

Response to Reviewers

We thank the reviewers for their comments and insightful suggestions that help improve the manuscript. We have addressed all the reviewer comments point by point below. To facilitate the review process, the *reviewer comments* are shown in italics. Our **response** is in blue after each comment. The **revised text** in the manuscript is shown in red.

Response to Reviewer #1

General comments:

This manuscript describes field measurements aimed at understanding the potential role of ambient SO₂ and NH₃ concentrations in affecting the formation of isoprene-derived SOA tracers. Aerosol samples were collected for low and high SO₂ and NH₃ levels and analyzed by gas chromatography electron ionization mass spectrometry (GC/EI-MS) and ultra-performance liquid chromatography electrospray ionization high resolution quadrupole time of flight mass spectrometry (UPLC/ESI-HR-Q-TOFMS). Six isoprene-derived tracers were quantified and were found to be enhanced under high SO₂ conditions, which is suggestive that SO₂ is supplying the acidity necessary for acid-catalyzed formation of the tracers. However, the tracers were not found to be strongly correlated to NH₃ levels or to the calculated aerosol acidity itself. While these findings are somewhat less conclusive about the role of SO₂/aerosol acidity than was probably the hope of this study at the outset, the result is quite important because it suggests that the nature of isoprene-derived SOA formation may be influenced by a number of factors. Because the findings are relevant to the construction of accurate chemical mechanisms for the formation of isoprene-derived SOA, the work has been carefully planned and executed, and the manuscript is clearly written, this study is quite appropriate for Atmospheric Chemistry and Physics.

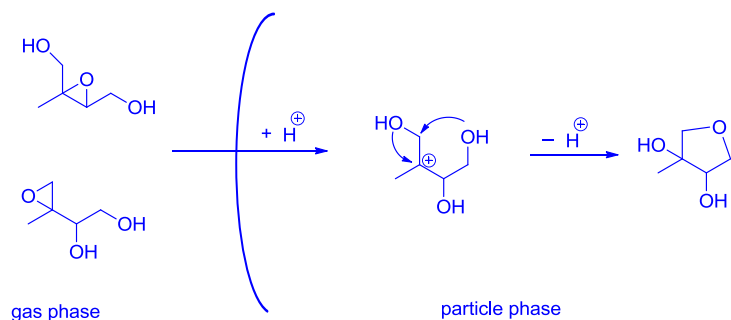
Specific comments

Line 284: I didn't find any mention in the manuscript concerning the (lack of) detection of IEPOX itself. It seems that the methods and sampling conditions are very similar to those described in Chan et al. 2010b in which IEPOX was first quantified in ambient SOA. It would be helpful for the authors to provide some insight (an upper limit concentration estimate, for example) regarding the lack of detection of IEPOX.

We thank the reviewer for raising this point. Here, we would like to clarify that the previous detection of particle-phase IEPOX in Chan et al. 2010b, which was characterized as m/z 262 with prior trimethylsilylation using GC/EI-MS analysis, has been shown to be a misidentification of 3-methyltetrahydrofuran-3, 4-diols (3-MeTHF-3, 4-diols) (Lin et al., 2012). This is confirmed through organic synthesis of both isomeric IEPOX and 3-MeTHF-3, 4-diol authentic standards (Zhang et al., 2012). 3-MeTHF-3, 4-diols are IEPOX-derived SOA tracers that result from reactive uptake of gas-phase IEPOX onto acidified sulfate particles, followed by acid-catalyzed rearrangement in the particle phase (reaction pathways shown below). The concentrations of 3-MeTHF-3, 4-diols detected in this study were estimated ranging from non-detectable (n.d.) to 35 ng m⁻³, which were comparable to the reported particle-phase IEPOX in Chan et al. 2010b (n.d. to 24 ng m⁻³).

