Can corals form aerosol particles through volatile sulphur compound emissions?

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Abstract. Acropora dominated coral reefs are a substantial source of atmospheric dimethylsulphide (DMS_a), one of the most abundant reduced sulphur gases present in the marine boundary layer. DMS is believed to act as a climate regulator of solar radiation and sea surface temperatures through the formation of non-sea-salt sulphate aerosols and cloud condensation nuclei (CCN), although this regulation has not yet been demonstrated. A bubbling chamber experiment was conducted on coral reef seawater containing a branch of *Acropora pulchra*, to investigate whether the coral-generated DMS_a could be oxidised to non-sea-salt sulphate aerosols under treatment with UV light and O_3. Results indicated that *A. pulchra* produced significant amounts of dimethylsulphoniopropionate (DMSP) and dissolved DMS although emissions of DMS_a in the chamber headspace were reduced by the presence of the coral, probably as a result of antioxidant activity in the coral tissue. Significant amounts of carbon disulphide (CS_2) and ethanethiol (ESH), other sulphur gases that could be involved in CCN formation, were also indicated in the bubbling chamber, most likely from coral production. A decrease in DMS_a and CS_2 in the presence of UV light and O_3 followed by an occurrence of freshly nucleated nanoparticles (<10nm) suggested that these two sulphur compounds were oxidised and potentially participated in aerosol particle formation and thus could be involved in CCN formation and possibly climate regulation. The study provided insights into the production of sulphur compounds by Acropora dominated coral reefs with potential impact on local climate.

Key words: Dimethylsulphide, Coral, Aerosols, Climate.

Introduction

According to the CLAW hypothesis, atmospheric dimethylsulphide (DMS_a) generated by phytoplankton is oxidised to non-sea-salt (nss) sulphate aerosols which go on to form cloud condensation nuclei (CCN), increasing the albedo of stratocumulus clouds and locally lowering solar radiation and sea surface temperatures (SST) in the ocean (Charlson *et al.*, 1987). Although supported by several studies (Ayers *et al.*, 1991; Modini *et al.*, 2009), the CLAW hypothesis has never been verified. On the other hand, oxidised organic compounds can also participate in newly-formed secondary aerosol particle formation (Vaattovaara *et al.*, 2006).

Research has shown that hard corals, through their symbiotic microalgae, produce DMSP, the main precursor of DMS (Jones *et al.*, 1994; Hill *et al.*, 1995), and emit DMS_a in chamber experiments on Acropora (Fischer and Jones, 2012). Continuous monitoring of sea surface temperatures (SST) in coral reefs worldwide has shown that pristine reefs within or near the Western Pacific Warm Pool have had fewer reported coral bleaching events relative to reefs in other regions of the world possibly because of an “ocean thermostat” mechanism that acts to depress warming beyond certain SST thresholds (Kleypas *et al.*, 2008). Research on DMS and aerosol formation suggests that oxidation of DMS_a from reefs could form nss-sulphate aerosols and thus could contribute to this phenomenon (Jones and Trevena, 2005; Jones *et al.*, 2007; Modini *et al.*, 2009; Jones and Ristovski, 2010).

Bubble bursting from breaking waves in the ocean is the primary source of sea-air exchange and sea spray aerosol production in the atmosphere, constituting a possible source for CCN formation (Modini *et al.*, 2009). Hydroxyl radicals in the atmosphere, which are formed as a consequence of photodissociation of ozone (O_3) by solar UV, are responsible for the oxidation of gaseous precursors such as DMS into atmospheric aerosols (Andreae and Crutzen, 1997). Thus, bubble bursting, O_3 and UV radiation are three major components in the emission and oxidation of DMS to aerosols.

Between May and June 2011, the CORACE-1 (**CO**ral **R**eef **A**erosol **C**haracterization **E**xperiment-1) campaign was conducted on Heron Island coral cay as a collaborative research project between QUT (Queensland University of Technology, Brisbane), SCU (Southern Cross University, Lismore) and UEF (University of Eastern Finland, Kuopio) in order to ascertain whether atmospheric DMS produced by coral reefs could, during bubble bursting and under O_3 and UV radiation, contribute to aerosol particle formation and hence potentially influence local climate (for more background information refer to Swan *et al.* 2012).

