Note: this manuscript was reviewered by three referees, whom we have referred to below as Reviewer 1, Reviewer 2, and Reviewer 3 based on dates that refereee comments were uploaded to ACPD. Our Final Response contains responses to twenty-five comments from Reviewer 1, fifteen comments from Reviewer 2, and three comments from Reviewer 3. In some cases, individual comments addressed several issues, which we annotated by using letters (a), (b), (c), etc. within the comment.

Reviewer 1 Comments

Comment 1. The f44 vs. f43 results presented in several figures clearly suggest that unit-resolution f44 and f43 data cannot be used to reliably derive elemental ratios of the organic aerosol component. High-resolution MS measurements are required to separate the isobars at these two nominal m/z values and resolve the contributions from less and more oxidized ion fragments (e.g. C3H7+ vs. C2H3O+). This deserves further discussion and reference to previous reports that have evaluated the reliability of using unit-mass AMS measurements to derive elemental ratios. On a related note, it was not discussed which experiments used the C-TOF-AMS instead of the HR-TOF-AMS. As only the HR measurements appear to be reliable for determining elemental ratios, due to the overlapping ion fragments at m/z 43 and 44, this is an important issue that needs addressing. The C-TOF measurements are not clearly discussed in the text or indicated in the Tables or Figures. Were elemental ratios derived from these measurements? If so how do they compare with the HR measurements? The elemental ratios from C-TOF measurements would seem quite unreliable based on the data presented here.

Response. The issues raised in this comment all appear to be directly connected to the fact that we were not initially clear on which data was obtained with the HR-AMS or C-AMS. We now state specific uses of these two spectrometers in the Experimental section of the paper, as well as which specific instrument was used when the results are presented in the text and Figures. An additional question raised by the reviewer concerns how f44, f43, H/C, and O/C ratios were derived.

Only the HR-ToF-AMS allows for direct determination of the O/C and H/C ratios. The data presented in Fig. 6, which shows H/C ratio versus O/C ratio, were all obtained with the HR-ToF-AMS. The data in Fig. 7, which shows kappa versus O/C ratio, were obtained with both instruments. For c-ToF-AMS measurements shown in Fig. 7, O/C ratios were derived from cToF-AMS f44 measurements using individual f44-to-O/C parameterizations for each system. These parameterizations were derived from HR-ToF-AMS measurements and were presented in the Supplement (Fig. S10a). We agree that the relationship between f43 and H/C ratio is more complex, and as a result we did not not use unit-resolution data to derive H/C ratios shown in Fig. 6.

All f44 and f43 data were obtained with either the c-ToF-AMS or the HR-ToF-AMS. Both of these instruments provide unit mass resolution or better—the c-ToF-AMS and HR-ToF-AMS used in these studies have mass resolutions of 800 and 3000 respectively. To answer the reviewer's concern directly, both the c-ToF-AMS and HR-ToF-AMS provide clearly resolvable signal at m/z = 43 and m/z = 44. If multiple species contribute to m/z =

43 and m/z = 44, only the HR-ToF-AMS can reliably resolve them.

In Fig. 3, we showed high-resolution measurements for those systems where m/z = 43 consisted of appreciable C3H7+ in addition to C2H3O+ (C10, C17, diesel fuel SOA). A result we did not present earlier, but which is now included in the revised manuscript, is high-resolution measurements of m/z = 44 in which ion contributions from C2H4O+ and CO2+ are resolved in SOA generated from C10, C17, and diesel fuel. We have revised Figure 3 by coloring the markers by the fraction $CO_2^+/(CO_2^+ + C_2H_4O^+)$. We have revised the text as follows (changes bolded):

p. 13626, line 21: “…High-resolution AMS measurements, which facilitate deconvolution of the total f_{43} signal into separate fractions of organic signal consisting of C_3H_{7+} (f_{C3H7+}) and $C_2H_3O_+$ (f_{C2H3O+}) ion fragments, revealed that the f_{43} curvature arises from the increase and subsequent decrease in f_{C2H3O+} with oxidation. **This curvature in f_{43} was observed for SOA generated from gas-phase alkanes, biogenic terpenoids, mesitylene, and naphthalene. Curvature in f44-f43 space suggests** a progression from formation of earlier-generation oxidation products containing carbonyl functional groups (**higher f_{C2H3O+}**) towards later-generation oxidation products containing acidic functional groups (**higher f_{44}, lower f_{C2H3O+}). These trends will be discussed further in Section 3.2. The f_{43} curvature observed in the present work has also been observed in other studies (Kroll et al., 2009; Ng et al., 2010; Chhabra et al., 2011; Lee et al., 2011). However, SOA/OPOA produced from glyoxal, lubricating oil, BES, toluene, and m-xylene did not exhibit the clear f_{43} curvature observed in Fig. S3. For each of these systems, there are plausible explanations for the absence of observable f_{43} curvature. However, we cannot support these explanations without introducing significant speculation to the discussion.**

For SOA generated from the oxidation of gas-phase alkanes **and longifolene**, both C_3H_{7+} and $C_2H_3O_+$ ions contribute appreciable **(>10%)** fractions **of** the total m/z = 43 signal at low OH exposures. **In these systems, f_{C3H7+} increases in the following sequence: longifolene < diesel fuel < n-C10 < n-C17. This trend suggests a correlation between carbon chain length of the precursor and f_{C3H7+} of the SOA**. If $C_2H_3O_+$ contributions to f_{43} are isolated in these systems, the extent of f_{43} curvature increases, as shown in Fig. 3 for SOA generated in the PAM from n-C_{10}, n-C_{17}, and diesel fuel. **In addition, for SOA generated from n-C_{10}, n-C_{17}, and diesel fuel, both CO_2^+ and $C_2H_4O^+$ ions contribute appreciable fractions of the m/z = 44 signal at low OH exposures, as indicated by the Fig. 3 colorbar. To our knowledge, in addition to SOA generated from isoprene at low OH exposures in this work and in previous studies (Ng et al., 2010), these represent the only measurements of laboratory SOA containing significant $C_2H_4O^+$ contributions to m/z = 44.** ”

Comment 2. The manuscript offers zero discussion of mass spectral features other than f43 and f44 to get insights into the products produced and their mechanisms. Other groups have used similar methods to learn a great deal about the products that form during oxidation of OA [e.g. George et al., 2008; Greishop et al., 2009; Tobias et al., 2000]. It is disappointing to see so little effort given here in this manuscript. Surely the HR-AMS can provide more chemical insight than just elemental ratios and PMF factor comparison? I can understand the desire to look for general trends when comparing so many different systems, but the analysis presented here is overly simplistic.

Response. The reviewer suggests that an article of the type we are presenting make an effort to discuss mass spectral features, as these are important in our understanding of SOA chemistry. We certainly agree with this premise, and we believe that we have done so. Our analysis is not restricted only to the f43 and f44 aspects of the spectra [as is suggested by the reviewer]. In fact, in addition to discussing the O/C and H/C ratios, in Fig. 5 we present correlations with PMF factors that use the entire mass spectra up to m/z = 300.

