

## ***Interactive comment on “The hygroscopicity parameter ( $\kappa$ ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: Relationship to degree of aerosol oxidation” by R. Y.-W. Chang et al.***

**M. Gysel (Referee)**

martin.gysel@psi.ch

Received and published: 13 January 2010

### General comments

This cloud condensation nuclei (CCN) closure study investigates the relationship between the composition of the organic fraction atmospheric aerosol particles and its influence on their ability to act as CCN. The organic aerosol fraction is known to be complex in composition and simplifying assumptions are typically required in e.g. climate or air quality models when it comes to describing CCN activation. The authors

C9653

explore the potential of two simplifying assumptions by linking the CCN activity of the organic aerosol fraction to its oxygen to carbon ratio (O/C) according to high resolution aerosol mass spectrometer (AMS) data, or similarly to more and less oxidized sub-fractions as inferred from the AMS data with statistical methods.

The topic of this study is highly relevant, field measurements were conducted with state-of-the-art experimental techniques and data analysis as well as manuscript preparation have been done with care. The pretended key result of this study is a correlation between O/C and CCN activity of the organic aerosol fraction (expressed as "kappa\_org"). However, no conclusive evidence for this relationship is given, instead the result is merely imposed by the assumptions of the chosen parametrization, as will be detailed below. The data presented in this manuscript just show that kappa\_org is larger than zero, i.e. the organic fraction enhances CCN activity beyond its mere contribution to particle size.

It is possible that the data set of this study also allows establishing a link between O/C and kappa\_org. However, showing this definitely needs additional data analysis. A major revision of this manuscript is required due to the vital gap in the line of argument.

### Major comments

p. 25335 and Figure 1: The results with the approach presented on p. 25335 and in Fig. 1 just show that the campaign mean kappa\_org is larger than zero, while no conclusive evidence of a correlation between the ratio of OOA to HOA and kappa\_org is given. The kappa of the oxygenated organic fraction (kappa\_ox) will always end up positive if the un-oxygenated fraction is assumed to be non-hygroscopic (kappa\_unox=0) and the campaign mean kappa is larger than zero at the same time, independent of the true cause for kappa\_org>0. Similarly one would end up with kappa\_unox>0 if kappa\_ox was assumed to be zero, while varying kappa\_unox until best closure was achieved. The analysis presented in this paper just shows that the assumption kappa\_org=eps\_ox\*kappa\_ox gives better CCN predictions than the

C9654

assumption  $\kappa_{org}=0$ . The latter assumption has previously been shown to be invalid in several environments (see e.g. references in this paper). The key thing to be shown here is that the assumption  $\kappa_{org}=\epsilon_{ox}\kappa_{ox}$  leads to significantly better individual CCN predictions compared to alternative approaches such as  $\kappa_{org}=\text{constant}$  ( $\sim 0.14$  according to p. 25342, line 16) or the counter-intuitive assumption  $\kappa_{org}=\epsilon_{unox}\kappa_{unox}$ . Without doing so, no evidence of a causal link between the ratio of OOA to HOA and  $\kappa_{org}$  is given. A further approach to be tested is leaving both  $\kappa_{unox}$  and  $\kappa_{ox}$  as free parameters in the optimization, similar to the approach in the study by Raatikainen et al. (2009), which investigated the link between different AMS-PMF-derived OA subfractions and hygroscopicity at subsaturated RH, volatility, etc.

p. 25339, first paragraph of Section 4.2: This approach just shows that  $\kappa_{org}>0$ , while it does not give evidence of a correlation between O/C and  $\kappa_{org}$ , similar to the previous comment. Starting off with the presumption that  $\kappa_{org}$  correlates with O/C (i.e. assuming  $\kappa_{org}=a \times (O/C)$ ) will always result in a positive value for  $a$ , if the campaign mean  $\kappa_{org}$  is larger than zero. With the "opposite" assumption that  $\kappa_{org}=b \times (C/O)$ , one would end up with something like  $b \sim 1/a$  I guess, which is also a positive value. The key thing to be shown with the data set of this study is not that the assumption  $\kappa_{org}=a \times (O/C)$  performs better than the assumption  $\kappa_{org}=0$ . Instead it has to be shown that  $\kappa_{org}=a \times (O/C)$  gives significantly better CCN predictions for the individual data points compared to alternative assumptions such as  $\kappa_{org}=\text{constant}$  (optimized of course) or  $\kappa_{org}=b \times (C/O)$ .

