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Atmospheric Chemistry and Physics Discussions

Interactive comment on "When does new particle formation not occur in the upper troposphere?" *by* D. R. Benson et al.

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We would like to thank Dr. Lovejoy for his helpful comments which will be taken into account in our revised manuscript. Responses to individual comments are given below. All cited figures or tables refer to the revised manucript

ACPD-2007-0383 "The Effects of Convection on New Particle Formation in the Free Troposphere: Case Studies" By Benson et al.

Response to Dr. E. R. Lovejoy (Referee 1's) Comments by S.-H. Lee

REF1: *This work poses an interesting and important question. Identifying the conditions where nucleation is absent should help to improve the understanding of the complex unresolved question of the mechanisms of new particle formation in the earth's atmosphere. This work presents some interesting observations of size resolved nanome-*

ter sized particles in the free troposphere. Unfortunately the particle observations are only weakly constrained by observations of other relevant parameters and the analysis and discussion are qualitative and inconclusive. This work may be publishable in ACP following extensive reanalysis and revision. Specific comments follow.

RE: We thank Dr. Lovejoy for his comprehensive review and the useful comments that improved our manuscript significantly. We also appreciate his understanding on this important topic. Because new particle formation (NPF) observations in the free troposphere usually require aircraft measurements and because of our limited capability to measure very low concentrations of aerosol precursors, it is very difficult to study the particle formation processes in this region. We also recognize that it is not ideal to study the nucleation mechanisms from aerosol size distributions alone. Rather, we show distinct examples of strong-, weak-, and non- NPF events from the measured aerosol size distributions to see how airmass history affects NPF. Even with the lack of chemical information, these atmospheric observations will provide an important dataset to the nucleation modelers to test and improve their nucleation theories.

REF1: *The title doesn't seem appropriate for this work, for two reasons. (1) Based on the criteria presented here for the classification of "new particle events" (N4-9>1 cm-3, N4-9>0.15 N4-2000, N4-6>N6-9), a "non-event" does not necessarily correspond to the absence of nucleation. (2) The non-events are not the focus of this manuscript. There are no plots of non-event data, and most of the discussion concerns weak and strong events.*

RE: We agree. The title is changed to "The Effects of Convection on New Particle Formation in the Free Troposphere: Case Studies".

(1) For our NPF criteria discussion, please see Section 2 (lines 90-107) in the revised manuscript: "The criteria for NPF are (i) N4-9 > 1 cm-3, (ii) more than 1/15 of N4-2000 are N4-9, and (iii) particles from 4 to 6 nm (N4-6) are higher than those from 6 to 9 nm (N6-9) (Young et al., 2007). A non-NPF event is defined when at least one of the above

three criteria is not satisfied. Non-events tended to have size distributions without a peak in the size range < 10 nm, a clear indication of more aged aerosols than for NPF cases (Figure 3c). Each NPF event can further be classified as a strong event when N4-9 > 500 cm-3 [that is, much higher than the background N4-9 (Table 1), similarly to Young et al., (2007)], or as a weak event when N4-9 < 100 cm-3 (much lower than the background N4-9). As shown in Figure 1, weak- and non-NPF cases show a similar upper level of N4-9, indicating that even though these two cases may have different size distributions (e.g., N4-6 vs. N6-9), they both have low N4-9. Previous NPF studies in the free troposphere made by other investigators have used the criterion that the measured total CN concentrations are higher than the background CN concentrations to identify NPF cases (Twohy et al., 2003 and numerous references cited therein), for example. In comparison, our criteria for NPF are more quantitative, yet consistent with these cited studies. For example, our non-NPF samples had much lower N4-9 and N4-2000 than the background concentrations (Table 1) so they will also be non-NPF cases even with the NPF criterion used in these cited other studies."

(2) We have included a non-event case (Figures 2c, 3c and 4c).

