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# **New particle formation and growth at a remote, sub-tropical coastal location**

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## **Abstract**

A month-long intensive measurement campaign was conducted in March/April 2007 at Agnes Water, a remote coastal site just south of the Great Barrier Reef on the east coast of Australia. Particle and ion size distributions were continuously measured during the campaign. Coastal nucleation events were observed in clean, marine air masses coming from the south-east on 65% of the days. The events usually began at ~10:00 local time and lasted for 1-4 hrs. They were characterised by the appearance of a nucleation mode with a peak diameter of ~10 nm. The freshly nucleated particles grew within 1-4 hrs up to sizes of 20-50 nm. The events occurred when solar intensity was high (~1000 W m<sup>-2</sup>) and RH was low (~60%). Interestingly, the events were not related to tide height. The volatile and hygroscopic properties of freshly nucleated particles (17-22.5 nm), simultaneously measured with a volatility-hygroscopicity-tandem differential mobility analyser (VH-TDMA), were used to infer chemical composition. The majority of the volume of these particles was attributed to internally mixed sulphate and organic components. After ruling out coagulation as a source of significant particle growth, we conclude that the condensation of sulphate and/or organic vapours was most likely responsible for driving particle growth during the nucleation events. We cannot make any direct conclusions regarding the chemical species that participated in the initial particle nucleation.

However, we suggest that nucleation may have resulted from the photo-oxidation products of unknown sulphur or organic vapours emitted from the waters of Hervey Bay, or from the formation of DMS-derived sulphate clusters over the open ocean that were activated to observable particles by condensable vapours emitted from the nutrient rich waters around Fraser Island or Hervey Bay. Furthermore, a unique and particularly strong nucleation event was observed during northerly wind. The event began early one morning (08:00) and lasted almost the entire day resulting in the production of a large number of  $\sim 80$  nm particles (average modal concentration during the event was  $3200 \text{ cm}^{-3}$ ). The Great Barrier Reef was the most likely source of precursor vapours responsible for this event.

## 1. Introduction

Marine aerosols constitute a significant fraction of global aerosol mass and therefore have an important role in the way aerosols impact global climate through their ability to scatter and absorb radiation and influence the microphysical properties (reflectance, lifetime, and precipitation efficiency) of clouds. The number concentration of particles in the pristine marine boundary layer (MBL) is relatively stable at around  $200\text{-}500 \text{ cm}^{-3}$ . Wet and dry deposition are continuously present sinks that act to decrease this number concentration. This implies that to maintain stable number concentration there must be natural sources of marine aerosols that are continuously replenishing the number of particles in the MBL. For a detailed discussion on the sources of marine aerosol see O'Dowd and De Leeuw (O'Dowd and De Leeuw, 2007).

This article will focus only on the secondary production of ultra-fine particles through the nucleation of low vapour pressure gases produced naturally in the MBL. The secondary production of atmospheric particles requires two (likely decoupled) processes: 1) the nucleation of stable atmospheric clusters (1-3 nm) and 2) the growth or activation of these clusters into observable aerosol particles ( $>3$  nm) (Kulmala et al., 2000). The first particle formation step requires sufficient concentrations of a low-vapour-pressure gas (typically sulphuric acid) and water vapour to form molecular clusters. This process may be enhanced by the presence of a third vapour (e.g. ammonia, low-volatility organics)

that participates in a ternary nucleation mechanism, or ions that increase the stability of molecular clusters (ion-induced nucleation). The second step of particle growth to observable sizes is controlled by the competition between particle growth, which may happen via a number of mechanisms, and scavenging of clusters by larger pre-existing particles. Particle growth or activation may (and, in fact, probably does) occur due to the condensation of extra vapours not involved in the initial particle formation process (such as low-volatility organics). Evidence, both theoretical and recently experimental (Kulmala et al., 2007b), is mounting to suggest that large amounts of charged and neutral clusters are almost always present in the atmosphere. Thus the second step of particle activation by extra, condensable vapours is likely to be the limiting step in the production of atmospheric particles. Once activated, continued condensation of vapours is required for particles to grow quickly to sizes greater than ~40 nm where they can participate in the direct and indirect effects of aerosols on climate. See Kulmala and Kerminen (2008) for a thorough discussion of the current state of knowledge regarding the secondary formation and growth of atmospheric particles.

Sulphates dominate the sub-micrometre particle number concentration in the MBL (Fitzgerald, 1991). Sulphuric acid may be derived from the oxidation of di-methyl sulphide (DMS) emitted by marine algae and phytoplankton (Cox and Sandalls, 1974; Lovelock et al., 1972). However, despite a significant number of field measurements, observations of sulphate particle formation in the MBL are rare. Clarke et al. (1998) observed a nucleation event on the Pacific Ocean during a 360 km long near-surface flight and linked the observed new particle formation event after precipitation to naturally produced DMS. However, the measurements combined with dynamic modelling of binary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation showed that sulphuric acid concentrations were too low for binary nucleation to occur and a third gas, likely ammonia, was posited to have induced a ternary nucleation process. Pirjola et al (2000) also showed that, under typical conditions in the MBL, binary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation will not occur and ternary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_4$  nucleation will only occur infrequently to produce particles with a detectable size (>3 nm). Within the free troposphere the conditions for DMS induced nucleation are much more probable due to the lower temperature and lower existing particle surface.

Nucleation events have been observed in the outflow of clouds during aircraft flights (Clarke and Kapustin, 2002; de Reus et al., 2001; Perry and Hobbs, 1994; Zaizen et al., 1996) as well as due to the entrainment of freshly nucleated particles from the free troposphere during dynamic weather events such as the passage of cold fronts (Bates et al., 1998; Covert et al., 1996).

Coastal nucleation events occurring locally in the boundary layer are much more frequently observed than nucleation events occurring over the remote ocean. Most of our information about coastal nucleation is based on comprehensive measurements performed at one location in particular: Mace Head, Ireland, where nucleation of particles has been observed on almost a daily basis for more than 15 years. These events correlate with tide and solar irradiance. However, dynamic modelling combined with precursor gas concentration measurements, TEM analysis and hygroscopic growth factor measurements have shown that sulphuric acid does not drive the particle production seen at this site (even if it potentially participates in the initial formation of stable atmospheric clusters). Instead, O'Dowd and Hoffman (2005) and references therein, suggested that during low tide the exposed marine biota emits iodine-containing compounds that act as the gas responsible for driving particle growth to detectable sizes. There is also evidence that secondary organic compounds contribute to nucleation mode particle growth at this site at sizes greater than about 5-6 nm (Vaattovaara et al., 2006).

In Moreton Bay on the east coast of Australia, the role of iodine in particle formation and growth is very small or even nonexistent (Johnson et al., 2005). The physicochemical characterisation of 14 and 18nm particles during nucleation events at this site showed that the majority of their volume could be attributed to partially and fully neutralised sulphates (or MSA) plus a volatile organic species. The nucleation mode particles also contained a small fraction (5% by volume) of material that evaporated at  $\sim 300\text{-}350^{\circ}\text{C}$  and had iodine-pentoxide-like hygroscopic properties. However, this result is uncertain because at  $\sim 300\text{-}350^{\circ}\text{C}$  the diameter of the nucleation mode particles was approaching the lower detection limit of the instrumentation. Consequently, whether particle formation occurred via a sulphate- or iodine-related mechanism in Moreton Bay is still

unclear. However, we can conclude that sulphates and/or organics were responsible for initial particle growth to sizes above 10 nm.

Lee et al. (2008) observed frequent nucleation events in the western coastal region of Korea. Sulphuric acid concentration was higher on event days than non-event days. Similarly at Preila environmental pollution research station on the Curonian Spit in Lithuania, Ulevicius (2002) observed nucleation events on days when the average daily concentrations of SO<sub>2</sub> or NO<sub>2</sub> were two to three times higher than the average monthly concentrations. However, neither of these studies provided enough evidence to completely attribute the events to sulphur-related (as opposed to iodine-related) nucleation. Coastal nucleation events have also been observed at Bodega Bay, California (Wen et al., 2006). During this study, no measurements were performed to identify the precursor responsible for particle nucleation and growth but coastal biogenic activity did play a role. Two studies have observed nucleation events in continentally-affected air masses arriving at coastal measurement sites. In both cases the events were attributed to continental, as opposed to marine/coastal sources and they will not be discussed in any further detail here (Coe et al., 2000; Russell et al., 2007). Apart from these studies and the large amount of research conducted at Mace Head, few other studies of coastal nucleation events are reported in the literature. The question of whether sulphates or iodine-containing species are responsible for particle formation and growth at other coastal locations around the world is yet to be thoroughly investigated

One method of investigating potential mechanisms of new particle formation and growth is to obtain information about the chemical composition of freshly nucleated particles. Current state-of-the-art techniques cannot measure the composition of stable atmospheric clusters < 3 nm in diameter and, therefore, cannot be used directly to investigate mechanisms of particle formation. Nevertheless a range of techniques exist, which can investigate the composition of particles in the observable nucleation mode size range (3-25 nm) immediately following a nucleation event. These techniques, listed with their approximate ranges of operation are as follows: CPC related physicochemical techniques, range 3-10 nm (Kulmala et al., 2007a; O'Dowd et al., 2002a); Thermal Desorption

Chemical Ionisation Mass Spectrometry (TDCIMS), range 5-20 nm (Smith et al., 2008; Smith et al., 2005; Smith et al., 2004); Aerosol Mass Spectrometry (AMS), lower limit ~20nm (Allan et al., 2006; Zhang et al., 2004); and Tandem Differential Mobility Analysis (TDMA) to measure particle hygroscopicity and/or volatility, lower limit 3nm (e.g. Ehn et al., 2007; Sakurai et al., 2005).

