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Atmospheric
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Interactive comment on "Cloud condensation nuclei activity of fresh primary and aged biomass burning aerosol" *by* G. J. Engelhart et al.

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(1) *This paper presents CCN derived hygroscopicity parameter of aerosol particles from a range of different biomass burning experiments, both before and after photochemical ageing in a smog chamber. A wide variety in kappas is observed for primary biomass burning aerosols in experiment with different types of fuel, which is related to effects of chemical composition. This variety decreases after photochemical ageing, and a secondary material from biomass burning is determined to have a CCN activity comparable to secondary organic aerosols from laboratory studies of monoterpenes. The paper is very well written and presents a well analyzed dataset, dealing with highly complex processes of atmospheric interest. I would recommend publication after a consideration of the minor and technical concerns, listed below.*

We thank the referee for the many helpful suggestions. Our responses are detailed below.

Specific comments:

(2) *In general, I miss either error bars in the figures or an estimate/discussion of the experimental uncertainties in determining kappa, organic mass fractions and f44.*

We have estimated the uncertainties in kappa and added the corresponding error bars to Figure 2.

(3) *P. 7524, l. 10: How much was the degree of dilution, and what were the emissions diluted with (purified air, free of particles, trace gasses, water etc.)?*

The emissions were diluted by a factor of approximately 25 using dried, HEPA- and activated-carbon filtered air. This information has been added to the paper.

(4) *P. 7524, l. 15: Can you characterize the UV lights compared to ambient sunlight?*

The UV bulbs used in this study were GE model 10526 with their emitted spectrum peaking at 368 nm. The ambient spectrum is broader than the spectrum generated from UV bulbs. We have added the bulb model number to the text.

(5) *P. 7524, l. 26: It is described how the emitted aerosols were preconditioned due to their fractal nature, but not what the effects of the treatment are (or at least what they are expected to be), or what the consequences had been if this preconditioning had not been carried out.*

The preconditioning of the aerosols collapses the fractal aggregates making the resulting particles close to spherical. A brief discussion has been added. Additional description of the humidification/drying process is contained in the references.

(6) *Section 3.1: Much of this section describes the practical, experimental operation rather than the theoretical background. You should consider combining it with Section 2.*

The section has been re-titled CCN Analysis and Theory to reflect the description of the offline analysis, which requires a basic understanding of the experimental operation. We do not believe the material in this section fits well in the experimental methods section.

(7) *P. 7526, l. 20: Is the density of 1 g cm^{-3} an arbitrary estimate, or is there a scientific reasoning behind this choice?*

The density of the particles was not calculated in this work. 1 g cm^{-3} allows for easy back of the envelope calculations based upon a given density estimate. For example, a density estimate of 1.3 g cm^{-3} would yield a mass peak of roughly 9 μg m^{-3}. Figure 1 is used to demonstrate the trends during the different experimental periods and is not intended to focus on the SOA mass yield. Details on the mass enhancement analysis can be found in Hennigan et al. (2011).

(8) *P. 7527, l. 8: Was a new nucleation mode clearly observable after lights on? It could be interesting to see examples of size distribution before and after lights were turned on, for example as supplementary material.*

Yes, the nucleation mode was clearly observable after the lights were turned on. The details of these nucleation events have been recently discussed by Hennigan et al. (Geophys. Res. Lett., 39, L09805, doi:10.1029/2012GL050930, 2012). An example of the evolution of the size distribution can be found in Figure 1 of that paper.

(9) *P. 7527, l. 13-15: What does a ratio less than 1 mean (as for example in burn no. 65)?*

A ratio of less than 1 indicates a loss of organic aerosol. This is most likely due to evaporation. This is now explained in the text.