REF1: *The present work and others show that nucleation is very common in the UT. What fraction of the observations has 4-9 nm particle concentrations above the detection limit? In the end, it seems that very few observations will show absolutely no evidence of nucleation. This is an intriguing possibility considering that the sub 4 nm particles are not even detected. The value of the nucleation event criteria is not clear.*

RE: This is an interesting comment and we would like to clarify this. The instrument we used to measure nano-particles is NMASS (Nuclei Mode Aerosol Sizing Spectrometer). As described in previous papers (Brock et al., 2000, 2002; Lee et al., 2003, 2004; Young et al., 2006), this instrument does not measure the sizes directly. Rather it measures the cumulative number concentrations of aerosols larger than 4, 8, 15, 30, and 60 nm with five different CN counters. And then with an inversion program, we retrieve particle size distributions. Because we are not directly measuring them, it is not feasible to directly estimate the detection limit of 4 nm particles. For the present study, we indirectly estimated a detection limit of N4-9 from the measured air temperature and pressure, sampling flow and particle count, and the typical detection limit is around 0.01 cm-3, for 30 second average data (similar to Lee et al., 2003). Note that this estimation depends on the total particle number concentration. For the data analysis, we used only data that are physically meaningful and above the instrumental detection limit.

REF1: *The nucleation criteria used in this work require that the 4-9 nm particles are at least 15% of all (4-2000nm) particles for the observation to be classified as a nucleation event. Does this discriminate against data that show nucleation at high surface areas (a few small new particles in the presence of many large particles), and bias the conclusions regarding the influence of surface area on nucleation?*

RE: First, 15% is corrected to "1/15 (that is about 6%)". The reason we have the 1/15 criterion is, we do not want to bias measurements against the lower stratospheric samples (especially those in polar regions) where total particle concentrations are on average only 15 cm-3 (Lee et al., 2003). So with this criterion, we have a consistent fraction of ultrafine particles for new particle formation events in an entire region of free troposphere and lower stratosphere at different altitude conditions.

The 1/15 (or 6%) cut for ultrafine particle fraction does not discriminate events data at high surface areas. For non-events (Figure 3c), the aerosol sizes are much larger with depleted ultrafine particles and in this case, the number concentrations are limited by the Aitken or accumulation number concentrations (and aerosol sizes are directly related to particle number concentrations in this case). On the other hand, for event cases, the aerosol surface area is not limited by total particle number concentrations because the majority of particles are small particles and they do not contribute to surface area concentrations (e.g., Figure 3a). In fact, for both event and non-event cases, the ranges of surface areas are similar (Figure 1a); the only difference is the median values (Table 1) which were rather related to different altitudes.

REF1: *p. 14210 Line 13: "the events were closely associated with convection" is too strong a statement considering the sparse data and qualitative analysis. I am not convinced that this work has established a direct link between convection and nucleation. See additional discussion below.*

RE: We rephrased this overstatement. Our reanalysis shows that for weak- or non-event cases, the air masses did not experience convection. For "strong" events, air masses often had convection, but there were also event cases where convection did not occur.

REF1: *p. 14210 Line 14: There is not a statistically significant difference between the average surface areas of the events and non-events. This data should be analyzed graphically as e.g. N4-9 versus surface area, to examine possible correlations. See additional comments below.*

RE: We agree. An N4-9 versus surface area plot is included in Figure 1a. The correlation of N4-9 and surface area is very weak, except that the median surface area is higher for NPF cases than for non-NPF event cases (Table 1). Please see Section 3.1 (lines 111-129) and Section 4 (lines 245-255) for more detail on the surface area discussion.

REF1: *p. 14210 Line 17: "where precursor concentrations are relatively low" implies that we know the identity of the aerosol precursors and their concentrations, which is not the case. Better wording would be "expected precursors" and state the identity of the expected precursors. Same comment for text in the conclusions.*

RE: Revised.

REF1: *p. 14210 Line 20 abstract: What is the basis of the comment "nucleation is thermodynamically favorable"? What is the significance of 250 K?*

RE: Lower temperatures are the favorable thermodynamic condition as shown from nucleation theories- but there was no significant indication of the 250 K threshold from

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our datasets, so we removed this discussion.

REF1: *p. 14211 Line 3: How are nucleation events classified by other investigators? Do they use similar criteria as in the present work? This is important for comparison of the occurrence statistics.*

RE: Please see Section 2 (lines 90-107), quoted in our earlier response, for the NPF criteria used in our study and other studies.

REF1: *p. 14211 Line 8: km-3=cm-3*
RE: Corrected.