On their own, measurements of particle volatility and/or hygroscopicity place relatively weak constraints on the actual composition of ultra-fine particles because different chemical species can display similar physical properties within a TDMA system. To address this problem the Volatility-Hygroscopicity-Tandem Differential Mobility Analysis (VH-TDMA) technique was developed by Johnson et al. in 2004. The VH-TDMA *simultaneously* measures the volatile and hygroscopic properties of atmospheric nanoparticles over a continuous temperature range to produce a unique signature for each particle type. Comparison of VH-TDMA signatures measured in the field with those of laboratory aerosols of known chemical composition can then help determine the composition of the atmospheric particles. Johnson et al. have previously employed this technique in a coastal environment and successfully inferred the composition of freshly nucleated particles (Johnson et al., 2005, see above).

The objective of this study was 1) to identify if, and to what degree new particle formation and growth occurs in a remote, sub-tropical coastal environment and 2) to investigate possible mechanisms of new particle growth through indirect determination of the chemical composition of nucleation mode particles using a VH-TDMA system.

## **2. Materials and Methods**

### **2.1. Site details**

Agnes Water is a remote coastal headland located on the East coast of Australia (24.2<sup>0</sup>S 151.9<sup>0</sup>W) (Fig. 1). The exact measurement site was a private dwelling located directly on the beach, far from any local anthropogenic sources of particles such as roads. The site has a large open ocean sector covering the range of bearings from 320-110<sup>0</sup> (all bearings

in this paper are measured from true north). Fraser Island (a sand island covered in vegetation) and the tidal flats comprising Hervey Bay (depth < 25 m) lay ~150 km away at a bearing of approximately 110-135°. Further south at a bearing of ~140° is the town of Bundaberg. The Great Barrier Reef (GBR) lies to the north of the measurement point. The southernmost reefs of the GBR are approximately 50 km away at a bearing of 050°. The intensive campaign was conducted over a 4 week period in autumn (March/April) 2007.

## **2.2 Instrumentation**

### **2.2.1 Meteorological measurements**

A portable weather station (Monitor sensors, Brisbane Australia) was erected directly on the dunes overlooking the beach in front of the house at a sufficient distance from any large objects to prevent local variations in the measured wind speed and direction. The temperature, atmospheric pressure, solar irradiance, wind speed, wind direction and relative humidity were measured at 5 minute intervals throughout the entire campaign. These measurements were validated against 3 hour observations of the same variables collected from a nearby (~2 km) Australian Bureau of Meteorology (BOM) weather station (Town of 1770).

### **2.2.2 Particle measurements**

Size distributions of particles ranging from 4 to 165 nm in diameter were measured using a TSI Scanning Mobility Particle Sizer (consisting of a TSI 3080 short column electrostatic classifier and 3022 CPC operated in low flow mode). The SMPS completed one scan every 5 minutes.

The volatile and hygroscopic properties of particles with diameters from 10 to 110 nm were measured with a VH-TDMA system that is described in detail elsewhere (Fletcher et al., 2007; Johnson et al., 2004). Essentially, the system first electrostatically classifies the sizes of the ambient aerosol to produce a nearly monodisperse distribution of particles



around a chosen diameter. These particles are then heated in a low-flow thermodenuder (built in house). After the thermodenuder, the aerosol flow is split; half flows to a dry SMPS (RH<25%) and half flows to a humidified SMPS (see Johnson et al., 2008 for details of the humidification technique). The volatilised-dry particle diameter is taken as the median of the dry size distribution and the volatilised-humidified particle diameter is taken as the median diameter of the humidified size distribution. The output variables of the system recorded at each step of the volatilisation process are volume fraction remaining ( $V/V_0$ ) - which is obtained from the chosen initial particle diameter and the volatilised-dry diameter - and, diameter Hygroscopic Growth Factor (HGF) which is obtained by dividing the volatilised-humidified diameter by the volatilised-dry diameter. The use of two separate SMPS systems in the VH-TDMA allows the HGF of atmospheric particles to be measured as a function of both humidity ( $\leq 95\%$ ) and volatilisation temperature ( $< 500^\circ\text{C}$ ).

The VH-TDMA technique lends itself particularly well to the analysis of the composition and structure of marine particles because marine aerosols are thought to consist of only a few classes of compounds, each of which has very different volatile and hygroscopic properties. To complement the atmospheric measurements performed for this study we compared them with VH-TDMA measurements of laboratory generated aerosols of known composition that exist in the MBL. In particular, our database of laboratory VH-TDMA data includes measurements of ammoniated sulphates, sulphuric acid, MSA, ammonium nitrate (Johnson et al., 2004), sodium chloride, sea salt, iodine-containing compounds ( $\text{HIO}_3$ ,  $\text{I}_2\text{O}_5$ ) (Ristovski et al., 2006) and secondary organic aerosol (photo-oxidation products of  $\alpha$ -pinene) (Meyer et al., 2009).

Each presented VH-TDMA scan was performed with a different initial particle size and these are indicated in the individual figures. The initial particle size was chosen slightly above the centre of the nucleation mode (seen by the SMPS) at the beginning of the scan to account for growth of the mode during the scan. The scans involved increasing the thermodenuder temperature from ambient temperature to  $\sim 200^\circ\text{C}$  in  $5\text{-}10^\circ\text{C}$  steps. The RH in the humidified SMPS was kept constant at 90% (variation  $\pm 0.5\%$  during scan).

Volume fraction remaining ( $V/V_0$ ) and HGF (RH=90%) were simultaneously measured at each volatilisation temperature. Each VH-TMDA scan took ~1-2 hrs to complete.

The SMPS and VH-TDMA were set up on a second floor balcony of the dwelling directly facing the ocean. Ambient aerosol was drawn directly from a ~1m long conductive rubber tube connected to the roof of the balcony through a bipolar Kr85 aerosol neutraliser (TSI model 3077) and into the two instruments. The height of the instruments above the water line was approximately 5m.

### 2.2.3 Ion size distributions

The appearance of nucleation mode particles was also determined by measurement of the size distributions of atmospheric ions with an Air Ion Spectrometer (AIS, Airel Ltd. Estonia). The AIS measures the mobility distribution of both positive and negative ions spanning a diameter range of approximately 0.34 to 40 nm. The AIS consists of two cylindrical aspiration-type Differential Mobility Analysers (DMA), one for positive and one for negative ions. Each mobility analyser has 21 collector electrodes provided with individual electrometrical amplifiers for measuring the electrical current carried by ions of different mobilities (Mirme et al., 2007). The AIS was located next to the particle instrumentation.

## 2.3 Calculations of the ion and particle growth rates

Particle and ion growth rates (GR) during the nucleation events were calculated from the SMPS and AIS data by tracking the peak nucleation mode diameter over time. SMPS GR's over particular size ranges are not evaluated as statistically the total number of observed nucleation events is small (because this was a short, intensive campaign) and nucleation mode particles appeared at, grew to and were prominent at different sizes during each event. For this reason the SMPS derived GRs are presented with the corresponding size ranges that the calculations were made over as well as the sample sizes.

## 2.4 Supplementary data

Air mass back trajectories were calculated after the measurement campaign using the GDAS global dataset in the HYSPLIT model (Draxler and Rolph, 2003; Rolph, 2003). For an interesting air mass (e.g. new particle formation event) 96-hour back trajectories were calculated at altitudes of 10, 100, 1000 and 10000m to observe the passage of air in the marine boundary layer (MBL) and free troposphere before the air arrived at Agnes Water.

Biological activity in the waters surrounding the measurement site was examined using data from NASA's SeaWiFS Satellite (<http://oceancolor.gsfc.nasa.gov/>). In particular, chlorophyll *a* concentrations for the length of the campaign were determined from ocean colour data.

### **3. Results and discussion**

#### **3.1. Physical characterisation of nucleation events and comparison with meteorological variables**

##### **3.1.1. Wind direction**

Figure 2a is a polar plot of the total concentration of particles measured by the SMPS ( $4 \text{ nm} < d < 165 \text{ nm}$ ) as a function of wind direction. It is overlaid onto a map of the area surrounding Agnes Water and centred at the sampling point. The data are gathered into two main groups that reflect the prevailing wind directions during the campaign, which followed a very regular pattern. During the night winds came from the continental sector at bearing of  $220\text{-}145^\circ$  while during the day the winds moved progressively east ( $145\text{-}90^\circ$ ) and strengthened as the SE sea breeze commenced by the afternoon. The average concentration of particles ( $4 < d < 165 \text{ nm}$ ) over the entire length of the campaign coming from the whole marine/coastal sector (bearing range  $320\text{-}135^\circ$ ) was  $345 \text{ cm}^{-3}$ . The corresponding average concentration of particles coming from the continental sector (bearing range  $140\text{-}315^\circ$ ) was  $587 \text{ cm}^{-3}$ .

