

Response to reviewers for the paper “Characterization of a real-time tracer for IEPOX-SOA from aerosol mass spectrometer measurements”

By W.W. Hu et al

We appreciate the reviewer’s comments and support for publication of this manuscript after minor revisions. Following the reviewer’s suggestions, we have carefully revised the manuscript. To facilitate the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

Anonymous Referee #1

General Comments

R1.0. In this manuscript, the authors analyze AMS data from multiple sources to determine whether m/z 82 and, more specifically the C_5H_6O fragment, are robust AMS tracers for SOA formed from isoprene epoxydiols (IEPOX). The main goals of the manuscript are to determine the range of $f_{C_5H_6O}$ in ambient IEPOX PMF factors, determine the background $f_{C_5H_6O}$ in different ambient environments, and determine whether SOA generated from monoterpenes (MT) and analyzed with the AMS have significant signal at the C_5H_6O fragment. The authors quantify the $f_{C_5H_6O}$ for areas influenced by biomass burning and urban pollution, areas with heavy MT emissions, and areas with strong isoprene emissions. They present a method for estimating the SOA mass formed from IEPOX chemistry from $f_{C_5H_6O}$ and compare this method to PMF results from the SOAS campaign. They argue that IEPOX SOA mass estimated from $f_{C_5H_6O}$ should be within a factor of 2 of that determined by a more rigorous PMF analysis.

This manuscript will primarily be of interest to AMS users and less so to general readers of ACP. Nevertheless, the AMS is probably widespread enough to justify publication in ACP rather than a more specialized journal (e.g., AMT). In general, the conclusions are well-supported and the analysis seems to be carefully done and robust. There are however, several things that the authors should do before publication to improve the clarity and readability of the manuscript. First, many of the key figures are essentially illegible because a large amount of data is placed in multi-panel figures that end up being too small to read. Figures 3 and 5 are particularly bad though several others would also benefit from being larger and from multiple datasets being differentiated from one another more clearly. Second, there are several places where the authors could be more clear/specific in their writing. For example, when they refer to IEPOX SOA, it often isn’t clear whether they are talking about the PMF factor or the general concept of SOA formed from IEPOX. As another example it isn’t clear how exactly all the average $f_{C_5H_6O}$ values were calculated. There are a relatively large number of typos and grammatical mistakes and, while it was generally clear what the authors meant, it would be good if the authors gave the manuscript a more careful read before final publication. After these corrections are made, the manuscript should be publishable in ACP.

A1.0: All of the items mentioned here are addressed in response to the more specific comments below, in particular R1.1-R1.7, R1.9, R1.13, R2.1, R2.4 and R2.9.

Major Specific Comments

R1.1. P 11227, lines 1-2 and Page 11244 , lines 19-21. Can you be more specific about how you arrive at your conclusion that the IEPOX SOA estimate from $f_{C_5H_6O}$ will be accurate to within a factor of 2? Have you used your estimation method on more than the SOAS datasets to estimate the accuracy? As you mention, the SOAS data probably represents a best case scenario.

A1.1: The justification on how we obtain the method accuracy to be ~ 2 may not have been stated clearly enough. We have addressed this topic in detail in 1.2 part of the supporting information of the revised manuscript:

“To estimate the accuracy of our IEPOX-SOA tracer-based estimation method, we used this method to estimate IEPOX-SOA from another two ambient datasets with the lowest and highest $f_{C_5H_6O}^{IEPOX-SOA}$ in PMF-resolved IEPOX-SOA (IEPOX-SOA_{PMF}) among all the studies in this paper. The lowest value is from a dataset in the pristine Amazon forest (AMAZE-08) where $f_{C_5H_6O}^{IEPOX-SOA} = 12\%$ (Chen et al., 2015) and the highest value from a dataset in a Borneo forest with $f_{C_5H_6O}^{IEPOX-SOA} = 38\%$ (Robinson et al., 2011). Since the $f_{C_5H_6O}^{IEPOX-SOA}$ values in these two datasets are the two farthest from the average $f_{C_5H_6O}^{IEPOX-SOA}$ ($22 \pm 7\%$), the estimation method results from these two datasets represent the worst case scenarios for all datasets published so far.

The estimation results from both datasets are shown in Fig. S13 and Fig. S14. Both of the background OA corrections for areas strongly influenced by urban+BB emissions and by monoterpene emissions are used.

Overall, all variants of the estimated IEPOX-SOA correlate well with PMF-resolved IEPOX-SOA (all $R \geq 0.93$). When average $f_{C_5H_6O}^{IEPOX-SOA} = 22\%$ is used, the slope between estimated IEPOX-SOA vs PMF-resolved IEPOX-SOA is between 0.43-1.5, i.e. within a factor of 2.2. When the actual $f_{C_5H_6O}^{IEPOX-SOA}$ in each dataset is used, the slope between estimated IEPOX-SOA vs PMF-resolved IEPOX-SOA is in a range of 0.7-1.2, i.e. within 30%.”

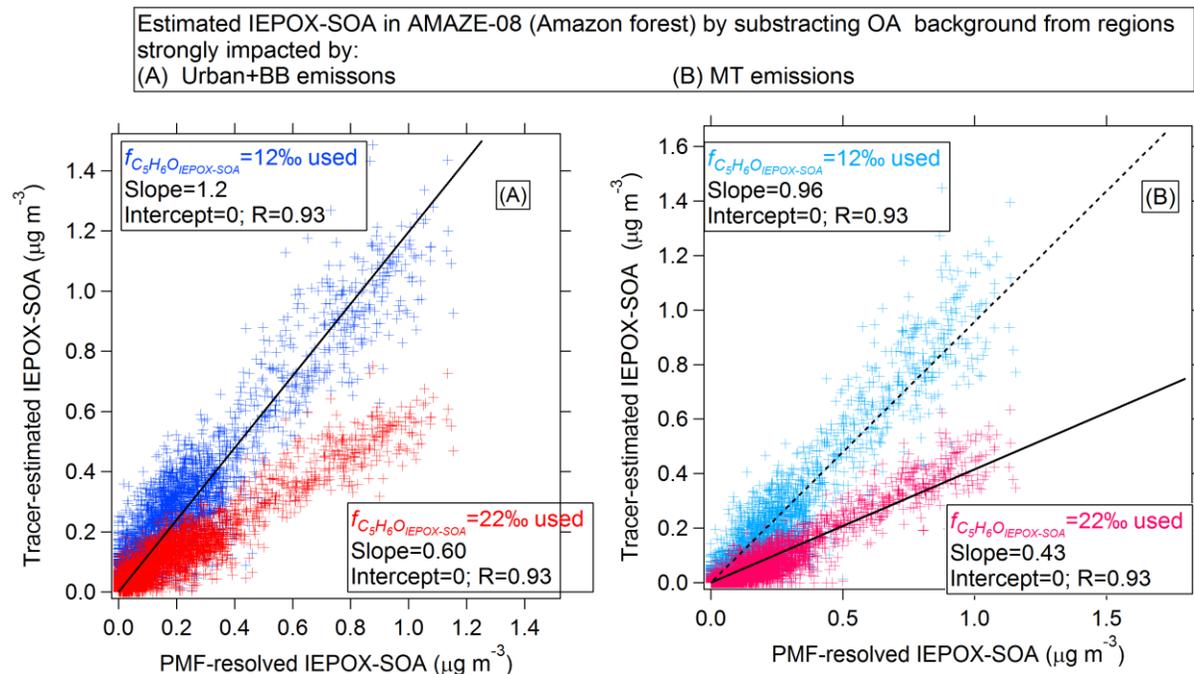


Figure S13. Scatter plot between tracer-estimated IEPOX-SOA and PMF-resolved IEPOX-SOA at a pristine Amazon forest site (AMAZE-08). The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each plot, we used two $f_{C_5H_6O}^{IEPOX-SOA}$, from the average IEPOX-SOA_{PMF} ($f_{C_5H_6O}^{IEPOX-SOA}=22‰$) and from the IEPOX-SOA_{PMF} in Amazon forest study ($f_{C_5H_6O}^{IEPOX-SOA}=12‰$).

