Atmos. Chem. Phys. Discuss., 10, C14314–C14326, 2011
www.atmos-chem-phys-discuss.net/10/C14314/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 2: Size-resolved aerosol chemical composition, diurnal cycles, and externally mixed CCN-inactive soot particles" *by* D. Rose et al.

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Received and published: 4 March 2011

Response to Referee #1

We thank Referee #1 for the review and the constructive suggestions for improvement of our manuscript, which will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee comment:

The conclusions are nicely summarized but the following statements in the abstract seem somewhat contradictory. The authors first state that "the constant kappa value [k=0.3] CANNOT account for the observed temporal variations in particle composition and mixing state (L28 P26843)" but then say "the results confirm that an average value of k=0.3 CAN approximate CCN concentrations when size distribution without chemical composition information are available (L3 P26844)". The following sentence (L6 P26844) then supports the original statement (L28 P26843) and says that more information is necessary to improve the k=0.3 predictions. Is it simply that that on a global and climate modeling scales the value of k=0.3 may be applied but it fails to capture regional and temporal variations of CCN? Can the authors simplify and clarify the logic in the abstract? This would apply a unifying message and improve the impact and importance of the paper.

Author response:

We agree that the argumentation in the abstract may be unclear and we intent to clarify this in the revised manuscript. The last paragraph of the abstract will then read as: "Overall, the results confirm that on a global and climate modeling scale an average value of kappa$\approx$0.3 can be used for approximate predictions of CCN number concentrations in continental boundary layer air when aerosol size distribution data are available without information about chemical composition. Bulk or size-resolved data on aerosol chemical composition enable improved CCN predictions resolving regional and temporal variations, but the composition data need to be highly accurate and complemented by information about particle mixing state to achieve high precision (relative deviations <20%)." Similar passages in the Summary and Conclusions will be also adjusted accordingly.

Referee comment:

L2. P 26849. What is the uncertainty associated with the density value (1.7 g cm-3), used to convert vacuum aerodynamic diameter to mobility equivalent diameters induce? How does this influence kappa_a,p?

Author response:

Assuming a particle density of 1.7 g cm-3 we are on the upper limit of what can be expected for a mixed aerosol with an organic fraction of on average 50%. Calculations based on the DMPS and AMS measurements performed during this campaign yielded a density increasing with particle size from $\sim$1.5 g cm-3 at 100 nm to $\sim$1.7 g cm-3 at 200 nm (Wolfram Birmili, personal communication).

For a density correction factor lower than 1.7, the resulting mobility diameter would turn out to be larger than what we calculated (e.g., 13% larger for a factor of 1.5). The mass concentrations and mass fractions displayed in Figs. 1 and 2 would be linearly shifted to the right and accordingly also the kappa_a,p values would be shifted (Fig. 11). Since we observed an increasing inorganic mass fraction with particle size (Fig. 2), this shift would lead to a smaller kappa_a,p value at a particular size. However, the effect would be small because the composition size dependence was small, except during the biomass burning event. For example, a density factor of 1.5 instead of 1.7 would change the average value of kappa_a,p by $\sim$1% at 50 nm and by $\sim$3% at $\sim$200 nm ($\sim$3% and $\sim$12%, respectively during the BBE). We will add this information in Sect. 2.2.3 of the revised manuscript.

Referee comment:

The viewer has several concerns regarding the conclusions drawn from AMS and CCN correlations. There is an evident bias towards the proposed empirical fit suggested by Gunthe et al., 2009. E.g., the authors state “kappa_a became too high compared to the expected hygroscopicity (P26353 L14)”. Is it not that the predicted value could

not fully describe the measured behaviour? The authors of this paper then reconcile this discrepancy and subsequent flaws in fits to AMS data at low mass concentrations. Should we not trust the measurement more than the prediction?

Author response:

We did not intend to value the prediction higher than the measurement and will reformulate the relevant sentences accordingly.

Referee comment:

The reviewer has concerns that the observed discrepancies between measurements and prediction may be real. Gunthe et al., 2009 proposed the mechanism from similarly low total mass concentrations in the Amazon. The Amazon is a somewhat pristine environment however low concentrations in the Guangzhou Region maybe indicative of very aged complex organic background aerosol. What is the composition of aerosol below 1 ug m-3? What is the fraction of organic constituents? Organic composition if soluble or surface active can contribute up to 40% variability in kappa-CCN activity (Juranyi et al., 2009). In regions where inorganics may dominate such as the range between “kappa_a =0.25 to 0.55, the predicted values deviate from the observed ones on average by less than 20% (L12 P26854)” thus closure between measured and predicted CCN properties is more likely to be in better agreement.

