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Atmospheric
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Interactive comment on "Cloud condensation nuclei (CCN) from fresh and aged air pollution in the megacity region of Beijing" *by* S. S. Gunthe et al.

Anonymous Referee #1

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This is a good paper, describing size resolved and supersaturation resolved CCN measurements near Beijing, and specifically highlighting time periods when CCN properties change due to different emission sources advecting to the sampling site. The CCN properties are further related to aerosol composition measurements, and a simple mixing state formula based on chemical composition is shown to fit the derived hygroscopicity parameter from the CCN measurements. I recommend that the paper be published after addressing the following points.

Page 2: "apparent elemental and organic carbon". I would remove the word "apparent"

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since it is not clear what you mean. You can say "observed elemental and organic carbon inferred from thermo-optical measurements" if that makes you feel more comfortable than simply removing the word "apparent". I would also remove the subscript "a" for the variable "EC_a" (which I assume stands for "apparent"). There is uncertainty in the EC measurement, and perhaps there are conditions where the measurement does not accurately describe the elemental carbon content of the aerosol, but every measurement is subject to uncertainties and caveats. For instance, particle size inferred from light scattering measurements may depend on the particle refractive index (which depends on composition) and particle shape. These unknowns add uncertainty to the sizing measurement - but measuring particle size with light scattering is still a valid technique. Putting the word "apparent" here makes it seem that the EC measurement technique is not valid. It would be better to quantify the uncertainty in the measurement, rather than to cast a vague doubt about the measurement technique.

Page 2: The equation assumes that EC is not contributing much to the CCN-active aerosol mass. This is a bit confusing when you say later in the abstract that EC mass fraction is ∼30% in the fresh pollution outflows. I would expect that the EC mass present in the fresh outflows can become internally mixed as the aerosol population ages, and therefore should be included in the kappa parameterization. I understand that EC does not contribute to soluble mass, but it can contribute to total mass (the denominator of your parameters "f_org" and "f_inorg") depending on how these mass fractions are defined. Please clarify this point, and be consistent and clear in your terminology. It is confusing that you apparently define mass fraction one way (relative to AMS organic + inorganic) and then in the next paragraph define it a different way (relative to soot + AMS organic + inorganic).

Page 4: replace "air particulate matter" with "atmospheric particulate matter". Also, is there another more permanent source you could reference for the population of Beijing? http://en.wikipedia.org/wiki/Beijing would be a better source (and it says 19.6 million, not 22 million). You write that in addition to the "domestic, industrial, and traffic emissions" there is "regional pollution originating from the highly industrialized areas to the south" – are agriculture/biomass burning and dust other important sources that you should mention here?

Page 7: the calibration line you report for S assumes that temperature is constant. You should at least mention this, and also mention how much a 10oC temperature change will effect supersaturation (10oC appears to be approx. how much the temperature changes over any given day, from Fig. 3). From Rose et al. 2008 (Fig. 8a), a temperature change of 10oC can change supersaturation by more than 15%. I'm guessing that pressure and CCNc flow rate do not change much, and therefore the temperature variability is your biggest source of uncertainty - but that is worth looking into as well. It is possible that a temperature increase of 10oC results in a >20% decrease in supersaturation (depending on the thermal efficiency of the instrument). therefore your reported uncertainty of < 10% seems a bit low to me, even though a precise solute activity model was used, since the operating parameters were not factored in to the estimated supersaturation (except for deltaT). Also, at high CCN concentrations the supersaturation in the CCNc can be significantly depressed, which should be at least mentioned (Lathem and Nenes, Water Vapor Depletion in the DMT Continuous-Flow CCN Chamber: Effects on Supersaturation and Droplet Growth, Aerosol Science and Technology, 45, 5, 2011) - How high were CCN concentrations at any given time in the instrument (a given size cut and supersaturation)?

Page 8: for the correction factor, you should say what units D is supposed to be in (presumably nm), or rather the units of x2. Also, report the Rˆ2 for this fit. For the multiply charged correction, do you just assume that all of the multiply charged particles you calculate from the aerosol size distribution and charge distribution act as CCN? (since they are larger and likely more hygroscopic, according to Fig. 6, than the singly charged particles). What kind of aerosol charger did you use upstream of the DMA? Also, why doesn't the cumulative Gaussian distribution function seem to fit very well for particle sizes just above the inflection point for your dataset?