Although there was variation in the wind direction at night and day, the calculated HYSPLIT back trajectories indicate that almost all of the air masses arriving at the sampling point during the night or day had spent at least 96 hours travelling over the open Pacific Ocean S or SE of Australia within the marine boundary layer (MBL) (see Fig. 3). The fact that HYSPLIT sees very little difference between the histories of air masses arriving during the night and day could be due to the temporal and/or spatial resolution of the GDAS dataset in the HYSPLIT model. However, this fact also presents a possible explanation of why the concentration of particles coming from the continental sector (defined by wind direction) was relatively low (average  $587 \text{ cm}^{-3}$ ); these air masses may have originated over the open ocean and only crossed land briefly before arriving at the sampling point.

Nucleation mode particles were observed on 65% of days during the campaign. Back trajectory analysis indicated that the air masses did not arrive from the free troposphere; therefore, the nucleation mode particles must have originated in the MBL. To help identify the MBL source of these particles, two more polar plots are shown in Figures 2b and 2c. Figure 2b shows the concentration of particles with diameter between 40 and 165 nm as a function of wind direction while Fig. 2c shows the concentration of particles smaller than 40 nm as a function of wind direction. The dividing diameter of 40 nm between these two figures was chosen because the median diameter of the Aitken mode was very rarely observed below this diameter, while the median diameter of the nucleation mode was frequently observed to grow up to (and sometimes beyond) this diameter. Figure 2b indicates that the continental sector produced higher concentrations of Aitken and accumulation mode particles compared to the marine/coastal sector. Over the length of the campaign the average concentration of particles with diameter between 40 and 165 nm coming from the continental sector was  $445 \text{ cm}^{-3}$ . The corresponding average for particles in this size range coming from the marine/coastal sector was only  $196 \text{ cm}^{-3}$ . From Figure 2c we can see that the occurrence of high concentrations ( $>1000 \text{ cm}^{-3}$ ) of particles smaller than 40 nm is significantly more prevalent in the marine sector than in the continental sector.

### 3.1.2. Ion and particle size distributions

The nucleation mode particles generally disappeared quite abruptly after 1-2 hrs as the wind direction moved more north from 100°. Only 3 days could be classified as having strong nucleation events characterised by a) the clear growth of particles from the nucleation to the Aitken mode and by b) the persistence of such events for longer than 2 hours. Two such strong events occurred on the 27 and 28 March 2007 (Fig. 4). Note that according to the classification system described by Buenrostro Mazon et al. (2009) even these very strong nucleation events would be classified as ‘tail events’ rather than ‘events’ because the nucleation mode particles were not observed below 10 nm. The classification scheme of Vana et al. (2008) is more appropriate to apply to this study because it was developed for coastal nucleation events (in particular, at Mace Head) where particle formation happens at a point or line source. According to this scheme all of the nucleation events observed during this campaign would be classified as class III (apple-type) events.

One particular day stands out from the rest. On the day of 30 March 2007 local wind direction was from NNE (10-15°). This was the only period during the campaign when the local wind blew from this direction. Figures 2a, b and c clearly show the elevated concentrations of particles coming from that direction on this particular day. Back trajectories indicated that the air mass had still travelled from the SE, but it had passed Agnes Water before looping in an anti-clockwise direction and travelling back south to the sampling point crossing the southernmost reefs of the GBR on the way (Fig. 5a). Based on calculations from both HYSPLIT back trajectories and wind speed data it would have taken 10-20 hrs for the air to travel from the GBR to Agnes Water. Contour plots of the AIS and SMPS data collected on this day (Fig. 5b) indicated a very strong nucleation event. Particles (~10 nm) were observed at 08:00 LT. The particles grew very quickly into the Aitken mode (up to ~80 nm) where they persisted for almost the entire day.

### 3.1.3. Ion and particle growth rates

Interestingly, particle growth was never seen by the AIS to occur from molecular cluster size (<1.5 nm) to the Aitken mode. Nucleation events were always characterised by the abrupt appearance of ~5 nm ions in the AIS data and ~10 nm particles in the SMPS data. Nevertheless, particle growth was observed with both instruments during most of the nucleation events. For the majority of nucleation events that occurred in air masses from the marine/coastal sector (100-135°), the SMPS-derived GR varied from 1.8-8.2 nm h<sup>-1</sup> (Table 1). On 30 March 2007, GR for nucleation-mode particles was significantly higher, 15.1 nm h<sup>-1</sup>.

The AIS-derived GRs for larger ions (7-20 nm) were generally higher than the SMPS derived GRs. This can be explained by the different size ranges the calculations were performed over. Interestingly, the ion GRs during the nucleation event on 30 March 2007 were similar or smaller than the ion GRs during all other nucleation events, in contrast to the SMPS-derived GR. The GRs of both positive and negative smaller ions (1.5-7 nm) are much smaller than the GRs for larger ions. A review by Kulmala et al. (2004) indicated that particle GRs in a range of different environments typically vary between 1-20 nm h<sup>-1</sup>, although particle GRs as high as 180 nm h<sup>-1</sup> have been observed close to the coastal source region at Mace Head (Dal Maso et al., 2002; O'Dowd et al., 2007). The GRs observed in this study are slightly higher than particle GRs typically seen in the atmosphere but lower than the GRs observed close to the coast at Mace Head.

### 3.1.4. Tide height, solar intensity, wind speed and RH

To investigate the necessary conditions for new particle formation, we compared time series of particle concentration, tide height (Agnes Water), solar intensity, wind speed, wind direction and RH during strong and weak nucleation events (Figs. 6 and 7, respectively). The strong nucleation events plotted in Fig. 6 are the same events plotted in Fig. 4 and the weak events occurred daily from 6 to 9 April 2007. The oscillation in the wind direction from the continental to marine/coastal sector from night to day (and corresponding increase in wind speed) is seen in both Figs. 6 and 7. Immediately before

each event there was a decrease in particle concentration corresponding to the daily shift in the wind direction from the continental to the marine/coastal sector. The observed nucleation events caused total particle concentration to increase from several hundred particles/cm<sup>3</sup>, typical for remote marine background concentrations, to over 1000 particles/cm<sup>3</sup> during the nucleation events. The majority of nucleation events occurred at ~10:00 LT although some events appeared later in the day at 12:00-13:00. This means solar intensity was very high (~1000 W m<sup>-2</sup>) during each nucleation event and RH was relatively low (~50-60%). A striking feature of the nucleation events is that they are not related to tide height at the measurement site.

The majority of air masses in which nucleation events occurred also passed over another coastal area surrounding Fraser Island some 150 km upwind of the measurement site. A time series of tide heights at this coastal area throughout the campaign is plotted in Fig. 8. The times when the air masses containing nucleation mode particles (observed at Agnes Water) passed over this coastal region were calculated according to measured wind speed data at Agnes Water and Fraser Island. Again there was clearly no relationship between the occurrences of nucleation events and tide height at this coastal region.

### **3.2. Physicochemical characterisation of nucleation mode particles**

Figure 9 presents typical VH-TDMA scans on nucleation mode particles during one strong and one weak nucleation event. Each VH-TDMA scan showed a two-step volatilisation process and corresponding change in HGF which means the nucleation mode particles contained two components of differing volatility and hygroscopicity. Because the two components have different HGFs, there would be two modes in the humidified size distributions if the components were externally mixed. Only one mode was ever observed in the humidified size distributions, which indicates that these two components were internally mixed within the nucleation mode particles. For particles observed during the strong nucleation event (top of Fig. 9) the transition between the two components was very pronounced. The first component was relatively volatile and completely evaporated by ~110<sup>0</sup>C where the volatility curve flattened out. Over the same temperature range HGF increased rather abruptly from 1.26 to 1.44. For particles

observed during the weak nucleation event (bottom of Fig. 9) the volatilisation of the first component was more gradual as temperature increased. This was also reflected by the gradual increase in HGF with temperature. Whether gradual or abrupt, the increase in HGF as the first component evaporated means that this component was less hygroscopic than the second component. This information and the fact that the first component was relatively volatile (more so than sulphates) indicate that this component was most likely organic.

The volatilisation temperature of the second component corresponded to the volatilisation temperature of ammoniated sulphate (partially or fully neutralised sulphuric acid) nanoparticles. To further investigate this in Fig. 9 we compared ambient data with the volatility curves for 29 nm ammonium sulphate (AS) particles generated by atomising a dilute solution of ammonium sulphate in ultra-pure de-ionised water. Excellent agreement was obtained between the ambient and laboratory measurements when the volatility curves of the laboratory generated AS particles were normalised to the apparent volume fraction of the second component in each VH-TDMA scan. The measured HGFs of the nucleation mode particles also approached the modelled, dry size dependent AS HGF curves (Fig. 9). Therefore, based on the combined volatility and hygroscopic data, we can conclude that the second component of the nucleation mode aerosol was most probably ammoniated sulphate. Unfortunately, our method is unable to determine the degree of neutralisation of the ammoniated sulphate particles as partially and fully neutralised sulphate particles have similar growth factors and decompose via the same route. However, our results still clearly show that the majority of the volume of these nucleation mode particles can be attributed to internally mixed sulphate and organic components. Assuming that the particles were only composed of these two species, the 17 nm particles observed during the strong nucleation event consisted of ~60% sulphates-40% organics by volume and the 22.5 nm particles observed during the weak nucleation event consisted of ~76% sulphates- 24% organics by volume.