REF1: *p. 14211 line 20: Lee et al (2003) = Lee et al. (2004)?*
RE: Corrected.

REF1: *p. 14212 line 17: "nighttime studies in this area are rare". Are there other studies, and what was observed?*

RE: Nighttime studies in the free troposphere were made by Mauldin et al., (JGR, 2003) and by Hermann et al. (JGR, 2003). These studies show ultrafine particle concentrations during the nighttime, but the mechanisms are unclear. We have also seen a similar feature during the 3 days of the HIAPER sun exposure experiments, but these results are discussed in Lee et al. (JGR, in press) separately.

REF1: *p. 14214 Line 2 and table one: The average values of the surface area are different for non-events and events, but the standard deviations encompass both averages. This is not "a clear indication that low surface area is necessary for new particle formation" (line 4 p. 14214). The authors should plot number of 4-9 nm particles (or some other measure of recent nucleation) as a function of the surface area to examine possible correlations. Evaluate the statistical significance of the slopes and intercepts of these plots. These figures should be included in the manuscript. Similar analyses should be used to explore possible correlations between nucleation and temperature, RH, convection, rainfall, etc. Use all of the available data in these plots.*

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RE: We agree. Figure 1 includes plots of N4-9 vs. surface, temperature and RHI. Surface areas have high standard deviations (Table 1), and when considering that the measurements covered a wide range of altitude (from the ground up to 14 km) and latitude (18 °N - 62 °N), it is very understandable. For both the event and non-event cases, the surface areas range in the same way but only with different median values and from these results (Figure 1), we also agree that it is difficult to derive a straight conclusion between surface area and ultrafine particle concentration and revised the discussions on surface area (Sections 3.1 and 4). We also did not see a strong correlation of ultrafine particles vs. temperatures and RHI (Figure 1b and c).

We have a quantitative definition of convection based on the rate of air uplifting (Section 3.1). Since this convection information is coming from NOAA HYSPLIT trajectory calculations, it is not feasible to do correlation plots of in-situ ultrafine particle concentrations vs. convection events. The same is true for rainfall. Instead, we thus provide Table 2, which lists the meteorological parameters derived from trajectory calculations including rainfall, solar flux and altitude of the air masses for the case study events. Table 2 is discussed in detail in Section 4 (lines 277-295).

REF1: *p. 14214 line 4: Are the authors suggesting that the observations are consistent with ion-induced nucleation, or simply that the apparent anticorrelation with surface area is consistent with nucleation models? If the latter, then there are many more appropriate references than Lovejoy et al. Same issue p. 14218 Line 18 of the conclusions. If the authors are proposing that the observations are consistent with ion induced nucleation, then there needs to be more discussion.*

RE: We meant the nucleation theory in general. However, as mentioned earlier, the surface area ranges largely for both event and non-event cases and this anti-correlation is not shown clearly in Figure 1a. (Sections 3.1 and 4).

REF1: *p.14214 line 8: The criteria used to classify convection and non-convection seem arbitrary and should be justified. It would be better to quantify some important*

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characteristics of the convection process, e.g. by rate of uplift, and plot N4-9nm versus these convection parameters to examine possible correlations.

RE: Convection is defined by the rate of uplift (Section 3.1), as mentioned earlier.

REF1: *p. 14214 line 15: The authors state that they "analyzed several strong new particle formation events and non-events", with reference to the data presented in figures 1 through 8. The figure captions refer to these events as strong and weak (not non-events). This is an important difference. In this work, observations of 4-9 nm particles are referred to as "new particle events", whereas by definition the new particles are formed when they grow past the critical cluster, which is very likely much smaller than 4 nm. Hence the particles are "formed" hours before they are observed. Therefore statements like "showing a strong new particle formation event that occurred at night" (p. 14214 line 27) may be more accurate as "showing high concentrations of 4-9 nm particles observed at night". Note that it will take >4 (40) hrs to grow to >4 nm with 10**7(6) H2SO4 cm-3, assuming that H2SO4 is the main growth agent. Note also that [H2SO4] should drop when the actinic flux drops at night. It would be a very important observation if it could be shown that nucleation occurred in the dark. However one cannot rule out nucleation during the previous day as the source of the nightime ultrafines, without knowing the particle growth history. Does the growth history information exist?*

RE: We agree. Based on this comment, we include an "absolute" non-event case in this study (Figures 2c, 3c and 4c). We also completely agree on "nighttime observations of ultrafine particles". It would be very helpful to have particle growth history to identify if these high numbers of ultrafine particles are related to nucleation or not, but, unfortunately, we do no have that information. Note, it is also difficult to derive growth information from aircraft studies, due to the large spatial and temporal fluctuations.