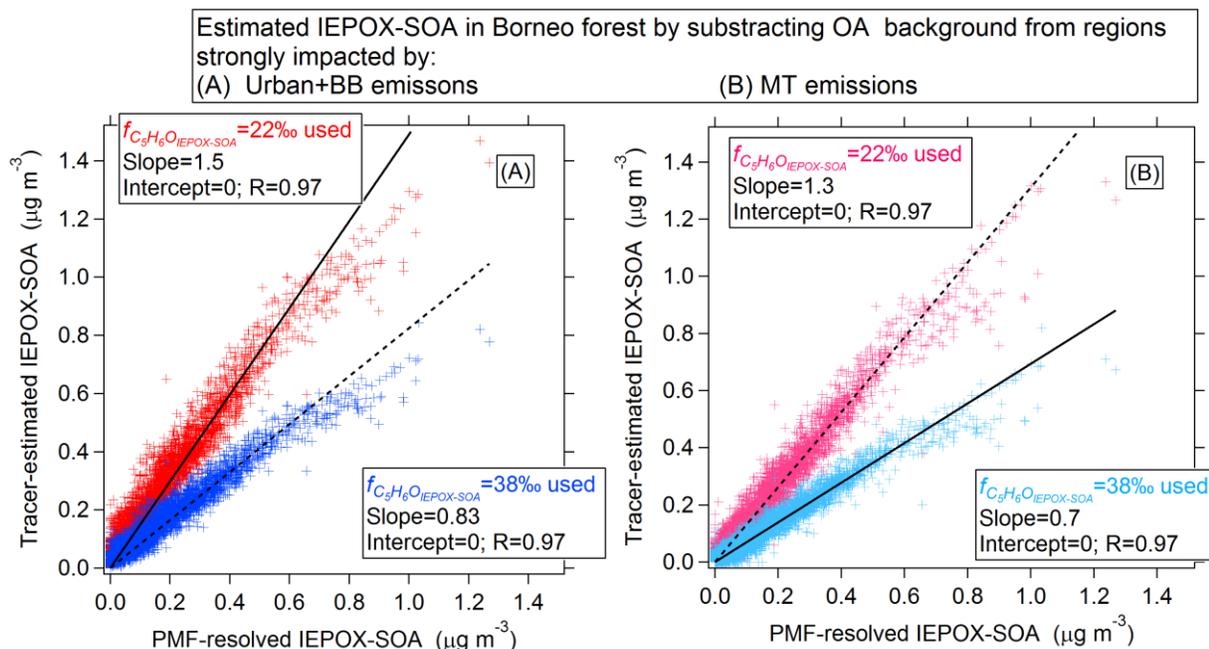


Figure S14 Scatter plot between estimated IEPOX-SOA and PMF-resolved IEPOX-SOA at a Borneo forest site. The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each plot, we used two $f_{C_5H_6O}^{IEPOX-SOA}$, from the average IEPOX-SOA_{PMF} ($f_{C_5H_6O}^{IEPOX-SOA}=22\%$) and from the IEPOX-SOA_{PMF} in Borneo forest study ($f_{C_5H_6O}^{IEPOX-SOA}=38\%$).

R1.2. Can you explain the bounds of when your $f_{C_5H_6O}$ estimation method can/can't or should/shouldn't be used? Is there a lower limit on $f_{C_5H_6O}$ (relative to the total organic particle mass) below which the estimation method is no longer accurate? In general it would be a benefit to the AMS community if you can explain the limits and bounds of your estimation method more clearly.

A1.2: Following the reviewer's suggestion, we have addressed this point in the supporting information.

In the main text, we have added a mention of this new information in the last part of section 3.9:

“Several scenarios based on different $f_{C_5H_6O}^{OA}$ values to use this tracer-based method are addressed in the supporting information. The justification from users on using this method is needed.”

In the supporting information part 1.1 we have added the following text:

“In theory, our method can easily produce an estimate of “IEPOX-SOA” from an AMS dataset, but the errors could be substantial in some cases. The guidelines below are meant to limit the errors when applying this method:

- 1) We first recommend making the scatter plot of $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ and then compare it to Fig. 5 in this study to help evaluate the possible presence of IEPOX-SOA.**
- 2) For datasets where an important influence of MT-SOA is suspected: if all the $f_{C_5H_6O}^{OA}$ in total OA are $\sim 3.1\%$ or lower within measurement noise, the estimated IEPOX-SOA will show negative and positive values scattered around zero, indicating negligible IEPOX-SOA in the dataset. A similar conclusion can be reached for urban or BB-dominated locations when $f_{C_5H_6O}^{OA} \sim 1.7\%$ or lower for most data points.**
- 3) When the scatter plot between $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ shows obvious enhanced $f_{C_5H_6O}^{OA}$ above the most-relevant background value, users can easily use the tracer-based method to estimate the IEPOX-SOA mass concentration. If the source of the background OA is not known, we suggest using both background corrections and reporting the range of results.**

- 4) Cases intermediate between No. 2 and 3 above, i.e. when $f_{C_5H_6O}^{OA}$ is only slightly above the relevant background level will have the largest relative uncertainty. In this case we recommend applying the method and evaluating the results carefully, as exemplified for the Rocky Mountain dataset in this paper (section 3.5). E.g. diurnal variations of $f_{C_5H_6O}^{OA}$ and SOA precursors (e.g., isoprene and monoterpene) and of estimated IEPOX-SOA provide useful indicators about whether the results are meaningful. For cases in which the fraction of IEPOX-SOA in total OA is relatively low (e.g., <5%) and the fraction of MT-SOA in total OA is high (e.g., >50%), the uncertainty of the IEPOX-SOA estimate will be very high. For this type of situation the full PMF method may be required.

Besides ease of use, another advantage of the tracer-based estimation method is that it can be used to quantify IEPOX-SOA based on brief periods of elevated concentrations, e.g. as often encountered in aircraft studies. In those cases it may be difficult for PMF to resolve an IEPOX-SOA factor, but no such limitation applies to this estimation method.”

R1.3. Abstract, lines 18-19 and several other places in paper (e.g., p 11243 lines 13-16). Several times in the manuscript, the authors compare $f_{C_5H_6O}$ of a bulk OA sample (for example, monoterpene SOA) to the $f_{C_5H_6O}$ found for the PMF factor attributed to IEPOX SOA. They authors do this to illustrate that $f_{C_5H_6O}$ is enhanced in IEPOX SOA and presumably to imply that the IEPOX $f_{C_5H_6O}$ signal is enhanced relative to other potential interferences (i.e., monoterpene SOA). However, it isn't really relevant to compare the $f_{C_5H_6O}$ of a PMF factor that is ~15% of the total OA to the $f_{C_5H_6O}$ for the entire OA sample. To me this is misleading.

A1.3: We thank the reviewer for pointing out this ambiguity, which appears to have been the largest source of confusion for the ACPD version. To avoid confusion we have changed this notation in the revised paper to always make explicit what we are referring to, as described in the added text below:

“We use a superscript to clarify the type of OA for which $f_{C_5H_6O}$ is being discussed: $f_{C_5H_6O}^{OA}$ refers to $f_{C_5H_6O}$ in total OA, $f_{C_5H_6O}^{IEPOX-SOA}$ to $f_{C_5H_6O}$ in IEPOX-SOA, $f_{C_5H_6O}^{MT-SOA}$ to the $f_{C_5H_6O}$ value in pure MT-SOA and $f_{C_5H_6O}^{OA-Bkg-UB}$ and $f_{C_5H_6O}^{OA-Bkg-MT}$ refer to background $f_{C_5H_6O}^{OA}$ from areas strongly influenced by urban+biomass-burning emissions and by monoterpene emissions, respectively. If we refer to $f_{C_5H_6O}$ in general, we will still use $f_{C_5H_6O}$.”

R1.4. From reading the manuscript, it seems the background $f_{C_5H_6O}$ is a minimum of 2 per mil and up to 4 per mil for areas of high MT emissions. The $f_{C_5H_6O}$ for all OA seems to be 5-6 per mil in many areas heavily influenced by isoprene emissions. So the $f_{C_5H_6O}$ “signal” from IEPOX SOA relative to the background $f_{C_5H_6O}$ “noise” isn't very elevated in most areas. Borneo (and perhaps the Amazon) seems to be an exception. Can the authors comment more on this issue?

A1.4: We have emphasized the differences of $f_{C_5H_6O}$ between IEPOX-SOA and MT-SOA in the abstract to be clearer:

“The average laboratory monoterpene SOA value ($5.5 \pm 2.0\%$) is 4 times lower than the average for IEPOX-SOA ($22 \pm 7\%$), which leaves some room to separate both contributions to OA.”

