

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.

R. Y.-W. Chang et al.

rchang@chem.utoronto.ca

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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 sur-

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face 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 gedanken-experiment). 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.

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Reply to general comments

We thank Reviewer 2 for their thoughtful comments, especially their discussion about the subtleties in different detection efficiencies for the organic and inorganic compounds. We have extensively re-written the paper to address all the reviewers's points.

To start, we note that the overprediction of CCN number is within our experimental uncertainties of 20% in CCN numbers (as stated in Sect. 2.2 and 4.1.1). This error estimate arises principally from errors in the counting accuracy of the Aerodynamic Particle Sizer and the size of the sample flow, i.e. we believe a systematic error is related to this slight overprediction. We do not feel that it necessarily arises from an error in the Köhler analysis procedure.

Nevertheless, to address the reviewer's point, we want to begin by clarifying the uncertainties in our analysis associated with the measurement of the chemical composition.

If the reviewer is referring to the AMS collection efficiency varying as a function of aerosol composition (e.g. in the Reviewer's gedanken experiment, an inorganic-rich particle is detected with a different efficiency than an organic-rich particle), then there are two reasons as to why we do not think that this is an issue. First, the collection efficiency of the AMS was not observed to vary greatly throughout the study, regardless of aerosol chemical composition. This is based on comparisons of: 1) single particle mass spectra with an integrated light scattering module (details of the general comparison can be found in Cross et al. (2009) and for our study in Slowik et al. (2010)), and 2) total AMS mass and estimated SMPS mass, also described by Slowik et al. (2010).

Second, our analysis depends on the fractional composition. This means that even if the collection efficiency varied with the chemical composition, as long as after an aerosol vapourizes in the oven, its components are detected by the mass spectrometer in the same way, independent of composition, then the mass fraction will also be independent of aerosol composition. For example, suppose the aerosol were inorganic-rich

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during one part of the study. Even if half of the aerosols bounce in the oven and are not detected by the mass spectrometer, so long as aerosol vapourization is independent of chemical composition, then the mass fraction will still be correct.

Although we consider it unlikely for the reasons just stated, we have nevertheless included additional cases in the uncertainty analysis which consider the sensitivity of our results to an increase in the mass of either the organic or inorganic fractions by 50%. Since the fractional composition is the important variable, this analysis can also be considered to represent the possibility should either of these components be over-measured instead.

What is more likely to have affected the aerosol composition is the mixing state of the aerosol, especially at the smaller sizes where there is a likelihood that the composition was different than that of the bulk aerosol. Because the smaller Aitken mode tends to be more organic-rich, this may have selectively affected the times when the bulk aerosol was inorganic-rich (since an organic-rich accumulation mode will still have an organic-rich Aitken mode), resulting in an over-estimation of the inorganic component. The general uncertainties associated with increasing the organic mass by 50%, as discussed in the previous paragraph, can also be used to consider the effects of external mixing. An additional case has been included to the Uncertainties section that uses the composition of the particles between 80–250 nm vacuum aerodynamic diameter, as measured by the AMS in particle time-of-flight mode, in an attempt to be more representative of the composition of the smaller mode.

Reply to 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!

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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 “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.

Thank you to the reviewer for these helpful suggestions. They have been corrected in the revised manuscript.

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?

The room temperature did vary throughout the study. However, the CCN counter actively monitors the temperature of the lower plate and heats the upper plate to the temperature needed to maintain the desired supersaturation. A computer program written in Labview (National Instruments) continuously monitors and controls the temperatures of the two plates. These details have been included in Sect. 2.2 of the revised manuscript.

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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?

