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Atmospheric
Chemistry
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Discussions

Interactive comment on "Aerosol optical properties relevant to regional remote sensing of CCN activity and links to their organic mass fraction: airborne observations over Central Mexico and the US West Coast during MILAGRO/INTEX-B" *by* Y. Shinozuka et al.

Anonymous Referee #1

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// General Comments: // This is an important paper describing the observed relationship between CCN activity, bulk aerosol composition and aerosol optical properties using in-situ measurements over two separate regions in North America. The authors suggest that their results may be useful for predicting the indirect effect of aerosol on climate using remote-sensing observations. This reviewer recommends that the paper be published with minor revisions.

——————- Minor comments Some people use d50, some use Dd. I have not seen people use "Ddc" to describe the threshold activation diameter.

For clarity, "chemistry" should be replaced with "chemical composition" or just "composition", where appropriate.

I think it would be helpful to include the time of day of the measurements and the altitude range.

// Specific Comments: //

Introduction Pg 12522 Ln 10-21 : You explain how chemistry influences CCN, but cite no evidence for how it influences optical properties and remote sensing (as posited in the first sentence of the paragraph).

Pg 12522 Ln 20-21 : "…the uncertainty in the threshold diameter would hamper estimation of CCN concentration." The threshold diameter is not the only necessary parameter for accurately predicting CCN. Aerosol mixing state should also be mentioned, especially in the context of a polluted environment like Mexico City.

Pg 12522 Ln 12-15 : "…determined by the solubility and surface tension of the particles… These chemistry-dependent parameters, expressed collectively as a single hygroscopicity parameter…" The way this is written makes it seem that surface tension is contained in the definition of the kappa-parameter. This is not correct. In actuality, these two properties are physically distinct from each other, and present themselves differently in the equations. I think it is important to be clear about this. If surface tension is not what you think it is, then your estimate for hygroscopicity will also be wrong.

——————- Experiments and Instruments Pg 12523 Ln 12: "Central Valley" add "…of California"

Pg 12523 Ln 16: "pass" replace with "transmit"

Pg 12523 Ln 20-22: "…for a few exceptional cases with heavy dust or sea-salt concentrations encountered during the experiments, the data are more uncertain than for the rest of the periods." add "… because a significant fraction of CCN could be lost in the inlet." or something to clarify this statement.

Pg 12524 Ln 1-2: "whose refractive index is 1.59" change to "with a refractive index of 1.59"

Pg 12528 Ln 3-5 "The "growth" factor for dry (∼20% RH) particles was usually found to be…" A bit confusing as written, since the growth factor is always determined for initially dry particles. For clarity, write "for dry particles also exposed to ∼20% RH in the conditioning section" or something like that.

———————- Observed Dcd vs bulk OMF

Pg 12528 Ln 21: "…Ddc is determined by seeking consistency between the simultaneous measurements of the total CCN concentration and the dry aerosol size distribution" Replace "determined" with "estimated". The only way to know Ddc for sure is by varying the dry particle size transmitted to the CCNc and simultaneously monitoring the total number of particles (both activated and unactivated) to get an activation curve. Externally-mixed nonhygroscopic particles will bias Ddc when estimated without size-resolved CCN data.

Pg 12528 Ln 23-24: "To illustrate this approach, Fig. 2a compares the CCN concentration at 0.15-0.20% supersaturation and the OPC number integrated from 100nm…" Is the DMA size distribution NOT used for this analysis? Since the smallest size the OPC reportedly measures is 100 nm, and the size distribution is often quite steep at this size, and the threshold diameter for CCN at 0.2% is also right around this size, it seems like a big mistake not to use the DMA size distributions to characterize the CCN. If I am correct that the DMA data was not used for this, can you explain why not? In that case, I am also unclear as to how Ddc is calculated from the CCN data (especially when Ddc is apparently smaller than 100 nm)...

Pg 12529 Ln 4: "…as if particles are homogeneously mixed" Explain what this assumption means in terms of the kappa-parameter. For instance, if there is a significant fraction of nonhygroscopic particles at 100 nm (which is quite possible, especially in a place like Mexico City, which has both dust and various types of local pollution) – then you will overestimate Ddc and thereby underestimate the amount of soluble material in the population of particles that does activate. Not everything about the aerosol composition can be lumped into one parameter, since, physically, different things can be happening at the same time. For instance, externally-mixed soot particles can have a fairly consistent diurnal variation controlled by primary emissions, while internally-mixed organic components can have a distinct diurnal variation based on photochemistry… Again, without identifying these independent factors, CCN prediction becomes much less precise, and more importantly, the mechanisms driving changes to the CCN distribution are much more difficult to tease out.

Pg 12529 Ln 13: "…reflecting the fact that aerosols of identical chemical properties…" It should be mentioned that at higher supersaturations smaller particles will activate, and these particles may have a substantially different chemical composition and mixing-state, so this technique can only be applied for a small change in supersaturation. Since the 0.05% supersaturation difference is barely outside the supersaturation uncertainty, I'm not going to make a huge deal out of this.

Pg 12529 Ln 25-27: These last two sentences are confusing and do not seem to add to the discussion of measurement uncertainties…

Pg 12529 Ln 29: "This indicates that the natural variability in the critical diameter…" Is it possible that some of the variability in Ddc is due to the intermittent presence of externally-mixed nonhygroscopic particles, which are not taken into account?