We have modified the main text and added a new Fig. S8 to more clearly illustrate this difference in the supporting information:

“We note that the average lab-generated MT-SOA value is still 4 times lower than the average for IEPOX-SOA_{PMF} and IEPOX-SOA_{lab} (Fig. S8), and thus there is some room to separate both contributions”

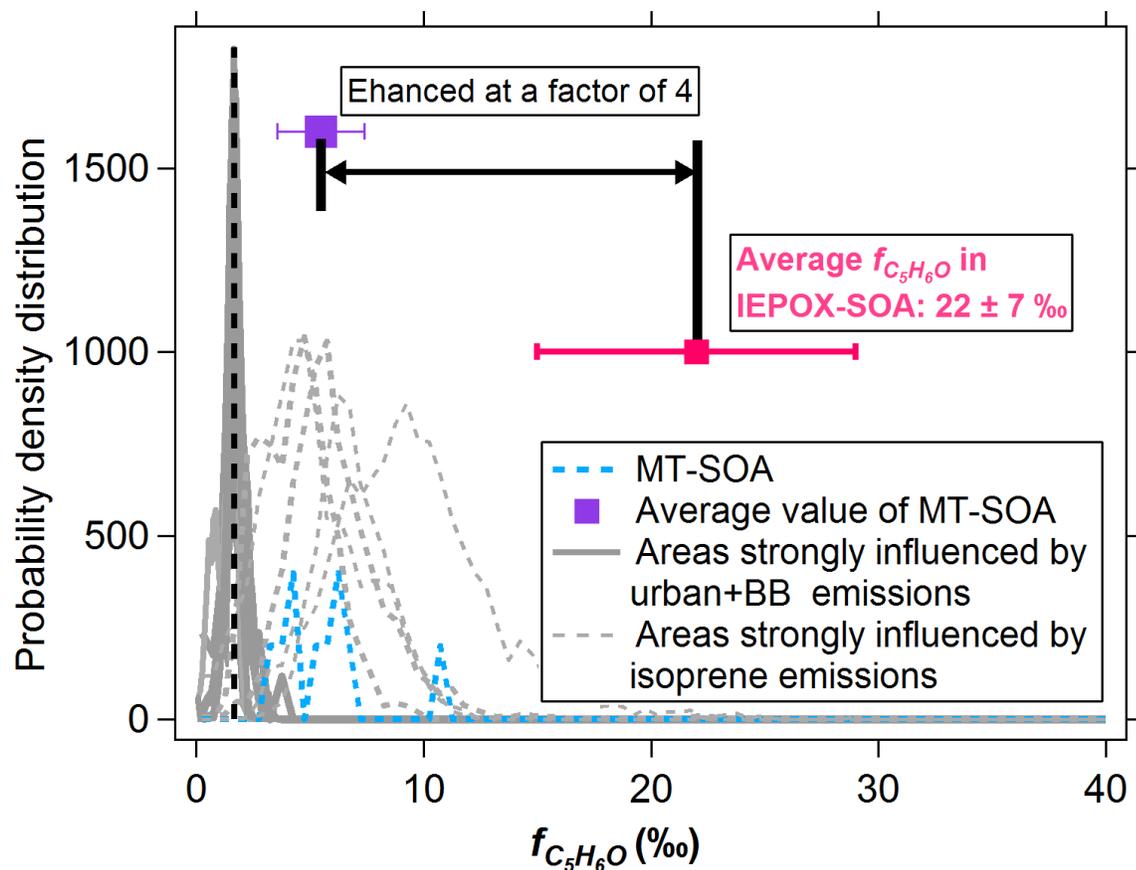


Figure S8 Comparison between $f_{C_5H_6O}^{MT-SOA}$ and $f_{C_5H_6O}^{IEPOX-SOA}$, $f_{C_5H_6O}^{OA}$ from areas strongly influenced by urban + biomass burning and isoprene emissions are also shown.

We also address the reason why smaller differences are observed in $f_{C_5H_6O}^{OA}$ between areas strongly influenced by isoprene emissions and by monoterpene emissions in the last part of section 3.5:

“Note that the difference between $f_{C_5H_6O}^{OA}$ in areas strongly influenced by monoterpene emissions ($3.1\pm 0.6\%$) and isoprene emissions ($6.5\pm 2.2\%$) is reduced, compared to a factor of 4 difference between pure MT-SOA ($5.5\pm 2.0\%$) and IEPOX-SOA ($22\pm 7\%$). This is likely due to the physical mixing of OA from different sources and in different proportions at each location.

R1.5. Abstract lines 15-20 and through paper. Please explain how you are weighting the average $f_{C_5H_6O}$ when combining data from many different studies, if at all. I can easily imagine that high frequency data from one study would completely overwhelm the average because of the larger number of points. As an example, aircraft data are recorded generally at 0.1 – 1 Hz, but ground data are typically averaged over significantly longer timescales. How do you treat this?

A1.5: We have added the following text to clarify this issue:

“When we report the average $f_{C_5H_6O}^{OA}$ in each campaign, as shown in the Table 1, we used the average from the time series of $f_{C_5H_6O}^{OA}$ at their raw time resolution (secs to mins). During this process, we exclude points whose OA mass concentrations are below twice the detection limit of OA in AMS (typically $2 \times 0.26 \mu\text{g m}^{-3} = 0.5 \mu\text{g m}^{-3}$). When averaging $f_{C_5H_6O}^{OA}$ values across datasets, we counted each dataset as one data point.”

R1.6. Related to this point, in the abstract, you list the average $f_{C_5H_6O}$ for MT influenced airmasses as 3.1 per mil. The Rocky Mountain data average is 3.7 per mil, the DC3 data influenced by MT emissions average 4.1 per mil and the boreal forest data average 2.5 per mil. From these values, it seems like the $f_{C_5H_6O}$ for MT background should be a little higher than 3.1. How do you calculate the 3.1 number given in the abstract?

A1.6: The 3.1‰ comes from the average value of 2.5‰ in boreal forest and 3.7‰ in Rocky Mountain dataset. We did not include 4.1‰ from DC3 dataset in this calculation, because 4.1‰ is only a single data point that we observed in an aircraft flight, and using that value could bias the average high. When we average all the enhanced $f_{C_5H_6O}^{OA}$ values (from 1.7‰-4.1‰) corresponding to the enhanced monoterpene concentrations for the DC3 flight in the Fig. 6, we obtain a $f_{C_5H_6O}^{OA}$ estimate of $3.0\pm 0.3\%$ from this period, which is similar to the average of 3.1‰ averaged from the Rocky mountain site and boreal forest site. We have modified the text in section 3.5 to clarify this point as:

“The average $f_{C_5H_6O}^{OA}$ in areas strongly influenced by monoterpene emissions is $3.1\pm 0.6\%$, obtained by averaging the values from the Rocky mountain forest (3.7‰), European boreal forest (2.5‰), and DC3 flight (3.0‰).”

R1.7 Through paper: There are a large number of unpublished studies cited in this manuscript. 11 cited referenced are unpublished; 6 are under review (i.e., discussion manuscripts) and 5 are “in preparation”. Some of the “in preparation” datasets, primarily from PMF analysis of field data, are used in the manuscript. To me this seems unusual because there has been no peer-

review of this data and insufficient details are provided in the manuscript to assess the data quality. I was unable to find ACP's policy on this, so I leave it to the editor to decide if this is an issue or not. The "in preparation" data are used heavily in the figures and it is difficult to say whether the authors would have come to the same conclusions or whether their conclusions would have been as robust, if this data were to be excluded.

A1.7: We understand the reviewer's concern about citing unpublished studies in our paper. Unfortunately when working on new and very active areas of research, this can sometimes be the case as the other relevant studies are mostly being conducted at the same time. Also importantly our paper should be considered the reference that presents the data for the unpublished studies, and the additional references are provided as a linkage to the literature for readers interested in additional detail on those studies. In addition, excluding the results for which a cited reference is unpublished does not change our conclusions.

In detail, in the ACPD version of our paper, 5 papers were under review but publicly accessible (in ACPD or AMTD) and 5 papers were in preparation. As of the submission of the revised version of our paper, the number of unpublished references has been reduced from 10 to 3. Five papers have been accepted for publication while our paper was under review and revision (an indication of the very active state of this area of research).

One paper is a citation to a referee comment on an ACPD paper that suggested the potential interference of MT-SOA in $f_{C_5H_6O}^{OA}$. We have kept this reference as it was the only mention of this issue that we could find in the literature, and since we only use this reference to suggest a problem that we proceed to explore in detail in our paper. This reference is:

"Anonymous_referee: Interactive comment on "Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA" by J. D. Allan et al., Atmos. Chem. Phys. Discuss., 14, C5277–C5279, 2014."

We also cited the overview paper for the SEAC4RS study, which is still in preparation.

"Toon, O. B.: Planning, implementation and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS) field mission, in prep., 2015".

However, since the SEAC4RS and DC3 datasets used here have been described in another paper, we change this citation to be:

"Liao, J., Froyd, K. D., Murphy, D. M., Keutsch, F. N., Yu, G., Wennberg, P. O., St. Clair, J. M., Crouse, J. D., Wisthaler, A., Mikoviny, T., Jimenez, J. L., Campuzano Jost, P., Day, D. A., Hu, W., Ryerson, T. B., Pollack, I. B., Peischl, J., Anderson, B. E., Ziemba, L. D., Blake, D. R., Meinardi, S., and Diskin, G.: Airborne measurements of organosulfates over the continental US, Journal of Geophysical Research: Atmospheres, 120, 2990-3005, 10.1002/2014jd022378, 2015."

As of the submission of this revised paper, only 1 paper is submitted and 2 papers are in preparation (listed below).

Submitted

Hu, W., Hu, M., Hu, W., Jimenez, J.-L., Yuan, B., Chen, W., Wang, M., Wu, Y., Wang, Z., Chen, C., Peng, J., Shao, M., and Zeng, L.: Chemical composition, sources and aging process of sub-micron aerosols in Beijing: contrast between summer and winter, submitted to JGR, 2015.

