

Review of Palm et al.

The authors present results from measurements of SOA formation made using an oxidation flow reactor in a forested environment. They provide a detailed discussion of the physical mechanisms at play, and find some interesting relationships between the SOA formation potential and the ambient concentrations of monoterpenes, in particular. They find that the SOA that they would predict to form based on the observed MT concentrations is lower than the observed formation. They use this, along with some direct measurements of the concentrations of S/IVOCs, to estimate effective yields for these species and to explain the observation-prediction gap. I find this section to be a bit weaker than it could be, I think because the authors are working to not show data that is under review elsewhere (Hunter et al., Submitted to Nat. Geosci.). I suggest that the authors be more direct in this section. Overall I think that this study is well done, provides interesting results and should be publishable once the authors address the comments below.

P30414, L13: Although it seems very likely that S/IVOCs are contributors to SOA formation from biomass burning and vehicle exhaust, some of the difference between the observed and predicted SOA formation from VOCs in the two cited studies (Ortega et al., 2013; Tkacik et al., 2014) could potentially be explained by the assumed SOA yields used to make the predictions being too low, a consequence of the losses of semivolatile gases alluded to on the previous page. It seem appropriate to also mention this here.

P30415, L25: I find the statement here regarding the NO⁺ ion to be a bit unclear how specifically this links to the first part of the sentence. Do the authors mean whole air samples analyzed using a CIMS technique with NO⁺ as the reagent ion?

P30416, L13: Is the mesh smaller than the ID of the OFR body (14 vs. 19.7 cm)? This makes it difficult to understand how this really acted as a screen (not that this really matters to the results of this study, but it could be clarified in case someone else wants to apply this methodology).

P30417, L22: It would be useful if the authors were to elaborate as to what “a small number means.” If, for example, the number of compounds influenced is small but they are the most abundant, then the influence on the system would not be small.

P30418, L2: It would be useful if the authors were to define “external OH reactivity” further here, so the reader doesn’t have to look this up in the Li et al. paper. Additionally, the authors could elaborate as to how this was estimated.

I suggest the authors just write out “equivalent” rather than using the abbreviation “eq.”, which I find awkward.

Line 30420, L24 and elsewhere: Given that the net change in the amount of particle volume observed can either increase or decrease, I suggest that the authors move away from using the terminology “volume added,” which to me implies that things only increase, to something like ΔV (where delta is the delta symbol) to capture that this is not unidirectional.

P30421: Although I understand the arguments as to why the OFR185 and OFR254 measurements are different, given that they apparently “give consistent results” I do not see why the OFR254 measurements would be excluded from the bulk of the analysis. Why not merge the data sets, which should be straight forward if they are “consistent”.

P30424, L14: The authors note that as the OH exposure is increased the SO₄ mass formed continued to increase. However, in looking at Fig. 2 it appears that the SO₄ mass increases to a point, but plateaus at high OH exposure. Is this generally true? If so, it should be mentioned.

P30426, L5: The authors here note that the accuracy of the model-derived OH exposures could be assessed by comparing the measured vs. predicted depletion curves. However, since the factor of 2 scaling was determined by comparing the model results with the observations, I don't really think that this is an assessment of the accuracy of the “model-derived OH_{exp}”. I realize the authors have the caveat “(including the factor of two decrease)”, but I don't find this sufficient. I suggest that the authors very simply replace “accuracy” with “reasonableness”.

P30427, L2: I think that here the authors are more specifically defining LVOCs as species that “irreversibly” condense, not just condense. I suggest they add this word.

P30427: Regarding the fates of the LVOCs relative to their fate in the atmosphere, given that this study focuses on a forested area where the available surface area may be low, do they think that (perhaps) the LVOCs may condense onto things like leaves, trees, rather than onto particles? If this were to occur, then some of the loss processes discussed here might actually be relevant to this particular environment. I am speculating here, but perhaps something to consider adding a note about? Of course, such high exposures as considered here would not be relevant for the particles within the canopy, in general, but for those transported far downwind and so perhaps this line of thinking on my part is generally irrelevant.

