

Ortega et al. report measurements of secondary organic aerosol generated by OH oxidation of ambient urban emissions in a PAM oxidation flow reactor during the CalNEX campaign. An aerosol mass spectrometer was used along with a scanning mobility particle sizer to obtain mass spectra, elemental ratios, and aerosol size distributions of the SOA. Selected VOCs were detected with a proton-transfer reaction mass spectrometer. The authors characterize organic aerosol enhancement factors as a function of OH exposure in the PAM reactor. The following results are obtained:

1. SOA formation peaks at an intermediate photochemical age in the reactor (~1-6 days' equivalent atmospheric OH exposure) prior to decreasing. This result is interpreted as a transition from functionalization- to fragmentation-dominated reactions.
2. SOA formation is largest during the nighttime. The authors interpret this result to suggest that the most SOA precursors have an atmospheric oxidation lifetime that is shorter than the source->receptor transit time (0.3 day) during the day, but not at night.
3. Campaign-average SOA oxidation state and $\Delta(\text{SOA})/\Delta(\text{CO})$ emission factors are generally consistent with previous studies, although the magnitude and trend of observed $\Delta(\text{SOA})/\Delta(\text{CO})$ emission factors is difficult to reproduce with conventional chemistry and transport models.

Overall, this manuscript addresses an important research topic regarding the characterization of ambient SOA formation and chemical evolution with oxidative aging. It demonstrates the unique capability of oxidation flow reactors to simulate *in situ* photochemical aging of air masses and complements previous studies through its application in an urban receptor location. I would support publication in Atmospheric Chemistry and Physics after incorporation of my comments below.

Main Comments

1. P21914, L19-21: Please add data to the Supplement to support the claim that removal of the inlet plate reduces losses.
2. P21915, L1-4: Please add data (such as residence time distributions of tracer species) to the Supplement to support the claim that this flow configuration maintains plug flow characteristics.
3. P21915, L29: More information/clarification about the particle loss correction is needed. Specifically, it's not clear to me how the UV dependence to particle losses was determined if particle losses are measured with the lamps off. Also, shouldn't there be a size dependence to the magnitude of the particle losses?
4. P21918, L3-4: "It is assumed that products after five oxidation steps with OH at kOH..." I found this sentence confusing. Couldn't you equivalently just state the OH exposure at which you assume that OH oxidation products no longer condense? For example, doesn't 5 oxidation lifetimes at $k_{\text{OH}} = 1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ correspond to an

OH exposure of 5×10^{11} molec cm^{-3} sec? If so, the first sentence in the next paragraph states: “At OH_{exp} lower than 1×10^{12} molec cm^{-3} sec ... the dominant LVOC fate is condensation to the aerosol”. While self-consistent, these two statements suggest a different OH exposure at which the transition to fragmentation-dominated reactions occurs (unless I am misinterpreting the method that is being applied). Please clarify.

5. P21918, L10-24: After reading this section, I found it difficult to come away with definitive conclusions about the relative importance of LVOC loss pathways as a function of OH exposure. Figure S6 demonstrates the corrections that are used, but the information in this figure does not come across clearly in the text. I suggest moving this figure out of the supplement and into the main paper because it seems to be important for interpretation of results. Some suggested text to incorporate is provided below (paraphrase and update highlighted quantities as appropriate), which I think would make it clearer:

“The modeled fractional loss of LVOCs to condensation on pre-existing aerosols decreases from a maximum of 0.75 at $\text{OH}_{\text{exp}} = 1 \times 10^{11}$ molec cm^{-3} sec to a minimum of 0.15 at $\text{OH}_{\text{exp}} = 1 \times 10^{13}$ molec cm^{-3} sec. Over the OH_{exp} range, the modeled fractional loss of LVOCs to gas-phase fragmentation reactions with OH increases from a minimum of 0.15 to a maximum of 0.83, and the fractional loss of LVOCs to the reactor walls and sampling line walls decreases from 0.10 to 0.02.”

