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 (ie: 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.

We thank the reviewer for their helpful comments as they have helped to improve the quality and clarity of the manuscript.

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, bit 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.

Heterogeneous liquid phase chemistry of IEPOX was added to a research version of CMAQ in the work of Pye et al. (2013, ES&T). The chemistry predicts the uptake of IEPOX (and MAE) via acid-catalyzed particle-phase reaction using many of the same parameters in simpleGAMMA, but with a slightly different approach. The publicly available version of CMAQv5.1, planned for release in Fall 2015, will include heterogeneous IEPOX chemistry for both research and regulatory simulations. The initial work of Pye et al. indicated that there were a number of uncertain parameters (such as the Henry's Law coefficient and particle-phase reaction rate constants) that affect the magnitude of IEPOX-OA. This work provides important insight into the effect of the magnitude of the Henry's law-coefficient and rate constants on IEPOX-derived SOA. This work also provides insight into the contribution of species like 2-methyltetrols, which are explicitly predicted in CMAQv5.1, to total IEPOX-OA, which could be underpredicted by the bottom-up approach of models such as CMAQ and simpleGAMMA, since many IEPOX-derived constituents have not been identified (see Karambelas et al., 2014 ES&TL).

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).

We have greatly simplified the PMF section as suggested by the reviewer.

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.

The MVK and MACR were measured by PTR-TOF-MS. The sentence has been revised as follow:

"July CIMS data was corrected by comparing it to collocated MVK+MACR measured by PTR-TOF-MS (Section 2.4.2)…."

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?

Wall loses for IEPOX and MAE in the chamber are 5.91×10^{-5} s^{-1} and 1.12×10^{-5} s^{-1}, respectively (Riedel et al., 2015). Over the course of calibration (~40 min), we expected to lose 14% and 3% of IEPOX and MAE, respectively.

We added this information to the main text as follows:

"During the course of the calibration experiments, we accounted for the fact that we would lose 14 and 3% of IEPOX and MAE, respectively. Wall loss rates for IEPOX and MAE have been measured in the chamber and are 5.91×10^{-5} s^{-1} and 1.12×10^{-5} s^{-1}, respectively (Riedel et al., 2015)."

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?

Practices vary as to employing a filter at the sample inlet when making PTR-MS measurements in ambient air. Below are a couple of additional references to studies where a filter was used. References to studies that did not use a filter can also be found in the literature. The argument for using a filter is that it will prevent particulate matter, which may contain semi-volatile organic compounds, from collecting on the walls of the sample lines. Any semi-volatile organic material that is deposited on the sample lines may later evaporate, leading to signals that could be attributed erroneously to gas phase species. In addition, organic material on the walls of the sample system may adsorb additional volatile or semi-volatile organic species from the gas phase, resulting in losses. On the other hand, as the reviewer points out, losses of semi-volatile species on the filter itself are also possible, as is subsequent evaporation and detection of these species at a later time. One advantage of a filter is that its effects can be evaluated more easily (by changing or removing the filter) than the effects of deposition of particulate matter on the walls of the sample system. We have performed tests of the effect of the filter by monitoring gas phase concentrations with and without a filter and before and after filter changes and have observed no measurable loss of volatile species such as isoprene, methyl vinyl ketone, and methacrolein to the filter. The filter may have a more significant effect on compounds of lower volatility, however, such compounds are not reported in the current study.

References:

Park, J.-H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karlik, J., and Holzinger, R.: Eddy covariance emission and deposition flux measurements using proton transfer reaction – time of flight – mass spectrometry (PTR-TOF-MS): comparison with PTR-MS measured vertical gradients and fluxes, Atmos. Chem. Phys., 13, 1439-1456, doi:10.5194/acp-13-1439-2013, 2013.

Eerdekens, G., Ganzeveld, L., Vilà-Guerau de Arellano, J., Klüpfel, T., Sinha, V., Yassaa, N., Williams, J., Harder, H., Kubistin, D., Martinez, M., and Lelieveld, J.: Flux estimates of isoprene, methanol and acetone from airborne PTR-MS measurements over the tropical rainforest during the GABRIEL 2005 campaign, Atmos. Chem. Phys., 9, 4207-4227, doi:10.5194/acp-9-4207-2009, 2009.

