the marine boundary layer (MBL); [DMS_t] is the concentration of DMS_a in the atmospheric transition layer or entrainment zone, E_v is the MBL - lower troposphere entrainment velocity; H is the mean height of the MBL; [OH] is the diurnally averaged concentration of hydroxyl radical;

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and K is the first order overall rate constant for reaction of OH with DMS. The HYSPLIT transport and dispersion model was used to obtain midday mixed layer heights, which were averaged for each season to provide input values for H. Seasonal contributions of the coral reef to F_{DMS} at Heron Island were estimated from the difference between fluxes calculated using mean and median DMS_a dataset concentrations.

3 Results and Discussion

3.1 Wet season 2012

Here we describe four instances of clearly observed DMS_a spikes in the dataset of results obtained during the wet season campaign. Meteorological conditions, tidal information and air parcel back trajectories are examined to provide detailed information of the circumstances leading to these DMS_a spikes. These spikes were superimposed on the oceanic background DMS_a signal derived from phytoplankton and other pelagic marine biota. This background signal was observed as a continuum coupled to WS (Fig. 3a), which provides kinetic energy for factors that directly drive DMS air-sea exchange such as turbulence and micro-breaking waves (Huebert et al., 2010). However, the four distinct spikes of DMS_a (10, 14, 16-17 March) were notably uncoupled from WS suggesting that they were derived from a source other than the open ocean. By closely examining the environmental conditions when each DMS_a spike was detected it was possible to attribute three of these intermittent spikes to DMS emissions from the platform reef surrounding Heron Island. In these instances, each spike was detected at low tide under WS of < 2 m s^{-1}, indicating that the prevailing SE trade winds (Fig. 2) acted as a diluent to disperse plumes of DMS_a emitted from the coral reef. It is, therefore, likely that the SE trade winds masked other instances of DMS emissions from the platform reef by diluting the DMS_a to the point that it was indistinguishable from the oceanic background DMS_a signal. The circumstances surrounding the largest wet season DMS_a spike on 16 March (Fig. 3a) were unique, suggesting that it resulted from longer range transport of DMS_a derived from the Capricorn Bunker Group of coral reefs to the SE of Heron Island (Fig. 1b). We saw no evidence of coral bleaching on the Heron Island platform reef during the summer wet season of 2012 to affect its usually high biodiversity. Complementary measurements of DMSP concentrations in *Acropora aspera* branching coral growing on the Heron Island reef flat in March 2012 indicated that the coral reef was in good health and not temperature stressed (Swan et al., 2016b).

The first of the DMS_a spikes indicated to be derived from the platform reef surrounding Heron Island was detected on 10 March between 3:33 to 6:08 under low WS of 0 - 0.7 m s^{-1}. In the early morning of the 10 March back trajectories show that high altitude (+1000 m) continental air was directed to Heron Island (Fig. 4). This dry free tropospheric non-marine air flow was characterised by a rapid drop in the water vapour mixing ratio from 17.4 to 13.0 g kg^{-1}, and also resulted in the lowest DMS_a wet season concentration of 0.6 nmol m^{-3} which occurred shortly after high tide under calm conditions. As the tide dropped, the DMS_a steadily increased, and in the period 10 March 3:59 to 5:42 the anemometer was becalmed. Between 3:07

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Deleted: , where the circumstances surrounding this event implicates the Heron Island reef flat as the source of the DMS_a spike and 3:33 the DMS_a rapidly increased from 2.1 to 6.2 nmol m^{-3} and, thereafter, five consecutive DMS_a concentrations of ~6 nmol m^{-3} were recorded over a period of nearly two hours when WS was 0 m s^{-1}. The low tide at 4:50 occurred near the middle of this period of no air movement. A peak DMS_a concentration of 6.4 nmol m^{-3} was recorded at 5:16; however, it decreased to 2.6 nmol m^{-3} by 7:00 with the onset of a southerly change at 6:36 when WS sharply increased from 0.3 to 2.4 m s^{-1}. The WS continued to increase in strength, and by 10 March 7:26 DMS_a had returned to the background concentration of 2.2 nmol m^{-3} (Fig. 3b). These observations indicate that the relatively low WS of 2.4 m s^{-1} was sufficient to rapidly dilute the DMS plume with marine air containing less DMS_a. The meteorological conditions under which this DMS_a spike occurred provide compelling evidence that it was a point source emission derived from the lagoonal platform reef surrounding Heron Island.

The second DMS_a spike was observed on 14 March at 21:12, which resulted in a peak DMS_a concentration of 10.6 nmol m^{-3}. This DMS_a spike appeared to result from rain enhanced air-sea exchange of DMS from the Heron Island reef flat at low tide. The increase in DMS_a began in the evening at 19:02 and returned to the background level at midnight. At the start of this event the WS was between 3 and 4 m s^{-1}, and the background oceanic-derived DMS_a was ~4 nmol m^{-3}. There had been no rain during the day; however, between 19:28 and 22:04 a local convection generated storm delivered a total of 12 mm of precipitation which fell during a 0.8 m low tide. The DMS_a rose sharply from 3.9 to 10.6 nmol m^{-3} in a 2.5 h period as a result of these two simultaneous events. Three steps were observed in this DMS_a spike and appeared to be linked to variations in rainfall intensity and WS. After the onset of the rainfall there was a pause in the rain and the WS increased to 5.1 m s^{-1} resulting in a pause in the rise of DMS_a; the WS then dropped to 2 m s^{-1} as the precipitation intensity increased, resulting in the next rise in the DMS_a spike. When the rainfall was most intense the WS had dropped to 1.4 m s^{-1} and this resulted in the peak DMS_a concentration which also occurred at the tidal minimum. As the rain eased, the WS again increased and the DMS_a concentration rapidly decreased with the rising tide, returning to the background concentration of 4.3 nmol m^{-3} at 1:05 on 15 March. This combination of a 0.8 m low tide coupled with a 2.5 h convective rainfall event resulted in an increase of 6 nmol m^{-3} above the prevailing background ocean DMS_a signal. The peak DMS_a concentration which co-occurred with the lowest recorded WS was apparently due to reduced mixing of the rain-enhanced local DMS_a plume from the reef with background marine air containing less DMS_a. Later, on 15 March between 12:40 and 14:50, another local convection storm delivered 7.2 mm of rain under a higher average WS of ~4 m s^{-1}. This later rain event did not coincide with low tide and did not induce a detectable DMS_a spike from the Heron Island reef flat (Fig. 3c).

