

Interactive comment on “A comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO₂” by D. C. Draper et al.

Anonymous Referee #1

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Interactive comment on "A comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO₃" by Draper et al. Anonymous Referee #1

Draper et al. present results from laboratory experiments investigating the effect of varying NO₂ concentrations on ozonolysis (and subsequent SOA formation) of four different biogenic terpenoids: alpha-pinene, beta-pinene, delta-3-carene, and limonene. These are the first reported results on this topic for a range of different monoterpenes

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rather than using alpha-pinene alone as a “model compound”. The results demonstrate different effects for different monoterpenes and thus highlight the importance of this research related to biogenic SOA formation via nitrate radical chemistry. Authors also demonstrate the effects of nitrate chemistry on resulting SOA composition, and postulate that the higher molecular weight compounds that emerge in the high NO₂ scenarios point to oligomerization as a key mechanism for SOA production from reactions with nitrate radical. Furthermore, the lack of high molecular weight compounds in alpha-pinene/NO₂ experiments could explain the low SOA yields observed here and previously from the alpha-pinene/NO₂ system. The results are well within the scope of ACP and constitute a valuable contribution to the existing literature on biogenic SOA production by filling in important gaps related to biogenic SOA production from nitrate radical chemistry. Overall the paper is very well-written and organized in a logical manner. Particular strengths of this paper are presented in results from Section 3.1 that compare aerosol formation trends under different experimental scenarios and results from Section 3.5 that compare SOA composition between the different experimental scenarios. There are some major weaknesses in Sections 3.2-3.4 that are discussed in detail in the comments below. Specifically, all results and discussion related to the SOA yield comparisons will need to be significantly revised before final publication in ACP.

General Comments

SOA Yields

As stated in the title of this manuscript, comparing “SOA yields” between different experimental scenarios was a major objective of this research. However, it is quite clear that the experimental set-up and design were not optimized to make comparisons of SOA yields between the experiments. I have listed the major concerns with regard to the SOA yield calculation/discussion with associated explanations below.

1) Yield is calculated as the amount of organic aerosol mass produced from the mass

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of VOC reacted. Consequently, accurately measuring the mass of VOC reacted is crucial for calculating SOA yields. The authors used a GC-FID to measure monoterpene concentrations at the outlet of the Reed Environmental Chamber (REC), but did not directly and continuously measure the monoterpene concentration at the inlet (Figure 2; P. 14928 L. 27-29; P. 14929 L. 1-4; P. 14931 L. 2-5). While it is true that the initial VOC concentration was measured from the source flask before and after each experiment (P. 14928 L. 27-29), the authors also state that the “Source concentrations were somewhat variable over time” (P. 14929 L. 2). The authors dealt with this issue by modeling the initial VOC concentration based on the measured change in oxidant concentrations, which obviously introduces additional uncertainties to SOA yield calculations that could have been avoided with a simple modification to the set-up. Why was the GC-FID only sampling from the REC outlet and not from both the inlet and outlet? Sampling from the inlet and outlet is a commonly used approach for flow-through SOA chamber experiments with a variable VOC source (i.e. Joutsensaari et al., 2015; Mentel et al., 2009; VanReken et al., 2006). This approach allows one to calculate reacted VOCs in the chamber from the difference between measurements of the inlet and outlet concentrations. The authors do not provide suitable justification for why this approach was not used. On P. 14928, L. 27-28, authors state, “Since experiments were initiated by introducing BVOC into an oxidant-rich chamber, online measurement of the reaction of the BVOC was not possible”, but this is an unsatisfactory defense because this would in no way prohibit VOC monitoring at the inlet and outlet with a simple valve-switching system.

