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Atmospheric Chemistry and Physics Discussions

Interactive comment on "New particle formation and growth at a remote, sub-tropical coastal location" *by* R. L. Modini et al.

R. L. Modini et al.

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We thank the reviewer for his/her constructive comments. Our replies follow each of the specific points raised by the reviewer below.

Comment: "1. Unfortunately, there is little time spent comparing and reconciling the measurements; they appear not to agree. From the gray scale it is difficult to tell how far off they are in the size range of overlap; perhaps a scatter plot at a series of relevant size ranges and some quantification of uncertainties, as well as some references to detailed instrument descriptions."

Response: We assume that the reviewer is referring to the discrepancy in initial particle/ion sizes measured by the AIS and SMPS (seen for example in Fig. 4). The

reviewer is correct in pointing this discrepancy out. We refer to this discrepancy on page 12114 line 3. We have now added a sentence after this stating that, "we cannot determine whether the discrepancies in initial sizes measured by the AIS and SMPS were due to measurement artefacts or actual physical differences between particles and ions." Because this difference does not effect the conclusions of our paper we believe it is sufficient to simply point it out.

Comment: "2. The more insidious problem with the manuscript is the extensive speculation above and beyond the evidence. Not a single gas or particle phase chemical species is measured by the instruments reported, and yet a large fraction of the paper, abstract, and conclusions is devoted to attributing the condensing species to organics and sulphur species, with specific attribution to DMS products. I am afraid the length and specifics of the discussion are entirely unwarranted. Here is an example from the abstract, where a physical volatility difference is used to attribute not only particle composition but precursors and their sources: "These particles contained internally mixed sulphate and organic components. We therefore conclude that sulphate and/or organic vapours were responsible for driving the initial particle growth to the observed sizes. 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: : :" 3. In short, these are very interesting physical measurements of particle growth, and the focus of the conclusions should be limited accordingly. If the mechanism is based largely on references, then specific reasons why the same mechanism should be cited and compared quantitatively."

Response: Firstly we would point out that the reviewer is referring to an earlier version of this manuscript, which was already revised following similar comments in the initial review stage before being published in ACPD. The quotation used by the reviewer is taken from the old version of the manuscript. Secondly we are not simply using a

volatility measurement to infer particle composition. We are using simultaneous measurement of volatility and hygroscopicity to infer chemical composition. A paragraph explaining the advantage of this compared to standard TDMA measurements was added after the initial review stage (page 12106 line 28). Finally in the paper we highlight in many places that from VH-TDMA data we are only capable of inferring chemical composition. We do not claim to be making detailed measurements of chemical composition. Taking these considerations into account we still contend that the VH-TDMA provides useful composition information.

Based on similar comments from both reviewers we agree that the discussion of possible particle precursors and their sources is too long and detailed based on the data we have collected. We have made major changes to 'Section 3.4 Possible particle precursor sources' (page 12118-12121) and removed Fig. 10 entirely. Specifically, we have removed the first 3 paragraphs of Section 3.4 and replaced them with the following two paragraphs:

"The question remains: what was the source of the particle precursors and the sulphur/organic vapours that were responsible for observed particle growth? Nucleation events generally occurred when wind direction was from the marine/coastal sector covering the range of bearings 100–145° (see Fig. 2c). This sector contains the shallow, biologically-active waters of Hervey Bay, the vegetation covered Fraser Island and the open ocean. This does not necessarily indicate that these marine/coastal regions contained the sources responsible for particle formation and growth because the land-sea breeze effect must be taken into account. This effect refers to the oscillation in local wind direction from the continent (160–200°) during the night to the ocean/coast (100–145°) during the day. It is clearly seen in the periodic nature of the wind direction time series (Figs. 6 and 7) but not in the HYSPLIT back trajectories (Fig. 3). Particle precursors may have been emitted from the continent and advected offshore during the night, before being photo-oxidised, nucleated into the particle phase and carried back to our coastal measurement site as solar intensity increased and the wind direction moved

progressively east during the morning. The fact that nucleation event occurrence did not depend on tidal height (Fig. 8) supports this hypothesis.