The third DMS_a spike during the wet season was detected on 16 March at 6:27, resulting in the highest recorded concentration of 11.5 nmol m^{-3} in the wet season dataset. This DMS_a spike lasted for 8.4 h, was a factor of 3.3 above the oceanic background level at its peak, and according to back trajectories occurred during a low-elevation marine air stream from a SE direction (Fig. 5). Unlike previous observations, this DMS_a spike started on a 2.5 m high tide and was rapidly decreasing by the time of the following 0.9 m low tide. WS data indicated that the DMS_a spike was not derived from wind enhanced air-sea exchange because DMS_a increased from 3.5 to 11.5 nmol m^{-3} as the WS eased from 4.1 to 3.1 m s^{-1}, and the DMS_a peak returned to the background DMS_a level as the WS increased from 3.4 to 5.8 m s^{-1} (Fig. 3c). According to back

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trajectories at that time the source of this long lasting maximum DMS_a spike in the wet season dataset is suspected to have originated from air that traversed the Capricorn Bunker Group, an extensive array of coral reefs to the SE of Heron Island that span a distance of ~70 km (Fig. 1b). This observation supports a previous report of elevated DMS_a in SE trade winds that travelled over dense coral biomass areas of the GBR and western Pacific Ocean (Jones and Trevena, 2005). Additionally, at a Queensland coastal site (24.21°S, 151.90°E) elevated new particle number concentrations, reflecting a strong nucleation event, were detected in an air stream that travelled over the Capricorn Bunker Group of southern GBR reefs on 30 March 2007 (Modini et al., 2009).

The fourth DMS_a spike which occurred between 21:20 16 March and 00:48 17 March (3.5 h duration), was observed as the WS abated from 3.4 to 0.7 m s^{-1} indicating that it did not result from increased air-sea exchange. The background DMS_a signal before and after this spike was, however, clearly decreasing with the abating WS (Fig. 3c). The peak DMS_a concentration of 8.2 nmol m^{-3} occurred at midnight on a 0.8 m low tide under a low WS of 1.7 m s^{-1}. These meteorological conditions again implicate the reef flat surrounding Heron Island as the source of this DMS_a spike, which was detected under relatively calm conditions when the water level over the reef was low.

3.2 Dry season 2013

During the dry season campaign at Heron Island, *spring* tides were experienced from 18 to 24 July with low tide heights ranging from -0.1 to 0.3 m. During these particularly low tides ten clearly defined DMS_a spikes of varying magnitude were observed above the background oceanic DMS_a signal. Three of these spikes were detected in WS exceeding 5 m s^{-1} which suggests that they were intense emission events from the lagoonal platform reef. An extreme DMS_a spike was detected in the early evening of 25 July when a convection storm deposited only 1.8 mm of rainfall onto the Heron Island reef flat when much of it was aerially exposed by a *spring* low tide of 0.2 m. Under this scenario, the background DMS_a concentration of 1.4 nmol m^{-3} at 17:26 increased to 45.9 nmol m^{-3} (1122 ppt) by 17:50 (Figs. 6a & 6b). This rain-reef-atmosphere interaction was characterized by a strong odour of DMS, and to our knowledge is the highest DMS_a concentration measured over a coral reef. It was also the sharpest DMS_a spike detected during both campaigns; the DMS_a returning to the background level within 1 h. This 45.9 nmol m^{-3} DMS_a peak concentration occurred under a low rain rate (1.5 mm h^{-1}) and one of the highest WS (9.5 m s^{-1}) measured during the dry season campaign. At this WS rain effects on air-water gas exchange are minor (Harrison et al., 2012) and cannot account for the sudden intensity of DMS_a observed. Since physical reasons alone cannot explain this extreme DMS_a spike, we propose that rainfall onto the aerially exposed coral reef induced a biological shock, where the coral reacted to a rapid decline in seawater salinity by utilizing intracellular DMSP to maintain osmotic pressure balance and to cope with the associated rapid decline in temperature (Stefels, 2000 and references therein). DMSP is recognized as an osmotically active intracellular compatible solute in unicellular algae that may act to buffer cell volume changes during the initial period after an osmotic shock (Kirst, 1996). Since unicellular algae (zooxanthellae) are abundant within the coral symbiosis, it is likely that corals use DMSP for osmotic regulation. Utilization of DMSP, a sulfonium zwitterion, for osmotic pressure balance could generate significant quantities of DMS as a metabolic by-product resulting in the extreme DMS_a spike observed, even under strong atmospheric mixing. It is suspected that the brevity of this DMS_a spike was because DMS was directly exchanged to the atmosphere from aerially exposed coral on the very low tide, and was rapidly diluted by horizontal advection under strong winds.

