

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.

Anonymous Referee #2

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The reviewed work by R. Y.-W. Chang et al. contains interesting new approaches on how to connect measured aerosol particle composition with the particle hygroscopicity. However, as I will explain in more detail below, the values for parameters derived in this work can only be upper limits. In this respect, a more detailed sensitivity study could be of interest. Also, in some parts the order in which things were described was backwards, complicating the understanding of the text. The manuscript needs major changes before it can be published.

In the study under review, data from one month of measurements of atmospheric

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aerosol was used. Information on the chemical composition from AMS data was taken to derive concentrations of CCN (Cloud Condensation Nuclei). The AMS delivered the fraction of inorganic and organic material. Data analysis was done twice, dealing with the organic fraction in two different ways. Once, additional information from the AMS about the fraction of “oxidized” and “unoxidized” OC (organic carbon) was used. The second approach employs the total molar ratio of oxygen to carbon (O/C). For both approaches, Koehler theory was formulated such, that one free parameter existed: the hygroscopicity parameter for the oxidized OC ($\kappa(\text{ox})$) in the first approach, and a factor “a” connecting O/C to the hygroscopicity parameter for all of the OC ($\kappa(\text{org})$) in the second approach.

The idea was, to adjust these free parameters such that the therewith derived number of CCN ($N(\text{CCN})$) matched the one that had been measured in parallel to the AMS data.

This could yield interesting information about $\kappa(\text{ox})$ and the factor “a”. But I see a (likely general) problem:

When the aerosol was largely dominated by inorganic compounds and $\kappa(\text{ox})=0$ was assumed, $N(\text{CCN})$ was already overpredicted by the calculations by 20%. Increasing $\kappa(\text{ox})$ only increases this overprediction, i.e. it is not easy to find a reason for the overprediction. Such an overprediction of $N(\text{CCN})$ has often been reported in the past, while an underprediction occurs much less frequent. However, it would be much easier to find reasons for an underprediction. E.g. increasing $\kappa(\text{ox})$ or decreasing the surface tension (which might be reasonable in the presence of organic substances), would increase $N(\text{CCN})$.

However, in the present study the authors have to deal with an overprediction. They try to overcome this by using the 20% overprediction from the inorganic aerosols as their base-line, to which they adjusted $\kappa(\text{ox})$ or the factor “a” for all examined aerosols. I think this is problematic. Here comes why:

Imagine there might have been a problem with the AMS detection efficiency for one (or all) inorganic compounds (I do not say there was, this is just a gedankenexperiment). Let us assume the inorganic mass, and therewith the inorganic fraction, was overpredicted. This could explain the 20% overprediction of $N(\text{CCN})$ for aerosols with mostly inorganic compounds. For aerosols with a smaller fraction of inorganic compounds, this overprediction of the inorganic fraction is still there, but it causes a smaller overall overprediction ($<20\%$) in $N(\text{CCN})$. But now you adjust $\kappa(\text{ox})$ or the factor “a” so, that it leads to an overprediction of 20%, i.e. you transfer some of the error of one measurement into the numbers you want to derive. This could explain why your values for $\kappa(\text{ox})$ exceed those values often found for organic aerosol. And with this, likely, the 0.3 derived for “a” is too large, as well.

There might be other explanations for the overprediction. If this originated in a constant measurement error of the CCN counter, it would be justified to do the analysis as it was done. However, it is more likely that the overprediction is different for different aerosol types. Therefore, it can only be said that the derived numbers are upper estimates. This limitation has to become clear in the work.

Also, I strongly suggest a more detailed sensitivity study, including e.g. values for epsilon as one source for uncertainty, $\kappa(\text{inorg})$ as a further one.

Specific comments:

page 25324, line 9 and 16 (abstract) and in the introduction: You use “O/C” four times, before you finally define it as “total molar ratio of oxygen to carbon (O/C)” in section 2.4. Correct this!

page 25324, line 18: Better start the first line with “Atmospheric aerosols” or “Atmospheric aerosol particles”, otherwise you include all kinds of aerosol, e.g. from spray cans, which you certainly don’t mean to include.

page 25324, line 20: “The efficiency of aerosols as CCN ...” – replace “aerosols” by

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“particles”

page 25325, line 6: should it not be “properties ARE known”?

page 25325, line 24: should it not be “signals” (plural)?

page 25326, line 1: replace “found” with “used”

page 25326, line 3: Lanz et al., 2007 already used PMF, and you cite this work later anyway. I suggest citing it here also.

page 25328, line 22: How stable was the room temperature in the laboratory? This should have a major influence on the stability of the supersaturation reached in the CCN counter. How does this lab-temperature variation relate to the uncertainty range of 0.03% that you give for the supersaturation on the next page?

page 25329, line 1 and 2: You mention that your measured CCN concentration was highest for a residence time of 19 s. What is your explanation for this? Is this instrument-specific, or does it come from the aerosol?

page 25330, line 4-6: The analysis below could be affected if the aerosol was not internally mixed and if one fraction would bounce off more easily than others. Also, collection efficiency may vary for different substances. These factors, indeed, determine the uncertainty of the AMS measurement, which, of course, has an influence on the results of the PMF. So please weaken your statement here accordingly, or remove it.

page 25331, line 9-21: It is confusing to read such a paragraph first, without knowing how you knew or derived your kappa. I suggest you define kappa first. So, following the description of the general Koehler theory and each of your approaches, you could show how kappa finally is defined: $\kappa = \epsilon(\text{inorg}) \cdot \kappa(\text{inorg}) + \epsilon(\text{ox}) \cdot \kappa(\text{ox})$, with $\kappa(\text{ox})$ being the free variable, and similar for the second approach with “a” being the free variable and the other parameters being known from the AMS measurements. The description of how then $\kappa(\text{ox})$ or “a” are varied to match the measured number of CCN would follow.

