

Interactive comment on “Dependence of SOA oxidation on organic aerosol mass concentration and OH exposure: experimental PAM chamber studies” by E. Kang et al.

E. Kang et al.

ekang@korea.ac.kr

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Authors comments to Referee 1

We are pleased that all the referees think that this work should be published after we address their concerns. We agree with many of their suggestions and have modified the manuscript as described below. We respond to the comments of each referee separately. Their comments are included in italics with numbers, followed by our responses.

In reviewing Table 1, we found an error in the VOC concentration numbers in the studies of SOA chemical composition dependence on OH exposure. The correction of the

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precursor VOC concentrations does not affect the results or the conclusions of those experiments. The corrected Table 1 is separately uploaded as a supplemental material. The VOC concentration numbers are listed in ‘Minor and technical corrections by Authors’ at the end.

Re-arrangement of paragraphs by Authors:

We re-arranged the paragraphs and section orders as suggested by referee 2’s comment and by authors’ decision.

We re-arranged the introduction section by moving the 2nd and 3rd paragraphs under Section 2 to Introduction section. Thus, we switched the number of figure 2 and 3 each other to be consistent with the manuscript revision.

We moved the “Section 3.1.2 The determination of OA mass concentration for this study” to “Section 2.4 The determination of OA mass concentration”.

We deleted the section title “Section 3.1.3 Oxidation indicators f_{44} and f_{43} ” and moved the paragraph under that section to Section 2.4.

We deleted the section title “3.1.1 Mass spectra of SOA”.

Major comments:

This paper examines the changes in composition that result from exposing VOCs (and the SOA produced upon oxidation) to a highly oxidizing environment in a PAM chamber. It is compelling that to see that the degree of oxidation of OA in the PAM chamber spans lab and field measurements. The manuscript is very clear and well written.

1-My only major concern is that these results be properly qualified, particularly when these results are compared to other lab/field studies. The PAM chamber represents a very different kind of oxidizing environment from the ambient atmosphere – differences in chemical products as well as kinetics could limit whether this chamber is a suitable proxy for the atmosphere. In some ways, this study represents a first step in

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the direction of examining whether the PAM chamber represents realistic processing.

I would encourage the authors to be realistic when making comparisons – there are many reasons that the PAM chamber environment could produce different results from atmospheric conditions. A discussion of these in Section 3.4 would be very interesting/ helpful for the community. The authors primarily focused on differences in AMS analysis and wall-effects (which of course can also contribute). It would be ideal to see some evidence of the scaling of chemical effects with exposure time (same overall OH exposure). Could the authors make a first step in this direction by decreasing/ increasing the flow rate and the OH concentrations to maintain the overall OH exposure but slow/speed the system? It appears from Kang et al., 2007 that experiments at different flow rates have been performed in the past.

We agree that oxidation in the PAM chamber could be different from the oxidation that occurs in the atmosphere, as well as large environmental chambers or flow tubes for that matter. However, all chambers are imperfect simulations of the atmosphere; yet it is important for us to understand how these chambers are both like and unlike the atmosphere. We can only develop this understanding by doing studies like these. This paper provides evidence that the PAM chamber does produce OA with characteristics that are quite similar to those observed in the atmosphere. None-the-less, we agree with the reviewer that we should not overstate these similarities between OA produced in the PAM chamber and those produced in the atmosphere. We have gone through the paper to make sure that we correctly represent the evidence.

For instance, we have added the following changes to qualify the comparisons.

Page 24054 Line 17-18: "... provide evidence that some characteristics. . . ."

Page 24075 Line 12: "... constancy of the sum of f_{44} and f_{43} . Third, the causes. . . ."

Page 24075 Line 14: We added the sentence, "And fourth, comparisons must be made

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of all characteristics of SOA produced in the PAM chamber and in the atmosphere to test the ability of small, highly oxidative chambers to simulate the behavior of SOA in the atmosphere.”

We agree with the reviewer that it would be interesting to vary the OH while keeping the OH exposure the same, but were not able to do that study when we had the AMS in the laboratory at Penn State. We mention some work on this issue in Kang et al. (2007) using the TEOM, but for those experiments we did not have the AMS. This would be another good study for future work. There are a number of additional studies that would be interesting to carry out, and our paper is intended to be a starting point for those studies.

Otherwise, I have only minor suggestions for improvement, primarily related to phrasing. Once these comments are addressed, I recommend that the article be published in ACP.

Minor comments:

1-Abstract, Line 5: *one can question whether oxidation in the PAM chamber “is equivalent” to atmospheric oxidation of longer duration, given potential differences in chemistry. I suggest modifying this phrasing to “approximates” or something similarly qualified.*

We modified the sentence as follows. The following statement is factual and does not imply that the oxidation processes are the same in the PAM chamber and the atmosphere but only that the OA have had a similar exposure to OH.