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3.3 Estimation of seasonal DMS flux

During both campaigns at Heron Island, daily backward trajectory air parcel analysis showed that clean marine air flows were received the majority of the time. Occasionally, when air was received from over the Australian continent, it was derived from high altitude (+1000 m), and was indicated to be clean free-tropospheric air. These conditions support use of the applied photochemical ambient mass balance Eq. (1) which specifies that DMS_a is predominantly removed from the clean MBL by reaction with OH. In polluted regions, where significant concentrations of NO_3 are often present, it is necessary to include NO_3, another DMS oxidant, in the mass balance equation used to determine DMS flux (Chen et al., 1999; Shon et al., 2005). Equation (1) balances factors that alter mean concentrations of DMS_a over time within seasonal average MBL box volumes. The MBL is composed of the surface layer, immediately above the sea, and the mixed layer (sub-cloud layer); it is through these layers that the ocean and the atmosphere are coupled. The mixed layer is capped by a transition layer that is ~100 to 200 m deep over tropical oceans (Johnson et al., 2001). This zone, often referred to as the entrainment zone, is characterised by a decrease in humidity together with a sharp increase in stability leading into the free troposphere (Clarke et al., 1998).

Mean concentrations of DMS_a measured in this study were 1.3 ($1\sigma = 1.6$, $n = 923$) and 3.9 nmol m^{-3} ($1\sigma = 1.5$, $n = 651$) for the dry and wet seasons, respectively (Table 1). The number of DMS_a measurements is sufficiently large that these mean concentrations for each campaign are expected to be representative of DMS_a in the MBL over Heron Island during the wet and dry seasons. The concentration of DMS_a in the entrainment zone is reported to be typically ~10 % of the MBL concentration (Ayers et al., 1995; Chen et al., 1999) so this percentage was applied to determine $[DMS_t]$. The sensitivity of this variable in Eq. (1) is low; when values for $[DMS_t]$ of 5% and 20% of MBL concentrations are entered into Eq. 1, F_{DMS} varies by only 1.4-2.6%. Average mixed layer heights (MLH) at noon were 977 m (± 231 m, range 680 to 1460 m, $n = 15$ days) and 786 m (± 290 m, range 346 to 1312 m, $n = 19$ days) during the 2012 wet season and 2013 dry season campaigns, respectively. These average values are consistent with a study of the MLH at Heron Island in June 2009 and February 2010, which ranged from 375 to 1200 m above the surface (MacKellar et al., 2013). Maximum MLHs were observed under stable anti-cyclone conditions, while minimum MLHs were observed during periods of heavy precipitation with convective downdrafts. Given that the MLH is the major part of the MBL, which is typically around 700 to 800 m (Stull, 1988); the average MLH values of 977 m (wet season) and 786 m (dry season) were, therefore, applied for H in Eq. (1). We were

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unable to measure the other input variables for Eq. (1) so representative values for the study location were derived from the literature. A value of 0.004 m s^{-1} was applied for E_v according to average data obtained from Lagrangian experiments in the southern hemisphere remote MBL (Wang et al., 1999). The entrainment rate from the lower troposphere into the MBL is typically low, and when E_v is varied by ± 100 % in Eq. 1 it has a sensitivity effect of 12-19 % on F_{DMS}. A value of 6.5 x 10^{-12} cm molecule^{-1} s^{-1} was applied for K, which is the sum of the abstraction and addition rate reactions of OH with DMS at 25°C and 1 atm (Finlayson-Pitts and Pitts Jr, 2000), which represents the temperature and pressure during the campaigns. The major variable altering OH concentrations in the atmosphere is the intensity of solar UV-B radiation, which controls the generation of OH from the photolysis of ozone (Rohrer and Berresheim, 2006). At Heron Island on the Tropic of Capricorn, the average daily solar irradiance measured at the surface during the 2013 winter dry season was only 10 % lower than during the 2012 wet season campaign (Table 1). According to this seasonal variation in surface solar irradiance and reported average OH concentrations over the South Pacific Ocean (Seinfeld and Pandis, 1998), values for [OH] of 1.8 x 10^6 (wet season) and 1.6 x 10^6 molecules cm^{-3} (dry season) were applied to Eq. (1).

Solving Eq. (1) for F_{DMS} using the mean DMS$_a$ concentrations and other specified values, gave surface fluxes of 5.0 and 1.4 µmol m^{-2} d^{-1} for the wet and dry season campaigns, respectively. These fluxes were clearly dominated by the oceanic background DMS$_a$ source; they reflect expected seasonal surface ocean primary productivity, and are temporally and spatially consistent with predicted fluxes calculated from a database of global surface ocean DMS concentrations (Lana et al., 2011). These seasonal fluxes, calculated using the photochemical mass balance approach, are expected to have a relative uncertainty of ~50 % (Chen et al., 1999). The highest DMS$_a$ concentrations in both seasonal datasets could be attributed to coral reef emissions. This was most apparent in the dry season dataset (Fig. 6), where the relatively stable oceanic background DMS$_a$ signal was occasionally elevated by spikes of DMS$_a$ from the Heron Island reef flat at low tide. In both seasons the reef spikes positively skewed the dataset distributions resulting in larger mean values than median values. If median DMS$_a$ concentrations (Table 1) are instead entered into Eq. (1), F_{DMS} equates to 4.8 and 1.2 µmol m^{-2} d^{-1} for the wet and dry season campaigns, respectively. Entering median DMS$_a$, concentrations into Eq. (1) provides an estimate of the oceanic flux in both seasons since the median values act to negate the contribution from the coral reef DMS$_a$ spikes. The difference between F_{DMS} calculated using mean and median values for [DMS] equates to 0.2 µmol m^{-2} d^{-1} for both the wet and dry season campaigns, thereby providing an estimate of the previously unquantified contribution of the coral reef to F_{DMS} at Heron Island. When this 0.2 µmol m^{-2} d^{-1} coral reef flux estimate is expressed as a fraction of the overall F_{DMS} in each season, it is apparent that the coral reef played a significantly greater contribution during the dry season. The coral reef enhanced the dominant oceanic F_{DMS} by 4 % during the wet season and 14 % during the dry season campaign, where the dry season flux enhancement resulted largely from the 45.9 nmol m^{-3} DMS$_a$ spike generated by a rain rate of only 1.5 mm h^{-1} onto the aerially exposed coral reef at low tide. Clearly, considerable uncertainty is inherent in the estimated coral reef DMS flux due to the difficulty of distinguishing the coral reef and oceanic DMS$_a$ source contributions; however, it provides a starting point for future improvement.

