Interactive comment on "CCN activity of organic aerosols observed downwind of urban emissions during CARES" by F. Mei et al.

Anonymous Referee #2
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General Comments
This paper presents an analysis of the CCN activity of organic aerosols during the CARES field study in 2010. The paper is not ground-breaking, but it does include some interesting findings concerning the relative value of f44 versus O:C ratio as a predictor of the hygroscopicity of the organic aerosol component (section 5.4). This core finding is worthy of publication, but in its current form the manuscript has major issues that must be addressed before publication.

One major concern with this present manuscript is its striking similarity with a recently published paper in JGR-Atmospheres involving some of the same authors (Mei et al., 2013). There are several paragraph-length passages that are virtually identical between the two papers, including (but not limited to) the first paragraph of section 1, all of sections 2.2 and 2.3, all of section 4, and parts of section 5.3. Figure 1 in this paper is identical to Figure 1 in the JGR paper, and Figure 3 here is functionally identical to Figure 4 in the JGR paper (i.e., identical ideas are communicated with different data). Figures 2, 4, and 5 in the ACPD paper also have very close analogues in the earlier JGR paper. The supplemental information is also virtually identical to material in the JGR paper and its supplement. It should be noted that some but not all of the authors are common to the two papers, and that the copyright to the JGR paper is held by the American Geophysical Union.

Some similarity between the ACPD and JGR papers might be expected, since they present similar analyses with similar instrumentation from two field studies closely spaced in time. In this case though, the documents overlap to an unacceptable degree. The separate scientific contributions of the two papers must be distinguished more clearly to merit separate publication. Given that the JGR paper has already passed peer review and is available to the public, sections 2 and 4 of this paper should be greatly reduced and readers should instead be referred to the appropriate sections of the existing paper. The supplemental material should be removed completely, as well as Figures 1 and 3. Section 1 should probably be rewritten to reduce redundancy and avoid copyright complications.

In addition to the above major critique, it also seems that the analysis in Section 3 (including Figure 2) has relatively limited value to the overall goals of the paper. The motivation to include the section seems to be to provide a foundation for the fuller data analysis later in the paper- an overview, as the section title suggests. If that is the primary intended goal then there should also be some discussion of the day-to-day variability in addition to the diurnal variation. Either time series plots or error bars on the mass concentration and size distribution plots would be good additions.

We thank the reviewer for the thoughtful and constructive comments. We agree that as the earlier paper (Mei et al., 2013) is now published, we should remove the description of analysis

methods and reference the paper when appropriate. We have made changes to the Section 1, especially the 1st paragraph. We also rewrote Sections 2.2 and 2.3, greatly reduced their lengths, and now the two sections are combined. Sections 4 and 5.3 were rewritten and greatly reduced, descriptions similarly available in Mei et al., (2013) are removed and referenced. Descriptions of instrument operation conditions (in Sections 2.2 and 2.3) and assumptions for the analysis (in Section 4) are kept. Figures 1, 3, and 4 are also removed following the reviewer's suggestion.

The section on "Uncertainty in derived κ_{org}" in removed from Supplementary Information. The section on "Derivation of particle hygroscopicity and mixing state" is kept in SI as the approach is somewhat different from that in Mei et al. (2013). During CalNex-LA, the dispersion in S_c of size selected particles was dominated by the heterogeneity in particle composition, therefore the contribution due to the width of the DMA transfer function was neglected. This contribution needs to be taken into consideration as the composition of size selected particles was much more homogeneous during CARES.

Section 3 is included because some of the main assumptions about particle composition employed in our analysis are based on the data shown in Figure 2. The reference to the figure is now included where the assumptions are described. We also changed the title of the section to "Diurnal variation of aerosol properties", which better describes the content of this section.

Specific comments

Page 9357, Lines 20-23: 'Essentially identical' is too broad here. Presumably the authors of the later studies saw their work as improvements over what existed previously are these improvements trivial? If you are making that assertion, then it must be supported.