Material and Methods

Study design and terminology

A bubbling chamber experiment was conducted on seawater collected from the Heron Island Reef flat (23°26'35.80"S/151°54'44.23"E) in which a branch of *Acropora pulchra,* a widely spread coral in the Indo-Pacific and Great Barrier Reef (GBR) (Veron, 2000), was immersed (coral seawater). Three control bubbling chamber experiments were also conducted on coral reef seawater collected at high tide (high tide seawater), low tide (low tide seawater) and from the Heron Island's tap seawater system that pumps water directly from the reef flat (reticulated seawater) (Fig. 1). A control air sample (CAS) was also taken from the "aquaria room" in which the experiment was held. In order to simplify the terminology used for this experiment, "high tide seawater", "low tide seawater" and "reticulated seawater" are referred to as "control seawaters".

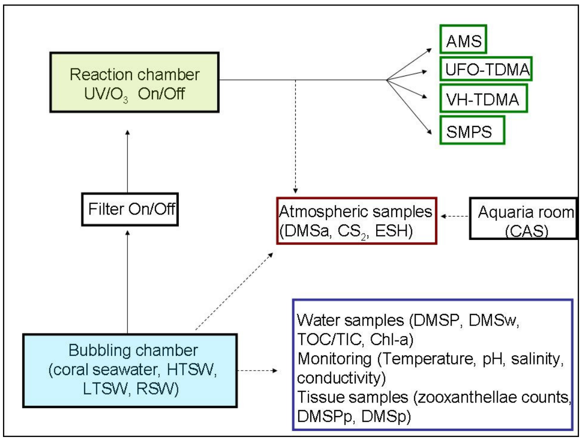

Figure 1: Experimental design of the bubbling chamber experiment conducted at Heron Island, May-June 2011, on coral seawater, high tide seawater (HTSW), low tide seawater (LTSW) and reticulated seawater (RSW).

Bubble bursting, simulating sea-air exchange of volatile substances present in the seawater, was intermittently applied to the four types of seawater using dried and filtered compressed air. The air flushed out of the bubbling chamber intermittently went through a particle filter before reaching the reaction chamber in which UV light (40W) and O_3 (200-500ppb) treatments were also applied intermittently. When filtration was applied, the bubble burst primary particles were removed leaving the gaseous compounds to enter the reaction chamber. When applied, UV and O_3 were simulating and accelerating oxidation processes that may occur to DMS_a and to other organic compounds that are released from the reefs to the atmosphere during air-sea exchange.

Sampling

Two types of samples were collected during the experiment: air samples from the headspace of the bubbling chamber simulating atmospheric sulphur emissions from the reef; and water samples from the bubbling chamber, simulating the dissolved sulphur compounds produced within the water column from the reef. Air samples collected onto gold-wool tubes (Kittler *et al.*, 1992) were taken from either the top of the bubbling chamber (before the air was flushed through the reaction chamber) or from the reaction chamber's outlet (Fig.1). Both air and water samples were collected in various conditions: 1) before and after bubbling, 2) with or without air filtration, 3) with or without UV and O_3 treatments and, 4) before and after the coral branch was placed in and taken out of the chamber (coral seawater only). Air samples were collected for atmospheric sulphur compounds. Water samples were collected for total organic and inorganic carbon (TOC and TIC), chlorophyll-a, pheophytin, dissolved DMS (DMS_w) and DMSP. Temperature, salinity, conductivity and pH were monitored throughout the experiment.

Number and size of primary and secondary particles were determined using a SMPS (scanning mobility particle sizer). Particle chemical properties (composition, volatility, hygroscopicity, oxidised organic fraction) were determined using an Aerodyne ToF-AMS (time-of-flight aerosol mass spectrometer), VH-TDMA (volatilisation and humidification tandem differential mobility analyser) (Fletcher *et al.*, 2007) and UFO-TDMA (ultrafine organic tandem differential mobility analyser) (Vaattovaara *et al.*, 2005) that were placed in-line with the reaction chamber and bubbling chamber.

Analysis

Sulphur samples were analysed with a purge and trap technique coupled to a gas chromatograph (GC) with a pulsed flame photometric detector (PFPD) using a dual eight-port/six-port two-position manual valve switching system (Swan and Ivey, 1994). Acidified DMSP samples were analysed by alkaline hydrolysis in a purging chamber whereas acidified DMS_w samples were analysed from the headspace (note: values for

DMSP were corrected for free DMS_w content). Analysis of TOC and TIC samples was carried out using a total organic carbon analyser. Absorbance of chlorophyll-a and pheophytin samples was determined by spectrophotometry (APHA, 1998).

