

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 #1

This article seeks to assess the reversibility of aqueous secondary organic aerosol (aqSOA). The methodology, in this work, is implemented to sample tropospheric aerosols and probe the aqSOA contents within. The authors infer that the aqSOA is primarily isoprene-derived, and attempt to elucidate the influence of NO_x on the extent of reversibility. They use a Particle-Into-Liquid-Sampler (PILS) coupled to a Total Organic Carbon (TOC) analyzer to measure aqSOA / water soluble organic carbon (WSOC) content, with a custom-made mist chamber and denuders as conditioning apparatus prior to sampling. The gas-phase measurements however were not conducted by the authors, rather they were obtained by the Maryland Department of the Environment (MDE) located ~20 km from their sampling site. Taken together, the results from the PILS/TOC and gases (isoprene and NO_x) seem to suggest that low- NO_x isoprene derived aqSOA is more prone to reversibility than high- NO_x isoprene-derived aqSOA. The literature does not seem to be abundant enough – in context of reversibility – to compare to the measurements, making this study unique. Perhaps the most interesting segment of this article is the time-lag analysis that correlates isoprene to water-soluble organic carbon (WSOC), acting as a proxy that crudely considers transport of isoprene-laden air from the source to the sampling site. Some seasonal analysis is done that suggests both secondary organic aerosol (SOA) and aqSOA abundance is correlated to summertime isoprene mixing ratios, further suggesting the reversibility of aqSOA is driven by isoprene oxidation products. That said, no back trajectories are included in the article. If the authors are correct, accounting for reversibility of aqSOA (or SOA in general) can non-negligibly influence aerosol loadings in certain continental areas. Overall, this article presents an interesting study and tackles an important area of aerosol chemistry and isoprene chemistry. However, in my view, it is not clearly written. Concepts do not come across easily, neither in explanations nor in inferences. While the science is appropriate for ACP and an ACP audience, the analysis and language need to be cleaned up. I recommend this be published in ACP once my comments are addressed, as it can lay groundwork for more studies of its kind.

Major comments:

1. While the authors demonstrate there is a relationship between isoprene and aqSOA (or WSOC, depending on the definition) reversibility, implying isoprene-derived aqSOA is at least ~25% reversible, their data analysis could be a lot stronger. Several figures (3-6) don't have error bars nor do they include the full data, e.g. scattered behind the trends. Because this is not a modeling paper, rather a purely experimental one, rigorous data analysis needs to be included for ACP standards.

We have updated Figures 2, 3, 4, 5, and 6 in response to the Referee's comment (see also our response to comments #55 through #59 below).

2. Furthermore, the Atmospheric Implications section and any discussion that follows lacks some key components. For example, peroxyethacryloyl nitrate (MPAN) is a known NO_x reservoir formed through the photooxidation of biogenic hydrocarbons (Bertman and Roberts, 1991; Tuazon and Atkinson, 1990), yet it is not mentioned in any high-NO_x scenarios. Perhaps it would be worthwhile to include some mention of MPAN and how it can affect aqSOA reversibility. Have any studies of MPAN formation from aqueous uptake of isoprene been done that can help in this discussion (Surratt et al., 2009)? Without this, the discussion of NO_x influence on aqSOA appears shallow.

From Sander (2015), the Henry's law constant for MPAN is quite low (1.7 M atm^{-1}), \approx five orders of magnitude (at least) lower than the Henry's law constant for glyoxal. Further, Pye et al. (2017) suggest that organic nitrates are among the least soluble SOA species. Therefore, we do not anticipate a significant contribution of MPAN uptake to form aqSOA.

3. Several times throughout the document the authors specify that low-NO_x conditions are responsible for reversible aqSOA yet the only compounds mentioned are isoprene epoxydiol (IEPOX), glyoxal, methylglyoxal, and other low- NO_x products. With the increase of anthropogenic activity, this may warrant further discussion.