To clarify this point, we have added a short discussion in the manuscript, starting on **Line 321**:

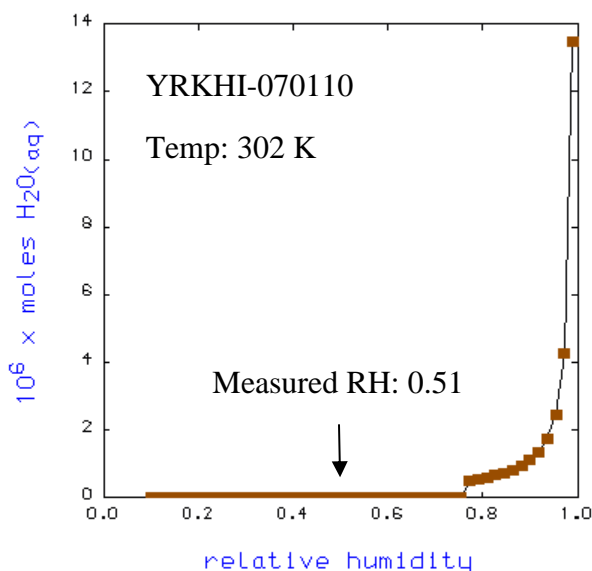
“.....It is noteworthy that the previous detection of particle-phase IEPOX in Chan et al. (2010b), which was characterized as m/z 262 with prior trimethylsilylation using GC/EI-MS analysis, has been shown to be a misidentification of 3-MeTHF-3, 4-diols (Lin et al., 2012). This is confirmed through organic synthesis of both isomeric IEPOX and 3-MeTHF-3, 4-diol authentic standards (Zhang et al., 2012). The concentrations of 3-MeTHF-3, 4-diols detected in this study were estimated ranging from non-detectable (n.d.) to 35 ng m^{-3} , which were comparable to the reported particle-phase IEPOX in Chan et al. (2010b) (n.d. to 24 ng m^{-3}).



Line 391: The determination of aerosol pH could also benefit from some further elaboration. In particular, the method for the modeling of liquid water content should be described. It's quite surprising that only 6% of the SOA samples were calculated to contain any LWC, especially given that one would expect high RH values during the SOA collection period (the summer months in Georgia).

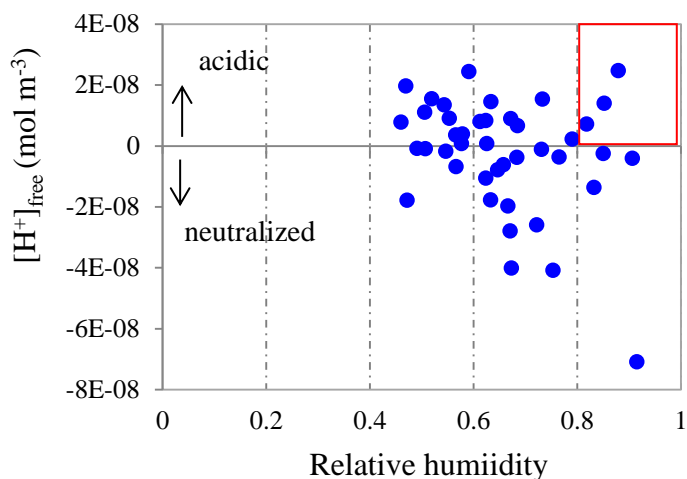
The amount of water (LWC) in an aerosol particle calculated using the E-AIM Model II system ($\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$) is dependent on the inorganic materials (electrolytes) present, the ambient relative humidity, and temperature.

Below is an example of modeling output showing no LWC from a high- SO_2 filter sample collected on 07/01/2010. The measured RH for this sample is 0.51.



Inorganic composition	moles m^{-3}
H^+	1.11E-08
NH_4^+	1.17E-07
SO_4^{2-}	6.29E-08
NO_3^-	2.1E-09
NH_3	2.87E-08

In addition, although there were some other high RH episodes observed during the sampling period (with $RH > 0.8$), these samples in fact have been fully neutralized ($[H^+]_{free} < 0$), and thus have to be excluded from the data set in the first place, since a charge imbalance in the ionic composition of the system is not allowed for the model input. As a result, only very limited number of samples could be modeled using this approach.