Section 4.1.2, Table 1 and Figure 5: Deriving  $\kappa_{ox}$  and  $\kappa_{unox}$  separately for different time periods is a step towards testing the generality of the "postulated" relationship  $\kappa_{org} = \epsilon_{ox} \times 0.20$ . However, my interpretation of the results is opposite from the author's interpretation. The fact that the retrieved  $\kappa_{ox}$  is massively different for one out of just three periods rather indicates that  $\kappa_{org}$  is mainly controlled by other factors than the just ratio of HOA to OOA, and that the above rela-

C9655

tionship cannot be recommended for general use, as it is put in abstract and conclusions.

p. 25339, line 24 - p. 25340, line 6: This whole paragraph including Table 2 is pure speculation and has to be removed. The  $\kappa$  values of the different PMF factors were not independently derived, they are just calculated under the assumption that the relationship inferred between  $\kappa_{org}$  and O/C is generally applicable. Above I argued that validity of this relationship has not been proven and the authors themselves state that "The oxygenated factors were grouped together because our model was not sensitive enough to elucidate separate hygroscopicities for each factor." on p. 25333 of their manuscript.

Minor comments

p.25327, lines 2-5: In the mean time Jimenez et al. (2009) have published a paper in which the O/C of the organic aerosol component of laboratory generated and ambient aerosols is linked to the hygroscopicity at subsaturated relative humidity (RH). Another study by Raatikainen et al. (2009) investigates the link between different AMS-PMF-derived OA subfractions and hygroscopicity at subsaturated RH, volatility, etc.

p. 25329, lines 3-7: Please cite the source of thermodynamic data used for calculating the CCN properties of calibration substance ammonium sulfate. Did you assume a  $\kappa$  value of 0.61 as mentioned later in the manuscript for the closure calculations? The  $\kappa$  value of pure ammonium sulfate at the point of CCN activation depends on the supersaturation (SS). It changes from  $\sim 0.65$  at  $SS=0.1\%$  to  $\sim 0.55$  at  $SS=1.0\%$  and it is  $\sim 0.59$  at  $SS=0.42$ .

p. 25330, lines 12-20: I recommend using the terminology of Jimenez et al. (2009) for the PMF factors. "low volatility OOA" and "semi-volatile OOA" are more meaningful terms than OOA-1 and OOA-2.

p. 25332, lines 14-19: Is the simplification to approximate ammonium nitrate by am-

C9656

monium sulphate needed. The calculations would hardly become more complex with distinguishing them. Furthermore, if this simplification is maintained, then the associated uncertainty in the derived kappa of the organic aerosol fraction has to be added to the (nice) sensitivity analysis presented in Section 4.3). Furthermore, please make sure that the kappa value of ammonium nitrate at the point of activation at SS=0.42% is indeed 0.67 as stated.

p. 25333, line 11: Duplissy et al. (2008) have shown that O/C has a strong influence on hygroscopicity of alpha-pinene SOA at RH=95%. The effect of varying O/C, caused by varying precursor concentration, on CCN activation of alpha-pinene SOA was not shown in Duplissy's study, instead it was just inferred from the behavior at RH=95% and the presumption that CCN activity will change similarly (CCN data very only available for high O/C from low precursor concentration experiments). However, a follow up study by Juranyi et al. (2009) showed that varying O/C of alpha-pinene SOA has virtually no influence on CCN activation, while the strong effect on hygroscopicity at lower RH was confirmed. Petters et al. (2009b) provides theoretical arguments that for this difference between "low" RH and very dilute solutions at the point of CCN activation. See also references therein for further experimental studies.

