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

P. Vaattovaara, H. B. Swan, G. B. Jones, E. Deschaseaux, B. Miljevic, A. Laaksonen, Z. D. Ristovski

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

Petri Vaattovaara is with the Department of Applied Physics, University of Eastern Finland, Kuopio, Finland (phone: +358 44 578 4226; e-mail: petri.o.vaattovaara@gmail.com).

Hilton B. Swan is with School of Environment, Science and Engineering, Southern Cross University, Lismore NSW, Australia and with National Measurement Institute, Chemical and Biological Metrology, North Ryde NSW, Australia (e-mail: hilton.swan@measurement.gov.au).

Graham B. Jones is with the School of Environment, Science and Engineering, Southern Cross University, Lismore NSW, Australia and with the Marine Ecology Research Centre, Southern Cross University, Lismore NSW, Australia (e-mail: Graham.Jones@scu.edu.au).

Elisabeth Deschaseaux is with the School of Environment, Science and Engineering, Southern Cross University, Lismore NSW, Australia and with the Marine Ecology Research Centre, Southern Cross University, Lismore, NSW, Australia, and with the Centre for Coastal Biogeochemistry, Southern Cross University, Lismore NSW, Australia (e-mail: elisabeth.deschaseaux@gmail.com).

BrankaMiljevic and Zoran D. Ristovski are with the Faculty of Science and Engineering, Queensland University of Technology, Brisbane, QLD Australia (e-mail: b.miljevic@qut.edu.au,z.ristovski@qut.edu.au).

Ari Laaksonen is with the Finnish Meteorological Institute, Helsinki, Finland and with the Department of Applied Physics, University of Eastern Finland, Kuopio, Finland (e-mail: Ari.Laaksonen@fmi.fi).

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 occursand 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 than1% 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/cm^3. Measurements made on the seaward side of the GBR were much lower (mean = 640 particles/cm^3) and

typical of remote marine aerosols. Since the CLAW hypothesis [6] suggested a feedback link in oceanic DMS emissions to the number of CCN and cloud albedo, the hypothesis of [6] has given a good reason to study DMS concentrations at biologically productive marine regions such as the GBR as a precursor for those particles. Reference [7] noted on the northern GBR that atmospheric DMS (DMS_a) concentrations often increased after low tide when the reef was exposed to the atmosphere. On the southern GBR, at the Capricorn Bunker Group of reefs, [8] found a DMS_a mean value of 6.5ppt (ranging from 0.12ppt to 23ppt). Additionally, [3] suggested the presence of significant secondary organic material in newly-formed secondary particles formed in biologically active marine areas. Importantly nearby the southern GBR at Agnes Water, [9] observed a strong new particle formation event when the air mass arrived from the GBR direction.

Understanding the role of clouds in regulating the temperature of the oceans and how that role changes is one of the biggest uncertainties for climate change researchers. A key feature in this regard is the formation and properties of CCN.

This *in situ* coral reef 2011 study, the first coral reef aerosol characterization experiment (CORACE-1), aimed to determine the contribution of sulfate and organic components to ultrafine (d < 15nm) particles formation and growth in the southern GBR environment at Heron reef.

II. METHODS

A. The Measurement Site

This CORACE-1 study was conducted at the Heron Island Research Station (HIRS, 23°26'34"S, 151°54'48"E) on the southern end of the GBR on South Pacific Ocean during 26 May-14 June 2011.

HIRS is located on the Heron Island coral cay near the Tropic of Capricorn at the northern end of the Capricorn and Bunker group of reefs, 72km north-east of Gladstone city (Queensland, Australia) and 539km north of the state capital Brisbane. The island is situated on the western side of Heron Reef, a fringing platform reef of significant biodiversity, supporting around 900 of the 1,500 fish species and 72% of the coral species found on the Great Barrier Reef [10].

Heron Island is about 800 meters long and 300 meters at its widest, giving an area of approximately 16 hectares. The highest point, near the western tip, is 3.6 meters above sea level (ASL). A dune ridge along the southern shore rises some 3 meters ASL; lower dunes on the northeastern side are only about one meter above the sea [11]. The sampling inlet used was built 15 m ASL at the HIRS.

Unfortunately, another previously planned measurement site building at Mission Beach on the northern Queensland coast close to the GBR was totally destroyed by the strong austral summer cyclone Yasi(3.Feb.2011).

