**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Characterization of particle cloud droplet activity and composition in the free troposphere and the boundary layer during INTEX-B" *by* G. C. Roberts et al.

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Response to Reviewer #1:

We thank the reviewer for their comments and suggestions that improve the quality of the manuscript. We have revised the manuscript accordingly to address their specific comments below.

Major points: 1. I don't doubt that the HTDMA measurements are of high quality, but there needs to be some discussion of the HTDMA measurement technique. I can't even find a reference.

We thank the reviewer for pointing out this omission and have added a brief description of the H-TDMA measurements in the text.

Size-resolved particle hygroscopicity was measured with a humidfied tandem differential mobility analyzer (H-TDMA) of Texas A&M University (Gasparini et al., 2004; Tomlinson et al., 2007). Dry classified particles (RH < 5%) of 50, 100, 200 and 300 nm diameter were exposed to an elevated RH at 84%; a second DMA measured the hygroscopic growth of the particles. The resulting hygroscopic growth factors are used to determine H-TMDA-derived kappas, which are compared to CCN-derived kappas in Section 4 (Discussion).

2. The AMS observations are used with respect to the volume measurements from the SMPS/DMA. These are used to assess potential refractory material in the particles, and this is critical for the assessment of kappa (e.g. Figures 6a and 8). There is no discussion of the comparison of the AMS results with the SMPS/DMA. This is fundamental to this work and it needs to be clear in this work how these measurements compare.

Airborne sample times were, unfortunately, too short for size resolved measurements with the AMS; therefore, we cannot report a size dependence comparison between the AMS and SMPS observations. Intercomparisons of the AMS concentrations to those from other instruments had been discussed in previous publications, and we have inserted the following text in the revised manuscript:

The AMS concentrations have been compared to those determined from the SMPS, a particle-into-liquid sampler, and an independent comparison method with light scattering measurements as described by DeCarlo et al. (2009) (Fig. 2 and associated discussion) and Dunlea et al. (2009) (Figs. 2 & 3 and associated discussion). The comparisons show consistent quantification of the AMS data, which is more obvious at the higher signal levels of Mexico City where the effect of noise in all the measurements is lower (DeCarlo et al., 2009).

Nonetheless, on Page 3524, line 13 the text reads "Ratios of NR+BC to SMPS volume was on average 0.74 ± 0.32." While this comparison is not exact, we use it to estimate potential volume contributions of refractory material. For the range of kappas reported here (particularly kappa ∼ 0.1), a 25% variability in the soluble fraction is related to a ca. 25% variability in kappa. This variability with respect to AMS measurements is well within the reported range of kappas reported here, especially given the noise and uncertainties of the measurements at these low concentrations.

3. Page 3525, lines 10-12 and Figure 8 - You make the statement that the results in figure 8 provide "evidence that nrOM O/C can be used to predict κ_{org}." The data in Figure 8 shows no relationship of kappa organic with m/z44/OM, and certainly provides no evidence in support of Jimenez et al. (2009) other than a vertical line crosses through a sloped line; if anything it refutes Jimenez et al. If not for this, the paper would be easily acceptable. Substantial revision of this point is required.

We did not intend to suggest that O/C ratios can be used to predict korg since only CCV measurements were included in Fig. 8 (due to large uncertainties in results from the other air masses types). These results neither support nor refute the linear relationship reported by Jimenez et al. 2009 – instead, our intent was to show that for the CCV measurements and the the more realistic limit (refractory material = dust) that korg is consistent with Jimenez et al. 2009.

The text has been reworded to clarify this point, and ensure that the reader does not interpret discussion to overstate this result:

"The κ_{org} calculated for the CCV (dust-limit) is in acceptable agreement with the relationship described in Jimenez et al., (2009) (i.e., 0.18 ± 0.06 compared to 0.15 from fit), ..."

Minor points for consideration: 4. Page 3501, line 24 – H"TDMA".

done; all references to TDMA changed to H-TDMA

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5. Page 3502, lines 11-16 – another relevant feature of Chang et al. (2007) is that they showed that as the organic fraction of the fine particle aerosol reaches relatively high values that the composition of the organic becomes more important for CCN activity.

True; it's also worth noting that Wang et al., 2008 found similar results for marine aerosols during a stratoculumus study off California. The following sentence has been added to the text. "Chang et al. (2007) and Wang et al. (2008) show that when organics dominate the aerosol mass, the composition of the organic fraction becomes more important for estimating CCN activity."

6. Page 3507, lines 15-16 – not important in the present context, but could not there have been HNO3 in these particles instead of NH3NO3, especially if they contained some water and the sulphate was neutralised? The effect would be the same; this just goes to process.