6. P21919, L22-L24: I would be careful to avoid over-interpretation of a single event in claiming that the OFR can be used as a predictive tool. Figure 3b indicates that maximum nighttime OA concentrations ranging from 15 – 30 $\mu\text{g m}^{-3}$ are observed at 6 separate intervals over 12 hours. Figure 2 shows a ~ 1.5 hr measurement cycle, suggesting that six OFR sampling cycles are conducted over this period. However, the corresponding OH_{exp} at which these $[\text{OA}] = 15 - 30 \mu\text{g m}^{-3}$ periods are attained is not discussed. If OH_{exp} in the reactor is the same as the ambient OH_{exp} during the following day (5-Jun-2010, peak OA $\sim 25 \mu\text{g m}^{-3}$), over multiple days of the campaign (instead of just one day), then it might be appropriate to highlight “the reactor’s potential for estimating the next day’s OA concentrations.” Otherwise, it is an interesting observation but (in my opinion) inconclusive. For example, Figure 2 suggests that maximum reactor OA concentration during a nighttime cycle on 2-Jun-2010 are observed at $\text{OH}_{\text{exp}} \sim 2 \times 10^{12}$ molec cm^{-3} sec (15 days of equivalent atmospheric oxidation), which is presumably much higher than the ambient OH_{exp} later that day.

7. P21920, Section 3.2: The mean inorganic aerosol concentration is greater than the mean organic aerosol concentration (11 $\mu\text{g m}^{-3}$ INORG versus 8.4 $\mu\text{g m}^{-3}$ ORG in reactor, 8.2 $\mu\text{g m}^{-3}$ INORG versus 6.8 $\mu\text{g m}^{-3}$ ORG in ambient). However, aside from a brief mention in the Supplement relating to discussion AMS collection efficiency, the magnitude and OH exposure-dependent inorganic aerosol enhancements in the reactor are never discussed despite being comparable to the organic aerosol enhancements. This is especially evident from the nitrate time series in Figures 3a and 3b. There is likely valuable information here that complements the discussion of OA enhancements:

- Nitrate, sulfate, ammonium and chloride enhancements as a function of photochemical age. Are the trends the same or different as OA trends, and what does this reveal about their sources?
- Are nitrate and sulfate neutralized by ammonium in the reactor and in ambient? At the moment this information is buried in L21-L29 of the Supplement.

As an aside, as noted in Comment #13 below, the mean “total mass” listed in Figure 3c ($22.4 \mu\text{g m}^{-3}$ in reactor, $14.9 \mu\text{g m}^{-3}$ in ambient) is not equal to the sum of the organic, nitrate, sulfate, ammonium and chloride components ($19.4 \mu\text{g m}^{-3}$ in reactor, $15.0 \mu\text{g m}^{-3}$ in ambient). If this is a typo it should be fixed, if it is a real difference it should be explained.

8. P21930, L12-L15. It is not clear how you distinguish gas-phase fragmentation of condensable species from heterogeneous oxidation of SOA here because to first order, the timescales for gas-phase fragmentation of condensable species and heterogeneous oxidation of SOA appear to be similar. Because this comparison is speculative and doesn't seem to add much to the discussion anyway, I would consider removing it.

9. P21930, L16-L29: To complement this discussion, I suggest adding a scatter plot of “measured oxygen added” versus “predicted oxygen added” to the main paper, and rephrasing the discussion accordingly. I am unable to draw this conclusion from Figure S10; I think this alternative figure would make the point a little clearer. Figure S10 could then be removed.

10. P21932, L8-L29 and P21934-P21935, L28-2: In making the comparison with Tkacik et al. (2014), I would consider the following points in the discussion:

- High NO levels (>400 ppb) in Tkacik et al. might minimize the relative rate of $\text{RO}_2 + \text{HO}_2$ reactions in their reactor that would otherwise lead to multifunctional, condensable species (and possibly higher $\Delta\text{OA}/\Delta\text{CO}$).
- High NO and NH_3 levels in Tkacik et al. result in nitrate and ammonium enhancements ~3x higher than the organic aerosol enhancements
- Thus, while vehicle emissions presumably dominate SOA formation in both studies, the ensuing RO_2 oxidation chemistry could be very different.
- Given that inlet losses of semivolatiles is pretty much discounted in this discussion, I would remove (or significantly shorten) that discussion and instead focus on the different photochemical conditions and how they might result in different secondary aerosol composition despite similar precursor makeup.
- The sum $\Delta(\text{OA} + \text{Nitrate} + \text{Sulfate} + \text{Ammonium})/\Delta(\text{CO})$ would also be worth calculating and comparing between the two studies.