B. The Measurement Instrument

An ultrafine organic tandem differential mobility analyzer (UFO-TDMA, Fig. 1; [12], [13]) was used to determine the

contribution of sulfate and organic components to nucleation mode size (d<15nm) particles composition. The main principle of operation of the DMA ([14], [15]) is to select a narrow band of an aerosol size distribution by applying high voltage to its central rod thus selecting particles with a particular electrical mobility. Thisway, a monodisperse aerosol distribution is allowed to pass through the instrument. The UFO-TDMA uses ethanol vapor as the working fluid. The first DMA selects a monodisperse aerosol distribution which is brought to a selected sub-saturated ethanol vapor environment where particles can grow to a new size in accordance to their composition and size; the second DMA then measures the final size. The ratio between the measured size in the second DMA and the size selected in the first DMA is called the organic growth factor (OGF). Depending on the chemical composition of the particles, different amounts of ethanol are consumed at a given saturation ratio by the particles. We applied the UFO-TDMA to ultrafine 10-15nm particles. The saturation ratio was $82 \pm 2\%$.
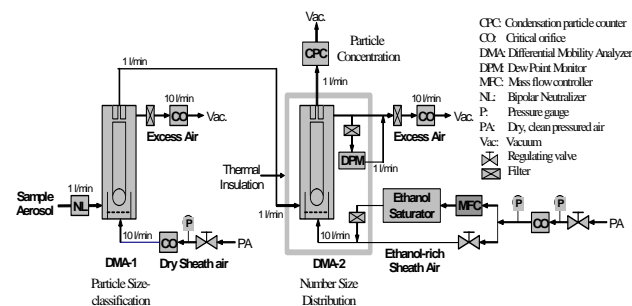

Fig. 1 A schematic of the UFO-TDMA system

The basic analysis principle is based on the fact that inorganic particles such as sodium chloride and ammonium sulfate do not grow (i.e. OGF is 1) in the sub-saturated ($S = 84\%$) ethanol vapor when the particle diameter is 20nm or smaller. Ammonium bisulfate would grow in 20nm size particles to an OGF of 1.02–1.03 but growth does not occur at 10nm size at 82–84% subsaturation [11]. Importantly, sulfuric acid is expected to be neutralized to ammonium sulfate in particle phase atmospheric conditions [16]. Indeed, [17] recently studied in CLOUD (Cosmics Leaving Outdoor Droplets) chamber nanoparticle formation and growth experiments that sulfuric acid was transformed to pure ammonium sulfate from 2nm diameter. Furthermore, iodine compounds do not grow [12]. On the other hand, particles composed of biogenic organics (e.g. citric acid or tartaric acid; [12]) or 10nm diameter secondary organics [18] do grow (i.e. OGF is clearly over 1) and generally, moderately oxidized organic do grow very well [18]. It is also notable that if particles are composed of organic non-polar compounds or if they are highly aged, they grow less.

The organic volume fraction (OVF) was calculated based on the principle introduced in [3]. The OVF is obtained from the following comparison: the volume corresponding to the measured size OGF is compared with the volume

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<15nm) 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 22ppb, 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 O_3. 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 10nm 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 100m height was received from the direction of Gladstone on the Queensland coast, which gave an OVF of 11% for 10nm 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 10nm particles during CORACE-1.

TABLE I
THE CONTRIBUTIONS OF SOA AND SULFATES

Experiment	Conditions	SOA (%)	Sulfates (%)	DMS_a(ppt_v)[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 chemi-adsorption of DMSa. Under calm conditions just after low tide on 3 June 2011 a peak DMSa of 12.8 ppt was detected, and again under similar conditions on 6 June 2011 a peak DMSa concentration of 13.1ppt 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 50km 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 (~1000W 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 17nm size during weak and 76% sulfates and 24% organics by volume in 22.5nm 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.
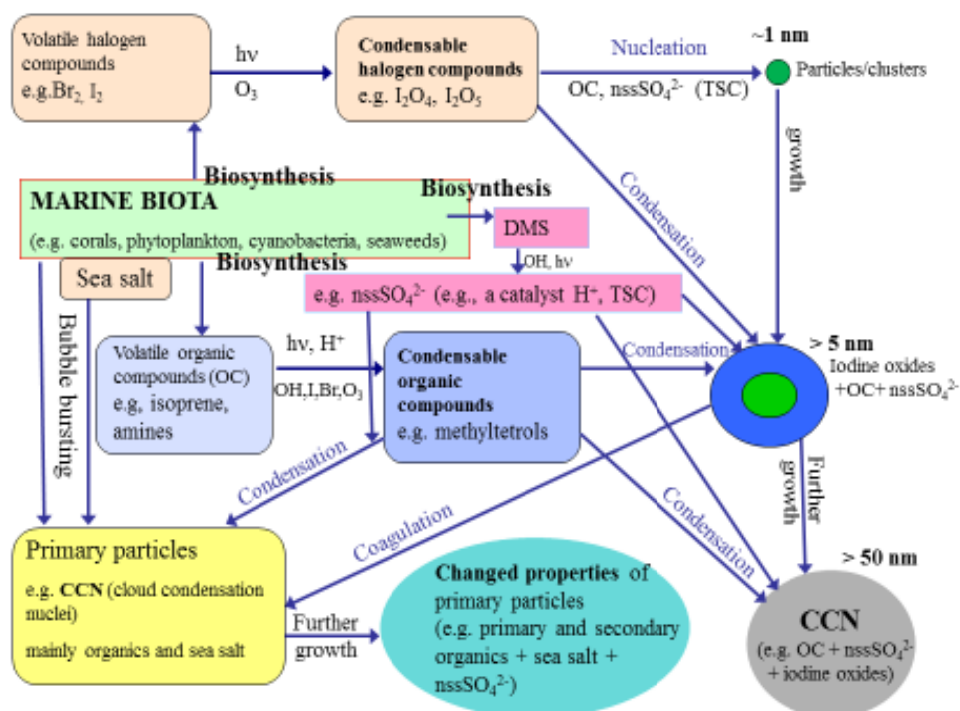
Fig. 2 A schematic of potential biogenic nucleation, Aitken and accumulation mode particle formation, growth, and composition during daylight hours at the Heron reef marine environment

