We thank the reviewers for the detailed and insightful comments. We have addressed the reviewers' comments point by point as indicated below.

Reviewer #1:

This paper shows some interesting results from a novel experiment involving taking ambient air in an urban environment and conducting a chamber experiment after enhancing the concentrations of VOCs. The main emphasis of this paper is the use of α-pinene and β-caryophylene, the characterisation of the SOA produced using aerosol mass spectrometry and inferences are drawn regarding their contribution to particulate concentrations in the region.

1. Overall, this is a nice piece of work and well within the journal's remit. However, I do think that the significance is a little overblown in places and the authors need to express more caution in how they interpret some of the results. In spite of their statements otherwise, this is not a true simulation of atmospheric processes (see below), there are a few PMF-specific subtleties that aren't taken account of and how reliably this can be projected onto the wider world is open to question on a number of levels. But in spite of these issues, the conclusions are largely sound and this deserves to get published. I therefore recommend publication with minor revisions.

Response: We thank the reviewer for the thoughtful insights. To address the reviewer's major concerns, we have toned down the significance of our conclusions and expanded discussions on PMF-specific subtleties in the revised manuscript. We think that the lab-in-the-field experiments can mimic certain atmospheric processes, shed light on understanding the sources of OA factors, and reflect potential issues that PMF analysis encounters. These responses will be discussed in detail when we address the reviewer's specific comments. Meantime, we agree with the reviewer that more studies are warranted to test the reliability of our conclusions to the wider world.

General Comments:

2. This paper makes the assumption of α-pinene and β-caryophylene being representative of monoterpenes and sesquiterpenes respectively. While these are common assumptions made in the community and the VOCs are both very well studied, their overall representativeness is in question because the level of oxidation in SOA from different precursors are known to vary substantially between compounds (Alfarra et al., Atmos. Chem. Phys., 13, 11769-11789, 10.5194/acp-13-

11769-2013, 2013). This is especially true of the sesquiterpenes, as difficulties in working with a number of these compounds means that we lack data on a large subset of these. This should be discussed and any evidence to support this assumption properly cited.

Response: In this study, we selected α-pinene and β-caryophyllene as representatives due to the following reasons. Firstly, both VOCs are widely studied in the literature. Secondly, they are the most abundant species in monoterpenes and sesquiterpenes, respectively (Guenther et al., 2012; Helmig et al., 2007). Thirdly, the mass spectra of SOA from VOCs in the same class generally share similar features. For example, the correlation coefficient (i.e., R) between the mass spectra of SOA from the β-caryophyllene and α-humulene is 0.97 (Bahreini et al., 2005). Still using the mass spectra reported in Bahreini et al. (2005), the R between α-pinene SOA and other monoterpenes SOA (β-pinene, α-terpinene, myrcene, and terpinolene) is larger than 0.9. Fourthly, in addition to the similar mass spectra, the time series of α-pinene in the southeastern U.S. is similar to that of other monoterpenes, such as β-pinene and camphene (Xu et al., 2015a). The above reasons have been added in the revised SI. We also add a caveat that future studies using other monoterpenes and sesquiterpenes are still in need.

We agree with the reviewer that many properties of SOA (i.e., yield, hygroscropicity, etc) from different monoterpenes or sesquiterpenes are different. To be precise, we have replaced "representative" with "important" in some sentences in the revised manuscript.

3. Throughout the manuscript, there is a general tendency to treat LO-OOA and MO-OOA as defined chemical entities, whereas the truth is that these represent reductions of highly complex chemical systems and the exact factors reported are known to vary dataset to dataset. While common trends have been noted in terms of behaviour and mass spectral profile, their exact mass spectral nature depends on the measurement location and season and in many cases (particular in the wintertime), PMF will fail to separate them at all, instead returning a single OOA factor. This must be discussed in a meaningful manner in the introduction and discussion because it adds an extra layer of nuance to the results.

Response: We agree with the reviewer that OA factors from PMF analysis represent complex chemical systems. Understand what these OA factors represent is one of many motivations of this study. In the revised manuscript, we have modified the language to avoid the confusion to treat OA factors as defined chemical entities. We also agree with the reviewer that the exact mass spectral nature of OA factors varies with locations. We would like to point out that the mass spectra of LO-OOA are highly similar (R > 0.95) across all the seven datasets in our study (Fig. R1). This is one of many evidence to suggest that LO-OOA at different datasets may have similar sources. Regardless, we clearly limit our conclusions to the southeastern U.S.

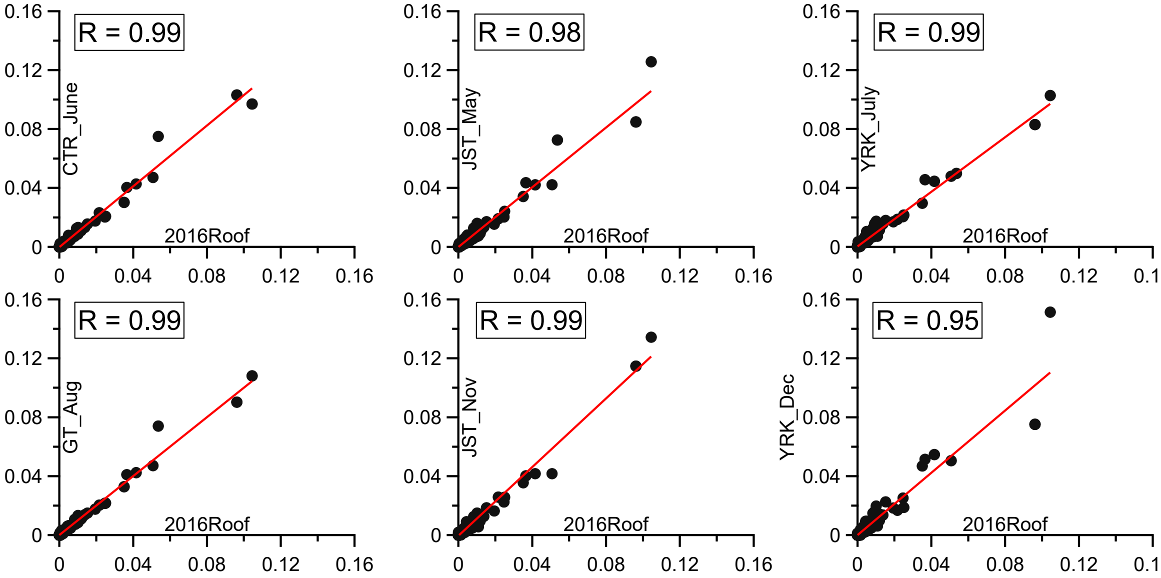

Fig. R1. The correlation plot between the mass spectrum of LO-OOA for 2016 rooflab perturbation study and the LO-OOA obtained in other six ambient datasets in the southeastern U.S.

In the introduction and implications sections of the revised manuscript, we have added the discussion that a single OOA factor is resolved in some cases, especially in winter.

4. Related to the above point, there seems to be a general assumption that PMF had adequately accounted for the new SOA being formed, but in my mind, the decrease in MO-OOA in response to the β-caryophylene experiments in particular raises a number of red flags because this implies that the data model didn't hold and the factorization wasn't sound. The authors need to pay much closer attention to whether the factorisations 'worked' or not; a good starting point would be inspecting the residuals (e.g. Q/Qexp) as a function of time over the course of the experiments and if they positively correlate at all with the amount of additional SOA, this would imply that PMF has failed to capture the chemistry perfectly.

Response: We agree with the reviewer that the decrease in MO-OOA after β-caryophyllene injection raises a red flag and implies that factorization is not perfect. We have examined the PMF residual (i.e., Q/Q_{exp}) in α-pinene and β-caryophyllene perturbation experiments. As shown in Fig. R2a, in α-pinene experiments, the difference in Q/Q_{exp} between “Chamber_Bf” (before α-pinene injection) and “Chamber_Af” (after α-pinene injection) is not statistically significant. This suggests that PMF analysis has adequately accounted for the newly formed α-pinene SOA. This is consistent with the observation that in α-pinene experiments, no OA factors show unexpected dramatic decrease after α-pinene injection.

In contrast, in β-caryophyllene experiments, there is a clear pattern that Q/Q_{exp} in “Chamber_Af” is larger than that in “Chamber_Bf” (Fig. R2b). This is likely because of the rapid change in the subtleties of OA composition caused by the newly formed β-caryophyllene. However, the behavior of Q/Q_{exp} is not quite expected because the OA mass spectra after injecting β-caryophyllene are almost identical to those before perturbation (i.e., R between Chamber_Bf and Chamber_Af is >0.99 as shown in Fig. R3b). The larger Q/Q_{exp} in β-caryophyllene experiments than α-pinene experiments may be a result of that ΔOA (i.e., the difference in OA concentration between “Chamber_Af” and “Chamber_Bf”) is larger in β-caryophyllene experiments (average value 1.95 μg m^{-3} over 6 experiments) than α-pinene experiments (average value 0.98 μg m^{-3} over 14 experiments). Regardless, under the simulated circumstances, PMF analysis cannot adequately capture the newly formed β-caryophyllene SOA.

We would like to clarify that our conclusions are not dependent on if PMF has perfectly accounted for the newly formed SOA, mainly because similar issues could also happen in the analysis of ambient data. The β-caryophyllene perturbation experiments simulate a scenario when there is a sudden change in the OA composition caused by an airmass encountering a plume or change in OA sources due to shift in wind direction. Under these circumstances, PMF analysis may have difficulty in accurately apportioning the OA sources. The simulated scenarios and the observed PMF issues have been observed in previous studies. For example, in the Figure 9 of Sun et al. (2016), an increase of hydrocarbon-like OA (HOA) is usually accompanied by a decrease in cooking OA (COA) and verse vice. Another example is that figure 5 of Reyes-Villegas et al. (2018) showed that a biomass burning plume leads to unexpected rapid variations in the concentration of many OA factors on the time scale of minutes. Last example is that in the figure S10 of Milic et al. (2017), the PMF residual during a biomass burning plume is orders of magnitude higher than other sampling periods. Emphasizing the limitations of PMF analysis is one goal of this study.

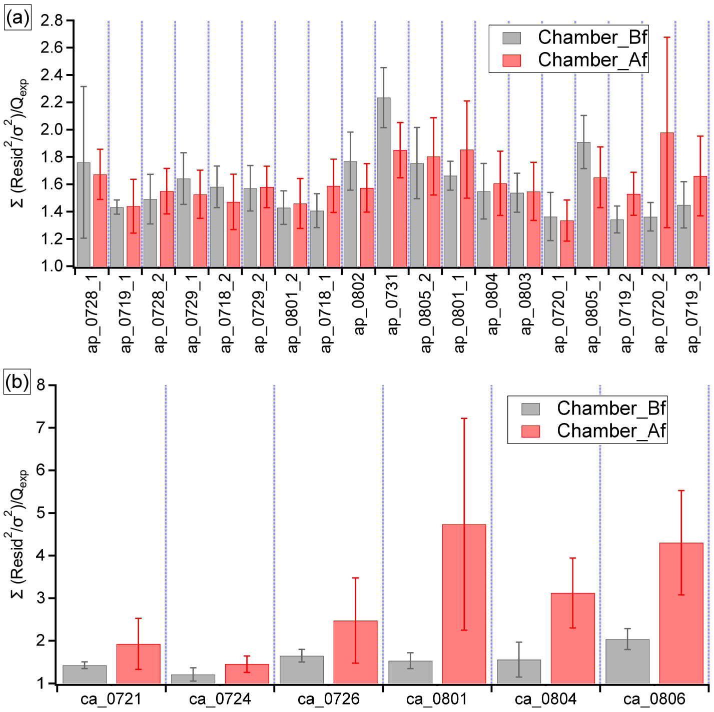

Fig. R2. The PMF residual (Q/Q$_{exp}$) during "Chamber_Bf" and "Chamber_Af" periods for (a) α-pinene and (b) β-caryophyllene perturbation experiments.

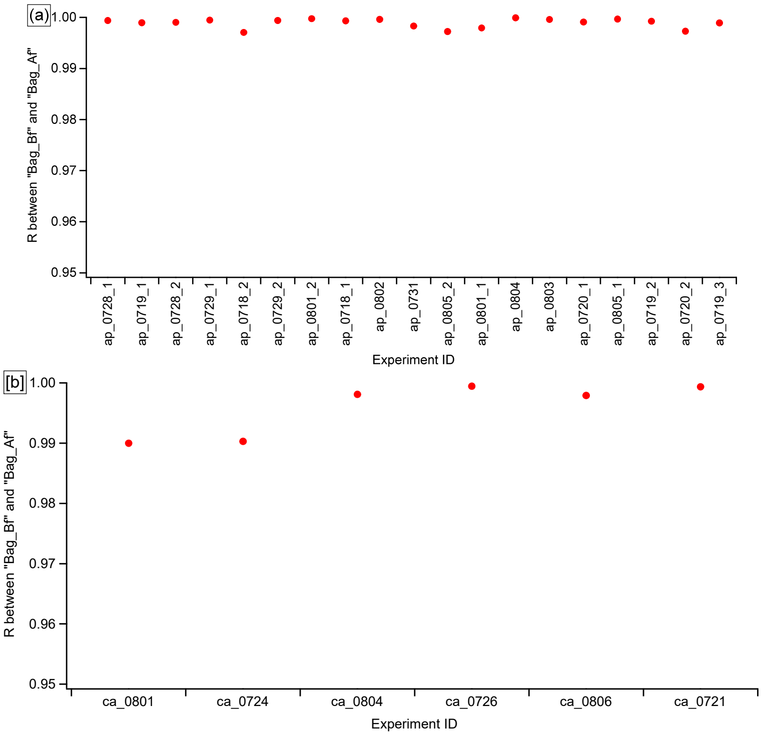

Fig. R3. The correlation coefficient by comparing the OA mass spectra between "Chamber_Bf" and "Chamber_Af" in (a) α-pinene and (b) β-caryophyllene perturbation experiments.

5. The modelling work presented in section 3.6 left me slightly confused as to what the authors were trying to achieve and how. The text in the main article would suggest that an updated scheme is being compared with a very old one, but the supplement seems to say that specific mechanisms have been added here. This must be clarified.

Response: We use the modelling work as one of the evidence to support our hypothesis that the major source of LO-OOA in this region is the oxidation of MT and SQT by various oxidants. In section 2.6, we described two simulations (i.e. “default simulation” and “updated simulation”) with different organic aerosol treatment. Compared to “default simulation”, we incorporate two recent findings in the “updated simulation”. Firstly, we implemented MT+NO_3 chemistry to explicitly account for semivolatile organic nitrate compounds that contribute to SOA. Secondly, we improved the parameterization of SOA formation from MT+O_3/OH based on a recent study by Saha and Grieshop (2016). In section 3.5 of revised manuscript, we pointed out that SOA_{MT+SQT} in the updated simulation reasonably reproduces the magnitude and diurnal variability of LO-OOA for each site. The model bias is within ~20%. The reasonable agreement between modeled SOA_{MT+SQT} and LO-OOA at multiple sites and in different seasons serves as one piece of evidence to support our hypothesis that LO-OOA largely arises from the oxidation of MT and SQT in the southeastern U.S.

6. Also, as pointed out later in this section, this work does not directly preclude that other precursors may be contributing and the discussion dealing with this relies heavily on inferences drawn from the literature, so this work isn’t really that dramatic a result in how it is presented now. I would suggest a more defined modelling experiment is constructed around a clear working hypothesis. This could just be a case of making the work shown here clearer and moving material from the supplement to the main article.

More generally, I noted a very odd tendency to leave certain pertinent (and in many cases interesting) details in the supplement that maybe should have been given more prominence or at least linked to the main article better. For example, the box modelling described in section S6 was very interesting, but it wasn’t clear at all how this fit into the narrative of the main article. I also had a hard time reconciling the information about the CMAQ runs in the main article and the supplement as well (see above). I would revise what information goes where, using the main article *for the discussions relating to the scientific arguments and making sure the material in the supplement is purely technical detail in support of this.*

Response: We have toned down the significance of conclusions in the revised manuscript. We have also re-organized the main text and SI, and improved the linkage between two parts. Many details, although interesting, are kept in the Appendix or SI, because we prefer to focus on the main message and keep the logic of manuscript easy to follow.

Specific comments:

7. Line 95: When saying 'representative urban', please be specific about what type of urban site this (e.g. background) and how you qualify this statement.

Response: We have deleted the word "representative".

8. Line 115: What counts as 'too much' SOA and why?

Response: As discussed in response to reviewer's comment #4, when there is a sudden change in the OA composition, PMF analysis may have difficulty in accurately apportioning the OA sources, as shown in β-caryophellene perturbation experiments and previous studies. This is why we tried to avoid producing too much SOA in the perturbation experiments.

It is challenging to quantify what counts as "too much". As shown in β-caryophellene perturbation experiments, even though (1) the newly formed β-caryophyllene SOA only increases the OA concentration by roughly 2 μg m^{-3} and (2) the OA mass spectra after injecting β-caryophyllene are almost identical to those before perturbation (i.e., R >0.99 as shown in Fig. R3b), PMF analysis encounters difficulty in accurately apportioning the OA sources.

9. Line 265: It has long been shown that α-pinene SOA produced in chambers produces a mass spectrum that is similar to LO-OOA and given that this mass spectral profile is also seen in the presence of strong emitters of this VOC (e.g. temperate and boreal forests), the case for α-pinene SOA being a strong contributor to LO-OOA has never really been in doubt in this reviewer's opinion. Why is the evidence presented here any more 'direct' than those published previous? While the perturbation experiment does indeed produce LO-OOA as retrieved using PMF, this retrieval is still based solely on mass spectral similarity, so I would contend that this does not really present any new evidence to this effect.

Response: We thank the reviewer for pointing this issue out. The “directness” of our conclusions is not clearly communicated in the original manuscript and caused some confusions. While we acknowledge that the mass spectra comparison approach largely improves our understanding of OA factors, we think that the perturbation experimental approach provides more objective and quantitative conclusions by addressing some limitations of the mass spectra comparison approach. The mass spectra comparison approach has the following limitations. Firstly, the similarity between two mass spectra is a subjective determination. In other words, what correlation coefficient ® value implies SOA from a certain source contributes to one OA factor? For example, the R values between laboratory-generated α-pinene SOA (using HONO as OH source) with LO-OOA, isoprene-OA, and MO-OOA in this study are 0.96, 0.88, and 0.81, respectively. Using these R values to imply whether α-pinene SOA contributes to a certain OA factor or not is subjective. As another example, Jimenez et al. (2009) showed that the mass spectrum of α-pinene SOA becomes more similar to that of MO-OOA (i.e., LV-OOA in older study) than that of LO-OOA (i.e., SV-OOA in older study) with photochemical aging. The ability to determine when and how much α-pinene SOA is apportioned to MO-OOA based on an R value is subjective. Secondly, the conclusions from mass spectra comparison approach are qualitative. Even if the mass spectrum of α-pinene SOA is the most similar to LO-OOA, this similarity does not guarantee that all α-pinene SOA is apportioned into LO-OOA and this similarity does not provide information regarding what fraction of α-pinene SOA is apportioned into LO-OOA.

The perturbation experiments could address the limitations of mass spectra comparison approach and provide more objective and quantitative conclusions. Firstly, the perturbation experiments simulate a short period of time with increasing α-pinene SOA concentration. we perform PMF analysis on the combined ambient data and perturbation data. PMF analysis does not distinguish SOA from natural α-pinene vs. from injected α-pinene, so that PMF analysis can objectively apportion α-pinene SOA into factors. Thus, the conclusions from the perturbation experiments are directly drawn without any subjective judgement on the similarity in mass spectra. Secondly, using the perturbation data, we attempt to quantify the fraction of fresh α-pinene SOA that is apportioned into different factors (i.e., ~80% into LO-OOA, ~20% into isoprene-OA, 0% into MO-OOA, COA, and HOA). Although further studies are required to extrapolate the conclusions from perturbation experiments to real atmosphere, a similar quantitative understanding cannot be obtained from simple mass spectra comparison approach. Thirdly, the perturbation experiments have the potential to utilize subtle differences across the entire the mass spectrum to evaluate the sources of OA factors. Based on previous laboratory study, the mass spectrum of α-pinene SOA is highly correlated (R = 0.97) with that of β-caryophyllene SOA (Bahreini et al., 2005). Using a mass spectra comparison approach would suggest that these mass spectra are too similar to be differentiated by PMF analysis. However, perturbation experiments show different behaviors of α-pinene SOA and β-caryophyllene SOA. That is, a fraction of the fresh β-caryophyllene SOA is apportioned into COA factor, but similar behavior is not observed for α-pinene SOA. The different behaviors are likely due to the subtle differences in their mass spectra. For example, f_{55} (i.e., the ratio of *m/z* 55 to total signal in the mass spectrum) is typically higher in β-caryophyllene SOA than α-pinene SOA (Bahreini et al., 2005; Tasoglou and Pandis, 2015), and the mass spectrum of COA is characterized by prominent signal at *m/z* 55 (Fig. 2). Overall, the perturbation experiments provide more objective and quantitative insights into the sources of OA factors than traditional mass spectra comparison approach.

We have added the above discussions in the revised manuscript.

10. Line 280: The fact that the oxidation rate of VOCs is dependent on oxidant concentration is very well established in kinetics. The discussion regarding this observation would be considered pointing out the obvious to many. It would be far more useful if a quantitative relationship with ozone concentration could be reported here.

Response: In Line 280, we are not making the conclusion that the oxidation rate of VOCs depends on oxidant concentration. Instead, we use this well-established conclusion to explain our observation that the LO-OOA enhancement amount correlates with oxidant concentration. As the SOA formation depends on a number of variables, including temperature, relative humidity, the concentrations of oxidants, NO_x, and existing particles, etc, the VOCs oxidation rate is not equivalent to SOA formation amount. In this study, the α-pinene perturbation experiments were conducted at different times of day (i.e., from 9am to 9pm) and under different conditions (i.e., T, RH, oxidant, NO_x, etc). Despite the large difference in reaction conditions, the LO-OOA enhancement amount correlates well with O_3 concentration, suggesting that the oxidant concentration plays a more controlling role in the amount of OA formed in α-pinene experiments than other reaction variables do.

As a side note, we also want to point out that the oxidant concentration is not the sole variable in determining the SOA formation from β-caryophyllene, which is in contrast to α-pinene experiments. As shown in Fig. S22 in revised SI, the LO-OOA enhancement amount in β-caryophyllene perturbation experiments is greatly affected by NO_2 level. For example, for two experiments with similar O_3 concentration and injection time, more LO-OOA is formed in the experiment with a lower NO_2 level (Fig. S22f in revised SI).

11. Line 286: An alternative explanation here is that the experimental set-up here was not conducive to HOM formation for whatever reason. This should be added as a caveat.

Response: We agree with the reviewer and have added this caveat in the revised manuscript.

12. Line 309: There is a major problem with this statement; the results indicate that the β-caryophylene SOA spectrum to be represented by PMF as a combination of the LOOOA and COA mass spectra, but it would be a mistake to imply in any way that it is producing two 'types' of OA (this is clarified later in the manuscript but it is ambiguous here). Issues about the quality of the PMF retrieval aside (see above), in the hypothetical situation that there is an environment with a mixture of cooking and biogenic SOA, PMF will likely still separate these because it determines factors not just by mass spectral profile but by temporal profile, so would still return factors corresponding to cooking and an average of biogenic SOA from all sources. The only situation I could think where this would be a problem is if monoterpene and sesquiterpene SOA formation were not well matched temporally, in which case I could see how the COA-like component of sesquiterpene SOA would manifest as 'mixing' between the cooking and biogenic SOA factors, but this would be evident in the temporal profiles.

Response: We agree with the reviewer that PMF separates factors based on features in both mass spectrum and time series. However, we note that the temporal variations of COA and SOA from monoterpenes and sesquiterpenes do not guarantee a clean separation between different sources. For example, the concentrations of many oxidation products of monoterpenes (e.g. pinonic acid, pinic acid, etc), COA, and LO-OOA show similar increasing trend near sunset (Allan et al., 2010; Xu et al., 2015b; Zhang et al., 2018). The emissions of sesquiterpenes and diurnal variations of sesquiterpene SOA are not well-studied. Thus, it is possible that some sesquiterpene SOA is apportioned into COA.

As mentioned in the manuscript, we agree with that COA is mainly from cooking emissions. However, the perturbation experiments show the possibility that COA could include β-caryophyllene SOA. There is no evidence in the literature to support that cooking OA factor is purely from cooking and does not have any biogenic SOA.

13. Line 350: How much more 'realistic' is this? While this would give a more life-like oxidant and NOx background, given that the chamber walls will act as a sink of VOCs, radicals and particles, I would still expect that the precursor perturbations would have to be higher than typical atmospheric concentrations to achieve realistic SOA concentrations and consequently have a higher VOC:NOx ratio. This must be discussed in an objective manner and while some of this is touched on in the supplement, it's kind of glossed over in the main article.

Response: We would like to clarify that we did not want to produce realistic SOA concentration. Instead, we aimed to produce small amount of SOA, which would not significantly perturb the composition of existing organic aerosol. Based on the chamber volume and injected α-pinene volume, we injected about 14ppb α-pinene. Most of injected α-pinene is carried out of the chamber by dilution air and we estimated that only 2-5 ppb α-pinene is reacted in the chamber. We have added this information in the main text.

14. Figure 6: The caption of this figure is excessively long.

Response: We prefer to keeping the caption descriptive of the figure, such that the readers could comprehend the figure after reading the caption.

15. Line S477: This doesn't make sense. Why would the solver reduce the concentration of MO-OOA because it had been added to? I find it more likely that there was a breakdown in the data model and mass was being erroneously rotated out of the factor. This is undesirable, but also feeds into the discussion above regarding the relationship with COA.

Response: As stated in the SI, the reason why MO-OOA decreases after adding β-caryophyllene is unknown. One possible explanation is that since the mass spectrum of β-caryophyllene SOA is more similar to LO-OOA than MO-OOA, PMF solver somehow decreases the concentration of MO-OOA to reduce the overall fitting residual. We agree with the reviewer that this result is undesirable. However, as pointed out in response to reviewer's comment #4, similar situation could happen in ambient measurements. This issue deserves more attention.

16. Line S480: What other studies?

Response: Please see response to comment#4.

Technical comments:

17. Line 113: Please be more specific over which VOCs are anthropogenic vs biogenic. The word 'respectively' does not work when four are listed.

Response: We have deleted the word "respectively".

18. Line 179: Why not saturated fatty acids?

Response: We have deleted the word "unsaturated", so that the "fatty acids" in the revised sentence includes both unsaturated and saturated compounds. We have also cited Allan et al. (2010) in this sentence.

19. Line 119: Correct 'concentration' to 'concentrations'.

Response: We have made this correction in the revised manuscript.

20. Line 184: What are the oxidation states in each instance?

Response: We have added the oxidation states (i.e., -0.70 to -0.34 for LO-OOA and from -0.18 to 0.71 for MO-OOA in the southeastern U.S.) in the revised manuscript.

21. Section 2.2: Please specify the materials used for the aerosol and gas sampling lines.

Response: Teflon tubing and stainless steel tubings were used for gas and aerosol sampling lines, respectively.

Reviewer #2:

The manuscript presented by Xu et al. proposes an interesting study on the contribution of the oxidation of alpha-pinene and caryophyllene to the SOA mass observed in the S.E.-US. The characterization of SOA generated in the lab-in-the-field smog chamber was performed using an aerosol mass spectrometer. Overall the work performed in this study is good and fall within the scope of the journal. However, I think the conclusions proposed from the PMF analysis/chamber experiments are not always well sustained and more caution should be taken when extrapolating the results.

Response: We thank the reviewer for the positive comments. In the revised manuscript, we have added more caveats regarding our conclusions drawn from the perturbation experiments.

General comments

1. The authors should carefully review their paper and avoid the repetition between the main text and the SI. At many places, sentences are duplicated and are not useful. However, some important details are left within the SI and should be moved to the main manuscript.

Response: We have re-organized the main text and SI, and improved the linkage between two parts.

2. The authors should provide more information in the PMF analysis and provide the elementary checks to validate their analysis. For instance, it is a bit surprising that the factors don't change throughout the experiments (i.e. bf vs af) while significant perturbation has been made to the system. Or do the authors consider/claim that most of the SOA sampled in the ambient are formed from the oxidation of alpha-pinene or caryophyllene? In addition, we could expect that the fresh LO-OOA (formed within a few minutes, without lights) would have different signatures that LO-OAA formed in the atmosphere (aged SOA, formed from different chemistry, …). How do the factors correlate throughout the experiments: e.g. LO-OOA_Amb_Bf vs LO-OOA_Chamber_Af?

Response: We respond to the reviewer's comment by addressing some confusions regarding PMF analysis. Firstly, we performed PMF analysis on the combined ambient and perturbation data. Each OA factor has a constant mass spectrum throughout the study, regardless of ambient or chamber periods. In other words, the mass spectra of factors do not change between "Chamber_Bf" and "Chamber_Af". Secondly, we did not introduce significant perturbation to the system. In contrast, our goal is to produce small amount of SOA, which would not cause dramatic change in the OA composition and would not bias PMF analysis. For example, the difference in average OA concentration between “Chamber_Bf” and “Chamber_Af” is within 4 μg m^{-3} for all perturbation experiments. Thirdly, we did not consider/claim that most of the SOA sampled in the ambient are formed from the oxidation of α-pinene or β-caryophyllene. This assumption is not related to our conclusions.

Regarding the last question in this comment, we believe that the reviewer suggests to compare the OA mass spectra between “Chamber_Bf (before VOC injection)” and “Chamber_Af (after VOC injection)”. As shown in Fig. R3 (in response to reviewer#1), the mass spectra between two periods are almost identical, with R larger than 0.99 for all experiments. This is desired because we do not intend to introduce significant change in the OA composition after perturbation.

3. How do the identified factors correlate with the reference MS? How do the residuals evolve throughout an experiment? How does alpha-pinene-derived LO-OOA correlate with caryophyllene derived LO-OOA? Overall, the authors should provide more statistical analyses in order to give a robust validation of the analysis.

Response: In this study, we resolve and evaluate PMF factors according to the standard procedure outlined in Zhang et al. (2011). The detailed description on OA factors and justification of PMF results have discussed in section S3 of SI. As discussed in the SI, the PMF factors have the same features as those in the literature. More importantly, the PMF results in this study are consistent with our previous measurements (from 2012 to 2015) at the same site and in similar seasons, as shown in Fig. S14 in revised SI. The mass spectra of LO-OOA are similar (R > 0.95) across all the seven datasets in this study (Fig. R1 in response to reviewer#1’s comment#3).

In α-pinene perturbation experiments, the PMF residual is not significantly different between “Chamber_Bf” and “Chamber_Af”, suggesting that PMF analysis has adequately accounted for the newly formed α-pinene SOA. More detailed discussions can be found in response to reviewer#1’s comment #4.