### **3.3. Comparison with other coastal nucleation sites**



Besides Mace Head there are only few locations where coastal nucleation events have been observed but unfortunately without detailed analysis of particle formation and growth mechanisms and particle precursor sources. Therefore we will focus on comparing our results with the results from Mace Head.

The nucleation events observed during this study were characterised by the appearance of a nucleation mode with peak diameter  $>10$  nm. At Mace Head the size at which the nucleation mode occurred depended on the distance of the tidal source region and varied from 3 to 10nm for source region distances from 100m to more than 10km, respectively (O'Dowd et al., 2002c). In our case the particles grew at a rate from 1.8-8.2 nm h<sup>-1</sup>, which is significantly lower than the growth rate of nucleation mode particles observed at Mace Head (Dal Maso et al., 2002; O'Dowd et al., 2007). The initial appearance of larger particles with lower growth rates in this study indicates that the source region for nucleation mode aerosol is further away from the measurement point. Assuming constant GRs we calculated that the source region is at a distance greater than 20 km from the measurement site. It is worth mentioning that in other locations such as forests the observed growth rates even close to the source are much lower indicating that the source location could be even further away.

Similarly to the events observed at Mace Head, solar radiation was a necessary condition for a nucleation event to occur, indicating that photochemical oxidation processes were an important stage in new particle formation. In contrast to the Mace Head observations, the occurrence of a nucleation event was not related to tide height during this study. Although a relationship between particle production and low tide has been observed at Mace Head and other coastal sites (Bigg and Turvey, 1978; Johnson et al., 2005; O'Dowd et al., 2002b), coastal particle production that is not related to tide height has been observed before at Bodega Bay, California (Wen et al., 2006).

Finally, iodine-containing compounds released by exposed macro-algae are primarily responsible for the particle production observed at Mace Head (O'Dowd and Hoffmann, 2005). Physicochemical characterisation of nucleation mode particles (17-22.5 nm)

during both strong and weak nucleation events in clean, marine air masses at Agnes Water indicated that the majority of their volume could be attributed to sulphate and organic components. It should be reiterated that the lower size limit of our VH-TMDA was 10 nm. Therefore from this analysis we cannot make any conclusions regarding the species that participated in the initial particle formation process. However, we can make conclusions regarding the mechanism responsible for nucleated particle growth. Simple calculations using basic polydisperse coagulation theory (Baron and Willeke, 2001) show that for the observed nucleation mode concentrations the process of coagulation could only account for a very small fraction of the observed particle growth rates (1.8-8.2 nm h<sup>-1</sup>). This means the majority of nucleation mode particle growth most likely occurred due to the condensation of sulphates and/or organic vapours. No evidence was obtained in this study to suggest that iodine-containing compounds were involved in new particle growth. Nevertheless we can not rule out the possibility that such compounds participated in the initial stage of particle formation.

#### **3.4. Possible particle precursor sources**

The question remains whether the sulphur or organic precursors responsible for driving the particle growth at Agnes Water were emitted by biomass in the open Pacific Ocean or by biomass in the coastal area SE of the sampling point? That is, to what extent did coastal biomass contribute to the observed particle production at this site? Chlorophyll *a* concentrations derived from the SeaWiFS satellite were used as an indicator of biological activity in the waters surrounding Agnes Water. Figure 10 highlights two areas of high biological activity over which air masses passed before arriving at Agnes Water. Firstly high chlorophyll *a* concentrations are observed in a large area in the remote Pacific Ocean between Tasmania and New Zealand (below latitude 40<sup>0</sup>S). Air masses would have passed over this area 3-4 days prior to arriving at Agnes Water. Secondly, much closer to Agnes Water, there is high biological activity in the waters of Hervey Bay. Fraser Island, which lies between Hervey Bay and the open ocean, prevents these two bodies of water from mixing well. This allows nutrients to build up in Hervey Bay and it is known to be an area rich in marine life.

Wind speed data indicates that the air masses in which nucleation events occurred passed over Hervey Bay 14-18 hrs before arriving at the sampling point. Depending on the precursor vapour, this may not be enough time to complete the necessary steps of photo-oxidation, nucleation into the particle phase and particle growth to ~10 nm. For example if DMS was the precursor vapour in question it would take 2-3 days to complete the complex oxidation pathway from DMS to SO<sub>2</sub> then to H<sub>2</sub>SO<sub>4</sub> before particle nucleation could even begin. This rules out DMS emitted from the coastal areas comprising Hervey Bay as the gaseous precursor responsible for the nucleation mode particles observed at Agnes Water. However it is quite possible that there could be another, as yet unknown, source of naturally emitted sulphur or organic vapours in that coastal region that could photo-oxidise to a low vapour pressure product that nucleates into the particle phase and grows to a size ~10 nm before being observed a few hours later downwind at Agnes Water. An observation that works against this hypothesis is that the occurrence of nucleation events was not related to tidal height at the coastal region around Fraser Island (see Fig. 7).

A second hypothesis is that the precursor gases ultimately responsible for particle nucleation may have been emitted by biomass in the region of high biological activity in the open ocean between Tasmania and New Zealand. Also, Vallina and Simo (2007) have shown that ocean surface DMS concentrations are dependent on solar radiation dose in the upper mixed layer of the ocean regardless of plankton biomass. Thus at these latitudes in the Pacific Ocean surface DMS concentrations are expected to peak in summer and remain relatively high moving into autumn (Simo and Pedros-Alio, 1999). As air masses travelled for 3-4 days over the open ocean before reaching Agnes Water the complex oxidation pathway from DMS to SO<sub>2</sub> then H<sub>2</sub>SO<sub>4</sub> could have been completed during this time resulting in the formation of stable sulphate clusters. Modelling studies and observations have shown that gaseous H<sub>2</sub>SO<sub>4</sub> concentrations in the MBL are rarely high enough to drive the growth of stable sulphate clusters into the observable particle size range before they are scavenged by pre-existing aerosol. However, some extra condensable vapours such as NH<sub>3</sub> or low-volatility organics may have been emitted from the vegetation on Fraser Island and/or the nutrient rich waters of Hervey Bay. These extra

condensable vapours could have activated the sulphate clusters into observable aerosol particles and continued condensing on the new particles to drive their growth to climatically relevant sizes (>40 nm). This hypothesis of DMS-derived remote marine nucleation with subsequent growth due to the coastal emission of condensable vapours is supported by the identification of a sulphate and organic component in the freshly nucleated particles observed at Agnes Water. To further test this hypothesis we would need concurrent measurements of potential gaseous precursors or a seasonal study to determine whether particle nucleation still occurs during winter and early spring when DMS concentrations in the surrounding ocean would be expected to be low.

The above discussion does of course not apply to the large nucleation event observed on 30 March 2007. No air masses with the same history, excepting the passage over the GBR, had such strong nucleation events throughout the campaign. Particle GR was also much higher during this event compared to all other events during the campaign (although ion GR was not). This suggests that the precursor source of these particles was different, or stronger, than the precursor source for all other nucleation events. The initial size of the nucleation mode particles observed at Agnes Water was ~10 nm, which indicates particle formation occurred somewhere upwind of the sampling point. Therefore we conclude that the GBR was the likely source of precursor vapours for these freshly formed particles. Coral reefs comprising the GBR are known to be large sources of DMS (Broadbent and Jones, 2004) and the GBR has long been suspected as a major source of freshly nucleated particles (Bigg and Turvey, 1978). However to our knowledge this is the first direct observation of particle formation from the GBR. Unfortunately on this day no physicochemical characterisation of the nucleation mode particles was completed and the mechanism of particle production and growth remains unknown. The particles produced from the GBR grew quickly up to ~80 nm in diameter. If we assume that similar particle production occurs along the whole 2600 km length of the GBR then it would constitute a major, natural source of ultrafine particles and cloud condensation nuclei (CCN) that would have a very significant role in regulating climate.

#### **4. Conclusions**

Coastal nucleation events were observed on 65% of the days during a month-long measurement campaign at the remote coastal location of Agnes Water. The events occurred in clean, marine air masses that had travelled from the SE over Hervey Bay. Solar intensity was high ( $\sim 1000 \text{ W m}^{-2}$ ) and RH was low ( $\sim 60\%$ ) during each event but there was no relationship between event occurrence and tide height. The growth rates of the nucleated particles were relatively high ( $1.8\text{-}8.2 \text{ nm h}^{-1}$ ). Nucleation mode concentrations were too low for coagulation to have a significant contribution to these observed growth rates. Therefore the condensation of low-volatility vapours was responsible for the majority of new particle growth. Based on the physicochemical characterisation of 17-22.5 nm particles with a VH-TDMA during both strong and weak nucleation events we attributed the majority of the volume of nucleated particles to sulphate and organic components. Therefore we conclude that the condensation of sulphate and/or organic vapours was most likely responsible for the growth of freshly nucleated particles to climatically relevant sizes. Two possible particle formation and growth mechanisms were suggested, both of which involved precursor vapours being emitted from the coastal area surrounding Hervey Bay. In addition, a unique and particularly strong nucleation event observed under northerly winds was attributed to the Great Barrier Reef.