REF1: *P 14215 last paragraph: The possibility that convection enhances aerosol precursor concentrations in the UT is intriguing. However, without measurements of aerosol precursors and even knowledge of the identity of aerosol precursors, these*

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arguments are highly speculative. Also, one can not rule out the importance of earlier trajectory history due to possible long lifetimes of aerosol precursors. For example, the atmospheric lifetime of SO2 with respect to OH reaction is roughly two weeks. Therefore it may be very difficult to draw any conclusions regarding the role of convection based on 5 day trajectories without knowledge of precursor concentrations.

RE: We agree. Aerosol precursor concentrations are needed- unfortunately, this was the first science mission on the GV and no aerosol chemical information was available. We also agree that SO2 has a lifetime of about two weeks, but as shown in atmospheric observations, SO2 clearly has an altitude dependence in the free troposphere (Thornton et al., 1999) and in this case, convection and air mass history can be very important (lines 264-272). Trajectory calculations have been used in many field studies to determine the airmass origins for both the ground and aircraft studies. Since aerosol precursor measurements are very rare for aircraft studies, trajectory calculations can be particularly useful and with such help, one still can provide useful information on airmass history and the associated aerosol precursor source information indirectly.

REF1: *p. 14216 line15: Please clarify if "polluted" and "clean" are supported by trace gas measurements, or just assumed. These are not good assumptions solely based on the trajectories presented in figure 6.*

RE: This information is based on the trajectory calculations. This discussion is now removed.

REF1: *p. 14216 line 19: The authors state that rainfall reduces surface area. However the weak nucleation event (fig. 5) has a surface area comparable to the strong event (fig. 4) despite more intense recent rainfall.*

RE: We agree. See the earlier responses related to surface area discussion (Sections 3.1 and 4).

REF1: *Do the observations presented in this work support the postulate that rainfall*

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reduces surface area? Is there enough data to plot surface area versus a measure of recent rainfall to test this postulate? The authors should indicate the number of observations that are the basis for the data presented in table 1.

RE: We have discussed rainfall vs. surface area in our earlier work by Young et al. (2007). Rainfall is not necessary correlated with low surface area. Rather surface area is associated with altitudes. Rainfall is discussed in Section 4 (lines 285-291): "Precipitation may have affected the strength of the event as in both cases the strong event experienced more cumulative precipitation (Table 2). Precipitation is believed to lower the surface area density because of scavenging, but since for all these events the surface areas were in fact very low in this region, the precipitation effects can be less important under such a condition".

REF1: *p. 14218 line 2 conclusions: The statement that new particle formation is active in the UT due to low temperatures needs some justification and references.*

RE: We added a reference (Carslaw and Karcher, 2006) for this statement.

REF1: *p. 14218 conclusions: The conclusions are overstated. See comments above.*

RE: Revised.

REF1: *Figure 2: It is difficult to discern the number concentrations from the plot. It would help to make the number concentration scale 0-1000 cm-3. Panels (a) and (b) are not self consistent (although this may be an optical illusion due to the scaling). The size distribution has a significant fraction of large particles, but panel (a) suggests that all the particles are small. In all of the data figures the time period that the "average size distribution" represents should be indicated.*

RE: Now revised figures are provided.

REF1: *Figure 3 caption "...where the event occurred" is really "where the elevated ultrafine concentrations were measured".*

RE: Agree. Note that "elevated ultrafine concentrations" are in fact the NPF criterion used for other NPF studies (Twohy et al., 2003 and references therein).

REF1: *Figure 1,2,4,5,7, and 8 captions: x,000 km = x km?*

RE: Corrected.

REF1: *Figure 10: It would be very interesting to see the altitude and/or temperature of the observations on the plot.*

RE: Ultrafine particles vs. altitude is now filtered by temperature in Figure 8.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14209, 2007.