

Interactive comment on “A new source of oxygenated organic aerosol and oligomers” by J. Liggió and S.-M. Li

Anonymous Referee #1

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GENERAL COMMENTS

The authors present results from studies where ambient urban air was exposed to either acidic or non-acidic sulfate seed aerosols. Under neutral conditions, the authors show that primary oxygenated species condensed on the seed aerosol, increasing the aerosol organic mass. In the presence of acidic seed, the uptake of primary oxygenated organics was enhanced relative to the neutral seed experiments which was attributed to non-reversible oligomerization reactions. Particle acidity correlated with the rate of increase of higher MW products, further indicating these oligomerization reactions are acid catalyzed. Although the impact of this organic aerosol source is small when considering typical SOA loadings in regions where this chemistry could be expected (urban, downwind regions), it could be on the same order of magnitude

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as POA. As processes and compounds contributing to organic aerosol formation and growth are not fully understood, this manuscript provides valuable insight into a previously unknown source of oxygenated organic aerosol in the atmosphere which will be of interest to the ACP readership.

The manuscript is well written, however there are some data and conclusions that need clarification, as detailed below. In particular, the presented data and conclusions are based on whether the experiment was with either neutral or acidic seed aerosols; however, the grouping of experiments based on this criterion is inconsistent in the manuscript. Also, in most cases, only data from select experiments within each seed group are included in the figures. This makes it difficult to determine if it is valid to draw clear conclusions based on the type of seed aerosol. I recommend this manuscript for publication after addressing this and the following comments.

SPECIFIC COMMENTS

P 29071, lines 2-3: “Typically, SOA dominates the OM mass...” This should read either “...OA mass...” or remove “mass” and define OM.

P 29071, lines 6-7: What do the authors mean by, “...and oligomer formation via aerosol-phase chemistry potentially increasing in importance.”? Is our knowledge of these reactions increasing or are they truly contributing more to aerosol phase chemistry with time?

P 29071, lines 6-7: With regards to the statement, “...traditional oxidation mechanisms... unable to account for SOA observations.”, currently unknown oxidation mechanisms are not the only possible source of the discrepancies between models and measurements for SOA. For example, another source may be the treatment of particles as liquids with regards to partitioning in current models. Recent studies (e.g., Cappa et al.; Kuwata et al.; Perraud et al.; Vaden et al.; Virtanen et al.) have shown that particles can be non-liquid, which can affect partitioning and reactivity and thus model calculations.

P 29072, line 18: It is unclear what is being contrasted in this paragraph. The second half of the paragraph applies to acidic seed aerosols, but it is not clear if the first half of the paragraph is meant to refer to the neutral seed or to both neutral and acidic seeds. Please clarify or remove “In contrast.”

P 29073, line 17: Was the elemental analysis carried out using APES? If so, add references for Aiken et al.

P 29074, lines 11-12: Please clarify that exposure of H₂SO₄ aerosols to organic free air and NH₃ resulted in “no measurable organic uptake.”

P 29075, lines 3-5: I disagree that “. . .those experiments with excess NH₃ fall closest to the best fit line.” I don’t see a clear trend in [NH₃/SO₄]_i and agreement with the best fit line. If there is a trend, what does this imply or what is the explanation for this? Either remove this part of the sentence or discuss and show this more clearly.

P 29075, line 16: “. . .the average organic spectrum for the experiments with highest [NH₃/SO₄]_i in the present study are shown in Fig 2b.” Please state in the text which specific experiments are included in this average. It is listed in the figure legend only. What is the rationale behind only averaging the experiments with the highest [NH₃/SO₄]_i, as opposed to averaging all experiments categorized as neutral (E4-E14)? If there is a dependence of the mass spectra on [NH₃/SO₄]_i which is considered neutralized, this should be discussed in the text.

P 29078, lines 23-24: The authors have provided approximate O:C values/ranges for the gasoline derived POA and OA from this study and Li et al (2011). Can the authors also provide literature values/ranges of O:C for HOA and SOA?

P 29080, line 4: The statement “. . .orders of magnitude above the noise level. . .” seems to be an exaggeration, even taking into account the log scale. From the peaks which are on scale in Figure 5, most peaks seem to be roughly an order of magnitude or less. I suggest changing “orders of magnitude” to “an order of magnitude”.

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P 29081, line 14: It is unclear if the O:C ratio is associated with $m/z > 300$ or for the entire mass range. Based on the following discussion in the text, I am assuming it is for the entire range, however the use of the word “associated” makes this unclear.