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

The low correlation between gaseous IEPOX and IEPOX-OA factor was asserted due to time gap from IEPOX uptake and formation of IEPOX-OA. The lifetime of ISOPOOH will affect time series of IEPOX formation and thus the IEPOX-OA factor. CIMS sensitivities toward IEPOX and ISOPOOH were measured to be similar at 1.3×10^{-7} and 9.9×10^{-8} signal ppt^{-1}, respectively. We have investigated lowering the IEPOX mixing ratio by a constant factor between 100 and 10% of total *m/z* 177 signal. In this exercise, which will be reported in future study, we found that the model correlations are not sensitive and only tracers mass loadings vary with the IEPOX:ISOPOOH ratio. The inability to distinguish IEPOX from ISOPOOH is a limitation in our study.

We added this information to the main text as follows:
"We synthesized ISOPOOH (see Fig. S10 for nuclear magnetic resonance (NMR) data) and measured CIMS sensitivities toward ISOPOOH and IEPOX. Results indicated that response factors of both compounds were similar (see Fig. S11). Investigation of lowering the IEPOX mixing ratio by a constant factor of total *m/z* 177 signal, which will be reported in a future study, showed that SOA tracer model correlations are not sensitive to this and only tracers mass loadings vary with the IEPOX:ISOPOOH ratio. The inability to distinguish IEPOX from ISOPOOH is a limitation in our study."

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.*

What we meant in this is that the lack of diurnal variation of gaseous IEPOX and thus IEPOX-OA were due to continuous oxidation of isoprene emitted at the site (which was in a forest) and the surrounding forested areas, as well as from forests further upwind of the site. IEPOX reactive uptake, although it is only few hours, would mean that it could continue on given that there is aerosol sulfate (which is not formed on site).

To make this clearer, we have revised the text as follows:

"… IEPOX-OA was not only formed on site but could also transported from surrounding forested and isoprene-rich areas. Despite the strong diurnal profile of isoprene at the LRK site, diurnal variations of the gas-phase products of isoprene photooxidation, particularly IEPOX, were small during this campaign (Fig. 4). The lack of strong diurnal profile of IEPOX and the fact that reactive-uptake of IEPOX is influenced by aerosol sulfate (Lin et al., 2012) that is not formed on site, might explain the lack of significant diurnal variation (Fig. 3) of the IEPOX-OA factor at LRK. …"

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.

We added more discussion on this issue as follow:

"…Diurnal profile of LV-OOA observed at LRK is similar to more-oxidized OOA (MO-OOA) observed at Centerville (Xu et al., 2015), suggesting their regional sources. At LRK average mixing ratios of monoterpenes and isoprene were <1 ppb and ~2 ppb (Fig. 4), respectively. Low anthropogenic emissions at LRK (<1 ppb; Fig. S16) suggests that BVOCs could be the source of LV-OOA (50% of OA) formation. Anthropogenic emissions as well as nitrate chemistry in the valley could also influence LV-OOA formation that oxidized during transport to the LRK site."

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.

Part of this paragraph has been removed and placed into the SI.

We added in the text the following:

"Potential sources of 91Fac is discussed in more detail in the SI (Fig. S15) and its association with biogenic SOA chemistry will be the focus of future studies."

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

There were some miscalculation and typos. This has been fixed as follows:

"In sum, IEPOX- and MAE-derived tracers contributed 96.6% and 3.4%, respectively, of total isoprene-derived SOA mass quantified from filter samples."

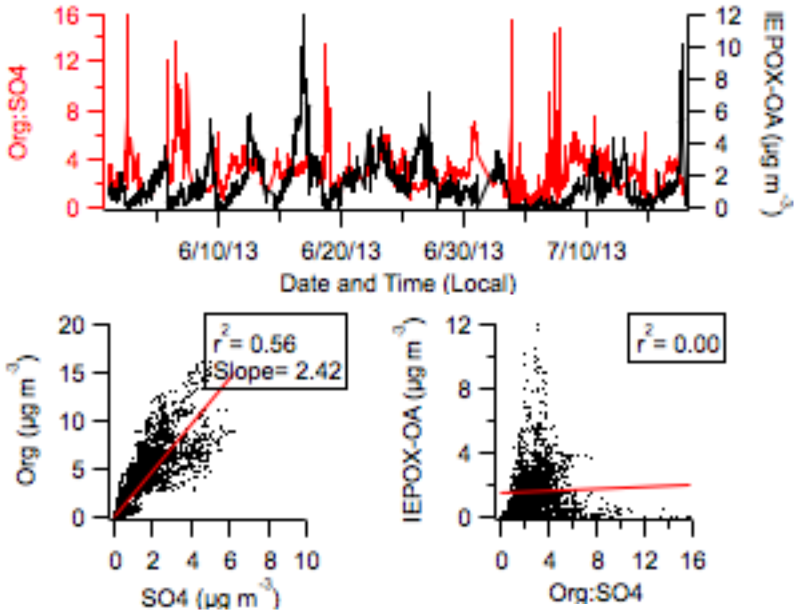
Pg 25,lines 9-10: This is a bit confusing here. In the above lines you say IEPOX and MAE derived tracers are ~97% of isoprene derived SOA, but here you say 25% of the IEPOX-OA factor mass...what is the difference between isoprene derived SOA and IEPOX-OA mass? I assume you mean one form offline and one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