Author response:

On average, the organic mass fractions observed at low aerosol mass loadings (m_D < 1 μg m-3) were not much different from those observed at high mass loadings (m_D > 1 μg m-3): f_org = 0.51+/-0.19 at low mass and f_org = 0.52+/-0.16 at high mass (mean +/- standard deviation). In a plot of kappa_a,p/kappa_a vs. m_D the scatter goes up a lot for small m_D but no bias was observed (that is, no systematic over- or under-prediction). Thus, we still consider uncertainties in the AMS measurement

to be the most plausible explanation. Nevertheless we agree that other factors might possibly also influence the results obtained for low aerosol mass loadings (different proportions of primary and secondary organic matter with different molecular and hygroscopic properties). This will be clarified in the revised manuscript.

Referee comment:

"Non-volatile is considered to be mostly soot but contains non-refractory material" (L26849. L28). The authors should address the implications of this statement for kappa-hygroscopicity. This suggests that using assuming k_org as fully soluble will induce discrepancies in closure, especially since it is supported in this paper that the lower volatility stuff is non-hygroscopic and accounting for it improves closure.

Author response:

The non-volatile material is supposed to be soot, which consists of black or elemental carbon and perhaps also of refractory organics. Besides AMS imprecision, deviations between predicted and measured kappa may also result from different and temporally varying molecular composition and hygroscopic properties of the organic fraction of the investigated aerosols. This will be clarified in the revised manuscript (P. 26861 L. 16).

Referee comment:

L24. P26854. Non-constant kappa values for varying S maybe indicative of either solubility or surface tension effects in addition to error caused by steep slope of aerosol size distribution.

Author response:

We agree that the increasing difference between the predicted and the observed CCN concentrations with decreasing supersaturation might be also due to different solubility

of the particles and surface tension effects. This will be implemented in the revised version on P. 26855 L. 4: "Alternatively or in addition the changing degree of overprediction with changing supersaturation may be caused by different solubility of the particles and surface tension effects."

Referee comment:

Fig 3. Are the slopes different for BBE and non-BBE?

Author response:

The slope of a linear fit of the data points that exclude the biomass burning event (BBE) is the same as for the entire campaign (-0.54) and the fit of the data points that belong only to the BBE is -0.51.

Referee comment:

L5. P26856. This correlations supports previous work that the volatile organic components are hygroscopic and CCN-active. Why are the soot particles assumed to be externally mixed? It is not clear to the reader how the authors are inferring mixing state from this data set. In addition, the utility of the kappa-hygroscopcity CCN model is that predictions are independent of mixing state, hence internal and external mixture considerations are not required for kappa based predictions.

Author response:

As detailed in Sect. 2.2.4, the size distribution of non-volatile residuals measured by the VTDMA usually separates in two or more distinct modes, which suggests the external mixture of the particles with respect to volatility. The mode which appears in the size range of the initially selected diameter represents particles of low volatility (diameter reduction <5% at 300°C). The other mode(s) represent(s) particles of higher volatility,

i.e., particles with a non-volatile core and a significant coating of volatile material. As has been done in several other VTDMA studies the particles of low volatility are referred to as externally mixed soot particles (e.g., Rose et al., 2006; Wehner et al., 2009).

In the CCN efficiency spectra, the observed non-unity plateaus suggest the external mixture. As detailed by Su et al. (2010) these plateaus cannot be explained by an internally mixed particle population. They are most plausibly explained by different modes of externally mixed particles.

Referee comment:

How significantly does kappa_a differ from kappa_t in this data set? Can you provide a plot of one value against the other (in addition to Fig. 11) ? If they are similar in value, then kappa_t_p is essentially a function of the observed kappa_t. Inotherwords, at larger S equations (3) and (4) are only modifications of measured values and the closure between predictions and measurements may never be perfect.

Author response:

At low supersaturation, where MAF is low, kappa_t is significantly smaller than kappa_a (e.g., on average by 25% at S = 0.068%). At medium to high supersaturation (S >= 0.47%), however, kappa_t and kappa_a are about the same because MAF $\approx$ 1 (see Tab. 3 and 4). The requested plot is attached at the end of this interactive comment. As expected and in accordance with Part 1 of this study (Rose et al., 2010), kappa_t is closely related to kappa_a at high supersaturation (MAF $\approx$ 1), whereas strong scattering is observed at low supersaturation (highly variable MAF). These and other differences between kappa_a and kappa_t were already discussed in Part 1 of this study (Rose et al., 2010). Thus, we do not consider it appropriate to include this plot in the revised manuscript.

We are not sure about the meaning of the second half of the above comment ("If they

are similar ... In other words ..."). In Sect. 3.2.2 we present how kappa_t,p can be calculated, first from taking only CCN measurement results into account (kappa_a, MAF_m, Eq. (3)) and second from applying also VTDMA results (phi_LV,D_a, Eq. (4)). Indeed kappa_t,p and the observed kappa_t agree very well (Figs. 9a, b) because kappa_t,p is mainly a function of the observed kappa_a, which is linked to the observed kappa_t as mentioned above. Only kappa_t,p calculated with Eq. (5) is independent of the CCN measurements and therefore kappa_t,p and the observed kappa_t do not agree as well (Fig. 9c).

