**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Aerosol mixing-state, hygroscopic growth and cloud activation efficiency during MIRAGE 2006" *by* S. Lance et al.

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This manuscript presents results from measurements outside Mexico City over a 16 day period. The measurements focus on the water uptake properties of the ambient aerosols. Several state of the art instruments were used including an aerosol mass spectrometer for measurements of aerosol chemical composition, a continuous flow CCN counter for determination of critical supersaturations and a HTDMA system for measurements of hygroscopic growth.

The experimental data are analyzed in the framework of kappa-Köhler theory. Kappa values derived from the different techniques are compared. Kappa_CCNc decreases as function of size during all time periods while the ccn active fraction increases with particle size. Kappa derived from AMS measurements agrees reasonable well (with

some deviations) with the kappa values derived from CCN measurements.

The authors find that there is a correlation between new particle formation events and increased kappa values. Particles are externally mixed during morning rush hours and internally mixed at mid-day. The authors point out that it is important to account for aerosol mixing state, otherwise one can overestimate CCN concentrations by 50-100%.

The manuscript is well written, the figures are very nice and interesting data are presented. I have some comments as outlined below which the authors should address before publication can be recommended.

We thank the reviewer for the positive and constructive feedback. Our responses to the issues raised are given below in italic.

General comments

In several places it is unclear what the averaging period is. For example: Fig 2: "Average diurnal profile: : :" – average over which period – the whole campaign Fig 5: is this average over NPF days? This should be clearly stated.

Yes, averaged over the whole campaign for Fig. 2. No, Fig. 5 is also the average diurnal profile throughout the whole campaign (not just NPF days). The captions for these two figures have been modified to explicitly state the averaging period.

Specific comments

Page 15713 The authors provide nominal and real dry particle diameters – how were the "real" values determined?

The high voltage settings were constant throughout the campaign, however the temperature and pressure fluctuated, which resulted in small changes to the classified particle sizes. The real dry particle sizes were determined using calculations (Knutson and Whitby, 1975) that took into account the pressure and temperature measured at

the inlet of the CCNc, just after the nanoDMA.

P. 15714 Why are the points at 40 and 60 nm at the lowest set points excluded? Please explain.

We allow extra time for the supersaturation to stabilize when going from the highest to the lowest temperature setting. We always step from the smallest particle size set-point to the largest particle size setpoint. By skipping the 40-60nm setpoints at the lowest supersaturation setting we gained 32 seconds more time for the temperature and therefore supersaturation to stabilize. This is mentioned in the methods section.

How was the CCNC calibrated?

Supersaturation in the CCNc was calibrated in the field using atomized and classified NaCl particles, which were also used to simultaneously calibrate the HTDMA system. This is now clearly mentioned in the paper.

P.15715 Since the HTDMA system as I understand was employed here for the first time it could be described in a little more detail. For example: what is the residence time in the nafion humidifier tube. With respect to the calibration – it says that the expected growth factor for NaCl is 1.3 at 90% RH based on Petters and Kreidenweis and that the RH was calibrated accordingly. The growth factor for NaCl at this RH is higher, see for example (Brechtel and Kreidenweis, 2000) or (Carrico et al., 2008). Was a kappa value used? If so why? Would it not seem more direct to use a growth factor at the specific relative humidity? Was a shape factor used/assumed for the NaCl particles?

The residence time in the permapure Nafion humidifier between DMA1 and DMA2 was 1.1 seconds (diameter of the tubes = 0.06 in, length of tubes = 24 in, number of tubes = 18 and flow rate = 1.07 L min^{-1}).

The NaCl growth factor of 1.3 was a typo and now corrected. The growth factor of classified 44.6nm NaCl particles was 2.2 (equilibrium humidified diameter = 98nm) at the 90% RH setpoint for which the HTDMA was operated during MILAGRO. To derive

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relative humidity from growth factor, the composition of the particles (or kappa) must be known (Petters and Kreidenweis, 2007). Using equation 6 from Petters and Krei-denweis (2007), with kappa = 1.3, D = 98nm, and Dd = 44.6nm, the equilibrium relative humidity is 90.0%. The same calculations were obtained for NaCl calibrations with dif-ferent dry particle sizes, and a range of RH values were obtained (90.4% +/- 0.56%). Using a dynamic shape factor of 1.02 for dry NaCl particles, the range of RH values is 91.03% +/-0.50%. We have now updated the text with this information.

P. 15616 To help the reader, I suggest to show an activation spectrum (non-averaged) or at least refer the reader to figure 7 to get an idea of what it looks like. How was double charged particles accounted for – looking at fig 7 it seems like they were somehow removed before fitting?

The multiply charged particles were not removed from Fig 7. The only place where the effect of multiply charged particles was subtracted was from the total CCN concentra-tions reported in Figs 4 and 9. We will refer the reader to Fig 7 here.

P. 15719: Is there a reference for how multiple charging was accounted for that could be given? As discussed by the authors later in the manuscript it complicates the fitting when the ccn-spectrum does not reach a stable activated fraction (for the smallest particles) – it could be described in 2.2.1 how that was handled.