In preparation:

Carbone, S., De Brito, J. F., Andreae, M., Pöhlker, C., Chi, X., Saturno, J., Barbosa, H., and Artaxo, P.: Preliminary characterization of submicron secondary aerosol in the amazon forest– ATTO station, in preparation, 2015.

de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Newburn, M. K., Brito, J., Liu, Y., Isaacman-VanWertz, G., Yee, L. D., Goldstein, A. H., Artaxo, P., Souza, R., Manzi, A., Jimenez, J. L., Alexander, M. L., and Martin, S. T.: Mass spectral observations of fine aerosol particles and production of SOM at an anthropogenically influenced site during GoAmazon2014wet season, in preparation, 2015.

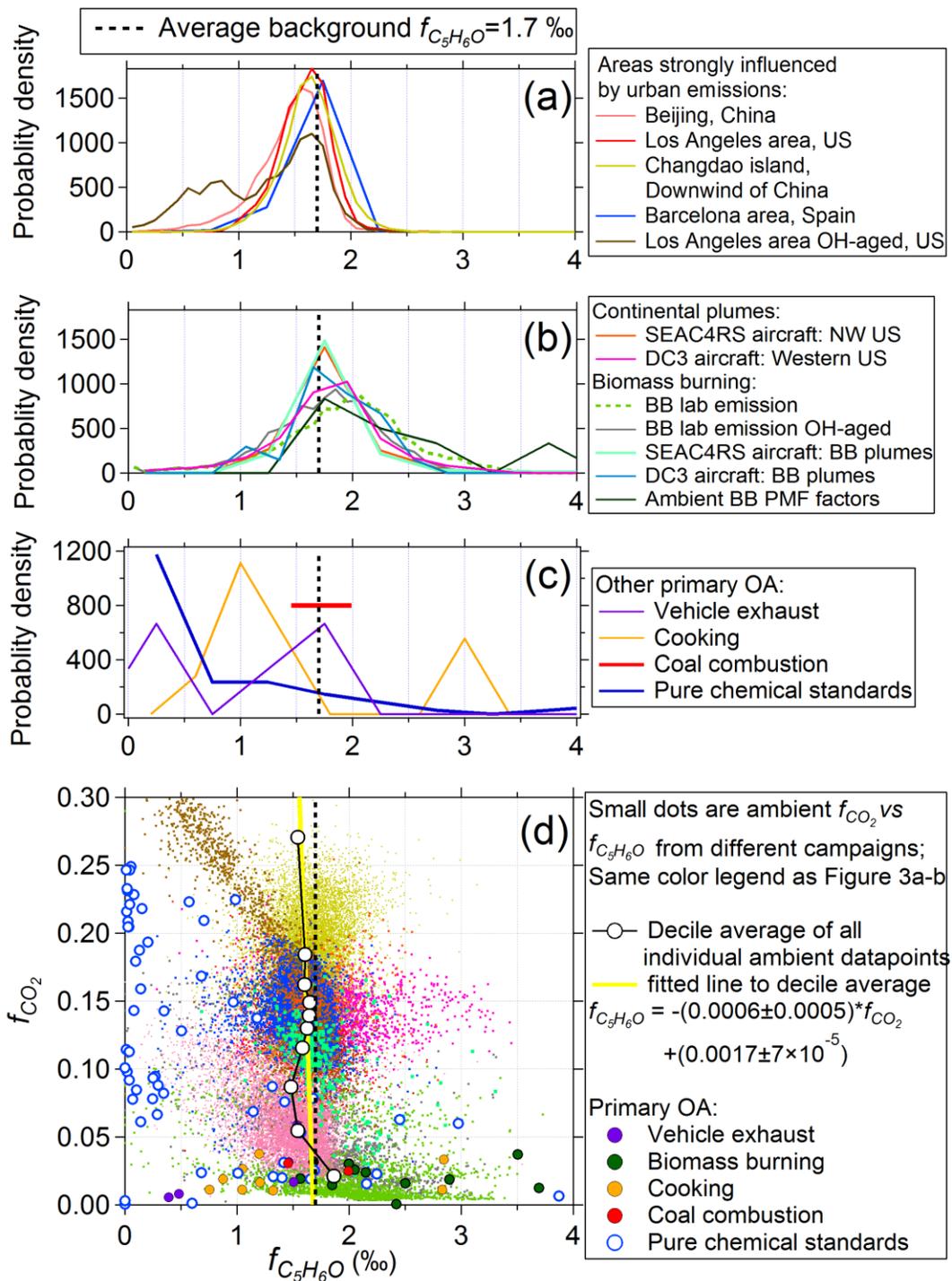
R1.8. Page 11233, line6-8. $f_{C_5H_6O}$ has a very specific meaning as does f_{82} . They are not the same. I find it highly objectionable that UMR f_{82} data are included in the $f_{C_5H_6O}$ average and labeled as $f_{C_5H_6O}$. Further, it isn't clear which datasets were analyzed for $f_{C_5H_6O}$ and which for f_{82} . Please either remove the f_{82} from the $f_{C_5H_6O}$ average or call the average f_{82} .

A1.8: We disagree with the reviewer on this point. We have updated the text to clarify this issue:

“The average $f_{C_5H_6O}^{IEPOX-SOA}$ value shown here also includes f_{82} data from four UMR IEPOX-SOA_{PMF} spectra. This is justified since $C_5H_6O^+$ accounts for over 95% of m/z 82 in IEPOX-SOA based on results from SOAS-CTR and other lab studies (Kuwata et al., 2015). Indeed the average does not change if the UMR studies are removed from the average.”

R1.9 Figure 3: This figure is generally illegible, with the legends particularly so. Please revise. What are the arrows pointing to on the right Y axes?

A1.9: Following the reviewer's suggestion, we have revised our Fig. 3 for clarity as shown below. The arrows have been removed for clarity.



R1.10. Figure 4. It looks like, if a PDF of $f_{C_5H_6O}$ for monoterpene SOA were placed on this figure, it would be very similar to the PDFs of the isoprene influenced field data. Can you also include the PDF for monoterpene SOA in the figure? Doesn't this argue that there is in fact a

very significant contribution of monoterpene SOA to $f_{C_5H_6O}$? It looks like the Borneo data PDF is significantly higher in $f_{C_5H_6O}$ than the others field data PDFs and the monoterpene lab SOA PDF.

This figure seems to suggest that the “interference” from monoterpene SOA could be worse than the authors argue. If the Borneo data are excluded from the average $f_{C_5H_6O}$, does it change significantly?

A1.10: We have updated the two figures below (Fig. 4 and Fig. S8, shown above in response A1.4) by adding the PDF of $f_{C_5H_6O}^{MT-SOA}$ (dashed blue line) from pure MT-SOA (10 data points). A detailed response to this comment can be found in the response to R 1.4.

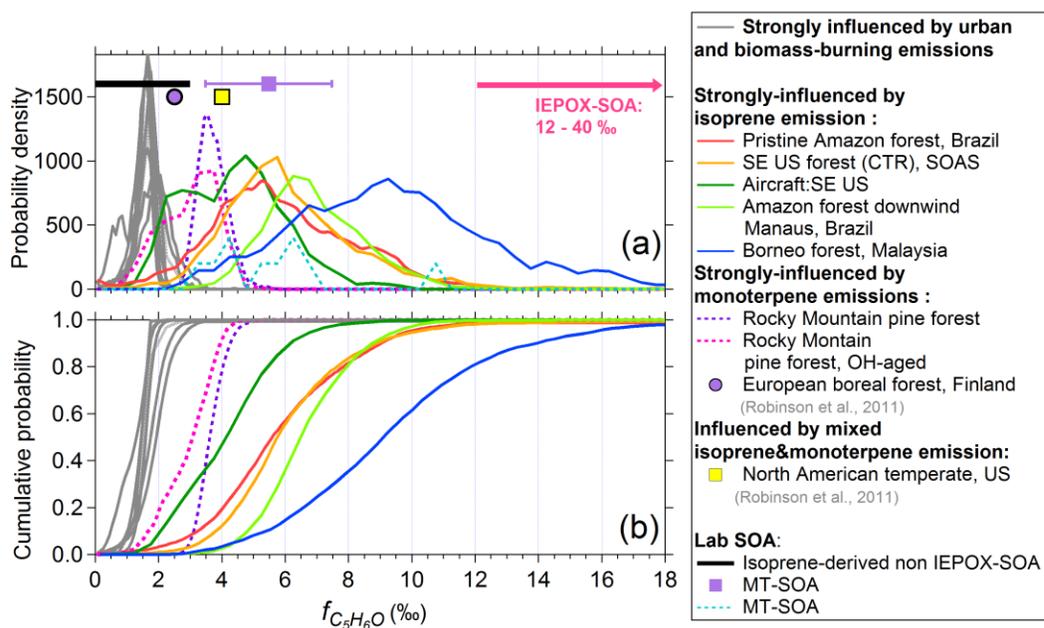


Figure 4. (a) Probability density and (b) cumulative probability distributions of $f_{C_5H_6O}^{OA}$ in studies strongly influenced by isoprene and/or monoterpene emissions. The ranges of $f_{C_5H_6O}$ from other non IEPOX-derived isoprene-SOA and MT-SOA are also shown. The background grey lines are from studies strongly influenced by urban and biomass-burning emissions and are the same data from Fig. 3a – b. The arrow in Fig. 4a indicates the range of $f_{C_5H_6O}^{IEPOX-SOA}$ between 12‰ (start of the arrow) to 40‰ which is beyond the range of x-axis scale.