(10) *P. 7527, l. 19: What was the range of kappa in the described regression? I would suggest that you made a figure of the paired kappa sets and added it as supplementary material, possibly with a table showing for which experiments/fuels the differences were most significant. Have you considered if the variation in kappa for different experiments with the same fuel could be due to variations in the dilution system? And have you considered that variation in kappa for different supersaturation could be caused by evaporation in the CCN counter, similar to the effect described by Asa-Awuku et al. (2009)?*

The kappa values ranged from 0.06 to 0.6. The most significant difference was for wire grass and it is discussed in the text. We could not explain the variation in kappa to variations in the dilution system. The variation in kappa was not consistently higher at one supersaturation something that would be expected if evaporation in the CCN counter was causing an experimental bias. We measured the volatility of the particles with a thermodenuder and their evaporation at the CCN counter conditions was negligible.

(11) *P. 7528, l. 12: The abbreviation "Q-AMS" has not been defined, and the purpose and concept of this technique should be introduced in Section 2 (Experimental methods).*

A description of the Q-AMS as well as the aethelometer for black carbon measurements has been added.

(12) *P. 7528, l. 13: The high volume filter measurements should also be described in Section 2, unless these results have already been described in an earlier study – in which case this study should of course be referenced.*

A brief description has been added as well as a reference to McMeeking et al. (2009).

(13) *P. 7528, l. 23: This is the first mention of the study's experimental characterization of POA (excluding the abstract). The concept (i.e. that POA is the organic particulate matter present after filling but before photo-oxidation) should be clearly defined, either here or in an earlier section. Be sure to make it clear, that the primary material has both an organic component (POA) and an inorganic component.*

We have added text in the first paragraph of Section 5 to clarify this point.

(14) *P. 7529, l. 2: You should discuss that some studies have observed more complex dependencies between CCN activity and the degree of oxidation, see for example Massoli et al., (2010); Chang et al. (2010) and Frosch et al. (2011), and also that CCN activity seems less sensitive to oxidation than hygroscopicity (compare with e.g. Tritscher et al. (2011) and Duplissy et al. (2011)).*

The above CCN references have been added together with their corresponding conclusions. Massoli et al. and Chang et al. both observed an increase in CCN activity with oxidation while Frosch et al. did not see such a trend for a large range of O:C. The discussion was not broadened to include HTDMA measurements given the known discrepancies in behavior of a lot of organic aerosol systems in sub-saturated and super-saturated conditions.

(15) *P. 7529, l. 5-8: Although concentrations of aerosol, oxidants and trace gasses are listed in the earlier study by Hennigan et al. (2011), it would be helpful to have a summary of concentrations of the main components available in the present study.*

A consistent numbering system for burns is used in these two papers to allow interested readers to combine information from the two papers without major duplication.

(16) *P. 7530, l. 7ff: You discuss very thoroughly how photo-chemical ageing decreases CCN activity. However, I miss some discussion on the chemical reactions and processes leading to an increase in CCN activity, observed in at least some experiments.*

A sentence has been added in this section to explain this process. The discussion of the SOA at the end of Section 5 will help to reinforce this point. Essentially, the organic component of the primary aerosol can undergo oxidation at the same time as SOA is condensing on the particles to make them more oxidized. The greater oxidation leads to more CCN active particles. This change is far less dramatic than the increased organic content in inorganic dominated particles. "Conversely, while the changes were more subtle for fuels with high organic content in the primary aerosol, the difference between the kappa of the photo-chemically generated organic aerosol and the POA drove a change in the CCN activity. The more oxidized SOA typically led to an increase in CCN activity for the heavily organic primary aerosols."

(17) *P. 7530, l. 21-25: Have you considered that an organic coating on the primary particles might also hinder water uptake, change growth droplets and delay activation, (similar to for example the effect of b-caryophyllene SOA reported by Asa-Awuku et al., 2009)?*

We did not see evidence of delayed growth kinetics in our data for any of the experiments. Therefore, this is probably not a significant issue for this study.

