Interactive comment on “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” by S. H. Budisulistiorini et al.

Anonymous Referee #2

Received and published: 15 April 2015

This paper describes the results of a recent field campaign at the look-rock site during SOAS, investigating the formation of isoprene derived SOA through the PMF analysis of AMS data along with the measurement of select isoprene-OA tracers. The authors are able find that a significant amount of the OA measured at the site was from isoprene derived SOA (∼30% based on the PMF analysis), but that the specific isoprene-SOA tracers measured accounted for only a small portion of this. The analysis performed in
this paper seems well done, and overall this is a good paper.

However, when all is said and done, it would seem that the results of this paper do not dramatically improve our state of knowledge when it comes to isoprene SOA. A significant fraction of isoprene SOA has been observed in other locations, and this paper simply reaffirms that this can be the case here as well. The expected correlations with other species (i.e., SO4, pH, NOy) based upon known chemistry for isoprene SOA formation are not significantly observed, partly because of the complex nature of the air masses intercepting the site. The results generally do not fit what we think we know about isoprene SOA formation. As a result, this paper does not provide any major new insights, except for emphasizing how little we in fact understand about this chemistry. For this reason alone it should be publishable after some relatively minor issues are addressed and commented on as outlined below.

Introduction, pg 8: The authors mention that the results of this paper will help the regional modelling of isoprene SOA via better parameterizations, since they are currently under predicting this. However, right now what are models for this part of the USA using for isoprene SOA? I know that this group had modified CMAQ with some new isoprene chemistry, but I did not think that explicit heterogeneous or liquid phase chemistry was included (but maybe they are??). If the current chemistry is insufficient for understanding field work, how can it be used to provide a better parameterization for a model?, If regional models are using a simple overall yield approach for isoprene SOA (under high or low NOx) then how will this work here be useful to them, and more importantly why are those models under predicting isoprene SOA in the first place? Some more information on the current model developments and issues would be useful here.

Pg 10: by this point we have a pretty good idea what PMF is. There is no need to repeat it all here, so I suggest it is put in the SI (or what you have in the SI is good enough).

Pg 12, line 2: The CIMS does not measure MVK or MACR, so how is this done? It is
not clear what you mean here.

Pg 13, lines 5-10: What about wall loses for IEPOX and MAE in the chamber? I would expect there to be some losses. How do you account for this?

Pg 13, line 28: typically I did not think a filter was used in front of a PTR-MS. How do you know that some gases are not also lost to the filter?

Pg 22, lines 10-15: If indeed the CIMS data is partly or mostly ISOPOOH, what effect will this have on your hypothesis here?

Pg 23, lines 3-5: This may or may not make sense. On the one hand since MVK and MACR are formed very quickly from isoprene one would expect a diurnal profile for these products as well as isoprene. The lifetime of isoprene is very short, presumably making MVK etc...On the other hand there does seem to be a small diurnal profile to these species as well, but less than isoprene possibly for good reason. You would need to model the system to truly understand if the diurnal profile of these others should be as pronounced as isoprene. Based upon the figure alone I do not think you can make the assertion that it is all transported in.

Pg 23, lines 10-12: If both LV-OOA and the IEPOX-OA are both transported from elsewhere (as hypothesized), then why does the LV-OOA have a diurnal cycle of some kind and IEPOX-OA not? You need more analysis here on this issue.

Pg 23, lines 17-29: I am not sure why this paragraph on terpenes is needed if this is a paper about isoprene SOA. Seems to stick out and does add much overall. I suggest it is removed or at least placed in the SI.

Pg 25, line 5: This is more than 100%. How is this possible?

Pg 25, lines 9-10: This is a bit confusing here. In the above lines you say IEPOX and MAE derived tracers are $\sim 97\%$ of isoprene derived SOA, but here you say 25% of the IEPOX-OA factor mass...what is the difference between isoprene derived SOA and IEPOX-OA mass? I assume you mean one form offline and one from On-line AMS C1603
data? If so you need explicitly state that here.

Pg 27, lines 1-5: it may also suggest that additional organics may result in the acidity being not accessible to the IEPOX eventually. This has been observed in some lab studies for other systems (although I do not recall the references), and may also explain why there is no diurnal profile, since the uptake occurred quickly then was slowed by this organic addition. You might also expect a moderate correlation with sulfate if this were to be occurring. Perhaps looking at the correlation between IEPOX-OA and the ratio of Org:SO4 might be helpful in this regard, as a means to isolate older vs local air masses, and possibly to get a hint if the added organics are self-limiting for this process.

Pg 27, lines 15-16: And yet since the particles remained acidic why should it not be taken up? Again this may point to a particle phase issue; possibly viscosity/mass transfer limitations caused an organic barrier of some kind.

Pg 28, lines 1-2: The NOx should also be from upwind, thus still correlated, and yet they are not. The fact that species of both high and low NOx seem to be not correlated to what is expected, seems to be a little odd. On the one hand you are saying that both are not formed locally, but it is non-local where the NOx is, so how can they both formed elsewhere and transported in? Unless they were from two separate regions, one with NOx and one without. This needs to be clearer here.

Pg 29, line 9: typo – should be "a" subset. . .

Pg 29, line 27-28: Despite this consistency, a correlation does not exist with acidity in the measurements. The model does not include transport along a trajectory and processing along the way, and yet this is what the authors are asserting is happening. So how can one use initial inputs of IEPOX etc... from the site when the initial inputs should be from at the source? Therefore there is not much reason to have faith in the so-called good correlation between box model and measurements since the model output is for 12 hrs of local emissions and the measurements are of processed SOA.
from elsewhere. It would seem then that the correlation is just fortuitous. In fact, it is not clear what the point of running this model was in the first place, especially if you didn’t expect it to agree anyways. The authors need to justify this model’s use, and at the very least explain the reasons for trying to do this at all.

Figure 3: On my screen the black of IEPOX in the pie chart looks grey and different from the black below it. I presume this is not intended?

Figure 5: What is the purpose of this figure? Since the correlations are poor for everything, what is it telling you? I would sooner like to see the correlations of IEPOX-OA with NO.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 7365, 2015.