As noted in response to the reviewer’s comment#2, the mass spectrum of LO-OOA is the same throughout the study, regardless of ambient vs. perturbation and regardless of α-pinene vs. β-caryophyllene experiments.

4. The authors should report the concentration of the inorganics in their experiments and in case of significant concentrations of sulfate estimate the aerosol acidity. Indeed, the presence of acidic aerosols can lead to multiphase reactions (e.g. reactive uptake of IEPOX) that could greatly impact the SOA composition. In addition, an estimation (modeling?) of the concentrations of other VOCs would be interesting (especially isoprene). Ozonolysis of alpha-pinene leads to the formation of OH radicals, which could further react and oxidize alpha-pinene but also other VOCs present in the ambient air. The authors should discuss this possibility and provide more information in the background of the chamber/ambient air. As it is, the conclusions proposed in the paper on the potential increase of the IEPOX-OA or COA factors from the oxidation of alpha-pinene and caryophyllene, respectively appear speculative (correlations are not sufficient to validate such trend: r~0.5). For instance, the authors could estimate the amount of IEPOX (thus isoprene) formed in the chamber to explain the formation of IEPOX-OA and check if the numbers make sense or not.

Response: We interpret that the reviewer's key question as the following: "is the enhancement in isoprene-OA factor due to the oxidation of isoprene in the chamber after injecting α-pinene?" The most direct evidence to rule out this hypothesis is that the concentration of IEPOX+ISOPOOH ($C_5H_{10}O_3{\bullet}I^-$) and isoprene hydroxyl nitrates ($C_5H_9NO_4{\bullet}I^-$), measured by I^- HR-ToF-CIMS, did not change after α-pinene injection (Fig. S3b in revised SI). This suggests that the α-pinene injection does not introduce isoprene oxidation in the chamber.

The relatively weak correlation between Δisoprene-OA and ΔLO-OOA (where the Δ indicates the difference in concentration between the "Chamber_Af" and "Chamber_Bf") across all α-pinene perturbation experiments is not contradictory to the conclusion that α-pinene SOA influences isoprene-OA factor. The weak correlation could be because α-pinene SOA in different perturbation experiments were formed under different conditions (e.g., NO_x) and had different mass spectra (Fig. 7 in revised manuscript). Thus, the fraction of α-pinene SOA apportioned into isoprene-OA factor varies with experiments and results in the weak correlation. However, we would like to point out that although the correlation between Δisoprene-OA and ΔLO-OOA across all α-pinene perturbation experiments is relatively weak, the time series of isoprene-OA and LO-OOA in the same α-pinene perturbation experiment are strongly correlated. The R is 0.88 for the α-pinene perturbation experiment on 07/20 (Fig. R4a). It is well studied that isoprene produces

SOA slower than α-pinene, as isoprene SOA involves higher-generation products. If the enhancement in isoprene-OA factor is due to isoprene oxidation, the enhancement is expected to occur later than the enhancement in LO-OOA, but it is not observed in the experiments. Thus, the strong correlation between isoprene-OA and LO-OOA in the same α-pinene perturbation experiment serves as another evidence that the enhancement in isoprene-OA factor is due to interference from newly formed α-pinene SOA, rather than oxidation of isoprene after injecting α-pinene.

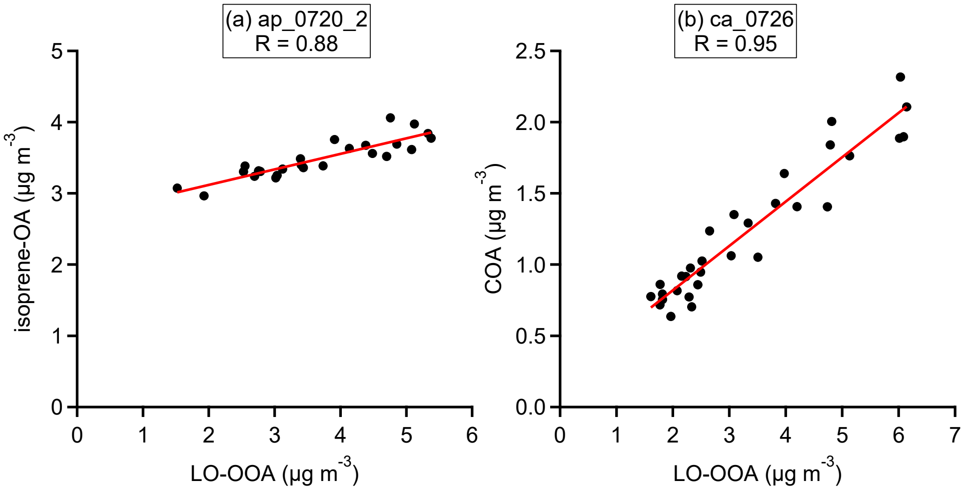

Fig. R4. (a) The correlation between isoprene-OA and LO-OOA in the “Chamber_Af” period of one α-pinene perturbation experiment (i.e., ap_0720_2). (b) The correlation between COA and LO-OOA in the “Chamber_Af” period of one β-caryophyllene experiment (i.e., ca_0726).

At the reviewer requested, the concentrations of inorganic species have been added into the revised SI.

Specific comments:

5. Lines 104:111. Did the authors characterize the chamber? Mixing, wall losses,

Response: Since our goal is to qualitatively understand which OA factors the α-pinene SOA is apportioned into, we did not characterize the mixing and wall loss of the chamber. We would like to note that because of the continuous exchange air between chamber and ambient air, the particle wall loss is difficult to characterize. The chamber characterization will be one focus of future work.

6. Lines 141: The authors claim that by having an overflow, it suppressed the particle loss. Did they mean reduce? Have you done some tests to validate such statement?

Response: We used a bypass flow to reduce the particle loss in sampling line. We have replaced "suppressed" with "reduced".

7. Lines 217-220: Why not using the outdoor chamber to do such experiments? Can the authors discuss the strategy here?

Response: In the laboratory studies, we follow traditional chamber experimental procedure produce α-pinene SOA under controlled conditions. Then we compare laboratory experiments with lab-in-the-field experiments to evaluate the representativeness of laboratory studies.

8. Lines 266-268: The decay of LO-OOA is quite fast and I do not think it can only explain by the dilution and or dead-volume. The residence time in the chamber is ~100 min. Where were located the sampling inlets?

Response: The ~100min residence time is calculated with the assumption of no dead volume. The existence of dead volume would largely decrease the residence time and change the decay rate of LO-OOA, as shown in Fig. S21 in revised SI.

The sampling inlets were inserted into the center of the chamber, which has been specified in the revised SI.

9. Lines 278:284: It is quite expected. What is the point of the authors?

Response: Please see response to reviewer#1's comment#10.

10. SI Line 150:157: These results are a bit intriguing. The data reported for the boreal forest do not exhibit prominent ions at m/z 53 or 82. The authors suggest that alpha-pinene/monoterpene can contribute to IEPOX-OA but according to Fig S7 the correlation is far to be obvious strong. The authors should compare the MS obtained in their study with other PMF data obtained from monoterpene-dominated areas (e.g. boreal forest).

Response: In SI Line 150-157, we suggest that monoterpenes SOA may influence isoprene-OA factor, if the isoprene-OA factor is present. In other words, for a location without isoprene-OA factor, the influence of monoterpenes SOA on isoprene-OA does not exist. Regarding the reviewer's comment on Fig. S7 (i.e., Fig S5 in revised SI), we have addressed it in response to comment#4. As the reviewer suggest, we compared the mass spectrum of LO-OOA in this study with that obtained in a coniferous forest mountain region in Whistler, British Columbia, Canada (Lee et al., 2016). The correlation coefficient is 0.99.

Reviewer #3:

This paper presents results from experiments and model runs focusing on the monoterpene contribution to biogenic SOA in the SE US. A small Teflon reactor was used to oxidize ambient air to which single VOC precursor was added. Based on simple PMF analysis and simple CMAQ model runs, it is concluded that monoterpenes are major contributors to ambient OA in the SE US. The authors are wellknown in the field and have published much excellent work, the paper falls within the scope of ACP, and has some interesting aspects. However, in my opinion the new evidence is weak, partially supported with circular logic, and is very overinterpreted. The new evidence is very insufficient to support the very strong conclusions. I don't see how this paper can be published in ACP in anywhere near its present form. I recommend that the authors go back to the drawing board and summarize the new experimental aspects into a paper whose conclusions are actually supported by the evidence presented. For example, the results on Appendix B seem more novel to this reviewer than the ones that are described in the main paper.

Note that I made this recommendation already in the access review, with the concurrence of the previous Editor, and hoping to avoid having to post this review in public. However, after an appeal by the authors, it was decided to publish the paper in ACPD anyway without significant revisions.

Response: We thank the reviewer for detailed comments in both access review and ACPD stages. We appealed the reviewer's suggestion in the access review stage because we respectfully disagree with many of the reviewer's comments. We would like to use the open discussion to clarify a number of issues.

1. Brief statement of the major issue

1) The main problem of this paper is that the evidence presented does not support the conclusions. The conclusions are summarized in the paper title "Large Contributions from Biogenic Monoterpenes and Sesquiterpenes to Organic Aerosol in the Southeastern United States." Or L80-84: "We provide direct evidence that newly formed SOA from α-pinene […] and β-caryophyllene (representative sesquiterpene) dominantly contributes to LO-OOA in the southeastern U.S."

The new evidence presented in this manuscript has two parts:

1.a) Some interesting, but incomplete, experiments with an ambient reactor, that have been analyzed using PMF. What the authors have really shown with these experiments is (in their own *words) "to qualitatively understand which OA factors the α-pinene SOA is apportioned into" (Supp. Info. L349-350). Most importantly, experiments with other precursors failed, and experiments using for example cloud pathways were not even attempted. It is highly likely (based on prior published work) that spectra from other precursors and pathways would also have looked similar to LO-OOA, so it is very problematic that those experiments failed or where not even attempted.*

The authors do acknowledge (L415) that based on the experimental work alone "we do not conclude that LO-OOA arises exclusively from MT and SQT." Next, they do acknowledge that their title is just a hypothesis, after all the experimental evidence has been considered: (L387-391): "we propose that the major source of OOA in this region is the oxidation of MT and SQT by various oxidants (O3, OH, and NO3). To test this hypothesis, we use CMAQ to simulate pollutant concentrations across the southeastern U.S."

So given how weak the evidence from (1.a) is in terms of supporting the paper's conclusions, how strong is the complementary evidence from the model?

1.b) The CMAQ model is run with a different parameterization for terpene SOA that has higher yields than a very old one. Not surprisingly, the terpene contribution to SOA in the SE US goes up in CMAQ. I understand that the parameterization is in principle improved compared to some older ones, but how do we know it is really accurate? The parameterization is still very simple, and does not included detailed chemistry such as a HOM mechanism. The justification about why this parameterization would be accurate when implemented in as complex a region as the SE US is very light and not satisfactory (sect. 2.6). I agree the model is "upgraded" (L25), but not that it has been shown to be accurate. There is a long history of simple parameterizations (after various "upgrades") being wrong when compared to ambient air. I do not see sufficient evidence that supports the accuracy of these model runs, so that strong conclusions about MT + SQT contributions (that could not be reached with the experiments alone) could now be reached with certainty.

In addition, the use of the CMAQ results suffers from circular logic. Section 1.a. ended with a hypothesis that LO-OOA was arising from MT & SQT. Now the fact that the CMAQ results are of the same order as LO-OOA is used as confirmation that indeed LO-OOA comes from MT & SQT.

But we did not know that LO-OOA came from MT & SQT yet, that was only a hypothesis. The logical structure here is therefore problematic.

Other evidence from the literature is mentioned, such as high emissions of MT & SQT in the SE US, and the fact that some previous results suggest that anthropogenic SOA is not a major contributor in this region. The first one has been known for decades. The second result is not quite consistent with some modeling studies and measurements of fossil carbon (when taking into account that urban pollution has a significant fraction of non-fossil carbon, see Kim et al. (2015) and references therein). Together, the combined evidence is still not sufficient for the sweeping conclusions.

Ten years ago we didn't know about the IEPOX-SOA pathway (Paulot et al., Science 2009), that has since proven to be a major contributor to SOA over the SE US. A paper written in 2008 may have used the existing literature to conclude that isoprene was a minor contributor to SOA in the SE US, and would have been sorely wrong in doing so. We also didn't know till very recently about autoxidation being important in the atmosphere (Ehn et al., 2014). The importance of autoxidation for urban emissions in the US has recently been demonstrated (Praske et al., PNAS 2018), and is not included in the CMAQ runs or literature studies cited here. SOA formation in clouds is also highly uncertain (Ervens et al., 2011), and could also lead to LO-OOA through various mixtures of precursors and pathways (which remain almost completely unexplored). For example perhaps there is an isoprene SOA pathway through clouds that has not been discovered yet and that contributes half of the LO-OOA in the SE US. The present paper is implicitly saying that other precursors and pathways are not important in the SE US, and risks shutting down research on other alternatives. Is that justified? In my opinion it is not, and the evidence is this paper is not anywhere near sufficient to justify its title and sweeping conclusions.

Response: We think the reviewer over-states the "weakness" of our evidence and the "strongness" of our conclusion. In many places of reviewer's comments, the reviewer indicates "the authors draw the conclusion that LO-OOA is exclusively monoterpenes SOA based on a single evidence" and that is a significant shortcoming. Our hypothesis is that "the major source of LO-OOA in the southeastern U.S. is the fresh SOA from the oxidation of monoterpenes (MT) and sesquiterpenes (SQT) by various oxidants (O_3, OH, and NO_3)". We never argue that LO-OOA is exclusively MT and SQT SOA and never state that SOA from other sources/pathways is not important. While monoterpenes have been recognized an important SOA source for some time, until Zhang et al. (2018), there was no evidence for them being a contributor on the order of half of the ambient OA. Even with Zhang et al. (2018), the scientific literature lacks information on the role of monoterpenes on larger spatial (e.g. entire southeast U.S.) and temporal (different times of year) scales which are included in our work. We support our hypothesis based on a weight of evidence provided in the literature and this study, as listed and discussed below.

(1) The large emissions of MT and SQT in the southeastern U.S. (Guenther et al., 2012), which has been established in decades and the reviewer agrees with.

(2) The majority (roughly 80%) of carbon in SOA is modern in the southeastern U.S. The reviewer suspects that this evidence is not quite consistent with some modeling studies. We beg to differ due to following reasons. Firstly, Weber et al. (2007) measured that the biogenic fraction of carbon is roughly 70-80% at two urban sites in Georgia that were also used in our study. Note that measurements in Weber et al. (2007) were performed in 2004 and the biogenic fraction is expected to be higher in 2016 than 2004, as a result of reductions in anthropogenic emissions (Blanchard et al., 2010). Secondly, we checked Kim et al. (2015) and found that the paper clearly stated that "we estimate that 18% of the total OC burden is derived from fossil fuel use. This is consistent with an 18% fossil fraction from radiocarbon measurements made on filter samples collected in Alabama during SOAS." In brief, Kim et al. (2015) is consistent with other studies (Zhang et al., 2018; Lewis and Stiles, 2006; Weber et al., 2007).

(3) Previous studies suggest that the oxidation of β-pinene (another important monoterpene) by nitrate radicals (NO_3) contributes to LO-OOA in the southeastern U.S. (Boyd et al., 2015; Xu et al., 2015a) and this reaction alone cannot replicate the magnitude of LO-OOA (Pye et al., 2015).

(4) The mass spectra of LO-OOA are almost identical (i.e., R ranges from 0.95 to 0.99 in Fig. R1) across all the seven datasets in our study. In addition, LO-OOA across all datasets also shares the same diurnal trends (Xu et al., 2015a). The similarity in LO-OOA features suggests that LO-OOA may share similar sources across multiple sites and in different seasons in the southeastern U.S.

(5) Perturbation experiments in this study show that the majority of fresh SOA from the oxidation of MT and SQT contributes to LO-OOA. Previous studies, mainly based on mass spectra comparison, concluded that MT SOA contributes to LO-OOA, but did not quantitatively show the fraction of MT SOA that is apportioned into LO-OOA. In other words, previous studies did not

show whether 100% or 50% of MT SOA is apportioned in to LO-OOA. The quantitative understanding is the basis when comparing modeled MT SOA with PMF factors. The reviewer raises concern regarding this conclusion in next comment and we will address his/her concern later.

(6) CMAQ model calculations for the region showed consistency between modeled SOA_{MT+SQT} and observed LO-OOA in terms of both magnitude and diurnal trend at different sites and in different seasons when an updated monoterpene SOA parameterization was used.

The new VBS parameterization implemented in the updated simulation represents a significant scientific improvement over the Odum 2-product parameterization currently used in the public version of CMAQ (v5.2). Specifically, the VBS parameterization does promptly form low volatility species, likely from autoxidation, which were absent from the previous Odum-2 product parameterization. In addition, the new parameterization allows for enthalpies of vaporization that are more consistent with species of the specified volatility, since the parameterization was produced from a richer dataset than the original Odum 2-product representation. The work shown here is an important step in the right direction and will allow for an improved representation of monoterpene SOA in current models while mechanistic pathways are still being determined. As shown in Fig. S16 in revised SI, implementing the new parameterization of MT SOA substantially reduces the normalized mean bias (NMB) between modeled and measured OA for all six datasets.

(7) A recent study by Zhang et al. (2018), which was published after our manuscript submission, offered other evidence to support our hypothesis. Zhang et al. (2018) characterized the molecular tracers of MT SOA at Centreville, AL (a site included in our study as well) and concluded that monoterpenes are the largest source of summertime organic aerosol in the southeastern U.S.

Therefore, we use above weight of evidence to support our hypothesis. We have revised the manuscript to clarify the logic and avoid confusions.

At last, we fully acknowledge the progress already made and the need to improve our understanding of atmospheric chemistry and all the unknowns the reviewer brought up. In fact, our study is motivated by many unknowns that the reviewer brought up. For example, due to the high O:C ratio of highly oxygenated molecules (HOMs) formed during monoterpene oxidation, it is hypothesized that HOMs maybe a potential source of MO-OOA. This hypothesis challenges our current understanding that MO-OOA represents aged SOA and also raises the question if monoterpenes SOA is exclusively apportioned into LO-OOA. Although previous studies repeatedly showed the similar mass spectra between α-pinene SOA and LO-OOA, the mass spectra comparison approach cannot tell us what is the fraction of α-pinene SOA apportioned into LO-OOA vs. other factors. The limitations of mass spectra comparison approach motivate us to explore alternative approaches to understand the sources of PMF factors. Another example is still related to HOMs. As the reviewer is aware of, the formation of HOMs and the contributions of HOMs to SOA are not captured by the Odum 2-product model implemented in current regional models which do not include prompt formation of material with saturation concentrations less than 10 $\mu g/m^3$. This is one of the reasons we replaced Odum 2-product model with VBS parameterization in the updated simulation. The new parameterization based on Saha and Grieshop (2016) considers the HOMs contribution to SOA and the HOMs yield in Saha and Grieshop (2016) is consistent with recent observations.

Throughout the manuscript, we never imply that SOA sources, other than monoterpenes and sesquiterpenes, are not important. Based on our measurements, LO-OOA accounts for 19-34% of total OA in the southeastern U.S. The sources of MO-OOA, which accounts for 24-49% of OA in the southeastern U.S., are highly uncertain. Many reaction pathways the reviewer brought up are actually potential sources of MO-OOA. For example, SOA produced from aqueous-phase chemistry is generally highly oxidized (Lee et al., 2011) and is likely apportioned into MO-OOA, instead of LO-OOA. A recent study by Xu et al. (2016) suggests that aqueous-phase reaction has a dominant impact on MO-OOA in China. There are also hypotheses in the literature that the SOA formed through cloud chemistry together with long-range transport and entrainment from aloft may contribute to MO-OOA (Crippa et al., 2013; Robinson et al., 2011; Xu et al., 2015b). In brief, we never make any implication that SOA from other sources/pathways are not important in the southeastern U.S.

A little more detail on the major issues

2) A very important problem with the manuscript is the logic of the PMF analysis (with both of the other reviewers explicitly pointing out serious problems in it). Indeed the a-pinene SOA is most similar to LOOOA (also referred to as SV-OOA in older works). This has been known for a decade, see for example Fig 2C of Jimenez et al. (2009) (cited in the manuscript) and several other papers. Or in the words of reviewer 1: "the case for a-pinene SOA being a strong contributor to LO-OOA has never really been in doubt in this reviewer's opinion. Why is the evidence presented here any *more 'direct' than those published previous?" The same conclusion can be deduced quickly by comparing spectra of chamber apinene SOA and ambient LO-OOA from the AMS spectral databases (much like the authors do again in their Fig. 6). So this it is not a new finding of this work. Here an interesting (though not completely new) experimental procedure is used to reach once again a conclusion that was already firmly established in the literature. See for example the figure below (Kiendler-Scharr et al., 2009, as an example, but there are quite a few such comparisons in the earlier AMS literature. Note that the Chebogue BSOA represents the outflow for the E US, similar to the work in the present paper).*

Therefore the conclusion is not really new and has been known for over a decade. So it seems surprising that suddenly the same specific result allows the present authors to reach far more general conclusions. The critical flaw is in the logic flow. It is true that (a) a-pinene SOA is most similar to LO-OOA. However, that cannot be used to conclude that (b) ambient LO-OOA in the SE US is mostly from apinene. Hypothesis (a) being true is a necessary, but not sufficient condition for the converse hypothesis (b) to be true. Much more evidence is needed to prove hypothesis (b) and to disprove alternative hypotheses.

A critical piece of additional evidence would include proving that spectra from other sources of SOA likely to be present in the region are not spectrally similar to LO-OOA. This is not shown in the manuscript. Experiments with other precursors were attempted (L313): "by injecting isoprene, mxylene, or naphthalene, which are major biogenic and anthropogenic emissions, respectively. However, the SOA formation from these VOCs is not detectable." So the experiments failed, and as a consequence no spectra from other likely sources are available to establish that spectra from those sources do not look like LO-OOA. A look at the AMS literature and the AMS databases suggest that spectra from these and other precursors have spectra which are indeed very similar to ambient LO-OOA. So it is very problematic that the experiments did fail.

Inexplicably the authors do not use the publicly available database spectra, nor perform regular chamber experiments for other precursors, and have a very handwavy section (sect. 3.4) trying to justify that. This is simply not acceptable. I do not agree that the ambient perturbation experiments are better than regular chamber experiments, but I would agree that they can be just as good. Adding a-pinene to ambient air, and using the oxidants (O3 and OH) and OA seed from ambient air, is not significantly different to injecting O3 in a chamber and using either a sulfate seed or no *seed. If the authors expect that the spectra would be significantly different, they should explain why this would be. But their own Figure 6 indicates that the spectra from the ambient perturbation experiments and a regular chamber are indeed very similar. Why then not use chamber experiments (either from the literature database, or the authors' chamber) to obtain spectra from other precursors and pathways, and see whether they are similar to the ambient LO-OOA or not?*

Response: The reviewer's comment targets on why our conclusions from perturbation experiments are more "direct" than previous studies based on mass spectra comparison method. We have carefully addressed this question in response to reviewer#1's comment#9. In brief, in the authors' opinion, the mass spectra comparison approach is subjective and qualitative. It relies on subjective judgement to determine whether lab SOA is similar to OA factor. Also, even if the mass spectrum of α-pinene SOA is similar to LO-OOA, the similarity is not equivalent to that α-pinene SOA is exclusively apportioned into LO-OOA. In contrast, in the perturbation approach, PMF analysis does not distinguish SOA from natural α-pinene vs. from injected α-pinene, so that PMF analysis can objectively apportion α-pinene SOA into factors. Further, we attempt to quantify the fraction of α-pinene SOA that is apportioned into different factors.

The reviewer also argued that it is problematic that the perturbation experiments with other VOCs (isoprene, m-xylene, or naphthalene) failed. In fact, the results with other VOCs are expected and explainable as will be discussed in response to reviewer's comment #7.

3) Similar experiments and analysis (VOC addition to ambient air in a flow reactor, followed by spectral comparison) have already been conducted and published by Palm et al. (2018) as part of the GoAmazon campaign, an area comparable to the SE US with high biogenic impact, but also other sources. In that work multiple VOCs were added to ambient air individually, and oxidized to form SOA in an oxidation flow reactor, which was then measured by an HR-AMS. Those authors were able to oxidize bcaryophyllene, longifolene, limonene, b-pinene, α-pinene, toluene, and isoprene, and to obtain yields and HR-AMS mass spectra for all of them. They further state: "The mass spectrum of the SOA formed from OH oxidation [of ambient air] was correlated (R2=0.72-0.93; shown in Fig. S12) with spectra of the SOA formed from the injected VOCs from the standard injection experiments in Sect. 3.4. These correlations show that the SOA formed from OH oxidation of ambient air appeared similar to SOA from known precursors, but the spectra from the different *precursors appear too similar to be able to differentiate the SOA sources in ambient air from the spectrum alone." Fig. S12 of that work is reproduced below for reference.*

Thus the difficulty of apportioning the SOA in ambient air through this type of experiments, and given the high fragmentation and limited information content of AMS spectra is clear and has been previously documented. If the authors disagree, the burden of proof is on them to show that they can unequivocally associate ambient air spectra with those of specific VOC precursors, including disproving that ambient LO-OOA may have major contributions from other precursors and pathways. Let's imagine that Palm et al. had only conducted experiments with limonene, and the rest of the experiments had failed. Then they would have observed R2 of 0.9 between SOA of those experiments and SOA from ambient air. Would that have been sufficient evidence to justify the title "Large Contributions from limonene to Organic Aerosol in the Amazon"? That paper performed additional analyses, and concluded instead that biomass burning and anthropogenic precursors were also important contributors at that particular location, in addition to biogenics. Therefore one has to avoid making expansive conclusions based on narrow evidence.

Response: Firstly, we do not agree with the reviewer that the analysis in Palm et al. (2018) is similar to our study. Palm et al. (2018) focused on the SOA formation from oxidizing ambient air with OH in an oxidation flow reactor. This SOA is referred to as "potential SOA". Both the mass spectra comparison and the "additional analysis" the reviewer referred to aim to understand the "potential SOA", instead of the existing SOA in the atmosphere. As clearly stated in Palm et al. (2018), "Importantly, this analysis does not provide information about what amounts or fractions of the preexisting (i.e., ambient) OA measured at the T3 site came from each of these sources." Thus, the analysis in Palm et al. (2018) is not similar to our study, as our study aims to understand the sources of preexisting OA.

The reviewer quote from Palm et al. (2018) that "…*but the spectra from the different precursors appear too similar to be able to differentiate the SOA sources in ambient air from the spectrum alone.*". The R^2 in Palm et al. ranges from 0.72 to 0.93. We would like to ask the question what counts as "too similar"? We believe that the mass spectra comparison method cannot provide an objective answer to this question, but the PMF analysis as done in our study can potentially answer the question. That is, if Palm et al. (2018) performed PMF analysis on the combined ambient data and perturbation data, SOA from different precursors may be apportioned into different factors.

Secondly, the reviewer raised one question that if Palm et al. had only conducted experiments with limonene, would that have been sufficient evidence to justify the title "Large Contributions from Limonene to Organic Aerosol in the Amazon"? We agree with the reviewer that the answer is definitely no, because this conclusion is drawn based on simply mass spectra comparison, instead of cumulative evidence as in our study. Let's imagine that Palm et al. simulate the SOA formation from limonene in Amazon, would that match the LO-OOA in both magnitude and diurnal trend at multiple sites and in different seasons? Is limonene the most abundant monoterpenes in the Amazon? Is there any study to objectively show that the majority of limonene SOA contributes to LO-OOA, instead of other factors? We state again that our hypothesis is supported by a weight of evidence, instead of simple mass spectra comparison.

Thirdly, to support the hypothesis that LO-OOA is largely from the oxidation of monoterpenes and sesquiterpenes in the southeastern U.S., we have shown cumulative evidence in response to this reviewer's comment#1. Below, we list more evidence to support that LO-OOA unlikely has major contributions from anthropogenic VOCs.

(1) m-xylene, an important and abundant anthropogenic VOC is likely apportioned to MO-OOA. The mass spectrum of laboratory-generated m-xylene SOA (Bahreini et al., 2005) is more similar to the MO-OOA (R = 0.97) than LO-OOA (R = 0.83), using the standard mass spectra in Ng et al. (2010). Using the reviewer's recommendation to leverage the similarity of spectra between laboratory experiments and the ambient measurements, m-xylene SOA contributes to MO-OOA, instead of LO-OOA.

(2) As indicated in Fig. S8 in revised SI, the modeled concentration of SOA from anthropogenic VOCs is on the order of 0.1 μg m^{-3}. Even if we double the SOA yields of anthropogenic VOCs to account for the potential vapor wall loss in laboratory studies (Zhang et al., 2014) and even if we assume all SOA from anthropogenic VOCs oxidation contributes to LO-OOA, anthropogenic SOA only account for a small fraction of LO-OOA. Also, the modeled anthropogenic SOA peaks in the day, which is different from that of LO-OOA, which reaches daily maximum at night. This small amount of anthropogenic SOA is consistent with Zhang et al.

(2018), who performed molecular-level characterization of OA and showed that anthropogenic SOA only accounts for 2% of total OA in Centreville, AL.

4) Some results of the PMF analysis appear to have been misinterpreted. The ambient data had 10 times as many points in time as the perturbation experiments. In such a situation, the ambient data effectively "dictates" the spectra due to its much higher fractional contribution to the Q value (weighed residual that PMF is minimizing). As expected in this situation (L167) "the perturbation experiments do not create a new factor that does not already exist in the ambient data." Under that setup, the PMF results for the chamber time periods are similar to multiple linear regression onto the spectra already predetermined for ambient air (since the chamber results have a low contribution to Q, and then are unable to change the factor spectra much).

As the spectra of SOA from the chamber are being forced to be represented by a linear combination of a limited set of ambient spectra (which they cannot influence in practice), it is normal that some SOA spectra from the chamber VOC additions "project" onto more than one ambient spectrum. That is, if an SOA spectrum produced in the chamber is not exactly similar to one of the ambient spectra, PMF may be able to reduce the residual by representing those experimental spectra as a linear combination of two of the "basis" spectra that were determined primarily from the ambient data. Those results are expected and not surprising. They do not "clearly demonstrate" at all that if a given type of SOA was present in an ambient dataset, it would be split into two factors in the same way. Mathematically these are two very different situations, with very different structures and residual contributions. For example an ambient cooking OA (COA) factor would have a different time variation, which PMF would also exploit in extracting the factors, but such structural difference in the variance is not present here. Experiments (for example using simulated data) could be carried out to investigate the interference point for ambient data alone. Unfortunately, the authors misinterpret their results for a very specific PMF situation for non-ambient data, into completely unsupported general statements for PMF analyses of ambient data (that for example ambient COA may contain caryophillene SOA, or that isoprene SOA may have interferences from a-pinene SOA), even though such analyses have not been performed in this work! Perhaps those interferences exist, but they have not been proven by this study. Rather here the results of a complex PMF analysis are being misinterpreted.