We have added a short discussion to further explain the limitations of modeling aerosol pH in the manuscript, starting on [Line 404](#):

“..... More specifically, the amount of water (LWC) in an aerosol calculated using the E-AIM Model II system ($H^+ - NH_4^+ - SO_4^{2-} - NO_3^- - H_2O$) is dependent on the inorganic materials (electrolytes) present, the ambient relative humidity, and temperature. Although there were some other high RH episodes observed during the sampling period (with $RH > 0.8$), these samples in fact have been fully neutralized ($[H^+]_{free} < 0$), and thus, have to be excluded from the data set since a charge imbalance in the ionic composition of the system is not allowed for the model input. Thus, aerosol pH could not be calculated for those samples either. As a result, only very limited number of samples could be modeled using this approach. Only 3 samples (out of 50) could be modeled for their *in situ* aerosol pH , and the average was found to be 1.71, ranging from 1.69 to 1.75.”

Line 393: For the pH values that could be determined from the few samples, the values were found to be quite low. For these samples, the IEPOX hydrolysis rate constants from Cole-Filipiak et al., (Env. Sci. Tech., 44, 6718-6723, 2010) indicate IEPOX processing times were less than 1 hour. Therefore, it seems that the acidity (and pH) data indicates that SOA was sampled both during conditions very conducive to IEPOX processing (low pH) and conditions not very conducive to IEPOX processing (neutralized), yet IEPOX was apparently not observed even for SOA that was neutralized (and the tracer product concentrations also seem to indicate significant IEPOX processing under neutralized conditions). Do the authors have an explanation for this apparent conundrum? I wonder if it is possible for a single SOA particle to be on average, neutralized, but to spend enough time as an acidic particle (depending on ambient SO_2 and NH_3 levels) to allow significant IEPOX processing.

We agree with the reviewer that the history of ambient aerosol acidity is complicated. The aerosol could be neutralized on average with time, but start as an acidic aerosol that has already provided sufficient acidity to allow significant IEPOX processing.

We have added a short discussion in the manuscript to stress this point, starting on **Line 432**:

“.....It should also be noted that the history of ambient aerosol acidity is complicated. The aerosol could be neutralized on average with time, but start as an acidic aerosol that has already provided sufficient acidity to allow significant IEPOX processing.”

Line 405: It would be helpful to provide some estimate of the SO₂ to SO₄²⁻ conversion time scale for the conditions at Yorkville, and then compare this number to the time scale of the sampling approach.

As the reviewer and we suggested in the previous comment above, the history of ambient aerosol is quite complicated, and thus, conversion of SO₂ to SO₄²⁻ is a bit challenging to accurately capture without measurements upwind of our site. As a result, we have removed this statement from our revised manuscript.

Response to the Short Comment

In a literature group meeting in our research group, we read this manuscript, and comments are based on that group discussion. We certainly enjoyed the publication and appreciated that it provides strong evidence through the molecular speciation and quantification of SOA oxidations that a large portion of the ambient organic carbon can be related to the photo-oxidation of isoprene under low NO_x conditions. We really enjoyed this story.

We had two comments that we think the authors could consider for greater clarification of the manuscript.

- 1. The first comment relates perhaps more to our own group's work and less to the authors, but nevertheless is quite germane to use of the AIM and Figure 9 of the manuscript. The authors appear to have run the AIM model with the assumption of no interaction between the organic material and the inorganic material. Our findings presented in Smith et al., ACP, 2012, 12, 9613-9628 show that isoprene-derived secondary organic material mixes miscibly with aqueous ammonium sulfate. In this case, the efflorescence and deliquescence points of the mixed particles are shifted. The bottom line result is that Figure 9 of the authors' manuscript might not be accurate with respect to the cases of "no LWC".*

We thank the reviewer for this very helpful comment. It is true that the E-AIM model was run under the assumption of no interaction between the organic phase and the inorganic phase. Although modeling output showed no modeled LWC for these samples, this could be inaccurate, especially since the Smith et al. (2012) paper has provided direct evidence of the shifted efflorescence and deliquescence points. We have changed the description of “no LWC” to “no modeled LWC” in Figure 9 to stress this limitation, and included this information the revised manuscript, **starting on Line 413**:

“.....However, the E-AIM model in this study was run under the assumption of no interaction between the organic phase and the inorganic phase. In a recent study by Smith et al. (2012), isoprene-derived secondary organic materials have been shown to mix miscibly with aqueous ammonium sulfate, and the resultant mixture shifted efflorescence and deliquescence points of pure ammonium sulfate. As a result, the modeling results could be inaccurate under this assumption, and thus, did not capture the actual particle LWC.”