(18) *P. 7531, l. 2: Change "ponderosa pine experiment" to "Burn number 40" (to avoid confusion, since there are two ponderosa pine experiments). Have you any explanation for the high value in burn number 40, or of why you could determine kappa in only 14 of the 18 experiments? And why only 14 experiments?*

Burn 40 has been added as a descriptor to ponderosa pine. The following sentence has been added to address the 4 experiments without SOA CCN activity information. "The nucleation mode SOA was not determined in 4 experiments for three reasons: lack of measurement information at the higher supersaturations, lack of growth into the measurable size window, or insufficient particle concentration late in the experiment to determine the activation diameter." The lack of nucleation in the chamise experiment (burn 59) was also noted. We do not have an explanation for the high value in burn 40.

(19) *P. 7531, l. 12: It would be good if you could show initial organic mass fractions for each experiment, for example in Table 1. It would also be interesting if you discussed the change in CCN activity caused by photo-oxidation in relation to the change in f44, which is probably also seen due to photo-oxidation and chemical ageing.*

The initial organic mass fractions have been added to Table 1. A detailed discussion of the behavior of the f44 in the various burns can be found in Hennigan et al. (2011). Relating these changes to the change in CCN activity is complicated by the presence of the inorganic fraction, the size dependence of the organic/inorganic ratio and the evolution of all of these with time during the experiments.

(20) *P. 7531, l. 12: I am not entirely sure of your meaning: Do you mean that SOA and POA have similar CCN activity/hygroscopicity, or SOA and PA (primary aerosols, meaning both organic and inorganic) have similar CCN activity/hygroscopicity?*

Separating the effects of the primary organic aerosol (POA) from that of the primary aerosol (PA) is challenging because of the size dependence of the organic/inorganic ratio. Fortunately, some experiments had low inorganic content (conversely written as high organic content), which minimized the influence of the inorganics, thus allowing some (rough) comparison of the POA and the SOA. While we are trying to discuss the comparison to POA and SOA these instances are highlighted because the PA is similar to the POA due the low inorganic content. We hope that the example will clarify this. The text has been rewritten as follows to help make this clearer: "In experiments where the primary aerosol had a high initial organic mass fraction (greater than 80 percent), the behavior of the primary aerosol is dominated by the organic aerosol (POA) content. The addition of SOA mass did not produce significant changes to kappa in these experiments suggesting that the hygroscopicity of the POA and SOA were similar (Figures 2 and 7)."

(21) *P. 7531, l. 13-18: The simple mixing rule for determining kappa for a multicomponent system (eq. 3) has been presented in Section 3. Have you considered to actually test it, using for example the kappa listed for example in the black spruce experiment? You already have kappa for the primary material (i.e. before photo-chemical ageing) and kappa for SOA. Using SMPS data (or AMS masses with some assumption regarding density), you could determine relative volumes of primary and secondary aerosols.*

This is a good idea and we have performed the corresponding analysis. Unfortunately, the results are inconclusive. The primary hurdle we were unable to overcome was appropriate measurements of the size-resolved inorganic content. The AMS does not measure all inorganic species and while the average PM composition was measured using filters the composition of particles smaller than 200 nm is uncertain. We have added the following text to explain this point: "This is qualitatively due to the mixing rule (Equation 3) and the fact that inorganic compounds have significantly higher kappa values than organics (Petters and Kreidenweis, 2007). More complete inorganic sizing information would have been required to test the mixing rule quantitatively."

(22) *P. 7532, l. 17-23: The comparison with the studies by Moore et al., Rose et al. and Petters et al. could be expanded to include more details and would fit better in Section 4.*

We have expanded this discussion as suggested and moved it to Section 5.2 which presents the aged aerosol CCN measurements. The following text has been added: "The convergence of kappa with photo-chemical aging in our chamber experiments agrees with ambient measurements of CCN activity in biomass burning plumes where kappa values show much less variability than the primary emissions in this and previous studies (Petters et al., 2009). One study of ambient aerosols in China near an area of active biomass burning found that using a campaign average kappa value (0.3) and measured size distributions predicted CCN number concentrations on average within 20 percent of measurements (Rose et al., 2010). This was despite the measured kappa value range of 0.1-0.5. Additionally, ambient measurements of aerosol plumes transported to Alaska showed a low variance in kappa (0.1-0.3) despite chemical compositions ranging from biomass burning plumes to pristine sea ice boundary layer air (Moore et al., 2011)."