In fact, the result that some of the a-pinene and carophyllene SOA apportions to other factors in the authors' methods weakens the main stated conclusions further. Even these types of SOA are not quite well represented by LO-OOA and need to "lean" on other ambient factors to reduce the residual in PMF. Therefore making the conclusion that ambient LO-OOA is mainly from MT & SQT is even more weakly supported.

Response: As stated in the manuscript, we designed our experiments in a way that the perturbation experiments do not influence the mass spectra of OA factors and would not create a new factor.

The reviewer argued that "*PMF results for the chamber time periods are similar to multiple linear regression onto the spectra already predetermined for ambient air*". Let's put aside whether this interpretation is correct, we think the same argument/interpretation also applies for ambient monoterpenes SOA. Imagine that there is a short period of ambient data with increasing monoterpenes SOA concentration. For this short period, one can also argue that this short period has small contribution to overall Q value and thus PMF results for this period are similar to multiple linear regression onto the spectra already predetermined for ambient air. The perturbation experiments simulate this short period with increasing α-pinene SOA concentration. It does not matter how PMF treats the perturbation experiments, as long as the treatment is the same for ambient data. Therefore, conclusions drawn from perturbation experiments are applicable to ambient data from a similar situation. The perturbation experiments point out the possibility that isoprene-OA factor could have interference from α-pinene SOA. This interference has not been acknowledged in previous studies and there is no study in the literature to prove that this interference does not exist. In fact, the interference of α-pinene SOA on isoprene-OA factor helps to address some uncertainties regarding the isoprene-OA factor in the literature. For example, Liu et al. (2015) compared the mass spectrum of laboratory-derived IEPOX SOA with isoprene-OA factors at some sites. The authors observed stronger correlation for isoprene-OA factors resolved at Borneo (Robinson et al., 2011a) and Amazon (Chen et al., 2015), and weaker correlation at Atlanta, U.S. (Budisulistiorini et al., 2013) and Ontario, Canada (Slowik et al., 2011). As another example, the fraction of measured total IEPOX-SOA molecular tracers in isoprene-OA factor highly varies with location, ranging from 26% at Look Rock, TN (Budisulistiorini et al., 2015) to 78% at Centreville, AL (Hu et al., 2015). To address the uncertainties in above two examples, one possible reason is that the isoprene-OA factors resolved at different sites are not purely from IEPOX uptake. Isoprene-OA factors likely have interference from monoterpenes SOA or other sources, but the interference magnitude varies with locations. We hope to use this study to raise the public awareness of the possible interference in OA factors.

The reviewer proposed a great suggestion to use simulated dataset to investigate the potential interference. However, a great amount of work is required to fully carry out this idea, as the creation of the simulated dataset (i.e., what mass spectrum, time series, and concentration of α-pinene SOA should be used?) is complicated and subjective. It would be an entire study in itself.

We agree with the reviewer that the perturbation experiments do not simulate all scenarios in the atmosphere and do not consider the temporal variation. The applicability of the conclusions drawn from the specific scenario to general atmosphere warrants further exploration. We have clearly discussed the caveats of the conclusions in the revised manuscript.

We agree with that PMF separates factors based on features in mass spectrum and time series. However, we do not agree that the temporal variations of monoterpenes and sesquiterpenes SOA and COA can guarantee a clean separation between different sources. For example, the concentrations of many oxidation products of monoterpenes (e.g. pinonic acid, pinic acid, etc), COA, and LO-OOA show similar increasing trend near sunset (Allan et al., 2010; Xu et al., 2015b; Zhang et al., 2018). As an attempt to test if our conclusion is affected by the temporal variation, we performed perturbation experiments at different times of day (9am to 9pm) in this study.

5) No uncertainty analysis, such as from bootstrapping, is performed for the PMF results. This is more glaring given that very strong conclusions about the identity of a major fraction of the ambient OA, and of potential interferences between factors are made, but we are not shown that the results are even statistically significant or what the uncertainties in the analysis may be.

Response: As the reviewer requested, we performed 100 bootstrapping runs to quantify the uncertainty of PMF results. As shown in Fig. R5. The statistical uncertainties in the time series and mass spectra of 5 factors are small and the PMF results reported in this study are robust.

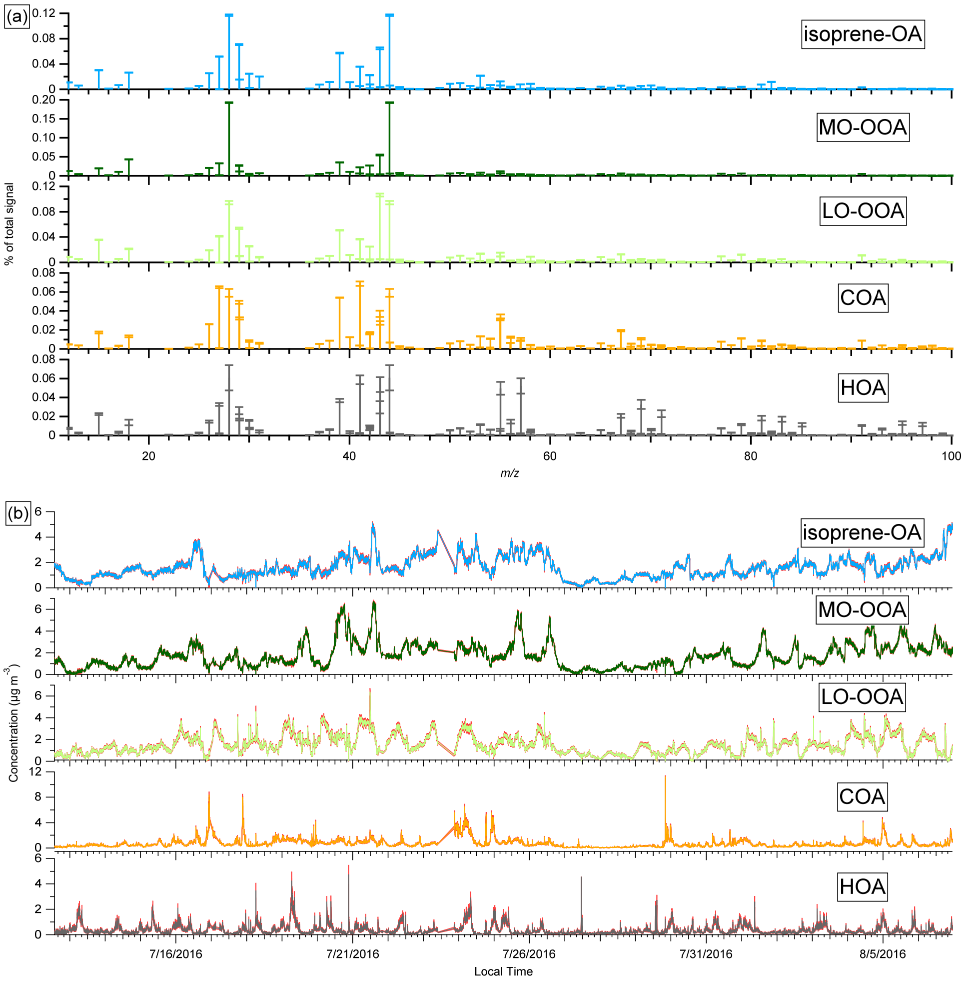

Fig. R5. PMF results from bootstrapping analysis. (a) Average mass spectra (sticks) with 1-σ error bars (caps). (b) Average time series and 1-σ error bars (red).

6) The statements about the novelty of the approach (L19, L21, L87-88, L457-458) are exaggerated. As cited in the paper, both Leungsakul et al. (2005) and Palm et al. (2017) have already published results from very similar experiments. The only difference between the present experiments and those previous ones is (in the authors' words, L22-123) that "no extra oxidant precursors were added into the chamber." That is correct, but would the authors expect that ambient O3 or OH produced from ambient air would be that different than those produced in other ways? I am sure that the a-pinene molecules don't care about how the O3 or OH colliding with them were formed. If the authors expected that adding a-pinene to ambient air but using ambient oxidants was going to significantly change the results compared to standard chamber experiments, the reasons for such expectations should be discussed in detail.

Otherwise the experiments are interesting, but follow on prior publications. I mention this because in some places (e.g. abstract L20-25, also in L87-88, L457-458) the statement that the experiments were "novel" is somehow used to prop the weak conclusions. As if somehow the "novel" experiments would have allowed the authors to reach some conclusions that were not reachable by previous authors. But the novelty is very minor. And the one reason why the experiments are a little different from previous experiments (no added oxidants) is the reason why the experiments failed in multiple cases! Therefore the "novelty" does not provide any real support for the conclusions.

Response: As the reviewer noted, we already referenced and acknowledged previous studies which used ambient air. However, the goals of previous studies are completely different from that of our perturbation experiments. In Leungsakul et al., the main purpose of using rural ambient air is to flush the 270m^3 outdoor chamber reactor. In Palm et al., their main goal is to measure the SOA yield from individual VOCs in the OFR under ambient RH and temperature conditions. Our goal to use ambient air is to examine which factor the fresh α-pinene and β-caryophyllene SOA is apportioned into by PMF analysis. With our goal in mind, we want to produce SOA only from α-pinene and β-caryophyllene. The reviewer is totally right that the α-pinene molecules don't care about where the O_3 or OH comes from. However, adding extra oxidants will produce SOA via a number of reactions (i.e., oxidize other existing VOCs/SVOCs/IVOCs). If so, we would not unambiguously know if the LO-OOA enhancement in the perturbation experiments arise from injected VOC or from other pathways.

We realize that the description of the novelty of our approach is not accurate in many places and we have modified the language in the revised manuscript.

7) Statements such as (L316-318) "The perturbation experiments with other VOCs confirm the stronger ability of α-pinene and β-caryophyllene to produce SOA" are misleading, and frankly just perplexing. A lot was already known about the relative potential of different VOCs to make SOA before this paper, and nothing new is learned from the experiments here about this point. The low SOA observed for other precursors is attributed (SI, L405-406 "to the low SOA yields or slow oxidation rates of these VOCs (Ng et al., 2007). Yields for naphthalene are certainly not low, but are higher than for a-pinene (Chan et al., 2009). Later it is acknowledged (SI L412-414) that "isoprene oxidation products which form SOA are mostly second or higher generation products.

They are not formed in large amount in the relatively short perturbation experiments (i.e., 40min)." The main issue is that a-pinene has a lifetime of ~1 h under the conditions of the ambient perturbation experiments (using well-known rate constants) and caroyphyllene has an even shorter lifetime. m-xylene has a lifetime of ~10 hrs, and therefore it reacts too slowly under the conditions of these experiments with no added oxidants. And for some precursors (other than isoprene) second or higher generation products are also needed to make SOA, which results in even longer time constants. However, those timescales are readily accessible in the atmosphere.

Response: The confusion regarding the referred statement mainly arises from the phrase "stronger ability". We realize that this phrase is not properly defined, but we do not think this statement is fundamentally wrong. Here, the "stronger ability of α-pinene and β-caryophyllene to produce SOA" means that under the same atmospheric conditions (i.e., oxidants level, NO_x, per-existing particles, etc) and the same initial VOC concentration, more SOA would be produced from α-pinene and β-caryophyllene than from other VOCs (i.e., isoprene, m-xylene) after the same oxidation time (i.e., 40min in perturbation experiments). This conclusion is well supported by laboratory studies in the literature. This is why we used the word "confirm" in the sentence.

The "*main issue is that …*" brought up by the reviewer is exactly the same meaning as "the low SOA yields or slow oxidation rates of these VOCs", which we wrote in the original manuscript. The timescale required to produce SOA of other VOCs (i.e., isoprene and m-xylene) is longer than our perturbation experiments. This is why we did not detect SOA formation from these VOCs in our experimental approach. Thus, the results are expected and explainable.

After submitting the manuscript, we realize another reason for the lack of SOA formation in naphthalene experiments. We injected naphthalene by passing pure air (1 liter per min) over the solid naphthalene flakes under ambient temperature for 1 min. Due to the relatively low vapor pressure of naphthalene (23.6Pa at 30°C) and rapid dilution in the chamber, the injected naphthalene concentration could be very low. We add this possible reason in the revised SI.

8) The discussion in the introduction about MO and LO OOA is unclear. Those factors do not represent the same sources or pathways in different studies. In some locations and times they are tied to biomass burning, in others to urban emissions, in others to biogenic SOA, and in others to various combinations. In older studies in which Isoprene-SOA (or "IEPOX-SOA) was not separated, it was necessarily part of MO and LO OOA. Care should be taken to clearly *communicate that any interpretations about sources contributing to MO or LO OOA are specific to a given location and time period. And the possibility should be considered (including in the SE US) that different periods may have larger contributions to these factors from different sources, for example BB during one period, pollution during another, and biogenics during another (if the sources impacting a site change substantially in time due to air mass changes or other causes). See e.g. Palm et al. (2018) for an example of such a situation.*

Response: We agree that the OOA factors represent different sources or pathways in different regions. For example, in the original manuscript, we stated that "There is evidence that LO-OOA in California is related to the oxidation of anthropogenic VOCs, as radiocarbon analysis suggests 68-75% of carbon in LO-OOA in California stems from fossil sources (Hayes et al., 2013; Zotter et al., 2014)." We have further emphasized these points in the revised manuscript and expanded the discussions on OOA factors in the introduction, as the reviewer requested.

While we agree with the reviewer that interpretations about the sources contributing to OOA factors are location- and time-specific, we would like to point out that our study includes measurements at multiple sites in the southeastern U.S. and in different seasons. The LO-OOA across all datasets have similar diurnal variation (Xu et al., 2015a) and mass spectra (Fig. R1). Moreover, the modeled SOA_{MT+SQT} can capture the magnitude and diurnal variation of measured LO-OOA at all datasets. These evidence suggests a general source of LO-OOA on a regional scale.

Other points

9) L71-72: "The assumption that LO-OOA represents fresh SOA has yet to be directly verified." Fig 2C, 2D, 2E in Jimenez et al. (2009) (where the older terminology SV-OOA was used for LO-OOA), and similar results in other publications, would appear to have directly verified that long ago.

Response: Please see response to reviewer#1's comment#9.

10) A paper with a similar title to this one, but using different lines of evidence, has been recently published (Zhang et al., 2018).

Response: Thanks for pointing this out. We note that Zhang et al. (2018) was published after our manuscript submission. The conclusion in Zhang et al. (2018) is consistent with our study and has been discussed in the revised manuscript.

Reference

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, Atmos. Chem. Phys., 10, 647-668, 10.5194/acp-10-647-2010, 2010.

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L.: Measurements of Secondary Organic Aerosol from Oxidation of Cycloalkenes, Terpenes, and m-Xylene Using an Aerodyne Aerosol Mass Spectrometer, Environ Sci Technol, 39, 5674-5688, 10.1021/es048061a, 2005.

Blanchard, C. L., Hidy, G. M., Tanenbaum, S., Rasmussen, R., Watkins, R., and Edgerton, E.: NMOC, ozone, and organic aerosol in the southeastern United States, 1999-2007 1 Spatial and temporal variations of NMOC concentrations and composition in Atlanta, Georgia, Atmospheric Environment, 44, 4827-4839, DOI 10.1016/j.atmosenv.2010.08.036, 2010.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.

Crippa, M., Canonaco, F., Slowik, J. G., El Haddad, I., DeCarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand, N., Temime-Roussel, B., Abidi, E., Poulain, L., Wiedensohler, A., Baltensperger, U., and Prévôt, A. S. H.: Primary and secondary organic aerosol origin by combined gas-particle phase source apportionment, Atmos. Chem. Phys., 13, 8411-8426, 10.5194/acp-13-8411-2013, 2013.

Guenther, A., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.

Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., and Sakulyanontvittaya, T.: Sesquiterpene Emissions from Pine Trees − Identifications, Emission Rates and Flux Estimates for the Contiguous United States, Environ Sci Technol, 41, 1545-1553, 10.1021/es0618907, 2007.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525-1529, DOI 10.1126/science.1180353, 2009.

Kim, P. S., Jacob, D. J., Fisher, J. A., Travis, K., Yu, K., Zhu, L., Yantosca, R. M., Sulprizio, M. P., Jimenez, J. L., Campuzano-Jost, P., Froyd, K. D., Liao, J., Hair, J. W., Fenn, M. A., Butler, C. F., Wagner, N. L., Gordon, T. D., Welti, A., Wennberg, P. O., Crounse, J. D., St. Clair, J. M., Teng, A. P., Millet, D. B., Schwarz, J. P., Markovic, M. Z., and Perring, A. E.: Sources, seasonality, and trends of southeast US aerosol: an integrated analysis of surface, aircraft, and satellite observations with the GEOS-Chem chemical transport model, Atmos. Chem. Phys., 15, 10411-10433, 10.5194/acp-15-10411-2015, 2015.

Lee, A. K. Y., Herckes, P., Leaitch, W. R., Macdonald, A. M., and Abbatt, J. P. D.: Aqueous OH oxidation of ambient organic aerosol and cloud water organics: Formation of highly oxidized products, Geophysical Research Letters, 38, n/a-n/a, 10.1029/2011GL047439, 2011.

Lee, A. K. Y., Abbatt, J. P. D., Leaitch, W. R., Li, S. M., Sjostedt, S. J., Wentzell, J. J. B., Liggio, J., and Macdonald, A. M.: Substantial secondary organic aerosol formation in a coniferous forest: observations of both day- and nighttime chemistry, Atmos. Chem. Phys., 16, 6721-6733, 10.5194/acp-16-6721-2016, 2016.

Lewis, C. W., and Stiles, D. C.: Radiocarbon Content of PM2.5 Ambient Aerosol in Tampa, FL, Aerosol Sci Tech, 40, 189-196, 10.1080/02786820500521007, 2006.

Milic, A., Mallet, M. D., Cravigan, L. T., Alroe, J., Ristovski, Z. D., Selleck, P., Lawson, S. J., Ward, J., Desservettaz, M. J., Paton-Walsh, C., Williams, L. R., Keywood, M. D., and Miljevic, B.: Biomass burning and biogenic aerosols in northern Australia during the SAFIRED campaign, Atmos. Chem. Phys., 17, 3945-3961, 10.5194/acp-17-3945-2017, 2017.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prevot, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos Chem Phys, 10, 4625-4641, DOI 10.5194/acp-10-4625-2010, 2010.

Palm, B. B., de Sá, S. S., Day, D. A., Campuzano-Jost, P., Hu, W., Seco, R., Sjostedt, S. J., Park, J. H., Guenther, A. B., Kim, S., Brito, J., Wurm, F., Artaxo, P., Thalman, R., Wang, J., Yee, L. D., Wernis, R., Isaacman-VanWertz, G., Goldstein, A. H., Liu, Y., Springston, S. R., Souza, R., Newburn, M. K., Alexander, M. L., Martin, S. T., and Jimenez, J. L.: Secondary organic aerosol formation from ambient air in an oxidation flow reactor in central Amazonia, Atmos. Chem. Phys., 18, 467-493, 10.5194/acp-18-467-2018, 2018.

Pye, H. O. T., Luecken, D. J., Xu, L., Boyd, C. M., Ng, N. L., Baker, K. R., Ayres, B. R., Bash, J. O., Baumann, K., Carter, W. P. L., Edgerton, E., Fry, J. L., Hutzell, W. T., Schwede, D. B., and Shepson, P. B.: Modeling the Current and Future Roles of Particulate Organic Nitrates in the Southeastern United States, Environ Sci Technol, 49, 14195-14203, 10.1021/acs.est.5b03738, 2015.

Reyes-Villegas, E., Priestley, M., Ting, Y. C., Haslett, S., Bannan, T., Le Breton, M., Williams, P. I., Bacak, A., Flynn, M. J., Coe, H., Percival, C., and Allan, J. D.: Simultaneous aerosol mass spectrometry and chemical ionisation mass spectrometry measurements during a biomass burning event in the UK: insights into nitrate chemistry, Atmos. Chem. Phys., 18, 4093-4111, 10.5194/acp-18-4093-2018, 2018.

Robinson, N. H., Newton, H. M., Allan, J. D., Irwin, M., Hamilton, J. F., Flynn, M., Bower, K. N., Williams, P. I., Mills, G., Reeves, C. E., McFiggans, G., and Coe, H.: Source attribution of Bornean air masses by back trajectory analysis during the OP3 project, Atmos. Chem. Phys., 11, 9605-9630, 10.5194/acp-11-9605-2011, 2011.

Saha, P. K., and Grieshop, A. P.: Exploring Divergent Volatility Properties from Yield and Thermodenuder Measurements of Secondary Organic Aerosol from α-Pinene Ozonolysis, Environ Sci Technol, 10.1021/acs.est.6b00303, 2016.

Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., Xu, W., Zhao, J., Han, T., Worsnop, D. R., and Wang, Z.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, Atmos. Chem. Phys., 16, 8309-8329, 10.5194/acp-16-8309-2016, 2016.

Tasoglou, A., and Pandis, S. N.: Formation and chemical aging of secondary organic aerosol during the β-caryophyllene oxidation, Atmos. Chem. Phys., 15, 6035-6046, 10.5194/acp-15-6035-2015, 2015.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States, J Geophys Res-Atmos, 112, Artn D13302 Doi 10.1029/2007jd008408, 2007.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences, 112, 37-42, 10.1073/pnas.1417609112, 2015a.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, Atmos. Chem. Phys., 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015b.

Xu, W., Han, T., Du, W., Wang, Q., Chen, C., Zhao, J., Zhang, Y., Li, J., Fu, P., Wang, Z., Worsnop, D. R., and Sun, Y.: Effects of Aqueous-Phase and Photochemical Processing on Secondary Organic Aerosol Formation and Evolution in Beijing, China, Environ Sci Technol, 10.1021/acs.est.6b04498, 2016.

Zhang, H., Yee, L. D., Lee, B. H., Curtis, M. P., Worton, D. R., Isaacman-VanWertz, G., Offenberg, J. H., Lewandowski, M., Kleindienst, T. E., Beaver, M. R., Holder, A. L., Lonneman, W. A., Docherty, K. S., Jaoui, M., Pye, H. O. T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Guo, H., Weber, R. J., de Gouw, J., Koss, A. R., Edgerton, E. S., Brune, W., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Kreisberg, N. M., Spielman, S. R., Hering, S. V., Wilson, K. R., Thornton, J. A., and Goldstein, A. H.: Monoterpenes are the largest source of summertime organic aerosol in the southeastern United States, Proceedings of the National Academy of Sciences, 10.1073/pnas.1717513115, 2018.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., and Sun, Y. L.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Anal Bioanal Chem, 401, 3045-3067, DOI 10.1007/s00216-011-5355-y, 2011.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, Proceedings of the National Academy of Sciences, 10.1073/pnas.1404727111, 2014.

Large Contributions from Biogenic Monoterpenes and Sesquiterpenes to Organic Aerosol in the Southeastern United States

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Abstract

Atmospheric organic aerosol (OA) has important impacts on climate and human health but its sources remain poorly understood. Biogenic monoterpenes and sesquiterpenes are critical precursors of OA. The OA generation from these precursors predicted by models has considerable uncertainty owing to a lack of appropriate observations as constraints. ~~Here, we perform novel lab-in-the-field experiments, which allow us to~~In this study~~ OA formation under realistic atmospheric conditions and offer a connection between laboratory and field studies. Based on the lab-in-the-field experimental approach and ~~, we propose that the less-oxidized oxygenated organic aerosol (LO-OOA) factor resolved from positive matrix factorization (PMF) analysis on aerosol mass spectrometry (AMS) data~~, we provide a measure of OA~~ can be used as a surrogate for fresh SOA from monoterpenes and sesquiterpenes in the southeastern U.S. We support this hypothesis based on a weight of evidence, including lab-in-the-field perturbation experiments, extensive ambient ground-level measurements, and state-of-the-art modeling. We performed lab-in-the-field experiments, in which the ambient air is perturbed by the injection of selected monoterpenes and sesquiterpenes and subsequent SOA formation. PMF analysis on the perturbation experiments provides an objective link between LO-OOA and fresh SOA from monoterpenes and sesquiterpenes as well as insights into the sources of other OA factors. Further, we use an upgraded atmospheric model and show that modeled SOA concentrations from monoterpenes and sesquiterpenes could reproduce both the ~~measured OA concentration from monoterpenes~~magnitude and ~~sesquiterpenes~~diurnal variation of LO-OOA at multiple sites in the southeastern U.S., building confidence in ~~the observed attribution of monoterpene SOA. We show that~~ our hypothesis. We predict the annual average concentration of ~~OA~~SOA from monoterpenes and sesquiterpenes in the southeastern U.S. is ~2.1 μg m^{-3}. This amount is substantially higher than represented in current regional models and accounts for 21% of World Health Organization PM$_{2.5}$ standard, indicating a significant contributor of environmental risk to the 77 million habitants in the southeastern U.S.

1 Introduction

Organic aerosol (OA) constitutes a substantial fraction of ambient fine particulate matter (PM) and has large impacts on air quality, climate change, and human health (Carslaw et al., 2013; Lelieveld et al., 2015). OA can be directly emitted from sources (primary OA, POA) or formed by the oxidation of volatile organic compounds (VOCs) (secondary OA, SOA). Global measurements revealed the dominance of SOA over POA in various atmospheric environments (Jimenez et al., 2009; Ng et al., 2010). The VOCs can be emitted from natural sources (i.e., biogenic) or human activities (i.e., anthropogenic). However, the relative contribution of biogenic and anthropogenic sources to SOA formation in the atmosphere is poorly constrained. This knowledge is critical for formulating effective pollution control strategies that aim at reducing ambient PM concentrations and accurately assessing the climate effects of OA (Hallquist et al., 2009). Biogenic VOCs such as monoterpenes (MT, $C_{10}H_{16}$) and sesquiterpenes (SQT, $C_{15}H_{24}$) are recognized as critical precursors of SOA (Tsigaridis et al., 2014; Hodzic et al., 2016; Pye et al., 2010). The predicted global SOA production from MT and SQT varies from 14 to 246 Tg yr^{-1} (Spracklen et al., 2011; Pye et al., 2010). This large variation in model estimates arises from a number of factors (including uncertainty in SOA yield) and introduces significant uncertainties in estimating OA concentrations and its subsequent influences on climate and human exposure.

The large model uncertainties call for ambient observations to constrain model results. Isolating and measuring SOA production from specific sources are challenging because SOA is a complex mixture consisting of thousands of compounds and SOA evolves dynamically in the atmosphere. A widely used method to apportion OA into different characteristic sources is positive matrix factorization (PMF) analysis on the organic mass spectra measured by aerosol mass spectrometer (AMS) (Ulbrich et al., 2009; Jimenez et al., 2009; Ng et al., 2010). PMF-AMS analysis groups OA constituents with similar mass spectra and temporal variations into characteristic OA subtypes (i.e., factors). This analysis has revealed ~~two ubiquitous OA subtypes in ambient environments, less-oxidized~~ that concentration of oxygenated OA (~~LO-OOA) and more-oxidized oxygenated OA (MO-~~OOA), which ~~are differentiated by their degree of carbon oxidation. LO-OOA and MO-OOA together account for more~~is a surrogate of SOA, is much greater than ~~half of total submicron OA~~that of hydrocarbon-like OA (HOA), which is a surrogate of POA (~~Crippa~~Zhang et al., ~~2014; Xu et al., 2015a; Jimenez et al., 2009~~2007)~~. Primarily based on comparison of their mass spectra with those of laboratory-generated SOA, previous studies~~

~~proposed that LO-OOA is freshly formed SOA from various sources and evolves into MO-OOA with photochemical aging in the atmosphere~~. In many circumstances especially in warmer months, more than one SOA factor is resolved from PMF analysis, often including less-oxidized oxygenated OA (LO-OOA, also denoted as semi-volatile oxygenated organic aerosol in older studies) and more-oxidized oxygenated OA (MO-OOA, also denoted as low-volatility oxygenated organic aerosol in older studies). LO-OOA and MO-OOA are differentiated by their degree of carbon oxidation. These two factors together account for more than half of total submicron OA (Crippa et al., 2014; Xu et al., 2015a; Jimenez et al., 2009~~; Ng et al., 2010~~)~~. These studies have significantly advanced our knowledge of the composition and evolution of ambient OA; however, there are still uncertainties associated with the sources of these OA factors. Firstly, the current understanding on LO-OOA and MO-OOA offers little mechanistic information regarding the specific sources of these factors at a measurement site. Atmospheric models typically use the lumped LO-OOA and MO-OOA concentration to constrain simulated total SOA concentration~~. Despite of their large abundance, the sources of LO-OOA and MO-OOA are unclear and likely vary with location and season. Early studies, primarily based on comparison of the mass spectra of OA factors with those of laboratory-generated SOA, proposed that LO-OOA is freshly formed SOA from various sources and evolves into MO-OOA with photochemical aging in the atmosphere (~~Spracklen~~Jimenez et al., ~~2011; Tsigaridis~~2009; Ng et al., ~~2014~~2010)~~, which hinders our ability to diagnose the cause for the discrepancies between modeled and observed aerosol concentrations (Spracklen et al., 2011). Secondly, the assumption that LO-OOA represents fresh SOA has yet to be directly verified. Also, it is not known whether fresh SOA is exclusively apportioned into LO-OOA. For example, rather than being produced from continued photochemical aging, recent studies hypothesize that the rapidly produced HOMs (highly oxygenated molecules) from the oxidation of VOCs may contribute to MO-OOA~~. Later, a number of possible sources have been proposed for MO-OOA, including SOA from long-range transport (Hayes et al., 2013; Robinson et al., 2011b), aged biomass burning OA (~~Ehn~~Bougiatioti et al., 2014; Grieshop et al., 2009)~~. Thus, considering the large abundance of these two OA subtypes and that they are surrogates for ambient SOA, understanding the sources of compounds composing these two OA subtypes is critical to constrain atmospheric models and~~, humic-like substances (El Haddad et al., 2013), highly oxygenated molecules (HOMs) formed in the oxidation of monoterpenes (Mutzel et al., 2015; Ehn et al., 2014), and aqueous phase processing (Xu et al., 2016c). Regarding the sources of LO-OOA, Zotter et al. (2014) applied radiocarbon analysis and showed that 68-75% of carbon in LO-OOA in California stems from fossil sources. In the southeastern U.S., Xu et al. (2015a) suggested that the oxidation of biogenic β-pinene by nitrate radicals (NO_3) contributes to LO-OOA, though this reaction alone cannot replicate the magnitude of LO-OOA (Pye et al., 2015). These studies significantly advanced our knowledge of the sources and evolution of ambient OA; however, uncertainties associated with the sources of these OA factors still exist. As a result, atmospheric models typically use the lumped LO-OOA and MO-OOA concentration to constrain simulated total SOA concentration (Spracklen et al., 2011; Tsigaridis et al., 2014), which hinders our ability to diagnose the cause of discrepancies between modeled and observed aerosol concentrations (Spracklen et al., 2011). Many sources of LO-OOA and MO-OOA are proposed based on comparing the mass spectra between OA factors and laboratory-generated SOA (Jimenez et al., 2009; Palm et al., 2018; Kiendler-Scharr et al., 2009). However, the similarity between two mass spectra is a subjective determination. Further, the subjectively-defined similarity cannot tell what is the fraction of SOA from a certain source contributes to one OA factor. Overall, considering the large abundance of OOA subtypes and their use as surrogates for ambient SOA, understanding the sources of compounds composing these two OA subtypes is critical to constrain atmospheric models and the SOA budget.