Referee comment:

P26844 L 17. What is meant by "source processes"? This phrase is somewhat ambiguous.

Author response:

Source processes are the processes that form new particles including primary emission and secondary formation of particulate matter.

Referee comment:

P26844 L25. Please include Wang et al., 20010

Author response:

Thanks, we will include Wang et al. (2010) in the revised manuscript.

Referee comment:

P26845 L26. Please include Antilla et al. 2010.

Author response:

Thanks for the suggestion. We will include Anttila (2010) in the revised manuscript.

Referee comment:

P26846 L 1. Remove “how”

Author response:

As far as we can tell, this would not be grammatically correct (and omitting the word “how” would also change the meaning of our sentence).

Referee comment:

P26848. L11. CDF?

Author response:

The abbreviation CDF stands for “cumulative Gaussian distribution function” and is explained in Tab. 1, to which it is referred here in the text.

Referee comment:

P26855, L12. Why is it an external mixture?

Author response:

Please see our response above.

Referee comment:

P26858. L23. Is it (kt,p) is as follows?

Author response:

Thanks for pointing out the inconsistencies regarding kappa_t and kappa_t,p in this and also in some following comments. We will change kappa_t into kappa_t,p where necessary. The same we will do for kappa_a and kappa_a,p as well as for N_CCN,S and N_CCN,S,p. When we use the acronyms without the subscript “p” (e.g., kappa_a, kappa_t, N_CCN,S) we do not necessarily refer to the “observed/measured” values of these variables but to the general meaning, i.e., effective hygroscopicity parameter or CCN number concentration. For clarification in the revised manuscript, we will adjust the description of these acronyms in Tab. 1 and we will add the word “observed” in front of kappa_a, kappa_t, N_CCN,S in those case where we really talk of the observed/measured values. When we talk of the predicted variables we will either use the acronym with subscript “p” or add the word “predicted” in front of the acronym without subscript “p”. That is, “kappa_t,p” and “predicted kappa_t” are equivalent formulations.

Referee comment:

P26859. L1. Replace, “the predicted k_t values” with “the predicted k_t,p values”

Author response:

See response above.

Referee comment:

Does Table 3, include or exclude BBE?

Author response:

Table 3 and 4 present average data including the BBE which we will explicitly mention

in the revised version of this manuscript. “Arithmetic means. . . for the entire campaign.”

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Referee comment:

Fig 4. What is the closure fit? What is the slope of the data points? How much uncertainty do the points lie between?

Author response:

The equation and correlation coefficient of a linear fit through the data points are y = 0.53 x + 0.15 and Rˆ2 = 0.44, respectively. This information will be added in the revised manuscript on P.26854, L.9.

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Referee comment:

Fig. 9. Axis titles are very small.

Author response:

Thanks, we will enlarge them in the revised manuscript.

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Referee comment:

Fig 12. Figure is very small and difficult to read.

Author response:

This figure will be larger in the ACP version of this paper.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26841, 2010.

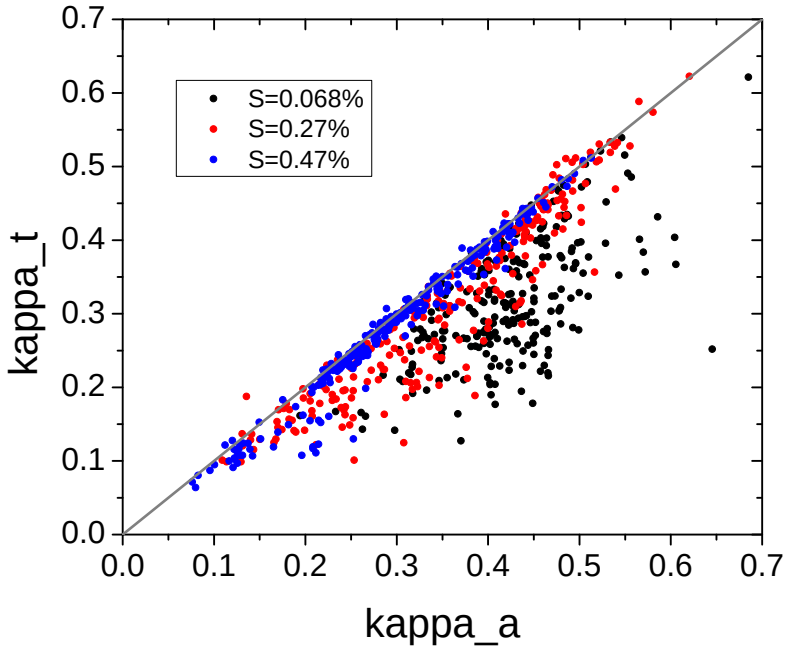

Fig. 1. Observed kappa_t plotted versus observed kappa_a.