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Deleted: Average mixed layer depths (MLD) at noon were 977 m (range 680 to 1460 m, n = 15 days) and 786 m (range 346 to 1312 m, n = 19 days) during the 2012 wet season and 2013 dry season campaigns, respectively. These average values are consistent with a study of the MLD at Heron Island in June 2009 and February 2010, which ranged from 375 to 1200 m above the surface (MacKellar et al., 2013). Deepest MLDs were observed under stable anti-cyclone conditions, while shallowest MLDs were observed during periods of heavy precipitation with convective downdrafts. MLDs often coincide with the MBL height, which is typically around 700 to 800 m (Stull, 1988); the average MLD values of 977 m (wet season) and 786 m (dry season) were, therefore, applied for H in Eq. (1).

Deleted: Mean concentrations of DMS$_a$ measured in this study were 1.3 (1σ = 1.6, n = 923) and 3.9 nmol m^{-3} (1σ = 1.5, n = 651) for the dry and wet seasons, respectively (Table 1). The number of DMS$_a$ measurements is sufficiently large that these mean concentrations for each campaign are expected to be representative of DMS$_a$ in the MBL over Heron Island during the wet and dry seasons. The concentration of DMS$_a$ in the entrainment zone is reported to be typically ~10 % of the MBL concentration (Ayers et al., 1995; Chen et al., 1999) so this percentage was applied to determine [DMS_t].

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4 Conclusions

This study has provided environmental evidence that coral reefs in the vicinity of Heron Island are point sources of DMS_a, where emissions may at times be detectable as spikes of DMS_a above the background oceanic signal. Detection of these DMS_a spikes relies on extended continuous measurements with sufficient frequency to resolve the spikes from the background source signal. The automated GC used here has served that purpose; however, further on-site continuous sampling of DMS_a at the GBR is required to more closely examine factors that cause coral reefs to emit DMS to the atmosphere. For example, the higher temporal resolution possible with proton transfer reaction mass spectrometry (Lawson et al., 2011) and atmospheric pressure chemical ionisation mass spectrometry (Bell et al., 2013) may provide additional insights into those factors and their interaction, while also improving the estimation of F_{DMS} from the GBR. We found the ocean to be the dominant source of DMS_a at Heron Island, where the ocean source was supplemented by occasional coral reef-derived spikes of DMS_a that were highly variable irregular events generally occurring at low tide when conditions exist that can stress the reef. The extreme DMS_a reef spike recorded in the dry season of 2013, which we conclude was an acute biological response to suddenly unfavourable environmental conditions, demonstrates that the Heron Island lagoonal platform reef has a unique DMS emission mechanism when compared with the surface ocean, where wind driven turbulence largely controls the air-sea exchange of DMS. Furthermore, the extreme DMS_a spike in the winter dry season demonstrates that the Heron Island lagoonal platform reef can be a seasonally aberrant source of DMS_a in comparison to the surface ocean, where increased primary production in the summer provides consistently higher concentrations of DMS_a than the dormant winter period (Ayers et al., 1991). The seasonal aberration of the coral reef as a source of DMS_a is supported by the flux estimates, where the coral reef enhanced the dominant oceanic F_{DMS} by 14 % during the dry season but only 4 % during the wet season campaign. Another significant finding from this study is that convective precipitation intensified the low tide emission of DMS from the coral reef surrounding Heron Island. On a broader regional scale this process may contribute to sulfate-derived secondary aerosol that may ultimately influence the radiation budget over the GBR; however, the extent to which DMS_a contributes to aerosol production and its role in CCN formation over the GBR is currently unknown. Aerosol formation and evolution studies are, therefore, required to determine if the GBR is a climatically influential source of marine aerosol.

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Author contributions. H.B. Swan configured the instrumentation, collected, processed and interpreted the data, and wrote the manuscript, gaining edits and textual contributions from the co-authors. G.B. Jones initiated the field study program and, together with E.S.M. Deschaseaux, participated in some of the field work to assist data collection. All authors approved the study design.

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and DP160100248 awarded to B.D. Eyre. H.B. Swan would like to thank George Tannous for constructing the autosampler, the National Measurement Institute Australia for providing some of the equipment used to collect the DMS_a datasets, Edith Swan for assistance with preparation of graphics, and John Ivey for helpful comments on the manuscript. All authors would like to thank the Heron Island Research Station staff and management for assisting with our experimental needs, and Melissa MacKeller (University of Queensland) for providing Fig. 1b. We gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for provision of the HYSPLIT transport and dispersion model and READY website (http://www.ready.noaa.gov) used to obtain back trajectories and mixed layer heights.