2) In the absence of VOC measurements at the inlet and outlet, the modeling approach utilized here could provide a less-than-ideal, but reasonable, alternative. For example, no yields were presented for the highest NO₂ experiments because of difficulties modeling the initial VOC under these conditions (P. 14932 L. 9-11). This highlights the fact that using this modeling approach to calculate the yields is not the best approach for an experiment with the objective to compare SOA yields. A brief discussion of the model uncertainties was provided on P. 14931 L. 11-22. A much more detailed discussion of

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the model uncertainties including comparisons with measurements is presented in the supplement on pages 4-6 (section entitled “BVOC measurement and characterization of uncertainties”). If one of the major objectives of this work is to discuss SOA yields then this information should be included in the main body of the text rather than the supplement because it has significant implications for interpreting the SOA yield results. For example, on page 5 of the supplement the authors state that the estimated yields presented in the manuscript in Table 3 “would be lower limits to the true yields” based on their measurement/model comparison. This is important information that should not be tucked away in the supplement.

3) On P. 14931 L. 23-15, the authors state that the SOA yields were not constant in a given experiment and go on to say that the SOA yields they present in Table 3 are the “maximum yield observed during the course of the experiment”. This is not a meaningful or appropriate approach to calculate and compare SOA yields between experiments using a flow-through chamber. A flow-through chamber will eventually reach a steady-state condition after a period of time dependent on the chamber residence time (an important number that was not provided anywhere in the manuscript). For flow-through chamber experiments, SOA yield should be calculated from the steady-state condition. This is in contrast to a batch chamber experiment where time-dependent SOA yields could be meaningful assuming only first-generation oxidation products contribute significantly to SOA growth (Ng et al., 2006). Based on the schematic in Figure 2, I estimated the residence time in the REC would have been approximately 90 minutes. Thus steady-state would likely not be reached until at least two (or possibly three) chamber lifetimes—3 to 4.5 hours. The SOA yield results that were presented were calculated within the first two hours of introducing VOCs to the REC (P. 14931, L. 27) so it is evident that the chamber had not reached steady-state. This “maximum yield” is not a meaningful number for this experimental design. Furthermore, the yield presented in Table 3 is actually not always the “maximum yield”, which immediately calls into question making any comparisons between the yields; authors state on P. 14931 L. 27-28 and P. 14932 L. 1-3, “In some cases, the aerosol growth rapidly exceeded the

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size range of the SEMS (20-800 nm). Aerosol data presented here is truncated as soon as the size distribution exceeds the range of the SEMS instrument and is represented as a lower limit to the maximum aerosol yield because all subsequent data will be an underestimation of mass." It is not clear from Table 3 which experiments exceeded the SEMS range and represent the "lower limit to the maximum aerosol yield". Was it just the beta-pinene experiments (this guess is based on Figure 3)? Regardless, none of these yield values were calculated from the steady-state condition in the chamber and an unidentified number of "some cases" were calculated at a different point than the others prohibiting any comparisons between them and other literature values.

4) In addition to the concerns raised above in comments, there are also some serious concerns about the authors' interpretation of the SOA yield data. On P. 14932 L. 4-5 the authors state, "With the mass yield effectively normalizing these mass yields across varying ΔHC [...]". This statement displays a serious gap in understanding about factors affecting SOA yields. SOA yield is affected by a complex suite of variables including, but certainly not limited to, precursor concentration (Kang et al., 2011; Kroll et al., 2008; Pfaffenberger et al., 2013; Presto and Donahue, 2006), seed particle composition/loading (Ehn et al., 2014; Hamilton et al., 2011), and mass of absorbing organic aerosol material present in the chamber (Pankow, 1994; Odum et al., 1996). Presumably no seed was used in these experiments (because it was not stated anywhere in the manuscript) and perhaps the range of VOC concentrations used was not variable enough to have a major effect on yields (substantially higher concentrations can push equilibrium toward partitioning of higher volatility compounds to the condensed phase), but the mass of organic aerosol was clearly quite different between experiments (Figure 4). The authors recognize that this could be a factor on P. 14933 L. 10-11 "[...] which may simply be explained by having the lowest background aerosol mass and thus smaller absorptive partitioning contributions", but then they continue to make general comparisons between the different scenarios using the calculated SOA yields anyway. To present the SOA yields in more meaningful way, the mass of organic aerosol that was used to calculate the yields in Table 3 must be included in the