We are unclear what the Referee is specifically referring to with "the increase of anthropogenic activity"? Most relevant to the context of this study, NO_x concentrations in the eastern U.S. are declining, and we note in the manuscript that isoprene oxidation in this region occurs approximately equally between the high- and low-NO_x pathways (citing Travis et al. (2016)).

Is the Referee instead suggesting that we be more specific instead of using "other low-NO_x products"? This will be challenging with the current body of literature. Surratt et al. (2010) show that ISOPOOH does not undergo uptake to aqueous particles (acidic or neutral). Wong et al. (2015) show reversible aqSOA from non-IEPOX products of low-NO_x isoprene oxidation, but they do not provide molecular identification of the gaseous precursors. Studies also show non-IEPOX isoprene SOA (e.g., (Liu et al., 2016)), but under lab conditions not relevant to the eastern U.S. (without acidic aqueous seed particles). In summary, there is simply not enough known about the molecular identities of other low-NO_x isoprene oxidation products that may form aqSOA.

4. With regards to timeseries, I wonder why the authors do not include them anywhere (except for isoprene). In the Supplement, there is a diurnal (diel) profile that suggests data was taken, or averaged, every hour, at least during the summertime. It would be great to have a timeseries for the year of isoprene, NO_x, and WSOC so that the data in this manuscript can come into context, e.g. Fig. 1. This time series can fit in the Supplement in my opinion. In the same vein,

Fig. S2 could come with confidence intervals, and perhaps Fig. 1 could have 12 box-and-whiskers (one for every month) to better capture seasonal variability. If data is insufficient, the authors should place more effort in explaining that.

Figure 2 presents a climatology of isoprene concentrations averaged over five years. Our WSOC measurements were not carried out for a year continuously, so a time series of these species would look very different than that of Figure 2 (with a lot of empty space). Table 1 in the manuscript clearly identifies the dates that correspond to the sampling within each season. We have added standard deviations to Figure 2, and Figure S2, and have added to the Supplement box plots showing individual data points (and their statistics) corresponding to Figures 3 and 4. We have also added box plots on top of the individual data plotted in Figures 5 and 6.

5. In addition, to bolster time lag arguments and correlations, if windroses are not available from MDE then perhaps some back trajectories can be calculated to ensure time lag air masses do not mix, e.g., with other air masses, the free troposphere, etc.

In this case, we do not agree that a back trajectory analysis is required to support our correlations. We have added the following discussion to Section 2 to better explain and justify our methods: “A key assumption employed in this analysis is that the WSOC measurements made at UMBC are representative of conditions at Essex, the location of the NO_x and isoprene measurements. Aerosol concentrations in the Baltimore-Washington region are spatially uniform over tens of kilometers (Beyersdorf et al., 2016). Further, WSOC_p concentrations exhibit small spatial variations across urban-to-rural gradients during the summertime (Weber et al., 2007). These prior analyses showed that aerosol concentrations, and in particular WSOC, were not dependent on wind direction. Isoprene emissions in the eastern U.S. are regional in nature, due to the expansive coverage of broadleaf forests (Guenther et al., 2012; Pye et al., 2013). NO_x emissions are spatially segregated from those of isoprene, and are far more localized. However, the isoprene-NO_x chemical regime (high- or low-NO_x) in the eastern U.S. is generally well-represented with model resolution of 28 x 28 km, suggesting that the chemistry occurring on small scales, such as in individual power plant plumes, does not significantly affect the regional isoprene-NO_x regime (Yu et al., 2016). NO_x concentrations at Essex (20 km ENE of UMBC) and HU-Beltsville (35 km SSW of UMBC) are strongly correlated (R = 0.89, Fig. S6), likely due to the overwhelming contribution of mobile source emissions along the heavily-traveled I-95 corridor to the region (Anderson et al., 2014). Together, this supports our analysis into the effects of isoprene and NO_x on reversible aqSOA using the measurements described above.”

6. While at the beginning of Section 3.3 the authors provide a brief discussion on atmospheric lifetimes, that can be expanded with the inclusion of transport. Further literature reading is encouraged on that front.

