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Biogeosciences
Discussions

Interactive comment on "Coral reef origins of atmospheric dimethylsulfide at Heron Island, southern Great Barrier Reef, Australia" *by* Hilton B. Swan et al.

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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 DMSa 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 DMSa 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 DMSa signal derived from phytoplankton and other pelagic marine biota, while occasional DMSa 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 DMSa 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 DMSa 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 Flux 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 Flux 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. [DMSa]. It is stated in Section 3.3 that the number of DMSa measurements is sufficiently large that the mean concentrations for each campaign are expected to be representative of DMSa in the MBL over Heron Island during the wet and dry seasons. Table 1 shows that the mean and SD for DMSa 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. [DMSt]. This is reported to be typically 10% of MBL concentrations. The sensitivity of this variable in Eq. 1 is small. When values for [DMSt] of 5% and 20% of MBL concentrations are entered into Eq. 1, Flux 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 106 (2012 wet season) and 1.6 x 106 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. Ev. 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 Ev value is varied by ±100% in Eq. 1 it has a sensitivity effect of 12-19% on Flux 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 DMSa 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 DMSa 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 DMSa 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 DMSa 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 species of branching coral during the campaigns in 2012 and 2013 showed that coral growing on the platform reef surrounding Heron Island was in good health. (This information will soon be reported in Analytical and Bioanalytical Chemistry). There was no evidence of coral bleaching in the 2012 wet season to affect the usually high biodiversity. 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 DMSa spikes detected at Heron Island. As is evident from the entire winter dataset, the intensity of the DMSa 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.

This information about the health conditions of the coral reef during the 2012 and 2013 campaigns at Heron Island will be incorporated into the revised manuscript.

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 was 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 was 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 environmental study conducted on-site at the GBR with sufficient sampling frequency to 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 DMSa 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 DMSa derived sulfate aerosol production over the GBR. In particular, it shows the oceanic DMSa source that provided the baseline DMSa 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 DMSa 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 DMSa, 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 DMSa spikes and the background DMSa signal. For example, the alignment of WS with the background DMSa signal shown in Fig 3a provides a convincing picture that it is the oceanic-derived DMSa 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 DMSa spikes detected from the coral reef. This complexity of interacting processes leading to the DMSa 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.

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