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table to be of any use for other researchers for making future comparisons with other SOA yield data. I would also recommend including the reacted hydrocarbon concentration and the initial hydrocarbon concentration as these numbers are also critical for interpreting the SOA yield data presented here. This would be valuable information to make available to the atmospheric chemistry community in general and could allow future comparisons of SOA yields from other experiments. However, to meaningfully compare SOA yields between different scenarios, SOA yield curves would need to be generated under each condition. Comparing yields at different organic aerosol loadings is not appropriate. For example, the yield of alpha-pinene can vary anywhere from 1%-35% depending on the organic aerosol loading in the chamber (Donahue et al., 2012, Figure 2). Consequently, in contrast to the statement made by the authors, calculating the yield alone does not "normalize" the yield values for comparison with one another. Ideally, there would be repeated experiments within each scenario spanning a range of different organic aerosol mass concentrations (Yield vs. Organic Aerosol Mass). Then, these mass yield curves for each scenario could be compared with one another. With the data presented here, this is unfortunately not possible, but the authors should not compare the yields between experiments. Comparisons between the yields is erroneously interpreted throughout the manuscript (i.e. P. 14932 L.6-9; P.14933 L.20-28; P. 14936 L. 14-15; P. 14937 L. 11)

Ultimately, the results and discussion related to "SOA Yield" constitute the weakest parts of this manuscript. The yield data should still be included (with the additional information in Table 3 included as I suggested above), but the emphasis on comparing the SOA yields between the experimental scenarios needs to be reduced. As a research community, we are already aware of the many factors that can affect SOA yields, and I think it is very important that we are more careful about how we present this type of data and how we use it to make comparisons between different chemical systems. I strongly suggest moving the emphasis of the paper away from a focus on SOA yields to focus more on the stronger sections/results. The data presented in Section 3.1, Figure 3 provides enough information to support authors' conclusions about nitrate effects on

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SOA production without making comparisons between yields that were calculated and interpreted in a potentially questionable manner. I would also recommend changing the title of the manuscript accordingly to be less focused on the SOA yield results.

Section 3.4: Determination of dominant nighttime oxidant using NO₂ to BVOC ratio
This section did not use any of the experimental laboratory data and was disconnected from the rest of the paper. The implications of the quick calculations performed here were potentially very interesting and valuable. However, to constitute an entire section of the manuscript it needs to be integrated into the rest of the paper more smoothly. For example, it could potentially fit better after all the laboratory measurements have been presented, after Section 3.5. It could also be strengthened with some elaboration. For example, how variable was the NO₂/BVOC ratio in the Fry et al., 2013 study? Authors calculate a crude NO₂/BVOC ratio by stating the nighttime peak of the BVOC concentration and the nighttime peak of the NO₂ concentration, but it is not stated anywhere that these two components peak at the same time during the night. Providing a range of the measured nighttime NO₂/BVOC ratios would be more useful and convincing.

Specific Comments

P. 14926 L. 24-26: "Ozonolysis of α -pinene has been previously observed to have high aerosol yields (Ng et al., 2006) but strikingly low (0-16%) SOA yields with NO₃". A range of yields is provided for the nitrate radical yields, but ozonolysis yields are simply described as "high". Please provide a quantitative range for ozonolysis yields of alpha-pinene for better comparison with the range provided for nitrate radical.

P. 14927 L. 23-24: how long did it take to reach steady-state? What was the residence time in the chamber? How does the ratio of O₃/NO₂ used in these experiments compare to ambient levels? What about absolute concentrations of O₃ and NO₂ compared to ambient levels?

Section 2, Methods: Please describe the procedure used to clean the chamber between experiments. Were these experiments unseeded? Please make this clear. Also,

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recent research has shown that yields can be significantly impacted by seed concentrations (Ehn et al., 2014; McVay et al., 2014; Zhang et al., 2014a, 2014b). Please include a short discussion about implications of these findings for the yields presented in this paper.

P. 14929 L. 2 "Source concentrations were somewhat variable over time". Please be more specific and provide a quantitative description of the variability.

P. 14931 L. 15: Please be more specific/quantitative about "reasonably well known" regarding the rate constant for RO₂ + NO₃. There should be a quantitative uncertainty associated with the rate constant.

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