

Review Report Graeffe et al. 2025: SOA yields from C10 alkanes and oxygenates and their relation to highly oxygenated organic molecules (HOM)

Graeffe et al. present a study about the Secondary Organic Aerosol yield from a number of C10 compounds from photooxidation in the presence of ozone and under very low NO_x concentrations in an Oxidative Flow Reactor (OFR). The list includes n-alkanes, branched, mono and bicyclic structures as well as the oxygenated compounds (aldehyde, ketone, alcohol). They find the expected trends for the SOA yields and try linking them with the observed Highly oxygenated Organic Molecules (HOM).

Such systematic, fundamental work furthers our understanding of SOA formation mechanisms in the atmosphere and is thus of interest for the audience of this journal. However, I found one important weakness in their methodology (the estimation of the VOC concentration, see Major Comment #1). Before publication, the impact of this issue needs to be discussed in detail to fully evaluate the findings of this study.

Major comments

- 1) Knowing the amount of reacted VOCs is crucial for the calculation of aerosol yields. Apparently due to some instrumental misfortune, the VOC concentrations (ingoing and outgoing) could not be measured for most of the experiments. The authors rely on the calculated concentrations from the injection method (flow of syringe pump) for the initial VOC concentration in the OFR. They then calculate the reacted amount from the OH exposure and known reaction constants. This method in itself is a valid approach if no measurements are available. But there are several sources of uncertainty for the calculated reacted VOC concentration which is the crucial parameter for the yield calculations.
 - a. Uncertainty of the initial VOC concentration. Do the authors have any indication of the accuracy of this estimation? E.g. how do the calculated and measured values of the initial VOC concentration compare for a case where they do have PTR data? (e.g. the OH exposure experiment with nonanal)
 - b. OH exposure. The authors use the OH estimator model from Li et al. (2016). They compared the calculated value with a test measurement for nonanal (a compound not used in the actual yield experiments) and report a more than two times higher OH exposure value from the measurements than from the model. Doing a simple calculation using a $k(\text{OH})$ of $1\text{e-}11 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, I calculate that the higher OH exposure leads to a 1.8 times higher amount of consumed VOC (see table below). The yield would be affected by the same factor.

Table 1: Calculation of consumed VOC with measured and modelled OH exposure

OHexp(meas)	6.20E+10	molec. /cm ³ /s
OHexp(model)	2.90E+10	
VOC initial	35	ppb
k	1.00E-11	cm ³ /molec./s
VOC consumed		
meas	16.2	ppb
calc	8.8	ppb
meas/calc	1.835474	

Since the authors use the model for all experiments, potentially all VOC consumed values are too low. Then the calculated yield would be too high. But this is just my first “top-of-the-head” thought and the authors need to go into the details.

- c. Residence time. It was not said explicitly, but I assume that the stated residence time was derived assuming plugged flow. PAM characterisation papers showed that due to the inlet geometry, the flow inside PAM is not represented by the “plugged flow” simplification. Fig 3 in (Lambe et al., 2011) shows an example of how much plugged flow and the actual residence time distribution can differ. The residence time is not used directly in the calculation, but it is folded into the calculated OH exposure where one single value is used for the residence time. Do the authors have any measurements for the residence time distribution in their PAM with their specific flow setup? What would the plugged flow residence time represent? Do most VOC molecules experience a shorter residence time? Is the plugged flow a representation of the average residence time? How would this affect the calculated vs measured OH exposure and thus Δ VOC?
- d. Reaction constants. What values were used for the reaction coefficients? I did not see any values or reference. Like any other parameter, reaction coefficients will have an uncertainty which will directly contribute to the uncertainty of the calculated Δ VOC concentration. From the typical values found in literature for these type of compounds (e.g. (Shaw et al., 2020)), I would guess a 10-20% uncertainty in the reaction coefficient values could be reasonable. How much does that add to the overall uncertainty for Δ VOC and thus the uncertainty of the aerosol yields?

With all this in mind, the authors should provide a thorough discussion of the overall uncertainty of their estimated VOC concentration values and how that will affect the calculated SOA yields. E.g., if the reported values are a lower or higher estimate and how much additional uncertainty stems from the VOC estimation. Such uncertainty needs to be taken into account in the discussion when comparing the yield values from this study with literature values.

- 2) The HOM part is too superficial in my opinion. I understand that the experiment design was not favourable for quantitative HOM measurements. But only two C10 HOM groups seem to be investigated in the text. In the appendix figures A2-A8, 6-8 ions (all C10) are identified. These do not seem to be the most prominent (strongest) signals in that m/z range. Why were these chosen? Are these identified HOM representative for the overall HOM population? Does the molar HOM yield in Fig 4 include all potential HOM in the system or also only a specific subset (e.g., only C10 compounds)? (See also specific comment 24)

In my opinion, the authors could strengthen the scientific impact of this manuscript by expanding the discussion of the HOM compounds.