Figure Comments

11. Figure 1: This figure could be moved to the supplement.

12. Figure 2:

- Given the range of $[O_3]$ (up to ~16 ppm), I suggest plotting in parts per million instead of parts per billion.
- I think it would be useful to have the colorbar scaled by the lamp voltages so that readers better the specific conditions that were used, especially if they want to reproduce the sampling protocols that were used here in their own work.
- In the caption, “oxidant cycle” is vague - something like “A typical OFR sampling cycle” would better describe the figure.

13. Figure 3c: The “total mass” is not equal to the sum of the non-refractory components listed here (OA + Nitrate + Sulfate + Ammonium + Chloride): $22.4 \mu\text{g m}^{-3}$ stated versus $19.4 \mu\text{g m}^{-3}$ calculated (PAM reactor) $14.9 \mu\text{g m}^{-3}$ stated versus $15.0 \mu\text{g m}^{-3}$ calculated (ambient). This discrepancy should be explained or sorted out as appropriate. Also, is there a reason why the reactor” and ambient pie charts are different sizes?

14. Figure 4: Analogous figures should be made for nitrate, sulfate and ammonium.

15. Figure 5: This figure could be removed or moved to the Supplement (see Comment #40)

16. Figure 6: It would make sense to show toluene here as well (rather than in Figure S8).

17. Figure 7: I assume that symbols representing the PMF factors are the same in Figures 7a and 7b, but this should be made clear. The “ambient” and “reactor” symbols are also the same, but whereas they appear in two legends, the PMF factor symbols do not.

18. Figure 9:

- I suggest adding vertical lines at photochemical ages corresponding to one e-fold decay of 1,3,5-trimethylbenzene, toluene, and benzene, to illustrate the relevant range of k_{OH} for important SOA precursors. This would convey the added information in Figure S9a in the main paper (and perhaps make that figure unnecessary in supplemental) more directly than the decay curves that are shown in Figure S9a.
- Define “BG” as “background” and “POA” as “primary organic aerosol in the figure caption.

19. Figure 10:

- The Hayes et al. 2014 ACPD citation shown in legend and caption is not in the listed references. Should this instead be Hayes et al. 2015?
- In the figure caption, the text “This difference is due...photochemical ages less than 1.2 h” would probably be better in the main text.
- Is there a reason why Figures 10a and 10b are different sizes?

20. Figure S6: Move to main paper

21. In addition to (or instead of) Figure S10, Add a scatter plot of “measured oxygen added” versus “predicted oxygen added” to the main paper.

Minor/technical comments

22. P21909, L6: Define the “CalNEX” acronym (it is not defined until the last paragraph in the Introduction).

23. P21909, L7: Might it be useful to spell out “California” and indicate it’s in the United States?

24. P21909, L11-13: “OH radical concentration was continuously stepped [...] 0.8 days – 6.4 weeks”. This sentence seems superfluous with the preceding sentence.

25. P21909, L19: Define LA-Basin

26. P21909, L25-28: “The mass added [...] fragmentation/evaporation.” I’m not certain if the abstract is the best place for this text.

27. P21911, L12: Quantify “long” aging timescales.

28. P21911, L19-21: “In order [...] changing air masses.” This sentence is unclear.

29. P21913, L12-14: “By combining results from the ambient aerosol and aged ambient aerosol measurements, we provide a stronger test of current SOA models.” Instead of ‘stronger’, I suggest “more rigorous.” Also, explain why the combination of ambient and PAM-oxidized ambient measurements is a better test of SOA models.

30. P21915, L23: Add “and” between “reactor” and “resultant”

31. P21916, L8: Isn’t residence time the governing parameter here (rather than flow rate)?

32. P21916, L18-19: “OH concentrations averaged up to $4 \times 10^6 \text{ cm}^{-3}$ during the daytime.” This sentence is confusing - was the mean daytime OH concentration $4 \times 10^6 \text{ cm}^{-3}$? If so, delete “up to”.