R1.11. Figure 4: It is very difficult to distinguish the colors of many of the lines from one another because of the color choices and size of the figure. Please revise.

A1.11: The revised figure is shown in response to comment R1.10.

R1.12. It isn't clear what the arrow pointing to the right Y axis is meant to indicate.

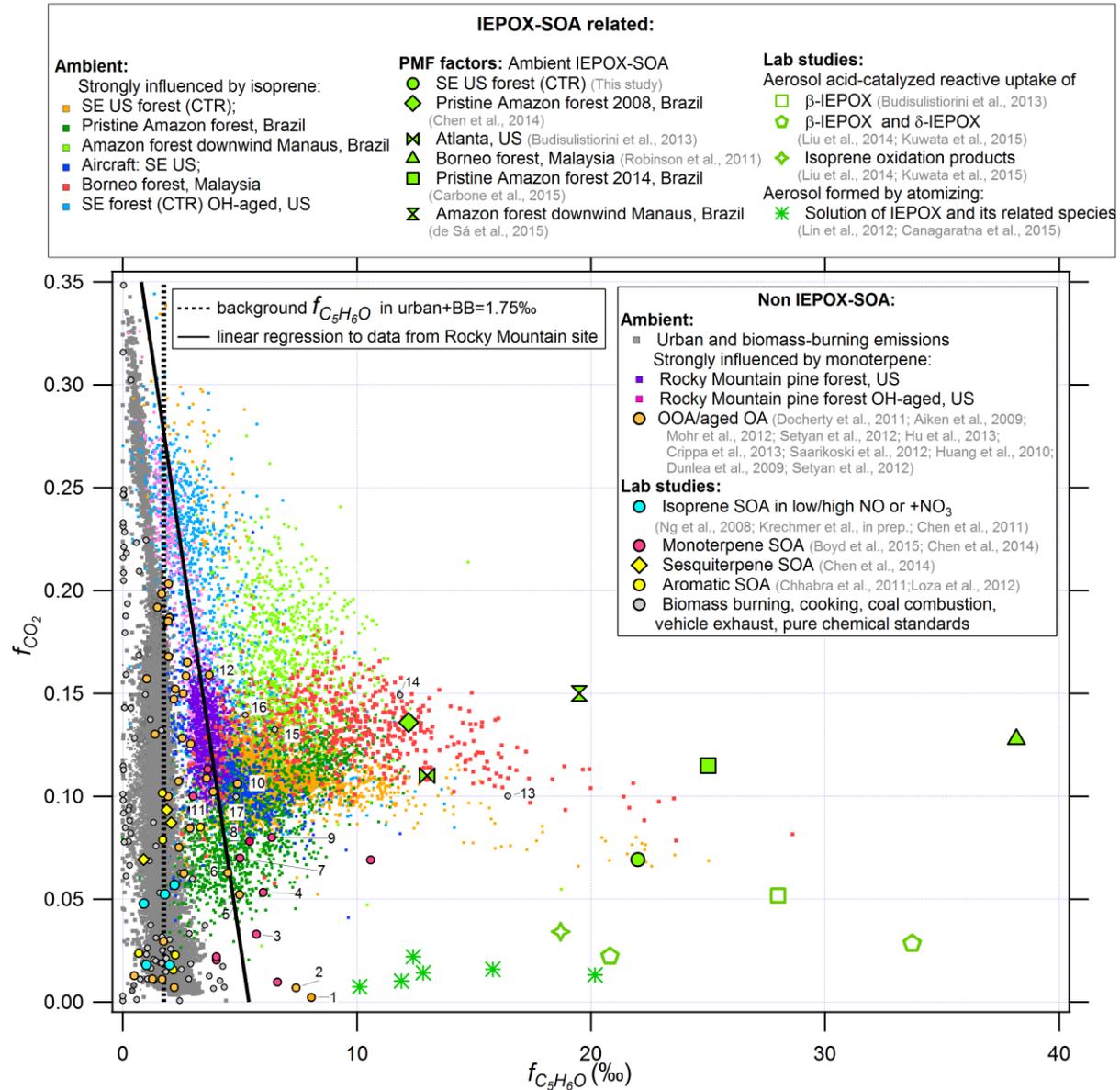
A1.12: We use this arrow to point out the highest $f_{C_5H_6O}^{IEPOX-SOA}$, which is beyond the range of the x-axis in Figure 4. We moved the arrow to the same height as MT-SOA and isoprene-derived

non IEPOX-SOA and added the corresponding explanation in the figure caption (as shown in the response to comment R1.10):

R1.13. Figure 5: The figure is generally illegible due to size and the amount of information on the figure. The symbols are indistinguishable from one another and the legend is impossible to read. I can't make out any of the numbered points aside from 1, 2, and 13. Please revise.

It isn't clear what the pink arrow in the middle of the figure is meant to indicate.

A1.13: Following the reviewer's suggestion, we significantly revised the figure as shown below:



Minor Comments and Technical Corrections

R1.14. Through paper: The authors often use the term average when the text seems to indicate they really mean mode (based on a vertical line drawn to the mode in most figures). Please clarify when/if you mean average and when/if you mean mode. This is relevant because few of the PDFs appear to be normally distributed.

A1.14: We have revised the text as needed to clarify what kind of value (average vs. mode) has used in the paper. Please see the details of the averaging methods used in the response to comment R1.5.

R1.15. Abstract and through paper. It would be helpful to define the per mil symbol the first time in is introduced.

A1.15: Following the reviewer's suggestion, we have defined the per mil in the abstract and main text when it show up in the first time.

In the abstract: **“A background of $\sim 1.7 \pm 0.1\%$ ($\%$ =parts per thousand) is observed”**

In the main text: **“ $f_{C_5H_6O}^{IEPOX-SOA}$ in IEPOX-SOA from SOAS and other field and laboratory studies (Table 1) ranges from 12% to 40% ($\%$ =parts per thousand)...”**

R1.16. Page 11226, line 4-5. What other low NO oxidation pathways would produce IEPOX-SOA? This is alluded to several times, but never defined. Do you mean IEPOX-SOA the PMF factor or do you mean SOA produced from IEPOX? It is confusing at times to discern whether the authors are talking about SOA formed from IEPOX (a mix of some known and some unknown organics produced by a specific process) or the PMF factor attributed to IEPOX SOA (an output of PMF). This is one clear case.

A1.16: We are referring to the recent finding in Jacobs et al. (2014): IEPOX can be formed in the oxidation of isoprene under high NO, via oxidation the 4-hydroxy-3-nitroxy isoprene (13%). Thus, we revised our sentence in the abstract to be:

“Total IEPOX-SOA, which may include SOA formed from other parallel isoprene oxidation pathways...”

We also added corresponding text in the introduction part to clarify:

“Note that some IEPOX can also be formed from isoprene in high NO region via oxidation of the product 4-hydroxy-3-nitroxy isoprene (Jacobs et al., 2014) , however this pathway is thought to be much smaller than the low-NO pathway.”

We agree with the reviewer's comment that the specific meaning of the term “IEPOX-SOA” in the paper text can be confusing. Thus, we have added the text below to clarify:

“We denote the IEPOX-SOA factor from PMF as “IEPOX-SOA_{PMF}” and IEPOX-SOA from lab studies as “IEPOX-SOA_{lab}”. If we use “IEPOX-SOA” in the paper, it refers to a broad concept of IEPOX-SOA.”

R1.17. Page 11226, line 9-11. Consider revising this sentence for clarity.

A1.17: We revised this sentence as:

“During the Southern Oxidant and Aerosol Study (SOAS) study, 78% of PMF-resolved IEPOX-SOA is accounted by the measured IEPOX-SOA molecular tracers (methyltetrols, C5-Triols and IEPOX-derived organosulfate), making it the highest level of molecular identification of an ambient SOA component to our knowledge”

R1.18. Page 11228, lines 22-25. Conversion of IEPOX to IEPOX-SOA requires gas-to-particle partitioning. I think you mean non-reactive partitioning here, but please clarify.

A1.18: Yes, the reviewer is correct. We mean non-reactive partitioning here. We revised the sentence to read:

“... because gas-phase IEPOX has high volatility, non-reactive gas-to-particle partitioning of IEPOX into OA is negligible under typical ambient concentrations in forest areas”

R1.19. Page 11230, lines 8-9. What is the rationale for including the polluted Amazon site in the “strongly influenced by isoprene” category as opposed to “strongly influenced by urban emissions” category? To me “polluted” in this context means influenced by Manaus emission. It would be good to clarify why the data were placed in one category rather than the other.

