

The Contribution of Sulfate and Oxidized Organics in Climatically Important Ultrafine Particles at a Coral Reef Environment

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Abstract—In order to investigate the properties of coral reef origin secondary aerosol and especially the contribution of secondary organic aerosol, ethanol affinity to atmospheric nucleation mode particles (diameter<15nm) was measured at the Heron reef marine environment in the South Pacific Ocean during the first coral reef aerosol characterization experiment in May-June 2011 using an ultrafine organic tandem differential mobility analyzer.

Our campaign study at Heron reef showed that the nucleation mode size particles (diameter =10nm) composition contain internally mixed sulfate and oxidized organic components in approximately equal proportion in sunny and still conditions around low tide time, indicating local biogenic sources. The produced secondary compounds and aerosols have potential to contribute to cloud condensation nuclei formation and properties that may affect local low-level cloud formation over the GBR. Additionally, primary marine sea-salt and organic material during windy conditions and anthropogenic/biogenic sources during continental air masses can affect the properties of these particles.

Keywords—Coral reef, DMS, particle composition, secondary organics.

I. INTRODUCTION

IN regards to climate change, one of the largest uncertainties is related to aerosols and their direct and indirect (via clouds) connections to the Earth's radiative balance and climate [1]. An important phenomenon associated with the climatically important direct and indirect aerosol effects is the formation of new nanometer-size particles. This phenomena

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consists of a set of processes that include the production of nanometer-size clusters from gaseous vapors, the growth of these clusters to detectable sizes (see e.g., [2]), and their growth to potential cloud condensation nuclei (CCN) and larger radiatively active sizes.

The aerosols typically consist of both organic and inorganic compounds whose relative ratios strongly depend on the environmental conditions where the interaction occurs and the ratio of anthropogenic and biogenic gases and particles define the overall composition and properties. In order to more fully understand the climatic effects of atmospheric aerosols, the composition of freshly nucleated nucleation mode particles and Aitken mode size particles (i.e. ultrafine particles < 100nm) needs to be properly understood in each environment.

One of the most important environments is marine areas which cover around 70% of the Earth's surface area. [3] suggested, using surface chlorophyll a concentrations (SeaWiFS satellite) as an indicator for the size of the plankton biomass and thus for overall marine productivity, that biologically productive marine regions are able to produce climatically important secondary particles worldwide (i.e. dimethylsulfide (DMS) and other organic vapors and their oxidation products), while so called marine deserts (typically 10-20 degree from equator) are not as productive. Depending on the availability of nutrients due to the strength of seasonal thermoclines and sunlight, the productivity in different parts of the ocean varies and thus the importance of these particles to regional climate also varies greatly.

Coral reefs form some of the most diverse ecosystems on the Earth, being one of those marine biologically active regions. They occupy less than 1% of the world's ocean surface but they provide a home for 25% of all marine species [4], including fish, mollusks, worms, crustaceans, echinoderms, sponges, tunicates and other cnidarians. They are most commonly found at shallow depths in tropical waters, but deep water and cold water corals also exist on smaller scales in other areas.

Stretching over 2600km, a long way along the coast of Queensland in Australia, the Great Barrier Reef (GBR) is one of the largest and most important ecosystems in Oceania. The regional climatic importance of the GBR emissions was identified when Bigg and Turvey [5] reported ca. 35 years ago that mean concentrations of aerosol particles in maritime air masses between the Australian mainland and the GBR to be 1590 particles/cm³. Measurements made on the seaward side of the GBR were much lower (mean = 640 particles/cm³) and

corresponding to the OGF value of a very high ethanol affinity compound. Typically, freshly formed secondary organics are moderately oxidized and they have a very high ethanol affinity. However, the presence of sulfate and oxidized organics also lead to low OGF organosulfates [18]; therefore, the calculated OVF values are minimum estimates.