However there is also evidence to suggest that the precursor vapours were actually of marine/coastal origin. Firstly, the change in wind direction from the continental to the marine/coastal sector was almost always accompanied by a decrease in particle number concentration. This indicates that the continentally affected air masses were being diluted by cleaner, marine air as the local wind direction changed from land to sea. If the vapours responsible for particle formation and growth were of continental origin, they would have been progressively more diluted as the sea breeze moved further east and strengthened throughout the day. Despite this nucleation events were still observed up to 3 hrs after the land-sea shift in wind direction (e.g. 6 and 7 April 2007; Fig. 7). In addition during the strong nucleation events particle growth is observed throughout the whole day (e.g. Figs. 4 and 5), which indicates a fairly constant vapour source. Therefore on the balance of the evidence we believe that the vapours responsible for particle formation and growth were most likely of marine/coastal origin. In particular, the biologically-rich waters of Hervey Bay and coastal region of Fraser Island are likely source regions for particle precursors. Nevertheless without any measurements of anthropogenic or continental tracers (e.g. black carbon, carbon monoxide, radon) we cannot prove this hypothesis by ruling out continental precursor sources."

We have also altered and limited our conclusions to reflect the modifications we have made. Specifically in the abstract we have replaced the statement (page 12102, line 17): "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." With the following statement: "Although there was a possibility that the precur-

sor vapours responsible for particle formation and growth had continental sources, on the balance of available data we would suggest that the precursors were most likely of marine/coastal origin."

In the Conclusions (Section 4 page 12121) we have replaced the statement (page 12121, line 22): "Two possible particle formation and growth mechanisms were suggested, both of which involved precursor vapours being emitted from the coastal area surrounding Hervey Bay." With the following statement: "It is possible that particle precursor vapours had a continental or a marine/coastal origin. However, based on all the available data, we suggest that the precursors were most likely coming from marine/coastal sources"

Comment: "4. The lack of "dependence" on tidal height is not really quantified. How was this determined? By lack of simultaneous occurrence? Does this really rule out a causative relationship if there is a time delay information? And what is meant by the following statement? "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).""

Response: We have expanded our analysis and discussion of the relationship between nucleation event occurrence and tide height. Specifically, we have replaced the 2nd paragraph of section 3.1.4 (beginning page 12115, line 12) with the following paragraph:

"To further examine the relationship between event occurrence and tide height we calculated the number distribution of nucleation events as a function of the time in hours between the beginning of a nucleation event and low tide (Δt). Negative Δt values indicate that low tide occurred after the nucleation event began (that is, the event occurred after a high tide). This was first done for tide data from Agnes Water (measurement location). 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 mea-

surement site. The times when the air masses containing nucleation mode particles (observed at Agnes Water) passed over this coastal region were back-calculated according to measured wind speed data at Agnes Water and Fraser Island, and these were used to calculate the number Δt distribution for this area. The tide data in this case was taken not from Agnes Water but from Fraser Island. Both distributions are relatively flat and uniform considering the data has been grouped into coarse, 2 hour time bins (Fig. 8). If there was a relationship between nucleation event and tide height we would expect to see a spike in the distributions in one of the Δt time bins. Rather, it was at least as likely for a nucleation event to occur after a high tide than a low tide. Therefore we conclude that there is no relationship between event occurrence and tide height. This finding is not particularly surprising for the Agnes Water measurement site because tidal amplitude was relatively small (average 0.9 m) and no visually obvious marine biota was exposed at low tides along the beach."

In addition we have now replaced Fig. 8 with a more quantitative figure showing the number distribution of nucleation events as a function of the time between the beginning of a nucleation event and low tide.

Comment: "5. Name the other coastal locations and their references, for geographical interest, even if they are not the "focus." An obvious reference missing from the discussion is the recent study at Appledore Island in the United States by Russell et al., 2007."

Response: This reference was already added to the manuscript following similar comments in the initial review stage before publication in ACPD. We have modified the sentence (page 12106, line 6) that contains the reference so it now includes the place name where the study was conducted for geographical interest: "Two studies have observed nucleation events in continentally-affected air masses arriving at coastal measurement sites at Appeldore Island, Maine USA (Russell et al., 2007) and on the north coast of Norfolk, United Kingdom (Coe et al., 2000)."