The reviewer cites 3 examples of papers that he/she feels is appropriate discussion of mass spectral features:

Grieshop et al. (ACP, 2009), who investigate the photochemical oxidation of wood smoke POA. Their mass spectral analysis includes:

(1) mass spectral comparison of wood smoke POA and aged wood smoke POA
(2) evolution of mass spectral tracers for wood smoke POA (e.g. m/z = 60, 73, 137, 167) and aged wood smoke POA (e.g. 43, 44) as a function of aging
(3) thermograms of mass spectral tracers in wood smoke POA and aged wood smoke POA
(4) correlations of wood smoke POA with ambient PMF factors (e.g. biomass burning organic aerosol, OOA, etc.)

George et al. (GRL, 2008), who studied the oxidation of ambient organic aerosol in a flow tube reactor. Their mass spectral analysis includes:

(1) mass spectral comparison of unoxidized and oxidized ambient organic aerosol, with specific annotations for alkane, alkene, aromatic, etc. peaks in the mass spectra
(2) evolution of mass spectral tracers for HOA (m/z = 57) and OOA (m/z = 44) as a function of aging

Tobias et al. (ES&T, 2000), who studied SOA formed from tetradecene ozonolysis at dry and humid conditions. Their mass spectral analysis includes:

(1) thermograms of tetradecene SOA products
(2) mass spectra of organic peroxides and secondary ozonides in the SOA

We have done a very similar analysis to that presented in these three papers. In our analysis, we discuss the evolution of m/z = 43 and m/z = 44 as a function of aging (Figs. 2,3,4,S2,S3) which we argue are the most relevant mass spectral tracers in this work. In this regard, we parallel the analyses of Grieshop et al. (#2) and George et al. (#2). Fig S2 also shows results from thermally denuded SOA; our analysis is not as detailed as that of Grieshop et al. (#3) or Tobias et al. (#1) because explicit characterization of SOA volatility is not a focus of this paper. Like Grieshop et al. (#4), we compared mass spectral features of PAM-generated SOA with PMF factors. We focus less on tracers for HOA/POA than Grieshop et al. (#1) and George et al. (#1). Also, we do not provide an explicit comparison “unoxidized” and “oxidized” organics.

We decided not to put the full analysis in the text because essentially the same conclusions are drawn whether one examines the complete mass spectra or focuses the discussion on m/z = 43, 44: at low-oxidation conditions, different precursors generate

SOA with complex, unique AMS spectra (larger range of f43). As the SOA is continually aged, the complexity and differences of AMS spectra of SOA generated from different precursors decrease significantly (smaller range of f43). A full treatment of this analysis in the text would result in an addition of about 20 mass spectra and would make the manuscript unnecessarily complex. However, the reviewer's comment convinced us to place this data into the Supplement and to make the following statement in the manuscript (on p. 13626; additions in the text are in bold script):

"**As shown in Figs. S6 – S8 of the Supplement, the wide range of precursor structures is captured by the complexity of AMS spectra for several types of SOA generated at low OH exposures.** The f43 spread is particularly wide for SOA generated […] reaching a maximum with mesitylene. **The range of measured f43, along with the overall complexity of the AMS spectra (Figs. S6 – S8), decreases with increasing OH exposure**."

Figures S6, S7, and S8 and 3 paragraphs of accompanying discussion were added to the Supplement. These figures present representative AMS spectra for SOA generated from alkane, terpenoid, and aromatic precursors at low and high OH exposures in the PAM.

Comment 3. It is also not clear what the lower limit of measurable kappa was here. This is determined by the dry particle diameters selected, and the CCN supersaturation range scanned. I would like to see data presented from the unoxidized POA precursors (elemental ratios, and an upper limit to their presumably small kappa values) to see if this data extends the trends reported here, prior to oxidation, or not. There is also no mention of the aerosol size distribution produced during these experiments, or what diameters were selected for CCN analysis.

Response. This is now taken into account. In Section 2.3 of the original manuscript, we specified the BES and lubricating oil particle diameters (145nm and 200nm). In Section 2.4, we added information about the diameters selected for CCN analysis. We added markers representing the upper limits of unoxidized POA kappa-values to Figure 7.

Given the wide range of diameters selected for CCN analysis, the range of lower-limit kappas was also large. We added two figures and discussion to the Supplement that shows: (1) lower-limit kappa-values as a function of diameter over the range of selected diameters (2) measured kappa versus O/C ratio for all SOA/OPOA measurements, (3) corresponding lower limit of kappa versus O/C ratio for SOA/OPOA measurements, (4) upper limit of kappa versus O/C ratio for unoxidized POA. Kappa-values were recalculated using the spreadsheet tool recommended by the reviewer (see Comment 7).

We added a two-panel figure to the Supplement (now Fig. S2) that shows representative SMPS volume distributions for SOA generated from a-pinene and naphthalene. Each figure shows volume distributions at "low" (1.6E11 molec/cm3*s), "medium" (6.7E11 molec/cm3*s), and high (2.1E12 molec/cm3*s) OH exposures in the PAM.

In addition, we have added the following statements to the text:

p. 13623, line 4: "**Representative size distributions of SOA generated from α-pinene and naphthalene are shown in Fig. S2 of the Supplement.**"

P. 13624, line 12: "**Selected dry mobility diameters ranged from 45 to 150 nm for SOA and from 145 to 200 nm for OPOA. The corresponding lower limits for κ-values ranged from 0.061 (45 nm) to $1x10^{-6}$ (200 nm). Lower limits for all κ-values are shown in Fig. S3 and S4 of the Supplement, along with upper limits for kappa-values of unoxidized POA.**"

Comment 4. Pg 13620, line 5: Should also include references to Jon Abbatt's work here.

Response. We added references to the George et al., Atmos. Environ., 2009 and George et al., ACP, 2010 studies as recommended by the reviewer.

Comment 5. Pg 13623, line 8: The activated carbon denuder would also alter gas-particle partitioning of OA components. This should be discussed later in the paper, along with the important roles that partitioning play in these experiments. These are not adequately discussed at present. It is not clear what mechanisms the authors believe dominate the production of SOA/OPOA. Gas-phase oxidation followed by nucleation/condensation? Dynamic evaporation-oxidation-condensation cycles? Heterogeneous oxidation?