A1.19: We added the reason why we classify this site as strongly influenced by isoprene emissions:

“Two pristine forest site and one forest site partially impacted by urban plumes in the Amazon rain forest (Brazil). The latter site is classified in this category because (i) high isoprene concentrations (e.g. 3 ppb in average peaks in the afternoon) were observed during the study; (ii) the impact of biogenic SOA formed during 1000 km where the air travels over the pristine forest upwind of Manaus; (iii) PMF results indicate an important impact of IEPOX-SOA at this site (de Sá et al., 2015); and (iv) PTRMS results indicate a substantial concentration of the isoprene hydroperoxyde formed by low-NO chemistry.”

R1.20. Page 11230, lines 14-15. Many of campaigns actually haven't been described in the literature and the referenced are listed as “in preparation” (see related comment in major comments section).

A1.20: Please see the response to comment R1.7.

R1.21. Page 11232, lines 26-28. Revise this sentence for clarity.

A1.21: Revised.

Original sentence: “The temporal variation of ion $C_5H_6O^+$ correlates best ($R=0.96$) with that IEPOX-SOA among all OA ions (Table S1), suggesting that it may be the best tracer among all ions for IEPOX-SOA”.

Revised sentence: **“The temporal variation of ion $C_5H_6O^+$ correlates best ($R=0.96$) with IEPOX-SOA_{PMF} among all measured OA ions (Table S1). This result suggests that $C_5H_6O^+$ ion may be the best ion tracer for IEPOX-SOA among all OA ions. ”**

R1.22. Page 11235, line 14. Add “that” between conditions and are.

A1.22: Added.

R1.23. Page 11240, line 4. Revise “Amazon forest down Manaus campaigns”.

A1.23: We modified this text to read: “**Amazon forest downwind of Manaus**”

R1.24. Page 11240, line 12. Revise “have low $f_{C_5H_6O}$ are”

A1.24: We revised the original sentence to be:

“...points with both lower $f_{CO_2}^{OA}$ (<0.08) and low $f_{C_5H_6O}^{OA}$ ($< 8\%$) values are thought...”

R1.25. Figure5, page 112340, lines 14-19. I’m struggling to see how the points group into a triangle. The points don’t seem to group into any shape at all. Please clarify.

A1.25: This trend was perhaps obscured by the complexity of the figure. We have added Figure S10, shown below, to more clearly illustrate the applicability of the “triangle area.”

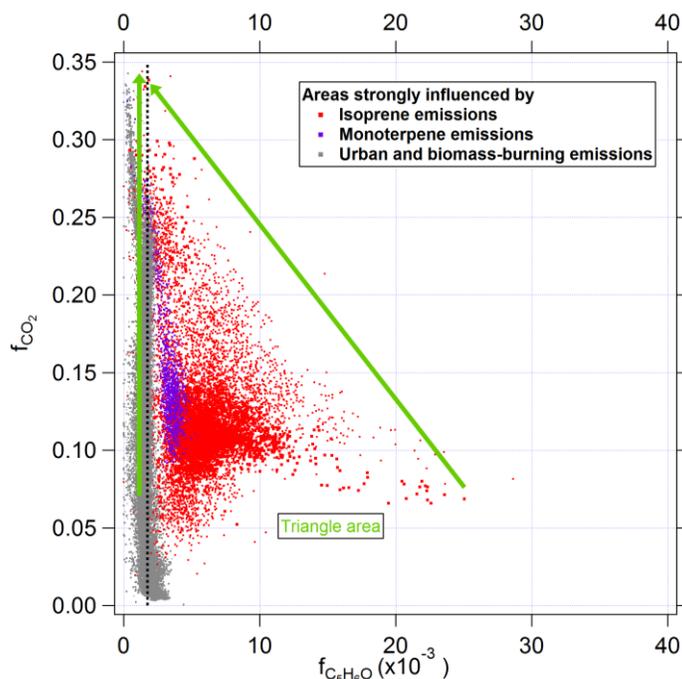


Figure S10. Scatter plot between $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ for all the ambient OA dataset. Green arrows are added to guide the eye.

R1.26 Page 11240, line 16-18. Revise for clarity.

A1.26: Revised.

Original sentence: “This “triangle shape” indicates that in most of campaigns of this study shows the local OA with IEPOX-SOA contributions is influenced by the ambient oxidation processes or mixing with more aged aerosols.”

Revised sentence: “This “triangle shape” indicates that as the ambient OA oxidation increases, the IEPOX-SOA signature is reduced, potentially by the ambient oxidation processes or by physical mixing with airmasses containing more aged aerosols.”

R1.27 Page 11243, line 13, Revise “An alternative estimate as $f_{C_5H_6O}$ from area”

A 1.27: We revised the sentence to be:

“An alternative estimate for background $f_{C_5H_6O}^{OA}$ in areas with strong monoterpene emissions”

R1.28 Section 3.10 and Figure 8. In the preceding section (3.9), you present two alternative expressions for estimating $f_{C_5H_6O}$ background for MT influenced areas. Which expression was used in Figure 8?

A1.28: In the Fig. 8, we applied the $f_{C_5H_6O}$ at the Rocky Mountain site estimated by $f_{C_5H_6O} = (0.41 - f_{CO_2}) \times 0.013$ as background $f_{C_5H_6O}^{OA}$ for areas with strong MT-SOA contributions. We added one sentence in the main text to clarify:

“Finally, we have decided to use $f_{C_5H_6O}^{OA}$ estimated from the Rocky Mountain site as $f_{C_5H_6O}^{OA-Bkg-MT}$ in the following calculation.”

Anonymous Referee #2

General comments

This manuscript presents a relatively comprehensive study using a variety of field and lab results to investigate the strength and limitation of using AMS data to represent ambient SOA formed from IEPOX. This study shows a positive relationship between AMS IEPOX-SOA and GEOSChem modeled gas phase IEPOX at many locations globally w and w/o isoprene emission. This study also estimates the interference in C₅H₆O signal from monoterpene and other sources (e.g urban, biomass burning). The authors found that IEPOX-SOA mass loading derived from AMS data is comparable to the measured molecular tracers concentrations in SOAS. The authors also provide a new method to estimate IEPOX-SOA w/o PMF, which may be useful when PMF is not available. This study brings the aerosol community a better understanding of IEPOX SOA derived from AMS measurements, which have been used in many studies of SOA formed from IEPOX. In general, the authors interpret their data carefully. However, there are a few places not clear in the manuscript. I think this manuscript is suitable for publishing in ACP after the authors address my comments below.

Specific comments

R 2.1. The manuscript uses both PMF IEPOX-SOA factor and $f_{C_5H_6O^+}$ to evaluate if AMS data can well represent SOA from IEPOX. I think the PMF IEPOX-SOA factor is the one that most people in the AMS community use to represent IEPOX SOA mass loadings. The authors checked the background values of $f_{C_5H_6O^+}$ in many non-isoprene dominant environments. Could the authors be clear about how those interferences would be reflected in the IEPOX-SOA factor ($\mu\text{g}/\text{m}^3$) ?

A 2.1: The PMF-resolved IEPOX-SOA factor is indeed the one reported as IEPOX-SOA in most of ambient measurements (Slowik et al., 2010;Robinson et al., 2011;Budisulistiorini et al., 2013;Xu et al., 2014;Budisulistiorini et al., 2015;Chen et al., 2015). One study from Allan et al. (2014) used f_{82} as a tracer for IEPOX-SOA in flight measurements over the Amazon forest. The tracer method was not available until the publication of our paper, and thus it has not been used in past literature.

We believe that the reviewer is asking us to quantify the uncertainty of the IEPOX-SOA mass concentrations reported from PMF. This uncertainty will depend on each specific case. As a representative example, we estimate this uncertainty for the SOAS dataset using the bootstrap method, which provides a quantitative assessment of the uncertainty of the factors (Ulbrich et al., 2009). 100 bootstrapping runs are carried out. The results are shown in the figure below, which was also added to the supporting information (Fig. S1).

The uncertainty (standard deviation) for C₅H₆O⁺ in IEPOX-SOA is around 3%. The average uncertainty of the IEPOX-SOA mass concentration time series is ~9%.

A summary of this result was added into the paper: “An uncertainty of IEPOX-SOA_{PMF} mass concentration of ~9% was estimated from 100 bootstrapping runs in PMF analysis (Ulbrich et al., 2009) (Fig. S1). This uncertainty concerns only the PMF separation method. In practice the uncertainty in IEPOX-SOA_{PMF} concentration is dominated by the larger uncertainty on the AMS concentrations arising from the collection efficiency and relative ionization efficiency (Middlebrook et al., 2012).”

