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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer” *by* P. S. Chhabra et al.

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Response to Referee 1:

The authors would like to thank the reviewer for the careful review and helpful comments and to our manuscript. We have prepared responses to each of the concerns and questions, which are listed below. The referee’s comments are in italics, followed by the authors’ responses.

1. In the last sentence of the abstract, a reference is made to PMF components without explicitly stating that this refers to components of ambient OA obtained from PMF analysis.

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Lines 10-14 have been changed as follows: "Although chamber SOA has generally been considered less oxygenated than ambient SOA, single-ring aromatic- and naphthalene-derived SOA can reach O/C ratios upward of 0.7, well within the range of ambient PMF component OOA, though still not as high as some ambient measurements. The spectra of aromatic and isoprene-high-NOx SOA resemble that of OOA but the spectrum of glyoxal uptake does not resemble that of any ambient organic aerosol PMF component."

2. In the experimental section (2.2 specifically), the authors detail the sampling mode of the AMS during the chamber reactions and state the AMS mode was switched every minute between the high resolution "W-mode" and the higher sensitivity "V-mode". W-mode data was used for the elemental analysis results while the O/C ratio was estimated as the fraction of m/z 44 to total organic signal using V-mode data. Calculated O/C ratios and estimated O/C were later compared to evaluate whether the ratio of m/z 44 to total organic signal was an adequate estimate of O/C for chamber reactions. I am curious as to why V-mode data was used to estimate O/C ratios instead of applying the same fragmentation tables to the W-mode data which was the basis of the elemental analysis as it would lead to a more direct comparison of the two metrics (e.g., tuning differences between the two modes would have no impact, etc.).

We decided to use V-mode data to estimate O/C ratios so as to maximize the signal to noise in the calculation. The reviewer is correct in stating that W-mode data could have been used for the O/C estimation for experiments that were not signal limited. We compared f_{44} between both modes of operation and found little difference across all systems that were studied. This discussion has been included in the paper.

3. At page 27493, line 10, the authors discuss the correction for CO2+ needed to remove the contribution from air. However, the authors end this sentence by stating that the air contribution to CO2+ is removed to "determine the organic signal at m/z 44". It would be more correct to state that this determines the organic signal at CO2+as there are additional organic fragments at nominal m/z 44 including C2H4O+ as evidenced by

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Figure 5A.

Lines 9-10 have been changed to “The CO2+ signal originating from ambient air CO2 is removed to determine the organic contribution of CO2+ to m/z 44”

4. On page 27497, the authors compare elemental analysis values obtained using AMS data for alpha-pinene ozonolysis with those calculated using the offline analysis results of Yu et al. (1999). Although the elemental ratios obtained from each measurement are similar, there is some question whether this is merely coincidental as the AMS and off-line analyses would not measure the same species due to the labile nature of many of the SOA constituents in this case. For example, Yu et al. (1999) claim that > 90% of SOA resulting from the ozonolysis of alpha-pinene is contributed by compounds containing carbonyl, hydroxyl, and carboxyl groups. However, using an iodometric-spectrophotometric technique, Docherty et al. (2005) found that nearly half of the SOA mass from this reaction consists of organic peroxides. These results were supported by additional experiments conducted by Surratt et al. (2006). These compounds would not likely be amenable to gas chromatography and may decompose to the products measured by Yu et al. The potential for this discrepancy should, at a minimum, be discussed in section 4.3 where other potential sources of uncertainty regarding offline analytical techniques are discussed.

The reviewer makes an excellent point. We have edited sections 3.2 and 4.2 as follows:

In Section 3.2 – “In contrast to Yu et al. (1999), using an iodometric-spectrophotometric technique, Docherty et al. (2005) estimated that nearly half of the SOA mass formed in α-pinene ozonolysis comprised organic peroxides. Suggested compounds such as peroxy pinalic acid (O/C=0.44) and peroxypinic acid (O/C=0.56), generally have higher O/C ratios than those measured by Yu et al. (1999) but still close to the range measured in this study. A comparison of elemental analyses in this work and other is given in Table 3.”

In Section 4.2 – “For α-pinene/O3 and naphthalene photooxidation SOA, a substantial portion of the total organic mass has been identified and quantified by coupled gas or liquid chromatography/mass spectrometry (GC/MS or LC/MS) methods and iodometric-spectrophotometric techniques (Yu et al., 1999; Docherty et al., 2005; Kautzman et al., 2009). The discrepancy between the α-pinene ozonolysis products measured by Yu et al. (1999) and Docherty et al. (2005) could be due to the reactive nature of organic peroxides which decompose to the products suggested by gas chromatography. However, the products suggested by Docherty et al. (2005) and the mole-weighted calculations of H/C, O/C, and N/C ratios of the quantified species in those systems are very close to the measured elemental composition of the HR-ToF-AMS."

5. Combining Tables 1 and 2 should be considered so that elemental analysis results can be reported for each replicate reaction. This would clearly show the range of O/C ratios which are depicted in Figure 16. Again considering Table 2, this table claims to provide the average ratio for each experiment. The O/C range for the four alpha-pinene + O3 reactions is 0.30-0.43, but the average is 0.43. How can that be? Please recheck these numbers.

The authors acknowledge the suggestion by the reviewer but feel the information is best conveyed in two separate tables. However, we have provided a table in the supplemental section that lists the maximum O/C ratios for each experiment. Table 2 lists the average maximum O/C ratio for each system, not the average O/C ratio.

Page 27487, line 21: the range of O/C ratios provided is incorrect (0.010 should be 0.10).

Fixed.

Page 27490, line 7: incorrect units for volume concentration (m3 cm-3 should be cm3 m-3).

Fixed

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Page 27491, line 24: the abbreviation HR-MS was never introduced and is unnecessary as it is only used once in the manuscript. I would suggest simply using "high-resolution mass spectra".

“HR-MS” replaced with “high-resolution mass spectra”

Page 27492, line 15: "by" or "in" should follow "described".

Changed to “described by”

Page 27492, line 21: "HR-AMS" abbreviation is used to refer to the high-resolution time-of-flight aerosol mass spectrometer when the abbreviation "AMS" was introduced at page 27491, line 12. Please correct.

“HR-AMS data” changed to “high-resolution analysis”

Page 27503, lines 1-4: The first sentence here is a fragment and may need to be combined with the second. Please revise.

The first sentence has been changed to “Under high-NOx conditions, organic nitrogen is expected as evidenced by the presence of nitroaromatics (Hamilton et al., 2005; Sato et al., 2007; Jang and Kamens, 2001).”

Page 27505, line 5: Comma following "chemical bond" should be removed.

Comma after “double bond” has been removed

Page 27505, line 28: "that" appears to be a typo and should be "than".

Fixed

Page 27507, line 23: Sentence reads " monomers measured detected through..." Remove either "measured" or "detected".

“detected” removed.

Page 27508, line 16: "oligioesters" is misspelled.

Fixed

Page 27509, line 8: omit "in" after "sulfonic".

Fixed

Page 27510, lines 1-5: Sentence beginning "It is likely..." is a fragment. Please revise.

Sentence now reads “It is likely that such processes are occurring, either heterogeneously or in the gas phase, in the systems evaluated here...”

Page 27510, line 29: Comma following m/z 44 is unnecessary.

Fixed

Table 3: "This Study" for toluene + OH should be bold to be consistent.

Fixed

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