2. *The second comment, unlike the first, relates strongly to the authors' thesis, both in the title and in particular in the strong sentence in the abstract, which reads: "IEPOX-derived SOA tracers were enhanced under high-SO₂ sampling scenarios..." We as readers were not able to locate a compelling data set or argument presented in the manuscript in this regard, so the authors might want to consider some clarification or clearer statements.*
 - a) *For instance, the highest Sum IEPOX/OM between Tables 2 and 3 is 19.1% and occurs for the case of high NH₃. Our understanding would be that this data set on its face would then be entirely opposite to the statement in the manuscript.*

Here we would like to clarify that the SO₂ conditional sampling and NH₃ conditional sampling experiments were two independent experiments. We didn't inter-compare samples collected from SO₂ and NH₃ conditional sampling experiments for the following reasons:

(1) SO₂ conditional sampling experiments were conducted during 06/25/2010-07/14/2012 and that the ambient SO₂ mixing ratio was the only controlled variable for PM_{2.5} sample collection. Thus, we could only compare high- and low-SO₂ samples collected on the same day (as a paired sample), since other variables, including NH₃, were not controlled.

(2) Similarly, NH₃ conditional sampling experiments were conducted during 07/29/2010-08/06/2012, and only the NH₃ level was controlled. We considered high- and low-NH₃ samples collected on the same day as a paired sample to distinguish the effects of ambient NH₃. As for the contributions of IEPOX SOA to OM were observed to be higher during the time of NH₃ conditional sampling experiments (high-NH₃: 19.1% and low-NH₃:18.6% vs. high-SO₂:13.3% and low-SO₂: 11.9%), this is likely due to the meteorological conditions more favorable for isoprene emissions during this time period of late summer.

We have made these points above clearer in the manuscript, starting on **Line 266**.

- b) *In Table 2, we wonder why "low SO₂" and "high SO₂" have yields of 11.9% and 13.3%, i.e., again not a strong statement of an influence of acid and perhaps just a correlation with total available surface area.*

The enhancement of IEPOX SOA formation could be in part due to the increased particle sulfate loadings that facilitate IEPOX uptake, and in part due to the enhanced aerosol acidity that catalyzes the oxirane ring-opening reactions. Since under high-SO₂ conditions these two effects occur hand-in-hand, we suggest that both factors would play a role in this process.

- c) *We would wonder, in relation to the authors' thesis of the importance of acidity, of why there are yields >0% for either "low SO₂" (Table 2) or "high NH₃" (Table 3).*

As isoprene SOA has been found to be influenced by both particle sulfate loadings and aerosol acidity, the amount of sulfate present in ambient aerosols would still affect isoprene SOA formation.

- d) *The organic carbon data of Table 1 appears to us, within uncertainty, to be independent of the 4 conditional sampling strategies.*

The OC data of Table 1 shows the average data of each condition from the whole data set. Since there are still numerous species that could contribute to the total organic carbon measurements other than isoprene SOA tracers, the organic carbon data might not reflect the influences of SO₂ or NH₃ we were trying to look for with conditional sampling strategies. Instead, the focus of this study is to look for shifts in the amounts of isoprene SOA tracers on a daily basis under SO₂ or NH₃ conditional sampling strategies, and particle sulfate loadings have been found to be important for this chemistry.

In regard to these comments, likely we as readers have a misunderstanding and so in this regard some clarification from the authors would be valuable for the readers (at least for us). One possibility occurring to us is that acidity is important but that the history of the particles in the atmosphere is complicated (e.g., perhaps starting as acidic and then becoming more neutralized with time) and, if this is the case, the fact remains that the data that could be collected (i.e., representing an observation after integration) does not appear (at least to us) to provide positive evidential support to the statement in the abstract.

We have revised the abstract as follows to address the reviewer's concerns, starting on **Line 39**:

"...Although IEPOX-derived SOA tracers were enhanced under high-SO₂ sampling scenarios, weak correlations between aerosol acidity and mass of IEPOX SOA tracers were observed. This suggests that IEPOX-derived SOA formation might be modulated by other factors rather than only aerosol acidity....."

