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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.

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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: "The measurements are very well made and quite complementary, but I have a major concern about their interpretation. For this reason, I recommend quite major modification of the manuscript. The concern is as follows: from the AIS and SMPS data it is obvious that any apparent nucleation leading to the observed "nucleation" mode was non-local (nothing really seen sub-10 nm). It is stated that the particle number decreased before every nucleation event as a result of the daily shift in wind direction from continental to marine / coastal. It appears very likely that the condensable vapours responsible for the nucleation / growth had a continental origin and were

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simply photochemically processed to produce nucleation as the airmass returned to the coastal measurement site. Were there ever nucleation events that were not contaminated by this sea-breeze effect? Such effects have been well-known for decades for gaseous secondary pollutants such as ozone, when the precursors are advected out to sea by land breezes and ozone returned onshore after photochemical processing. It would be important to eliminate such effects by a null event where there was no land-sea breeze effect – the only other way to eliminate it is by an anthropogenic tracer such as CO or black carbon measurements which should both be at background MBL concentrations if the landsea breeze is not the source of the particles. It is essential that the authors screen their data for such effects before drawing conclusions about the nucleation / growth precursor sources. In the absence of being able to screen for such an eventuality, this should be clearly stated as the likely source of the nucleation precursors - moreso than any remote marine sources. This interpretation is obvious from figures 6 and 7. It is, of course, possible that the clusters were advected and grew offshore rather than being nucleated from vapours offshore - however, these two options must be eliminated before anything can be said about coastal or marine sources. It was particularly interesting to note the difference in growth rates from the Barrier reef event and all other events, though of course this may simply be the result of different continental precursor strengths being advected offshore in the different wind direction. In any case, one would not expect to see a tidal signature in particles of a continental origin - only a landsea breeze signature. Likewise, one would not see such local meteorological effects in trajectory data as these are based on mean geostrophic winds and will not capture such effects. Because of these reasons, the source study and conclusions should be rewritten after further analysis. Given any amendments to the conclusions if the continental influence cannot be removed, reference to the tidal and open ocean productivity figure should be minimised - probably removing the figures entirely."

Reply: We acknowledge the reviewers point about the importance of the land-sea breeze effect and the difficulty of ruling out continental particle precursor sources with the available data. In light of this we have made major changes to 'Section 3.4 Possible particle precursor sources' (page 12118-12121) and removed Fig. 10 (the ocean productivity figure) 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 ob-

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served 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 precursor 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"

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Comment: I have one further criticism of note: I feel it must be better distinguished between the growth to detectable and growth to observed sizes. As the authors state, it may correctly be inferred that sulphate and organic material was responsible for the mass determining the volatility and hygroscopic growth of 17 to 22.5 nm particles. However, since the particles are detectable at 3 nm, the mass of newly detectable particles would be (at constant density) a maximum of 3ËĘ3 / 17ËĘ3 = 0.005 times (or 0.5% of) the mass of the particles whose properties were being measured. It is therefore regrettably impossible to deduce the properties of the material contributing to the growth to detectable sizes of the particles. The authors must therefore remove the reference to INITIAL growth being driven by sulphate and organic vapours in the abstract and throughout the manuscript - it is merely the growth to sizes above 10 nm. There has been care to make this clear in many places of the manuscript, but this point cannot be too strongly made.

Response: We agree with the reviewers comments. Although this point was originally made in the manuscript (page 12118, line 7-10) we have now tried to make it more clearly throughout the entire manuscript. Specifically, in the abstract we have slightly modified a statement (page 12102, line 16) to read, “we conclude that the condensation of sulphate and/or organic vapours was most likely responsible for driving particle growth at sizes greater than 10 nm during the nucleation events.”

In the introduction section we have added the following sentence after page 12106, line 13: “In the current study we focus only on the question of particle growth at sizes greater than 10 nm. “

Comment: Minor comments: Intro it’s stated that marine aerosols constitute a significant fraction of the aerosol mass. This seems an odd way to justify studies into marine aerosol (I’d probably normally expect a statement of the high contribution to radiative forcing); if the authors choose to phrase it this way, the fraction should be stated and referenced. It is also stated that a relatively stable number implies MBL replenishment. Continuous entrainment from the FT and reasonable lifetimes with respect to deposition will also result in stable numbers. Entrainment will have continuous and sporadic components- variation in number can result from gentle fluctuations in the continuous entrainment rate and vigorous changes in sporadic entrainment and boundary layer ventilation under less stable conditions. Why is this discounted? In any case, entrainment should be mentioned.

Response: In accordance with the reviewers concerns we have changed the opening paragraph of the introduction section (page 12103, line 2-11) to the following: "Marine aerosols have an important impact on 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 200-500 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 and particles entrained from the free troposphere 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 (2007). "

Comment: The arguments surrounding the composition of the first step in MBL aerosol production seems very skewed towards sulphuric acid. Firstly, there is no unambigous evidence for the participation of sulphuric acid playing a role in MBL nucleation. Admittedly there is no unambiguous direct evidence for any component of nucleation mode aerosol – but where there is evidence, it points to iodine, not sulphuric acid, ammonia or organics. Admittedly this is at the coast and is tidal, but non-coastal MBL nucleation (and not entrained from the FT) has not been unambiguously observed. This is mentioned, but less prominently than is necessary.

Response: In the introduction we refer to a number of studies that are related to sulphuric acid nucleation but ultimately state that sulphate particle formation in the MBL is most likely a very rare occurrence (based on modelling and a lack of observations). We also mention the importance of iodine related particle formation with reference to the large body of work conducted at Mace Head. We agree with the reviewer that there is no unambiguous evidence for the participation of any component in MBL particle nucleation. This is why we think the question of what species are involved in MBL particle nucleation at other sites around the world is still an open one.

Comment: Reference to Whitehead et al. (2009) should be made when discussing the other studies of nucleation at a coastal site on page 5. (Whitehead, J. D., G. B. McFiggans, M. W. Gallagher and M.J. Flynn, Direct linkage between tidally driven coastal ozone deposition fluxes, particle emission fluxes and subsequent CCN formation, Geophys. Res. Lett., 36, L04806, doi:10.1029/2008GL035969, 2009)

Response: Reference added on page 12106, line 9: "Finally a very recent study has reported particle formation events during low-tide at a coastal site in Brittany, France (Whitehead et al., 2009). Ultra-fine particle emission fluxes were directly linked to both increased ozone depositional loss to exposed macro-algae and the photochemical destruction of ozone. There is the suggestion that this could indicate iodine-mediated new particle formation."

Comment: Referencing In-line citations should consistently be in correct ACP format e.g. O'Dowd and DeLeeuw (2007), not O'Dowd and DeLeeuw (O'Dowd and DeLeeuw, 2007)

Response: Referencing format has been corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12101, 2009.