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Table 1. Summary of atmospheric DMS and some meteorological data for the 2012 wet season and 2013 dry season campaigns at Heron Island, southern Great Barrier Reef

	Atmospheric DMS nmol m^{-3} (ppt)		Wind speed m s^{-1}		Air temp °C		Water vapour mixing ratio g kg^{-1}		Daily solar irradiance[a] MJ m^{-2} d^{-1}	
Season	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Mean	3.9 (95)[b]	1.3 (32)[c]	4.5[d]	3.5[e]	26.5	20.8	17.3	8.9	27.4	24.7
SD	1.5 (37)	1.6 (39)	2.4	2.3	1.7	2.2	1.6	2.2	10.6	8.6
Median	3.7 (90)	1.2 (29)	4.1	3.3	26.0	20.4	17.6	9.2	32.0	28.3
Minimum	0.6 (15)	0.2 (5)	0	0	22.7	15.6	12.8	2.2	4.7	5.0
Maximum	11.5 (281)	45.9 (1122)	13.6	9.9	32.6	29.0	20.8	13.2	37.2	33.2

[a]Daily solar irradiance is for the 24 h period.
[b]The number of DMS measurements for the 2012 wet season campaign was 651.
[c]The number of DMS measurements for the 2013 dry season campaign was 923.
[d]The number of meteorological observations for the 2012 wet season campaign was 1313.
[e]The number of meteorological observations for the 2013 dry season campaign was 1716.

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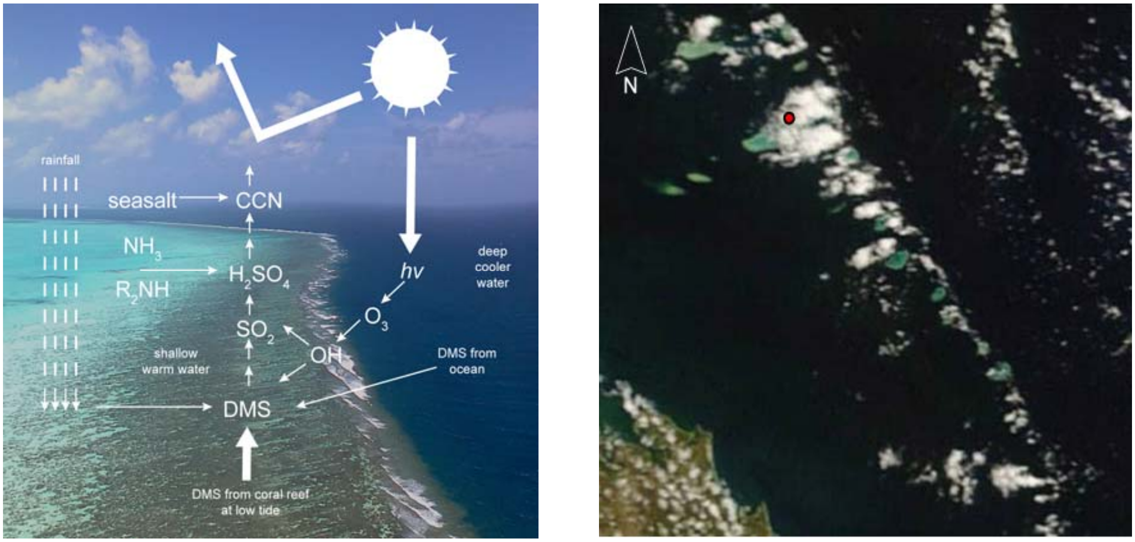


Figure 1: The Capricorn Bunker Group of coral reefs, southern Great Barrier Reef, Australia (23.13°S, 151.85°E to 23.92°S, 152.60°E). (a), an aerial photo of Wistari Reef near Heron Island (Image: H.B. Swan). Superimposed on this image is a conceptual model of factors controlling DMS_a derived sulfate aerosol production over the GBR. Ocean derived DMS_a and spikes of DMS_a from the coral reef at low tide are oxidized by photochemically produced hydroxyl radical (OH) forming sulfate aerosol that can grow to cloud condensation nuclei (CCN). This process can assist formation of high-albedo low-level marine clouds that influence the radiation budget of the GBR. (b), MODIS (Moderate Resolution Imaging Spectroradiometer) satellite image of daytime low-level convective clouds aligned over the Capricorn Bunker Group of coral reefs. Heron Island, near Wistari Reef (cloud covered), is indicated by a red circle. Part of the east Australian coastline is seen in the bottom left-hand corner.