III. RESULTS AND DISCUSSION

In order to investigate the properties of coral reef origin secondary aerosol and especially the contribution of secondary organic aerosol (SOA), ethanol affinity to atmospheric nucleation mode particles (diameter < 15 nm) was measured in-situ at the Heron Island marine environment during CORACE-1 using the UFO-TDMA described. OGFs determined on 30 May and 3 June 2011 (ozone ca 22 ppb, RH~58%) under calm and sunny daytime conditions at low tide were 1.08 and 1.09, giving a minimum estimate of 46-52% (6% uncertainty) for the OVF of 10 nm particles. This finding was supported by an on-site coral seawater chamber experiment, where bubble-burst particles were filtered and then treated with UV and O₃. The chamber experiment showed that freshly formed secondary particles consisted of at least 50% moderately oxidized organic compounds [19]. Similar OVF values were measured for 10 nm particles under variable wind conditions at low tide on 26, 27 and 28 May and 13 June 2011 at Heron reef. However, air-masses during the days with higher wind speeds may also contain continentally derived compounds. A continentally polluted air-mass was measured on 31 May 2011 when air from 100 m height was received from the direction of Gladstone on the Queensland coast, which gave an OVF of 11% for 10 nm particles. Overall (Table I), the UFO-TDMA measurements typically showed that both sulfate and oxidized organics related volume fractions were close to 50% in new 10 nm particles during CORACE-1.

TABLE I
THE CONTRIBUTIONS OF SOA AND SULFATES

Experiment	Conditions	SOA (%)	Sulfates (%)	DMS _a (ppt.) [20]
26-28.5 and 13.6	variable winds	50	50	-
30.5	calm and sunny	46	54	-
31.5	continentally influenced	11	-	-
3.6	calm and sunny	52	48	12.8
6.6	calm and sunny	-	-	13.1
Chamber [19]	oxidation and UV	50	50	-

Additionally, during CORACE-1, the biological activity and the ability of coral reef waters to form atmospheric particles was additionally supported by gold-wool chemisorption of DMS_a. Under calm conditions just after low tide on 3 June 2011 a peak DMS_a of 12.8 ppt was detected, and

again under similar conditions on 6 June 2011 a peak DMS_a concentration of 13.1 ppt was detected [20].

Previously, [9] found that the majority of the volume of Aitken mode size particles detected at Agnes Water, on the Queensland coast 50 km south of the GBR, could also be attributed to internally mixed sulfate and organic components. The majority of nucleation events observed at Agnes Waters occurred between 10:00-13:00 LT under high solar intensity (~1000 W m⁻²) and low relative humidity (~50-60%) [9]. Generally, they assumed in the marine air mass new particle formation events at Agnes Water (a part of Pacific Ocean) that the particles consisted of around 60% sulfates and 40% organics by volume in 17 nm size during weak and 76% sulfates and 24% organics by volume in 22.5 nm size during strong nucleation events.

Along the Atlantic coast, a significant iodine oxide contribution to new particle formation may be derived from emission of iodine from brown seaweed ([20]-[22]). However, local Australian studies suggest that the role of iodine in particle formation is likely to be minor over the GBR ([23], [24]). Those observations are supported by the fact that the brown seaweed contribution is relatively small compared to the amount of total GBR or Heron reef biota.

Instead, [25] highlighted high DMS and DMSO levels in coral mucus. Therefore, microalgae and the corals, and especially the mucus of corals could be the main sources for DMS and non-DMS volatile organic emissions which are necessary for SOA formation at coral reefs. Secondary compounds can also contribute to the composition and thus the properties of primary particles produced by bubble bursting which can potentially form CCN. A schematic of the potential for biogenic nucleation, Aitken and accumulation mode particle formation, growth, and composition during daylight hours at the Heron Island marine environment is shown in Fig. 2.

Sunlight is required for nanoparticle formation from volatile organic compounds (VOC) such as DMS or alkenes (e.g. isoprene). Photochemically mediated oxidation of DMS results mainly in the formation of SO₂, although lesser amounts of methanesulfonic acid (MSA) are also produced [26]. Oxidation of SO₂ leads to sulfuric acid which may undergo nucleation with other gases such as neutralizing ammonia and oxidized organics to produce thermodynamically stable clusters of nanoparticles. These may grow further to radiatively and climatically important sizes with VOC oxidation products and iodine oxides to form atmospherically important SOA. Additionally, those secondary compounds can change the properties of primary organic material and sea salt, producing climatically relevant CCN ([27], [28], [3]), Fig. 2.