In this study, we integrate lab-in-the-field experiments, extensive ambient ground measurements, and state-of-the-art modeling to improve the understanding of the sources of OA factors and better constrain the OA budget from MT and SQT. ~~We~~Based on lab-in-the-field experiments, we provide ~~direct~~objective evidence that newly formed SOA from α-pinene (~~representative~~an important monoterpene~~, which accounts for about half of monoterpenes emissions (Guenther et al., 2012))~~) and β-caryophyllene (~~representative~~an important sesquiterpene) is dominantly ~~contributes~~apportioned to LO-OOA in the southeastern U.S. ~~The modeled SOA~~In addition, we model the SOA concentration from the oxidation of MT and SQT (denoted as SOA_{MT+SQT}) ~~accurately~~and show that SOA_{MT+SQT} reasonably reproduces the magnitude and diurnal variability of LO-OOA measured at multiple sites in the southeastern U.S. ~~The agreement between model and measurements supports the hypothesis~~Together with other evidence in the literature, we propose that LO-OOA can be used as a measure of SOA_{MT+SQT} in the southeastern U.S. ~~The~~Finally, we discuss how the lab-in-the-field approach allows for the study of SOA formation under realistic atmospheric conditions, which bridges laboratory studies and field measurements and provides a direct way to evaluate the atmospheric relevancy of laboratory studies.

2 Method

2.1 Lab-in-the-field perturbation experiments

The perturbation experiments were performed in July-August 2016 on the rooftop of the Environmental Science and Technology building on the Georgia Institute of Technology campus. This measurement site is ~~a representative~~an urban site in Atlanta, Georgia. Multiple ambient field studies have been performed at this site previously (Xu et al., 2015b; Hennigan et al., 2009; Verma et al., 2014). A 2m^3 Teflon chamber (cubic shape) (Fig. 1) was placed outdoor on the rooftop of the building. The eight corners of the chamber were open (~2”×2”) to the atmosphere to allow for continuous exchange of air with the atmosphere. The perturbation procedure is briefly described below and illustrated in Fig. A1. Firstly, we continuously flushed the chamber with ambient air using two fans, which were placed at two corners of the chamber. During this flushing period, all instruments sampled ambient air and were not connected to the chamber. The flushing period lasted at least 3 hours to ensure that the air composition in the chamber is the same as ambient composition. Secondly, we stopped both fans and connected all instruments to chamber. Because of the continued sampling by the instruments (~20 liter per minute) and the open corners of the chamber, ambient air continuously entered the chamber, even though the two fans were turned off. Thirdly, after sampling the chamber for about 30min, we injected a known amount of VOC (liquid) into the chamber with a needle, where the liquid vaporized upon injection. We continuously monitored the chamber composition for ~40 min after VOC injection. Lastly, we disconnected all instruments from the chamber, sampled ambient air, and turned on two fans to flush the chamber to prepare for the next perturbation experiment.

~~We perturbed the chamber content by injecting one of the following VOCs: isoprene, α-pinene, β-caryophyllene, *m*-xylene, or naphthalene, which are major biogenic or anthropogenic emissions, respectively. The injected VOC amounts were carefully selected. If the injection amount is too large, it is not atmospherically relevant, produces too much SOA, and will bias subsequent analysis. If the injection amount is too small, the produced SOA would fall below the detection limit of the experimental approach. The OA concentration in the chamber after perturbation ranges from 4 to 16 µg m~~$^{-3}$~~, which is within the range of typical ambient OA~~

~~concentration. The VOC oxidation occurred in ambient air (inside the chamber) and lasted ~40 min. Several previous studies have used ambient air as background (Palm et al., 2017; Leungsakul et al., 2005). An important distinction between our study and pervious work is that we perturbed the ambient air only by injection of VOCs and no extra oxidant precursors (i.e., O_3, photolysis of H_2O and O_2, or photolysis of NO_x) were added to the chamber. Our approach allows for study of SOA formation from the specific VOCs injected and evaluate into which PMF factor the SOA is apportioned.~~

Each perturbation experiment can be divided into the following four periods: Amb_Bf (30min ambient measurement period before sampling chamber), Chamber_Bf (from sampling chamber to VOC injection, a period ~30min), Chamber_Af (from VOC injection to stop sampling chamber, a period ~40min), and Amb_Af (30min ambient measurement period after sampling chamber). We calculate the changes in the mass concentration of OA factors after perturbation based on the difference between Chamber_Bf and Chamber_Af, after taking ambient variation into account. The detailed procedure is presented in Appendix A. We develop a comprehensive set of criteria to determine if the changes are statistically significant and if the changes are simply due to ambient variations. The details of these criteria are also discussed in Appendix A.

We perturbed the chamber content by injecting one of the following VOCs: isoprene, α-pinene, β-caryophyllene, *m*-xylene, or naphthalene, which are major biogenic or anthropogenic emissions. We focused on α-pinene and β-caryophyllene, because they are widely studied in the literature (Eddingsaas et al., 2012a; Kurtén et al., 2015; Tasoglou and Pandis, 2015; Ehn et al., 2014; Pathak et al., 2007) and they have large abundances in their classes. For example, α-pinene accounts for about half of monoterpenes emissions (Guenther et al., 2012) and β-caryophyllene is one of the most abundant sesquiterpenes (Helmig et al., 2007). The injected VOC amounts were carefully selected. If the injection amount is too large, it is not atmospherically relevant, produces too much SOA, and will bias subsequent analysis. If the injection amount is too small, the produced SOA would fall below the detection limit of the experimental approach. The VOC oxidation occurred in ambient air (inside the chamber) and lasted ~40 min. The OA concentration in the chamber after perturbation ranges from 4 to 16 μg m^{-3}, which is within the range of typical ambient OA concentrations.

We note that several previous studies have used ambient air (Palm et al., 2017; Leungsakul et al., 2005; Peng et al., 2016), but experimental approaches and purposes of previous studies are different from this study. For example, In Leungsakul et al. (2005), the rural ambient air was used to flush and clean the 270m^3 outdoor chamber reactor. After the flushing, both VOCs and oxidants were injected to produce SOA, the concentration of which were orders of magnitude higher than atmospheric levels. In this study, we use ambient air with pre-existing OA in order to examine which factor(s) the fresh α-pinene and β-caryophyllene SOA are apportioned into by PMF analysis. We aim to produce SOA only from injected α-pinene or β-caryophyllene, so that an important distinction between our study and pervious work is that we perturbed the ambient air by only VOCs, not extra oxidant.

2.2 Analytical instruments

A suite of analytical instruments was deployed to characterize both the gas-phase and particle-phase compositions. The particle-phase composition was monitored by a scanning mobility particle sizer (SMPS, TSI) and a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne), which shared the same stainless steel sampling line. A diaphragm pump (flow rate ~8 liter per minute) was connected to this sampling line, which increased the sampling flow rate and ~~suppressed~~reduced particle loss in the sampling line by reducing the residence time in the tubing. The HR-ToF-AMS measures the chemical composition and size distribution of submicron non-refractory species (NR-PM$_1$) with high temporal resolution. The instrument details about HR-ToF-AMS have been extensively discussed in the literature (Canagaratna et al., 2007; DeCarlo et al., 2006) and the operation of HR-ToF-AMS in this study is described in the section S2 of Supplement.

The gas-phase composition and oxidation products was monitored by an O$_3$ analyzer (Teledyne T400, lower detectable limit 0.6ppb), an ultrasensitive chemiluminescence NO$_x$ monitor (Teledyne 200EU, lower detectable limit 50ppt), and a high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS). The HR-ToF-CIMS with I$^-$ as regent ion can measure a suite of oxygenated volatile organic compounds (oVOCs) at high frequency (1Hz). Detailed working principles and sampling protocol can be found in Lee et al. (2014). The concentrations of VOCs were not measured in this study. All gas-phase measurement instruments shared the same Teflon sampling line. Similar to the particle sampling line, a diaphragm pump (flow rate ~8 liter per minute) was connected to the gas sampling line to reduce the residence time in the tubing.

2.3 Positive Matrix Factorization (PMF) analysis

PMF analysis has been widely used for aerosol source apportionment in the atmospheric chemistry community (Jimenez et al., 2009; Crippa et al., 2014; Xu et al., 2015a; Ng et al., 2010; Ulbrich et al., 2009; Beddows et al., 2015; Visser et al., 2015). PMF solves bilinear unmixing factor model ~~(Paatero and Tapper, 1994; Ulbrich et al., 2009)~~ by minimizing the summed least squares errors of the fit weighted with the error estimates of each measurement~~.~~ (Paatero and Tapper, 1994; Ulbrich et al., 2009). We utilized the PMF2 solver, which does not require a priori information and reduces subjectivity. In this study, we performed PMF analysis on the high-resolution mass spectra of organic aerosol (inorganic species are excluded) of combined ambient and perturbation data in the one-month measurements. Considering that (1) the perturbation data only account for ~10% of total data and (2) the OA concentration is similar ~~in~~between the perturbation experiments and typical ambient measurements, the perturbation experiments do not create a new factor that does not already exist in the ambient data. This is desirable because it allows PMF analysis to apportion the newly formed OA in the perturbation experiments into pre-existing OA factors in the atmosphere.

We resolved five OA factors, including hydrocarbon-like OA (HOA), cooking OA (COA), isoprene-derived OA (isoprene-OA), less-oxidized oxygenated OA (LO-OOA), and more-oxidized oxygenated OA (MO-OOA). The time series and mass spectra of OA factors are shown in Fig. 2. The same 5 factors have been identified at the same measurement site and extensively discussed in the literature (Xu et al., 2015a; Xu et al., 2015b; Xu et al., 2017). Below, we only provide a brief description on these OA factors and more details are discussed in section S3 of Supplement. The mass spectrum of HOA is dominated by hydrocarbon-like ions ($C_xH_y^+$ ions) and HOA is a surrogate of primary OA from vehicle emissions (Zhang et al., 2011). For COA, its concentration is higher at meal times and its mass spectrum is characterized by prominent signal at ions $C_3H_5^+$ (*m/z* 41) and $C_4H_7^+$ (*m/z* 55), which likely arise from ~~unsaturated~~ fatty acids (Huang et al., 2010; Mohr et al., 2009; Allan et al., 2010). The mass spectrum of isoprene-OA is characterized by prominent signal at ions $C_4H_5^+$ (*m/z* 53) and $C_5H_6O^+$ (*m/z* 82) and it is related to the reactive uptake of isoprene oxidation products, isoprene epoxydiols (IEPOX) (Budisulistiorini et al., 2013; Hu et al., 2015; Robinson et al., ~~2011~~2011a; Xu et al., 2015a)~~. LO-OOA and MO-OOA are named based on their differing carbon oxidation state~~. LO-OOA and MO-OOA are named based on their differing carbon oxidation state, that is, from -0.70 to -0.34 for LO-OOA and from -0.18 to 0.71 for MO-OOA in the southeastern U.S. (Xu et al., 2015b). We performed 100 bootstrapping runs to quantify the uncertainty of PMF results. As shown in Fig. S1, the statistical uncertainties in the time series and mass spectra of 5 factors are small and the PMF results reported in this study are robust.

2.4 Details of multiple ambient sampling sites

Measurements at multiple sites in the southeastern U.S. were performed as part of Southeastern Center for Air Pollution and Epidemiology study (SCAPE) and Southern Oxidant and Aerosol Study (SOAS~~).~~) in 2012 and 2013. Detailed descriptions about these field studies have been discussed in the literature (Xu et al., 2015a; Xu et al., 2015b) and section S4 of Supplement. The sampling periods are shown in Table S1 and the sampling sites are briefly discussed below.

- Georgia Tech site (GT): This site is located on the rooftop of the Environmental Science and Technology building on the Georgia Institute of Technology (GT) campus, which is about 30-40m above the ground and 840m away from interstate I75/85. This is ~~a representative~~an urban site in Atlanta. This is also where the perturbation experiments in this study were conducted.

- Jefferson Street site (JST): This is a central SEARCH (SouthEastern Aerosol Research and Characterization) site, which is in Atlanta's urban area with a mixed commercial and residential neighborhood. It is about 2 km west of the GT site. The JST and GT sites are in the same grid cell in CMAQ.

- Yorkville site (YRK): This is a central SEARCH site located in a rural area in Georgia. This site is surrounded by agricultural land and forests and is at about 80 km northwest of JST site.

- Centreville site (CTR): This is a central SEARCH site in rural Alabama. The sampling site is surrounded by forests and away from large urban areas (55km SE and 84 km SW of Tuscaloosa and Birmingham, AL, respectively). The is the main ground site for the SOAS campaign.

2.5 Laboratory chamber study on SOA formation from α-pinene

To compare with results from the lab-in-the-field perturbation experiments, we performed laboratory experiments to study the SOA formation from α-pinene photooxidation under different

NO_x conditions in the Georgia Tech Environmental Chamber (GTEC) facility. The facility consists of two 12 m^3 indoor Teflon chambers, which are suspended inside a temperature-controlled enclosure and surrounded by black lights. The detailed description about chamber facility can be found in Boyd et al. (2015). The experimental procedures have been discussed in Tuet et al. (2017). In brief, the chambers were flushed with clean air prior to each experiment. Then, α-pinene and oxidant sources (i.e., H_2O_2, NO_2, or HONO) were injected into chamber. Once the concentrations of species stabilize, the black lights were turned on to initiate photooxidation. The experimental conditions are summarized in Table S2. Considering that the OA mass concentration affects the partitioning of semi-volatile organic compounds (Odum et al., 1996) and hence affects the organic mass spectra measured by AMS, we calculated the average mass spectra in these laboratory studies by only using the data when the OA mass concentration is below 10 μg m^{-3}, which is similar to that in our ambient perturbation experiments.

2.6 Community Multiscale Air Quality (CMAQ) Model

We used the Community Multiscale Air Quality (CMAQ) atmospheric chemical transport model to simulate the pollutant concentrations across the southeastern U.S. CMAQ v5.2gamma was run over the continental U.S. for time periods between May 2012 to July 2013 with 12km × 12km horizontal resolution. We focus our analysis on the southeastern U.S., which comprises 11 states (Arkansas, Alabama, Florida, Georgia, Kentucky, Louisiana, Mississippi, North Carolina, South Carolina, Tennessee, and Virginia). The meteorological inputs were generated with version 3.8 of the Weather Research and Forecasting model (WRF), Advanced Research WRF (ARW) core. We also applied lightning assimilation to improve convective rainfall (Heath et al., 2016). Anthropogenic emissions were based on the EPA (Environmental Protection Agency) NEI (National Emission Inventory) 2011 v2. Biogenic emissions were predicted by the BEIS (Biogenic Emission Inventory System) v3.6.1. The gas-phase chemistry was based on CB6r3 (Carbon Bond v6.3).

We performed two simulations with different organic aerosol treatment. The "default simulation" generally follows the scheme of Carlton et al. (2010), with the addition of IEPOX SOA following Pye et al. (2013) and documented in Appel et al. (2017) (Fig. ~~S1a~~S2a). The traditional two-product absorptive partitioning scheme (Odum et al., 1996) is used in "default simulation" to describe SOA formation from monoterpenes using data from laboratory experiments by Griffin et al. (1999). In the “updated simulation”, we incorporate two recent findings. Firstly, we implemented MT+NO_3 chemistry to explicitly account for the organic nitrate compounds that have recently been shown to be a ubiquitous and important component of OA (Pye et al., 2015; Kiendler-Scharr et al., 2016; Lee et al., 2016; Ng et al., 2017). We follow the scheme described in Pye et al. (2015) to represent the formation and partition of organic nitrates from monoterpenes via multiple reaction pathways (i.e., oxidation by NO_3 and oxidation by OH/O_3 followed by RO_2+NO). Secondly, we improved the parameterization of SOA formation from MT+O_3/OH based on a recent study by Saha and Grieshop (2016), who applied a dual-thermodenuder system to study the α-pinene ozonolysis SOA. The authors extracted ~~SOA yield~~ parameters (i.e., SOA yields and enthalpies of evaporation) by using an evaporation-kinetics model and volatility basis set (VBS). The SOA yields in Saha and Grieshop (2016) are consistent with recent findings on the formation of HOMs (Ehn et al., 2014; Zhang et al., 2015) and help to explain the observed slow evaporation of α-pinene SOA (Vaden et al., 2011). In the updated simulation, we use the VBS framework with parameters derived from Saha and Grieshop (2016). The new parameterization allows for enthalpies of vaporization that are more consistent with species of the specified volatility. The properties of ~~7~~the volatility bins in the VBS framework are listed in Table S3. A schematic of SOA treatment in “updated simulation” is shown in Fig. ~~S1b. Additional details of the CMAQ simulations are given~~S2b. In the following discussions, we focus on the results from “updated simulation”. The comparison between “default simulation” and “updated simulation” can be found in the section S5 of Supplement.

3 Results and Discussions

3.1 α-pinene perturbation experiments

A total of 19 α-pinene perturbation experiments were performed at different times of the day (i.e., from 9am to 9pm) to probe a wide range of reaction conditions. The injection time and concentrations of O_3 and NO_x during α-pinene perturbation experiments are summarized in Table S4. ~~Initially~~Based on the chamber volume and injected liquid α-pinene volume, initially ~14 ppb α-pinene is injected into chamber~~, but~~. Due to lack of VOC measurements, we build a box model to simulate the fate of α-pinene in the chamber (section S6 of Supplement). We estimate that only a small fraction (2-5ppb) of α-pinene is reacted in the chamber~~, with~~ and most of α-pinene ~~being~~is carried out of the chamber due to dilution with ambient air ~~(section S6 of Supplement).~~.

Fig. 3 shows the time series of OA factors in a typical α-pinene perturbation experiment. ~~The most striking feature is a~~An evident burst and increase of LO-OOA after α-pinene injection occurs. This ~~is the most~~provides direct~~ and compelling~~ evidence that freshly formed α-pinene SOA contributes to LO-OOA. About 15 min after α-pinene injection, LO-OOA concentration starts to decrease, as ambient air continuously flows into the chamber and dilutes the concentration of LO-OOA (section S6 of Supplement). As shown in Fig. ~~S2~~S3, the major known gas-phase oxidation products of α-pinene measured by HR-ToF-CIMS (Eddingsaas et al., ~~2012; Yu et al.;~~2012b; Lee et al., 2016; Yu et al., 1999) show an immediate increase after α-pinene injection. This verifies the rapid oxidation of α-pinene in the chamber.

Fig. 4a shows the perturbation-induced changes in the concentrations of OA factors for all α-pinene experiments. Out of 19 experiments, the LO-OOA concentration is enhanced in 14 experiments. Also, among all OA factors, LO-OOA shows the largest enhancement. This directly supports that freshly formed α-pinene SOA contributes to LO-OOA. The enhancement in LO-OOA concentration differs between experiments, mainly because the perturbations were performed at different times of day ~~under~~(i.e., from 9am to 9pm) and with different reaction ~~conditions. Although~~variables (i.e., temperature, relative humidity, oxidants concentrations, NO_x, etc). Despite the large difference in reaction conditions~~ vary between experiments~~, we note that both LO-OOA enhancement amount and LO-OOA formation rate (i.e., slope of LO-OOA increase) correlate positively with ozone concentration (Fig. 5). This correlation suggests that the concentration of oxidants, both ozone and hydroxy radical (OH, which is not measured in this study but is known to positively correlate with ozone in the atmosphere), ~~is~~plays a more controlling ~~variable for~~role in the amount of OA ~~formation~~formed in α-pinene ~~experiments~~experiment than other reaction variables do. This is likely because higher oxidant concentrations lead to more α-pinene consumption and hence more OA production with the same reaction time.

MO-OOA only increases in 1 out of 19 α-pinene experiments. ~~The~~The highly oxygenated molecules (HOMs), which are rapidly produced from the oxidation of α-pinene, are a hypothesized source of MO-OOA, because of the high O:C ratio of HOMs (Ehn et al., 2014; Mutzel et al., 2015). However, HOMs are first generation monoterpene products co-formed with semivolatile SOA species, and the lack of enhancement in MO-OOA suggests that the HOMs~~, which are rapidly produced from the α-pinene oxidation (Ehn et al., 2014),~~ are unlikely contributors to MO-OOA~~, though more~~. We cannot rule out the possibilities that HOMs are not formed under our experimental conditions, and future studies on the simultaneous verification of HOMs formation and apportion of HOMs by PMF analysis are warranted.

Isoprene-derived OA (isoprene-OA) increases in 7 out of 19 α-pinene experiments. This increase is surprising because the isoprene-OA factor ~~is typically interpreted as SOA from the reactive uptake of IEPOX. Our results demonstrate that the isoprene-OA factor (also referred to as "IEPOX-OA" in some studies) could have interferences from α-pinene SOA. This conclusion could be applicable to isoprene-OA factor resolved at other monoterpenes-influenced sites.~~ (also referred to as "IEPOX-OA" in some studies) is typically interpreted as SOA from the reactive uptake of IEPOX, but our results suggest that the isoprene-OA factor could have interferences from α-pinene SOA. The isoprene-OA enhancement is due to interference from newly formed α-pinene SOA, rather than that the injected α-pinene affecting the oxidation of pre-existing isoprene or affecting the gas/particle partitioning of pre-existing semi-volatile species in the chamber, because of the following reasons. Firstly, based on I^- HR-ToF-CIMS measurement, the concentration of isoprene oxidation products, such as IEPOX+ISOPOOH ($C_5H_{10}O_3 \bullet I^-$) and isoprene hydroxyl nitrates ($C_5H_9NO_4 \bullet I^-$), did not change after α-pinene injection (Fig. S3b). In addition, after injecting α-pinene, the SOA concentration increases less than 4 µg m^{-3}, which does not substantially perturb the gas/particle partition of pre-existing semi-volatile species. Finally, the time series of isoprene-OA and LO-OOA in the same α-pinene perturbation experiment is strongly correlated (Fig. S4a). It is well studied that isoprene produces SOA slower than α-pinene, as isoprene SOA involves higher-generation products. If the enhancement in isoprene-OA factor is due to isoprene oxidation, the enhancement of isoprene-OA is expected to occur later than the enhancement of LO-OOA, but it is not observed in the experiments. Thus, the strong correlation between isoprene-OA and LO-OOA in the same α-pinene perturbation experiment serves as another evidence that the enhancement in isoprene-OA factor is due to interference from newly formed α-pinene SOA, rather than oxidation of isoprene after injecting α-pinene.

The interference of α-pinene SOA on isoprene-OA factor helps to address some uncertainties regarding the isoprene-OA factor in the literature. For example, Liu et al. (2015) compared the mass spectrum of laboratory-derived IEPOX SOA with isoprene-OA factors at some sites. The authors observed stronger correlation for isoprene-OA factors resolved at Borneo (Robinson et al., 2011a) and Amazon (Chen et al., 2015), and weaker correlation at Atlanta, U.S. (Budisulistiorini et al., 2013) and Ontario, Canada (Slowik et al., 2011). As another example, the fraction of measured total IEPOX SOA molecular tracers in isoprene-OA factor highly varies with location, ranging from 26% at Look Rock, TN (Budisulistiorini et al., 2015) to 78% at Centreville, AL (Hu et al., 2015). To address the uncertainties in above two examples, one possible reason is that the isoprene-OA factors resolved at different sites are not purely from IEPOX uptake. Isoprene-OA factors likely have interference from monoterpenes SOA or other sources, but the interference magnitude varies with locations.

While the perturbation experiments clearly point out the possibility that isoprene-OA factor could have interference from α-pinene SOA, two caveats should be kept in mind. First, in this study, the enhancement magnitude of isoprene-OA is ~20% of LO-OOA enhancement (Fig. S5a), but the interference magnitude would vary with locations and seasons. Second, the perturbation experiments simulate a period with increasing α-pinene SOA concentration. The applicability of the conclusions drawn from this specific scenario to general atmosphere with more dynamic variations of OA sources warrants further exploration.

Primary OA factors, i.e., HOA and COA, only show slight increases in 1 or 2 α-pinene experiments, indicating a lack of interference from α-pinene SOA in these factors.

3.2 β-caryophyllene perturbation experiments

A total of 6 β-caryophyllene perturbation experiments were performed. Initially ~10 ppb β-caryophyllene is injected into the chamber. The concentrations of O_3 and NO_x during β-caryophyllene perturbation experiments are summarized in Table S4. In all β-caryophyllene perturbation experiments, LO-OOA also shows a significant enhancement (Fig. 4b). This clearly ~~demonstrates~~shows that the freshly formed SOA from β-caryophyllene oxidation can be another source of LO-OOA. In addition to LO-OOA, COA shows an unexpected increase in 5 out of 6 β-caryophyllene experiments. We have ample evidence that the COA factor at the measurement site has contributions from cooking activities. Firstly, the diurnal variation of COA peaks during meal times (Fig. ~~S3a). Secondly~~S6a). Additionally, the COA concentration shows clear increase on football days, consistent with barbecue activities on campus and close to the measurement site. ~~Thirdly~~Finally, the COA concentration is enhanced on the days right before the start of a new semester when there are many fraternity/sorority rush events (i.e., barbecue activities) on campus (Fig. ~~S3b~~S6b and ~~S3c~~S6c). However, the COA enhancement in β-caryophyllene experiments underscores the fact that COA may not be purely from cooking activities in areas with large biogenic emissions.

3.3 Perturbation experiments with other VOCs

In addition to α-pinene and β-caryophyllene, we also performed a few perturbation experiments by injecting isoprene, *m*-xylene, or naphthalene~~, which are important biogenic and anthropogenic emissions, respectively~~. However, the SOA formation from these VOCs is not detectable. This is mainly due to either lower SOA yields (of isoprene) or slower oxidation rates (of *m*-xylene and naphthalene) compared to α-pinene and β-caryophyllene~~ (section S6 of Supplement). The perturbation experiments with other VOCs confirm the stronger ability of α-pinene and β-caryophyllene to produce SOA (Kroll et al., 2006; Ng et al., 2007; Griffin et al., 1999).~~, which are discussed in section S6 of Supplement.

We have also performed four perturbation experiments by injecting acidic sulfate particles to probe reactive uptake of IEPOX. We observed enhancement in isoprene-OA concentration after the injection of sulfate particles. The detailed results are included in Appendix B.

3.4 ~~Perturbation experiments~~ Compare conclusions from lab-in-the-field perturbation experimental approach vs. mass spectra comparison approach

~~The~~ Based on the lab-in-the-field perturbation experiments~~provide more insights~~, we show that fresh SOA from α-pinene and β-caryophyllene oxidations are mainly apportioned into ~~the sources of OA factors than traditional mass spectra comparison. Previous~~LO-OOA. This finding is consistent with previous studies which concluded that LO-OOA (also denoted as semi-volatile oxygenated organic aerosol, SV-OOA, in older studies) represents freshly formed SOA~~,~~. The conclusion from previous studies is mainly based on ~~the observation that~~mass spectra comparison approach, that is, the mass spectra of laboratory-generated fresh SOA from various sources ~~better resemble the mass spectrum~~are similar to that of LO-OOA~~ than other factors~~ (Jimenez et al., 2009; Ng et al., 2010; Marcolli et al., 2006; Kiendler-Scharr et al., 2009)~~. While this mass spectra comparison approach sheds light on the potential sources of LO-OOA, it does not allow for evaluating whether freshly formed SOA in the atmosphere is exclusively apportioned into LO-OOA. The perturbation experiments, on the other hand, provide a way to evaluate this explicitly. Here, we directly produce SOA from a specific known VOC in ambient air matrix and determine where it is apportioned into. For example, we show that while fresh SOA from α-pinene and β-~~

~~caryophyllene oxidations are mainly apportioned into LO-OOA, they could also be possibly apportioned into isoprene-OA factor and COA, respectively.~~

~~The~~. While we acknowledge that the mass spectra comparison approach largely improves our understanding of OA factors, we believe that the perturbation experimental approach provides more objective and quantitative conclusions by addressing some limitations of the mass spectra comparison approach. The mass spectra comparison approach has the following limitations. Firstly, the similarity between two mass spectra is a subjective determination. In other words, what correlation coefficient (R) value implies SOA from a certain source contributes to a specific OA factor? For example, the R values between laboratory generated α-pinene SOA (using HONO as OH source) with LO-OOA, isoprene-OA, and MO-OOA in this study are 0.96, 0.88, and 0.81, respectively. Using these R values to imply whether α-pinene SOA contributes to a certain OA factor or not is subjective. As another example, Jimenez et al. (2009) showed that the mass spectrum of α-pinene SOA becomes more similar to that of MO-OOA than that of LO-OOA with photochemical aging. The ability to determine when and how much α-pinene SOA is apportioned to MO-OOA based on an R value is subjective. Secondly, the conclusions from mass spectra comparison approach are qualitative. Even if the mass spectrum of α-pinene SOA is the most similar to LO-OOA, this similarity does not guarantee that all α-pinene SOA is apportioned into LO-OOA and this similarity does not provide information regarding what fraction of α-pinene SOA is apportioned into LO-OOA.