Abstract Line 4-5: We removed the sentence starting with “Oxidation for a few minutes. . .” , and added the sentence “The OH exposure from a few minutes in the PAM chamber is similar to that from days to weeks in the atmosphere”

2-Abstract, Line 16: *This statement is poorly worded. Do you mean “the least oxidized OA” from this study or from the environmental chambers?*

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We modified the sentence for clear understanding as follows.

Page 24054 Line 14-16: We removed the sentence starting with “The degree of oxidation. . .” , and added the sentence “In this study, the degree of SOA oxidation spans much of the range observed in the atmosphere.”

3-Page 24055, line 12-13: This sentence is a little misleading in that it suggests that “with further oxidation” the only fate of organics is fragmentation. But not everything goes to CO₂! Clearly organics can also functionalize with oxidation. And even for the most non-volatile (highly functionalized) organics, much of the organic material will deposit out of the atmosphere before fragmentation occurs. This is also a little unclear in the second paragraph of Section 3.3

We agreed to comments. We modified the manuscript as follows.

Page 24055 Line 12-14: We removed the sentence starting with “With further oxidation, the. . .”, and added the sentence “With further oxidation, the organics are subject to fragmentation that cleaves carbontocarbon bonds and functionalization that adds oxygen containing functional groups (Kroll et al., 2009).”

Page 24067 Line 15-16: We changed the words in the sentence from “. . . fragmentation can occur, resulting in more volatile organics and loss of OA mass concentration” to “. . . fragmentation can occur, resulting in breaking carbon bonds and loss of OA mass concentration.”

Page 24067 Line 16-19: We removed the sentence starting with “Oxidation pathways. . .”. We added the sentences “Functionalization and oligomerization can also occur (Gross et al., 2006; Jimenez et al., 2009), but in this study functionalization was not the dominant process based on the O:C ratio increase and OA mass concentration decrease with oxidation, which is similar to the conclusion of Kroll et al. (2009) and Heald et al. (2010). In this study, oligomerization is difficult to study because of the extensive fragmentation by the Q-AMS”

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4-Page 24056, line 6: suggest the qualification of “unmeasured precursor VOCs” – clearly only those VOCs which lead to SOA formation are relevant. Also in this sentence, can you clarify whether “measurement errors” applies to ambient or lab (or presumably both)?

Yes, “unmeasured precursor VOCs” should be specified to “the VOCs which lead to SOA formation”, because not all VOCs are transforming to SOAs. But, VOCs measurements should not be limited to currently well known SOA precursors, because the VOCs that were not known to be SOA precursors in the past (e.g. isoprene) later have been found to generate SOAs (Carlton et al., 2009).

Page 24056, Line 6-7: We replaced the words “unmeasured VOCs, unknown oxidation processes, or measurement errors” with “unmeasured precursor VOCs that can lead to SOA formation, unknown oxidation processes, or measurement errors for OA and precursor VOCs in both the atmosphere and the laboratory.”

5-Page 24066, line 10: This is a detail but Fig 6b of Ng et al. shows a number of points above f_{44} of 0.15 (equivalent to O:C of 0.6+). I would revise your 0.5 number to 0.6

Thank you. Indeed the f_{44} values in Fig. 6 of Ng et al. (2010) were above 0.15. So, we will change the O:C ratio from 0.5 to 0.6 as you suggest.

Page 24066, Line 10: We replaced the words “some flow tubes are less than 0.5” with “some flow tubes are less than 0.6”.

References:

Carlton, A. G., Wiedinmyer, C., Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987-5005, 2009.

Minor and Technical corrections by Authors:

Abstract line 14: We changed the words “. . . , with linear f_{44} increase and f_{43} decrease.” to “. . . , with f_{44} increasing and f_{43} decreasing.”

Page 24055 Line 29: We changed the words “by the ultraviolet light (UV)” to “by the ultraviolet (UV) light”.

Page 24058 Line 13: We changed the words “UV grid lamps” to “ultraviolet (UV) grid lamps”.

Page 24056 Line 29: We changed the words “During those experiments, . . .” to “During some additional experiments, . . .”.

Page 24059 Line 18: We corrected the typos from “60 pptv to 500 pptv” to “60 pptv to 480 pptv”.

Page 24060 Line 27: We corrected the typos from “60 pptv to 500 pptv” to “60 pptv to 480 pptv”.

Page 24060 line 18: We added the reference list here “ 1.5×10^6 molecules cm^{-3} (Mao et al., 2009)”.