(23) *Table 1: You state that aged kappa was averaged from measurements from the last 30 minutes of data (footnote c). Was there any temporal variation? And did all experiments last the same number of hours, or could different exposures to oxidants explain some of the experimental variations discussed in the paper?*

There was little temporal variation in the initial, fresh, primary aerosol CCN activity. Once the lights were turned on to initiate photochemical reactions SOA was formed which caused a change in the CCN activity. Figure 5 shows examples of some fuels that seemed to continue to show changes in activity. Many fuels, however, did not seem to be changing in activity within the measurement uncertainty. We wanted to compare the most oxidized state within our experimental limitations to estimate how similar the fuels would be with extended atmospheric processing. 30 minutes is a long enough period of time to average the data to have a robust hygroscopicity estimate. The experiments were carried out for a similar amount of time with the protocol allowing 90 minutes for characterization of the primary aerosol and then 3-4.5 hours of analysis of the photochemical aging within the limitations of smog chamber volume and particle concentrations (signal). The oxidant concentrations, experiment length, chamber temperature, etc. are all factors which may explain some of the experimental variations discussed in the paper.

(24) *Figure 3: I wish I could see which types of fuel resulted in the various organic mass fraction – perhaps this information could be included in the figure, or initial organic mass fractions could be listed in Table 1?*

The initial organic mass fractions have been added to Table 1 for reference.

(25) *Figure 4: SS (in the label on the y-axis) has not yet been defined (supersaturation was defined as S in eg. 1). Make clear that "primary aerosol" is not the same as POA. Why does the figure only contain data from supersaturation 0.26 percent?*

SS has been changed to S to indicate supersaturation consistently throughout the paper. We have attempted to reinforce the inherently confusing primary aerosol versus primary organic aerosol (a part of the whole) in the text. The results are quite similar for the different supersaturations, so only the results at 0.26 percent was shown to simplify the figure.

(26) *Figure 5: Throughout the paper, you mainly describe kappa. Why do you suddenly choose to display activation diameter on the y-axis, and not kappa? And does the shaded area represent an estimate of the experimental error? From the data, it looks like uncertainties increase with time – which one would also expect from the decreasing particle concentration caused by wall losses. However, this is not reflected by the shaded areas.*

Figure 5 is used to describe changes during the experiment. Since activation diameter is the measured variable we feel that this is the most appropriate value to plot. Kappa is a very useful parameterization of the data and has immense value for comparing across CCN studies, so most of the analysis discussion centers around kappa. The shaded regions are provided to guide the eye and are not an estimate of experimental error.

(27) *Figure 6: Consider giving all three subplots the same y-axis (from 0 to 1), which would make them easier to compare. Change "kappa" in the x-axis label to "k"*

We are now using the same y-axis in all three plots. The x-axis has also been revised to the symbol.

(28) *Figure 7: As for Figure 4, SS (in the label on the y-axis) has not yet been defined* *(supersaturation was defined as S in eg. 1). Consider centering y-axis around 0 and marking 0 with a horizontal line. Is "Fresh POA mass fraction" identical to the "initial organic mass fraction", which is mentioned in Section 4? If so, you should use the same phrase – or alternatively describe the differences. Also, it could be very good if you discussed for which experiments/fuel types you observe the largest change in kappa.*

The y-axis has been updated to the consistent S rather than SS for supersaturation. Yes, fresh POA mass fraction is identical to organic mass fraction and the figure has been altered to reflect this. The text now reads "The most significant changes to kappa were observed in experiments with high initial inorganic mass fractions (Figure 7). " Table 1 now includes the initial organic mass fractions (and thus the inorganic mass fractions can be inferred).