The perturbation experiments could address the limitations of mass spectra comparison approach and provide more objective and quantitative conclusions. Firstly, the perturbation experiments simulate a short period of time with increasing α-pinene SOA concentration. We perform PMF analysis on the combined ambient data and perturbation data. PMF analysis does not distinguish SOA from natural α-pinene vs. from injected α-pinene, so that PMF analysis can objectively apportion α-pinene SOA into factors. Thus, the conclusions from the perturbation experiments are directly drawn without any subjective judgement on the similarity in mass spectra. Secondly, using the perturbation data, we attempt to quantify the fraction of fresh α-pinene SOA that is apportioned into different factors (i.e., ~80% into LO-OOA, ~20% into isoprene-OA, 0% into MO-OOA, COA, and HOA). Although further studies are required to extrapolate the conclusions from perturbation experiments to real atmosphere, a similar quantitative understanding cannot be obtained from simple mass spectra comparison approach. Thirdly, the perturbation experiments have the potential to utilize subtle differences across the entire the mass spectrum to evaluate the sources of OA factors. Based on previous laboratory ~~studies~~study, the mass ~~spectra~~spectrum of ~~fresh SOA from~~ α-pinene ~~oxidation and~~SOA is highly correlated (R = 0.97) with that of β-caryophyllene ~~oxidation share much similarity, but there are subtle differences in the mass spectra~~ SOA (Bahreini et al., 2005~~; Tasoglou and Pandis, 2015~~)~~. For example, in the perturbation experiments~~. Using a mass spectra comparison approach would suggest that these mass spectra are too similar to be differentiated by PMF analysis. However, perturbation experiments show different behaviors of α-pinene SOA and β-caryophyllene SOA. That is, a fraction of the fresh β-caryophyllene SOA is apportioned into COA factor, but ~~we do not observe~~ similar behavior is not observed for α-pinene SOA. ~~This is~~ The different behaviors are likely ~~because~~due to the subtle differences in their mass spectra. For example, f_{55} (i.e., the ratio of *m/z* 55 to total signal in the mass spectrum) is typically higher in β-caryophyllene SOA than α-pinene SOA (Bahreini et al., 2005; Tasoglou and Pandis, 2015), and the mass spectrum of COA is characterized by prominent signal at *m/z* 55 (Fig. ~~2).~~2). Overall, the perturbation experiments provide more objective and quantitative insights into the sources of OA factors than traditional mass spectra comparison approach.

3.5 LO-OOA as a surrogate of SOA$_{MT+SQT}$ in the Southeastern U.S.

We propose that the major source of LO-OOA in the southeastern U.S. is the fresh SOA from oxidation of MT and SQT by various oxidants (O_3, OH, and NO_3), based on the following piece of evidence. First, the southeastern U.S. is characterized by large biogenic emissions, including monoterpenes and sesquiterpenes (Guenther et al., 2012). Second, the majority of carbon in SOA is modern in the southeastern U.S. Weber et al. (2007) measured that the biogenic fraction of SOA is roughly 70-80% at two urban sites in Georgia that were also used in our study. We note that measurements in Weber et al. (2007) were performed in 2004 and the biogenic fraction of SOA is expected to be higher in 2016 than 2004, as a result of reductions in anthropogenic emissions (Blanchard et al., 2010). Third, previous studies suggest that the oxidation of β-pinene (another important monoterpene) by nitrate radicals (NO_3) contributes to LO-OOA in the southeastern U.S. (Boyd et al., 2015; Xu et al., 2015a), though this reaction alone cannot replicate the magnitude of LO-OOA (Pye et al., 2015). Fourth, the mass spectra of LO-OOA are almost identical (i.e., R ranges from 0.95 to 0.99 in Fig. S7) across all the seven datasets in our study. In addition, LO-OOA across all datasets also shares the same diurnal trends (Xu et al., 2015a). The similarity in

LO-OOA features suggests that LO-OOA generally share similar sources across multiple sites and in different seasons in the southeastern U.S. Fifth, the lab-in-the-field perturbation experiments provide objective evidence that the majority of freshly formed SOA from the oxidation of MT and SQT contributes to LO-OOA. Sixthly, using the updated CMAQ model (i.e., explicit organic nitrates and Saha and Grieshop (2016) VBS for MT+O_3/OH SOA), we found that the simulated SOA_{MT+SQT} reasonably reproduces both the magnitude and diurnal variability of LO-OOA for all sites (Fig. 6a). The model bias is within ~20% for most sites, except for Centreville, Alabama (i.e., 43% for CTR_June dataset). Fig. 6b present maps of ground-level SOA_{MT+SQT} concentration corresponding to the time periods of observational data, and the SOA_{MT+SQT} concentration is substantially higher in the southeast than other U.S. regions. While, the SOA_{MT+SQT} is present throughout the year, it reaches the largest concentration in summer. The spatial and seasonal variation of SOA_{MT+SQT} concentration is consistent with MT and SQT emissions (Guenther et al., 2012). The consistency between modeled SOA_{MT+SQT} and measured LO-OOA at multiple sites and in different seasons builds confidence in our hypothesis that LO-OOA largely arises from the oxidation of MT and SQT in the southeastern U.S.

We note that we do not conclude that LO-OOA arises exclusively from MT and SQT. SOA from other precursors or other pathways may contribute to LO-OOA, but the related contributions are expected to be much smaller than MT and SQT in the southeastern U.S. Firstly, the contributions of anthropogenic SOA to LO-OOA are likely small. The emissions of anthropogenic VOCs are much weaker than that of biogenic VOCs in the southeastern U.S. (Goldstein et al., 2009). We modeled that the concentration of anthropogenic SOA is on the order of 0.1 $\mu g\ m^{-3}$ for our datasets (Fig. S8). Even if we double the SOA yields of anthropogenic VOCs to account for the potential vapor wall loss in laboratory studies (Zhang et al., 2014), the concentration of SOA from anthropogenic VOCs oxidation is still negligible compared to SOA_{MT+SQT}. The low modeled concentration of anthropogenic SOA is consistent with Zhang et al. (2018), who showed that the measured tracers of anthropogenic SOA only account for 2% of total OA in Centreville, AL. Secondly, other reaction pathways, like aqueous-phase chemistry or some unexplored reaction, may contribute to LO-OOA. However, the consistency between modeled SOA_{MT+SQT} and LO-OOA suggests that LO-OOA can be reasonably represented by a model based on current knowledge and it is not necessary to invoke any unexplored mechanisms. In addition, SOA produced from aqueous-phase chemistry is generally highly oxidized (Lee et al., 2011) and may be apportioned into MO-OOA, instead of LO-OOA. A recent study by Xu et al. (2016c) suggests that aqueous-phase SOA is a major source of MO-OOA in China.

We limit our hypothesis that major source of LO-OOA is the oxidation of MT and SQT to the southeastern U.S. There is clear evidence that LO-OOA factor represents different sources at different locations. For example, radiocarbon analysis shows that 68-75% of carbon in LO-OOA in California stems from fossil sources (Hayes et al., 2013; Zotter et al., 2014), suggesting the contribution from anthropogenic SOA to LO-OOA. Also, in the wintertime of many locations, LO-OOA and MO-OOA are not separated and a single OOA factor is resolved (Xu et al., 2016b; Lanz et al., 2008).

3.6 Connection between laboratory and field studies

Due to the difficulties associated with accurately measuring complex chemical processes in the atmosphere, laboratory studies have been an integral part in our understanding of atmospheric chemistry (Burkholder et al., 2017). However, the representativeness of laboratory studies under simplified conditions with respect to the complex atmosphere is difficult to evaluate. One unique feature of our lab-in-the-field approach is that the VOC oxidation and SOA formation proceed under realistic atmospheric conditions. Taking advantage of this, we provide a direct link between laboratory studies and ambient observations. Previous laboratory studies have shown that NO can affect SOA composition by influencing the fate of organic peroxy radical (RO_2, a critical radical intermediate formed from VOC oxidation) (Kroll and Seinfeld, 2008; Sarrafzadeh et al., 2016; Presto et al., 2005). To evaluate the representativeness of laboratory studies and ~~directly~~ investigate the effects of NO on SOA composition, in Fig. ~~6~~7, we compare the chemical composition of α-pinene SOA formed in laboratory studies under different NO conditions (denoted as SOA_{lab}) with those in α-pinene ambient perturbation experiments (denoted as $SOA_{ambient}$). The degree of similarity in OA mass spectra (i.e., evaluated by the correlation coefficient) between laboratory α-pinene SOA generated under NO-free condition (i.e., denoted as $SOA_{lab,NO\text{-}free}$, using H_2O_2 photolysis as oxidant source) and $SOA_{ambient}$ shows a strong dependence on ambient NO concentration, under which the $SOA_{ambient}$ is formed. The degree of similarity in mass spectra decreases rapidly when ambient NO increases from 0.1 to 0.2ppb, and then reaches a plateau at ~0.3ppb NO. The opposite trend is observed when laboratory α-pinene SOA generated in the presence of high NO concentrations (i.e., denoted as $SOA_{lab,high\text{-}NO}$, using the photolysis of NO_2 or nitrous acid as oxidant source) are compared with $SOA_{ambient}$. These observations ~~directly demonstrate~~show the transition of RO_2 fate as a function of NO under ambient conditions. For the perturbation experiments performed when ambient NO is below ~0.1ppb, the mass spectra of $SOA_{ambient}$ are similar to $SOA_{lab,NO\text{-}free}$, consistent with that RO_2 mainly reacts with hydroperoxyl (HO_2) or isomerizes. In contrast, for the perturbation experiments performed when ambient NO is above ~0.3ppb, the mass spectra of $SOA_{ambient}$ are similar to $SOA_{lab,high\text{-}NO}$, consistent with that the RO_2 fate is dominated by NO. This NO level (~0.3ppb) is consistent with the NO level required to dominate the fate of RO_2 in the atmosphere, as calculated by using previously measured HO_2 and kinetic rate constants (section S8 of Supplement). These observations also ~~directly~~ illustrate that the SOA composition from laboratory studies can be representative of atmosphere. We note that the mass spectra of $SOA_{ambient}$ are generally more similar with that of laboratory SOA generated using NO_2 photolysis as oxidant source than using nitrous acid photolysis. This suggests that laboratory experiments using NO_2 photolysis as oxidant source better represent ambient high NO oxidation conditions in the southeastern U.S. than experiments using nitrous acid do. Possible explanations are discussed in section S7 of Supplement. This finding provides new insights into designing future laboratory experiments to better mimic the oxidations in ambient environments.

4 Implications

~~3.6 Abundance of SOA_{MT+SQT}~~ In this study, we performed lab-in~~-~~the ~~Southeastern U.S.~~

~~The ambient~~-field perturbation experiments ~~provide direct~~and provided objective evidence that the majority of ~~freshly formed~~fresh SOA from the oxidation of MT and SQT contributes to LO-OOA. ~~Previous studies suggest that the oxidation of β-pinene (another important monoterpene) by nitrate radicals (NO_3) contributes to~~ Based on weight of evidence, we propose that LO-OOA can be used as a surrogate of fresh SOA from MT and SQT in the southeastern U.S. ~~(Boyd et al., 2015; Xu et al., 2015a), though this reaction alone cannot replicate the magnitude of LO-OOA, particularly during the daytime (Pye et al., 2015). Considering the large biogenic emissions in the southeastern U.S.~~We showed that modeled SOA_{MT+SQT} could reasonably reproduce both ~~(Guenther et al., 2012) and the new results from our perturbation experiments, we propose that the major source of LO-OOA in this region is the oxidation of MT and SQT by various oxidants (O_3, OH, and NO_3). To test this hypothesis, we use CMAQ to simulate pollutant concentrations across the southeastern U.S.~~

~~The SOA$_{MT+SQT}$ concentration in the default simulation (i.e., no explicit organic nitrate partitioning, Griffin et al. (1999) photooxidation parameterization) is significantly lower than LO-OOA by 55-84% (Fig. 7). In contrast, SOA$_{MT+SQT}$ in the updated simulation (explicit organic nitrates and Saha and Grieshop (2016) VBS for MT+O$_3$/OH) accurately reproduces~~ the magnitude and diurnal variability of LO-OOA ~~for each site (Fig. 8a). The model bias is reduced to within ~20% for most sites, except for Centreville, Alabama (i.e., 43% for CTR_June dataset). The consistency between modeled SOA$_{MT+SQT}$ and measured LO-OOA~~ at ~~multiple~~different sites and in different seasons~~ supports our hypothesis~~. Based on the model simulation, we estimate that ~~LO-OOA largely arises from the oxidation of MT and SQT in the southeastern U.S. Fig. 8b present maps of ground-level SOA$_{MT+SQT}$ concentration corresponding to the time periods of observational data. The SOA$_{MT+SQT}$ concentration is substantially higher in the southeast than other U.S. regions. The SOA$_{MT+SQT}$ is present throughout the year and reaches the largest concentration in summer. The spatial and seasonal variation of SOA$_{MT+SQT}$ concentration is consistent with MT and SQT emissions (Guenther et al., 2012). The~~the annual concentration of SOA$_{MT+SQT}$ in PM$_{2.5}$ in the southeastern U.S. is ~2.1 μg m^{-3} (i.e., average concentration over the six sampling periods and over the southeastern U.S. in the updated simulation). This accounts for 21% of World Health Organization PM$_{2.5}$ guideline (i.e., 10 μg m^{-3} annual mean) and indicates a significant contributor of environmental risk to the 77 million habitants in the southeastern U.S. Also, the estimated ~~concentration~~abundance of SOA$_{MT+SQT}$ is substantially ~~higher~~larger than represented in current models (Lane et al., 2008; Zheng et al., 2015)~~.~~, but in line with the conclusion from Zhang et al. (2018). Zhang et al. (2018) used a different methodology, characterization of molecular tracers of MT SOA at Centreville, AL (a site included in our study as well), to conclude that monoterpenes are the largest source of summertime organic aerosol in the southeastern United States. The oxidation of MT and SQT is likely an under-estimated contributor to ~~natural PM in~~PM in the present day and perhaps during the pre-industrial period, which determines the baseline state of atmosphere and the estimate of climate forcing by anthropogenic emissions (Carslaw et al., 2013). Models need to improve the description of the MT and SQT oxidation to reduce the uncertainties in estimated OA budget and subsequent climate forcing.

~~We note that we do not conclude that LO-OOA arises exclusively from MT and SQT, SOA from anthropogenic VOCs may also contribute to LO-OOA. However, the SOA contribution from anthropogenic VOCs is expected to be much smaller than that from biogenic monoterpenes and~~

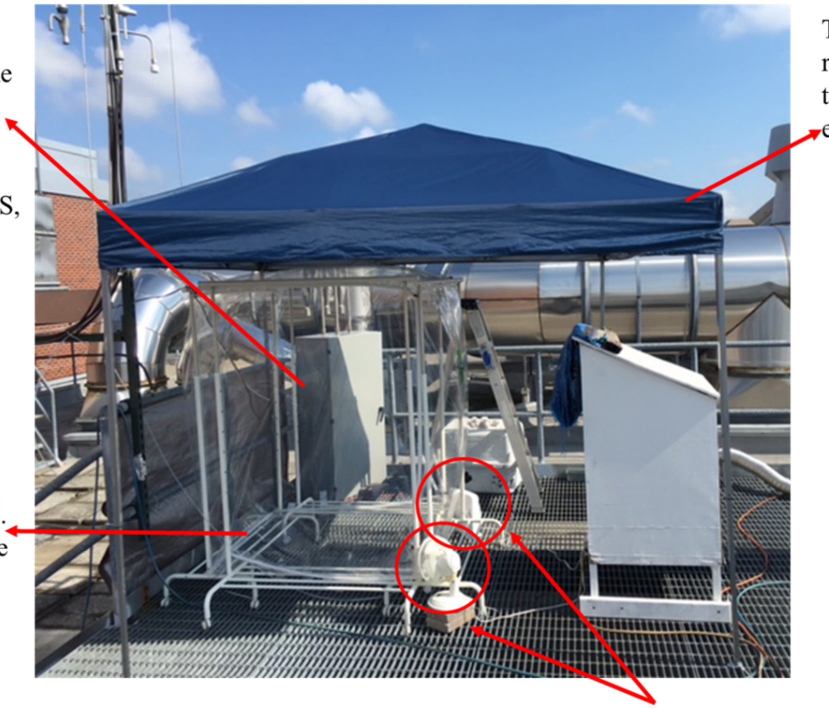
~~sesquiterpenes in the southeastern U.S. Firstly, as shown in the perturbation experiments, α-pinene and β-caryophyllene produce more SOA than *m*-xylene and naphthalene using the same experimental approach in ambient air matrix. Together with weaker emissions of anthropogenic VOCs than biogenic VOCs in the southeastern U.S. (Goldstein et al., 2009), the small contribution to SOA from anthropogenic VOCs is expected. Secondly, as indicated in Fig. S5, the modeled concentration of SOA from anthropogenic VOCs is on the order of 0.1 μg m^{-3}. Even if we double the SOA yields of anthropogenic VOCs to account for the potential vapor wall loss in laboratory studies (Zhang et al., 2014), the concentration of SOA from anthropogenic VOCs oxidation is still negligible compared to SOA$_{\mathrm{MT+SQT}}$. SOA from anthropogenic VOCs oxidation could be abundant in urban areas of the western U.S. There is evidence that LO-OOA in California is related to the oxidation of anthropogenic VOCs, as radiocarbon analysis suggests 68-75% of carbon in LO-OOA in California stems from fossil sources (Hayes et al., 2013; Zotter et al., 2014). The contribution from anthropogenic VOCs to LO-OOA awaits exploration through ambient perturbation experiments in various locations around the world.~~

~~4 Implications~~

~~In this study, we propose that LO-OOA can be used as a surrogate of fresh SOA from MT and SQT in the southeastern U.S., based on the weight of evidence provided by: (1) the large emissions of MT and SQT in this region; (2) the contribution from MT + NO$_3$ to LO-OOA as shown in previous studies; (3) perturbation experiments providing direct evidence that the majority of fresh SOA from the oxidation of MT and SQT contributes to LO-OOA; (4) the consistency of modeled SOA$_{\mathrm{MT+SQT}}$ with the magnitude and diurnal trend of LO-OOA at different sites and in different seasons.~~

Using LO-OOA as a surrogate of SOA$_{\mathrm{MT+SQT}}$ in the southeastern U.S., our ambient ground measurements suggest that at least 19-34% of OA in the southeastern U.S. is from the oxidation of biogenic monoterpenes and sesquiterpenes (Xu et al., 2015a). The fraction of biogenic OA in the southeastern U.S. is even larger if we consider that isoprene-OA could account for 21-36% of OA in summer (albeit potential interferences of SOA from monoterpenes oxidation) and that MO-OOA (24-49% of OA) likely contains SOA from long-term photochemical oxidation of biogenic VOCs. The dominant biogenic origin of SOA poses a challenge to control its burden in the southeastern U.S., if the roles of anthropogenic oxidants and other controlling factors are not recognized. Previous studies have shown that the SOA formation from biogenic VOCs can be mediated by anthropogenic emissions, such as nitrogen oxides and sulfur dioxide (Hoyle et al., 2011; Goldstein et al., 2009; Surratt et al., 2010; Rollins et al., 2012; Xu et al., 2015a). Thus, regulating anthropogenic emissions could help reduce SOA concentration (Lane et al., 2008; Pye et al., 2015; Zheng et al., 2015). For example, as observed in our ambient perturbation experiments, one controlling parameter of α-pinene SOA formation is the concentration of atmospheric oxidants (O_3, OH, and NO_3), which are known to strongly depend on NO_x concentration. As it has been shown that anthropogenic emissions exert complex and non-linear influences on biogenic SOA formation (Zheng et al., 2015), the effectiveness of regulating anthropogenic emissions on biogenic SOA burden requires careful investigations. ~~Importantly, the novel~~

The lab-in-the-field perturbation experiments ~~substantially improve our understanding of ambient~~provide insights into the OA ~~sources~~factors. This experimental approach ~~is~~can be easily ~~applicable to other regions in the world~~adapted. Future experiments conducted under various ambient environments and with diverse SOA precursors would facilitate ~~accurate quantification of global OA sources as well as their climate and health impacts.~~the understanding of OA factors in other regions of the world.



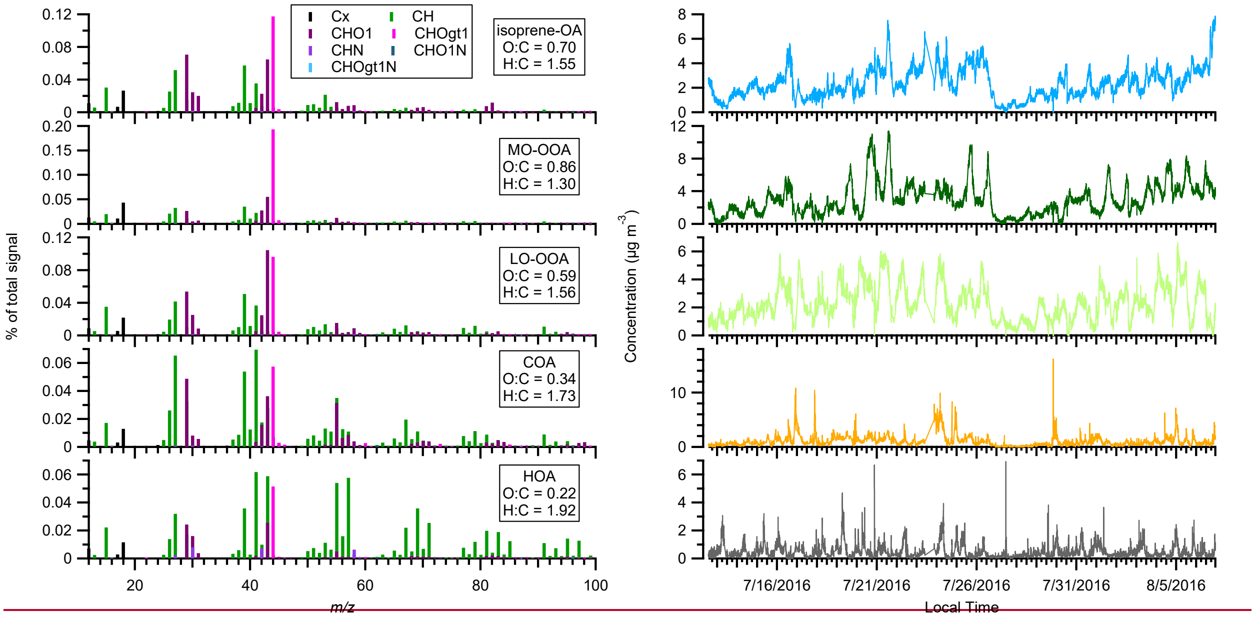
Instruments are located inside the lab (not shown).
Particle phase: AMS, SMPS
Gas phase: CIMS, O_3, NO_x

The tent is removed during the perturbation experiments.

The chamber volume is ~2 m^3. Eight corners are open.

Two fans are used to flush the chamber. The fans are turned off after VOC injection. After turning off the fans, flow rate of air going into the chamber is equal to the instruments pulling flow rate.

Fig. 1. The instrument setup for ambient perturbation experiments.



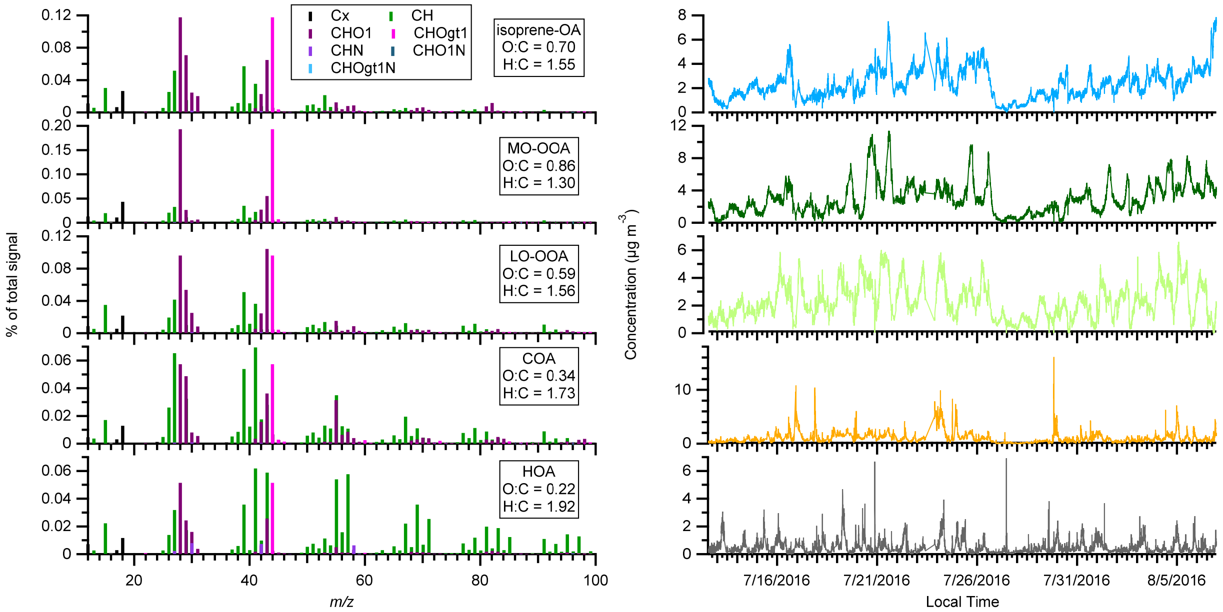


Fig. 2. The mass spectra and time series of OA factors in perturbation study. The time series includes both the ambient data and perturbation experiments data.

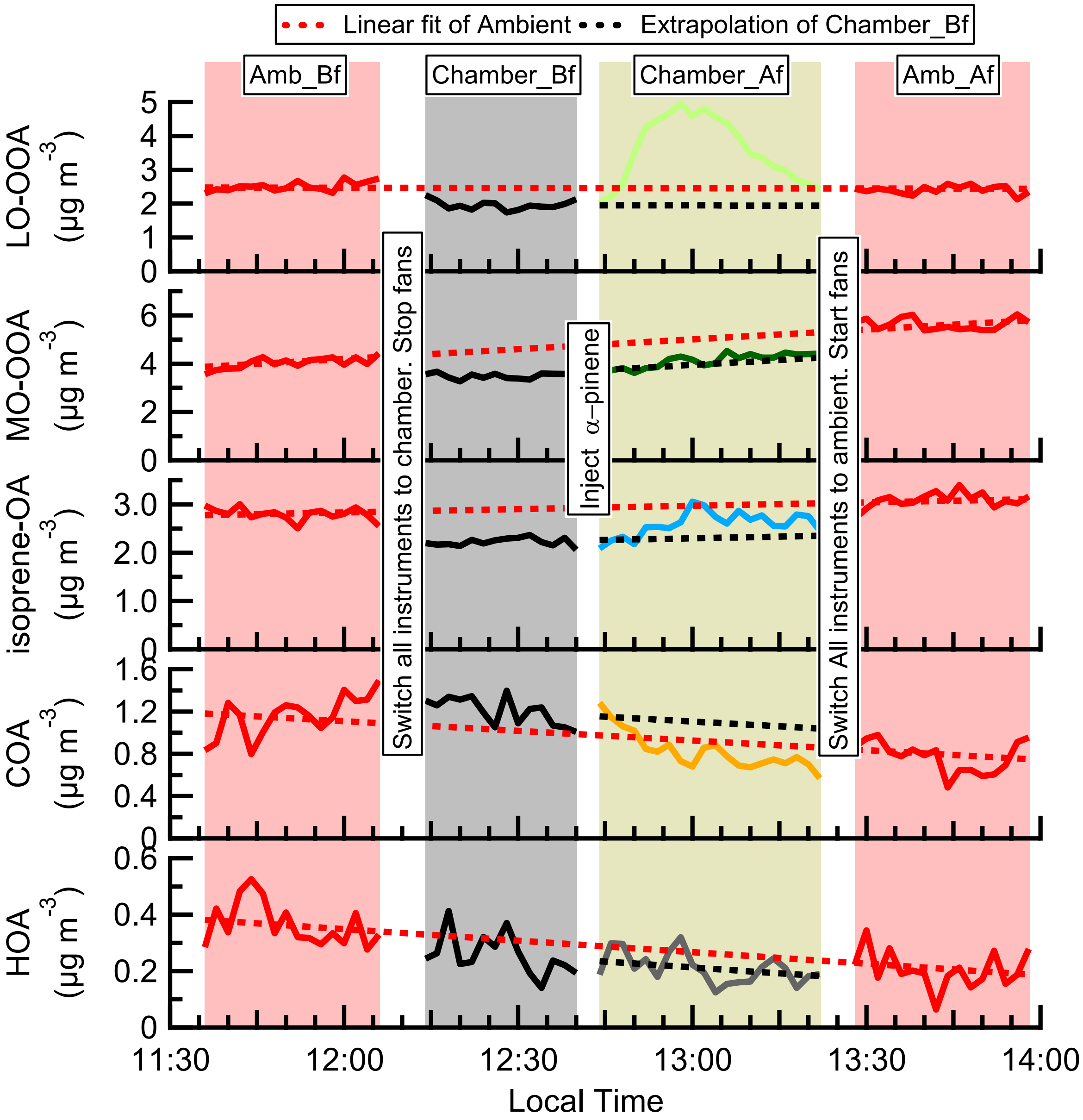
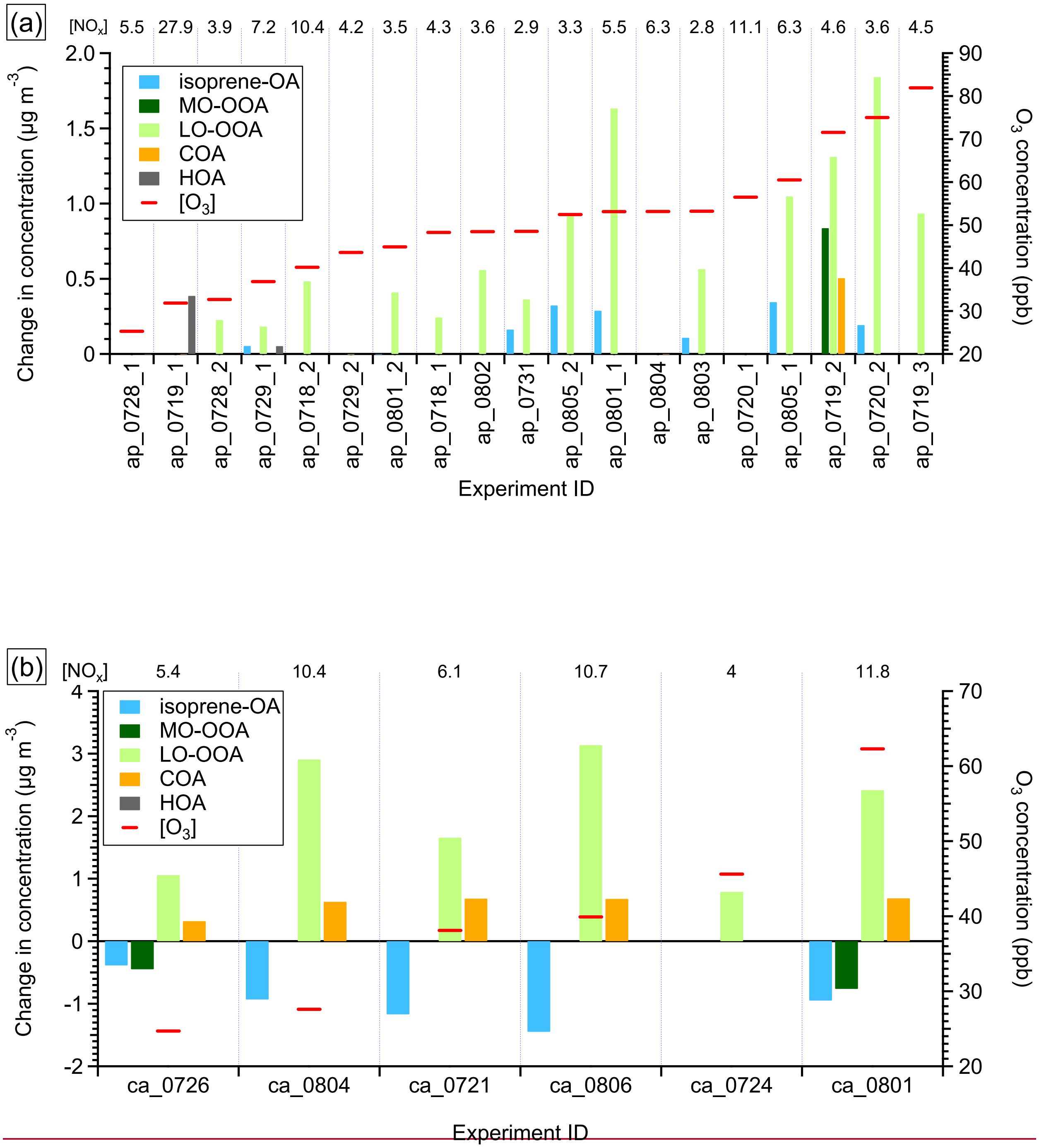


Fig. 3. The time series of OA factors in an α-pinene perturbation experiment (Expt ID: ap_0801_1). Each perturbation experiment includes four periods: Amb_Bf (~30min), Chamber_Bf (~30min), Chamber_Af (~40min), and Amb_Af (~40min). "Amb" and "Chamber" represent that instruments are sampling ambient and chamber, respectively. "Bf" and "Af" stand for before and after perturbation, respectively. The solid lines are measurement data. The dashed red lines are the linear fits of ambient data (i.e., combined Amb_Bf and Amb_Af). The slopes are used to extrapolate Chamber_Bf data to Chamber_Af period (i.e., dashed black lines). The validity of the linearity assumption is discussed in Appendix A. The difference between measurements (i.e., solid lines) and extrapolated Chamber_Bf (i.e., dashed black lines) represents the change caused by perturbation.