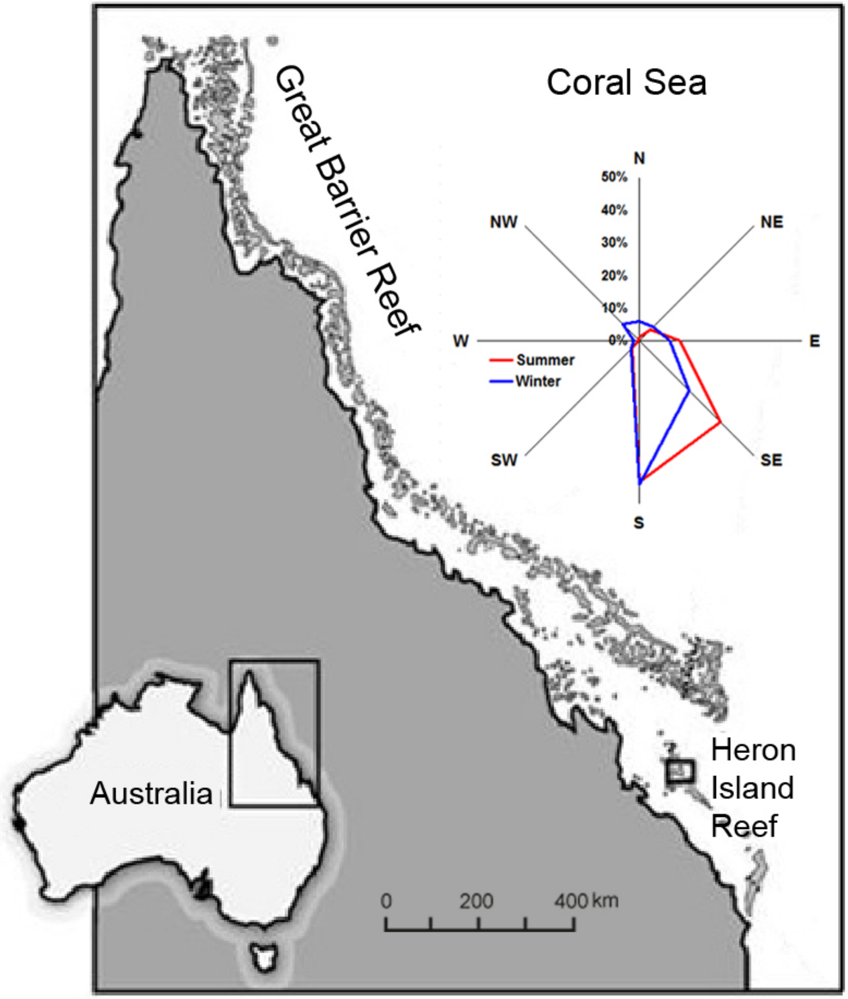
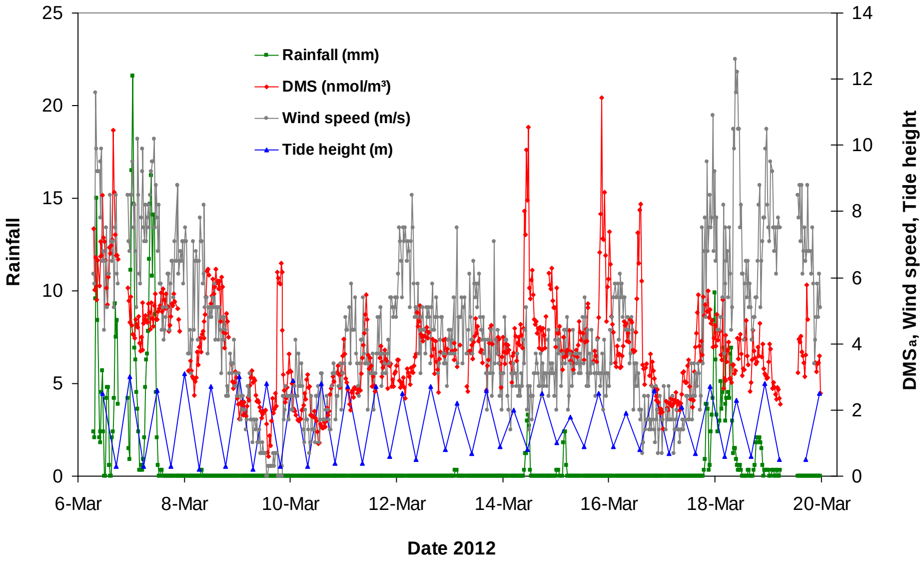


Figure 2: Location of Heron Island in the southern Great Barrier Reef, Australia, where continuous on-site analysis of DMS_a was conducted in the austral wet season of 2012 and dry season of 2013. The compass shows the directional frequency of winds received at Heron Island during the late summer wet season (red line) and mid winter dry season (blue line) measurement campaigns. Daily backward trajectory analysis showed that marine-derived air streams in the SE sector were received at Heron Island the majority of the time during both campaigns.

(a)



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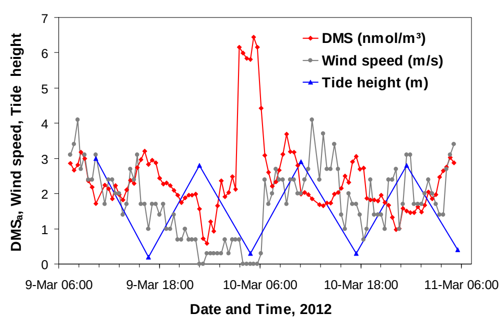

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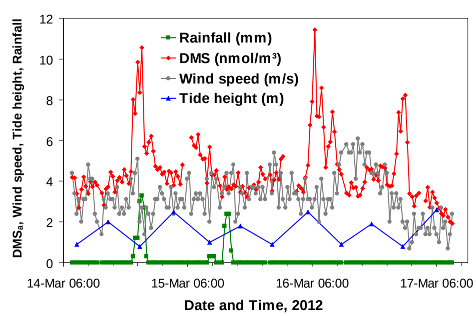


Figure 3: Data obtained from Heron Island during the wet season of 2012. (a), Entire time series of DMS_a (red line), wind speed (WS, grey line), rainfall (green line) and tide height (blue line). Four distinct spikes (10, 14, 16-17 March) above the background DMS_a signal are indicated to be coral reef-derived emissions. (b), Extracted time series showing the DMS_a spike on 10 March (red line) which occurred during a 0.3 m low tide under still conditions (grey line). There was no rainfall during the period shown. (c), Extracted time series showing three distinct coral reef DMS_a spikes. The first, detected between 21:12 on 14 March and 1:05 on 15

March (~4 h duration), was associated with convective rainfall (green line) during a 0.8 m low tide. The highest DMS_a concentration recorded during the wet season campaign (11.5 nmol m^{-3}) was detected on 16 March at 6:27, shortly after high tide. This tidally unique and longest lasting DMS_a spike (~8.5 h) is indicated to have originated from low-level marine air that traversed the length of the 70 km Bunker Group of coral reefs that lie to the SE of Heron Island (Fig. 1b). The third DMS_a spike seen on 17 March, which occurred on a 0.8 m low tide under abating WS, is indicated to be derived from the lagoonal platform reef surrounding Heron Island.