We can't completely rule out the effect of aerosol acidity here, owing to the lack of knowledge on the history of the particles arriving to us at our site, as suggested here by the short comment provided by the Martin group. Also, the effects of aerosol acidity in ambient aerosol samples might not be as linear as previous observations in laboratory studies, since aerosol neutralization process is dynamic and convoluted.

We enjoyed the paper in the literature discussion, and we hope that our feedback as readers can be useful to the authors.

We sincerely appreciate the Martin group taking interest in our discussion paper and providing such constructive feedback and helpful comments. We also appreciate being pointed to the

Smith et al. (2012) paper. We think that the incorporation of Martin group's suggestions have helped to improve the quality of our manuscript.

Response to Reviewer #3

General comments:

This is a carefully designed and conducted field study aimed at clarifying the effect of acidity by examining the role of ambient SO₂ and NH₃ concentrations on isoprene SOA formation. The results are of atmospheric relevance suggesting that under ambient conditions the formation of isoprene SOA depends on the atmospheric SO₂ concentrations and sulfate aerosol could be a surrogate for surface area in the uptake of IEPOX onto preexisting aerosols. Weak correlations are found between aerosol acidity and the mass of IEPOX-related SOA tracers, which is perhaps a little disappointing but not so surprising because information is lacking about the acid history of the particles. It is interesting to see that the correlations between the mass of the isoprene SOA tracers under all conditions correlated better with the particle sulfate loadings than with the acidity of the particles. The manuscript is very well structured and written, and reads fluently. I fully concur with the positive appraisal of the first reviewer and only have a few specific comments.

Specific comments:

Part 3.1 – page 3108 – lines 1-4: The authors write “In addition, strong correlations ($r= 0.71$) were observed between the IEPOX-derived organosulfate (m/z 215) and the MPAN-derived organosulfate (m/z 199), suggesting similar formation behaviors or limiting factors, since these two species are known to form from different NO_x-dependent pathways, as shown in Fig. 1. “It is not clear what the authors mean by “similar formation behaviors or limiting factors”. Isn't “similar formation behavior” in contradiction to “different NO_x-dependent pathways”?

We thank the reviewer for raising this point. In a recently published paper from our group, methacrylic acid epoxide (MAE) has been shown as a precursor to isoprene high-NO_x SOA formation arising from MPAN oxidation (Lin et al., 2013). Reactive uptake of epoxide precursors followed by particle-phase oxirane ring-opening reactions appears to be a common mechanism for both low-NO_x and high-NO_x isoprene SOA formation pathways, although yielding distinct SOA composition. We have updated this information in the revised manuscript for further clarification.

Line 76:

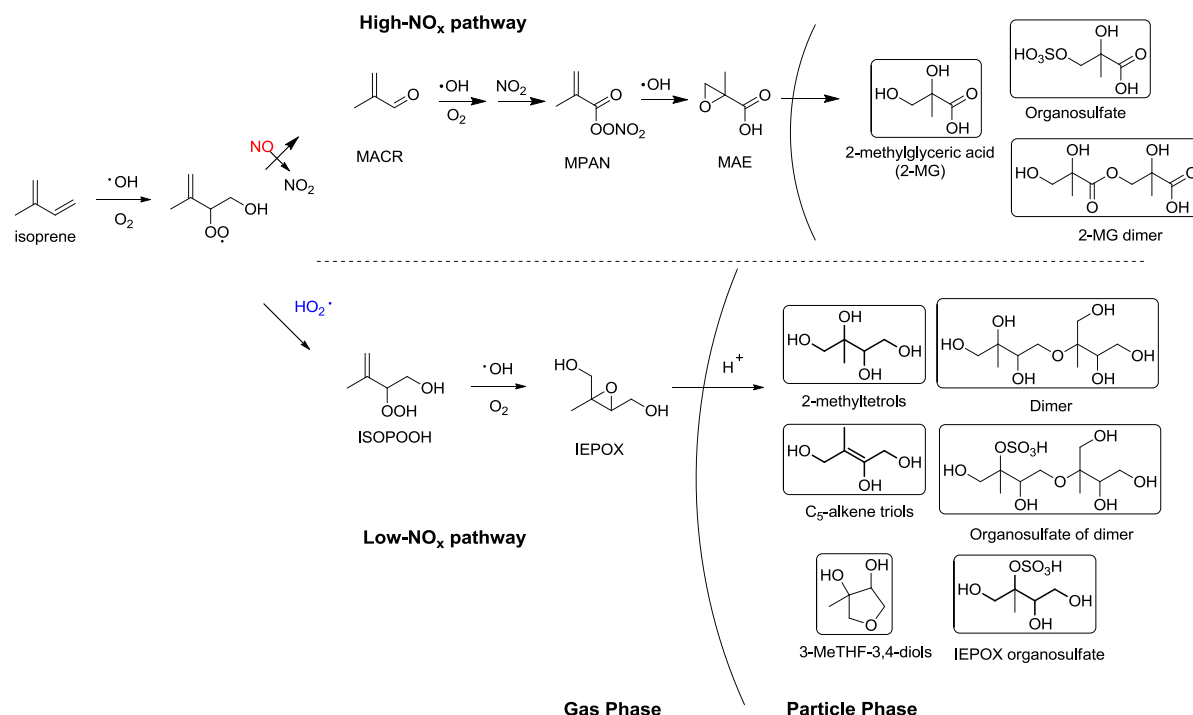
“.....Under high-NO_x conditions, isoprene SOA is enhanced with increasing NO₂/NO ratios (Chan et al., 2010a; Surratt et al., 2010a). This enhancement is explained by the formation and subsequent photooxidation of methacryloylperoxynitrate (MPAN) (Surratt et al., 2010b), forming methacrylic acid epoxide (MAE) (Lin et al., 2013), which leads to 2-methylglyceric acid (2-MG) formation and its corresponding oligoesters (Surratt et al., 2006; Surratt et al., 2010a).....”

Line 352:

“.....Reactive uptake of epoxide precursors followed by particle-phase oxirane ring-opening reactions appears to be a common mechanism for both low-NO_x and high-NO_x isoprene SOA formation pathways, although yielding distinct SOA composition.....”

MPAN-derived SOA has been revised as MAE-derived SOA throughout the text.

Figure 1 has been updated with this information.