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.

REFERENCES

[1] IPCC, climate Change 2007: Summary for Policymakers. IPCC WGI Fourth Assessment Report, ed. R. Alley. 2007, Geneva, Switzerland: IPCC.
[2] M. Kulmala and, V.-M. Kerminen, *Atmospheric Research*, 90, 132-150, 2008.
[3] Vaattovaara, P., Huttunen, P. E., Yoon, Y. J., Joutsensaari, J., Lehtinen, K. E. J., O'Dowd, C. D., and Laaksonen, A.: The composition of nucleation and Aitken mode particles during coastal nucleation events: evidence for marine secondary organic contribution, Atmos. Chem. Physics, 6, 4601-4616, 2006.
[4] Jell, J. S. and Flood, P. G. (1 April 1978) Guide to the Geology of Reefs of the Capricorn and Bunker Groups, Great Barrier Reef Province with special reference to the Heron Reef. Papers, Department of Geology,

University of Queensland, 8 3: 1–85 http://espace.library.uq.edu.au/view/UQ:10881

[5] Bigg, E. K., and Turvey, D. E.: Sources of atmospheric particles over Australia, Atmos. Environ., 12, 1643-1655, 1978.

[6] Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326, 655-661, 1987.

[7] Jones, G. B., and Trevena, A. J.: The influence of coral reefs on atmospheric dimethylsulphide over the Great Barrier Reef, Coral Sea, Gulf of Papua and Solomon and Bismarck Seas, Mar. Fresh. Res., 56, 85-93, 2005.

[8] Broadbent, A., and Jones, G.: Seasonal and diurnal cycles of dimethylsulfide, dimethylsulfoniopropionate and dimethylsulfoxide at One Tree Reef lagoon, Environ. Chem, 3, 260-267, 2006.

[9] Modini, R. L., Ristovski, Z. D., Johnson, G. R., He, C., Surawski, N., Morawska, L., Suni, T., and Kulmala, M.: New particle formation and growth at a remote, subtropical coastal location, Atmos. Chem. Physics Discuss., 9, 12101-12139, 2009.

[10] University of Queensland Centre for Marine Studies: Island Research Station. Retrieved 2006-JUL-14.

[11] Fosberg, F.R., Thorne, R.F. and Moulton, J.M. (1961): Heron Island, Capricorn Group, Australia. Atoll Research Bulletin82: 1–16.

[12] Vaattovaara, P., Räsänen, M., Kühn, T., Joutsensaari, J., and Laaksonen, A.: A method for detecting the presence organic fraction in nucleation mode sized particles, Atmos. Chem. Physics, 5, 3595-3620, 2005.

[13] Joutsensaari, J., Vaattovaara, P., Vesterinen, M., Hämeri, K., and Laaksonen, A.: A novel tandem differential mobility analyzer with organic vapor treatment of aerosol particles, Atmos. Chem. Physics, 1, 51-60, 2001.

[14] Knutson, E.O. and Whitby, K.T. Aerosol classification by electric mobility: apparatus, theory and applications: Journal of Aerosol Science, 6, 443-451-1975.

[15] Liu,B.Y.H., Pui, D.Y.H., Whitby, K.T., Kittelson, D.B., Kousaka, Y., and McKenzie, R.L. Aerosol mobility chromatograph – new detector for sulphuric-acid aerosols. Atmospheric Environment, 12, 99-104, 1978.

[16] Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics, John Wiley & Sons Inc, New York, 1326 pp., 2006.