Although a small amount of HNO3 may be adsorbed on the surface of atmospheric particles, it is well established from thermodynamic modeling and associated experiments that for substantial gas-phase HNO3 to be take up by the particle phase, formation of ammonium nitrate or another nitrate species is needed. See e.g. the Extended Aerosol Inorganics Model web page and references therein at: http://www.aim.env.uea.ac.uk/aim/aim.php/. As a side note the composition of ammonium nitrate is NH4NO3, not NH3NO3.

7. Page 3507, line 24 – "by two research groups ON THE C-130 during INTEX-B."

text added

8. Page 3509, line 13 – "a Single. . ."

text corrected

9. Page 3512, line 17 – "with possible vertical mixing with the marine boundary layer". By this, do you mean that the trajectory dipped down near the ocean surface?

yes, to clarify changed sentence to "vertical mixing that incorporated marine boundary layer air."

10. Page 3513, lines 6-7 - why not? This seems like an important distinction.

We have modified the manuscript to read: "The analysis presented here also does not differentiate between FT and Asan-influenced FT by the same definition described in Dunlea et al. (2009), as the two air mass categories were separated by sulfate loading greater or less than 1 ug SO4 m^{-3}, respectively. This distinction was not used in this manuscript since few of the FT air masses included in this analysis fit that criterion." Most of the airmasses in the FT have trajectories with Asian-origins. The two FT cases that originate in the Pacific Ocean have lower kappa values.

11. Page 3513, line 13 - the dominant mode of what?

"dominant mode of the aerosol size distribution." We have added this clarification to the text.

12. Page 3515, lines 11-14 – I don't understand "which may suggest that polluted air masses enhance the rate at which particles become hygroscopic." Are you suggesting that polluted air masses contain more sulphate or more organic, or something else?

It has been observed that Asian outlflow contains higher concentrations of sulfate and aerosol precursors (Clarke et al., JGR, 2004). We have added this clarification to text.

13. Page 3517, line 3 – there are also natural sources of CO, NOy and NOx.

yes – however, we cannot distinguish natural from background sources.

14. Page 3517, line 14 – why wasn't MSA estimated from the AMS?

The presence of MSA was detected with the AMS as indicated by the CH3O2S+ ion (Dunlea et al., 2009); however, it was generally present at low concentrations and we do not present the MSA analysis in this manuscript.

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15. Page 3518, lines 21-25 – this is stretch, and I suggest revision or removal. There are a number of ways to explain this observation. It can not be inferred that high CN and low sulphate implies organics; could as easily be nucleation of H2SO4.

We agree with the reviewer and certainly did not mean to imply that these conditions strongly support the presence of organics, rather it is one possible explanation of high concentration of small size modes in MBL. Given the lack of supporting data, we have removed this text from the manuscript.

16. Page 3519, line 3 – "formation" and emissions.

We have added "and emissions" to text

17. Page 3519, line 7 – 0.81 is different from the value in Table 4 (1.01).

Table 4 is correct. We changed the text to match the values in the table (1.01+/-0.46)

18. Page 3519, lines 7-8 – related to major comment 2 above. "the mean OM was more than 3 times the mean sulphate, yet the mean OMF is 50%. Table 4 shows that sulphate+nitrate+ammonium was about 1.9 compare with 2.9. Is the other 1.0 (needed to make the average 50%) from refractory material in the AMS size range or are there AMS collection efficiency issues?

The reviewer is correct in that the remaining mass needed to yield the OMF of $\sim$50% is the estimated refractory material (from the AMS-SMPS comparison). A collection efficiency correction was applied to the AMS measurements based on the acidity of the particles and varied from 0.5 to 1 (Dunlea et al., 2009). While this correction may be imperfect and contribute to the uncertainty of the measurement, we do not expect that it would result in a systematic bias.

We could add a column to Table 4 indicating the estimated refractory material; however the AMS-SMPS comparison yields an estimated "missing volume".

19. Page 3519, line 15 - but it doesn't mean that they were completely externally mixed.

comment refers to statement: The AMS size distributions from the CCV had sufficient signal-to-noise to show that the submicron particles were externally mixed with a sulfate mode centered at 350 nm and an nrOM mode centered at 200 nm.

The reviewer is correct. We have changed the text to reflect this point and it now reads "...the submicron particles showed evidence of external mixing with the sulfate mass mode centered at 350 nm and the nrOM mass mode centered at 200 nm."