Page 24062 Line 5: We changed the figure number from “are shown in Fig. 2” to “are shown in Fig. 3” because we rearranged the figure 2 and 3.

Page 24067 Line 4-6: We corrected the VOCs concentration by replacing the sentence to “Initial VOCs concentrations were 39 ± 6 ppbv of α -pinene, 170 ± 30 ppbv of m-xylene, 180 ± 30 ppbv of p-xylene, and a mixture of 37 ± 6 ppbv of α -pinene, 46 ± 7 ppbv of m-xylene and 47 ± 8 ppbv of p-xylene.”

Page 24065 Line 4: We corrected the number from “fixed to 259 pptv” to “fixed to 260 pptv” for 2-significant figure.

Page 24065 Line 5: We corrected the VOCs concentration numbers including error ranges from “. . . from 7 to 79 pptv, m-xylene from 87 to 426 pptv, and p-xylene from 141 to 371 pptv” to “from 7 ± 1 to 79 ± 13 ppbv, m-xylene from 87 ± 14 to 430 ± 70 ppbv, and p-xylene from 140 ± 30 to 370 ± 60 ppbv”.

Page 24061 Line 10: We changed the words “. . . species by evaporation. Aerosol

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mass...” to “... species by evaporation. The aerosol mass...”

Page 24061 Line 16: We changed the words “... and only brief description ...” to “... and only a brief description ...”

Page 24063 Line 18: We changed the words “... sensitivity or tune of the ...” to “... sensitivity or tuning of the ...”

Page 24065 Line 2: We corrected the typos from “... of three VOCs, α -pinene, ...” to “... of three VOCs: α -pinene, ...”

Page 24065 Line 26: We changed the words “a rapid decrease in the ratio with...” to “a rapid decrease in f_{44}/f_{43} with...”.

Page 24065 Line 26-27: We changed the words “, leveling off at higher OA mass concentrations” to “and a much smaller decrease at higher OA mass concentrations”.

Page 24065 Line 27: We changed the numbers “mixing ratio, 7 ppbv, ...” to “mixing ratio, 7 ± 1 ppbv, ...”.

Page 24066 line 6-7: We change the numbers with error range and 2-significant figure values from “11.8 to 216 $\mu\text{g}/\text{m}^{-3}$ within 16 and 271 $\mu\text{g}/\text{m}^{-3}$ ” to “ 12 ± 5 to 220 ± 18 $\mu\text{g m}^{-3}$., ... within 16 ± 5 and 270 ± 22 $\mu\text{g m}^{-3}$ ”.

Page 24066 Line 14: We removed the sentence “The ratio of f_{44} to f_{43} shows similar behavior” and added a new sentence “The decrease in the ratio of f_{44} to f_{43} with increasing OA mass concentration is another way to show this behavior”.

Page 24066 Line 21: We changed the words from “OA mass concentration than α -pinene ...” to “OA mass concentration than for α -pinene ...”.

Page 24067 Line 8: We changed the words from “... the relative humidity and added VOC amounts” to “... the relative humidity.”

Page 24068 Line 10: We corrected the typos in the reference list from “... Bahreini et

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al. (2006)” to “... Bahreini et al. (2005)”

Page 24068 Line 26: We changed the words from “... to all AMS masses,...” to “... to several AMS masses,...”.

Page 24071 Line 19: We added the words from “... Caltech environmental chamber are consistent ...” to “... Caltech environmental chamber (orange rectangle in Fig. 7) are consistent ...”

Page 24071 Line 21: We added the full name of LBNL here to “study at Lawrence Berkeley National Laboratory (LBNL) (Jimenez et al., 2009) ...”.

Page 24072 Line 24: We removed the full name of LBNL here to “The differences between the LBNL study...”.

Page 24072 Line 18: We corrected the typo by removing “... into m/z 43 and m/z44 groups (or that there...” to “... into m/z 43 and m/z 44 groups or that there...”

Page 24074 Line 3: We changed the words from “A caveat...” to “Other caveats ...”.

We used the consistent expression “vs.” instead of “versus” for the followings.

Page 24068 Line 18: “ f_{44}/f_{43} vs. OH exposure”

Page 24068 Line 21: “ f_{44} vs. OH exposure...”

Page 24068 Line 22: “ f_{43} vs. OH exposure...”

Page 24070 Line 17: “ f_{44} vs. f_{43} ...”

Page 24072 Line 1: “ f_{44} vs. f_{43} ...”

Figure 2 Line 3-4: We changed the words from “... are the 1σ standard deviation (precision).” To “... are at the 1σ confidence level.”

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