Response. We revised the text in Section 2.3 to take into account the reviewer's comment. The revised text is as follows (**changes bolded**):

p. 13622, lines 19-21: "SOA was generated via gas-phase oxidation of VOCs and IVOCs **followed by homogenous nucleation**. **Subsequent heterogenous oxidation of the SOA is possible, but is likely too slow to be of significance relative to much faster oxidation in the gas phase (Lambe et al., 2009).** OPOA was generated via heterogenous oxidation of condensed-phase precursors."

p. 13623, line 9: "…that removed gas-phase and **volatile condensed-phase species** before the particles entered into the PAM. **The purpose of the denuder was to maximize the role of heterogenous oxidation. The influence of the denuder on gas-particle partitioning was minimal for BES because of its low volatility, but was significant for lubricating oil: about 60% of the lubricating oil particle mass was removed from denuding. As a result, the influence of evaporation-oxidation-recondensation cycling of OPOA, which has been observed in previous studies (Miracolo et al., 2010), was minimized in the lubricating oil experiments".**

We have added the following citations to the list of references:

Lambe, A. T., Miracolo, M. A., Hennigan, C. J., Robinson, A. L., and Donahue, N. M.: Effective Rate Constants and Uptake Coefficients for the Reactions of Organic Molecular Markers (n-Alkanes, Hopanes, and Steranes) in Motor Oil and Diesel Primary Organic Aerosols with Hydroxyl Radicals, Environ Sci. Technol., 43, 8794-8800, 2009.

Miracolo, M. A., Presto, A. A., Lambe, A. T., Hennigan, C. J., Donahue, N. M., Kroll, J. H., Worsnop, D. R., and Robinson, A. L.: Photo-oxidation of low-volatility organics found in motor vehicle emissions: Production and chemical evolution of organic aerosol mass, Environ. Sci. Technol., 44, 1638-1643, 2010.

Comment 6. Pg 13624, line 5: Should make it clear that particle size was held constant while supersaturation was stepped through. What size particles were selected by the DMA for CCN analysis? The size distributions of the SOA, POA, and OPOA are never mentioned, what were they?

Response. We added the following to the manuscript on page 13624, line 5 (changes bolded):

"CCN activation curves were generated **by holding the particle size constant** while systematically varying the CCNC column temperature gradient to obtain controlled water vapor supersaturation between 0.1-1.5% or until 100% activation was reached, whichever occurred first.

On page 13623, line 9: "**BES and lubricating oil particle diameters were 145 nm and 200 nm respectively.**"

Also, please see our reply to Comment 3 where we state:

p. 13623, line 4: **"Representative size distributions of SOA generated from α-pinene and naphthalene are shown in Fig. S2 of the Supplement."**

Comment 7. Pg 13624, Eq 1: This equation used to derive kappa is an approximate expression, as stated in Petters & Kreidenweis (2007): "If kappa >0.2, then kappa alternatively can be calculated from paired sc –Dd values from the following approximate expression: [your Eq. 1]". As you derive kappa values that are typically significantly less than 0.2 this approximation is not valid. Kappa values should be re-calculated from your Sc – Dd data pairs. There are tools freely available for this available here: http://www4.ncsu.edu/ ~mdpetter/code.html, including a spreadsheet that can be used to calculate kappa easily.

Response. We recalculated kappa values using the code referenced by the reviewer. In fact, we found that the analytical expression used in the text (Equation 1, p. 13624) agrees with the web site-referenced calculation to within about 5% for kappa > 0.01. The results plotted in Fig. 7 are not noticeably altered. For kappa < 0.01, the web site-referenced calculation resulted in kappa-values 2-4 times lower than the analytical equation that was originally used. Those values have also been updated accordingly in Fig. 7.

In the manuscript itself, the analytical expression has been replaced with the equation provided on the web site, with the following added text on page 13624, lines 7-12 (changes bolded):

"The CCN hygroscopicity parameter, kappa, was calculated using Eq. (1) (Petters and

Kreidenweis, 2007) **which was solved using a κ-lookup table (http://www4.ncsu.edu/~mdpetter/code.html):**

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} exp\left(\frac{4\sigma_w M_w}{RT\rho_w}\right)$$

Here *S* is the saturation ratio over a droplet, *D* is the cloud droplet diameter, D_d is the dry diameter of the size-selected particles, *R* is the universal gas constant, *T* is the sample temperature, […] **The critical supersaturation s_c, which is determined from CCNC measurements, corresponds to the maximum value in the κ-Kohler curve; note that $s_c = S - 1$.”**

Comment 8. Pg 13625, line 29: I was surprised that the OH exposure was only varied by a factor of 20. In other work using the PAM the OH exposure has been one order of magnitude lower, ~1E10 molecules/cc. Why was a lower OH exposure not also tested here?

Response. From our perspective, the most interesting and atmospherically relevant results are obtained for OH exposures greater than ~1E11 molec/cm3*s, or about 1 day of aging at typical ambient OH levels. To attain higher OH exposures (up to 2E12 molec/cm3*s) than in previous studies, we used higher O3 levels and higher relative humidities in the PAM. This gave us the factor-of-20 range in OH exposure at a specific O3 level and relative humidity. To attain lower OH exposures would have required an alteration of several operating conditions, including varying the O3 and relative humidity. Therefore, working in the OH exposure range presented in the manuscript provided the most self-consistent set of results.

Comment 9. Pg 13626, line 2: You plot oxalic acid as an endpoint, do you detect ion fragments (Larger than m/z 44) indicative of oxalic acid or other carboxylic acids?

Response. Yes. For m/z > 44, the AMS spectrum of pure oxalic acid has prominent ion fragments at m/z = 45 (CHO_2^+) and at m/z = 56 ($C_2O_2^+$) that were readily detected. Both of these fragments were commonly present in highly oxidized SOA generated in the PAM during this study. The parent ion at m/z = 90 ($C_2H_2O_4^+$), which has a relative abundance of ~0.0002 as measured by the HR-ToF-AMS used in this work, was below detection limits with our AMS except for when we sampled very high concentrations of pure oxalic acid particles.

As stated in the text (p. 13625, line 16), we used oxalic acid as an oxidation endpoint marker because an analysis of atmospheric aerosols by several techniques has shown that it is “often the most abundant dicarboxylic acid in ambient OOA (Sorooshian et al., 2006; Takegawa et al., 2007), and represents the highest oxidation state of atmospheric organics other than CO_2 (Kroll et al., 2011).”

Comment 10. Pg 13627, line 12: A 50/50 mixture of a-pinene/naphthalene is hardly complex. Why weren’t other, more complex mixtures explored? This would help to determine how atmospherically relevant these experiments are.

Response. To the best of our knowledge, this paper is the first study to characterize f43 and f44 of a binary SOA mixture produced from oxidation of gas-phase precursors. It complements the work of Lee et al (GRL, 2011) who characterized f43 and f44 of a binary aqueous mixture of organics. We agree with the reviewer that more complex mixtures would be a worthwhile study. Characterization of more complex mixtures was beyond the scope of this paper but will be the subject of future work.

Comment 11. Page 13631, line 7: This explanation is confusing. A change in slope in Van Krevlen space indicates a change in reaction mechanism. If the same mechanism continues to replace one functional group with another then the slope would remain constant. From the data the former appears to be occurring – a change in reaction mechanism and products. This is an interesting finding that warrants much more detailed discussion.