This is an operational aspect that is unique to the design of our instrument. The optimal residence time in the chamber is a balance between giving the droplets sufficient time to grow to sizes large enough to be counted by the APS and preventing the aerosols from growing so large that they are lost to gravitational settling. The optimal residence time can also depend on the aerosol chemical composition. However, this was not explored systematically in this study and is therefore not discussed in this manuscript. Shantz et al. (2010), however, discuss the kinetics of activation during the Egbert 2007 study. For these measurements, we gave long residence times to ensure full activation. These details have been added to Sect. 2.2 of the manuscript.

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.

The reviewer brings up good points that have been addressed in our response to the general comments above. In short, the mixing state of the aerosol likely contributes the most to the uncertainties associated with the chemical composition. The Uncertainties section (Sect. 4.3) has been expanded to discuss these issues. The sentence referred to by the reviewer has been modified to:

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"In general, this does not affect the analysis below, which only uses the fractional composition and assumes an internally mixed aerosol. If the aerosol were not internally mixed, then the collection efficiency could be important, and potential effects will be considered in Sect. 4.3 by considering relative uncertainties in the organic to inorganic ratios."

Furthermore, uncertainties in the oxygenated and unoxygenated fractions have also been added to the Uncertainties section.

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: $\kappa = \epsilon(\text{inorg}) * \kappa(\text{inorg}) + \epsilon(\text{ox}) * \kappa(\text{ox})$, 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.

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 0.072 Nm⁻² "initially" - this is the value of water at 20 deg C. And you do not vary it, apart from in the uncertainty-section.

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Thank you to the reviewer for these suggestions. Section 3 has been largely restructured as recommended by the reviewer to explain the formulation of κ_{org} more clearly.

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

The acidity of the aerosol should always be considered. However, as mentioned two lines later, the aerosol that was measured at Egbert was not acidic during this study, so ammonium, sulphate and nitrate stoichiometrically added up.

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!

This value (i.e. 0.61) was derived from thermodynamic data (Clegg et al., 1996) and was originally published by Petters and Kreidenweis (2007). A value of 0.59 is actually the correct value for the supersaturation of our chamber, and is now used in our calculation (as suggested by Reviewer 1).

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?

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We have addressed these valid issues in the new version of the manuscript. In particular, ammonium nitrate is now grouped with ammonium sulphate for all the calculations. This was done to simplify the calculation. The uncertainties associated with this assumption have now been added to the Uncertainties section (Sect. 4.3) of the manuscript, although they are not large.

The organic component is now treated as two components, oxygenated and unoxxygenated, for all the calculations including the density. The oxygenated component, in particular the OOA component, is thought to be similar to secondary organic aerosol (SOA). As such, a density of 1500 kg m^{-3} (measured for monoterpene SOA by Kostenidou et al. (2007)) was used for the oxygenated component. On the other hand, the unoxxygenated component, i.e. HOA, is thought to be composed of, among other components, lubricating oil or hydrocarbon components, which have a density of 900 kg m^{-3} (e.g. Cylinder Lube 1000 from NOCO Energy Corp.). As such, this was the density used for the unoxxygenated component.

Both of these explanations have been added to Sect. 3 of the revised manuscript.

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.

Line 7 of the abstract and paragraph 3 of the Introduction now include the terms oxxygenated and unoxxygenated.

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

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need to clearly motivate that you try 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.

Thank you to the reviewer for this suggestion. This section has now been restructured and the statistical method has been moved to Sect. 3 so that the analysis reads more clearly in the Results and Discussion section. In this discussion of Fig. 1a, we are actually comparing the right-half (upper 50th percentile) of the all the data points with the left half (lower 50th percentile). This has been specified in the revised manuscript.

page 25335, line 9-26: You described in the last section, how you would use two different approaches. This now seems to be a third one. I have several complaints here: Again, the sequence is confusing: kappa(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(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.

This section has been restructured so that it is more clear. Also, as described above in the response to the general comments, we do not feel that there are significant biases in the AMS measurements due to collection efficiencies, for example, and that the level

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of overprediction is within the experimental uncertainties of the CCN measurements. As such, the comparison of one aerosol population to another is a valid approach, to better determine the hygroscopic properties of the oxygenated organic components. Nevertheless, errors in this approach that might arise from potential biases are now addressed in Sect. 4.3.