Results

Three main peaks (31µM, 39.6µM and 10.8µM) of DMSP and an increasing concentration of DMS_w (up to 0.3µM) were found in coral seawater containing the branch of *A. pulchra,* whereas DMSP and DMS_w were not found in control seawaters (Fig. 2).

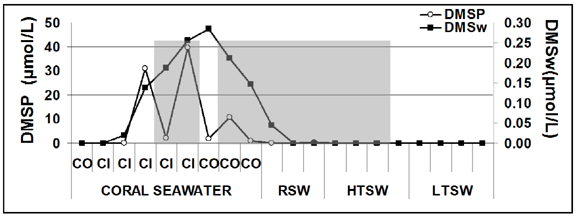

Figure 2: DMS_w and DMSP concentrations in coral seawater and control seawaters (RSW, HTSW, LTSW) during the bubbling chamber experiment. Shading shows bubbling periods. CO and CI stand for "coral out" and "coral in" respectively.

DMS_a as well as two background sulphur compounds, carbon disulphide (CS_2) and ethanethiol (ESH), were detected in the headspace of the bubbling chamber (Fig. 3). The concentrations of DMS_a, CS_2 and ESH measured in the "aquaria room" air were much lower than the concentrations of these sulphur compounds contained in the bubbling chamber.

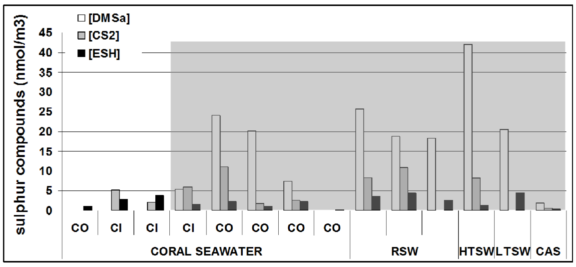

Figure 3: Sulphur gas concentrations in bubbling chamber experiments conducted on coral seawater and control seawaters (RSW, HTSW, LTSW). Atmospheric concentrations of the control air sample (CAS) is also shown. Shading shows bubbling periods. CO and CI stand for "coral out" and "coral in", respectively.

Although CS_2 (5.2 nmol/m^3) and ESH (2.8 nmol/m^3) were detected from the headspace of the chamber prior to applying bubbling, seawater-air exchange of DMS_a only took place when bubbling was applied. Then 5.5 nmol/m^3 of DMS_a was measured in the headspace of the bubbling chamber containing the branch of *A.pulchra*. However, five times more DMS_a and twice as much CS_2 were released from the coral seawater as soon as the coral branch was taken out of the chamber while maintaining constant bubbling.

Generally, the DMS_a concentration in the headspace of the chamber was similar when purging control seawaters and coral seawater, after the coral branch had been taken out of the chamber. ESH was present in all experiments but in lower concentration than both DMS_a and CS_2. CS_2 was found in all types of seawater except for low tide seawater.

Of particular interest was the finding that DMS_a and CS_2 tended to decrease as soon as UV and O_3 were applied to the reaction chamber. No decrease in ESH could be recorded as a result of UV and O_3 treatment.

A significant increase in chlorophyll-a and TOC, as well as a decrease in TIC, were found in coral seawater towards the end of the bubbling chamber experiment whereas no variation was observed in control seawaters, and concentrations remained very low (data not shown). Temperature, salinity, conductivity and pH did not vary throughout the entire experiment.

The SMPS data showed that new particle formation occurs when gaseous components released into the chamber headspace upon bubbling were exposed to UV and O_3. These newly formed particles were too small (count median diameter < 10nm) to be measured by the AMS and therefore their chemical composition has not been determined. The hygroscopicity and volatility profiles of these particles were lower and greater than for sulphates, respectively.

The UFO-TDMA measurements when bubbling, particle filtration, UV and O_3 were applied, showed that the freshly formed secondary particles included at least 50% oxidised organic compounds. The formed ultrafine particles were quickly further oxidised (aged) when they grew bigger in size, due to the production of high level of oxidants into the air.

Discussion

Bubbling chamber experiments conducted on *Acropora pulchra* and Acropora dominated coral reef water provided important information on the production of DMS_a in coral reef ecosystems and its potential role in aerosol formation and climate regulation.

DMSP was clearly produced by the coral *Acropora pulchra*. The coral-produced DMSP was then rapidly cleaved into DMS_w, probably as a result of DMSP lyase activity, by either the endosymbiont (Yost and Mitchelmore, 2009) or marine bacteria (Todd *et al.*, 2007) present in the seawater.