Response. We replaced the words "functional group composition" with "reaction mechanism" at the suggestion of the reviewer. We expanded the discussion by editing the text as follows (changes bolded):

p. 13631, lines 7-9: "For several types of PAM-generated SOA, the (H/C)/(O/C) slope changes significantly over the course of oxidation. This evolution suggests that the **reaction mechanism** changed as the SOA became more oxidized. **The changes in Van Krevelen slope are most pronounced for SOA generated from alkanes (Fig. 6a), where the slope increases from about -1.4 to -0.3 with increasing oxidation. Along with corresponding changes in f_{43} and f_{44}, the observed changes in slope may indicate a transition in the oxidation reaction mechanism from carbonyl and acid/alcohol formation with minor fragmentation to acid formation with significant fragmentation. This possibility will be examined in future work.**"

Comment 12. Page 13632, line 13: More discussion of kappa values for the low O:C systems is warranted. For example, what is the kappa of unoxidized POA (such as lubricating oil)? Is it truly 0? What is the lowest kappa value you could measure using your methods (dry diameter and CCN supersaturation range)?

Response. Please see our reply to the reviewer's Comment 3, that is:

P. 13624, line 12: **"Selected dry mobility diameters ranged from 45 to 150 nm for SOA and from 145 to 200 nm for OPOA. The corresponding lower limits for κ-values ranged from 0.06 (45 nm) to 1×10^{-6} (200 nm). Lower limits for all κ-values are shown in Fig. S3 of the Supplement, along with upper limits for κ-values of unoxidized POA (1×10^{-6}).**"

Comment 13. Page 13632, line 19: It is true that HTDMA measurements tend to produce smaller kappa values than CCN measurements, and this is usually attributed to solubility arguments. If k(org) is larger for CCN measurements than HTDMA, and Jimenez et al. used HTDMA data while CCN data is used here, why is their slope of k(org) vs. O:C (0.37) more than double that presented here (0.17)?

Response. The data from Jimenez et al were taken over a smaller range than in our study (O/C = 0.23 to 0.77 and kappa = 0 to 0.20, compared to O/C = 0.05 to 1.4 and kappa = 8E-4 to 0.28). Therefore, while the kappa(CCN) and kappa(HGF) values are similar in both studies, the slope (0.37) and intercept (-0.09) applied to the data in Jimenez et al. are less accurate when extrapolated over a wider range. In particular, the negative intercept is significant over the range of O/C ratios in their work, and as a result the k(HGF) values are less than or equal to the corresponding k(CCN) values.

At the suggestion of Reviewer 2, we have added this regression line to Fig. 7, which we think will help clarify this point.

[Note: we revised the linear fit parameters representing data from Jimenez et al. from kappa(org) = 0.37*O/C – 0.06 (ACPD manuscript) to kappa(org) = 0.37*O/C – 0.09 (revised manuscript). This revision was performed at the suggestion of authors from the Jimenez et al. Science paper, in order to better represent field measurements presented in that manuscript].

Comment 14. Figure 7 warrants much greater discussion in general, particularly in terms of the low O:C measurements that lie well off the trend line. I am highly skeptical of a fundamental relationship existing between O:C and hygroscopicity. If you compare measured kappa for a variety of pure organics with similar O:C ratios you get a large spread in kappa. You can see this using the data in the Supplementary Information of Petters et al. (2009) which you have cited. For example, at O:C ~ 1.0, aspartic acid has kappa ~ 0.29 while xylitol has kappa ~ 0.16.

Response. In this manuscript, based on results shown in Fig. 7, we present an empirical formula derived from a large dataset of measured kappa-values and O/C ratios. There may or may not be exceptions to this empirical relationship, but we feel this does not detract from the wide range of applicability of the presented relationship. However, we have removed oxalic acid from the linear fit presented in Fig. 7 to emphasize the empirical nature of the kappa-O:C relationship as it applies to SOA/OPOA (rather than pure compounds). The revised fit parameters (slope = 0.18, intercept = 0.03) have been adjusted accordingly in the paper.

The deviation of the kappa-to-O/C relationship at low O/C ratios is discussed on page 13632, lines 3-9. We think this discussion is sufficient, based on the measurements that are presented.

Comment 15. Page 13632, line 27: Only if the inorganics are soluble, which is not always the case.

Response. We clarified this sentence in accord with the reviewer's suggestion:

p. 13632, line 27: "Figure 8 shows the calculated fractional contribution of OOA to the κ-values of a mixture of ammonium sulfate and OOA (kappa(total) ; kappa(sulfate) = 0.6) as a function of the volume fraction of organics, assuming linear volume-weighted OOA and sulfate contributions to kappa […] **and complete solubility of the organics and inorganics (Petters and Kreidenweis, 2007).**"

Comments 16. Page 13633, line 5: The mixed glyoxal/ammonium sulfate experiments are confusing. A 50/50 mixed particle was oxidized by OH, which increased O:C but dramatically decreased the organic fraction? Please explain this more clearly.

Response. We believe the confusion is now removed by revising the text on p. 13633, line 5 (changes bolded):

"For these data, O/C ratio increased from 1.06 to 1.50 as a function of OH exposure. The organic volume fraction of SOA generated from glyoxal also decreased from 0.53 to 0.04 as a function of oxidation. **This observation suggests that the unoxidized glyoxal oligomers undergo fragmentation reactions that (1) increase the O/C ratio and (2) result in evaporation of some organic aerosol mass.**"

Comment 17. Page 13634, line 2: "Because ambient OOA contains organics from multiple precursors, the corresponding f44–f43 composition may provide information about OOA contributions from specific precursors." I find this very hard to believe. In fact, Russell et al. (2011) recently reported that O:C ratios alone were not sufficient to characterize particle sources.

Comment 18. Page 13634, line 18: "the position of OOA in Van Krevelen diagrams may provide information about contributions from specific precursors." While this would be nice I again find this highly doubtful as the analysis is overly simplistic and not supported by the presented data. This should be removed.

Response. We agree with the reviewer that O/C ratio alone is insufficient to provide information about precursors. However, the combination of f43 & f44, as well as O/C and H/C ratios, provides significantly more information (see discussion from line 4, p. 13626 to line 23, p. 13627 and line 7, p. 13630 to line 9, p. 13631). Oxidation of different precursors produces SOA/OPOA that lie in different locations on f44-f43 and H/C-O/C plots, suggesting a dependence on precursor structure. Further, the trends in f44-f43 and H/C-O/C space with oxidation vary in different systems. We feel our results may be useful in characterizing ambient measurements, which is the reason we made these statements. Previous studies support this notion, e.g. Ng. et al. (ACP, 2011).