p. 25333, lines 14-15: According to the arguments brought up in Petters et al. (2009b) one does not necessarily expect a strong dependence of CCN activity (CCN-derived kappa\_org) on O/C from a theoretical point of view. Molecular weight gains on importance compared to O/C when it comes to very dilute solutions, in contrast to the influence of O/C on hygroscopicity at lower water activity.

p. 25333, line 11-13: Please make clear that the study by McFiggans et al. (2005) presents hygroscopicity data at RH<=90%. The influence of O/C on hygroscopicity is expected to be larger at such "low" water activity compared to the point of CCN activation (see above comments).

p. 25333, line 26 - p. 25334, line 2: Adipic acid - which has a relatively low solu-

C9657

bility - may not be most representative for OOA. Cross et al. (2007) have reported experimental density data.

p. 25336, lines 4-7: An average ratio (R\_CCN) of 1.20 between predicted and measured CCN concentration seems inconsistent with a fitted slope of 1.02 between the same two quantities. First, is the distribution of individual R\_CCN values rather normal or lognormal? In the latter case it is better to report the geometric mean instead of the arithmetic mean of the R\_CCN values. Second, Fig. 2 shows that the R\_CCN are biased towards values >1 mainly at medium and low CCN concentrations, while they are near unity at the highest CCN concentrations. Fitting a line with axis intercept at the origin is most sensitive to the highest CCN concentrations unless a weighting is introduced.

p. 25338, lines 3-16: This is largely a repetition of text already given on page 25335. Please try to reduce redundancy.

p. 25341, line 16-20: The studies by Juranyi et al. (2009) and Petters et al. (2009b) indicate that O/C has little influence on CCN activity of organic compounds.

p. 25341, line 27ff: Ensemble mean molecular weight is also a key factor for CCN activity of organics, not just O/C.

p. 25343, lines 1-4: As detailed above I do not at all agree with this summary statement.

p. 25343, conclusions, lines 11-12: "most of the specific time periods for the study". Call 2 out of 3 "most" is audacious (see also corresponding major comment).

Technical corrections:

p. 25332, line 2: What do you mean with "initially"? Isn't it simpler to directly state that you assume surface tension of pure water in all closure calculations.

References:

E. S. Cross, J. G. Slowik, P. Davidovits et al., Aerosol Science and Technology 41, 343

C9658

(2007)

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., et al.: Evolution of organic aerosols in the atmosphere. *Science*, 326, 1525-1529, 2009.

Jurányi, Z., Gysel, M., Duplissy, J., Weingartner, E., Tritscher, T., Dommen, J., Henning, S., Ziese, M., Kiselev, A., Stratmann, F., George, I., and Baltensperger, U.: Influence of gas-to-particle partitioning on the hygroscopic and droplet activation behaviour of  $\alpha$ -pinene secondary organic aerosol. *Phys. Chem. Chem. Phys.*, 11, 8091-8097, 2009.

Petters, M. D., Wex, H., Carrico, C. M., Hallbauer, E., Massling, A., McMeeking, G. R., Poulain, L., Wu, Z., Kreidenweis, S. M., and Stratmann, F.: Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol - Part 2: Theoretical approaches. *Atmos. Chem. Phys.*, 9, 3999-4009, 2009b.

Raatikainen, T., Vaattovaara, P., Tiitta, P., Miettinen, P., Rautiainen, J., Ehn, M., Kulmala, M., Laaksonen, A., and Worsnop, D. R.: Physicochemical properties and origin of organic groups detected in boreal forest using an aerosol mass spectrometer. *Atmos. Chem. Phys. Discuss.*, 9, 21847-21889, 2009.

---

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 25323, 2009.