Isoprene-derived SOA mass was measured by offline analysis, while IEPOX-OA factor mass was resolved by PMF analysis of OA fraction measured by ACSM. This has been changed as follows:

"…. Total IEPOX-derived tracers masses quantified from filter samples were on average 26.3% (maximum 48.5%) of the IEPOX-OA factor mass resolved by PMF…."

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.

IEPOX-OA shows no correlation with ratio of Org:SO4 as illustrated below. The average ratio Org:SO4 of 2.42 indicates that the air masses is mostly aged. No-correlation between IEPOX-OA and ratio of Org:SO4 might suggest a mix of local and non-local (aged) air masses.



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.

Our recent flow tube studies have shown that organic coatings with PEG-300 can suppress IEPOX uptake (Gaston et al., 2014), and thus, lowering the uptake coefficient by upwards of a factor of 2 at similar acidities. However, organic coatings of more complex mixtures and of atmospheric relevance have not been systematically studied. It is unclear at this time how coatings will affect IEPOX uptake in the atmosphere.

To clarify this section, we have revised this sentence as:

"Further complicating factors may be viscosity or morphology changes of the aerosol as IEPOX is taken up by heterogeneous reaction, and thus, slowing of uptake kinetics as the aerosol surface is coated with a hydrophobic organic layer (Gaston et al., 2014). Additionally, liquid-liquid phase separation is likely to occur in the atmosphere due to changes of relative humidity that affect particles water content (You et al., 2012). Moreover, the effects of aerosol viscosity and morphology on IEPOX uptake is not well understood and warrant further study using aerosol of complex mixtures and of atmospheric relevance."

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.

The NO_x was from urban areas upwind of the site. MAE/HMML could be formed in the urban areas since they are downwind of forested areas where isoprene is emitted. We revised the sentence as follow:

"….The observation that neither the summed MAE/HMML tracers nor 2-MG correlated with NO_x, is consistent with the hypothesis that MAE/HMML is formed in urban areas upwind and transported to the sampling site. …"

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

This has been changed as suggested.

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.*

We were justified in using gas-phase IEPOX concentrations measured model inputs because atmospheric lifetime of IEPOX is a few hours (Gaston et al., 2014; and diurnal profile Fig. 4), meaning that it is all relatively local. Aerosol sulfate is regional, as indicated by the flat diurnal profile. Furthermore, measurements at all SOAS locations indicate highly acidic aerosol. Additional support for our choice of local data as model inputs is that aerosol acidity is instantaneously determined by the local thermodynamic equilibrium, which for the aerosol we have at hand is less than 1 hour. Given this, and that water equilibrates on the order of seconds strongly suggests that all the relevant chemistry here is fast and using local initial conditions of IEPOX etc. is appropriate.

Our goal in using the model was to help reconcile what we know about the chemical mechanism of IEPOX-OA formation, as represented in simpleGAMMA (which includes dependence on aerosol acidity, aerosol liquid water, sulfate, and ammonium content), with the apparent lack of expected correlation with acidity and aerosol liquid water. The model results provide estimated IEPOX SOA mass loadings, which we compare to observed concentrations. We feel that the demonstrated model-data agreement shows that the observations are consistent with the known chemical mechanisms, despite the lack of correlation between acidity and the tracers.

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?

We have fixed the figure.

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.

We relocated Fig. 5 to SI since it is mainly utilized to explore possible sources of 91Fac instead of the isoprene-derived SOA factor. Further investigation of the sources of 91Fac will be conducted in a future study.