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?

The reviewer asks a good question that does not appear to have a straightforward answer. The slope from the linear regression is a least-square fitting, whereas the R_{CCN} is a direct measure of the ratio of the predicted to measured concentrations. While past closure studies have always only considered the linear fit, it is biased towards the data points at high concentrations (since they would contribute more in magnitude to the residuals if fit poorly). The logarithm of the data points were taken and then linearly fit, in an attempt to reduce the weighting of the higher data points, but the slope only increased slightly to 1.03. If the data points are weighted by their estimated error ($\pm 20\%$ for measured CCN concentrations) and the intercept set to zero, then the slope can be increased to 1.10 (1.05 if the intercept is not forced through zero), which halves the discrepancy with the value obtained from R_{CCN} . Although our CCN concentrations are over-predicted, it is not entirely clear how this compares to other studies in the literature since the other studies have not published their comparisons in this manner. This discussion has been included in the Sect. 4.1.1 of the revised manuscript.

page 25338, line 9: You said earlier (first paragraph of Sect. 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

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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.?

This section of the work looks at specific time periods during the study when the air mass was thought to be constant and we could consider the degree to which a constant formulation for κ_{org} for the entire study was valid. As the reviewer notes, we use the anthropogenic period as a reference because it has a high fraction of inorganic components. As such, the overall hygroscopicity of that aerosol will be largely insensitive to the hygroscopicity of the organic components. In that context, it does not matter that the absolute numbers of CCN during the anthropogenic period are 20% over-predicted. Instead, this is only a relative comparison. That being said, it is a valid point that we now stress that the extraction of the individual kappa values for the different time periods are all extracted by using this approach of comparing data to the anthropogenic period.

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 $a=0.3$?

This sentence was originally meant to suggest that $a = 0.3$ is the value of κ_{org} if the O/C was extrapolated to one. However, since this was not stated clearly, it has been removed from the revised manuscript.

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

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Corrected.

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?

The O/C in the entire organic component ranged from 0.3 to 0.6, however, the PMF factors that make up the organic component can have O/C that are not in this range. However, if we were to average them for the aerosol, then they would fall into the range of 0.3 to 0.6.

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?

Thank you for bringing this to our attention. These values were meant to represent an average SOA component, considering both small diacids (with molecular weights of 104 g mol⁻¹ for malonic acid to 132 g mol⁻¹ for glutaric acid and densities of 1600 kg m⁻³ down to 1400 kg m⁻³, respectively, (Weast et al., 1983)) as well as monoterpene oxidation products (with molecular weights of 172 g mol⁻¹ for norpinic acid to 214 g mol⁻¹ for pinic acid and densities of 1500 kg m⁻³ (Kostenidou et al., 2007)). This has been added to the revised manuscript in Sect. 4.4.

page 25342, lines 7 and 9-10: Using Eq. 6, I cannot follow how O/C of 0.12 results in kappa(org)=0.16 (I obtain 0.036), nor does an O/C of 0.046 or 0.069 result in kappa(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

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given here, I cannot follow.

We apologize for the confusion. The values given are the fraction of the organic signal at *m/z* 44, which can be converted to an O/C by using the equation in Fig. 4b of Aiken et al. (2008):

$$\text{O/C} = (3.82) \times (m/z\ 44 / \text{Total Organic Signal}) + 0.0794.$$

This value for the organic signal at *m/z* 44 results in an O/C of 0.538 and κ_{org} of 0.16 for the results of Duplissy et al. (2008) and an O/C of 0.255–0.343 and κ_{org} of 0.07–0.1 for the results of George and Abbatt (2010). This has been added to the revised manuscript to improve on the clarity of Sect. 4.4.

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

Thank you for suggesting this.

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