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Table 1: Nucleation mode particle growth rates (GRs) calculated from the SMPS data

<b>Date in 2007</b>	<b>Growth rate (nm h<sup>-1</sup>)</b>	<b>Size range (nm)</b>	<b>Sample size (no. of data points in regression)</b>
27 March	1.8	17-21	26
28 March	8.2	16-24	15
30 March	15.1	20-46	23
04 April	4	16-20	15
05 April	6.5	17-23	13
06 April	7.2	19-31	18
08 April	2.9	16-22	25
09 April	5.4	15-21	15
10 April	5.8	15-22	18
11 April	7.9	17-25	15
12 April	6.1	12-26	28

Table 2: Nucleation mode negative (-) and positive (+) ion growth rates (GRs) calculated from the AIS data. Blank spaces indicate values that could not be reliably measured.

Date in 2007	Growth rate (nm h <sup>-1</sup> )					
	1.5-3 nm		3-7 nm		7-20 nm	
	-	+	-	+	-	+
27 March		0.9		1.9		
28 March			11.2	7.1		
30 March	2.8		8.7	5.8	15.1	12.4
04 April					15.1	5.8
05 April				0.6		14.5
06 April					17	19
08 April	0.4		2.1	2.6	22.5	36.5
09 April	2.7		3.8	5.4	43.3	26.1
10 April	6	1.7	3.5	2.5	19.7	18.6
11 April			3.4	1.8		
12 April					3.6	17.7
14 April						21.4

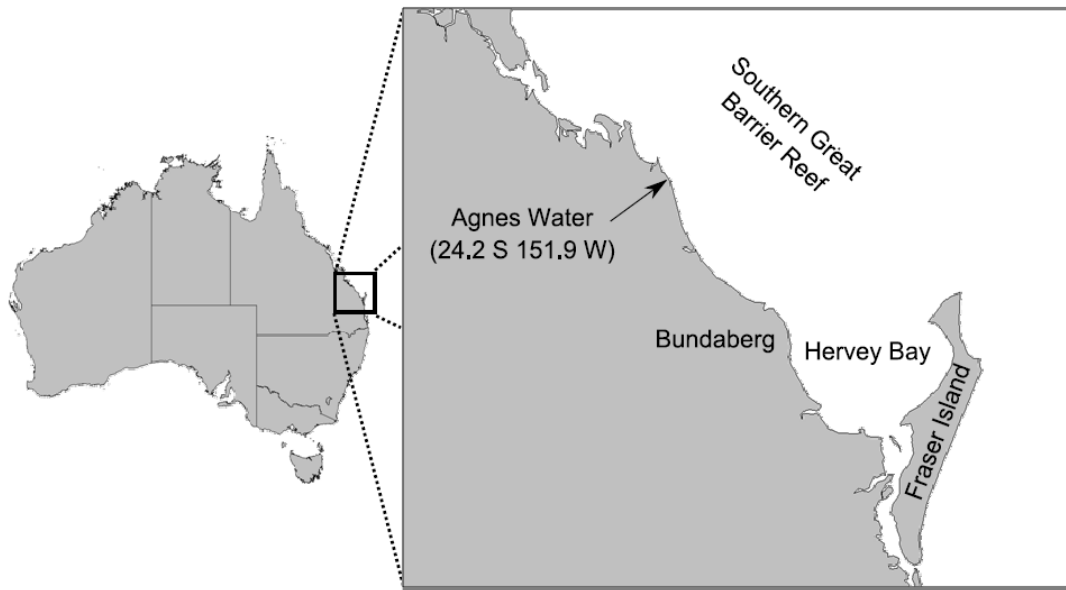


Figure 1: Map of Australia detailing the sampling point (Agnes Water) and surroundings

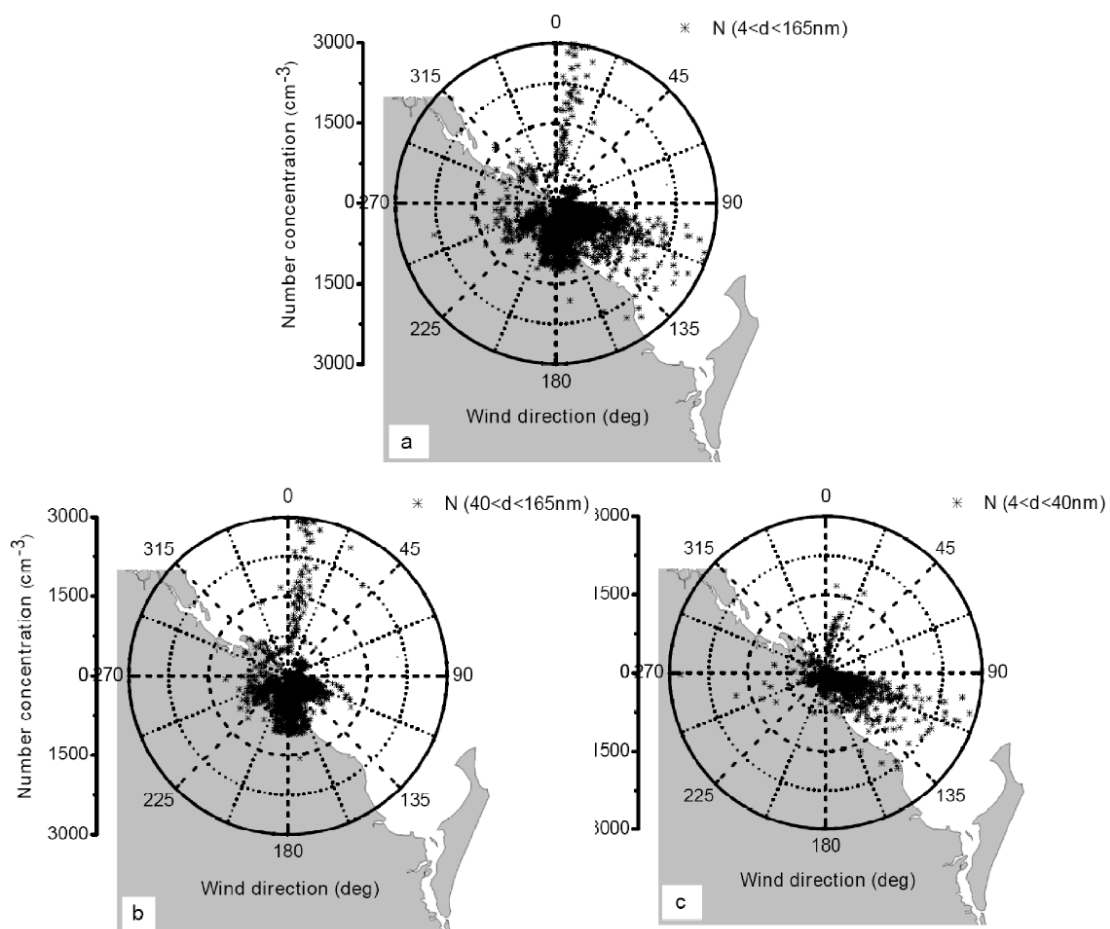


Figure 2: Polar plots of number concentration against wind direction for particles in the size range a) 4-165 nm, b) 40-165 nm and c) 4-40 nm.