These parameterizations are certainly not completely identical. We describe in the text that they are "essentially equivalent". In Petters and Kreidenweis (2007), the authors also describe that their parameterization (kappa) "is equivalent" to that described in Hudson and Da (1996) when κ >0.2 and S_c<1%, which are typical for atmospheric aerosols.

Page 9358, Lines 21-22: This line asserts that measurements of kappa_org for ambient organics are scarce, and no previous studies are cited. There are several previous studies looked at this same parameter for ambient conditions, and these should be mentioned. A very quick search revealed recent papers by Lathem et al. (2013) and Moore et al. (2011). The lack of citations combined with the phrasing of the sentence may lead to the impression that the present analysis is more isolated than it is.

The sentence is rephrased and the references are included.

Page 9361, Lines 6-16. The text suggests that the CCN counter was stepped through the six temperature gradients in order, so that each supersaturation was measured every four hours. However, Figure S1(b) suggests a sawtooth pattern. Under the pattern suggested by Figure S1, the 4.5 C temperature gradient would only be measured once every eight hours (approximately).

Please clarify this, and if the latter, please add text discussing the implications of this approach in your analysis.

As the reviewer correctly pointed out, the temperature gradient was stepped through using a "sawtooth" pattern. This provided measurements at 6 different temperature gradients every four hours. Obviously, due to the sawtooth pattern, in the first four hours, the temperature gradient of the CCN counter stepped up from 4.5 C to 12 C, and in the second four hours, it stepped down from 12 C to 4.5 C. The purpose of this "sawtooth" pattern was to minimize the change in temperature gradient at each step, and therefore reduce the wait time required for CCN counter to reach equilibrium between steps. This is now clarified in the text. Since our analysis was focused on periods with minimum variation in particle composition, whether the temperature gradient was stepped up or down should have negligible impact on the results.

Page 9364, Lines13-17: Isn't this an estimation rather than a derived solution? Why would a derived property be valid only for kappa>0.1? What is the uncertainty associated with using equation (2) rather than the analytical solution?

Yes, Eq. (2) is an approximation. For kappa>0.1 and S_c less than 0.5%, the uncertainty associated with using equation (2) is less than 2% (relative).

Page 9365, Lines 16-21: What advantage is gained by using two different methods to fit the curve describing the characteristic critical supersaturation? Neither this paper nor the earlier paper in JGR indicates why the second lognormal fit is sometimes superior, or whether the difference is sufficient to justify the added effort.

We found that lognormal distribution fits the data better when the critical supersaturation distribution of size-selected particles is relatively broad. This simply suggests that the distribution of critical supersaturation, or particle hygroscopicity, is better described by a lognormal function. One motivation to fit the data with two different functions is to make sure that the results are not sensitive to the fitting methods (and they are not for the CARES data). In addition, it is quite straightforward to fit the data with two different functions, and the added effort was very minimal.

Page 9365, Lines 24-27: The derivations of sigma_kappa and kappa_bar are not provided in the Supplement to the ACPD paper. The readers should be referred here to the JGR paper.
Thanks for pointing this out. We have modified the sentences and referenced the JGR paper here.

Page 9372, Lines 7-9: What is difference between a~100% increase and a factor of 2 increase?
This was a typo. It should be "a factor of 3 increase". This is now corrected.

Page 9372, Lines 25-29: This is an interesting point.
Thank you.

Page 9373, Lines 5-14: Are these periods evenly distributed through the study period.

Are they distributed evenly diurnally? What fraction of the total data set do they represent? Knowing this would better place the results that follow in the context of the overall conditions at the site.
Those periods are approximately evenly distributed diurnally. The total time of these periods is ~9 days, representing ~ 50% of the total sampling time (~18 days). We clarified this in the manuscript.

Page 9374, Line 21 – Page 9375, Line 7: The approach for relating size-resolved kappa_org to size-resolved O:C ratio seems somewhat faulty. Size-resolved O:C as described here is not a measured value, but rather a parameterized value based on size-resolved f44 and the bulk f44/O:C ratio. This approach implies an assumption the f44/O:C ratio is size-independent. This seems to be an ambitious assumption given that the point of the analysis is to evaluate how f44 and O:C ratio might vary relative to each other.