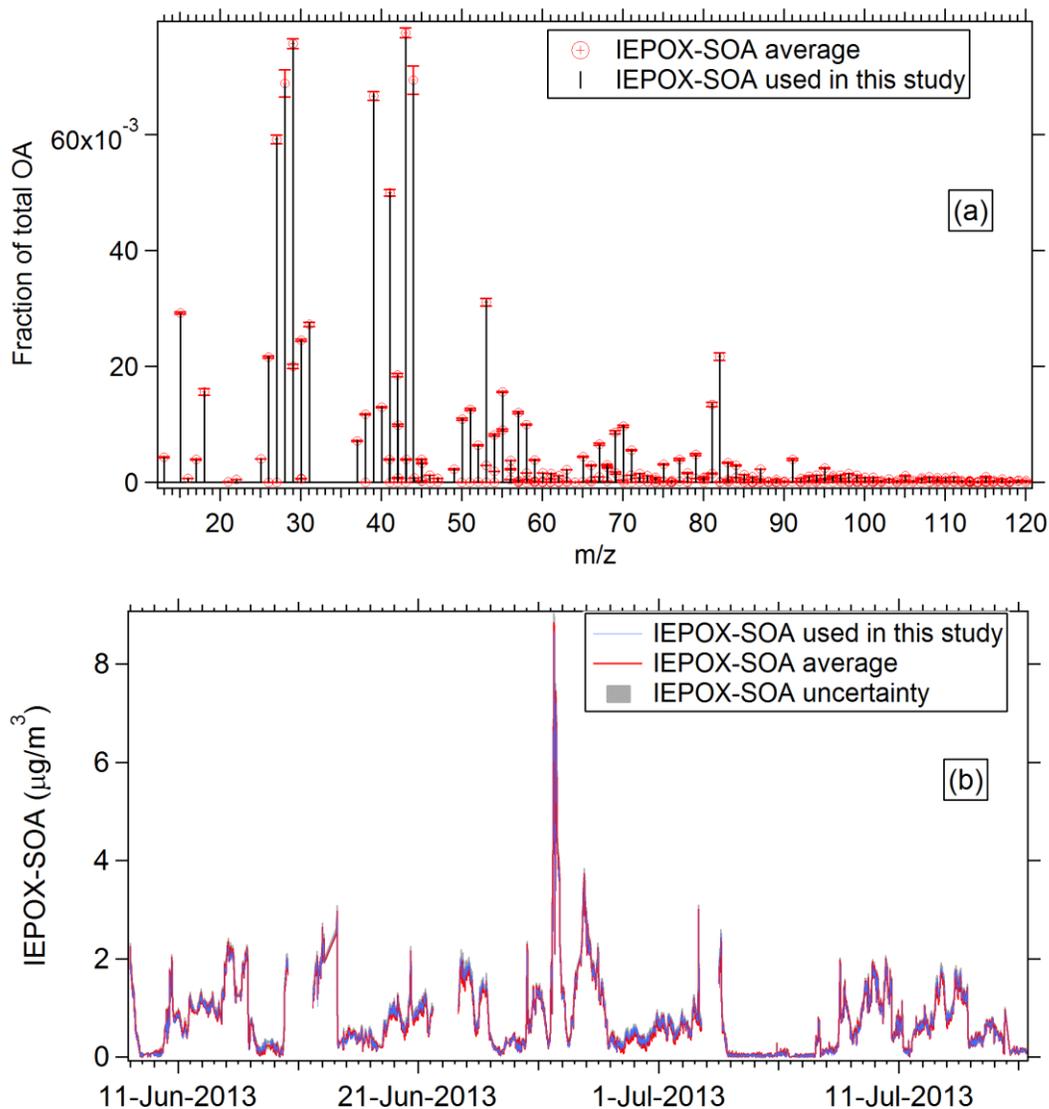


Figure S1. Results from bootstrapping analysis of the 4-factor solution of the SOAS dataset. Average IEPOX-SOA, with standard deviation, are shown for IEPOX-SOA (a) mass spectrum and (b) time series.

R 2.2. Also, it is often not clear when the $f_{C_5H_6O^+}$ values in the manuscript are $C_5H_6O^+/OA$ from IEPOX-SOA factor mass spectra only, from all data or from non-IEPOX-SOA factor data. I

think it is important to keep them consistent. I suggest using “ $f_{C_5H_6O+.all}$ ” or other symbol to represent from all data and using “ $f_{C_5H_6O+.IEPOX-SOA}$ ” or other different symbol to represent from IEPOX-SOA factor data only. I was misled at the beginning when I read the manuscript. For example, in the abstract, $f_{C_5H_6O}$ in IEPOX-SOA of (12–40 ‰) looks much higher than that influenced by monoterpene (3.1 ‰). These values are actually apples and oranges.

A2.2: Please see the response to comment R1.3

R2.3. Page 11226 line 24-25: Please state clearly if “the low $f_{C_5H_6O}$ (< 3 ‰) observed in non IEPOX-derived isoprene-SOA” is the result in the lab or in the ambient. Also I think the abstract should be clearer if this result is from part of this study or derived from previous published results.

A2.3: We revised our sentence to clarify this point as:

Original: “The low $f_{C_5H_6O}$ (< 3 ‰) observed in non IEPOX-derived isoprene-SOA indicates that this tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene”

Revised: **“The low $f_{C_5H_6O}$ (<3‰) reported in non IEPOX-derived isoprene-SOA from chamber studies indicates that this tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene”**

R2.4. Figure 2(b) What about the correlation between IEPOX-SOA and C5-alkene triols and IEPOX-derived organosulfates and dimers?

A2.4: We have added the relevant information to the main text (section 3.1) and also Fig. S2 to the supporting information:

“Other IEPOX-SOA tracers, such as C5-alkene triols, IEPOX-organosulfates, and dimers containing them, can also be measured by offline GC-EI/MS and LC/MS (Lin et al., 2014; Budisulistiorini et al., 2015), and they account for 28% and 24% in total IEPOX-SOA in SOAS (R=0.7), respectively (Fig. S2).”

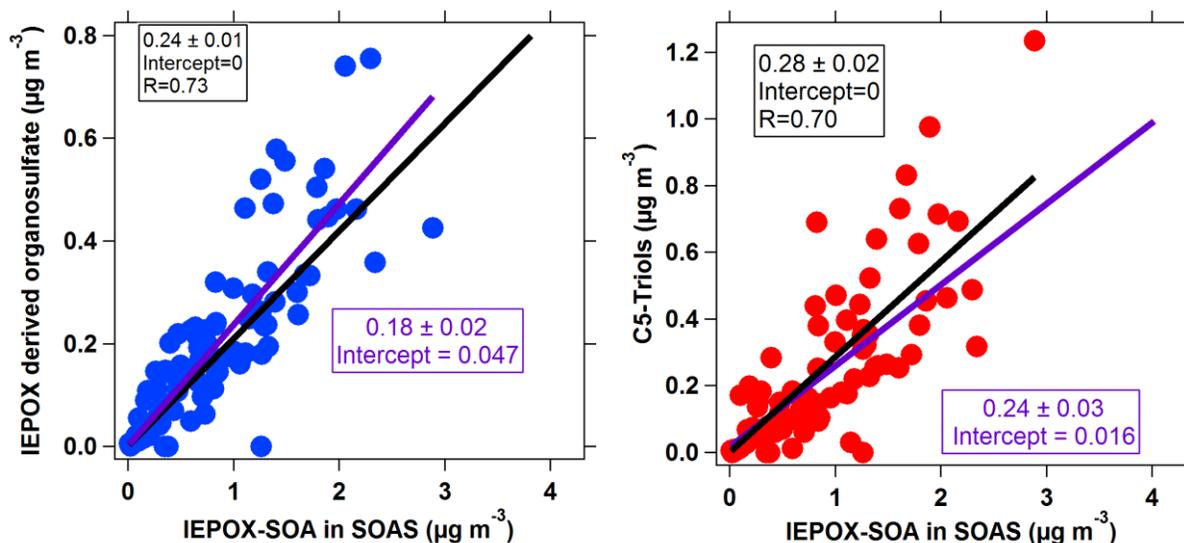


Figure S2. Scatter plots between IEPOX-derived organosulfate and C5-triols vs IEPOX-SOAP_{PMF} in the SOAS study. The IEPOX-derived organosulfate and C5-triols were measured in GC/MS and LC/MS analysis of filter extracts (Lin et al., 2014; Budisulistiorini et al., 2015).

R2.5. Page 11232:

“No IEPOX-SOA factor found in areas strongly influenced by urban emissions (e.g. Hayes et al., 2013)” does not give us information whether IEPOX pathway is suppressed by high NO unless you measured high isoprene levels there.

A2.5: We have modified this text to clarify this issue:

“No IEPOX-SOAP_{PMF} factor (i.e. below the PMF detection limit of ~5% of OA, Ulbrich et al., 2009) was found in areas strongly influenced by urban emissions where high NO concentrations suppress the IEPOX pathway, even in the presence of substantial isoprene concentrations (e.g. Hayes et al., 2013).”

R2.6. Page 11244: “Given the spread of values of f_{C5H6O} IEPOX-SOA (12–40 %) in different studies, if no additional local IEPOX-SOA spectrum is available for a given site, the estimation from this method should be within a factor of 2 of the actual concentration.”