The pulsed production of DMSP in coral seawater may mimic coral bleaching events and the loss of symbiotic zooxanthellae (Iglesias-prieto *et al.*, 1992). Eventually, mass release of zooxanthellae in the chamber led to an increase in chlorophyll-a and TOC (data not shown). The decrease in TIC, usually used as a proxy for CO_2, also suggests an increase in coral bleaching and mortality through a decrease in respiration. This conclusion was supported by observation of excessive cloudiness of the coral seawater, probably linked to a build up in coral mucus and zooxanthellae in the bubbling chamber. Thus, the present results confirmed previous findings that corals produce significant amounts of DMS and DMSP in coral reef seawater through release of coral mucus containing expelled zooxanthellae (Broadbent and Jones, 2004).

Acropora dominated coral reefs at Heron Island have already been shown to be a significant source of DMS and DMSP (Jones *et al.*, 2007; Fischer and Jones, 2012), and concentrations found in this experiment were similar to what is recorded in the literature. However, the presence of coral-reef-produced CS_2 and ESH was unexpected. Both CS_2 and ESH play an important role in the atmospheric sulphur cycle, with CS_2 oxidising into COS and SO_2, sulphate compounds that can influence CCN formation as well as global climate and are involved in the formation of acid rain (Yu *et al.*, 2004; Kachina *et al.*, 2006). Both compounds can be produced naturally in the environment (Watts, 2000) but can also be produced as a result of pollution (Yu *et al.*, 2004; Kachina *et al.*, 2006). In this study, bubbling chamber experiments were conducted in a closed chamber and the compressed air that was pumped through the chamber to create bubble bursting was pre-filtered. Also, concentrations of sulphur gases measured from the “aquaria room” were very low relative to that measured in the chamber headspace. Therefore, it is unlikely that CS_2 and ESH came from external pollution and thus, are indicated to be a result of reef production.

However, gas chromatography retention time alone cannot be considered as an absolute means to claim the identity of an analyte and a proper confirmation of identity, using spectral instrumental techniques, needs to be carried out for both CS_2 and ESH.

Meanwhile, emissions of DMS_a, CS_2 and ESH were similar in coral seawater and control seawaters, suggesting that coral reef seawater was already highly concentrated with these sulphur compounds. However, it appears that the presence of the coral inhibited the release of DMS_a and CS_2 into the bubbling chamber headspace, supporting the theory that under artificial stressful conditions DMS could be used as an antioxidant within the coral tissue (Sunda *et al.*, 2002; Jones *et al.*, 2007). However, increased concentrations of DMS_a and CS_2 following the removal of the coral branch could suggest that the bulk of these gases could be entrained within the coral mucus and tissue and were released when the coral was removed from the chamber, constituting an increase in DMS_a emitted from the water surface.

Bubbling was needed to transfer DMS_w to the chamber headspace as no DMS_a was measured from the headspace until bubbling was applied. However, the fact that ESH and CS_2 were detected in the headspace of the chamber prior to apply bubbling suggests that these two sulphur compounds are more volatile than DMS and thus could be more concentrated in the atmosphere relative to their production rates.

Of particular interest was the decrease of DMS_a and CS_2 under UV and O_3 treatment which indicated that both sulphur compounds could potentially become oxidised in the atmosphere, participating in secondary aerosol particles and possibly CCN formation (Chin and Davis, 1993; Liss *et al.*, 1997; Moore *et al.*, 2011). In contrast, the fact that ESH remained constant after UV and O_3 exposure suggests that ESH does not contribute to the production of atmospheric aerosols.

It is worth noting that the newly-formed nucleation mode particles included a remarkable and even dominating fraction of oxidised organic compounds. Additionally, hygroscopicity data indicate that newly formed particles might not necessarily originate only from DMS and that other sulphur-containing gaseous precursors or other volatile organic compounds could also be responsible for particle formation and growth. The volatility profile of these particles indicates that sulphates were not the dominant component in these particles.

Further bubbling chamber experiments, as described in this paper, need to be conducted on Acropora corals and artificial seawater to 1) confirm the identity of ESH and CS_2 measured during this first bubbling chamber experiment, 2) see if ESH and CS_2 are a result of coral production and 3) confirm that biogenic DMS_a and CS_2 are oxidised to aerosol particles and participated in forming CCN. By characterising aerosol particles formed in bubbling chamber experiments such as this one, as well as air masses over coral reefs, we are hoping to eventually ascertain whether reef aerosol emissions can affect local climate.

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