We point the Referee to our discussion in Section 4, Atmospheric Implications:

“The lifetime of organic compounds in the atmosphere is strongly dependent on their phase (Pye et al., 2017). Oxygenated organic compounds in the gas-phase often have much shorter lifetimes

than particle-phase organics due to significantly higher dry deposition velocities (Nguyen et al., 2015) and photolysis rates (Fu et al., 2008). Thus, the reversible uptake of WSOC_g to aerosol water may effectively shield these species from such loss processes, resulting in enhanced transport. Accounting for the reversible partitioning of water-soluble organic gases to aerosol water would likely improve model predictions of these compounds.”

7. Page 9 Line 8: In my opinion, this paragraph should be moved to the beginning of the results section! I found it to be a great paragraph. Readers may be confused as to why the authors don't explain what the results really mean – which if I understand correctly is that IEPOX reversibly partitions – until after a discussion of how aqSOA reversibility can affect model predictions! I felt as though I kept guessing what their results meant and why the authors chose this method of drying coupled to a mist chamber.

We agree with the Referee's suggestion and have moved this paragraph to the beginning of Section 4.

8. The Uncertainties section label may be misconstrued. There are no quantitative arguments in the section, let alone statistical error analyses, just qualitative interpretations of the data obtained. I would revise the section caption or move the text to a different section or subsection.

We agree with the Referee's comment. We have removed this section label, and have moved each of the paragraphs to their most relevant section.

9. In the Conclusion section, the first paragraph reads: “Lower NO_x leads to increase SOA production. . .” This needs to be revisited. It is believed (Spracklen et al., 2011), as the Southern Oxidant and Aerosols Study (SOAS) campaign also suggest, that higher NO_x mixing ratios enhance SOA production. If the authors are talking specifically about reversible aqSOA, they need to state that clearly, and that otherwise their surrogate is not representative of (urban) continental SOA.

The Referee is correct – we have clarified the sentence so that it now reads: “**Lower NO_x leads to a higher fraction of aqueous SOA formed reversibly.**”

10. A schematic / diagram of the setup is highly encouraged. This would help envision the split of WSOC_p and WSOC_g.

In two prior papers from our group (El-Sayed et al., 2016; 2015), both of which are cited here, we have included a schematic of the experimental setup. See our response to comment #55 below, as well.

11. For my clarification, can the authors explicitly state the difference between aqSOA and WSOC_p? I'm assuming a major difference is that WSOC_p can be primary organic aerosol (POA), but the audience may miss this. Also for my clarification, does 'reversible' imply physical partitioning or chemical equilibria? Or both?

We have added the following to the Methods section: “WSOC_p is operationally defined based upon the solubilities 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.”

To the Referee's second point: since the WSOC measurements do not provide molecular information, we do not have the tools to directly characterize the partitioning mechanism. However, we can infer some information about the process, as we have in the Atmospheric Implications section: “Note that Sareen et al. (2017) predict very low dissolved IEPOX in the eastern U.S. during summer ($< 0.01 \mu\text{g m}^{-3}$), suggesting reversibly formed reaction products are the dominant contributors to reversible aqSOA.”

12. Finally, I think the Supplement should at least contain the title and author list.

We have prepared the Supplement according to the ACP guidelines, which are as follows: “Supplements will receive a title page added during the publication process including title ("Supplement of"), authors, and the correspondence email. Therefore, please avoid providing this information in the supplement.”

Minor Comments:

13. Page 1 Line 27: “The oxidation of isoprene has important implications. . .” – consider revising or removing ‘important implications’ redundancy and nuancing how isoprene oxidation results in SOA, e.g.: “Isoprene oxidation is known to stimulate tropospheric O₃ production and contributes to SOA formation, thus affecting the local environment”. Relevant literature should be cited, e.g (Claeys, 2004; Kamens et al., 1982; Kroll et al., 2006).