Pg 12531 Ln 12-13: "For very hygroscopic aerosol similar to sodium chloride the hygroscopicity parameter [kappa] is 1…" 1.0 is not a limit for kappa (e.g. kappa for NaCl is 1.3). See Petters and Kreidenweis [2007]. Also, many people would say that ammonium sulfate is a “very hygroscopic aerosol”, but kappa for AS is only 0.6.

Pg 12531: It should be mentioned that Ddc estimated from hygroscopitiy studies can be biased because of slightly soluble compounds (like Calcium Sulfate, found in dust, and some organics) that may not dissolve until the aerosol particle grows nearer to its critical diameter. Also surface active species behave differently under dilute and concentrated conditions. Therefore determination of kappa from CCN measurements is typically preferred for prediction of CCN.

Pg 12532 Ln 7-8: “…black carbon and dust comprised only a small fraction of the submicron range in and around Mexico City”. Although the mass fraction of black carbon for submicron aerosol may be small for this study, I suspect that the number of black carbon particles can be significant (since the mass distribution for black carbon peaks at 200 nm). Even if on average only 10-20% of the particles at 100 nm are soot or dust particles, this could directly translate into a significant bias (not a random error) in the estimated Ddc. High loadings during dust events or interception of primary emission plumes may also contribute to the observed variability in Ddc.

Pg 12533 Ln 7-8: “…the lack of systematic biases means the average Ddc is neither significantly overestimated nor underestimated” I’m not convinced of this, for the reasons outlined previously (externally-mixed particles and slightly soluble compounds would both tend to overestimate Ddc).

Pg 12533 Ln 16: “chemical component” Change to “chemical composition”

Pg 12533 Ln 16-19: “This perhaps reflects the more diverse sources of particles (Central Valley pollution of urban and agricultural mix, Asian fossil fuel and biomass combustion, and possibly ocean surface), sampled over and off the US West Coast.” Does not Mexico City also have urban, Asian and marine influences…

Pg 12533 Ln 16-19: “In fact, the hygroscopicity tends to be higher for samples from California than those from the State of Washington for OMF greater than 0.6.” The

point of this statement escapes me. Please clarify.

Pg 12533 Ln 24-25: “The organics sampled in Asian plumes over the West Coast were essentially all aged and oxygenated (OOA-I)…” You should cite here the paper that describes these terms and the technical detail behind them.

Pg 12533 Ln 26-28: “It is possible that this is due to some potassium in the particles in Mexico due to biomass burning, which is excluded from the calculation of OMF.” I suspect that “this” is referring to the apparent discrepancy between the type of organics measured in the two regions and the hygroscopic growth estimated for the two regions. But this whole paragraph could be rewritten/reorganized to be clearer.

Pg 12534 Ln 19: “decreases more slowly” The time-rate of change of hygroscopicity is an important subject. However, this is not what is being presented in the current study. I suggest using the words “is less sensitive to”.

Pg 12535 Ln 7-8: If the “natural variability” in kappa is 0.1-0.2, and kappa is on average 0.2-0.4, then that translates into as much as 100% variability on average, which translates into a 26% variation in Ddc (at lower OMFs).

Pg 12535 Ln 13-15: “In other words, the CCN activity of particles does not noticeably vary among ionic species and among organic species, or with their state of mixing.” You have not shown this to be true. For instance, you do not measure the mixing-state, and therefore cannot say whether or not it is changing during the times that you are sampling. Some results from Mexico City show a strong diurnal cycle in externally mixed nonhygroscopic particles, with highest fractions late in the evening and early morning. If the flights always took place during the mid-day, then this variability may have been missed. It should also be mentioned that these results may not apply at higher supersaturations, with activation of smaller particles that are more likely to vary in concentration and composition.

—————- Optical signatures of OMF and hygroscopicity:

Pg 12538 Ln 24-26: “In contrast, that calculated for OPC particles up to 750 nm, which roughly corresponds to 1 um aerodynamic diameter, varies between 2.3 and 2.5 (thin triangles in Fig. 5a), a range narrower than observed. Hence the Angstrom exponent in this geographical region is determined by coarse particles. . .”. I do not understand this. From the caption of Fig 5a, the “thin triangles” represent calculations for the submicron pollution particles only, whereas the “thin squares” represent the total aerosol (including both submicron and coarse particles). Yet from the text it appears that the “thin triangles” represent the full size range (0.1-1 um). . . Please clarify.

Pg 12540 Ln 23-24: “Satellite retrievals of these optical properties would be helpful”. I think it would useful to add “in cloud-free, but not necessarily dry, regions” or something like that.

——————- Acknowledgements Pg 12542 Ln 25: “PDF” should be “PFD”

——————- Figures

Pg 12554 It is not completely clear whether or not only a subset of the HTDMA-derived kappa values (only at high angstrom coefficients) are plotted in Figs 3c and 3d (as in Fig 3b). In the caption, “tabulized” should be “tabulated”, and I believe “horizontal axes” describing the Petters and Kreidenweis tabulated values should be “vertical axes”. Is this data an average for all flights?

Pg 12555 Can we get more tick labels and/or ticks on the right axes (preferably in the range of the data presented), so that we can see what Ddc we’re looking at?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12519, 2009.