Referee report on Xu et al.

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 well-known 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.

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.**

<u>A little more detail on the major issues</u>

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 LO-OOA (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 a-pinene 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):

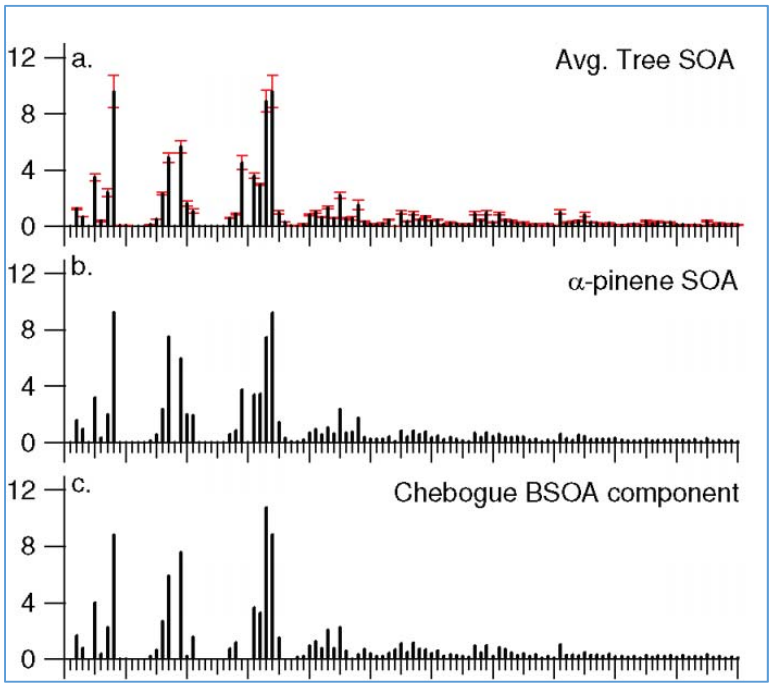

FIGURE 3. Mass spectra comparisons of average plant chamber BSOA (a) vs α-pinene SOA (b), a BSOA component derived from field data (c)

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 a-pinene. 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, m-xylene, 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?**

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 b-caryophyllene, 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.

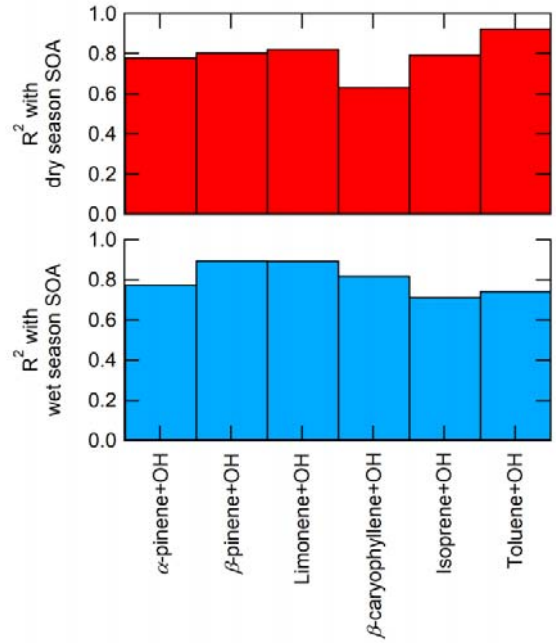

Fig. S12. Correlation coefficients between the SOA formed from OH oxidation of ambient air during the wet and dry with the SOA formed when injecting individual VOCs into the OFR. All spectra were calculated as the difference between the average spectrum of OA after OH oxidation in the OFR minus the average spectrum of concurrent ambient OA. For the spectrum of SOA formed form OH oxidation of ambient air, only data in the range of maximum SOA formation with >1 μg m^{-3} SOA formation were used.

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 pre-determined 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.

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.

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.**

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.

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.

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.

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

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