(a)
[NO$_x$]
5.5
27.9
3.9
7.2
10.4
4.2
3.5
4.3
3.6
2.9
3.3
5.5
6.3
2.8
11.1
6.3
4.6
3.6
4.5
Change in concentration (μg m^{-3})
2.0
1.5
1.0
0.5
0
isoprene-OA
MO-OOA
LO-OOA
COA
HOA
[O$_3$]
O$_3$ concentration (ppb)
90
80
70
60
50
40
30
20
ap_0728_1
ap_0719_1
ap_0728_2
ap_0729_1
ap_0718_2
ap_0729_2
ap_0801_2
ap_0718_1
ap_0802
ap_0731
ap_0805_2
ap_0801_1
ap_0804
ap_0803
ap_0720_1
ap_0805_1
ap_0719_2
ap_0720_2
ap_0719_3
Experiment ID
(b)
[NO$_x$]
5.4
10.4
6.1
10.7
4
11.8
Change in concentration (μg m^{-3})
4
3
2
1
0
-1
-2
isoprene-OA
MO-OOA
LO-OOA
COA
HOA
[O$_3$]
O$_3$ concentration (ppb)
70
60
50
40
30
20
ca_0726
ca_0804
ca_0721
ca_0806
ca_0724
ca_0801
Experiment ID

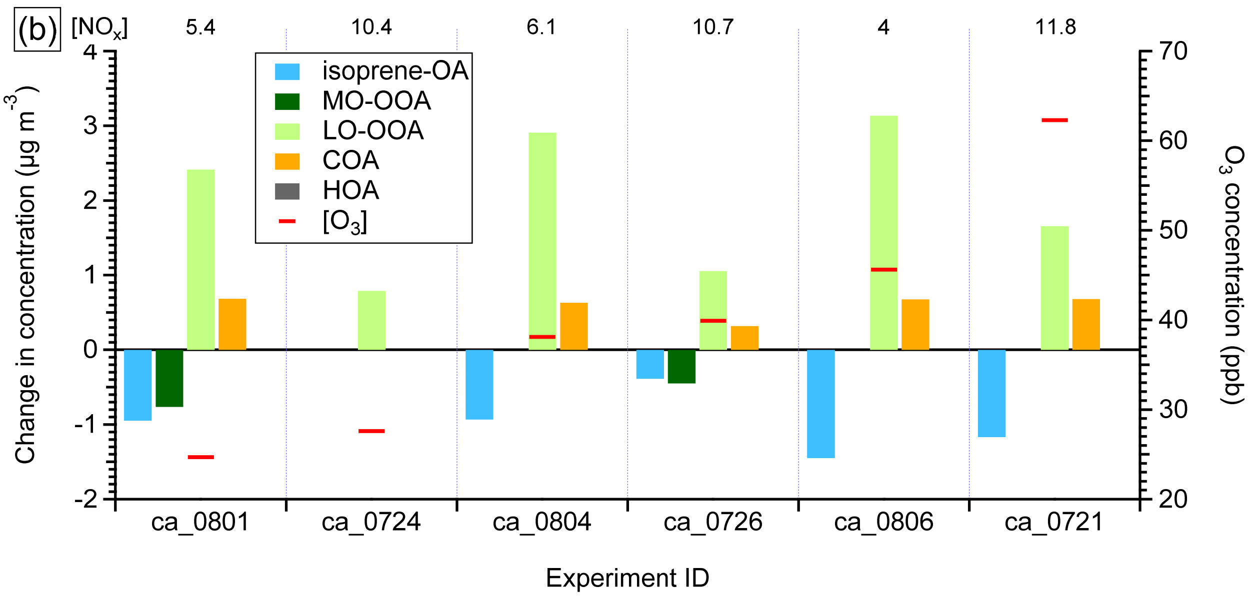


Fig. 4. The statistically significant changes in the concentrations of OA factors after perturbation by (a) α-pinene and (b) β-caryophyllene. The experiments are sorted by average $[O_3]$ during Chamber_Af. The average $[NO_x]$ during Chamber_Af are shown on top of the figure. The changes in concentration are the differences between measurements during Chamber_Af and extrapolated Chamber_Bf (Appendix A). A set of criteria are developed to evaluate if the changes are statistically significant and if the changes are due to ambient variation (Appendix A). Isoprene-OA decreases after β-caryophyllene injection. The reason for this decrease is unclear, but likely due to the limitations of PMF analysis, which assumes constant mass spectra of OA factors over time (section ~~S9~~S3 of Supplement).

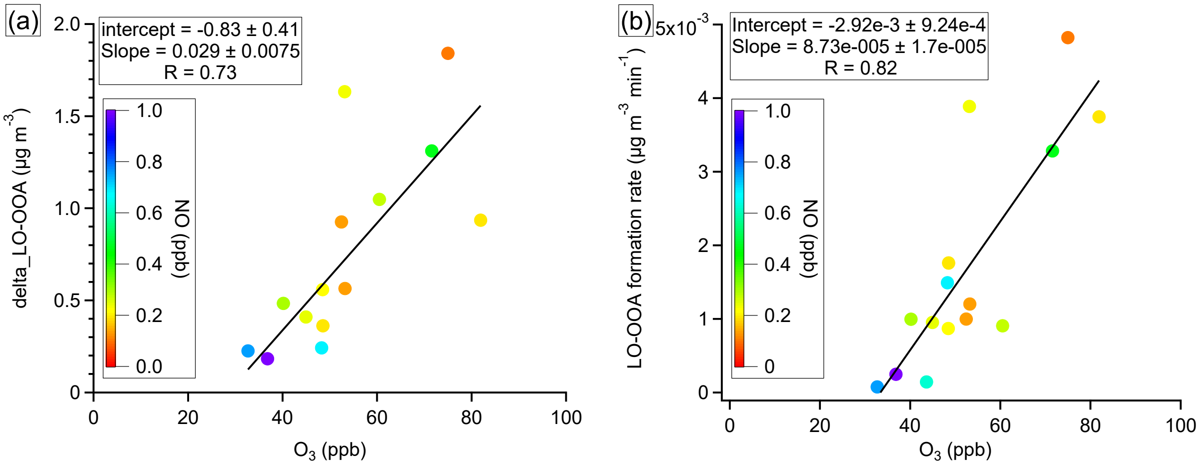
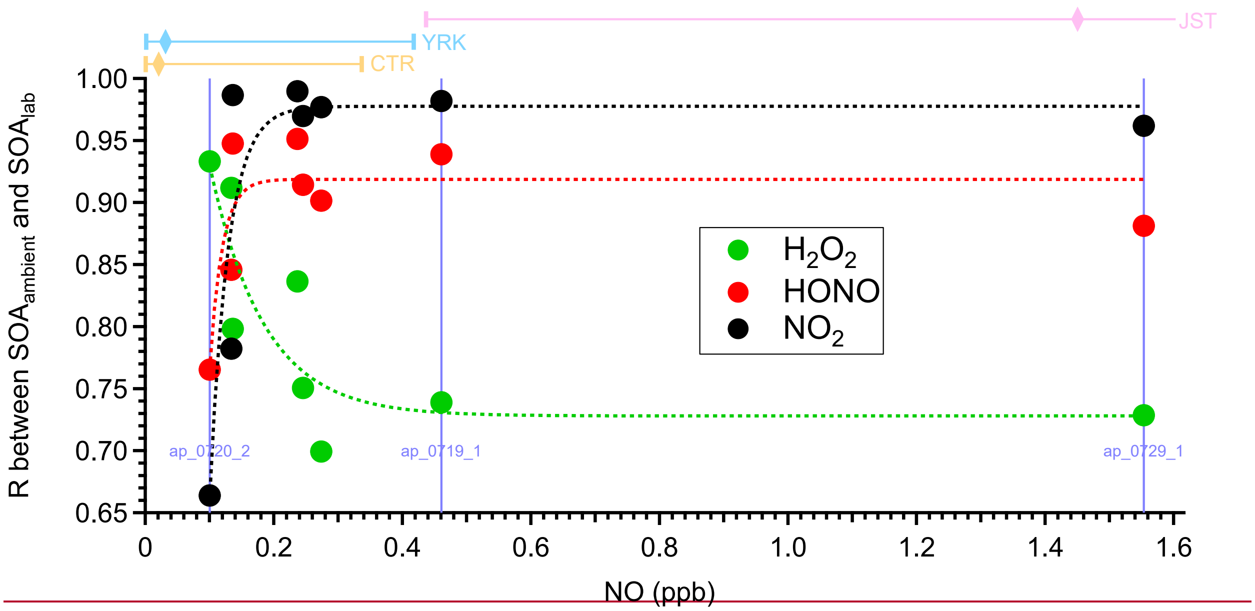


Fig. 5. Observations of trends in (a) LO-OOA enhancement amount and (b) LO-OOA formation rate with O_3 concentration in α-pinene perturbation experiments. The data points are colored by average NO concentration during Chamber_Af period. The slopes, intercepts, and correlation coefficients (R) are obtained by least square fit.


YRK
CTR
JST
R between $SOA_{ambient}$ and SOA_{lab}
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
ap_0720_2
ap_0719_1
ap_0729_1
H_2O_2
HONO
NO_2
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
NO (ppb)

~~Fig. 6~~

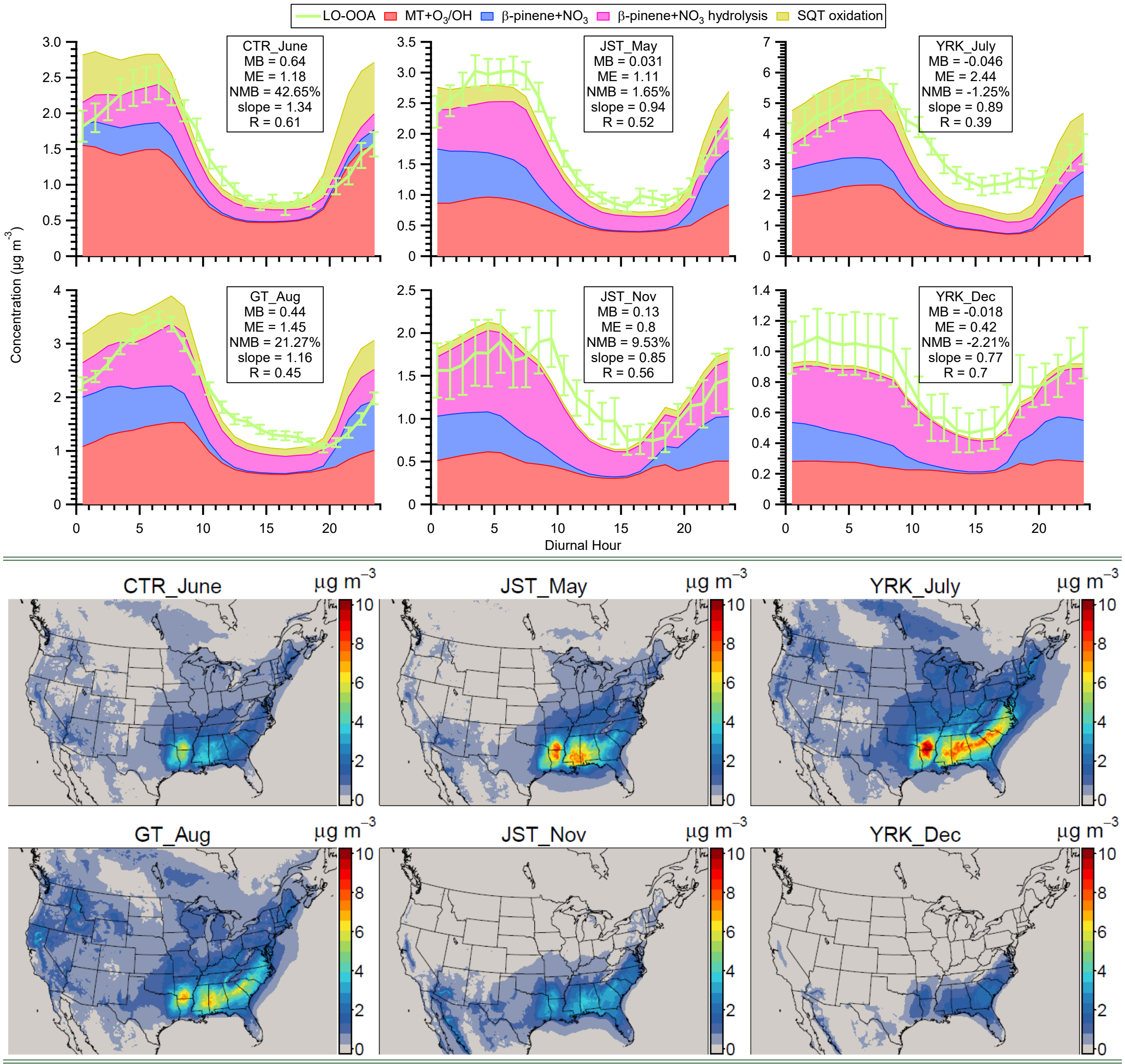


Fig. 6. (a) top panel: the diurnal trends of LO-OOA and modeled SOA from monoterpenes and sesquiterpenes (SOA_{MT+SQT}) at different sampling sites in the southeastern U.S. (b) bottom panel: maps of modeled ground-level SOA_{MT+SQT} concentration coinciding with the time periods of intensive ambient sampling. Model results shown here are from the updated simulation. Abbreviations correspond to Centreville (CTR), Jefferson Street (JST), Yorkville (YRK), Georgia Institute of Technology (GT). Detailed sampling periods are shown in Table S1. In panel (a), since the perturbation experiments show that 16% of SOA from α-pinene oxidation is apportioned into isoprene-OA (Fig. S5a), we only include 84% of modeled SOA from MT+O_3/OH when comparing with LO-OOA for the sites with isoprene-OA. The mean bias (MB), mean error (ME), and normalized mean bias (NMB) for each site are shown in each panel. The slopes and correlation

coefficients (R) are obtained by least square fit. The error bars indicate the standard error. In panel (b), average SOA_{MT+SQT} concentration in $PM_{2.5}$ during each sampling period is reported.

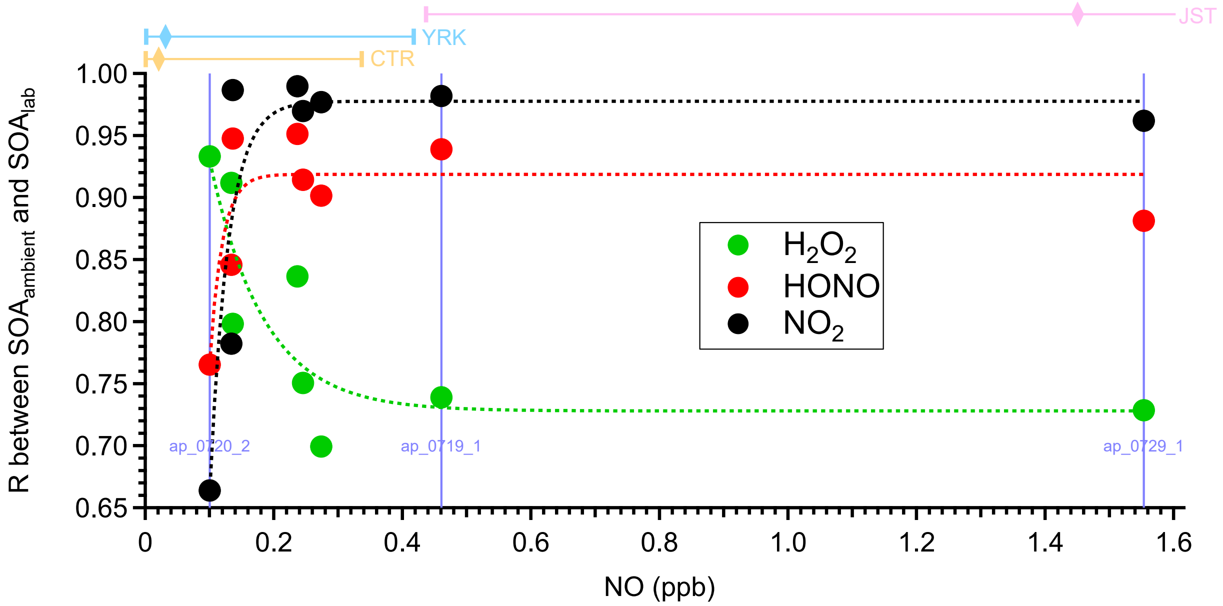
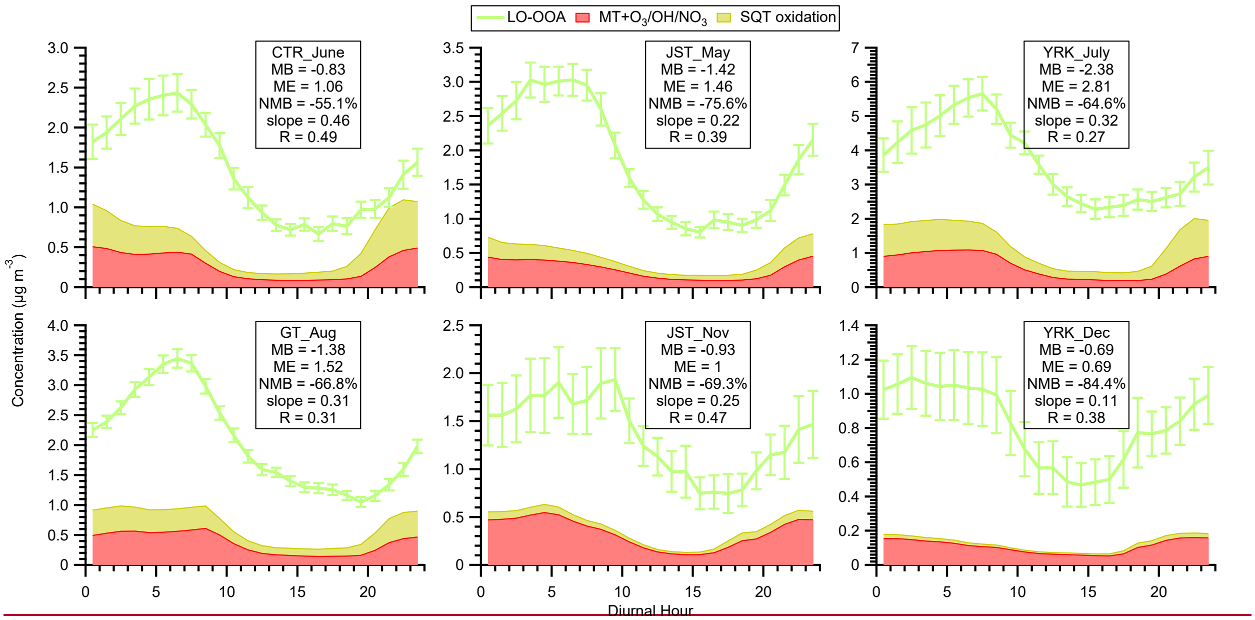
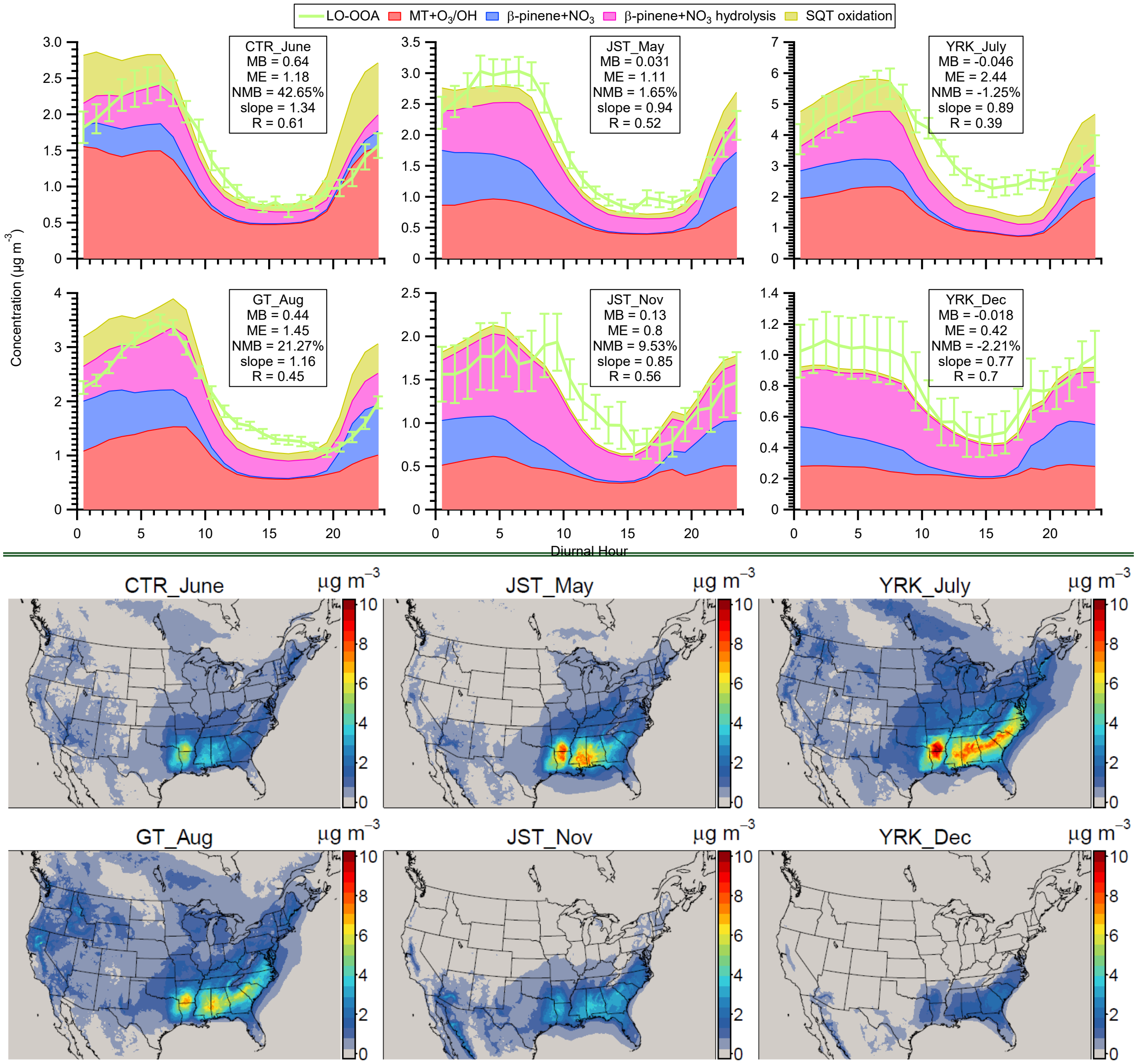


Fig. 7. The correlation coefficients between the mass spectra of OA formed in laboratory under different NO conditions (“SOA$_{\mathrm{lab}}$”) and those of OA formed in ambient α-pinene perturbation experiments (“SOA$_{\mathrm{ambient}}$”). The subscripts “$_{\mathrm{lab}}$” and “$_{\mathrm{ambient}}$” indicate the SOA formed under laboratory conditions and ambient conditions, respectively. Three different oxidant sources (i.e., H_2O_2, HONO, and NO_2) are used to create different NO concentrations in laboratory studies. The mass spectra of “SOA$_{\mathrm{ambient}}$” are calculated by comparing the mass spectra of OA during Chamber_Af and those of extrapolated Chamber_Bf (section S7 of Supplement). To calculate reliable mass spectra of “SOA$_{\mathrm{ambient}}$”, only the experiments with significant OA enhancement are analyzed and shown here (Appendix A). The x-axis is the average NO concentration during each perturbation experiment. The data points on the same vertical line (i.e., the same NO concentration) are from the same perturbation experiment, but compared to three different laboratory experiments. The dashed lines are used to guide eyes. The bars on top of the figure represent the 10th, 50th, and 90th percentiles of NO concentration for CTR (Centreville, AL), YRK (Yorkville, GA), and JST (Jefferson Street, GA) in 2013. The NO concentration is measured by the SouthEastern Aerosol Research and Characterization (SEARCH) network. The 90th percentile of NO concentration in JST is 14.8 ppb, which is not shown in the figure.



~~Fig. 7. The diurnal trends of LO-OOA and modeled SOA from monoterpenes and sesquiterpenes at different sampling sites in the southeastern U.S. in the default simulation. The mean bias (MB), mean error (ME), and normalized mean bias (NMB) are shown for each site. The slopes and R are obtained by least square fit.~~



~~Fig. 8. (a) top panel: the diurnal trends of LO-OOA and modeled SOA from monoterpenes and sesquiterpenes (SOA_{MT+SQT}) at different sampling sites in the southeastern U.S. (b) bottom panel: maps of modeled ground-level SOA_{MT+SQT} concentration. Model results shown here are from the updated simulation. Abbreviations correspond to Centreville (CTR), Jefferson Street (JST), Yorkville (YRK), Georgia Institute of Technology (GT). Detailed sampling periods are shown in Table S1. In panel (a), since the perturbation experiments show that 16% of SOA from α-pinene oxidation is apportioned into isoprene-OA (Fig. S7a), we only include 84% of modeled SOA from MT+O_3/OH when comparing with LO-OOA for the sites with isoprene-OA (Fig. S7a). The mean bias (MB), mean error (ME), and normalized mean bias (NMB) for each site are shown in each panel. The slopes and correlation coefficients (R) are obtained by least square fit. The error bars indicate the standard error. In panel (b), average SOA_{MT+SQT} concentration in $PM_{2.5}$ during each sampling period is reported.~~

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References

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, Atmos. Chem. Phys., 10, 647-668, 10.5194/acp-10-647-2010, 2010.

Appel, K. W., Napelenok, S. L., Foley, K. M., Pye, H. O. T., Hogrefe, C., Luecken, D. J., Bash, J. O., Roselle, S. J., Pleim, J. E., Foroutan, H., Hutzell, W. T., Pouliot, G. A., Sarwar, G., Fahey, K. M., Gantt, B., Gilliam, R. C., Heath, N. K., Kang, D., Mathur, R., Schwede, D. B., Spero, T. L., Wong, D. C., and Young, J. O.: Description and evaluation of the Community Multiscale Air Quality (CMAQ) modeling system version 5.1, Geosci. Model Dev., 10, 1703-1732, 10.5194/gmd-10-1703-2017, 2017.

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L.: Measurements of secondary organic aerosol from oxidation of cycloalkenes, terpenes, and m-xylene using an Aerodyne aerosol mass spectrometer, Environ Sci Technol, 39, 5674-5688, Doi 10.1021/Es048061a, 2005.

Beddows, D. C. S., Harrison, R. M., Green, D. C., and Fuller, G. W.: Receptor modelling of both particle composition and size distribution from a background site in London, UK, Atmos. Chem. Phys., 15, 10107-10125, 10.5194/acp-15-10107-2015, 2015.

Blanchard, C. L., Hidy, G. M., Tanenbaum, S., Rasmussen, R., Watkins, R., and Edgerton, E.: NMOC, ozone, and organic aerosol in the southeastern United States, 1999-2007 1 Spatial and temporal variations of NMOC concentrations and composition in Atlanta, Georgia, Atmospheric Environment, 44, 4827-4839, DOI 10.1016/j.atmosenv.2010.08.036, 2010.

Bougiatioti, A., Stavroulas, I., Kostenidou, E., Zarmpas, P., Theodosi, C., Kouvarakis, G., Canonaco, F., Prévôt, A. S. H., Nenes, A., Pandis, S. N., and Mihalopoulos, N.: Processing of biomass-burning aerosol in the eastern Mediterranean during summertime, Atmos. Chem. Phys., 14, 4793-4807, 10.5194/acp-14-4793-2014, 2014.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A., and Surratt, J. D.: Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor, Environ Sci Technol, 47, 5686-5694, Doi 10.1021/Es400023n, 2013.

Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site, Atmos. Chem. Phys., 15, 8871-8888, 10.5194/acp-15-8871-2015, 2015.

Burkholder, J. B., Abbatt, J. P. D., Barnes, I., Roberts, J. M., Melamed, M. L., Ammann, M., Bertram, A. K., Cappa, C. D., Carlton, A. M. G., Carpenter, L. J., Crowley, J. N., Dubowski, Y., George, C., Heard, D. E., Herrmann, H., Keutsch, F. N., Kroll, J. H., McNeill, V. F., Ng, N. L., Nizkorodov, S. A., Orlando, J. J., Percival, C. J., Picquet-Varrault, B., Rudich, Y., Seakins, P. W., Surratt, J. D., Tanimoto, H., Thornton, J. A., Zhu, T., Tyndall, G. S., Wahner, A., Weschler, C. J., Wilson, K. R., and Ziemann, P. J.: The Essential Role for Laboratory Studies in Atmospheric Chemistry, Environ Sci Technol, 10.1021/acs.est.6b04947, 2017.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, Mass Spectrometry Reviews, 26, 185-222, 10.1002/mas.20115, 2007.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6, 3649-3661, 10.5194/amt-6-3649-2013, 2013.