We have revising the text as follows (changes bolded):

p. 13634, line 2: "~~Because ambient OOA contains organics from multiple precursors, the corresponding~~ The ~~corresponding~~ f44-f43 composition **of ambient OOA** may provide information about **precursor structure(s)**".

p. 13634, line 18: "The position of **OA** in Van Krevelen diagrams may provide information about precursor composition **and reaction mechanism**. **For example, ambient HOA factors presented in Ng et al. (2011b) have H/C ratios ranging from 1.5 to 2.0 and are characterized by a Van Krevelen slope of approximately -2. These observations, combined with our laboratory measurements, suggest oxidation of alkane precursors forms OA with carbonyl functional groups**

Comment 19. Page 13634, line 20: "The work presented here provides the most extensive evidence that κorg depends on chemical composition." This is an over-exaggeration and not strictly correct. First, chemical composition of the oxidized OA was not determined here. Only elemental ratios, which say nothing about structure or actual composition, were determined. Second, this is not the most extensive evidence. Petters et al. (2009) summarize hygroscopicity data from a wide variety of organic systems, for example. It is true that this work likely represents the most extensive set of hygroscopicity experiments on oxidized organic precursors (OOA & OPOA). The text should be clarified to reflect these issues.

Response. We have modified the text as suggested by the reviewer by stating on page 13634, line 20: "The work presented here provides the most extensive set of **CCN-derived hygroscopicity measurements of laboratory-generated SOA and OPOA**."

Comment 20. Page 13634, line 23: I have significant problems with the parameterization of kappa(org) vs. O:C. First it treats particle properties as state functions, where only the final state (here O:C) matters, not the (reaction) pathway that was taken to reach the final state. I again question the atmospheric relevance of simulating oxidation of organic aerosol at more than five orders of magnitude higher OH concentrations, and very short exposure times. Second, the linear fit of kappa(org) vs. O:C has a significant amount of scatter, and data for low O:C systems fall well off the trend line. It is premature to claim that this fit can be extrapolated to realistically represent atmospheric aerosol hygroscopicity. While O:C may reflect the polarity of the organic compounds, it says nothing about structure or carbon chain length, which are also important parameters in controlling organic component hygroscopicity.

Response. There are two central issues addressed in this comment. A new and important issue is addressed here: the effect of high OH concentrations and short exposure times in the flow tube experiments described here (relative to the atmosphere). This is certainly a valid and important concern, and was the focus of a recent study by Renbaum and Smith ("Artifacts in measuring aerosol uptake kinetics", ACP, 11, 6881–6893). In this paper, flow tube experiments were performed to assess whether oxidant concentration and exposure time are interchangeable parameters, and if conserving the product of the two parameters (i.e. integrated oxidant exposure) allows extrapolation to atmospheric conditions. Renbaum and Smith studied the uptake kinetics of OH and Cl radicals on 2-ocyldodecanoic acid (2-ODA) organic aerosols at exposure times of 2 and 66 sec. Based on their results, they conclude:

"No difference is observed in the reaction kinetics of 2-ODA aerosols with OH or Cl when the decay profiles are constructed by changing the radical concentration […] or the reaction time […] as long as the [radical] precursor (O_3 or Cl_2) concentration is the same in both cases. Thus, it is appropriate to consider the radical concentration and reaction time as interchangeable parameters with the product of the two, the exposure (=[OH]·t or [Cl]·t), being conserved. Consequently, it seems reasonable to extrapolate results from laboratory aerosol flow tube studies, in which reactions are studied with high radical concentrations on the timescales of seconds to minutes, to atmospheric processes, which involve much lower radical concentrations and occur over several days to a few weeks."

We have revised the text as follows (changes bolded):

Page 13622, line 16: "**OH concentrations in these experiments (approximately $2*10^9$**

to $2*10^{10}$ molec cm^{-3}) are higher than ambient OH concentrations, although the integrated OH exposures are similar. To first order, a heterogenous oxidation kinetics study by Reinbaum and Smith (2011) found that increasing the OH concentration from $8*10^{8}$ to $2.6*10^{10}$ molec/cm3 while decreasing the flow tube residence time from 66 to 2 sec yielded similar results. From their analysis, they suggest that extrapolation of laboratory results, in which high OH concentrations and short exposure times are used, to atmospheric conditions is appropriate.

In addition, Renbaum and Smith found that increasing the radical precursor concentration (i.e. O3 for OH radicals) decreased the rate of reactive OH uptake. They proposed Langmuir-type competitive absorption on the particle surface to explain these results. In our work, it seems that nonreactive surface absorption of O3 could potentially decrease heterogenous oxidation kinetics between OH radicals and organic aerosols, and the work of Renbaum and Smith suggests that this effect can be up to ~50%. It seems unlikely that O3 absorption would otherwise influence the chemical composition or hygroscopicity of OPOA. Surface absorption of O3 would likely not significantly influence the formation and properties of SOA particles generated from gas-phase oxidation by OH.

We have revised the text as follows to put the findings of Renbaum and Smith in the context of the present work:

p. 13622, line 16: "The most significant experimental artifact arising from high OH concentrations is probably nonreactive absorption of O_3 (Renbaum and Smith, 2011). O_3 absorption may block active sites on the surface of particles that would otherwise be available for heterogenous oxidation by OH radicals. At O_3 levels used in the present work, the results of Renbaum and Smith suggest a ~30% decrease in the rate of heterogenous oxidation reactions as a result of O_3 absorption."

We have also added the following citation to the list of references:

Renbaum, L. H. and Smith, G. D.: Artifacts in measuring aerosol uptake kinetics: the roles of time, concentration and adsorption, Atmos. Chem. Phys., 11, 6881–6693, http://dx.doi.org/10.5194/acp-11-6881-2011doi:10.5194/acp-11-6881-2011, 2011.

In addition, our AMS measurements generally compare well to smog chamber measurements conducted at lower OH concentrations and longer exposure times. This was discussed in Sections 3.1 and 3.2 (p. 13626, lines 13-16; p. 13629, lines 9-10; p. 13630, lines 16-18). We have expanded on this discussion by revising the text as follows (changes bolded):

Page 13631, line 9: "**H/C and O/C ratios of SOA generated from six of the precursors used in this work were also characterized in smog chamber studies (Chhabra et al., 2011). For example, at O/C ratios ranging from 0.48 to 0.77 where our measurements overlap with Chhabra et al., the H/C ratio for SOA generated from naphthalene ranged from 0.77 to 0.78 in the PAM and 0.83 to 0.93 in the measurements of Chhabra et al. The agreement in H/C ratios for SOA generated from isoprene is similar (1.6 to 1.7 in the PAM and 1.5 to 1.6 in the measurements**

of Chhabra et al. for O/C ratios ranging from 0.45 to 0.65).”

The second issue raised in this comment questions the validity of a kappa-to-O/C parameterization, as was first brought up in Comment 14. Here we can only restate what we said in response to Comment 14:

“In this manuscript, based on results shown in Fig. 7, we present an empirical formula derived from a large dataset of measured kappa-values and O/C ratios. There may or may not be exceptions to this empirical relationship, but we feel this does not detract from the wide range of applicability of the presented relationship.”