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page 25331, line 23-24: Eq.1 does not show, how all the variables are combined into a single kappa, but Eq.3 does.

page 25332, line 2: Why is the surface tension 0.072Nm^{-2} “initially” – this is the value of water at 20°C . And you do not vary it, apart from in the uncertainty-section.

page 25332, line 14: Did ammonium, nitrate and sulphate add up, from a stoichiometric point of view? If not, how was the gap treated?

page 25332, line 16: When deriving kappa for ammonium sulphate from Eq. 3, I get a value of 0.53 (for a van't Hoff factor of 2.2, which seems reasonable). 0.61 seems too large to me!

page 25334, line 2: You said earlier, that you treated the inorganics as ammonium sulphate, and now you use different densities for them (which, actually, are really close). How did you do this, after you grouped them? And why?

page 25334, line 2: For the organic compound, you said two lines ago that the density you used was that of adipic acid, 1360 kg m^{-3} . For the overall organic you use 1200 kg m^{-3} . Where does this latter value come from?

page 25334, line 20: You emphasise the use of PMF factors during much of your paper. However, in the last section we saw, that this boils down to using epsilon(ox) and epsilon (unox), i.e. you have 2 factors left. Already explain that earlier in the text and the abstract, because this makes it easier to put your work into perspective.

page 25335, line 2-8: I again suggest a change in the order. I wondered which kappa you used to produce Fig. 1, until I found the solution some lines later. You need to clearly motivate that you try $\text{kappa(ox)}=0$ first to see if organic-rich and inorganic-rich periods behave similar or not. Also, you need to explain clearly, which colour in Fig. 1 is organic-rich or inorganic-rich, and what the black dots are. This only comes later in Sec. 4.1.2., but one needs to know that here already.

page 25335, line 9-26: You described in the last section, how you would use two

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different approaches. This now seems to be a third one. I have several complaints here: Again, the sequence is confusing: $\kappa(\text{ox})=0.2$ appears from nowhere, and only then you explain where the value came from. This is the wrong way around. But, as already said in the beginning of the review, I also have a problem with the basic assumption you made to obtain this value. An over- or underprediction for one kind of aerosol does not have to be the same than for the other, because the particles in the different aerosols could have different surface tensions or different growth kinetics. Also, you adjust $\kappa(\text{ox})$ so, that the overprediction obtained for the inorganic aerosols is met. This overprediction could be caused by an error (e.g. in AMS detection efficiency for the inorganics). I do not see what can be learned from this section and thus suggest erasing it completely. A very similar analysis follows in the next section, anyway.

page 25336, line 6: If $R(\text{CCN})$ is 1.2, then how can the slope in Fig. 2, which is (“predicted CCN” / “measured CCN”), i.e. which is exactly $R(\text{CCN})$, be 1.02?

page 25338, line 9: You said earlier (first paragraph of Sec. 3): “... ($\kappa(\text{org})$) was then iteratively varied (...) to yield predicted CCN concentrations consistent with those measured by the CCN counter.” Here, now, you use $R(\text{CCN})$ from the anthropogenic period as the reference, which means the CCN concentration to which you adjust $\kappa(\text{ox})$ is 20% larger than the measured one. This can hardly be accepted as a means to predict $\kappa(\text{ox})$, but rather shows that the overall measurement uncertainty, even for periods with mainly inorganic aerosol, likely is too large to do such a detailed analysis. (See beginning of the review.) Also, how is this part of your work different from section 4.1.1.?

page 25339, line 9: Was “O/C of one” the value that was derived from the AMS measurements? Or why did you use it to derive $a=0.3$?

page 25339, last line: “ κ ” should likely be a symbol.

page 25340, line 11: “... O/C for this study was limited to 0.3 to 0.6 ...” – how does this correspond to the O/C values given in Table 2?

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page 25341, line 13: Where do these values for molecular weight and density come from? Do you have a particular substance in mind, or do you want them understood as average values for an oxygenated organic compound? If so, how do these values connect to literature?

page 25342, lines 7 and 9-10: Using Eq.6, I cannot follow how O/C of 0.12 results in $\kappa(\text{org})=0.16$ (I obtain 0.036), nor does an O/C of 0.046 or 0.069 result in $\kappa(\text{org})$ of 0.08 or 0.1, respectively (I get 0.014 and 0.021). This could originate in information about the “entire aerosol”, but as this information is not given here, I cannot follow.

Table 3: This is the only time when you call “a” the “slope of O/C” – better call it “a” instead.

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

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