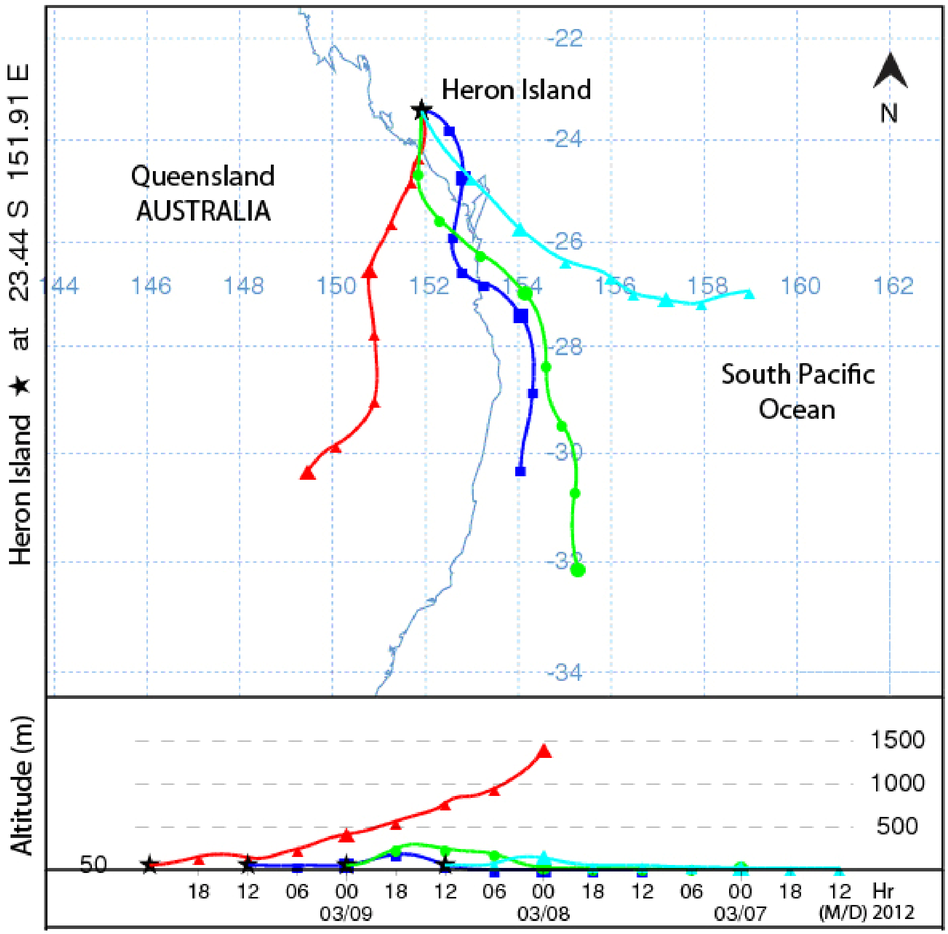


Figure 4: Twelve hour separated back trajectories of 48 hour duration ending 10 March 2012 showing air movement onto the Australian continent with high altitude free-tropospheric air (red line) being directed to Heron Island. This relatively dry non-marine air stream resulted in the lowest DMS_a concentration of 0.6 nmol m^{-3} during the wet season campaign, which occurred shortly after high tide. However, by low tide a DMS_a spike peaking at 6.4 nmol m^{-3} was detected in this air stream under calm conditions (Fig. 3b) prior to a southerly change that redirected the usual marine air flow. The tidal and meteorological conditions under which this DMS_a spike was detected strongly suggest that it was derived from the coral reef surrounding Heron Island.