Section 3.2.2: In Figure 6a, the O:C ratio during E14, which was grouped with the neutral seed experiments (P29074 lines 15-20) and not with the acidic seed experiments at the beginning of this section (P 29079, lines 15-16), is in fact increasing from ~ 0.15 at the start of the experiment to ~ 0.33 after ~ 250 minutes. However, the authors state, “. . . increases in the O:C ratios over time were not observed for experiments with neutral aerosols. . .” (P 29082, lines 1-2) Do the authors mean that the rate of increase in the O:C ratio does not change with the NH₃ pulse? Also, the $m/z > 300$ /Tot Org is increasing with time for E14 prior to the NH₃ pulse, although for the neutral experiments, it was stated that the mass remained constant after the initial uptake in the first 2 minutes. Perhaps it would be informative to include the $m/z > 300$ /SO₄ data in Figure 1a on the right-hand axis as done in Figure 1b, if in fact the fraction of $m/z > 300$ is increasing while the total organic loading is maintained in the neutral seed experiments. The large increase in $m/z > 300$ /Tot Org following the NH₃ pulse in E14 is not accompanied with the same large increase in O:C observed for the acidic E3, instead the O:C continues the steady increase observed before the NH₃ pulse. Can the authors comment on these points?

-In the caption for Figure 6b, I see that E14 (and E4 and E5) are now designated as experiments which remain acidic. Is this because the final NH₄/SO₄ is less than 2? Following this criteria, E6-9 and E11 should also be regrouped and included in Figure 6b. The regrouping of E4, 5 and 14 is not mentioned in the text and is confusing as they were originally grouped with the neutral seed experiments.

-Are the changes with NH₃ pulse observed for all experiments where it was added? For the acidic conditions, an NH₃ pulse was only added for one acidic experiment. However, an NH₃ pulse was added for E4, E5 and E14. Was the behavior shown in Figure 6a for E14 also observed for E4 and E5? A sentence added to the text would

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clarify this.

Table 1: It is useful to have the individual mixing ratios for toluene, benzene, terpenes and isoprene. However, to facilitate comparison of the experiments, it would be nice to also have the final values. Can these be added to the table, perhaps in parentheses following the individual values?

Figure 1a: Why were these 3 neutral seed experiments included and not all the neutral seed experiment time traces?

Figure 1b: Number 1 near arrow for addition of NH₃ is not mentioned in the text or caption.

Figure 2b: The authors state that the best fit line is through shaded points only, however all the data points are colored. There is also the shaded region. Please clarify in the caption, perhaps stating fit only includes the data denoted with square markers.

Figure 2b, 3 and 4: What does the subscript “a” on the y-axis label denote?

Figure 3: Please add A, B, C and D labels to the individual graphs (not just legend subscript), as done in Figures 1 and 2 for example.

Figure 6a: Why is the O:C data for E3 not shown for the entire experiment? It stops at ~180 min, whereas the corresponding m/z>300/SO₄ trace for this experiment continues to ~300min. There is a sharp increase after the addition of the NH₃ pulse and I would like to know if this value continues to increase or the plateaus.

TECHNICAL COMMENTS

P 29071, line 3: “remains” -> “remain”

P 29074, line 25: Awkward wording of “which for non-acidic aerosols is essentially complete.”

P 29075, line 10: Should read, “. . .and the fast organic uptake was found to be. . .”

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P 29078, line 17: “is” -> “are”

P 29079, line 20: Lower case “Aerosol-phase”

P 29086, lines 24-25: In the Jimenez, et al. reference, there is a web address inserted in the author list.

All Figures, but particularly 2, 3 and 6: It is very hard to see the figure labels, legends, etc. when printed at 100%. Please make labels larger for better readability.

Figure 2a: Dashed line in the legend is removed from the description (Li et al., 2011)

Figure 2b: The “41” label is partially missing.

Figure 5: X-axis “m/z” label on the main graph is partially missing.

Table 1: Footnote e: Capitalized “limit” or lowercase “ below detection” in “Below Detection limit”.

Table 1: Final column heading (Additional [NH₃] Pulse) is missing units.

Table 2: Subscript on E14 (NH₄/SO₄)_f entry should be “d”, not “g”.

REFERENCES

Aiken AC, DeCarlo PF, Jimenez JL (2007) Elemental Analysis of Organic Species with Electron Ionization High-Resolution Mass Spectrometry. *Anal Chem* 79: 8350-8358.

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