The multiply charged particles were not removed from the CCN activation spectra.

Page 15716-15717 For practical reasons the sheath to aerosol ratio in the DMA in front of the CCN counter is very low (2.7). It would be nice to show an example demonstrat-ing how much of the slope can be attributed to the DMA transfer function and how much to other effects (chemical heterogeneity, slightly soluble material, surface ten-sion). Other groups have also investigated such effects and the authors could consider citing some of those: e.g. (Rose et al., 2008) (Svenningsson and Bilde, 2008).

This issue is discussed in detail for the sigmoidal approach we use in Lance et al.

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(2007) and Cerully et al. (2011). For the conditions in this study the slope of the activation curve is considerably affected by the chemical heterogeneity of the particles as demonstrated by a laboratory calibration immediately following the MILAGRO 2006 study. Using the nanoDMA transfer function and the expected behavior of AS particles at each supersaturation, we derived an expected CCN activation spectrum for AS particles that matches well with the laboratory calibrations (slope parameter, C=13), which is considerably greater than the activation spectra of ambient Mexico City aerosol (C=5) with roughly the same characteristic supersaturation (S*).

We also will cite the work of Rose et al., and Svenningsson and Bilde whom also explored the information content of the activation curve slope.

Page 15719: "The measured and simulated CCN concentrations are inverted to determine nCCN(dp,S)=: : :." It is not clear how this was done and when these inverted number concentrations where used. This should be explained in more detail. What is shown in Fig 1 a and Fig9 – is it CCN concentration measured by the CCN counter or has it been somehow inverted? I find the use of the * a bit confusing. Why not call it kappa_CCNc, kappa_AMS, kappa_HTDMA for the experimentally determined values and then in eq (5) use kappa as also done in Petters and Kreidenweis eq 10?

We have clarified the procedure, citing previously published work that also use this approach.

Page 15728 The authors write in the conclusion that a linear fit is obtained with lower slope than observed in several other studies (I assume this refers to Fig. 6) but when discussing fig 6 in the main text it was concluded that the results fall within results from several other studies. This seems inconsistent.

Thank you for pointing this out. We agree that it is confusing as stated. The conclusions have been reworded to reflect the measurements and trends shown in Fig. 6.

P. 15723: The use of the term "often" in the discussion of five days is maybe too strong

– instead it should be specified on how many days out of the five considered this was the case.

For every one of the 5 NPF days, the concentration of 40nm CCN exceeded by more than twofold the concentration of 100nm CCN at S > 0.5%. CCN measurements were obtained every 3 minutes, so for the "daytime" hours (+/- 5 hours from the solar maximum), there are typically 200 CCN measurements per particle size, 40% of which are for S > 0.5%. For 33% of the time, nCCN (40nm, >0.5% S) > 2 nCCN (100nm, >0.5% S), and for 52% of the time are nCCN (40nm, >0.5% S) > nCCN (100nm, >0.5% S). The frequency is much higher using a more restrictive definition of "daytime" (e.g. +/- 2 hours from the solar maximum).

Page 15725: the authors state that the increase in both kappa_CCNC and kappa_HTDMA during NPF events is contrary to the observations of Dusek et al. 2010 – what could be the reason for this? The authors could consider also to compare/contrast with ccn activity and NPF events in other environments e.g. (Sihto et al., 2011).

One possibility is that the NPF events in the near-urban forested site in Germany described by Dusek et al (2010) are more heavily influenced by organic components (as suggested by the ~75% organic mass fraction for particles < 100nm in Germany, compared to the ~50% organic mass fraction in Mexico City during NPF events).

It may also be possible that we are describing a different phenomenon from what Dusek et al (2010) observed: 1) in our case, the effect of NPF events, and 2) in the case of the Dusek et al (2010), the effect of atmospheric conditions that also result in NPF events (e.g. wet scavenging of larger particles).

Dusek et al (2010) state that: "Aerosol properties differ significantly between time periods with and without NPF (Figure 1). During NPF events, number concentrations in the size range < 40 nm are strongly enhanced (Figure 1a). On average, number concentrations in the 50–100 nm size range are somewhat reduced, consistent with the

fact that NPF is facilitated when the surface area of preexisting particles is reduced."

The statement about the concentration of 50-100nm particles decreasing during NPF events is contrary to our observations, and perhaps indicates that the change in activation diameter seen for this size range is not a result of NPF, since one could argue that the most basic effect of NPF events is an increase in particle concentrations.

Sihto et al (2011) showed that NPF events resulted in a small decrease in dcrit, suggesting that particles became more hygroscopic, which agrees qualitatively with our results. There are other studies (e.g. Hameri et al., 2001 and Ehn et al., 2007) showing that hygroscopicity increases during nucleation days as well. We now add these references to the paper to put the Dusek et al (2010) into better context.

Page 15723: Please provide uncertainties on the determined kappa_inorg and kappa_org from the intercepts in fig. 6.

This has been added to the text.

Fig 3: a: critical supersaturation had distinct values – I would suggest to indicate those with separate colors rather than let it look like a continuum (right hand scale).