Page 9: It is not correct to say that not accounting for the externally-mixed CCN-inactive particles in calculation of kappa is the same as obtaining the "effective overall properties" of the aerosol population. kappa and MAF can vary independently from each other, and they have different effects on the shape of the CCN spectrum. The 2-parameter fit will only have predictive ability when the externally-mixed fraction is low. When MAF is < 1, the 2-parameter fit will always overestimate D_a. Just because this bias acts in the same direction as a lower MAF (reducing predicted CCN concentrations for a given S), this doesn't mean that the two biases (overestimate of MAF and overestimate of D_a) cancel each other out. Assuming MAF = 1 also does not help with understanding or modeling the physical processing that are occuring. Therefore, the 2-parameter fit is inferior, but it seems that you are stating the opposite. I don't know why the 2-parameter fit is used at all.

Although you are basically copying the text from Rose et al, 2010, it is not correct to say "The difference between unity and maximum observed CCN efficiency... represents the fraction of externally mixed CCN-inactive particles at D_max or averaged over the diameter range of D_a to the largest diameter of the measured spectrum (D_max)". Mixing state is defined for a given (constant) particle size. For a given size, if you increase the supersaturation, you activate more particles, until the point when all CCN-active particles have activated - at that point, you can say that what remains are the "externally-mixed CCN-inactive particles". In Fig. 2a, MAF(0.07%S)=0.81 - but when you increase the supersaturation, MAF(0.26%S)=0.98. Just because you

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measure MAF(0.07%S)=0.81, that doesn't mean 19% of the ~300nm particles are CCN-inactive - apparently, they just need a slightly higher supersaturation in order to activate. Therefore, your dataset shows that the aerosol composition for these large particles is a continuum, rather than two discrete populations.

by the way, Table 1 and Fig. 2a do not match up. For the entire campaign, MAF_m(0.26%S) appears from Fig. 2a to be 0.98, not 0.91 as reported in Table 1. and MAF_f(0.26%S) > 0.9 (from Fig. 2a) while Table 1 reports MAF_f(0.26%S) = 0.90. I did not check all values in the table.

In fact, I think it is incorrect to use the terminology maximum activated fraction (MAF) in this way, first of all because the fraction of activated particles for a given size maybe greater than what you measure at some arbitrary supersaturation (as explained above) and also because you cannot assume that the activated fraction will always increase with particle size (the activated fraction of large particles can actually be lower than smaller particles, due to differences in their composition and mixing state - therefore the activation spectrum as a function of particle size is not necessarily a cumulative distribution). To have a cumulative distribution, you would have to see how the activated fraction changes as a function of supersaturation, not particle size (See Fig. 3, Cerully et al, Aerosol hygroscopicity and CCN activation kinetics in a boreal forest environment during the 2007 EUCAARI campaign, ACPD, 11, 15029-15074, 2011).

I don't believe you are capable of determining the externally-mixed fraction of CCN-inactive particles for sizes < ~80nm with this dataset, since you have only 3 datapoints (supersaturations) for any given particle size. You can say that at least ~80% of 60 nm particles activate. and you can say that at least ~60% of 45 nm particles activate. but you do not know if the supersaturation were increased further slightly (> 0.86%) if more of the 45 nm particles would activate or not. Therefore, you cannot say how the externally-mixed fraction changes as a function of particle size. You can only say that particles > ~80nm do not have a significant externally-mixed CCN-inactive fraction (for the average).

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Page 10: again, even though it has been previously published in Rose et al, 2010, and Gunthe et al, 2009, I don't agree with the statement: "kt is better suited for the calculation of CCN number concentrations..." this statement assumes that MAF is not known. If the CCN activation spectra are obtained, then there is no reason why MAF would not be known, or why the 2-parameter fit would ever be used. Even if CCN activation spectra are not obtained, mixing state can be derived from single particle composition measurements or humidified tandem DMA measurements.

Page 13: Is it possible that the externally-mixed CCN-inactive particles at 250 nm are dust and not primary soot particles? From studies in other locations (e.g. Mexico City, Houston) I would expect the mean of the primary soot number mode to be much smaller (e.g. dp = ∼60nm mobility diameter). Also, I expect that there can be a significant amount of dust in Beijing. Dust can also be an absorbing aerosol, which might register as ECa? I understand that you will focus on the "abundance, properties and effects of the externally mixed, weakly CCN-active particles" in later studies, but I would like a short discussion on this here, since you say that these large (> 250 nm) particles are likely soot, but don't rule out the possibility (or even mention) that they could be dust (which seems more likely to me). If you believe that they are not likely dust, then I'd like you to give a short explanation why you think this.

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in general, more topic sentences would be nice. Especially for the paragraph introducing Fig. 2c on Page 14. This is an important paragraph - it would be nice to know that up-front.