33. P21916, L19-22: “Since a significant part of SOA formation ... peak OH observed during CalNex.” This sentence is unclear; please clarify or rephrase. Also, “peak OH” should be “peak [OH]” or “peak OH concentration”.

34. P21918, L24: This is the first instance of “ER_{OA}” in the manuscript, so it needs to be defined here.

35. P21919, L17: Typo (“attributes”->“attribute”)

36. P21919, L25: Replace “indicating” with “suggesting”
37. P21919-21920, L26-1: “At the peak of...removal by photochemical oxidation and condensation”. Delete, this is repetitive with the previous sentence.
38. P21921, L4-6: The last sentence of this paragraph is confusing.
39. P21921, L14: Please provide a reference for the stated 0.5 day transit time from downtown Los Angeles to Pasadena.
40. P21922, Section 3.3.1 and Figure 5: In my opinion this section is somewhat self-evident because the oxidant exposures attainable in the reactor are much higher than the ambient photochemical age. I don't think it adds much to the paper and would delete or move to the Supplement.
41. P21922, L19-20: I suggest a slight modification to the title of Section 3.3.2: “Further constraints on urban SOA formation timescales from OH reactivity of measured VOCs.”
42. P21923, L6: Typo (“moelcule”->”molecule”)
43. P21923, L14: Typo (“theses”->”these”)
44. P21923, L24-25: Somewhere in the paper S/IVOCs should be briefly defined. This sentence could be explained slightly to point out why these species are not often measured.
45. P21924, L6: f43, f44, H:C and O:C are never defined.
46. P21924, L10: Rather than “move up and to the left”, I suggest “f44 increases and f43 decreases.”
47. P21924, L13: Typo (“lay”->”lie”)
48. P21924, L17-L18: “The Van Krevelen diagram ... demonstrates results that are very consistent to those of the previous plot”. The connection between f44 – O/C and f43 – H/C has been documented in previous papers (e.g. the Ng et al. 2011b ref, among others), but is never made in this paper. Readers might not make this connection themselves. I suggest doing so here if you want to relate Figures 7a and 7b.
49. P21925, L12-13: “While ambient OSc is within the range of ...urban/anthropogenic OA”. Please provide reference(s).
50. P21925, L21: I suggest a modification to the title of Section 4.1: “Evolution of OA/ Δ CO with photochemical age”

51. P21926, L8-L19 and PL22-23: “Ambient photochemical age ... Fig. S9a for reference” and “Reactor data are shown... vapor loss-correction applied (see Sect. 2.3)”. Can this text be deleted or shortened significantly? Most of it is already in the Figure 9 caption or self-evident from viewing the figure, and it breaks up the flow of discussion of data in Figure 9.

52. P21926, L27: “To further illustrate the lifetimes of important urban SOA precursors”. This sentence confuses the point. Benzene, toluene, and 1,3,5-trimethylbenzene are not important urban SOA precursors. Rather, their OH oxidation lifetimes – in conjunction with timescale over which OA/ Δ CO increases -- constrain the range of OH reactivity (k_{OH}) of important urban SOA precursors: $5 \cdot 10^{-12} < k_{OH} < 5 \cdot 10^{-11} \text{ cm}^{-3} \text{ molec sec}$. This should be clarified here and elsewhere in the discussion.

53. P21927, L15: I suggest a modification to the title of Section 4.2: “Fit to the observed ambient and reactor OA/ Δ CO evolution” or perhaps “Parameterization of timescales for SOA functionalization and fragmentation processes.”

54. P21927, L22: “However, the evolution...”: Evolution of OA/ Δ CO?

55. P21928, L22: Isn't it implicit in the discussion that IVOCs and SVOCs are primary emissions? I suggest: “The second model variant represents SOA formation from IVOCs and SVOCs in addition to VOCs”.

56. P21930, L6: Define “TPOT”.

57. P21933, L14-L15: Didn't the George and Abbatt (2010) and Tkacik et al. (2014) studies that are already cited here also use an oxidation flow reactor to perturb ambient urban air?