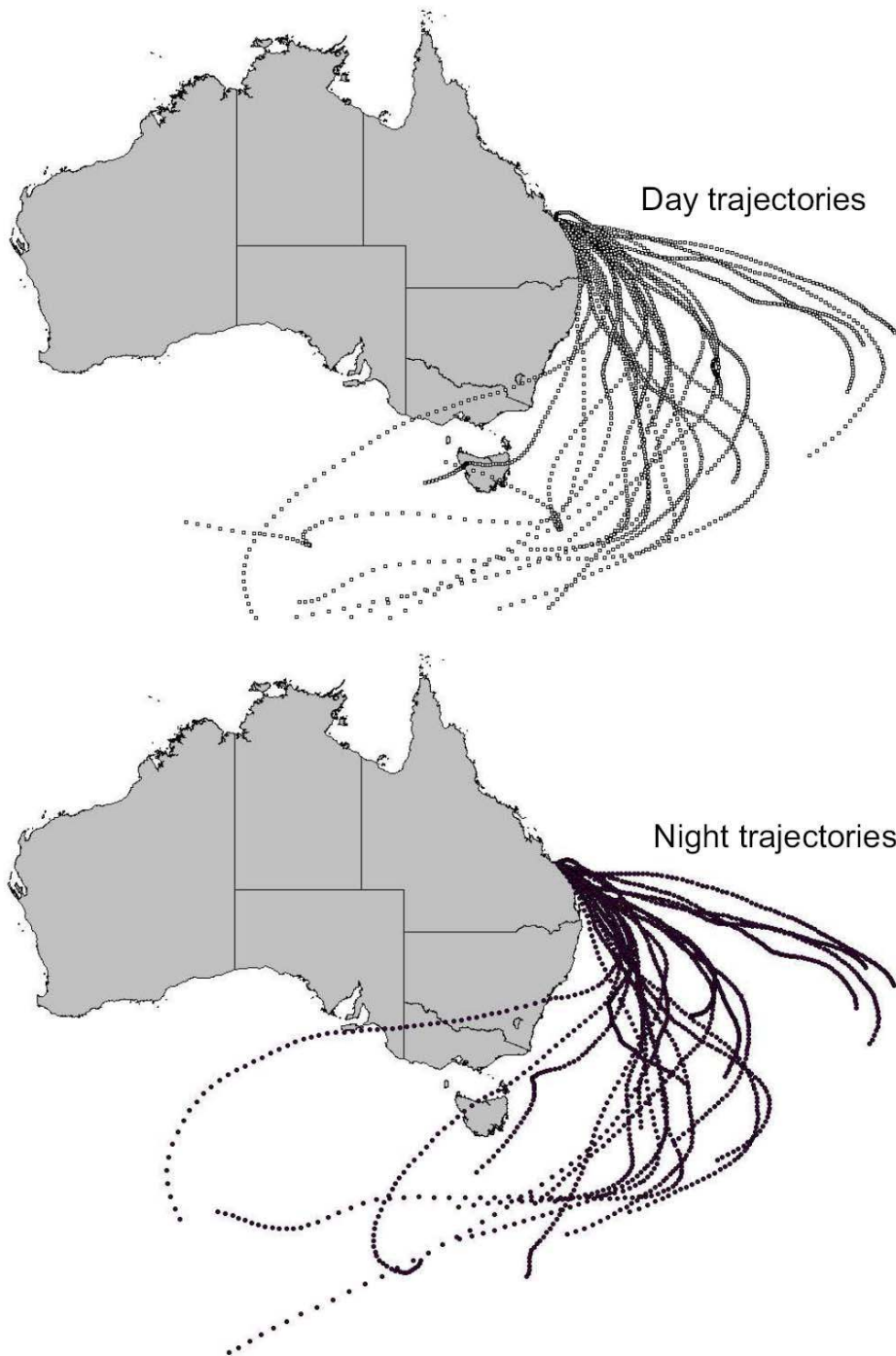


Figure 3: HYSPLIT 96-hour back trajectories for air masses arriving at Agnes Water at an altitude of 100 m on each day (12:00 local time) and night (02:00 local time) of the campaign. Note that there was no significant between these trajectories and the trajectories of air masses arriving at altitudes of 10 m and 1000 m.

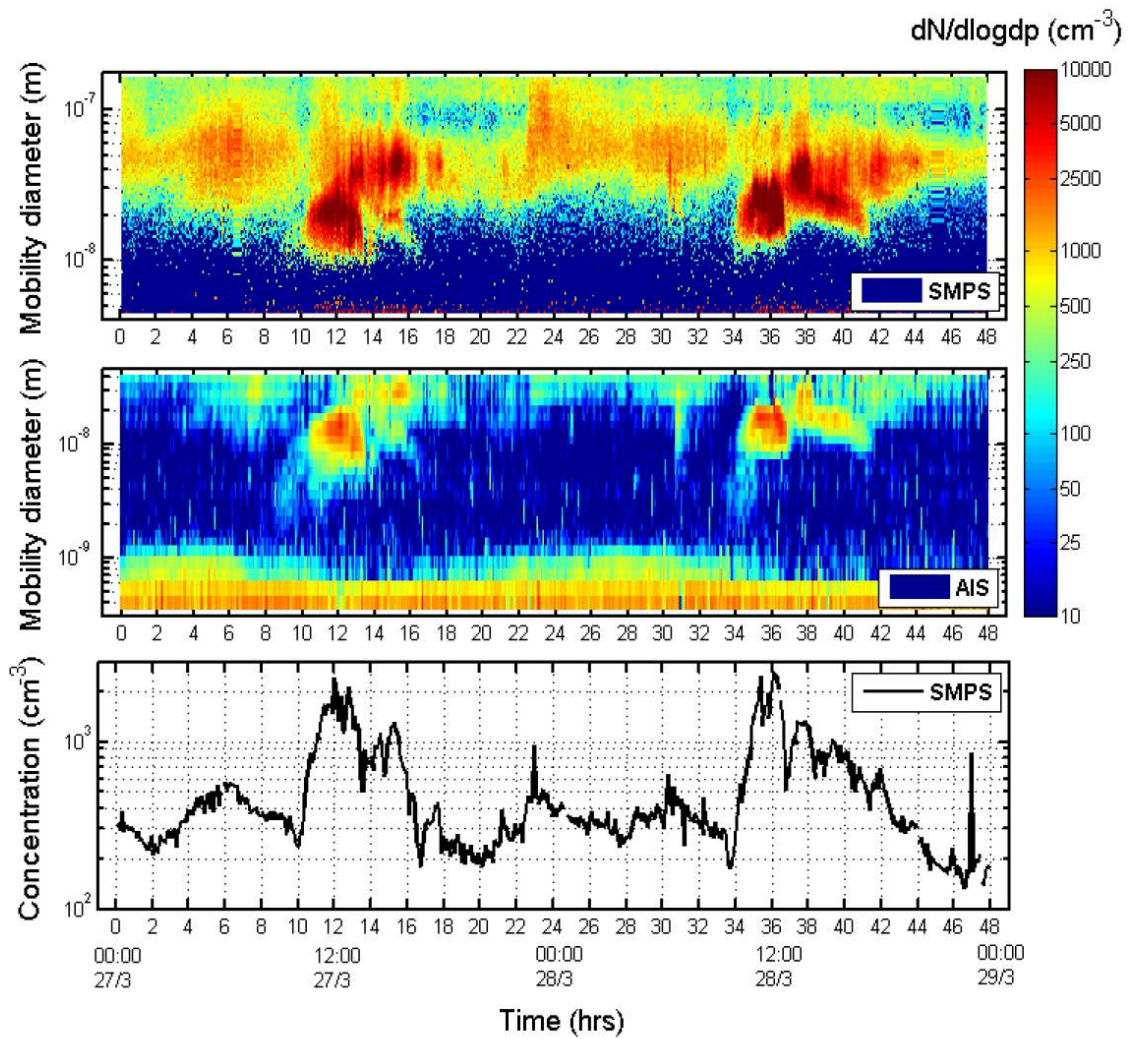


Figure 4: Contour plots of the AIS and SMPS data and a time series of particle concentration ( $4 < d < 165$  nm) for 27 and 28 March 2007. Legends indicate the instrument that measured the data in each graph. AIS data shown is for negative ions, the graph for positive ions looks very similar.

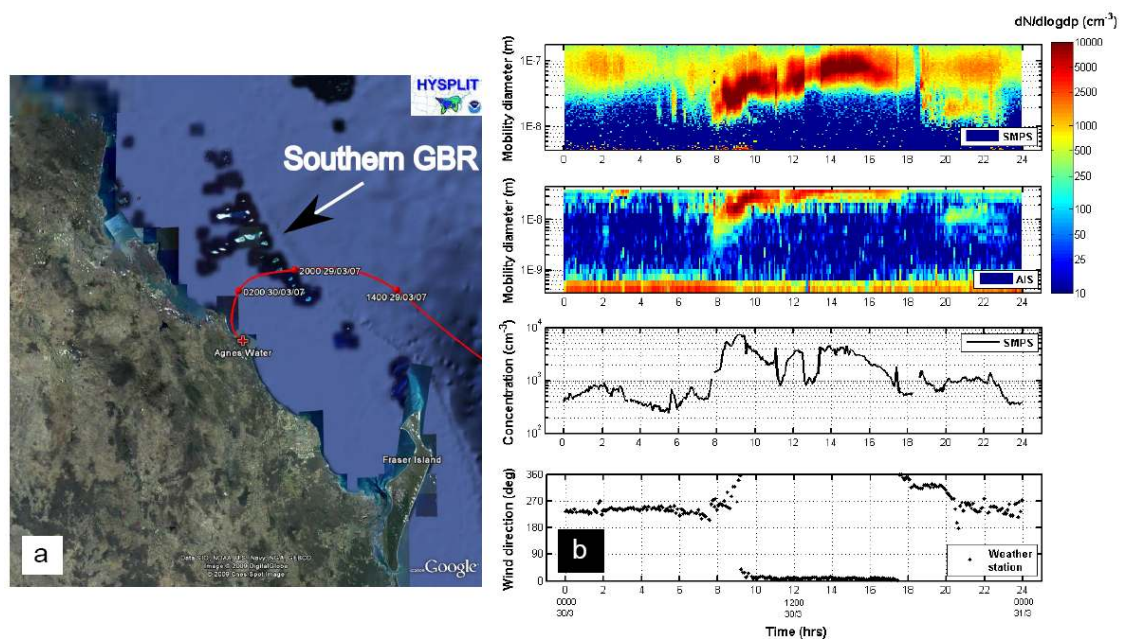


Figure 5: a) HYPLIT back trajectory for air mass arriving at Agnes Water at an altitude of 100m at 08:00 on 30 March 2007. The trajectory clearly shows the air mass crossing the southernmost reefs and islands of the Great Barrier Reef (GBR) on the previous night; b) Contour plots of the AIS and SMPS data plus time series of particle concentration ( $4 <d < 165$  nm) and wind direction for 30 March 2007. Legends indicate the instrument used to measure each data set.