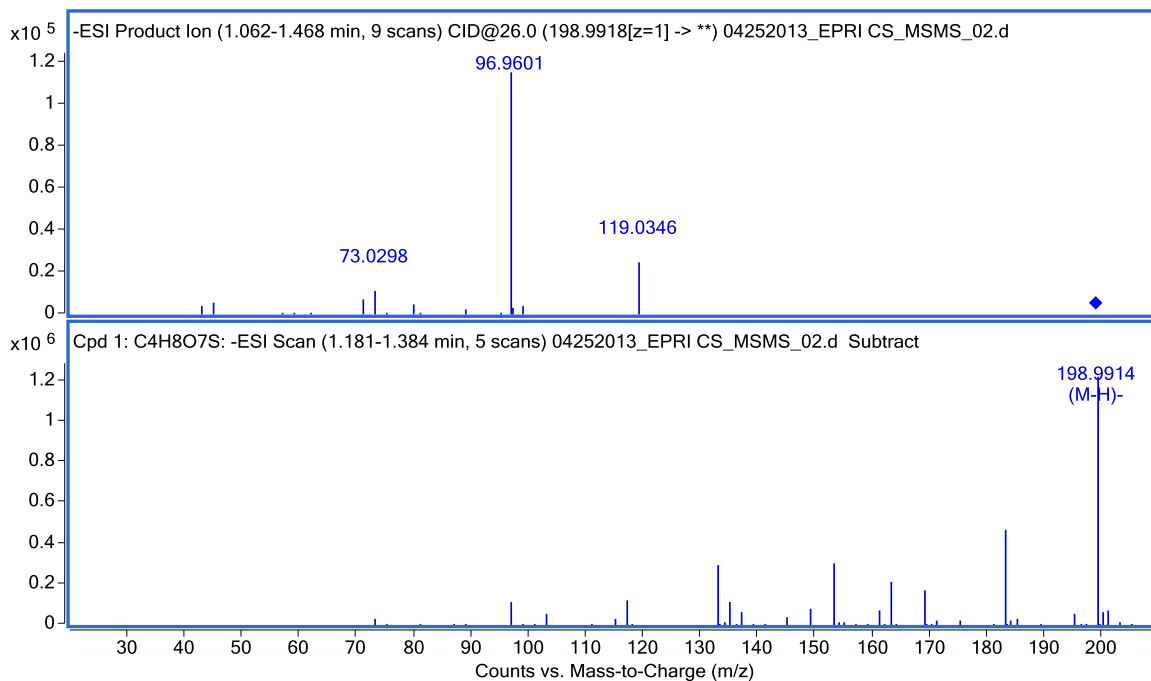
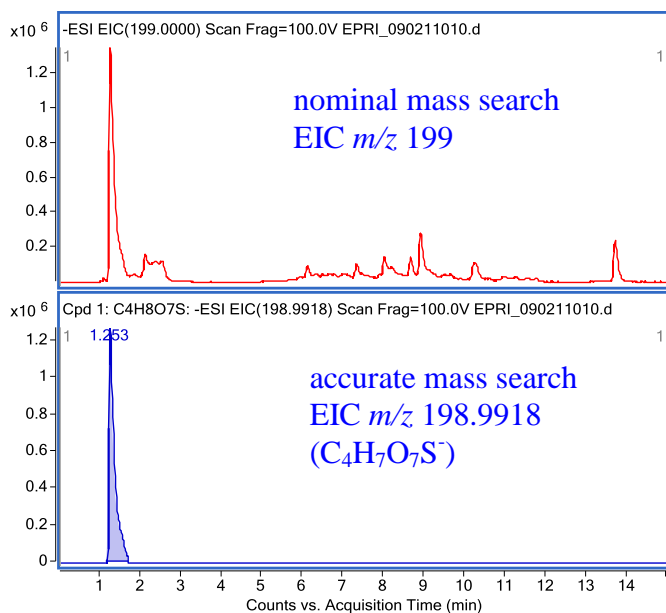


Furthermore, it is also possible that the m/z 199 organosulfate is more complex than thought as the chromatographic resolution using the ACQUITY UPLC HSS T3 column is limited and contains other species than the 2-methylglyceric acid-derived (or MPAN-derived) organosulfate. See the paper by Safi Shalamzari et al. which recently appeared in *Rapid Communications in Mass Spectrometry* (27, 784-794, 2013).

We thank the reviewer for this information. Based on the accurate mass data, the species of m/z 199 found in our samples could be mainly attributed to 2-methylglyceric acid-derived organosulfate; we more accurately describe this as the MAE-derived organosulfate ($\text{C}_4\text{H}_7\text{O}_7\text{S}^-$) based on our recent work in Lin et al. (2013). We have also collected MS/MS data for this chromatographic peak and it is consistent with prior work by Safi Shalamzari et al. (2013).

Starting on Line 338 in the revised manuscript we add the following statement:

“It should be noted that the MAE-derived organosulfate (detected as the $[\text{M}-\text{H}]^-$ ion at m/z 199) produced an MS/MS spectrum (Fig 1S, see Supplement) consistent with that recently shown by Shalamzari et al. (2013).”



Part 2.2 – lines 5-10: The polar isoprene SOA-related organosulfates were quantified using sodium propyl sulfate as surrogate standard. It is not clear how the actual quantitation was performed: was it done assuming a similar mass response or molar response? This should be mentioned.

The use of sodium propyl sulfate to quantify isoprene-derived organosulfates was performed under the assumption of similar ionization efficiency since the retention time (and thus the mobile phase composition) of this surrogate standard is similar to our target analytes. The quantification was done based on the mass response. We have added this information in the revised manuscript (starting on Line 202).