20. Page 3519 – Shantz et al (ACP, 2010) for example, suggests that the mass accommodation coefficient for growing droplets may be lower for anthropogenic organics compared with other organic types (e.g. biogenic). Since CCN are defined based on the ability for a particle to grow beyond some size threshold, could the lower kappa values you see in the CCV case be in part due to a kinetic effect rather than an equilibrium effect?

The reviewer raises an interesting point and accommodation coefficients have been explored in recent work by Ruehl et al., 2009. However, with the size threshold at 1 micron diameter for counting a droplet as CCN, we are not constrained by kinetic limitations for the following reasons: The residence time in the column (∼9 sec.) is considerably greater than the time required to achieve this threshold size (∼3 sec @ 0.3% Sc); the CCN instrument is not water vapor limited; and the CCN number concentration in CCV are well below concentrations at which the instrument has been calibrated. To detect kinetic effects, we would have to look into changes in the droplet size distributions or use a phase-Doppler detection system. Also, to increase the precision of the measurements, a constant pressure controller would be needed to maintain a well-defined supersaturation in the CCN column.

21. Page 3520, lines 22-23 – From Roberts et al (2006), the Wyoming chamber used in CIFEX based its CCN concentration on the peak light scattered. In that case the calibration is dependent on the chemical composition, and I believe a low value of the "true" kappa would be interpreted as a still lower value of kappa. Could this have

contributed to some of the difference? Differences in growth time and detection size between the two chambers might also make a difference.

The lower detection limit in the static chambers is related to the 'hang' time in the sample volume. If droplet growth rates are reduced (i.e., Hegg et al., 2001), under-counting will yield artificially low kappas. Nonetheless, Englehart at al., ACP, 2008 find that droplet growth kinetics of SOA are similar to Am. Sulfate except at low super-saturations (< 0.3% S). The limited comparisons between the static chamber and the streamwise instrument did not show systematic differences between the number concentrations in the CIFEX data (Figure 5; Roberts et al., 2006). It's also worth noting that calculations of kappa are influenced by not only the CCN instruments, but also the measurements of size distributions (Good et al., ACP, 2010). Systematic biases are nearly impossible to uncover, especially when CCN instruments and HTDMAs are not calibrated as a single unit. No change has been made to the text.

22. Page 3521, line 21 - I don't see any kappa value <0.05 in the above discussion.

This was a typographical error – should have read k < 0.1

23. Page 3521, line 23 – a substantial fraction? Phinney et al. (Deep Sea Research, 2006) measured the aerosol composition over the North Pacific in the summertime with an AMS. Considering the location, these measurements are somewhat relevant to your observations. For three weeks of measurements, they found for the fine mode aerosol that was sulphate was 0.74 ug m^{-3}, sea salt was 0.6 ug m^{-3}, organics were 0.3 ug m^{-3} and MSA was 0.16 ug m^{-3}. Depending on how you classify MSA, organics were about 17-25% of the total; perhaps substantial, but likely not sufficient to significantly influence kappa unless kappa-org is relatively large.

We agree with the reviewer that if the presence of organics is only 17-25% of the total volume fraction near the critical diameter of CCN active particles (as is the case reported by Phinney et al., (2006)), then the organic fraction is probably not sufficient to significantly influence kappa. However, as stated in the text, Wang et al. (2008)

also used an AMS and found that sulfate mass was large in bulk measurement, but organic mass dominated (up to 90% of mass) at the critical diameter relative to CCN (and influences kappa). Unfortunately, we cannot contribute to the results of either of these studies, as we do not have AMS size distributions in the MBL due to low signal levels and short averaging times. Nonetheless, we note in the text that the contribution of organics can be variable and cite Phinney et al. (2006).

In some cases, the impact of organic compounds on kappa in MBL aerosols can be profound (Wang et al., 2008; where the organic fraction approaches 95%). In other cases, the impact is likely less significant (Phinney et al., 2006; where the organic fraction is less than 25%).

On this same note we also added the following text (at the end of the paragraph) to include the effects of organic films on CCN activity in recent published research:

Furthermore, recent field studies (Modinia et al., 2010) suggest that organic films on marine particle may significantly suppress the water uptake of mixed particles in H-TDMA measurements.

24. Page 3525, line 4 – not coincidentally, the lower limit of your kappa values in figure 7 (for both the CCN- and htdma-derived values) looks to be close to 0.18.

true – we added text to point this out.

25. Page 3526, line 2 - perhaps "application" rather than "demonstration". The latter does not suggest confidence in the measurements, which is not the case.

we agree with the reviewer and have changed the text to 'application'.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3499, 2010.