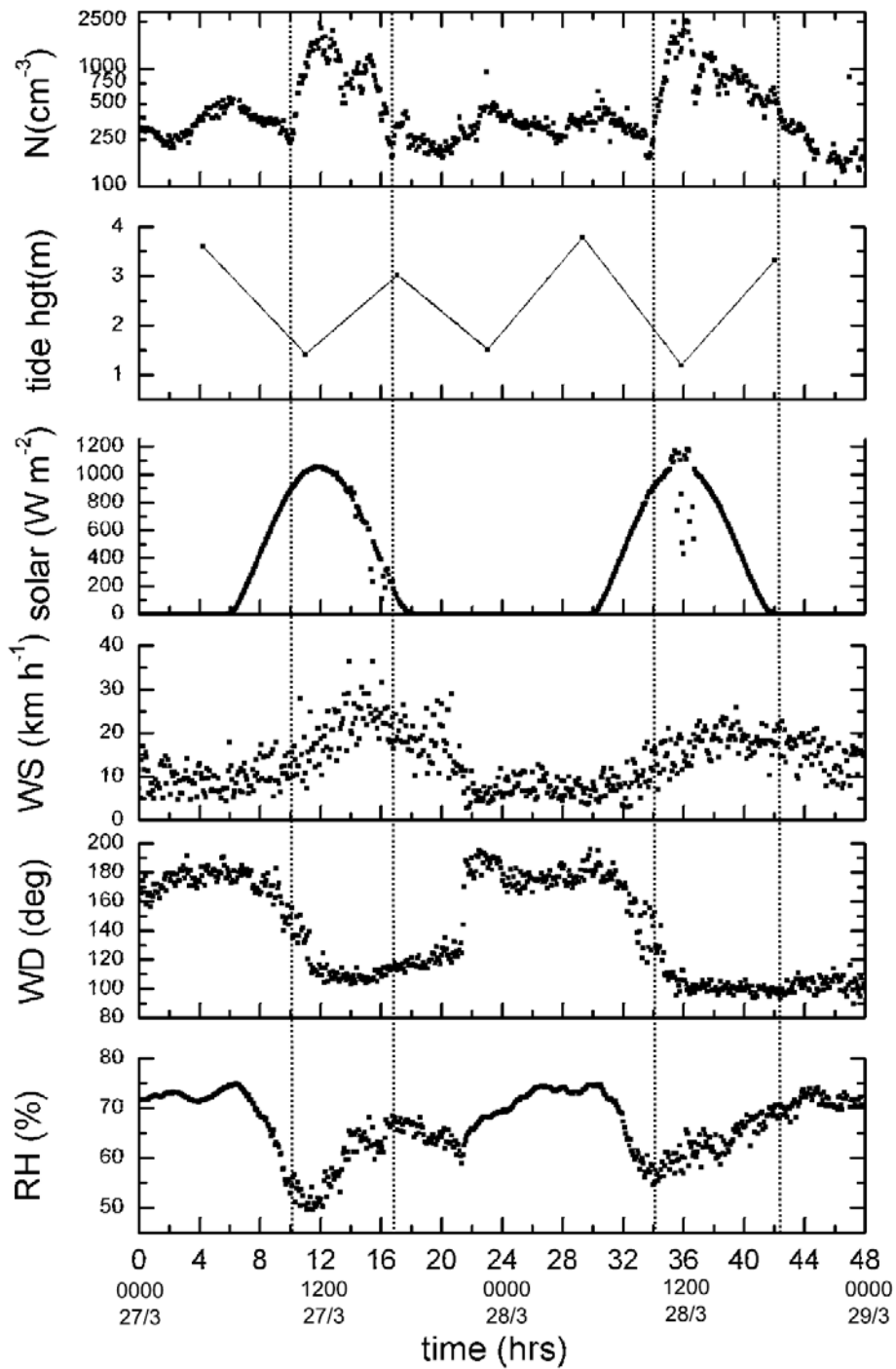


Figure 6: Time series of particle concentration ( $4 < d < 165$  nm),  $N$  ( $\text{cm}^{-3}$ ); tide height at Agnes Water, tide hgt (m); solar intensity, solar ( $\text{W m}^{-2}$ ); wind speed, WS ( $\text{km h}^{-1}$ ); wind direction from true north, WD (deg); and relative humidity, RH (%) for 27 and 28 March 2007. Dashed lines indicate the occurrence of 2 strong nucleation events.

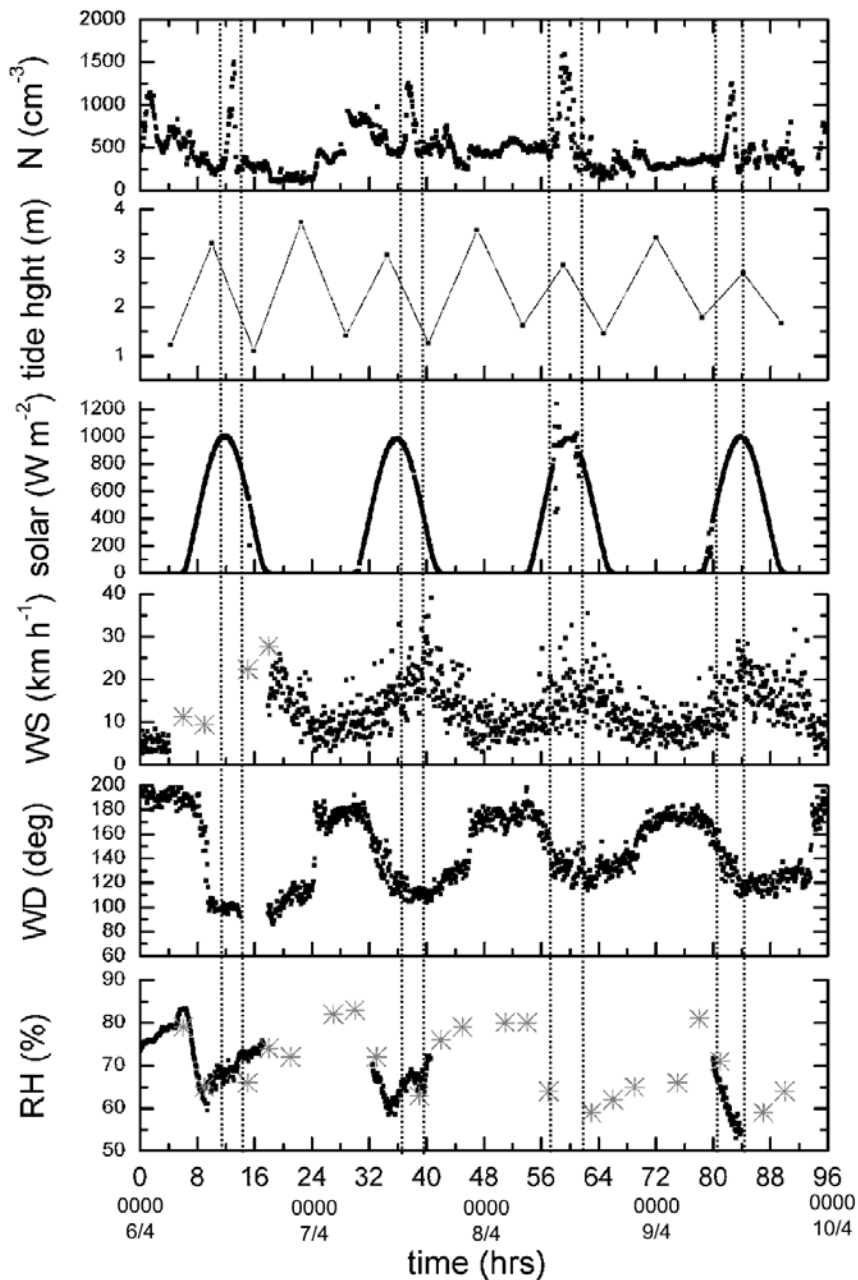


Figure 7: Time series of particle concentration ( $4 < d < 165$  nm),  $N$  ( $\text{cm}^{-3}$ ); tide height at Agnes Water, tide hght (m); solar intensity, solar ( $\text{W m}^{-2}$ ); wind speed, WS ( $\text{km h}^{-1}$ ); wind direction from true north, WD (deg); and relative humidity, RH (%) for 06 to 09 April 2007. Dashed lines indicate the occurrence of 4 weak nucleation events. Grey asterisks represent data collected from a nearby (Town of 1770) Australian Bureau of Meteorology weather station.