[17] H. Keskinen, A. Virtanen, J. Joutsensaari, G. Tsagkogeorgas, J. Duplissy, S. Schobesberger, M. Gysel, F. Riccobono, J. G. Slowik, F. Bianchi, T. Yli-Juuti, K. Lehtipalo, L. Rondo, M. Breitenlechner, A. Kupc, J. Almeida, A. Amorim, E. M. Dunne, A. J. Downard, S. Ehrhart, A. Franchin, M.K. Kajos, J. Kirkby, A. Kürten, T. Nieminen, V. Makhmutov, S. Mathot, P. Miettinen, A. Onnela, T. Petäjä, A. Praplan, F. D. Santos, S. Schallhart, M. Sipilä, Y. Stozhkov, A. Tomé, P. Vaattovaara, D. Wimmer, A. Prevot, J. Dommen, N. M. Donahue, R.C. Flagan, E. Weingartner, Y. Viisanen, I. Riipinen, A. Hansel, J. Curtius, M. Kulmala, D. R. Worsnop, U. Baltensperger, H. Wex, F. Stratmann, and A. Laaksonen. Evolution of particle composition in CLOUD nucleation experiments.Atmos. Chem. Phys., 13, 5587-5600, 2013

[18] Vaattovaara, P., Petäjä, T., Joutsensaari, J., Miettinen, P., Zaprudin, B., Kortelainen, A., Heijari, J., Yli-Pirilä, P., Aalto, P., Worsnop, D. R., and Laaksonen, A.: The evolution of nucleation and Aitken-mode particle compositions in a boreal forest environment during clean and pollution-affected new particle formation events, Boreal Environ. Res., 14, 662-682, 2009.

[19] Deschaseaux, E., Jones, G., Miljevic, B., Ristovski, Z., Swan, H., and Vaattovaara, P.: Can corals form aerosol particles through volatile sulphur compound emissions?, The 12th International Coral Reef Symposium, Paper 4A-3 in Water motion, abiotic and biotic processes on coral reefs, 1-5, 2012.

[20] Swan, H. B., Jones, G. B., and Deschaseaux, E.: Dimethylsulfide, climate and coral reef ecosystems, The 12th International Coral Reef Symposium, Paper 4A-5 in Water motion, abiotic and biotic processes on coral reefs 1-5, 2012.

[21] Carpenter, L. J., Hebestreit, K., Platt, U., and Liss, P. S.: Coastal zone production of IO precursors: a 2-dimensional study, Atmos. Chem. Physics, 1, 9-18, 2001.

[22] O'Dowd, C. D., and Hoffman, T.: Coastal new particle formation: a review of current state-of-the-art, Environ. Chem, 2, 245-255, 2005.

[23] Johnson, G. R., Ristovski, Z. D., D'Anna, B., and Morawska, L.: Hygroscopic behaviour of partially volatilised coastal marine aerosols using the volatilisation and humidification tandem differential mobility analyser technique, J. Geophys. Res., 110, 10.1029/2004 JD005657, 2005.

[24] Cainey, J. M., Keywood, M., Grose, M. R., Krummel, P., Galbally, I. E., Johnston, P., Gillett, R. W., Stein, T., Ibrahim, O., Ristovski, Z. D., Johnson, G., Fletcher, C. A., Bigg, E. K., and Gras, J. L.: Precursors to particles (P2P) at Cape Grim 2006: campaign overview, Environ. Chem, 4, 143-150, 2007.

[25] Broadbent, A.D. and G.B. Jones, DMS and DMSP in mucus ropes, coral mucus, surface films and sediment pore waters from coral reefs in the Great Barrier Reef. Marine and Freshwater Research, 55(8), 849-855, 2004.

[26] Finlayson-Pitts, B. J., and Pitts Jr, J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, experiments, and applications, Academic Press, San Diego, USA, 969 pp., 2000.

[27] Ristovski, Z. D., Suni, T., Kulmala, M., Boy, M., Meyer, N. K., Duplissy, J., Turnipseed, A., Morawska, L., and Baltensperger, U.: The role of sulphates and organic vapours in new particle formation in a eucalypt forest, Atmos. Chem. Physics, 10, 2919-2010, 2010.

[28] Zelenyuk, A., Imre, D., Earle, M., Easter, R., Korolev, A., Leaitch, R., Liu, P., MacDonald, A. M., Ovchinnikov, M., and Strapp, W.: In situ characterization of cloud condensation nuclei, interstitial, and background particles using the single particle mass spectrometer, SPLAT II, Anal. Chem., 82, 7943-7951, 2010.

[29] Leahy, SM, Kingsford MJ, and Steinberg, CR., Do Clouds Save the Great Barrier Reef? Satellite Imagery Elucidates the Cloud-SST Relationship at the LocalScale. PLoS ONE 8(7): e70400. doi:10.1371/journal.pone.0070400, 2013

[30] Woodhouse, M. T., Mann, G. W., Carslaw, K. S., and Boucher, O.: Sensitivity of cloud condensation nuclei to regional changes in dimethyl-sulphide emissions, Atmos. Chem. Physics, 13, 2723-2733, 10.5194/acp-13-2723-2013, 2013.