As discussed in Setyan et al. (2012), two distinct oxygenated organic aerosol (OOA) factors were identified during this study, including a more-oxidized OOA (f44 = 0.11; O:C = 0.54) and a less-oxidized OOA (f44 = 0.13; O:C = 0.42). These two OOA factors together account for almost all of the variances in O:C and f44. While it is true that the two OOA types have fairly different f44/O:C ratios, they appear to have similar size distributions, which can be deduced based on the similar size distributions of m/z 43 and 44 (see Fig. 6c in [Setyan et al., 2012]). As a result, it is reasonable to assume the f44/O:C ratios are independent of particle sizes. We have revised the text accordingly to clarify this point.

Minor Revisions
Page 9357, Line 2: 'Also' should be deleted.
Done.

Page 9357, Line 12: This sentence should be attached either to the preceding paragraph or the following one.
Done.

Page 9358, Line 1: 'Is' should read 'can be'. This sentence is also slightly awkwardly worded.
Changed as suggested.

Page 9358, Lines 16-17: Why no references after the clause about SOA?
The references were listed at the end of the sentence. We now moved the references to after "SOA".

Page 9358, Line 24: Needs a space after the first kappa.
This was an error during type setting. Thanks for pointing this out.

Page 9359, Line 21: 'Site' should be plural.
Done.

Page 9360, Line 17: 'Spectrum' does not need to be capitalized here.
Updated

Page 9361, Line 5: ‘CPC3771’ should just read ‘CPC’.
Done.

Page 9364, Line 16: Delete ‘and was’.
Done.

Page 9367, Line 18: ‘Combing’ should be ‘combining’, probably.
Corrected.

Figure 5 caption: ‘Expect for the outlines’ should read ‘except for the outliers’.
Corrected.

Supplement, Figure S1: The resolution on this figure is poor. Can it be improved?
Done.

Supplement, Page 1, Line 9: This is listed as Mei et al., 2013 in the main paper.
Updated.

References

Lathem, T. L., Beyersdorf, A. J., Thornhill, K. L., Winstead, E. L., Cubison, M. J., Hecobian, A., Jimenez, J. L., Weber, R. J., Anderson, B. E. and Nenes, A.: Analysis of CCN activity of Arctic aerosol and Canadian biomass burning during summer 2008, Atmospheric Chem. Phys., 13(5), 2735–2756, doi:10.5194/acp-13-2735-2013, 2013.

Moore, R. H., Bahreini, R., Brock, C. A., Froyd, K. D., Cozic, J., Holloway, J. S., Middlebrook, A. M., Murphy, D. M. and Nenes, A.: Hygroscopicity and composition of Alaskan Arctic CCN during April 2008, Atmospheric Chem. Phys., 11(22), 11807–11825, doi:10.5194/acp-11-11807-2011, 2011

Hudson, J. G., and Da, X. Y.: Volatility and size of cloud condensation nuclei, J. Geophys. Res., 101, 4435-4442, 1996.

Mei, F., Hayes, P. L., Ortega, A. M., Taylor, J. W., Allan, J. D., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Jimenez, J. L., and Wang, J.: Droplet activation properties of organic aerosols observed at an urban site during CalNex-LA, J. Geophys. Res., 118, 2903-2917 10.1002/jgrd.50285, 2013.

Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, 2007.

Setyan, A., Q. Zhang, M. Merkel, W. B. Knighton, Y. Sun, C. Song, J. E. Shilling, T. B. Onasch, S. C. Herndon, D. R. Worsnop, J. D. Fast, R. A. Zaveri, L. K. Berg, A. Wiedensohler, B. A.

Flowers, M. K. Dubey, and R. Subramanian (2012), Characterization of submicron particles influenced by mixed biogenic and anthropogenic emissions using high-resolution aerosol mass spectrometry: results from CARES, Atmospheric Chemistry & Physics, 12, 8131-8156.