Considering that the interference from monoterpene oxidation is important (e.g. f_{C5H6O} in rocky mountain comparable to SE aircraft data: Figure 4) and that estimation from monoterpene interference is derived from only one site (rocky mountain), I think more data are needed to testify the method and the above conclusion is a little bit too strong.

A2.6: Please see response to comment R1.1.

R2.7 Page 11245

Paragraph 2 “Low tracer values ($f_{C_5H_6O} < 3 \text{ ‰}$) are observed in non IEPOX-derived isoprene-SOA, indicating that the tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene.” Please also state if this is lab or ambient result because the paragraph starts with “ In ambient OA ...” and this sentence is somehow misleading when I read.

A2.7: This is effectively the same comment as R2.3, but here referring to the text in the conclusions, rather than the main text. Consistent with our response to R2.3, we have revised the next in the conclusions to read:

“Low tracer values ($f_{C_5H_6O} < 3 \text{ ‰}$) are observed in non IEPOX-derived isoprene-SOA from laboratory studies, indicating that the tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene”

R2.8 Figure 2 and Figure 7:

Could the authors give more information about how to get IEPOX-SOA in $\mu\text{g}/\text{m}^3$? The mass spectrum of IEPOX-SOA factor in Figure 2 (b) shows many other peaks besides 82 m/z. Is IEPOX-SOA in $\mu\text{g}/\text{m}^3$ a function of $f_{C_5H_6O}$ in IEPOX-SOA factor and the “weighing” of IEPOX-SOA factor compared to other OA factors? I think this is important to help non AMS people better understand AMS IEPOX-SOA data. The results in Figure 7 and the statement in abstract “During the SOAS study, 78% of IEPOX-SOA is accounted for the measured molecular tracers” rely heavily on this.

A2.8: We addressed this in section 3.1 with the text below, as well as with the description of the tracer-based estimation method in Section 3.9. The uncertainty of IEPOX-SOA_{PMF} is addressed in response to comment R2.1.

“The IEPOX-SOA_{PMF} mass concentration is the sum of mass concentrations of all the ions in the IEPOX-SOA_{PMF} mass spectra. The “mass concentration” of an ion is used to represent the mass of the species whose detection resulted in the observed ion current of that ion, based on the properties of electron ionization (Jimenez et al., 2003)”,

R2.9 In addition, could the authors provide the uncertainties (or error bars) of the data shown in Figure 7? The statement of “During the SOAS study, 78% of IEPOX-SOA is accounted for the measured molecular tracers, making it the highest level of molecular identification of an ambient SOA component to our knowledge.” in the abstract also points to the importance to know the uncertainty.

A2.9: The explanation was added in the main text:

“The uncertainty (standard deviation) of the fraction of IEPOX-SOA molecular tracers in IEPOX-SOA_{PMF} in SOAS study (42%) is estimated by combining the overall uncertainty from IEPOX-SOA molecular tracer measurement (24%), linear regression between tracer vs IEPOX-SOA_{PMF} (17%, see Fig. 2b and Fig. S2), IEPOX-SOA_{PMF} in PMF separation

method (9%) and the quantification of IEPOX-SOA_{PMF} based on AMS calibration (30%) (Middlebrook et al., 2012).”

The uncertainty bar was added to Fig. 7 as well.

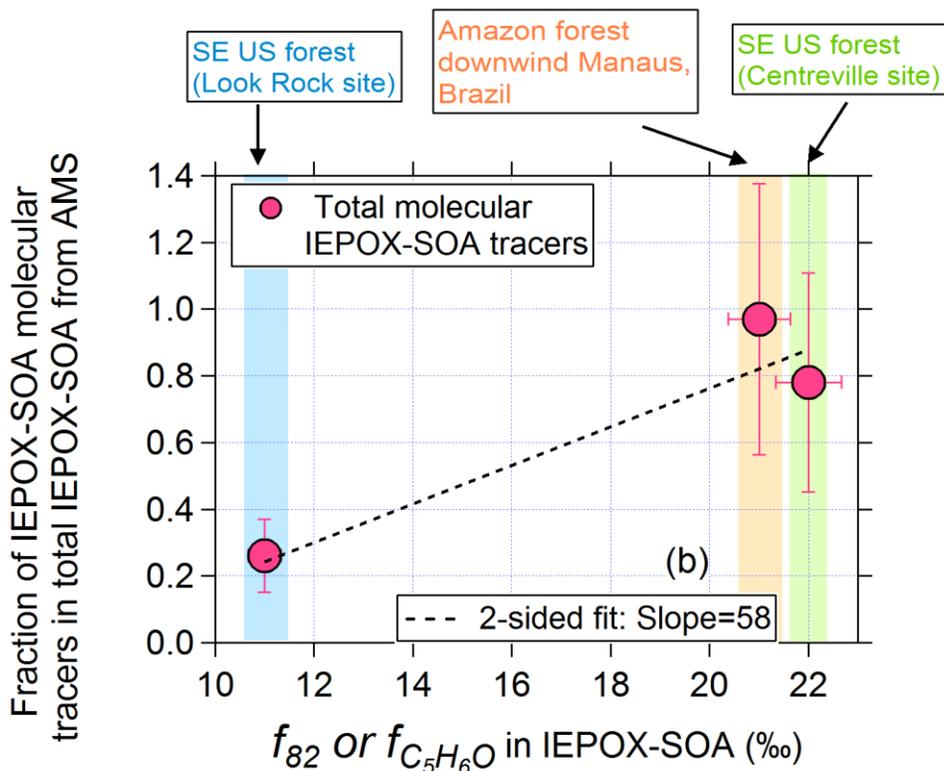


Figure 7. Scatter plot between total IEPOX-SOA molecular tracers (=Methyltetrol + C5-alkene triols +IEPOX-derived organosulfates and dimers) in IEPOX-SOA_{PMF} and $f_{82}^{IEPOX-SOA}$. Besides SOAS, the other two datasets in the graph are from Budisulistiorini et al. (2015) and de Sá et al.(2015). The relative uncertainty value estimated for the SOAS study is applied to the other two datasets.

Technical correction:

R2.10 Page 11226 Line 9: please define “SOAS”

A2.10: Corrected.

We revised the sentence to be: “**During the Southern Oxidant and Aerosol Study (SOAS) study...**”

R2.11 Figure 3: red curves in (a) are hard to distinguish. So are the green ones in (b). Please state clearly what the small dots are in (d).

A2.11: Following the reviewer’s suggestion, we revised our Figure 3. Please see the response to the comment R1.9.

R2.12 Figure 3 and 5: the legends are way too small and won't show up readable in print version.

A2.12: Please see the response to comments R1.9 and R1.13.

R2.13 Check the references to make sure they are recently updated.

A2.13: Thank for reviewer's reminder. We have checked through all the references and made sure they are all updated, and will check again on the ACP proofs after the paper is hopefully accepted. See also our response to comment R1.7.

References:

- Allan, J. D., Morgan, W. T., Darbyshire, E., Flynn, M. J., Williams, P. I., Oram, D. E., Artaxo, P., Brito, J., Lee, J. D., and Coe, H.: Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA, *Atmos. Chem. Phys.*, 14, 11393-11407, 10.5194/acp-14-11393-2014, 2014.
- 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, 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. Discuss.*, 15, 7365-7417, 10.5194/acpd-15-7365-2015, 2015.
- 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.
- de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Newburn, M. K., Brito, J., Liu, Y., Isaacman-VanWertz, G., Yee, L. D., Goldstein, A. H., Artaxo, P., Souza, R., Manzi, A., Jimenez, J. L., Alexander, M. L., and Martin, S. T.: Mass spectral observations of fine aerosol particles and production of SOM at an anthropogenically influenced site during GoAmazon2014 wet season, In prep., 2015.
- Jacobs, M. I., Burke, W. J., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, *Atmos. Chem. Phys.*, 14, 8933-8946, 10.5194/acp-14-8933-2014, 2014.
- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X. F., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, *J Geophys Res-Atmos*, 108, 8425, Doi 10.1029/2001jd001213, 2003.
- Kuwata, M., Liu, Y., McKinney, K., and Martin, S. T.: Physical state and acidity of inorganic sulfate can regulate the production of secondary organic material from isoprene photooxidation products, *Phys Chem Chem Phys*, 17, 5670-5678, 10.1039/c4cp04942j, 2015.
- Lin, Y.-H., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z., Gold, A., Kautzman, K. E., and Surratt, J. D.: Light-Absorbing Oligomer Formation in

- Secondary Organic Aerosol from Reactive Uptake of Isoprene Epoxydiols, *Environ Sci Technol*, 48, 12012-12021, 10.1021/es503142b, 2014.
- Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, *Aerosol Sci Tech*, 46, 258-271, 10.1080/02786826.2011.620041, 2012.
- 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, 10.5194/acp-11-1039-2011, 2011.
- Slowik, J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C., Chang, R. Y. W., Liggió, J., Makar, P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, *Atmos. Chem. Phys.*, 10, 2825-2845, 10.5194/acp-10-2825-2010, 2010.
- 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, 2009.
- 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, 2014.