Carlton, A. G., Bhave, P. V., Napelenok, S. L., Edney, E. O., Sarwar, G., Pinder, R. W., Pouliot, G. A., and Houyoux, M.: Model Representation of Secondary Organic Aerosol in CMAQv4.7, Environ Sci Technol, 44, 8553-8560, 10.1021/es100636q, 2010.

Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G. W., Spracklen, D. V., Woodhouse, M. T., Regayre, L. A., and Pierce, J. R.: Large contribution of natural aerosols to uncertainty in indirect forcing, Nature, 503, 67-71, Doi 10.1038/Nature12674, 2013.

Chen, Q., Farmer, D. K., Rizzo, L. V., Pauliquevis, T., Kuwata, M., Karl, T. G., Guenther, A., Allan, J. D., Coe, H., Andreae, M. O., Pöschl, U., Jimenez, J. L., Artaxo, P., and Martin, S. T.: Submicron particle mass concentrations and sources in the Amazonian wet season (AMAZE-08), Atmos. Chem. Phys., 15, 3687-3701, 10.5194/acp-15-3687-2015, 2015.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A. M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14, 6159-6176, 10.5194/acp-14-6159-2014, 2014.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, Anal Chem, 78, 8281-8289, 10.1021/ac061249n, 2006.

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Chan, M., Schilling, K. A., Chhabra, P. S., Seinfeld, J. H., and Wennberg, P. O.: α-pinene photooxidation under controlled chemical conditions – Part 2: SOA yield and composition in low- and high-NOx environments, Atmos. Chem. Phys., 12, 7413-7427, 10.5194/acp-12-7413-2012, 2012a.

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Seinfeld, J. H., and Wennberg, P. O.: α-pinene photooxidation under controlled chemical conditions – Part 1: Gas-phase composition in low- and high-NO_x environments, Atmos. Chem. Phys., 12, 6489-6504, 10.5194/acp-12-6489-2012, ~~2012~~2012b.

Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476-479, 10.1038/nature13032, 2014.

El Haddad, I., D'Anna, B., Temime-Roussel, B., Nicolas, M., Boreave, A., Favez, O., Voisin, D., Sciare, J., George, C., Jaffrezo, J. L., Wortham, H., and Marchand, N.: Towards a better understanding of the origins, chemical composition and aging of oxygenated organic aerosols: case study of a Mediterranean industrialized environment, Marseille, Atmos. Chem. Phys., 13, 7875-7894, 10.5194/acp-13-7875-2013, 2013.

Goldstein, A. H., Koven, C. D., Heald, C. L., and Fung, I. Y.: Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States, Proceedings of the National Academy of Sciences, 106, 8835-8840, 10.1073/pnas.0904128106, 2009.

Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass spectrometer data, Atmos. Chem. Phys., 9, 2227-2240, 10.5194/acp-9-2227-2009, 2009.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J Geophys Res-Atmos, 104, 3555-3567, Doi 10.1029/1998jd100049, 1999.

Guenther, A., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos Chem Phys, 9, 5155-5236, 2009.

Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W., Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappenglueck, B., Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., De Gouw, J. A., Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corrigan, A. L., Russell, L. M., Isaacman, G., Worton, D. R., Kreisberg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M., Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Offenberg, J. H., Dusanter, S., Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., and Jimenez, J. L.: Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign, J Geophys Res-Atmos, 118, 9233-9257, Doi 10.1002/Jgrd.50530, 2013.

Heath, N. K., Pleim, J. E., Gilliam, R. C., and Kang, D.: A simple lightning assimilation technique for improving retrospective WRF simulations, Journal of Advances in Modeling Earth Systems, 8, 1806-1824, 10.1002/2016MS000735, 2016.

Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., and Sakulyanontvittaya, T.: Sesquiterpene Emissions from Pine Trees − Identifications, Emission Rates and Flux Estimates for the Contiguous United States, Environ Sci Technol, 41, 1545-1553, 10.1021/es0618907, 2007.

Hennigan, C. J., Bergin, M. H., Russell, A. G., Nenes, A., and Weber, R. J.: Gas/particle partitioning of water-soluble organic aerosol in Atlanta, Atmos Chem Phys, 9, 3613-3628, 2009.

Hodzic, A., Kasibhatla, P. S., Jo, D. S., Cappa, C. D., Jimenez, J. L., Madronich, S., and Park, R. J.: Rethinking the global secondary organic aerosol (SOA) budget: stronger production, faster removal, shorter lifetime, Atmos. Chem. Phys., 16, 7917-7941, 10.5194/acp-16-7917-2016, 2016.

Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A., Hallar, A. G., Hartz, K. H., Petters, M. D., Petaja, T., Rosenoern, T., and Sullivan, A. P.: A review of the anthropogenic influence on biogenic secondary organic aerosol, Atmos Chem Phys, 11, 321-343, DOI 10.5194/acp-11-321-2011, 2011.

Hu, W. W., Campuzano-Jost, P., Palm, B. B., Day, D. A., Ortega, A. M., Hayes, P. L., Krechmer, J. E., Chen, Q., Kuwata, M., Liu, Y. J., de Sá, S. S., McKinney, K., Martin, S. T., Hu, M., Budisulistiorini, S. H., Riva, M., Surratt, J. D., St. Clair, J. M., Isaacman-Van Wertz, G., Yee, L. D., Goldstein, A. H., Carbone, S., Brito, J., Artaxo, P., de Gouw, J. A., Koss, A., Wisthaler, A., Mikoviny, T., Karl, T., Kaser, L., Jud, W., Hansel, A., Docherty, K. S., Alexander, M. L., Robinson, N. H., Coe, H., Allan, J. D., Canagaratna, M. R., Paulot, F., and Jimenez, J. L.: Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, Atmos. Chem. Phys., 15, 11807-11833, 10.5194/acp-15-11807-2015, 2015.

Huang, X. F., He, L. Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L. W., Liu, X. G., Zhang, Y. H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos Chem Phys, 10, 8933-8945, DOI 10.5194/acp-10-8933-2010, 2010.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525-1529, DOI 10.1126/science.1180353, 2009.

Kiendler-Scharr, A., Zhang, Q., Hohaus, T., Kleist, E., Mensah, A., Mentel, T. F., Spindler, C., Uerlings, R., Tillmann, R., and Wildt, J.: Aerosol Mass Spectrometric Features of Biogenic SOA: Observations from a Plant Chamber and in Rural Atmospheric Environments, Environ Sci Technol, 43, 8166-8172, 10.1021/es901420b, 2009.

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Äijälä, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H. C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophysical Research Letters, 43, 7735-7744, 10.1002/2016GL069239, 2016.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J Geophys Res-Atmos, 110, Doi 10.1029/2005jd006004, 2005.

Kroll, J. H., ~~Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, Environ Sci Technol, 40, 1869-1877, Doi 10.1021/Es0524301, 2006.~~

~~Kroll, J. H.,~~ and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmospheric Environment, 42, 3593-3624, DOI 10.1016/j.atmosenv.2008.01.003, 2008.

Kurtén, T., Rissanen, M. P., Mackeprang, K., Thornton, J. A., Hyttinen, N., Jørgensen, S., Ehn, M., and Kjaergaard, H. G.: Computational Study of Hydrogen Shifts and Ring-Opening Mechanisms in α-Pinene Ozonolysis Products, The Journal of Physical Chemistry A, 119, 11366-11375, 10.1021/acs.jpca.5b08948, 2015.

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Effect of NOx on Secondary Organic Aerosol Concentrations, Environ Sci Technol, 42, 6022-6027, 10.1021/es703225a, 2008.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., Szidat, S., Wehrli, M. N., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H., and Prevot, A. S. H.: Source Attribution of Submicron Organic Aerosols during Wintertime Inversions by Advanced Factor Analysis of Aerosol Mass Spectra, Environ Sci Technol, 42, 214-220, 10.1021/es0707207, 2008.

Lee, A. K. Y., Herckes, P., Leaitch, W. R., Macdonald, A. M., and Abbatt, J. P. D.: Aqueous OH oxidation of ambient organic aerosol and cloud water organics: Formation of highly oxidized products, Geophysical Research Letters, 38, n/a-n/a, 10.1029/2011GL047439, 2011.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R., and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, Environ Sci Technol, 48, 6309-6317, 10.1021/es500362a, 2014.

Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurtén, T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Xu, L., Ng, N. L., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., de Gouw, J., Olson, K., Goldstein, A. H., Seco, R., Kim, S., McAvey, K., Shepson, P. B., Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J. E., Miller, D. O., Brune, W., Schobesberger, S., D'Ambro, E. L., and Thornton, J.

A.: Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, Proceedings of the National Academy of Sciences, 113, 1516-1521, 10.1073/pnas.1508108113, 2016.

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air pollution sources to premature mortality on a global scale, Nature, 525, 367-371, 10.1038/nature15371, 2015.

Leungsakul, S., Jeffries, H. E., and Kamens, R. M.: A kinetic mechanism for predicting secondary aerosol formation from the reactions of d-limonene in the presence of oxides of nitrogen and natural sunlight, Atmospheric Environment, 39, 7063-7082, https://doi.org/10.1016/j.atmosenv.2005.08.024, 2005.

Liu, Y., Kuwata, M., Strick, B. F., Geiger, F. M., Thomson, R. J., McKinney, K. A., and Martin, S. T.: Uptake of Epoxydiol Isomers Accounts for Half of the Particle-Phase Material Produced from Isoprene Photooxidation via the HO2 Pathway, Environ Sci Technol, 49, 250-258, 10.1021/es5034298, 2015.

Liu, Y., Kuwata, M., McKinney, K. A., and Martin, S. T.: Uptake and release of gaseous species accompanying the reactions of isoprene photo-oxidation products with sulfate particles, Phys Chem Chem Phys, 18, 1595-1600, 10.1039/C5CP04551G, 2016.

Marcolli, C., Canagaratna, M. R., Worsnop, D. R., Bahreini, R., de Gouw, J. A., Warneke, C., Goldan, P. D., Kuster, W. C., Williams, E. J., Lerner, B. M., Roberts, J. M., Meagher, J. F., Fehsenfeld, F. C., Marchewka, M., Bertman, S. B., and Middlebrook, A. M.: Cluster Analysis of the Organic Peaks in Bulk Mass Spectra Obtained During the 2002 New England Air Quality Study with an Aerodyne Aerosol Mass Spectrometer, Atmos. Chem. Phys., 6, 5649-5666, 10.5194/acp-6-5649-2006, 2006.

Mohr, C., Huffman, J. A., Cubison, M. J., Aiken, A. C., Docherty, K. S., Kimmel, J. R., Ulbrich, I. M., Hannigan, M., and Jimenez, J. L.: Characterization of Primary Organic Aerosol Emissions from Meat Cooking, Trash Burning, and Motor Vehicles with High-Resolution Aerosol Mass Spectrometry and Comparison with Ambient and Chamber Observations, Environ Sci Technol, 43, 2443-2449, 10.1021/es8011518, 2009.

~~Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909-3922, 10.5194/acp-7-3909-2007, 2007.~~

Mutzel, A., Poulain, L., Berndt, T., Iinuma, Y., Rodigast, M., Böge, O., Richters, S., Spindler, G., Sipilä, M., Jokinen, T., Kulmala, M., and Herrmann, H.: Highly Oxidized Multifunctional Organic Compounds Observed in Tropospheric Particles: A Field and Laboratory Study, Environ Sci Technol, 10.1021/acs.est.5b00885, 2015.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prevot, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos Chem Phys, 10, 4625-4641, DOI 10.5194/acp-10-4625-2010, 2010.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, Atmos. Chem. Phys., 17, 2103-2162, 10.5194/acp-17-2103-2017, 2017.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/Particle Partitioning and Secondary Organic Aerosol Yields, Environ Sci Technol, 30, 2580-2585, 10.1021/es950943+, 1996.

Paatero, P., and Tapper, U.: Positive Matrix Factorization - a Nonnegative Factor Model with Optimal Utilization of Error-Estimates of Data Values, Environmetrics, 5, 111-126, DOI 10.1002/env.3170050203, 1994.

Paatero, P.: The Multilinear Engine—A Table-Driven, Least Squares Program for Solving Multilinear Problems, Including the n-Way Parallel Factor Analysis Model, Journal of Computational and Graphical Statistics, 8, 854-888, 10.1080/10618600.1999.10474853, 1999.

Palm, B. B., de Sá, S. S., Day, D. A., Campuzano-Jost, P., Hu, W., Seco, R., Sjostedt, S. J., Park, J. H., Guenther, A. B., Kim, S., Brito, J., Wurm, F., Artaxo, P., Thalman, R., Wang, J., Yee, L. D., Wernis, R., Isaacman-VanWertz, G., Goldstein, A. H., Liu, Y., Springston, S. R., Souza, R., Newburn, M. K., Alexander, M. L., Martin, S. T., and Jimenez, J. L.: Secondary organic aerosol formation from ambient air in an oxidation flow reactor in central Amazonia, Atmos. Chem. Phys. Discuss., 2017, 1-56, 10.5194/acp-2017-795, 2017.

Palm, B. B., de Sá, S. S., Day, D. A., Campuzano-Jost, P., Hu, W., Seco, R., Sjostedt, S. J., Park, J. H., Guenther, A. B., Kim, S., Brito, J., Wurm, F., Artaxo, P., Thalman, R., Wang, J., Yee, L. D., Wernis, R., Isaacman-VanWertz, G., Goldstein, A. H., Liu, Y., Springston, S. R., Souza, R., Newburn, M. K., Alexander, M. L., Martin, S. T., and Jimenez, J. L.: Secondary organic aerosol formation from ambient air in an oxidation flow reactor in central Amazonia, Atmos. Chem. Phys., 18, 467-493, 10.5194/acp-18-467-2018, 2018.

Pathak, R. K., Stanier, C. O., Donahue, N. M., and Pandis, S. N.: Ozonolysis of alpha-pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), J Geophys Res-Atmos, 112, Artn D03201

Doi 10.1029/2006jd007436, 2007.

Peng, J., Hu, M., Guo, S., Du, Z., Zheng, J., Shang, D., Levy Zamora, M., Zeng, L., Shao, M., Wu, Y.-S., Zheng, J., Wang, Y., Glen, C. R., Collins, D. R., Molina, M. J., and Zhang, R.: Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, Proceedings of the National Academy of Sciences, 113, 4266-4271, 10.1073/pnas.1602310113, 2016.

Presto, A. A., Huff Hartz, K. E., and Donahue, N. M.: Secondary Organic Aerosol Production from Terpene Ozonolysis. 2. Effect of NOx Concentration, Environ Sci Technol, 39, 7046-7054, 10.1021/es050400s, 2005.

Pye, Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y. H., Surratt, J. D., Zhang, Z. F., Gold, A., Luecken, D. J., Hutzell, W. T., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M., and Edney, E. O.: Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation, Environ Sci Technol, 47, 11056-11064, Doi 10.1021/Es402106h, 2013.

Pye, H. O. T., Chan, A. W. H., Barkley, M. P., and Seinfeld, J. H.: Global modeling of organic aerosol: the importance of reactive nitrogen (NOx and NO3), Atmos Chem Phys, 10, 11261-11276, DOI 10.5194/acp-10-11261-2010, 2010.

Pye, H. O. T., Luecken, D. J., Xu, L., Boyd, C. M., Ng, N. L., Baker, K. R., Ayres, B. R., Bash, J. O., Baumann, K., Carter, W. P. L., Edgerton, E., Fry, J. L., Hutzell, W. T., Schwede, D. B., and Shepson, P. B.: Modeling the Current and Future Roles of Particulate Organic Nitrates in the Southeastern United States, Environ Sci Technol, 49, 14195-14203, 10.1021/acs.est.5b03738, 2015.

Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest, Atmos Chem Phys, 11, 1039-1050, DOI 10.5194/acp-11-1039-2011, ~~2011~~2011a.

Robinson, N. H., Newton, H. M., Allan, J. D., Irwin, M., Hamilton, J. F., Flynn, M., Bower, K. N., Williams, P. I., Mills, G., Reeves, C. E., McFiggans, G., and Coe, H.: Source attribution of Bornean air masses by back trajectory analysis during the OP3 project, Atmos. Chem. Phys., 11, 9605-9630, 10.5194/acp-11-9605-2011, 2011b.

Rollins, A. W., Browne, E. C., Min, K.-E., Pusede, S. E., Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A., Russell, L. M., and Cohen, R. C.: Evidence for NOx Control over Nighttime SOA Formation, Science, 337, 1210-1212, 10.1126/science.1221520, 2012.

Saha, P. K., and Grieshop, A. P.: Exploring Divergent Volatility Properties from Yield and Thermodenuder Measurements of Secondary Organic Aerosol from α-Pinene Ozonolysis, Environ Sci Technol, 10.1021/acs.est.6b00303, 2016.

Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S. H., Wu, C., Mentel, T. F., Zhao, D., Hastie, D. R., and Kiendler-Scharr, A.: Impact of NOx and OH on secondary organic aerosol formation from β-pinene photooxidation, Atmos. Chem. Phys., 16, 11237-11248, 10.5194/acp-16-11237-2016, 2016.

Sen, P. K.: Estimates of the Regression Coefficient Based on Kendall's Tau, Journal of the American Statistical Association, 63, 1379-1389, 10.1080/01621459.1968.10480934, 1968.

Slowik, J. G., Brook, J., Chang, R. Y. W., Evans, G. J., Hayden, K., Jeong, C. H., Li, S. M., Liggio, J., Liu, P. S. K., McGuire, M., Mihele, C., Sjostedt, S., Vlasenko, A., and Abbatt, J. P. D.: Photochemical processing of organic aerosol at nearby continental sites: contrast between urban plumes and regional aerosol, Atmos Chem Phys, 11, 2991-3006, DOI 10.5194/acp-11-2991-2011, 2011.

Spracklen, D. V., Jimenez, J. L., Carslaw, K. S., Worsnop, D. R., Evans, M. J., Mann, G. W., Zhang, Q., Canagaratna, M. R., Allan, J., Coe, H., McFiggans, G., Rap, A., and Forster, P.: Aerosol mass spectrometer constraint on the global secondary organic aerosol budget, Atmos. Chem. Phys., 11, 12109-12136, 10.5194/acp-11-12109-2011, 2011.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, P Natl Acad Sci USA, 107, 6640-6645, DOI 10.1073/pnas.0911114107, 2010.

Tasoglou, A., and Pandis, S. N.: Formation and chemical aging of secondary organic aerosol during the β-caryophyllene oxidation, Atmos. Chem. Phys., 15, 6035-6046, 10.5194/acp-15-6035-2015, 2015.

Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P. J., Artaxo, P., Bahadur, R., Balkanski, Y., Bauer, S. E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T. K., Beukes, J. P., Bian, H., Carslaw, K. S., Chin, M., Curci, G., Diehl, T., Easter, R. C., Ghan, S. J., Gong, S. L., Hodzic, A., Hoyle, C. R., Iversen, T., Jathar, S., Jimenez, J. L., Kaiser, J. W., Kirkevåg, A., Koch, D., Kokkola, H., Lee, Y. H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G. W., Mihalopoulos, N., Morcrette, J. J., Müller, J. F., Myhre, G., Myriokefalitakis, S., Ng, N. L., O'Donnell, D., Penner, J. E., Pozzoli, L., Pringle, K. J., Russell, L. M., Schulz, M., Sciare, J., Seland, Ø., Shindell, D. T., Sillman, S., Skeie, R. B., Spracklen, D., Stavrakou, T., Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G., von Salzen, K., Yu, F., Wang, Z., Wang, Z., Zaveri, R. A., Zhang, H., Zhang, K., Zhang, Q., and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global models, Atmos. Chem. Phys., 14, 10845-10895, 10.5194/acp-14-10845-2014, 2014.

Tuet, W. Y., Chen, Y., Xu, L., Fok, S., Gao, D., Weber, R. J., and Ng, N. L.: Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds, Atmos. Chem. Phys., 17, 839-853, 10.5194/acp-17-839-2017, 2017.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918, 10.5194/acp-9-2891-2009, 2009.

Vaden, T. D., Imre, D., Beránek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proceedings of the National Academy of Sciences, 108, 2190-2195, 10.1073/pnas.1013391108, 2011.

Verma, V., Fang, T., Guo, H., King, L., Bates, J. T., Peltier, R. E., Edgerton, E., Russell, A. G., and Weber, R. J.: Reactive oxygen species associated with water-soluble PM2.5 in the southeastern United States: spatiotemporal trends and source apportionment, Atmos. Chem. Phys., 14, 12915-12930, 10.5194/acp-14-12915-2014, 2014.

Visser, S., Slowik, J. G., Furger, M., Zotter, P., Bukowiecki, N., Canonaco, F., Flechsig, U., Appel, K., Green, D. C., Tremper, A. H., Young, D. E., Williams, P. I., Allan, J. D., Coe, H., Williams, L. R., Mohr, C., Xu, L., Ng, N. L., Nemitz, E., Barlow, J. F., Halios, C. H., Fleming, Z. L., Baltensperger, U., and Prévôt, A. S. H.: Advanced source apportionment of size-resolved trace elements at multiple sites in London during winter, Atmos. Chem. Phys., 15, 11291-11309, 10.5194/acp-15-11291-2015, 2015.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States, J Geophys Res-Atmos, 112, Artn D13302 Doi 10.1029/2007jd008408, 2007.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences, 112, 37-42, 10.1073/pnas.1417609112, 2015a.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, Atmos. Chem. Phys., 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015b.

Xu, L., Middlebrook, A. M., Liao, J., de Gouw, J. A., Guo, H., Weber, R. J., Nenes, A., Lopez-Hilfiker, F. D., Lee, B. H., Thornton, J. A., Brock, C. A., Neuman, J. A., Nowak, J. B., Pollack, I. B., Welti, A., Graus, M., Warneke, C., and Ng, N. L.: Enhanced formation of isoprene-derived organic aerosol in sulfur-rich power plant plumes during Southeast Nexus, Journal of Geophysical Research: Atmospheres, 121, 11,137-111,153, 10.1002/2016JD025156, ~~2016~~2016a.

Xu, L., Williams, L. R., Young, D. E., Allan, J. D., Coe, H., Massoli, P., Fortner, E., Chhabra, P., Herndon, S., Brooks, W. A., Jayne, J. T., Worsnop, D. R., Aiken, A. C., Liu, S., Gorkowski, K., Dubey, M. K., Fleming, Z. L., Visser, S., Prévôt, A. S. H., and Ng, N. L.: Wintertime aerosol chemical composition, volatility, and spatial variability in the greater London area, Atmos. Chem. Phys., 16, 1139-1160, 10.5194/acp-16-1139-2016, 2016b.

Xu, W., Han, T., Du, W., Wang, Q., Chen, C., Zhao, J., Zhang, Y., Li, J., Fu, P., Wang, Z., Worsnop, D. R., and Sun, Y.: Effects of Aqueous-Phase and Photochemical Processing on Secondary Organic Aerosol Formation and Evolution in Beijing, China, Environ Sci Technol, 10.1021/acs.est.6b04498, 2016c.

Yu, J., Cocker, D. R., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products, J Atmos Chem, 34, 207-258, 10.1023/a:1006254930583, 1999.

Zhang, H., Yee, L. D., Lee, B. H., Curtis, M. P., Worton, D. R., Isaacman-VanWertz, G., Offenberg, J. H., Lewandowski, M., Kleindienst, T. E., Beaver, M. R., Holder, A. L., Lonneman, W. A., Docherty, K. S., Jaoui, M., Pye, H. O. T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Guo, H., Weber, R. J., de Gouw, J., Koss, A. R., Edgerton, E. S., Brune, W., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Kreisberg, N. M., Spielman, S. R., Hering, S. V., Wilson, K. R., Thornton, J. A., and Goldstein, A. H.: Monoterpenes are the largest source of summertime organic aerosol in the southeastern United States, Proceedings of the National Academy of Sciences, 10.1073/pnas.1717513115, 2018.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophysical Research Letters, 34, Artn L13801 Doi 10.1029/2007gl029979, 2007.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, Proceedings of the National Academy of Sciences, 10.1073/pnas.1404727111, 2014.

Zhang, X., McVay, R. C., Huang, D. D., Dalleska, N. F., Aumont, B., Flagan, R. C., and Seinfeld, J. H.: Formation and evolution of molecular products in α-pinene secondary organic aerosol, Proceedings of the National Academy of Sciences, 112, 14168-14173, 10.1073/pnas.1517742112, 2015.

Zheng, Y., Unger, N., Hodzic, A., Emmons, L., Knote, C., Tilmes, S., Lamarque, J. F., and Yu, P.: Limited effect of anthropogenic nitrogen oxides on secondary organic aerosol formation, Atmos. Chem. Phys., 15, 13487-13506, 10.5194/acp-15-13487-2015, 2015.

Zotter, P., El-Haddad, I., Zhang, Y., Hayes, P. L., Zhang, X., Lin, Y.-H., Wacker, L., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Surratt, J. D., Weber, R., Jimenez, J. L., Szidat, S., Baltensperger, U., and Prévôt, A. S. H.: Diurnal cycle of fossil and nonfossil carbon using radiocarbon analyses during CalNex, Journal of Geophysical Research: Atmospheres, 119, 2013JD021114, 10.1002/2013JD021114, 2014.

Appendix A. Data Analysis Method for Perturbation Experiments

The most challenging and important analysis is to determine if the perturbation results in a statistically significant change in the mass concentration of OA factors. We perform the following analysis to calculate the changes in the mass concentration of OA factors after perturbation, to determine if the change is significant, and to evaluate if the change is simply due to ambient variation.

The duration of one perturbation experiment is about 130min, including four periods: Amb_Bf (~30min), Chamber_Bf (~30min), Chamber_Af (~40min), and Amb_Af (~30min), as illustrated in Fig. A1. Firstly, we assume that the ambient variation is linear during both the Chamber_Bf and Chamber_Af periods (i.e., when instruments are connected to chamber and not sampling the ambient aerosol) and that the ambient variation can be represented by interpolating Amb_Bf and Amb_Af. The validity of this assumption will be discussed shortly. To obtain the slope of ambient variation, we analyze the combined Amb_Bf and Amb_Af data and use Theil-Sen estimator(Sen, 1968). The Theil-Sen estimator is a method to robustly fit a line to a set of two-dimensional points (i.e., concentration "*C*" and time "*t*" in this study). This method chooses the median of the slopes $(C_j-C_i)/(t_j-t_i)$ determined by all pairs of sample points. Compared to simple linear regression using ordinary least squares, the Theil-Sen estimator is robust and insensitive to outliers. Unless specifically noted, the slope is Appendix A is calculated from Theil-Sen estimator. Secondly, we use the slope to extrapolate the Chamber_Bf data to estimate aerosol concentration inside the chamber during the Chamber_Af period if there were no VOC injection. We refer to this estimated aerosol concentration as "extrapolated Chamber_Bf" and use it as the reference to calculate the change in aerosol mass concentration after perturbation. We extrapolate the Chamber_Bf data, instead of ambient data, because the OA concentration in chamber is lower than that in the atmosphere due to wall loss. Thirdly, we calculate the changes in the concentration of OA factors based on the difference between measured Chamber_Af data and "extrapolated Chamber_Bf".

For each perturbation experiment, after calculating the changes in the concentration of OA factors, we develop a set of criteria to determine if the changes are statistically significant and if the changes are simply due to ambient variation. The increase in the concentration of an OA factor needs to satisfy all criteria to be considered as statistically significant and not due to ambient variation.

Criterion 1: The difference in concentration between Chamber_Af and extrapolated Chamber_Bf must be significant. We use T-test and 95% confidence interval.

Criterion 2: The slope of all data points or the first 8 data points during the Chamber_Af period is significantly different from the slope of aerosol concentration during the Chamber_Bf period. The rationale behind this criterion is that if the perturbation causes a substantial change in the concentration of an OA factor, its slope during the Chamber_Af period should be different from that during the Chamber_Bf period.

The slope of aerosol concentration during the Chamber_Af period is obtained in the following way. We calculate the slope by using (1) all data points and (2) only first 8 data points during the Chamber_Af period. This is because the concentration of factors firstly increases after perturbation and then decreases due to dilution (Fig. A1). In this case, the slope obtained by fitting all data points might be negative and will not reflect the initial increase in concentration (e.g., LO-OOA of ap_0805_1 in Fig. ~~S4a~~S9a). Using only the first few data points during the Chamber_Af period can avoid this issue. We select the first 8 data points in this period because the concentrations of total OA and OA factors typically reach the highest at the 8th point (i.e., ~16min after injection). The slope is calculated by Theil-Sen estimator.

The slope of aerosol concentration during the Chamber_Bf period is analyzed in the following way. In order to determine if the slope in Chamber_Af is significantly different from that in Chamber_Bf, we use bootstrap analysis (1000 times) to obtain a distribution of the slope of Chamber_Bf. In brief, in each random resampling of Chamber_Bf with replacement, a slope is calculated by Theil-Sen estimator. Then, 1000 times resampling provides a distribution of slope in Chamber_Bf. The 5% and 95% percentiles of the slope distribution are compared to the slope of Chamber_Af to determine if the slopes are significantly different. If the slope of Chamber_Af (from either all data points or the first 8 data points) is smaller (or larger) than the 5% (or 95%) percentile, the slopes in Chamber_Bf and Chamber_Af are significantly different.

Criterion 3: The slope of all data points or the first 8 data points during the Chamber_Af period is significantly different from the slope of ambient data (i.e., combined Amb_Bf and Amb_Af). The rationale behind this criterion is the same as the second criterion. That is, if the perturbation causes a substantial change in the concentration of an OA factor, its slope during the Chamber_Af period should be different from that in ambient data. The procedure to obtain a distribution of slopes in the ambient data (combined Amb_Bf and Amb_Af) is same as Criterion 2.

As mentioned above, one critical assumption is that the ambient variation is linear during both the Chamber_Bf and Chamber_Af periods (i.e., when instruments are connected to chamber and not sampling the ambient aerosol) and that the ambient variation can be represented by interpolating Amb_Bf and Amb_Af. We design the following pseudo-experiment to test the validity of this assumption. In brief, we perform the same analysis as we did for the perturbation experiments, but using ambient data **only** (i.e., no perturbation data). We firstly randomly select a data point, which defines the start point of one pseudo-test. Secondly, based on the start point, we obtain the concentration of OA factors during “Amb_Bf” period, (i.e., from start point to start point + 30min), “Chamber_Bf” period (i.e., from start point + 30min to start point + 60min), “Chamber_Af” period (i.e., from start point + 60min to start point + 100min), and “Amb_Af” period (from start point + 100 min to start point + 130min). This mimics the sampling periods in a real perturbation experiment. Thirdly, we calculate the slope of ambient period (i.e., combined “Amb_Bf” and “Amb_Af” periods) and the slope of chamber period (i.e., combined “Chamber_Bf” and “Chamber_Af” periods). Fourthly, we calculate if the slope of chamber period is significantly different from the slope of ambient period. We repeat this test 1000 times and then obtain the probability of whether the slopes of chamber period and ambient period are significantly different.