Specific comments

- 1) Line 48: what is the “bimolecular reaction rate” referring to? O₂ addition to the alkyl radical? Or the initial OH+VOC reaction?
- 2) Lines 72-74: The description of the oxidant formation is not strictly precise. OH is not produced from water vapour, but from photolysis of O₃ and then consecutive reaction of O(1D) with H₂O. HO₂ radicals are mostly formed from photolysis but from the reaction of OH with O₃ (or VOCs). HO₂ is listed as an “oxidant” in the same way as OH is. But to my knowledge, HO₂ will not initiate oxidation reactions with the investigated VOCs but rather participate in the reaction mechanism, e.g. terminating RO₂ radical chemistry. This sentence needs rephrasing and clarification.

- 3) Line 76 & Fig A1: To my knowledge, most PAM systems use a Nafion humidifier and not a water bath for humidification.
- 4) Line 76: 22% RH is a rather low value. Often 40% RH are used in OFR or chamber studies as a representation of average atmospheric conditions. Furthermore, the recommendation to obtain atmospherically comparable VOC and RO₂ chemistry for OFR185 mode is to use high H₂O, low UV, and low OH_{ext} (see conclusions of (Peng et al., 2019)). Was there a reason for choosing 22% or did this stem from the limitation of the setup (i.e., the efficiency of the humidifier at the high flow needed for the instrumentation)?
- 5) Line 79: The UV lamps were set to 100V? To my knowledge PAM UV lights use a control voltage of 0-10 V. Was a different system used? Or is this a different voltage?
- 6) Line 77: I assume the residence time value is calculated assuming plugged flow. This needs to be clarified.
- 7) From the description, I assume PAM was operated in “OFR185” mode, i.e., using the 185 nm UV lamps inside PAM to generate O₃ and OH at the same time? Using this label may help clarify the mode of operation and facilitate comparison with other studies.
- 8) Line 111 and Figure A1: I understand that additional dilution after PAM was necessary to achieve enough sample flow. The sampling flows in Fig A1 add up to 14 lpm. Why was the dilution flow set to 10 lpm creating an overflow of 6 lpm?
- 9) Line 89f: I do not understand how the authors come to the conclusion that the measurements do not include the external reactivity. The presence of nonanal in the measurements is the “external OH reactivity”. The derived OH exposure values will be the values in the presence of the set amount of nonanal.

I assume that the authors used the “OFR exposure estimator” based on Li et al.

(<https://sites.google.com/site/pamwiki/estimation-equations>). Then the reason that the model estimates a lower value is that it assumes that the set external reactivity is present for the whole residence time. This is equivalent with assuming that the 35 ppb of nonanal are never consumed. Or that the reaction products of nonanal continue to react with OH at the same rate as the precursor and that they continue to do so for the whole residence time. Neither of these are of course correct – the truth is somewhat in the middle (precursor gets consumed, reaction products react). However, the discrepancy between the model and measurements does not stem from “not include the external reactivity”.

- 10) Line 96: If the authors provide the information about the AMS data acquisition interval, they should also mention if they were only alternating between open and closed or if they also ran pToF. Typical settings are 20sec for open/closed. Then only 2/3 of the 1 min would actually contain MS data.
- 11) Line 97: what is meant with an “overflow of 1L/min”
- 12) Line 102: what is meant by “area concentration”?
- 13) Line 104: How much uncertainty is introduced by using this density estimation? If AMS did acquire pToF data, do the estimated densities match the densities that can be derived from comparing aerodynamic and electromobility diameters (at least the trends between experiments)?
- 14) Line 102: The upper limit of the SMPS was 500nm (electromobility). How did the volume size distribution spectra look? Was there considerable mass/volume at the highest size and could this be an indication that some particles >500nm were omitted in the SMPS measurements? Few particles at that size can already contribute a large portion of the aerosol mass.
- 15) There is no mention of any O₃ scrubber being used. Was this indeed the case?
- 16) Line 155ff: I do not agree with the interpretation of SOA volatility from the yield data in this way. To me the point is that decaline produces a larger fraction of low volatility material already at low VOC conc. The acyclic ones produce less of those compounds. Hence, less SOA is formed. But the volatility of the condensing products cannot be derived from this. E.g., let’s assume that the system allows particle phase partitioning of compounds with $C^* < 1e-4$ ug/m³. VOC 1 has 10% of its oxidation products with $C^* = 1e-4$ ug/m³ and nothing below that. VOC 2 has 1% products at $C^* = 1e-6$ ug/m³. VOC 1 will form more SOA than VOC 2. At low precursor concentrations, VOC 2 may not

form any SOA as it does not create high enough concentrations to initiate nucleation (wall losses may also play a role). At higher precursor concentrations, SOA is formed in both cases. But the volatility of the SOA would be higher for VOC 1 than for VOC 2 – so the opposite of what would be expected from the SOA yield.