Comment 21. Page 13634, line 25: “average molar volume” is a poor predictor of kappa(org), as demonstrated by Petters et al. (2009).

Response. We removed this from the text at the reviewer’s suggestion.

Comment 22. Table 1: Please include data for unoxidized POA (BES, lubricating oil, and diesel fuel if this produced stable particles). Kappa for these systems is likely too low to determine; what is the lower limit of kappa that can be derived using your method? This should be used to report an upper limit for kappa for the POA (e.g. kappa(org) < x).

Response. Please see our reply to Comment 3, where we report an upper limit of kappa(org) < 1E-6 for the POA.

Comment 23. Fig.6 : The y-axis scale should be narrowed so differences in the data can be seen more clearly. Hard to distinguish the open symbols. Figures are too small.

Response. In Fig. 6, we narrowed the y-axis scale from 0 – 2.5 to 0.6 – 2.2. This revision allows the data to be presented more clearly.

In regards to the reviewer’s comment about open symbols, we assume he/she is referring to the overlapping symbols for linear alkanes and for biogenic precursors. We have revised the Fig. 6 caption on page 13651 accordingly (**changes bolded**):

“Van Krevelen diagrams showing H/C ratio as a function of O/C ratio for SOA and OPOA generated in the PAM […] Symbols are colored by OH exposure, except for open symbols which represent unoxidized precursors **(Note: for n-C_{10}, n-C_{17}: O/C = 0 and H/C = 2.2; for isoprene, α-/β-pinene, longifolene: O/C = 0 and H/C = 1.6)**.”

We made the figures larger by moving the OH exposure colorbars from the right-hand-side margins of Fig. 6a, 6b, and 6c to the top margin of Fig. 6a. This will consolidate the figures and make them larger after typesetting. We also updated the Ng et al. (2011) parameterization lines shown in Fig. 6. These lines changed slightly following the review of that manuscript.

Comment 24. Fig. 7: Please explain what the grey box represents in the figure caption. Unoxidized POA should be included here as well to test if it follows the trend or not, even if a kappa(org) < value can only be estimated for those systems.

Response. To explain the grey box, we added following text to the Fig. 7 caption on page 13652: “**Shaded rectangle represents typical range of κ_{org} and O/C values (Liu and Wang (2010); Ng et al. (2010)**”. We added markers for the unoxidized POA measurements, using measured O/C ratios and upper limits of kappa(org) < 1E-6 for POA.

Comment 25. Fig. 8: Please list the kappa(org) values used for O:C = 0.3 and 1.0 in the legend.

Response. In Fig. 8, we added the relevant kappa(org) values to the legend: for O:C = 0.3, kappa(org) = 0.084; for O:C = 1.0, kappa(org) = 0.21; for the glyoxal/sulfate mixture: kappa(org) = 0.18*O:C + 0.03.

Reviewer 2 Comments

Comment 1. (a) P13621. Can more details be provided for the experimental setup? For example what type DMA and CPC are used? Is it the same DMA on P13623. L8? What type of SMPS (TSI 3080?) What is the sheath to aerosol flow? (b) For which data points were the C-Tof-AMS used? Under what conditions (flow rate, supersaturation) was the CCNC operated? (c) Was the CCNC calibrated? If so, how? Or in other words, how do the authors know the supersaturation in the instrument? This value is critical for kappa calculations in Equation 1. (d) Are the kappa values presented an average of activation experiments? If so how many? The authors mention “the CCN activity of particles was measured with a previously described technique P13624. L1”. However this statement is very vague, as the papers cited mainly describe instrumentation parameters and several techniques exits for CCN activity measurement. The addition of experimental details will help future readers reproduce the work.

Response. This comment contains several issues which we delineated within the comment using letters (a), (b), (c) and (d):

(a) Experimental questions about the type of DMA/CPC used. This is now clarified in the text:

[Page 13621, line 12: Specified DMA (TSI 3080), CPC (TSI 3010), and sheath-to-aerosol flow (5:1) for the SMPS.]

(b) Which data points were measured by the c-ToF-AMS, and which by the HR-ToF-AMS. This is now clarified in the text and also in our response to Comment 1 by Reviewer 1:

[“We now state specific uses of these two spectrometers in the Experimental section of the paper, as well as which specific instrument was used when the results are presented in the text.”]

(c) Calibration and operating conditions of the CCNC. This is now clarified in the text.

[Page 13621, line 15: Specified CCNC flow (0.5 lpm).

Page 13624: added the following operation details for the CCNC (changes bolded):

"The CCN activity of particles was measured with a continuous flow CCN counter (CCNC) using a previously described technique (Roberts and Nenes, 2005; Lance et al., 2006). **Briefly, the aerosol was size-selected using a TSI 3080L electrostatic classifier prior to CCN number concentration measurements with the CCNC and total particle number concentration measurements with a CPC (TSI 3022A).** CCN activation curves were generated **by holding the particle size constant** while systematically varying the CCNC column temperature gradient to obtain controlled water vapor supersaturation between 0.1-1.5% or until 100% activation was reached, whichever occurred first. **The water vapor supersaturation was calibrated using size-selected ammonium sulfate particles with dry diameters ranging from 25 to 85 nm**."

(d) Whether presented kappa values are single measurements or averages of several replicate measurements. This is now clarified in the text.

[Page 13624, end of Section 2.4: "Each κ-value represents an average of 1-4 separate activation experiments.]

Comment 2. P13622. L4. How significant are 30% fluctuations in RH to OH production?

Response. This statement was confusing as written, which we apologize for. The RH does not fluctuate by 30% at a specific operating condition in the PAM. The relative humidity is usually constant to within 5% at a specific condition. We have now clarified this issue in the text as follows:

p. 13622, lines 3-5: "**Most experiments were conducted at relative humidities ranging from 30% to 40%, depending on the temperature in the PAM at different UV lamp settings. At a given measured relative humidity, this parameter remained constant to within +/-5%. A subset of experiments was performed at higher RH (52% - 60%) and is discussed in more detail in Section 2.3.**"

Comment 3. (a) Figures 2 and 3. How are the dashed lines for oxalic acid determined? How do the authors know the slope of the dashed line as f43 increases? This is not explicitly stated in the text but is critical to the interpretation of the results and the discussion. (b) Perhaps one of the most interesting graphs is Figure 4 where the authors explore the mixture of naphthalene and a-pinene. Figure 4 suggests that the mixture is not simply the additive contribution from both species. "f44 of the mixture was always lower than f44 of naphthalene SOA and apinene SOA. . ..results suggest that a more quantitative understanding (P13627 L19)" is required. This is somewhat contradictory to the statement in the summary (P13634, L2): ". . .ambient OOA contains organics from multiple precursors; the corresponding f44-f43 composition may provide information about contributions from specific precursors". (c) Do the authors have a similar Figure 5 for the mixture of a-pinene and naphthalene? Can the contributions of a mixed SOA species be characterized with PMF?