Table 2 and 3, and corresponding discussion of the data: To calculate the sum of the IEPOX SOA tracers the sum is made of the 2-methyltetrols determined using GC/MS with prior trimethylsilylation, IEPOX-derived organosulfate (m/z 215) determined using LC/MS, and some other isoprene SOA species. I doubt that this summation procedure can be followed since part of the 2-methyltetrols measured with the GC/MS procedure will originate from the acid-catalyzed hydrolysis/derivatization of IEPOX-derived organosulfate upon trimethylsilylation. Hence, a correction should be made for the part of the 2-methyltetrols that was counted double. It is not clear from the manuscript whether such a correction was done. The same comment applies to the MPAN SOA tracers. Thus, there could be an overestimation of the mass of IEPOX- and MPAN-related SOA tracers.

We agree with the reviewer that 2-methyltetrols and 2-methylglyceric acid could possibly be overestimated due to the hydrolysis and derivatization of IEPOX- and MAE-derived organosulfates upon trimethylsilylation. To evaluate the extent of this effect, we analyzed sodium octyl sulfate using GC/MS with prior trimethylsilylation, and compared the results to octanol with trimethylsilylation. Sodium octyl sulfate and octanol were used here as surrogates owing to the lack of authentic standards for IEPOX- and MAE-derived organosulfates, as well as their hydrolyzed products (i.e., 2-methyltetrols and 2-methylglyceric acid). The results indicate ~1.6% octyl sulfate was hydrolyzed during the process of trimethylsilylation. We have revised our manuscript to acknowledge this source of uncertainty for the estimated mass concentrations (starting on Line 328).

Technical corrections:

Page 3102 – line 10: ...of the GC/MS procedure...

Page 3103 – line 7: ...all isoprene-derived organosulfates

We thank the reviewer for the detailed technical corrections. These corrections have been incorporated in the revised manuscript.

References:

Chan, A., Chan, M., Surratt, J., Chhabra, P., Loza, C., Crouse, J., Yee, L., Flagan, R., Wennberg, P., and Seinfeld, J.: Role of aldehyde chemistry and NO_x concentrations in secondary organic aerosol formation, *Atmos. Chem. Phys.*, 10, 7169-7188, 2010a.

Chan, M. N., Surratt, J. D., Claeys, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., Eddingsaas, N. C., and Wennberg, P. O.: Characterization and quantification of isoprene-derived epoxydiols in ambient aerosol in the southeastern United States, *Environ. Sci. Technol.*, 44, 4590-4596, 2010b.

Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acid-catalyzed

reactive uptake studies with authentic compounds, *Environ. Sci. Technol.*, 46, 250-258, 10.1021/es202554c, 2012.

Lin, Y.-H., Zhang, H., Pye, H. O. T., Zhang, Z., Marth, W. J., Park, S., Arashiro, M., Cui, T., Budisulistiorini, S. H., Sexton, K. G., Vizuete, W., Xie, Y., Luecken, D. J., Piletic, I. R., Edney, E. O., Bartolotti, L. J., Gold, A., and Surratt, J. D.: Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, *Proc. Natl. Acad. Sci. USA*, 110, 6718-6723, 10.1073/pnas.1221150110, 2013.

Safi Shalamzari, M., Ryabtsova, O., Kahnt, A., Vermeylen, R., Hérent, M. F., Quetin-Leclercq, J., Van der Veken, P., Maenhaut, W., and Claeys, M.: Mass spectrometric characterization of organosulfates related to secondary organic aerosol from isoprene, *Rapid Commun. Mass Spectrom.*, 27, 784-794, 2013.

Smith, M., Bertram, A., and Martin, S.: Deliquescence, efflorescence, and phase miscibility of mixed particles of ammonium sulfate and isoprene-derived secondary organic material, *Atmos. Chem. Phys.*, 12, 9613-9628, 2012.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, *J. Phys. Chem. A*, 110, 9665-9690, 10.1021/jp061734m, 2006.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc. Natl. Acad. Sci.*, 107, 6640, 2010a.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc. Natl. Acad. Sci. USA*, 107, 6640-6645, 2010b.

Zhang, Z., Lin, Y. H., Zhang, H., Surratt, J. D., Ball, L. M., and Gold, A.: Technical Note: Synthesis of isoprene atmospheric oxidation products: isomeric epoxydiols and the rearrangement products cis- and trans-3-methyl-3,4-dihydroxytetrahydrofuran, *Atmos. Chem. Phys.*, 12, 8529-8535, 10.5194/acp-12-8529-2012, 2012.