P30427, L20: The authors here seem to be implying that the low volatility of SOA results solely from the condensing species being low volatility. However, this neglects that some of the low volatility nature of SOA may result from condensed phase reactions involving SVOCs. If such condensed phase reactions are fast, then distinguishing between SVOC and LVOC condensation may not be important.

P30427, L25: I find this to be an odd way to start a sentence.

P30429, L13: I think the units are incorrect on the surface area concentration.

P30432, L24: Do the authors mean by dividing the newly produced SO₄ mass, and not the total SO₄ mass, which would include pre-existing SO₄ that is not influenced by the loss to walls or exiting the OFR?

Figure 6: There does not appear to be a blue curve, as indicated in the legend. Do the authors mean black?

P30433: I agree that the H₂SO₄ results suggest a strong potential for the LVOC correction method to help/work, however I think that the authors should also note that there is a great deal of scatter at low enhancements, when the corrections are particularly large, meaning that these values are particularly uncertain.

P30435, L5: I suggest a reference to (Lambe et al., 2015) would be good here, as they compare OFR to chamber experiments for isoprene SOA.

P30435, L14: In Fig. 7, comparing the daytime points, the difference between OFR185 and OFR254 at the lowest OH exposure was fairly large. Although I agree that there are no major differences between the OFR185 and OFR254, I am not entirely convinced that “significant” is justified here.

P30439, L7: Given the authors acknowledgement on the previous page that the yields of SOA in chamber experiments due to losses of S/IVOCs to chamber walls might be low, I think that the authors should change their language to indicate that other S/IVOCs “contribute” to the discrepancy, don’t “cause” the discrepancy.

Section 3.6.2: Given that the Hunter et al. manuscript is not yet published and not available for consideration, I find it difficult to really assess this section. For example, the authors report here measurements of MT concentrations that are typically around 0.5-1 ppb, which corresponds to 2.5-5 ug/3m. The logC* of MTs is around 6 or 7. Either way, they should fall in one of the TD-EIMS bins shown in Fig. 12. However, the max concentration in those bins is only 0.5 ug/m³. Where are the MTs? I see the argument that “the TD-EIMS instrument experiences a loss of sampling efficiency in that bin and MT are not expected to be measured,” but without being able to read the Hunter paper I do not understand how one specific class within a bin would be missed (which is implied by the statement). If the authors simply mean that the overall efficiency in this bin is low, that I can understand.

S/IVOCs Diurnal Dependence? The authors note a substantial difference in day/night SOA formation. This correlates really well with the day/night variation in MT concentrations. What about for S/IVOCs?

P30440/L28: I don’t fully follow what is being compared here. I thought that the SOA yields from S/IVOCs were just derived by comparing the S/IVOCs to the SOA. But then here they are comparing the SOA predicted from S/IVOCs (and VOCs) to the observed SOA. Isn’t this circular? Is the point here only the R² value since the slope was effectively forced to one? This should be clarified. But given that the authors seem to use campaign-average values, not time-dependent values, for the S/IVOC concentrations it is not especially surprising to me that the R² decreases from when compared to just the SOA predicted from VOCs. Or am I missing that, in fact, time dependent S/IVOC concentrations were used here? I think I am confused because of the statements on the previous page that a “full time series analysis” was not possible. I suggest that this section could be somewhat clearer regarding what specifically is being done with the S/IVOC measurements. (I suspect the authors are trying to not show too much of this data given the other pending publication. If the Hunter paper has been published by the time this is revised, I strongly encourage the authors to use a figure to help facilitate understanding here.)

P30441, L8: I think the authors need to change “will produce” to “can potentially produce.” As I see what the authors have done, it is simply a matching exercise that does not definitively indicate that S/IVOCs form this much more SOA compared to VOCs in this environment because the authors have not addressed the issue of potential yield underestimates for VOCs in a quantitative manner.

P30441/L12: The authors here discuss how the correlation between SOA and MT concentrations indicates that S/IVOCs come from biogenic sources related to MTs. I believe it would be much more straight forward to compare the SOA formation to the S/IVOC concentrations or the MT concentrations to S/IVOC concentrations directly to make this point. As written, this conclusion seems one step removed from the desired actual comparison.

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