Response. This comment contains several issues which we delineated within the comment using letters (a), (b), and (c).

(a) It appears that we were not clear in defining the origin of the dashed lines. We have altered the text to clarify this issue as follows. First, we altered the text as follows (changes bolded):

p. 13626, line 12: "The range of measured f_{43} decreases with increasing OH exposure, presumably because oxidation converts the lesser-oxidized compounds contributing to f_{43} to products that contribute to f_{44}. **The region defined by the dashed-and-dotted lines shown in Fig. 2 was constructed to bound the extremes of the f43 and f44 measurements obtained in the laboratory, with oxalic acid as an oxidation endpoint. As is evident, measurements for SOA generated from glyoxal and mesitylene fall close to the dashed-and-dotted boundary lines.** Several SOA precursors examined in the present work have been characterized in smog chamber studies (Ng et al., 2010; Chhabra et al., 2011)."

(b) Based on this comment, along with Comment 17 raised by Reviewer 1, we have revised the Summary statement on p. 13634, line 2, to read:

"The f44 -f43 composition of ambient OOA may provide information about precursor structure(s)."

(c) We think the reviewer raises an excellent question about resolving contributions of a mixed SOA species, but that answering it beyond the scope of the present work.

Comment 4. Little discussion is provided for isoprene SOA. Isoprene is an important biogenic precursor and has been the discussion of several papers. (a) The reviewer is unaware of previously published work that has been able to produce isoprene SOA at low precursor levels (less than 330ppb) without the use of NOx. (b) A table with the precursor conditions would be valuable. If PAM is the first technique to do this, it should also be highlighted. (c) Furthermore, the isoprene SOA appears to "misbehave" in several figures (2,6,7). Have the authors given consideration as to why isoprene is not consistent with the empirical models? These details could add to the importance of the paper.

Response. This comment contains several issues which we delineated within the comment using letters (a), (b), and (c).

(a) We would like to bring two studies to the attention of the reviewer by Kroll et al. (ES&T, 2006) and Chhabra et al. (ACP, 2010) that produced isoprene SOA at isoprene levels less than 100 ppb under low-NOx conditions. These references are now cited in the text.

(b) At the reviewer's suggestion, we added to the Supplement a table with VOC precursor conditions and stated this in the text on page 13622, line 26.

(c) We assume that the reviewer is referring to the following features of isoprene SOA:

1. $f_{44,max} = 0.12 \pm 0.02$, compared to maximum f44 values ranging from 0.21 – 0.31

for SOA generated from other VOC/IVOC precursors (Fig. 2).

2. Higher H/C ratios (1.6 – 1.7) than monoterpene/sesquiterpene SOA (Fig. 6)

We added the following text to the discussion (changes bolded):

p. 13626, lines 13 – 16: "For a specific precursor, the f_{44} and f_{43} of SOA generated in smog chambers and in the PAM at low OH exposures are generally similar (Ng et al., 2010; Chhabra et al., 2010; Chhabra et al., 2011) . Because higher OH exposures are possible in the PAM than in smog chambers, the range of attained f44 increases significantly. **One exception is SOA generated from isoprene, which at higher OH exposures may have fragmented into more volatile products in the PAM (Kroll et al., 2006). This might have prevented the formation of SOA with f44 > 0.12**."

p. 13630, line 26: "As shown in Fig. 6a, the H/C ratios of SOA generated from alkanes and isoprene at low OH exposures range from 1.6 to 2.1, which is on the high end of H/C ratios typically measured in ambient OOA. **SOA generated from isoprene had higher H/C ratios than other biogenic SOA precursors, a trend which has been observed in previous studies (Chhabra et al., 2010).**"

This trend may correspond to high yields of tetrols and organic peroxides in isoprene SOA (e.g. Surratt et al., 2006), which are more saturated than acids and therefore have higher H/C ratios. (We didn't state this in the text because we weren't certain this could asserted from our measurements alone).

In regards to Fig. 7, it is not clear to us that isoprene SOA behaves differently than the other types of SOA that are presented, so we have not changed the discussion.

Comment 5. Figure 6. If the data fall outside of the associated uncertainty with the H/C and O/C parameterization, does not this suggest that the model is even less robust than assumed? Figure a has a concave (almost opposite trend) and Figures b and c have several points that lie outside of the shaded area. What percentage of points, actually fall within the described uncertainty levels, and for what conditions?

Response. The reviewer's suggestion of a poor H/C and O/C parameterization is one possible explanation for measurements falling outside the prescribed uncertainty range. The shaded grey region in the figure is obtained from field measurements. In the atmosphere, multiple types of SOA are measured simultaneously in a given air parcel. In such ensemble measurements, the extremes may be averaged out towards the center. Such a tendency is perhaps evidenced in our data (e.g. Figs. 2 and 4), where the ambient measurements fall within a smaller triangle than the laboratory measurements. The same could be true for data shown in Fig. 6.

Discussion of this issue has now been added into the text as:

Page 13627, line 19: **"In ensemble measurements of laboratory and ambient SOA mixtures, the extreme f43 values may be minimized due to averaging. Such a tendency is perhaps evidenced in Fig. 4 and also in Fig. 2, where the ambient OOA measurements fall within a smaller triangle than the laboratory measurements."**

Page. 13630, line 5: **"As in Figs. 2 and 4, mixing multiple SOA precursors may cause extreme H/C ratios to be averaged out towards the center."**

Comment 6. Fig 7. (a) Why is glyoxal not shown? (b) What is the meaning of the dashed lines?

Response. (a) In order to form glyoxal SOA, the glyoxal had to be solvated in an aqueous ammonium sulfate solution. Under such conditions, kappa(org) for glyoxal cannot be measured directly because the mixed particles contain CCN contributions from ammonium sulfate along with glyoxal. For these reasons, glyoxal is not shown in Fig. 7. We discussed the glyoxal /ammonium sulfate measurements as a separate case study of organic/inorganic mixtures, and therefore felt it was warranted to present glyoxal separately in Fig. 8.

(b) The dashed lines in Fig. 7 represent the confidence intervals for the linear fit; we altered the Fig. 7 caption to specify this.

Comment 7. Fig 7. For comparison, perhaps it would be more effective to show the parametrization of Chang et al. 2010 and Jimenez et al 2009 on the figure as well?

Response. At the reviewer's suggestion, we added these parameterizations to Fig. 7.

Comment 8. Fig 7. Can you provide a list of compounds that do not follow the trend at low O/C? It is difficult to read all the symbols that are grouped together.

Response. We revised Fig. 7 by adding an insert to the figure with an expanded scale from kappa = 0 to 0.025 and O/C = 0 to 0.3 to display the markers at low O/C ratios on an expanded scale.