A real example for a precursor with lower aerosol yield and also lower SOA volatility is the comparison of SOA from farnesene and α -pinene in (Ylisirniö et al., 2019).

My point here, aerosol yields cannot be interpreted directly into SOA volatility in this way without further composition information or information about the volatility distribution of the gas and particle phase products.

- 17) Section 3.1.2: was the basic parametrisation (Aiken et al., 2007) or the “improved” parametrisation (Canagaratna et al., 2015) used to derive O:H and H:C values from AMS? This should be stated in the methods section.
- 18) Line 191ff: The trends of O:C with overall yield seem to suggest that higher yields are linked to higher O:C values. But the decanal points are all >0.5 while decaline and butylcyclohexane shows O:C values that go much lower. But all decaline and butylcyclohexane points have a higher yield than even the highest decanal points. With this in mind, can the authors really make this claim about the trends?
- 19) Section 3.1.2: Both H:C and O:C values vary for all precursors. Did the authors look into using OSc (average oxidation state of carbon), a parameter which combine O:C and H:C, instead of just individually O:C and H:C? Would that reveal clearer trends?
- 20) Line 210ff: if the conditions were so different (namely VOC to oxidant ratio and residence time), are the HOM yields representative for this study?
- 21) Generally, HO₂ concentrations are very high in PAM when operated at low NO_x (very little recycling back to OH). How would that affect HOM production. Don't higher HO₂ concentrations enhance the quenching of RO and RO₂ radicals and thus suppress auto-oxidation type processes?
- 22) Fig 4: I wonder how useful this figure/comparison is knowing about the limitations of the HOM data. It may be doing more harm than good. Playing devil's advocate, I can look at this figure and state that decanal can show a aerosol yield of 0.08 with molar HOM yield of $\sim 3 \times 10^{-2}$ and decanone can have the same aerosol yield with “no HOM at all”. Thus, HOM cannot be that important for aerosol yields Looking only at the precursors that had a measurable HOM yield, I could claim that and increasing HOM yields show decreasing aerosol yields (decanal & decanol vs decaline and butylcyclohexane).
- 23) Line 237:”and thus high injected VOC concentrations will lead to the majority of OH radicals reacting with the VOC. “ I'm not sure if this is strictly true for PAM. A lot of the OH radicals will also react with O₃ (which is at 10s of ppm I assume).
- 24) Line 230ff: Only C₁₀ HOM compounds were investigated for the evaluation of the first/second generation products. Does this interpretation hold when other HOM species are included (e.g. with C₉ or C₈)?
- 25) Line 230ff: Does C-C bond cleavage become more important on successive oxidation? If that is the case, would that not mean that some of the second generation product are no longer C₁₀ and thus “hide” as C <10 HOM? Could this be more pronounced for acyclic compounds?
- 26) Line 230ff: This analysis (first/second generation) is only based on the gas phase data. If the multi gen products of decanal etc. are just a bit more low-volatility, they could be condensing into the particle phase, hiding from the gas phase measurements. Then it would look like there is less of them in the gas phase, right?
- 27) Line 273ff: I do not agree with finding “a clear link between the two yields” (see specific comment 22). If anything, the combination of the Wang et al. and this new study shows how much the experimental setup and chosen reaction conditions can impact the formed and detected HOM amounts and types. Thus, great care must be taken in the experiment design and when comparing HOM data from different studies.

28) Fig A1: This figure needs more explanations in the caption. None of the acronyms/abbreviations are explained. The main text does contain most of the information, but this figure will become much easier to understand if the information is also provided directly with it.

Language

+ line 11: “emitted in the atmosphere” – should be “emitted into”

+ line 112 “got enough of sample flow” – I would omit the “of”

+ line 212 “chosen from them” who is “them”? I guess the authors mean the Wang paper? Please rephrase to make clearer what the “them” is referring to.

+ line 235f: The way the increase/decrease trends are assigned in this sentence was a bit hard to wrap my head around. To paraphrase: “decrease of A to B ratio with increasing VOC conc means that lower VOC conc increases second gen oxidation” Consider rephrasing this. “the ratio of second to first generation product ions increased with decreasing VOC conc, i.e., lower precursor conc ”

+ line 237: “OH generation” maybe better use “OH production” to differentiate from the other meaning of the word generation (reaction generation) which is used in the same paragraph.

References

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