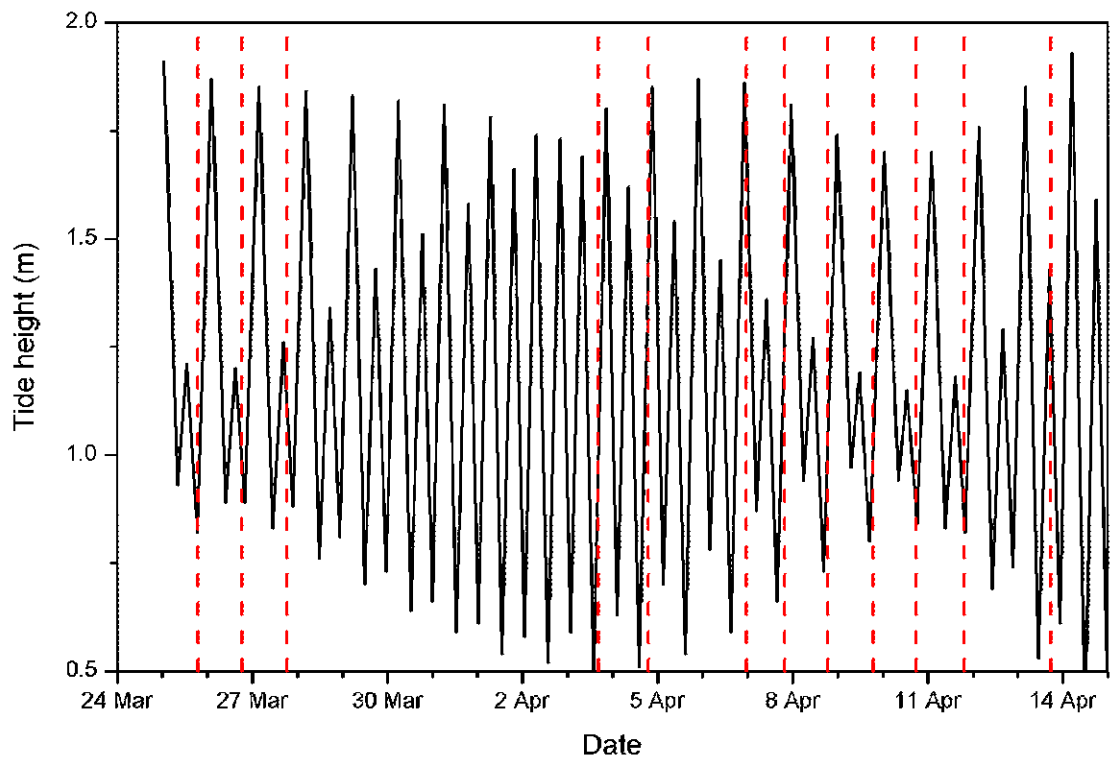


Figure 8: Tidal height at Fraser Island, a coastal area ~150 km upwind from the Agnes Water measurement site. Red dashed lines indicate the times when air masses that contained nucleation mode particles crossed this coastal region.

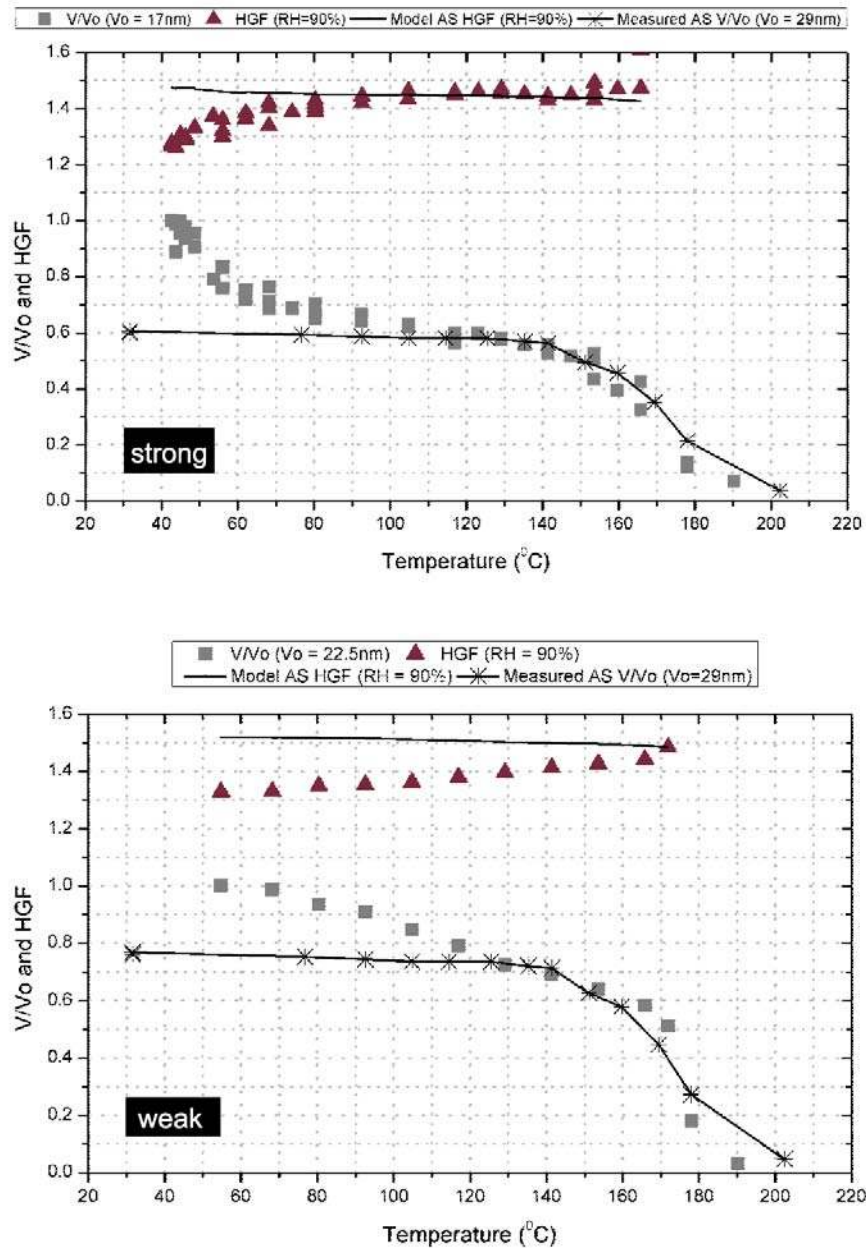


Figure 9: VHTDMA scans completed during a strong (top) and weak (bottom) nucleation event.  $V/V_o$  is volume fraction remaining and HGF (RH=90%) is the growth factor at 90% RH for the atmospheric particles. The solid black lines indicate measured volatility curve of ammonium sulphate (AS) particles normalised to the apparent volume fraction of the more hygroscopic component and theoretical, dry size dependent ammonium sulphate growth factors.

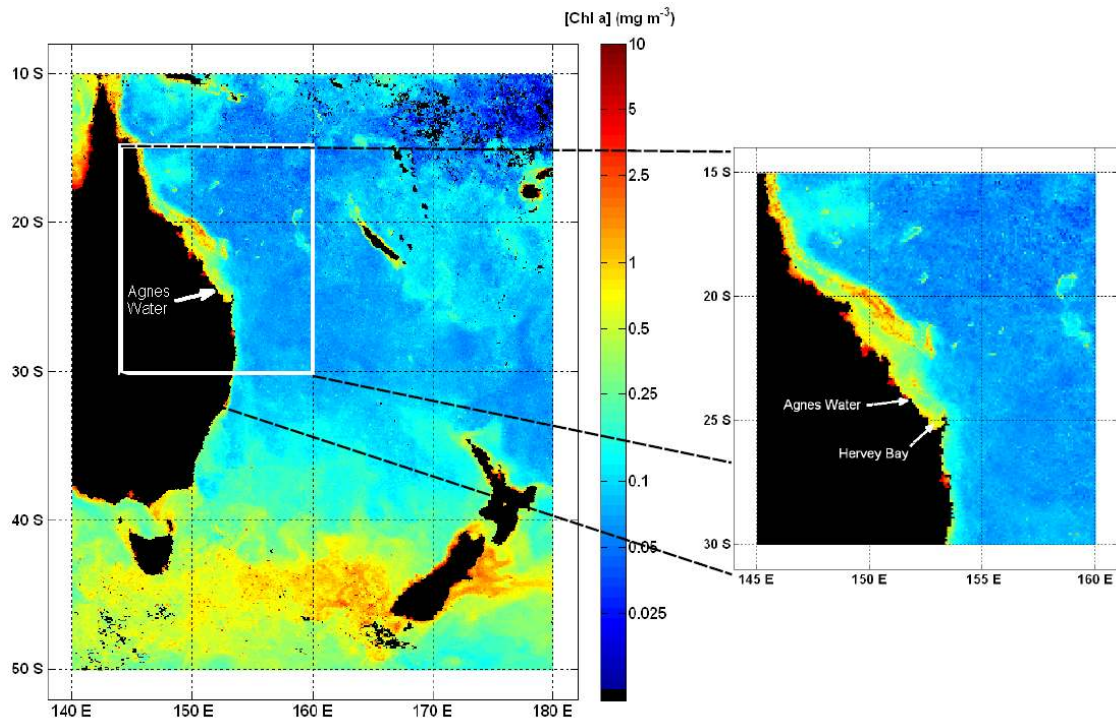


Figure 10: SeaWiFS derived surface chlorophyll concentrations off the east Australian coast averaged over the month of March 2007.