We assume that the reviewer meant this comment for Fig. 1. We have changed the color scale for Fig. 1a as requested (we also reordered the datapoints so that the higher supersaturations show up on top. Otherwise it is difficult to discern the colors).

Fig 2: "Average diurnal: : :" the time of the average should be given.

We added the word "campaign" before "average", to indicate that the entire dataset is averaged.

Fig3: red and grey lines should be explained in the caption

Done.

Fig 4: It would be nice to see error bars on the "all other days" data to see if there is a

significant difference between NPF days and "all other days".

The reason this was not done is because it looks messy and is difficult to discern from the error bars already shown. There is overlap between the error bars, indicating that the difference between "NPF days" and "all other days" is not statistically significant. We do show the datapoints in addition to the trends, which is another way to illustrate the variability. Note also that NPF events did occur on days that were not labeled as "NPF days". In the manuscript we have stated: "The days with the strongest NPF events at the T1 site were the 16, 18, 21, 23, and 24 March (Fig. 3). Weaker and shorter-lived NPF events occured on almost all other days throughout the campaign. In the following analysis, we include only the five days with the strongest NPF events to represent "NPF days", and contrast these days with all other days during the campaign." Therefore, we believe the variability is less important, and the difference in average concentrations is the point we want to make with this figure.

Fig 6: What were the particle sizes used in the literature studies shown? It should be stated in the figure caption which days are included in the figure-

We have added to the caption that these are averages over the whole campaign.

Fig 7: is the morning rush hour a campaign average?

Yes, all are campaign averages. However, we already show the "campaign average" results, which include all times of day, whereas the "morning rush hour" only includes observations made at 0600-0800 local time. We add this information to the caption.

Minor comments:

in the introduction it is explained what T1 is – it should also be explained what T0 is.

The text states: "A subset of this study, called MIRAGE (Megacities Impacts on Regional and Global Environments), included measurements at several ground-based sites (Fastetal2007, Molinaetal2010) over the month of March 2006." For people who are unfamiliar with the MILAGRO and MIRAGE campaigns, these two papers provide

background information on the different field sites. We feel it might be confusing to discuss the T0 field site in the introduction when the measurements shown are only from the T1 site.

On page 15712 it says that the campaign was in the period 16-31 March – in Figure 1 it looks like it is 15-30 March.

The text states: "The measurements presented here focus on the water uptake properties. . . from 16-31 March." This is in fact correct. The only measurements on 15 March shown in Figure 1 are the dry particle size distributions.

Was there air-condition in the container to keep the cold end of the CCN counter at a constant temperature? This could be stated.

Yes. We now state this in the "Measurement and Instrumentation" section of the paper.

P. 15721: Line 23: it should say in the text that this is for 1% supersaturation.

The requested change has been made. We also add here that the hygroscopic growth factor is for ∼90% RH

Page 15718: it says that measured values of kappa* are referred to as kappa_CCNc , I suggest to rephrase (kappa is not measured, it is derived from measurements.)

Good point. We change this to: "kappa derived from CCNc measurements are referred to as kappa_CCNc"*

References

Brechtel, F. J., and Kreidenweis, S. M.: Predicting particle critical supersaturation from hygroscopic growth measurements in the humidified TDMA. Part II: Laboratory and ambient studies, Journal of the Atmospheric Sciences, 57, 1872-1887, 10.1175/1520-0469, 2000.

Carrico, C. M., Petters, M. D., Kreidenweis, S. M., Collett, J. L., Engling, G., and Malm,

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W. C.: Aerosol hygroscopicity and cloud droplet activation of extracts of filters from biomass burning experiments, Journal of Geophysical Research-Atmospheres, 113, 10.1029/2007jd009274, 2008.

Ehn, M., Petaja, T., Aufmhoff, H., Aalto, P., Hameri, K., Arnold, F., Laaksonen, A., and Kulmala, M.: Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid, Atmos. Chem. Phys., 7, 211–222, 2007.

Hameri, K., Vakeva, M., Aalto, P. P., Kulmala, M., Swietlicki, E., Zhou, J., Seidl, W., Becker, E., and O'Dowd, C.D.: Hygroscopic and CCN properties of aerosol particles in boreal forests, Tellus B, 53, 4, 359–379, doi: 10.1034/j.1600-0889.2001.530404.x, 2001.

Knutson, E. O. and K. T. Whitby: Aerosol classification by electric mobility. Apparatus, theory and applications, J. Aerosol Sci., 6, 443, 1975.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Poschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, Atmos. Chem. Phys., 8, 1153-1179, 2008.

Svenningsson, B., and Bilde, M.: Relaxed step functions for evaluation of CCN counter data on size-separated aerosol particles, J. Aerosol Sci., 39, 592-608, 10.1016/j.jaerosci.2008.03.004, 2008.

Sihto, S. L., Mikkila, J., Vanhanen, J., Ehn, M., Liao, L., Lehtipalo, K., Aalto, P. P., Duplissy, J., Petaja, T., Kerminen, V. M., Boy, M., and Kulmala, M.: Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest, Atmos. Chem. Phys., 11, 13269-13285, 10.5194/acp-11-13269-2011, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15709, 2012.

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