

Interactive comment on “The hygroscopicity parameter (κ) 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.

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Chang et al. analyze cloud condensation nuclei and aerosol composition data from the Egbert 2007 field study to infer the relationship between the oxidation state of the organic components and organic aerosol hygroscopicity. To find the organic aerosol hygroscopicity, the authors model CCN concentration by convolving the aerosol size distribution and the chemical composition. Simultaneously, aerosol mass spectrometer data constrain the oxidation state of the organic fraction in form of derived oxygen-to-carbon ratios or commonly used PMF components such as HOA and OOA. Combined

the data allow to compute quantitative empirical relationships between organic component hygroscopicity and the degree of oxidation of those components for organic compounds present in the atmosphere.

I find that this is a nice study and I recommend it for publication in Atmospheric Chemistry and Physics. In particular it adds new data that fits into the unifying organic aerosol modeling framework recently proposed by Jimenez et al. (2009). However, I also find myself left with some conceptual difficulties regarding the advocated relationship between O/C and kappa as well as the derivation of organic aerosol kappa. I suggest that the authors provide better theoretical and experimental constraints and add a number of qualifications before this manuscript appears in print.

General comments

It seems that over the last few years a dramatic shift occurred regarding aerosol-to-CCN closure studies. Not too long ago, we as a community collectively failed to measure aerosol composition and predict CCN concentrations adequately (see McFiggans et al., 2006, ACP; Kreidenweis et al., 2009, Cloud particle precursors in Clouds in the Perturbed Climate System: Their Relationship to Energy Balance, Atmospheric Dynamics, and Precipitation. Struengmann Forum Report, vol. 2, Ervens et al., 2009, ACPD, and Kammermann et al., 2010, JGR for a list of studies), with a systematic trend to overpredict CCN concentrations from size and composition data. Recently, this trend has been reversed and closure is achieved more often than not. It is unclear to me what aspect of the measurements improved. My personal view on the failed closure story has always been the difficulty to match concentration measurements (CCN and integrated CN), as well as the propagation of sizing errors due to the high sensitivity of the Kohler equation to dry size. I should note that at least in the earlier studies there has been great difficulty to reconcile closure conditions with composition. The conceptual shift that has taken place is that closure is now a given, and that closure conditions are well enough constrained to infer the partial effects of a single sub-component of the aerosol, here the organic fraction. While the numbers presented

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here are plausible, I still also consider them highly uncertain. In particular, the issue is that the organic kappa reported here subsumes many of the perhaps compensating measurement errors. An incomplete list would be sizing errors, shape effect errors, mixing state uncertainty, and counting errors. For example, how much does the derived organic kappa change if the CCN instrument counts 10% low? How representative is the organic aerosol kappa, if the ratio of organic/inorganic fraction varies with size, if it leads to only 'average' closure? How well can hygroscopic inorganic and insoluble inorganic compounds be subtracted when the AMS measures only the non-refractory composition? How much do assumptions about the chemical state of the inorganic compounds matter? In summary, my criticism is that the derived organic kappa values are at least more uncertain than in studies that measure kappa more directly. To address my concerns the authors should present additional analysis that highlights these uncertainties. For example, the authors might want to do a classical error propagation analysis and report that in a supplement. Alternatively, plots of organic fraction vs. total kappa (e.g. Shinozouka et al. 2009, ACP) could show how noisy the data are, and how well organic kappa can be inferred from subtracting inorganic components. In particular the authors should be sensitive to the problem of overprediction at $k_{org} = 0$, which clearly reveals other experimental issues at play.

When I first saw the proposed relationship $k_{org} = 0.3 * O/C$, I was immediately tempted to 'break' this relationship. The reason for this is that we recently published a paper on the relationship between molecular size and kappa, and showed that the Flory-Huggins entropy of mixing well describes kappa over a broad range of molecular sizes. When we selected compounds to study, we did so based on O/C ratio. In particular we ran $O/C \sim 1$ (carbohydrates) for $C = 3..18$, and $O/C \sim 0.5$, for $C = 6..>60$, with the hope to learn something about the relationship of O/C and kappa. For example, maltotriose hydrate has an $O/C \sim 1$ but kappa of ~ 0.055 (Petters et al., 2009, GRL, Table S1), which does not conform to the proposed relationship here. Taking the argument to the limit, one might conclude from our work that the extent of oxidation has nothing to do with kappa. To add to this critique, one can also break the proposed relationship another

way, by considering nitroglycerin (1,3-dinitrooxypropan-2-yl nitrate), which has an O/C ratio of 3, but likely not $\kappa = 0.9$. The implication of this example is twofold: 1) How are organic nitrates accounted for using the AMS technique? 2) Should an O bound with N count the same than an O with C? So based on the above, I have great conceptual difficulty accepting the parameterization of O/C vs. κ . On the other hand, it is obvious that HOA (or pure hydrocarbons without oxygen) do have $\kappa \sim 0$, and that oxidizing these compounds will eventually increase κ . The likely mechanism is that compounds transition from being water insoluble, where they do not contribute to κ , to water soluble, where they express the κ according to their molecular size. Further, if acids are produced, the oxidized molecule will likely break apart and lead to smaller more oxidized fragment in the condensed phase. Such a process would also indirectly result in an increase of κ for more oxidized compounds. Finally, for ambient aerosol the matrix of possible oxygenated functional groups may be limited by the chemical pathways producing that aerosol, further leading to a streamlining of the empirical O/C vs. κ relationship. In fact, my personal view is that the observed linear relationship between κ and O/C provides more of a constraint on chemical oxidation mechanisms active in the atmosphere rather than offering a prognostic equation to predict CCN, but that is more a philosophical question. In light of my comment, I suggest the following specific changes to the manuscript

- 1) A couple of paragraphs that describe these issues and at least qualitatively argue why O/C and κ should be related.
- 2) A big qualification, to be also included in the abstract, that the equation $\kappa = 0.3 * O/C$ does not apply to arbitrary molecules, but only bulk O/C ratios measured for atmospheric aerosol using the AMS.
- 3) A qualifier on how AMS O/C ratios may differ from actual O/C ratios, e.g. for organic nitrates.
- 4) A qualifier that the O/C ratios explored here are only valid for the narrow range of

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O/C explore here (this should be part of the equation).

5) A statement that the relationship is likely due to the fact that the observed O/C correlates with solubility and molecular size and not directly controls kappa. If the authors have alternative or additional explanations to the ones I give here they should of course be included as well.

6) A detailed plot on the observed O/C vs. kappa relationship, including error bars in x and y. This is important to show if the observations are indeed linear (which I would not expect from theory), and how it compares with the Jimenez et al. data points.

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