Fig. A2a shows the probability that the slopes of chamber period and ambient period are not significantly different for five factors. The larger this probability is, the more reliable the linearity assumption is. The average probability is ~50% for all factors, without discernible diurnal trends. This suggest that there is ~50% chance that the linear variation assumption is valid. Since the linearity assumption is not perfect, we develop another criterion to constrain the potential influence of ambient variation on the interpretation of perturbation results.

Criterion 4: From the above pseudo-experiment on ambient data only, we can calculate the relative change in slope between “chamber period” and “ambient period” by

~~relative change in slope =~~ $\frac{\text{Slope}_{\text{Chamber}}\text{-Slope}_{\text{Amb}}}{\text{Slope}_{\text{Amb}}}$ $\underline{\text{relative change in slope} = \frac{\text{Slope}_{\text{Chamber}}\text{-Slope}_{\text{Amb}}}{\text{Slope}_{\text{Amb}}}}$

Eqn 1

In each pseudo-experiment test, we calculate a relative change in slope between "chamber period" and "ambient period". By repeating the pseudo-experiment test 1000 times, we obtain a frequency distribution of the relative change in slope for each OA factor (Fig. A2b). This frequency distribution indicates the probability that certain relative change in slope occurs due to ambient variation. Take LO-OOA as an example, the probability that the relative change in slope varies by a factor 8 due to ambient variation is ~1%. Thus, if the relative change in slope of LO-OOA in a α-pinene experiment is 8, the change is unlikely due to ambient variation. We use the 5% and 95% percentiles from the frequency distribution as the fourth criterion to determine if the changes in the concentrations of OA factors in each perturbation experiment are due to ambient variation. In other words, if the relative change in slope between Chamber_Af and ambient data in a real perturbation experiment falls outside of the 5% or 95% percentiles, the changes in the concentrations of OA factors are likely due to perturbing chamber with VOC, instead of ambient variation. This criterion strictly considers the influence of ambient variation. In general, the comparison in slope is an optimal option to account for ambient variation, because the influence of ambient variation is unlikely to coincide with the perturbation.

Based on these 4 criteria, the OA factors with significant changes in their mass concentrations as a result of perturbation are shown in Fig. 4. LO-OOA is enhanced in 14 out of 19 α-pinene experiments. However, total OA is only enhanced in 8 out of 19 α-pinene experiments. Several reasons can contribute to the different behaviors of LO-OOA and OA. Firstly, as total OA has multiple sources, the enhancement in one factor does not guarantee an enhancement of total OA. For instance, in some perturbation experiments, while LO-OOA is enhanced, the concentration of other factors steadily decreases due to ambient variation. The increase in LO-OOA and decrease in other factors compensate each other and result in a lack of enhancement in total OA. Secondly, based on the pseudo-experiment, we note that total OA is more easily affected by ambient variation than a single OA factor. For example, the 95% of the relative change in slope of total OA is 3.59, which is larger than any OA factors (Fig. A2b). Thus, the criteria for the change in total OA concentration to be considered as significant are stricter than those for a single OA factor. Thus, some experiments with significant changes in LO-OOA do not have significant changes in total OA.

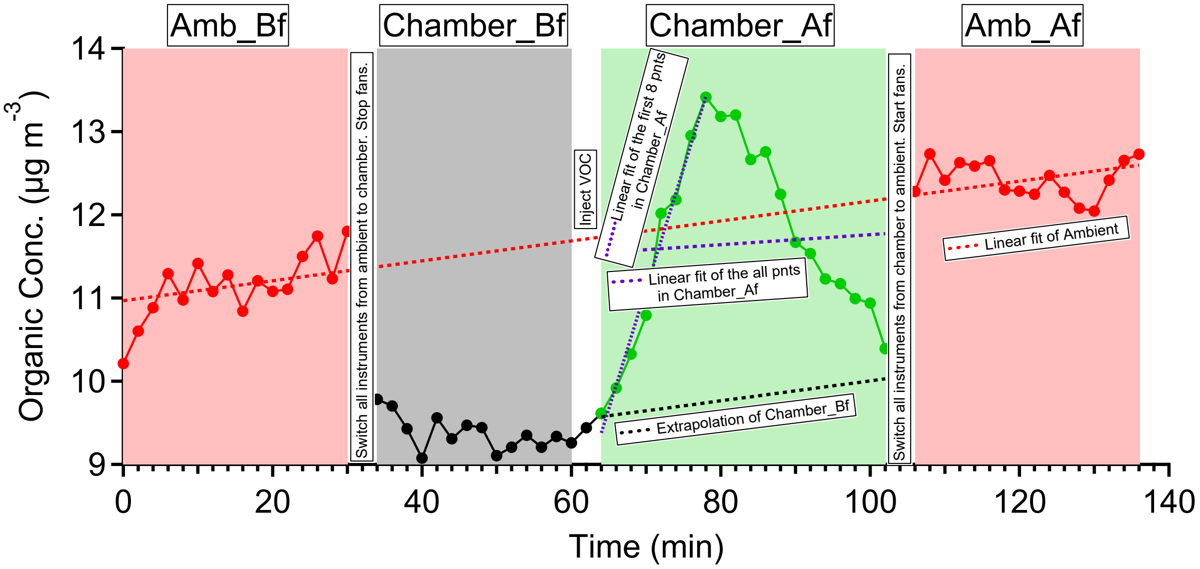
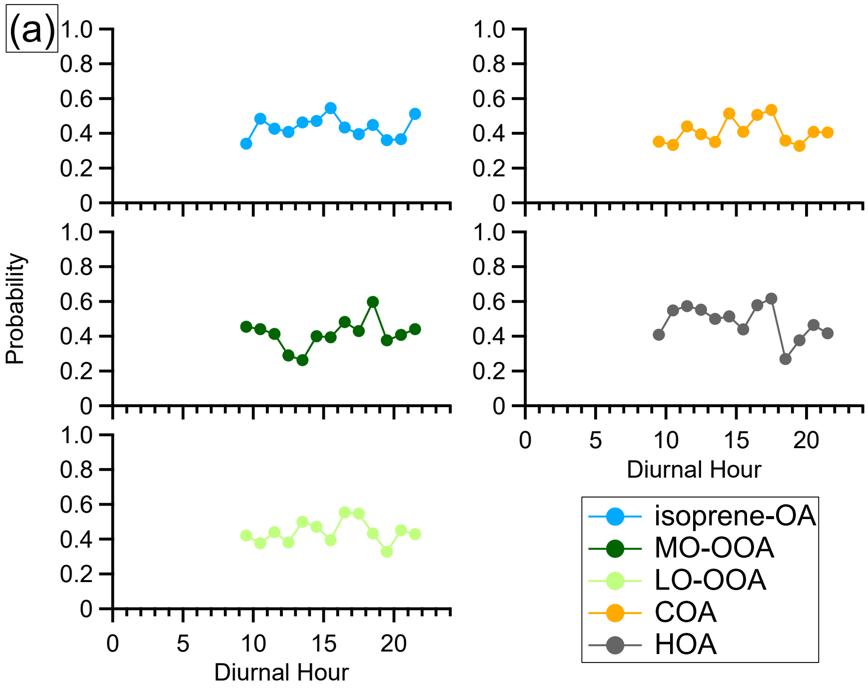


Fig. A1. Time series of OA in experiment ap_0801_1 to illustrate the analysis method. Each perturbation experiment includes four periods: Amb_Bf (~30min), Chamber_Bf (~30min), Chamber_Af (~40min), and Amb_Af (~40min). "Amb" and "Chamber" correspond to the periods when the instruments are sampling ambient and chamber, respectively. "Bf" and "Af" stand for before and after perturbation, respectively. The solid lines are measurement data. The dashed red lines are the linear fit of ambient data (i.e., combined Amb_Bf and Amb_Af). The slope is used to extrapolate Chamber_Bf data to Chamber_Af period (i.e., black dashed line). The dense dashed purple line is the linear fit of the first 8 points during the Chamber_Af period. The sparse dashed purple line is the linear fit of all data points during the Chamber_Af period. During this period, the difference between measurements (i.e., solid green data points) and extrapolated Chamber_Bf (i.e., dashed black line) represents the change in organic concentration caused by perturbation.



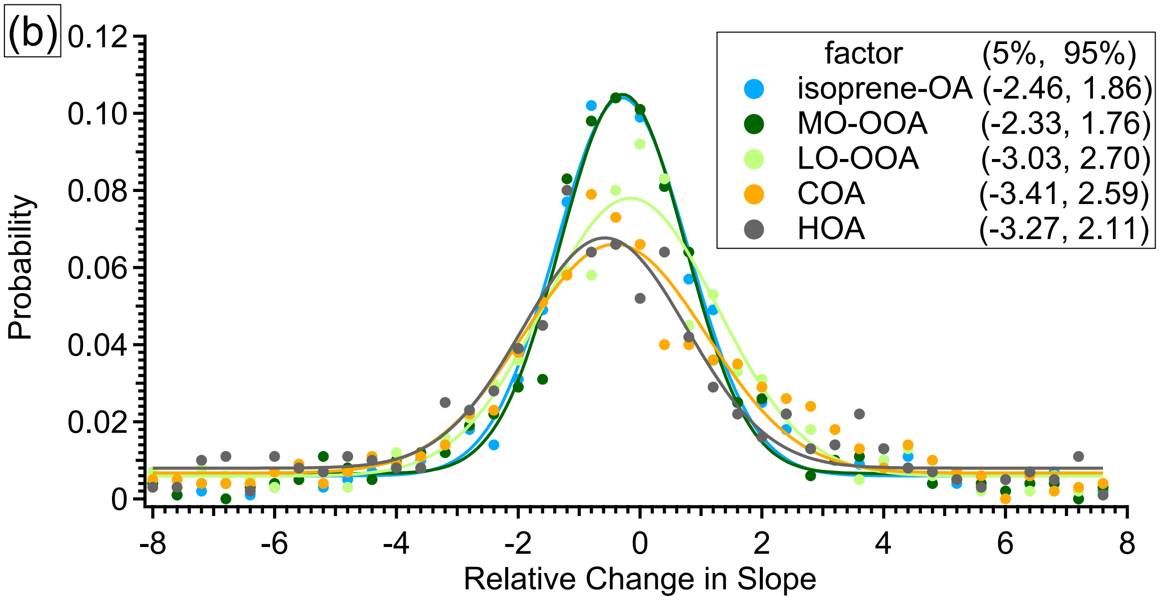


Fig. A2. (a) The diurnal trends of the probability that the slopes between ambient periods (i.e., Amb_Bf and Amb_Af periods) and chamber periods (i.e., Chamber_Bf and Chamber_Af periods) are not significantly different in the pseudo-experiment. (b) The frequency distribution of the relative change in slope. The data points are fitted using Gaussian function. The numbers in the box represent the 5% and 95% percentile of the Gaussian fit.

Appendix B. Ambient Perturbation Experiments with Acidic Sulfate Particles

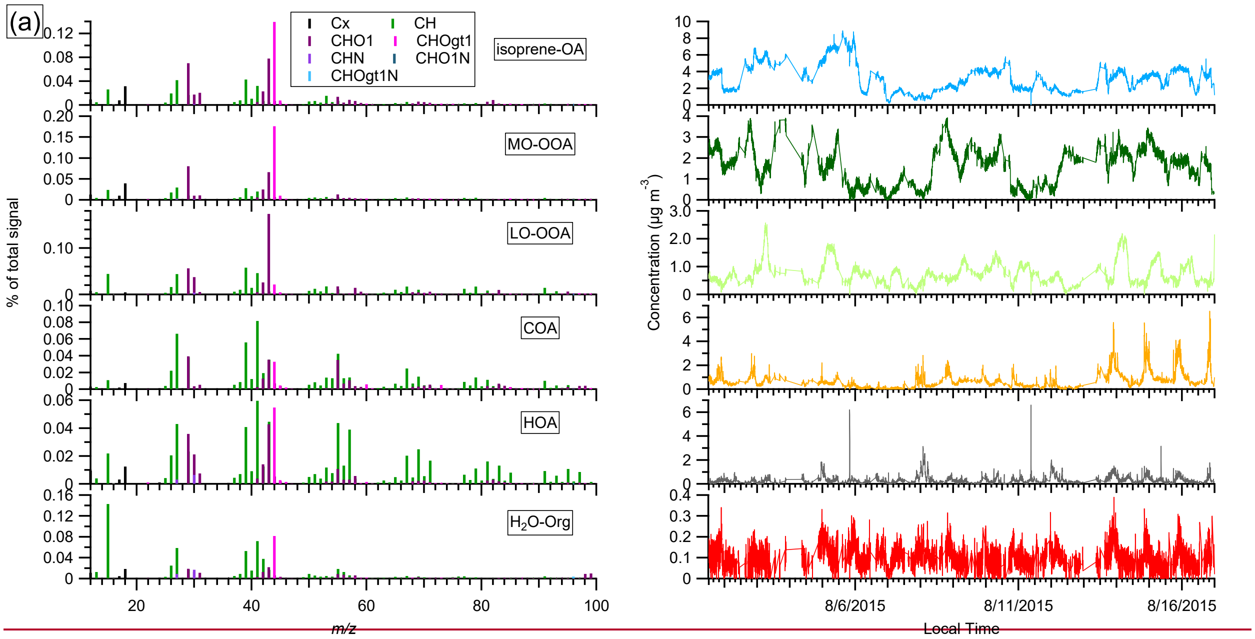
Previous field observations showed strong correlation between isoprene-OA and sulfate (Xu et al., 2015a; Xu et al., ~~2016~~2016a; Budisulistiorini et al., 2015). Moreover, airborne measurements over power plant plumes in Georgia, U.S. observed enhanced isoprene-OA formation in the sulfate-rich power plant plume ~~(Xu et al., 2016).~~(Xu et al., 2016a). To probe the relationship between isoprene-OA and sulfate, we conducted perturbation experiments in August 2015 by injecting acidic sulfate particles (i.e., a mixture of H_2SO_4 and $MgSO_4$) into the 2 m^3 Teflon chamber. This mimics the airborne measurements over power plants, which introduce sulfate into the atmosphere ~~(Xu et al., 2016).~~(Xu et al., 2016a).

The experimental procedure in 2015 experiments is generally similar to those in 2016 experiments, but has the following modifications. Firstly, in order to avoid the depletion of species which can uptake to sulfate particles, we kept one fan on during the Chamber_Bf and Chamber_Af periods to enhance the air exchange between chamber and atmosphere. Secondly, considering the fan is on during sulfate injection to enhance mixing chamber air with ambient air, we only use the Chamber_Bf and Chamber_Af periods to calculate the changes in OA factors. The Criteria (1)(2)(4) are applied in 2015 experiments. Thirdly, the Chamber_Bf period is ~40 min in 2015 experiments, which is slightly longer than the 30 min in 2016 experiments. Fourthly, the HR-ToF-CIMS was not deployed in 2015 experiments.

The acidic sulfate seed particles were introduced into chamber by atomizing 0.88mM H_2SO_4 + 0.48mM $MgSO_4$ mixture solution from a nebulizer (U-5000AT, Cetac Technologies Inc., Omaha, Nebraska, USA). One important interference in these sulfate perturbation experiments is the trace amount of organics in solvent water [i.e., HPLC-grade ultrapure water (Baker Inc.)], which is used to prepare the H_2SO_4+$MgSO_4$ solution. These organics were injected into chamber together with sulfate. We utilize the multilinear engine solver (ME-2) to constrain the organics from solvent water (i.e., H_2O-Org). Unlike the PMF2 solver which does not require any a priori information of mass spectrum or time series, the ME-2 solver uses a priori information to reduce rotational ambiguity among possible solutions(Canonaco et al., 2013; Paatero, 1999). We obtained the reference spectrum of organic contamination (i.e., the a priori information for ME-2 solver) by atomizing the H_2SO_4+$MgSO_4$ solution directly into AMS. The ME-2 solver successfully extracted a factor (i.e., denoted as H_2O-Org factor, Fig. B1), which showed a clear enhanced concentration during atomization (Fig. B2).

A total of four experiments were performed and details are summarized in Table B1. As shown in Fig. B2, the isoprene-OA factor increases in all three daytime experiments, but not the nighttime experiment. Based on current understanding of isoprene-OA factor, this enhancement is likely due to the reactive uptake of IEPOX. The lack of enhancement in nighttime experiment is consistent with low IEPOX concentration at night (Hu et al., 2015). Our results provide direct observational evidence that acidic sulfate particles lead to increase in isoprene-OA, which supports results from previous studies (Xu et al., 2015a; Xu et al., ~~2016~~2016a; Budisulistiorini et al., 2015). Due to lack of measurements of gas-phase organic compounds, we are unable to identify the reactive species. Other species, such as glyoxal (Kroll et al., 2005), isoprene hydroperoxides (Liu et al., 2016), and HOMs (Ehn et al., 2014), also have the potential to uptake to acidic sulfate particles and form SOA. Future experiments with comprehensive measurements of gas-phase organic compounds can provide more insights into the identities of reactive uptake species.

We note that in non-atomizing period, the concentration of H_2O-Org factor is close to zero, but not zero. Since H_2O-Org arises from the atomizing solution, it should only exist during atomizing periods. Thus, the non-zero concentration suggests the limitation of the ME-2 solver and cautions are required when using ME-2 solver to resolve one factor based on a specific mass spectrum. This limitation does not affect the conclusion that the enhancement in isoprene-OA is likely due to the reactive uptake of organic species, as we further verify that the organic increase in three daytime perturbation experiments with sulfate particles cannot be solely explained by the organic contamination in atomizing water, from the following two aspects. For example, we atomize the solution directly into AMS and find that the Org/SO_4 ratio is 0.025. This value is significantly lower than the Org/SO_4 ratio in the three daytime sulfate perturbation experiments (i.e., 0.048-0.059), but close to the nighttime sulfate perturbation experiment (i.e., 0.022) (Fig. B4).



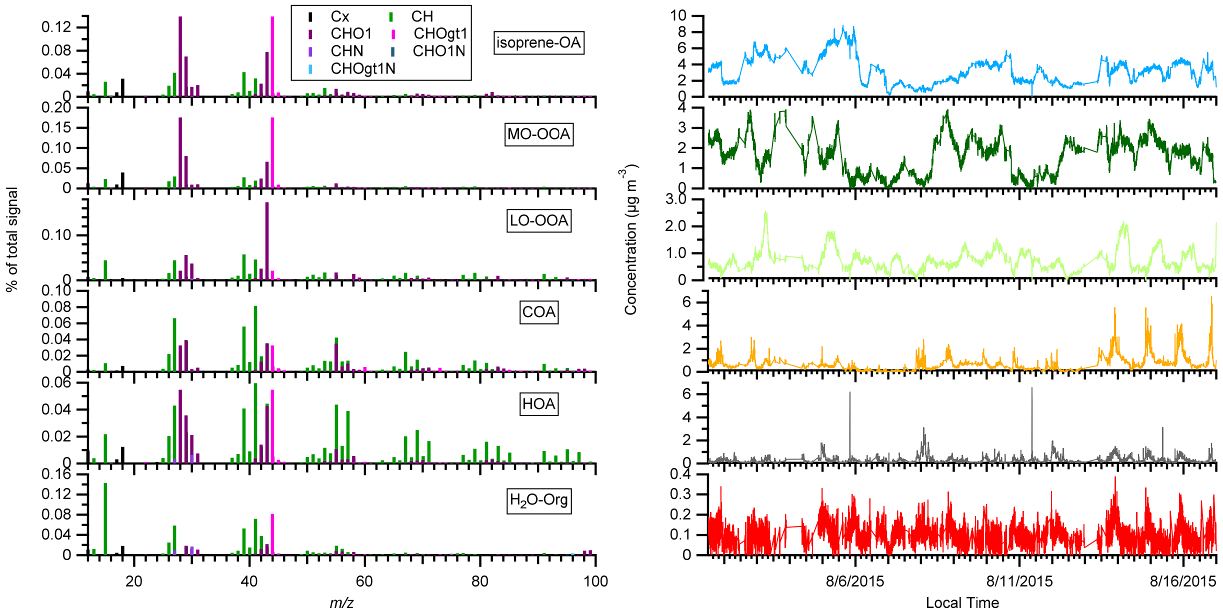


Fig. B1. The mass spectra and time series of OA factors in the 2015 acidic sulfate particle perturbation measurements. Note that the perturbation periods are included in the time series.

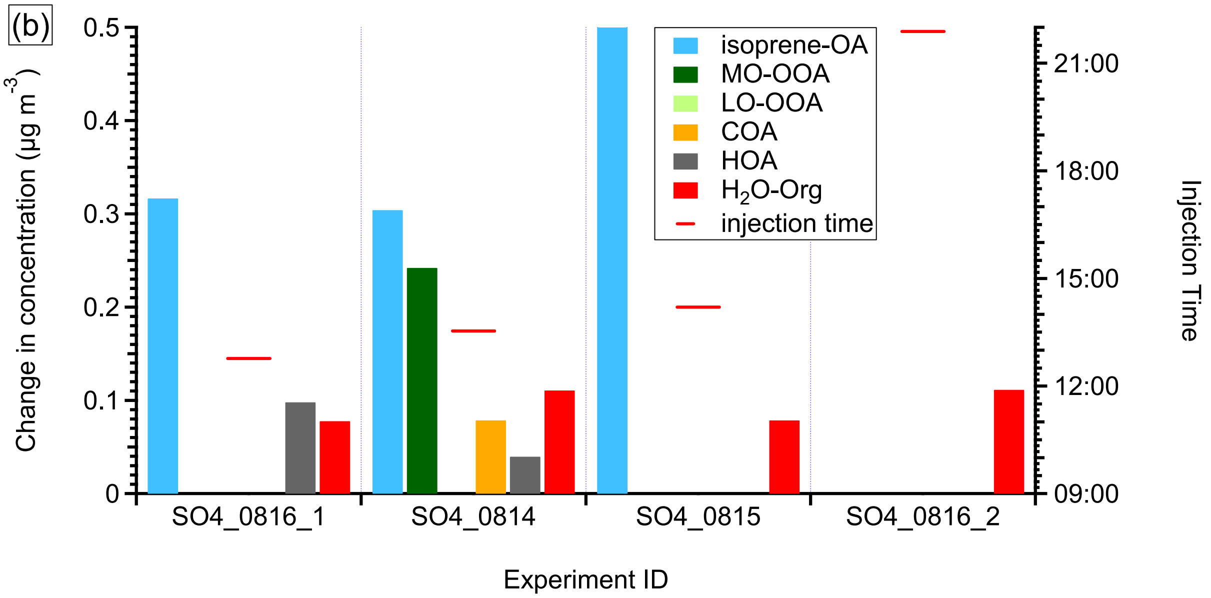


Fig. B2. The statistically significant changes in the concentrations of OA factors after perturbation by acidic sulfate particles. The experiments are sorted by perturbation time. The changes in concentration are the difference between measurements during the Chamber_Af period and mass concentration extrapolated from the Chamber_Bf period. A set of criteria are developed to evaluate if the changes are significant and if the changes are due to ambient variation (Appendix A). H_2O-Org factor in these sulfate perturbation experiments represents organic contaminations in atomizing water.

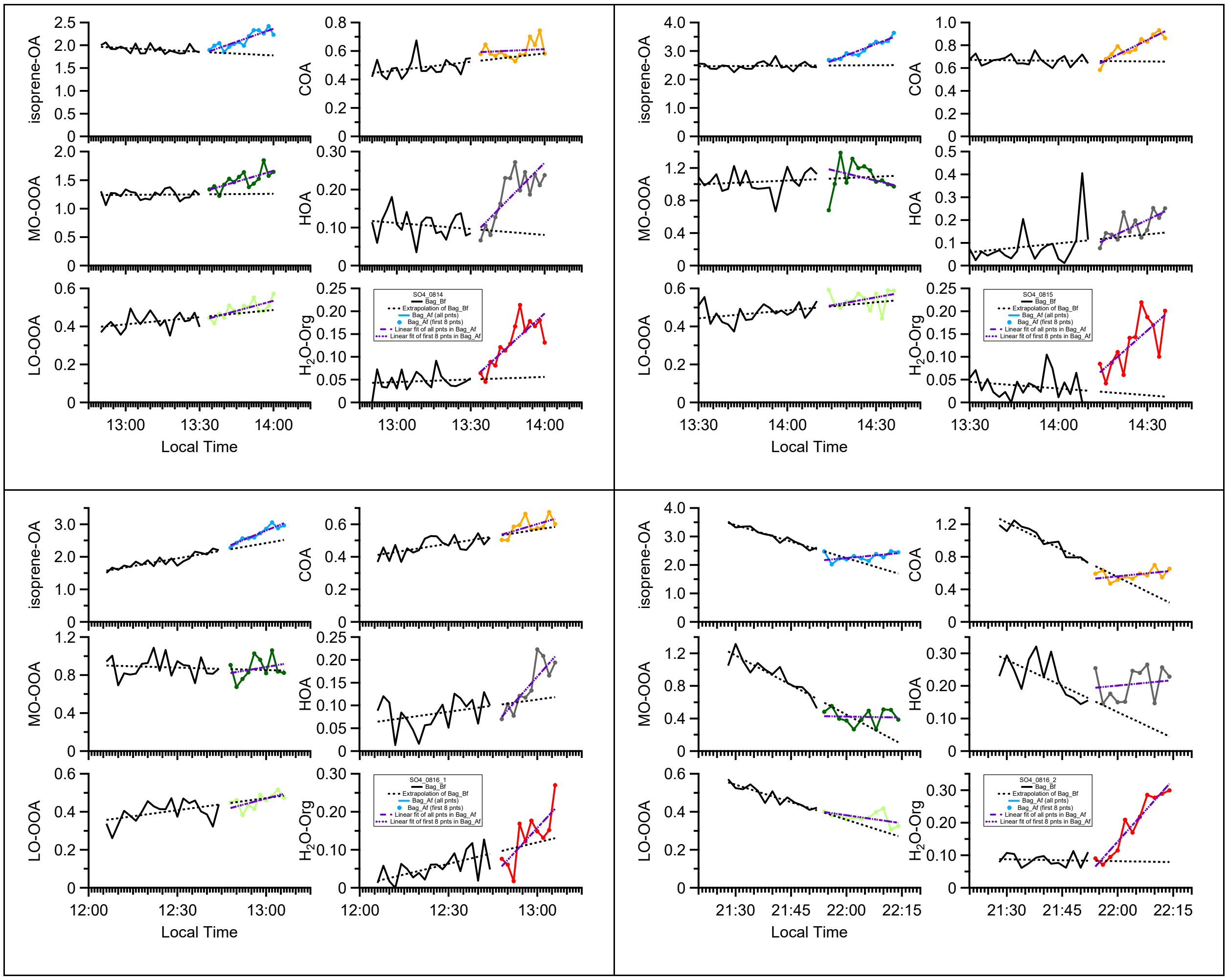


Fig. B3. Time series of OA factors in each sulfate perturbation experiment.

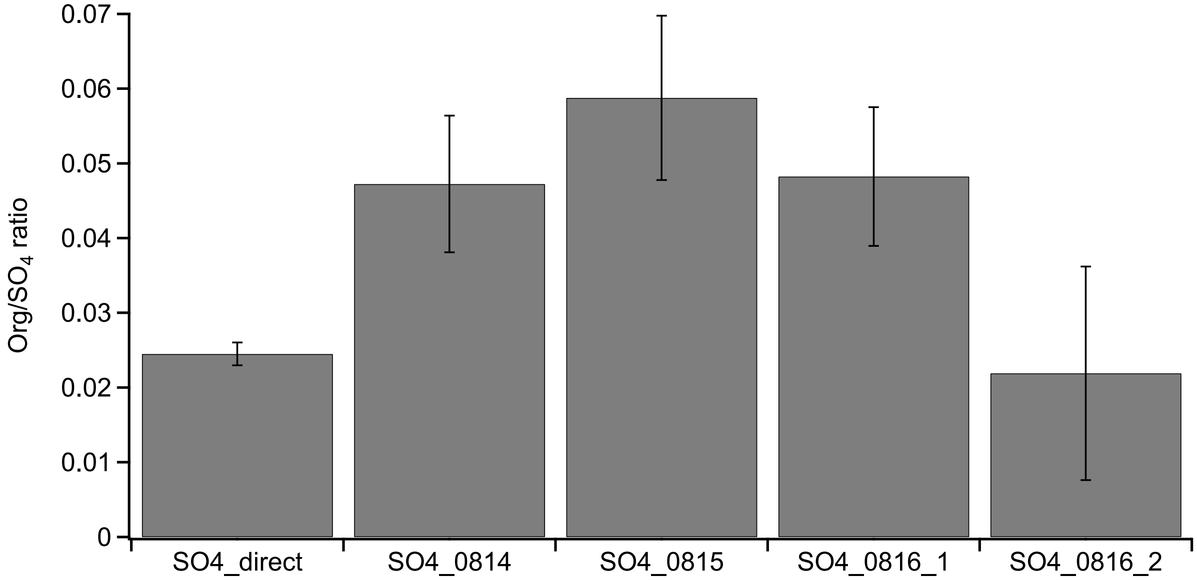


Fig. B4. The Org/SO_4 ratio in sulfate perturbation experiments and laboratory tests by directly atomizing H_2SO_4 + $MgSO_4$ mixture solution into AMS (i.e., SO4_direct).

Table B1. Experimental conditions for sulfate perturbation experiments.

Perturbation	Expt ID[a]	Date	Injection Time	Perturbation Amount[b]	NO[c] (ppb)	NO_2[c] (ppb)	O_3[c] (ppb)
sulfate	SO4_0814	8/14/2015	13:32	16.29	0.51	5.86	59.8
	SO4_0815	8/15/2015	14:12	14.33	0.18	4.79	63.0
	SO4_0816_1	8/16/2015	12:46	14.52	0.36	4.08	53.2
	SO4_0816_2	8/16/2015	21:53	13.92	0.03	5.40	35.6

[a] Expt ID is named as "perturbation species + date + experiment number". For example, SO4_0816_1 represents the first sulfate perturbation experiment on 08/16.

[b] The unit for the perturbation in sulfate experiments is $\mu g\ m^{-3}$. The perturbation amounts of sulfate are calculated from Chamber_Af – extrapolated Chamber_bf.

[c] Average concentration during the Chamber_Af period.