## Response to Reviews

We thank the reviewers for their detailed comments and helpful suggestions. We have addressed each comment below, with the Referee comment in bold italicized text, our response in plain text, and any manuscript changes noted in red text. In addition, the revised manuscript with changes marked up has been attached to the end of our response to Referee 3.

## Anonymous Referee #2

***General comments:***

***This work examines aqueous SOA, both reversible (able to evaporate upon drying) and irreversible, in the Eastern US using measurements of water-soluble compounds in both the gas and particle phase. Additional measurements (isoprene, NOx) are used to infer that the reversible SOA is a result of isoprene epoxydiol (IEPOX) uptake to an aqueous medium. This paper examines an important issue with implications for what controls IEPOX SOA formation. However, to further their conclusions it would be good to demonstrate stronger connections between isoprene and the reversible SOA since no chemical identity beyond WSOCp (particulate WSOC) and WSOCp,dry (dried WSOC) is known for the organic aerosol. The major pieces of evidence for IEPOX being the precursor to reversible SOA come from NOx and isoprene concentrations and time lag analysis. The WSOCp peaks 9 hours after isoprene (consistent with IEPOX being 2nd generation plus an additional lag), and the reversible SOA is highest when NOx/Isoprene is lowest which is consistent with our understanding of IEPOX formation in the gas-phase. However, formation of IEPOX may not be the limiting factor for IEPOX SOA formation (sulfate and its influence on particle surface area/volume as well as acidity may be responsible). In addition, other aspects of the ambient atmosphere are changing in addition to NOx and isoprene as a function of season. Two areas that could be furthered include:***

***1. Can mass closure be reached in terms of how much isoprene is present and the amount of WSOCp and WSOCg? E.g. Page 6 line 25: Do you get mass closure if you assume 5 ppbC of isoprene reacted forms 2 ugC/m3 IEPOX?***

We agree with the reviewer that such an analysis would be quite interesting; however, we are not able to quantitatively link the reacted isoprene and formed $WSOC_p$. This is an inherent limitation of the $WSOC_p$ and isoprene measurements at different locations. We have added detailed discussion about this point in the Methods section (see also our response to Referee 3, comment #1). Based on our methods and analyses, we are only able show a strong link between isoprene and reversible aqSOA: attempting a mass closure analysis would be too speculative and would have a prohibitively high uncertainty.

***2. Is the reversible IEPOX SOA just dissolved IEPOX or is it a reversibly formed reaction product? Are the levels of reversible IEPOX SOA consistent with dissolved IEPOX? Sareen et al. 2017 indicate dissolved IEPOX alone is a very small concentration (especially compared to IEPOX SOA from AMS PMF analysis).***

The reviewer brings up an excellent point. We have clarified several points in the text: "Note that Sareen et al. (2017) predict very low dissolved IEPOX in the eastern U.S. during summer (< 0.01 µg $m^{-3}$), suggesting reversibly formed reaction products are the dominant contributors to reversible aqSOA." and also: "For example, it is unclear how the instruments employed by Lopez-Hilfiker et al. (2016) and Hu et al. (2016) respond to reversible IEPOX reaction products present in the aqueous phase."

***3. Were other proxies for chemistry besides NOx/Isoprene examined? Page 7, near line 10: Is the diurnal variation in sulfate involved in IEPOX SOA?***

In the eastern U.S., sulfate typically shows little variability throughout the day (e.g., Fig. S2b in (Xu et al., 2015)). However, sulfate does play a critical role in IEPOX chemistry, so we have added substantial analysis and discussion related to this point. See our response to comments #4 and #5 below.

***4. Figure 7 shows seasonality in the WSOCp,dry/WSOCp ratio consistent with changes in NOx/Isoprene. What else changes as a function of season that could also explain the ratio? Oxidants? How is ALW changing? If the horizontal axis was sulfate or SOx divided by isoprene would it show the same behavior?***

ALW does not vary significantly across our late spring, summer, and fall sampling periods (≈20% differences, Paper in preparation). Ozone does exhibit a strong seasonal pattern in the eastern U.S., increasing in the spring, peaking during summer, decreasing during fall, with a minimum in winter. In terms of SOA contributions, ozone reactions with monoterpenes are far more important than ozone reactions with isoprene (Xu et al., 2015). However, monoterpene SOA is produced year round, and does not peak during summer in the eastern U.S. (see also our response to Referee 3, comment #2 for more detailed discussion of this point). Sulfate strongly affects isoprene SOA; however, we do not have sufficient sulfate data to incorporate such an analysis in the present study. $SO_2$ and sulfate are not correlated in Baltimore ($R^2 = 0.06$), indicating that a figure analogous to Fig. 7 but instead with $SO_2$/isoprene on the x-axis would not provide the desired insight into the effects of sulfate. Studies show that sulfate and NOx both affect isoprene SOA (e.g., (de Sá et al., 2017)), so even if there are other important species that we do not consider here, our analysis of NOx/isoprene is still valid.