Comment 9. The reviewer is thoroughly confused by the results presented in Figure 8. (a) Why is glyoxal mixture data the only one shown? Why not also show data for a mixture of organic with O/C = 0.3 with sulfate? (b) kappa assumes the aerosol is completely soluble and the volume contributions of each species are additive; hence the contributions of each component to the kappa total should be a function of the volume fraction. But Why is figure 8 not a linear line with a slope of 1? Does the data deviate from simple single parameter kappa theory? (c) Furthermore, the authors fit the glyoxal/sulfate data points with the parametrization based on O/C=1.0 but the text states that "For these data, O/C ratio increased from 1.06 to 1.50" (P13633 L7). How do the authors use a lower O/C ratio to fit the data? Perhaps the authors could elucidate and explain in detail the calculations for this figure.

Response. This comment contains several issues which we delineated within the comment using letters (a), (b), and (c).

(a) Glyoxal/ammonium sulfate was the only organic/inorganic mixture studied in the present work. It may certainly be worthwhile to expand on this study with other organic/inorganic mixtures in future work.

(b) With the curves in Fig. 8, we are showing the dependence of modeled organic contributions to kappa as a function of organics volume fraction. This relationship is nonlinear. The data points are derived from measured kappa-values, and are used to test the applicability of the model.

In response to this comment, we have revised the text as follows (changes bolded):

Page 13632-13633, lines 29-3: "Figure 8 shows the calculated fractional contribution of OOA to the κ-values of a mixture of ammonium sulfate and OOA (***kappa(total);*** $\kappa_{sulfate}$ = 0.6) as a function of the volume fraction of organics, assuming linear volume-weighted OOA and sulfate contributions to κ (King et al., 2007, 2010; Dusek et al., 2010; Prisle et al., 2010) **and complete solubility of the organics and inorganics** (Petters and Kreidenweis, **2007):**

$$f_{\kappa_{total,OOA}} = \frac{\nu_{org}\kappa_{org}}{\nu_{org}\kappa_{org} + (1-\nu_{org})\kappa_{sulfate}}$$

Where $f_{kappa(total,org)}$ is the fractional contribution of OOA to kappa(total) and v_{org} is the volume fractions of organics in solution. Two lines are shown for theoretical mixtures containing sulfate and OOA with O/C ratios of 0.3 and 1.0, respectively (the most common range of O/C in ambient OOA)."

(c) The glyoxal/sulfate data were fit by assuming $kappa(org) = 0.17 * O/C + 0.04$, i.e., independently of the O/C = 1.0 trace. This has been clarified in the revised text and in the Fig. 8 legend.

Comment 10. P13626 L2. What is meant by similar? What are the exact values observed in Lee et al., 2011?

Response. The reviewer is referring to f44 and f43 values of oxalic acid measured in this work and in the work of Lee et al. (2011). The exact f44 and f43 values are not provided by Lee et al., but can be estimated from the figures. To clarify this issue, we revised the text as follows (changes bolded):

p. 13626, lines 1-3: "The highest measured f_{44} and corresponding f_{43} for SOA generated from glyoxal are f44 = 0.39 +/- 0.05 and f43 = **0.001±0.01**. These values are similar to those measured in our experiment for oxalic acid **(f44 = 0.36, f43 = 0.0048). Lee et al. (2011) measured f44 and f43 for oxalic acid and for organics generated from the oxidation of aqueous glyoxal. In their manuscript they presented results graphically without stating numerical values. From their graphical representation, we estimate f44 ≈ 0.3 and f43 ≈ 0 for both oxalic acid and oxidized aqueous glyoxal.**"

Comment 11. P13627 L5. Insert "as observed in Fig. S3"

Response. The insertion was made.

Comment 12. Fig. 1. Is a DMA part of the particle-sizing (SMPS) system?

Response. Yes. Fig. 1 has been revised to clarify this.

Comment 13. Fig 2. And Fig. 3. The font on the graphs is very small and difficult to read.

Response. In Fig. 2, we increased the font size for the x- and y-axis labels. We consolidated the "OH exposure" colorbars from three vertical bars to one horizontal bar and placed it in the top margin of Fig. 2a. The font size for the colorbar label was also increased. In Fig. 3, we increased the font size for the x- and y-axis labels and for the legend text.

Comment 14. Fig. 6. Why not include oxalic acid dashed lines? (also addresses the previous question about the oxalic acid parameters)

Response. The dashed lines in Fig. 6 correspond to the dashed lines in Fig. 2 delineating the ambient f44-f43 measurements presented by Ng et al. (ACP, 2010). Ng et al. (ACP, 2011) mapped the ambient f44-f43 triangle onto a Van Krevelen diagram using:

1. The f44-to-O/C parameterization from Aiken et al. (2008): O/C = 3.82*f44 + 0.0794
2. The f43-to-H/C parameterization from Ng et al. (2011): H/C = 1.01+6.07*f43-16.01*f43^2

Motivated by the reviewer's comment, we used the same method to derive dashed-and-dotted lines for Fig. 6 corresponding to the dashed-and-dotted lines in Fig. 2 that bound laboratory PAM measurements (with oxalic acid as the vertex). Upon doing this, we realized that the f43-to-H/C parameterization from Ng. et al. (2011), which is quadratic and fit to f43 < 0.22, cannot be reliably extrapolated to the laboratory f44-f43 triangle shown in Fig. 2, which extends to f43 = 0.25. The quadratic nature of the Ng et al. fit causes the predicted H/C ratio to level off and then decrease significantly for f44 > 0.22, which may not be representative of real behavior in this regime.

Therefore, we have decided not to include dashed-and-dotted lines in Fig. 6 that map the laboratory f44-f43 triangle from Fig. 2 onto Van Krevelen diagram coordinates. We feel doing so creates more confusion than insight based on parameterizations that are currently available.

Comment 15. Fig 8. What is the meaning of the dashed line?

Response. The reviewer is referring to a horizontal line representing a 20% contribution by OOA to the kappa-value in a mixture of OOA and sulfate. We added the following text to the Fig. 8 caption: "Grey dashed line indicates level below which OOA contributions to kappa(total) are considered insignificant.

Reviewer 3 Comments

Comment 1. The SOA generated in PAM might not be representative of those formed in the atmosphere. I think at least this should be mentioned in the paper.

Response. Please see our reply to Comment 20 raised by Reviewer 1.

Comment 2. Lack of the details on the calibration and operation of the CCN counter, the measurements of Kappa, and how the uncertainties were derived.

Response. Please see our replies to Comment 3 by Reviewer 1, and Comment 1 by Reviewer 2.

Comment 3. I also think it would be very helpful to include direct comparison to previous results (e.g. in Figure 7), and discuss the significance of any differences.

Response. Please see our reply to Comment 7 raised by Reviewer 2, who suggested adding kappa-to-O/C parameterizations from Jimenez et al. (Science, 2009) and Chang et al. (ACP, 2010) to Fig. 7.