Technical comments:

(29) *You alternate between writing "-values" (e.g. P. 7528, l. 8) and " values" (e.g. P. 7522, l. 12) – please make sure you are consistent.*

Kappa values has been adopted throughout the paper as opposed to kappa-values.

(30) *P. 7525, l. 13: Change "is" to "was".*

Tense shift corrected as suggested.

(31) *P. 7527, l. 20: Consider changing "Values range . . . = 0.6" to "kappa values ranged from 0.06 to 0.6).*

The line now reads, "kappa values ranged from 0.06 to 0.6 as shown in blue bars in Figure 2 for 0.26 and 0.43 percent supersaturations."

(32) *P. 7528, l. 15-18: It is confusing that the sentence starts in the present tense,*

"There is a clear relationship", and ends in the past "mass fractions increased . . . primary aerosol decreased".

The tense shift has been revised to read "There is a clear relationship between these two parameters: as the organic mass fraction increases, the kappa value of the primary aerosol decreases, consistent with the results of Petters et al. (2009). "

(33) *P. 7532, l. 11: Change to: "These new particles nucleated and grew due to. . ."*

The addition has been made.

References

Asa-Awuku, A., Engelhart, G. J., Lee, B. H., Pandis, S. N., and Nenes, A.: Relating CCN activity, volatility, and droplet growth kinetics of beta-caryophyllene secondary organic aerosol, Atmos. Chem. Phys., 9, 795-812, doi: 10.5194/acp-9-795-2009, 2009.

Chang, R. Y.-W., Slowik, J. G., Shantz, N. C., Vlasenko, A., Liggio, J., Sjostedt, S. J., Leaitch, W. R., and Abbatt, J. P. D.: The hygroscopicity parameter of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation. Atmos. Chem. Phys., 10, 5047-5064, doi: 10.5194/acp-10-5047-2010, 2010.

Duplissy, J., DeCarlo, P. F., Dommen, J., Alfarra, M. R., Metzger, A., Barmpadimos, I., Prevot, A. S. H., Weingartner, E., Tritscher, T., Gysel, M., Aiken, A. C., Jimenez, J. L., Canagaratna, M. R., Worsnop, D. R., Collins, D. R., Tomlinson, J., and Baltensperger, U.: Relating hygroscopicity and composition of organic aerosol particulate matter. Atmos. Chem. Phys., 11, 1155–1165, doi: 10.5194/acp-11-1155-2011, 2011.

Frosch, M., Bilde, M., DeCarlo, P., Jurányi, Z., Tritscher, T., Dommen, J., Donahue, N. M., Gysel, M., Weingartner, E., Baltensperger, U.: Relating CCN activity and oxidation level of a-pinene secondary organic aerosol, Geophys. Res., 116, D22212, doi: 10.1029/2011JD016401, 2011.

Massoli, P., Lambe, A. T., Ahern, A. T., Williams, L. R., Ehn, M., Mikkilä, J., Canagaratna, M. R., Brune, W. H., Onasch, T. B., Jayne, J. T., Petäjä, T., Kulmala, M., Laaksonen, A., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles. Geophys. Res. Lett., 37, L24801, doi: 10.1029/2010GL045258, 2010.

Tritscher, T., Dommen, J., DeCarlo, P. F., Barmet, P. B., Praplan, A. P., Weingartner, E., Gysel, M., Prévôt, A. S. H., Riipinen, I., Donahue, N. M., and Baltensperger U.: Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber. Atmos. Chem. Phys. Discuss., 11, 7423-7467, doi: 10.5194/acpd-11-7423-2011, 2011. Interactive comment on Atmos. Chem. Phys. Discuss., 12, 7521, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 7521, 2012.