## ***Other Specific Comments:***

***5. Page 1: Lines 23-24 indicate that the trend towards lower NOx/Isoprene ratios may mean more IEPOX SOA in the future. Given the dependence of IEPOX SOA on sulfate, wouldn't we expect this pathway to decrease with decreasing sulfate levels in the future as demonstrated by Marais et al. 2017 ERL (http://iopscience.iop.org/article/10.1088/1748-9326/aa69c8/meta)?***

The Referee brings up an excellent point. We have removed the sentence from the abstract, and have added the following paragraph to the Conclusions: "Predictions of future $NO_x$ and isoprene emissions in response to regulations, technology, and climate change also suggest that this process may increase in importance going forward. Such an inference is complicated by concurrent reductions in $SO_2$ emissions in the U.S. and other developed nations. The consequent decreases in sulfate may offset the effects of $NO_x$ reductions on isoprene SOA (de Sá et al., 2017). However, we stress that prior studies into the $NO_x$-sulfate-isoprene system have not systematically determined how these species affect the reversibility of isoprene SOA. Therefore, while we hypothesize that future decreases in $NO_x$ and increases in isoprene will increase reversible isoprene SOA (or at least the reversible fraction), the role of changing sulfate will also need to be considered. Future laboratory and modeling studies will be needed to address this question directly."

***6. Page 1: Line 29 indicates isoprene is the dominant SOA precursor in summer. I would define dominant as responsible for >= 50% of SOA. Hu et al. 2015 ACP (https://doi.org/10.5194/acp-15-11807-2015) indicate isoprene (or IEPOX) is responsible for 17% to 36% of Southeast US SOA. So while it is important, it is not dominant.***

The Referee is correct that measurements and models constrain the IEPOX contribution to SOA in the eastern U.S. during summer to less than 50%. However, isoprene also forms SOA that is not necessarily associated with the IEPOX factor identified by the AMS. The studies we have cited here both predict that isoprene is the dominant SOA precursor, contributing more than 50% of SOA in the southeastern U.S during summer. These predictions have uncertainties, though, and to acknowledge this, we have changed the text to read: "In the southeastern United States, isoprene is likely the dominant SOA precursor during summer (Kim et al., 2015; Ying et al., 2015)."

***7. Page 2: Lines 21-23: I would characterize both Marais et al. 2016 and Pye et al. 2013 as irreversible IEPOX uptake since both use a reactive uptake formulation. The major difference between Marais et al. and Pye et al. is the Henry's law coefficient which leads to different amounts of IEPOX SOA. They also simulated different years. Budisulistiorini et al. 2017 has shown that reversible (simpleGAMMA, McNeill et al. 2012) and irreversible (CMAQ, Pye et al. 2013) models of IEPOX uptake can agree when the parameters going into them are identical (for ~6 hours of processing time).***

We agree with the reviewer's comment, and have removed this sentence.

***8. Page 3: Line 17-18: which instruments may not measure reversible SOA?***

These instruments may include: AMS, f(RH), $PM_{2.5}$ mass concentrations and others. We have a full discussion about instruments and methods that might not be able to measure reversible aqSOA due to particle drying in our previous publication (El-Sayed et al., 2016).

***9. Page 4: Near line 30: Can you clarify the relationship between WSOCp and aqSOA? What fraction of WSOCp is aqSOA? How was aqSOA identified?***

We have added the following to the Methods section: "$WSOC_p$ is operationally defined based upon the solubilites of the organics, themselves, and the level of dilution employed for the analysis (Psichoudaki and Pandis, 2013). In the eastern U.S., the $WSOC_p$ measurement is a surrogate for SOA, especially during summer (Weber et al., 2007). The measurement includes SOA formed through absorptive partitioning and through aqueous-mediated pathways (aqSOA). We consider any $WSOC_p$ that evaporates with drying to be reversible aqSOA, since this material exists in the condensed phase because of the aerosol water and partitions back to the gas phase when the water evaporates."

aqSOA is identified based upon the relationship between $F_p$ ($F_p = WSOC_p/(WSOC_p + WSOC_g)$) and relative humidity, according to Hennigan et al. (2008) and El-Sayed et al. (2016, 2015). We have another paper in preparation that focuses on the other question (***What fraction of WSOCp is aqSOA?***).

***10. Page 8: Line 35: How much higher is the fraction of reversible aqSOA? Insert value.***

We have changed the text so that it now reads: "The results in Fig. 1 show that ≈10 to 15 % of the total $WSOC_p$ evaporates with drying during the late spring and summer, on average. This suggests that the fraction of aqSOA that is formed reversibly is much higher than 15% since the measurement of $WSOC_p$ includes compounds formed through uptake to aqueous particles (aqSOA) and compounds formed through traditional SOA pathways."

***11. Page 8: Line 36: For the range of 0-60%, what is the typical value (mean, median, or similar)?***

We have changed the text so that it now reads: "The results in Fig. 1 show that ≈10 to 15 % of the total $WSOC_p$ evaporates with drying during the late spring and summer, on average. This suggests that the fraction of aqSOA that is formed reversibly is much higher than 15% since the measurement of $WSOC_p$ includes compounds formed through uptake to aqueous particles (aqSOA) and compounds formed through traditional SOA pathways."

***12. Page 9: Line 18-22: I am unclear as to whether or not the work of Wong et al., 2015 is atmospherically relevant if their experiments did not produce SOA from IEPOX. D'Ambro et al. 2017 ES&T (http://pubs.acs.org/doi/abs/10.1021/acs.est.7b00460) demonstrates that IEPOX is the atmospherically relevant pathway to isoprene SOA and laboratory experiments with unrealistic concentrations may be activating pathways that are not important in the atmosphere.***

We agree with the reviewer's comment and have added the following to our discussion: "Although the experiments of Wong et al. (2015) were performed in a chemical regime where

IEPOX formation is favored, it did not contribute to the SOA in their experiments due to high OH levels. Given the absence of IEPOX-SOA in the experiments of Wong et al. (2015), the atmospheric relevance of their results may be questionable. However, the uptake of other, non-IEPOX, low-$NO_x$ oxidation products may explain such observations (Liu et al., 2016; Riva et al., 2016)."

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