I wish you had used different variable names, because I have to keep referring back to page 8 for their definitions. They are not obvious. I think it would be a lot easier to keep track if the following names were used:

....

3 parameter fit:

MAF (instead of MAF_f, what does the subscript f stand for anyway? fit? it seems like the same subscript should be used as the other fit parameters, or no subscript at all)

Da_3 (instead of Da_a)

sigma_3 (instead of sigma_a)

....

2 parameter fit:

Da_2 (instead of Da_t)

sigma_2 (intsead of sigma_t)

....

I don't really understand why MAFm is useful. Since MAFf is fit to the activation spectrum, then it should correspond fairly closely to MAFm. Why does the variability of this one point (the activated fraction at Dmax) matter more than for the other points?

you could have simply used MAFf = MAF, since MAF for the 2-parameter fit is always 1, and since MAFm isn't really useful.

Also, some of the variables (e.g. NCN, tot and NCN,30) are defined in table captions, when they should be defined in the text. they should also be defined before they are used (Table 2, where NCN,30 is defined, is introduced after it is used, for example).

what does the subscript "p" stand for in "kappa_p"? why not use "kappa_AMS" to be more straightforward?

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Page 17: "...the mass concentrations determined by AMS were enhanced by factors of 1.5-2..." although I know what you mean, you should say explicitly, enhanced relative to what?

Page 19: "An apparent overprediction of κa in the Aitken size range during the focus period of fresh city pollution (< 100 nm, Fig. 6c) is likely due to enhanced mass fractions of soot and elemental carbon (Tab. 3), which are not captured by the AMS data." You need to rethink this statement. For kappa_p to overestimate kappa_a, a compound must be measured by the AMS, but not actually contribute soluble material. Presumably, soot is not measured by the AMS. Instead, perhaps some of the organic compounds measured by the AMS during this focus period are not actually soluble? It seems reasonable to suggest that kappa_org is lower (< 0.1) for these fresh organics than on average. In that case, not only the fraction of organics matters, but it can also matter (to a lesser extent) whether the organics are fresh or aged...

Page 21: "Thus, the CCN concentrations were generally larger (∼(0.8-13)×103 cm-3 vs. ∼(0.4-8)×103 cm-3), although the total CN number concentrations were smaller (∼1.8×104 cm-3 vs. ∼2.2×104 cm-3)." you should generally avoid words like "larger" and "smaller" when talking about particle concentrations (and instead used "greater" and "lesser", "higher" and "lower", or "more" and "fewer") to avoid confusion with statements about particle size.

Page 22: again I don't believe this statement is correct: "An apparent overprediction of κa in the Aitken size range during the focus period of fresh city pollution was likely due to enhanced mass fractions of soot and elemental carbon, which are not captured by the AMS"

Page 23: "...suggests that the fresh outflow from Chinese megacity centers may generally contain..." remove the word "may" or "suggests". both words together in the same sentence (along with "generally") makes it sound like you are not confident in your results.

Figure 2: It seems that your fits of the CCN activation spectra fit better to the smaller particles than to particle sizes just above the inflection point. Can you explain this? Does it have to do with the variable composition (or variable MAF) as a function of size? or multiply charged particles? What does it mean?

Figure 3 has a lot of information in it - it's very difficult to convey that much information in one figure. It would be nice to see a diurnal plot (data as a function of time of day, instead of one long timeseries) or a series of such plots that are colored by whatever variable you are interested in (e.g. temperature, organic mass fraction, humidity or wind direction). This would more directly illustrate the correlation(s) that you want to show. If you do decide to keep Figure 3, you should at least label all of the plots (a through i), in correspondence with the caption. Please discuss why the relative humidity (presumably after the drier) is so high (> 50% at times) during the green shaded periods. were you sampling in fog during those times? on page 16 you said there was a "frontal passage" during this period. If you were sampling in cloud, perhaps you were sampling interstitial aerosol, which appears to be consistent with your observations (e.g. lower CCN, lower kappa, lower MAF...)

Figure 5: Why are there so few data points at S = 0.86%? It might be nice to show the

different focus periods on this same plot (using different marker symbols?)

Figure 6: This figure is very nice. It would have been nice to see how the externally-mixed fraction varies as a function of particle size too. but I don't think you are capable of determining this from your dataset. However, if I am wrong about that, please include it here. you could at least show a lower limit for the externally-mixed fraction...

In generaly, you should order citations by date (oldest first, to give credit to the person originally doing the work).

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 9959, 2011.