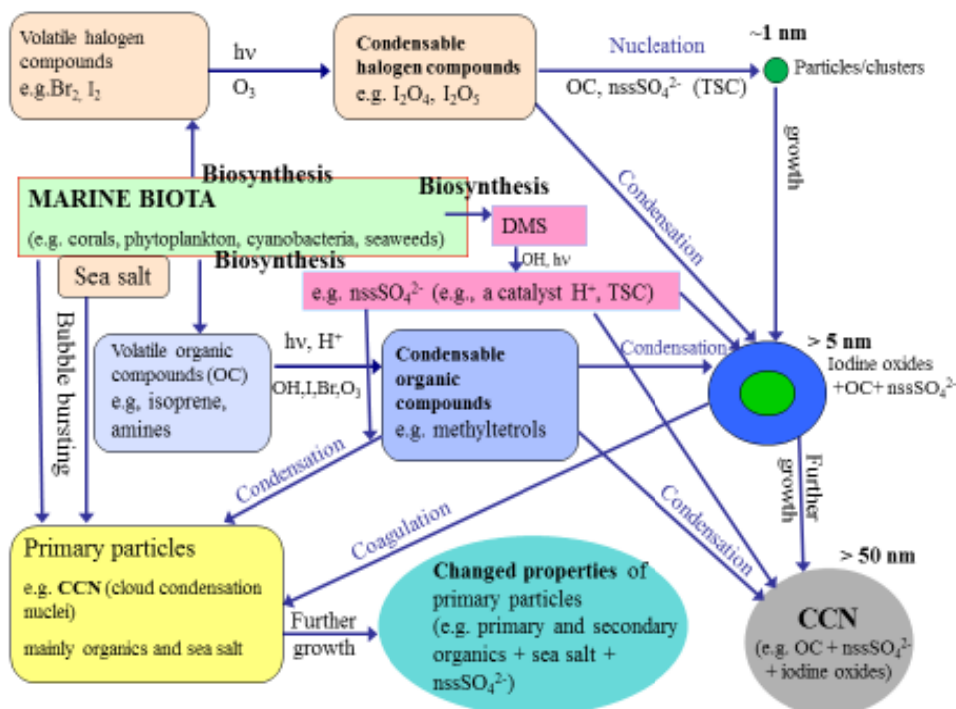


Fig. 2 A schematic of potential biogenic nucleation, Aitken and accumulation mode particle formation, growth, and composition during daylight hours at the Heron reef marine environment

Importantly on the GBR scale, the importance of clouds in regulating (cooling) sea surface temperature (SST) over the GBR has recently been quantified for the first time [29].

IV. CONCLUSION

In order to investigate the properties of coral reef origin secondary aerosols and especially the contribution of secondary organic aerosol, ethanol affinity to atmospheric nucleation mode particles (diameter < 15nm) was measured in-situ at the Heron Island marine environment in the South Pacific Ocean during CORACE-1 (May-June 2011) using an ultrafine organic tandem differential mobility analyzer.

Our 2011 campaign study at Heron reef showed that the composition of nucleation mode size particles (diameter < 15nm) consisted of internally mixed sulfate and oxidized organic components in approximately equal proportion under sunny still conditions at low tide, thus indicating local biogenic sources. The sea-to-air release of secondary compounds and resulting aerosols can potentially contribute to cloud condensation nuclei formation that may contribute to local low-level cloud formation over the GBR while also affecting cloud properties. Additionally, primary marine sea-salt and organic material generated during windy conditions, together with anthropogenic/biogenic sources during continental air masses can affect particle and cloud properties.

Generally, the aerosol processes that regulate the formation and properties of cloud condensation nuclei over large parts of the coral reef areas, and their effect on regional climate of these areas are poorly understood. At biologically active

marine regional scales, the particle formation can determine the population of aerosol particles that seed droplet formation in clouds [30]. These produced biogenic aerosol particles can therefore have a major influence on cloud properties and hence the climate and the hydrological cycle in biologically active marine areas such as the GBR region.

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