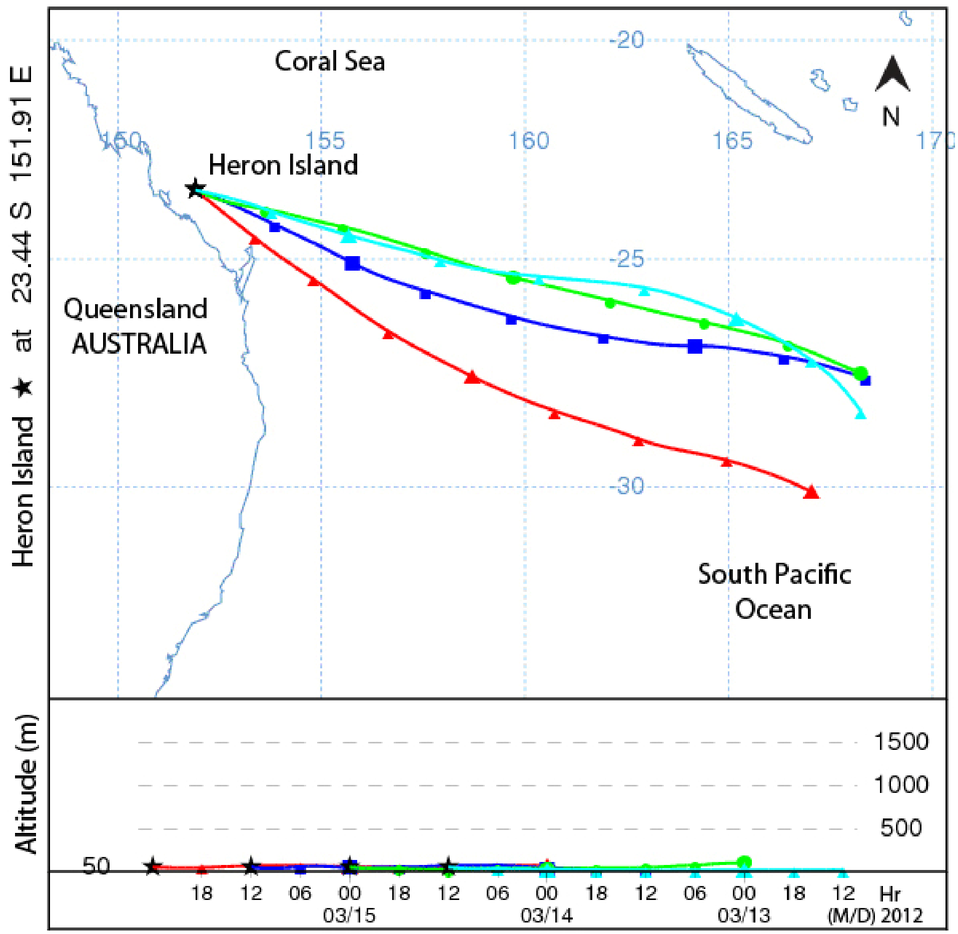
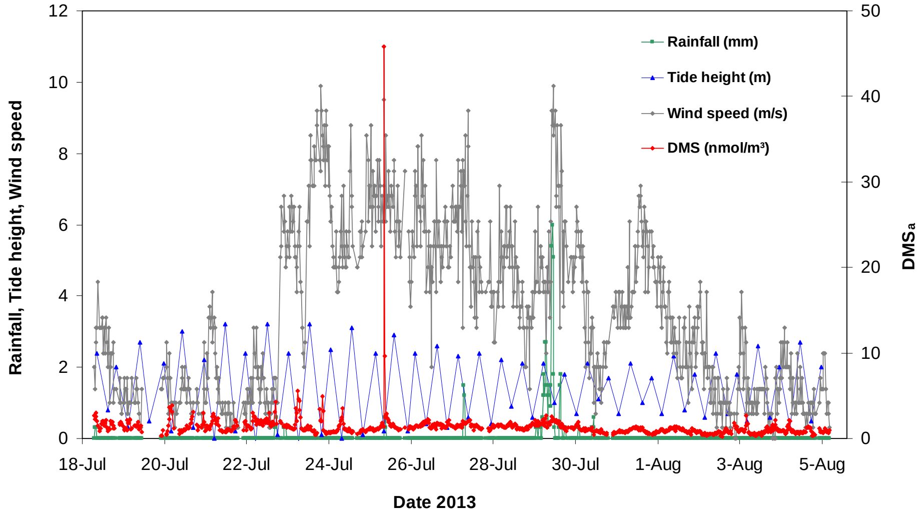


Figure 5: Twelve hour separated back trajectories of 48 hour duration ending 16 March 2012 showing the low-level SE marine air flow (red line) that is indicated to have traversed the ~70 km length of Capricorn Bunker Group of coral reefs (Fig. 1b) before arriving at Heron Island. This marine air flow resulted in the longest lasting DMS_a spike and the highest recorded DMS_a concentration of 11.5 nmol m^{-3} during the wet season campaign (Fig. 3c).

(a)



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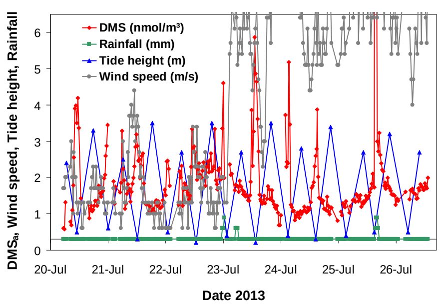

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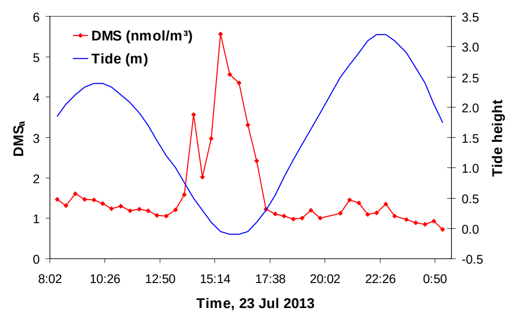

Figure 6: Data obtained from Heron Island during the dry season of 2013. (a), Entire time series of DMS_a (red line), WS (grey line), rainfall (green line) and tide height (blue line). The second axis for DMS_a is scaled to show the relative intensity of the coral reef DMS_a spike (45.9 nmol m^{-3}) detected at low tide in the early evening of 25 July. Even under relatively strong atmospheric mixing (WS = 9.5 m s^{-1}, grey line) this DMS_a reef-derived spike was detected as an intense event. (b), Extracted time series from 20 to 26 July showing ten low tide coupled DMS_a spikes from the Heron Island reef flat. The extreme DMS_a spike (off-scale) on 25 July can be seen to be linked to the 0.2 m low tide and a brief shower of rain that fell onto the aerially exposed coral reef. (c), Time-line magnification of the low tide induced DMS_a spike from the Heron Island coral reef on 23 July between 13:31 and 17:28. There was no rainfall during the period shown.

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