We have changed the sentence so that it now reads: “Isoprene oxidation stimulates tropospheric ozone production and contributes substantially to secondary organic aerosol (SOA) formation, thus impacting air quality and climate (Henze and Seinfeld, 2006; Pfister et al., 2008).”

14. Page 1 Line 28: “In regions with high isoprene emissions, such as the southeastern United States, isoprene is. . .” – perhaps consider revising sentence structure to

avoid repeating the word ‘isoprene’ twice in a sentence. Furthermore, citing two articles that don’t conclude isoprene by itself is the major SOA precursor can be scant.

We have revised the sentence to: “**In the southeastern United States, isoprene is likely the dominant SOA precursor during summer** (Kim et al., 2015; Ying et al., 2015).”

15. While the Ozarks are known as the ‘isoprene volcano’, other terpenes (with SOA yields much higher than isoprene) can compete for total SOA load. If the authors can either rephrase the sentence to imply that isoprene is an important SOA precursor versus ‘the’ dominant SOA precursor, the sentence can be justified by citing the two articles.

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).”

16. Page 1 Line 31: “. . .glyoxal and methylglyoxal.” – consider an Oxford comma unless aldehydes are meant to be lumped together as a class separate from epoxides.

Comma has been added.

17. Page 2 Line 1: “A body of work indicates. . .” – while studies suggest uptake of organic gases in water lead to brown carbon formation, it should be pointed out that photochemical SOA production from isoprene occurs during homogeneous and heterogeneous nucleation (chamber studies), implying aqueous uptake is not the only source of isoprene SOA. A clarification is encouraged.

We have clarified the following sentence so that it now reads: “**Isoprene oxidation products can form SOA in the presence and absence of aerosol water** (Nguyen et al., 2014; Surratt et al., 2006), though the majority of regional-scale isoprene SOA is currently thought to form through aqueous pathways (Marais et al., 2016).”

18. Page 2 Line 20: Consider replacing the semicolon by a full stop to break the sentence.

We have made the change, as suggested.

19. Page 2 Line 34: I would think this sentence is better fit at the end of the previous paragraph.

We agree and have moved the sentence.

20. Page 2 Line 37: Consider substituting 'reaction' with 'oxidation'.

We have made the suggested change.

21. Page 2 Line 37: "This includes a major effect on isoprene oxidation chemistry, . . ." what does that mean? Is the major effect simply high and low yield? Or is it differences in chemical pathways? Also consider expanding the literature cited.

We have changed this sentence to read: "This includes a major effect on the chemical pathway of isoprene oxidation, and on the resulting SOA yield (Ervens et al., 2008; Kroll and Seinfeld, 2008)."

As the Referee notes, we could cite far more studies, not just in this sentence, but in many other places (e.g., see comment #23 below). We already have > 70 references cited, which may be on the high end for an article of this length, but we think appropriate given the large body of literature on isoprene SOA.

22. Page 3 Line 5: Consider rewording "with our understanding" to "with the understanding".

We have made the suggested change.

23. Page 3 Line 9: Consider citing more literature, e.g. (Kroll et al., 2006; Lin et al., 2013; Surratt et al., 2006, 2009).

We have added (Surratt et al., 2010).

24. Last paragraph of Introduction: Seems redundant, consider revising or removing.

We agree with the Referee's suggestion and have removed most of this paragraph. We have edited the first sentence (and moved it to the end of the prior paragraph) so that it now reads: "The aim of this study was to characterize the effects of isoprene and NO_x on aqSOA formed reversibly and irreversibly at a site in the eastern U.S. heavily impacted by biogenic and anthropogenic emissions."

25. Page 3 Line 25: Consider using a comma, e.g. ". . .using a mist chamber (MC), and in the particle phase. . .". Furthermore, is a brief description of the MC available? For anyone

interested in the technique, which may not be as diffuse as the authors imply, it may be cumbersome to backtrack El-Sayed et al. 2015, then Hennigan et al. 2009, then Cofer and Edahl 1986. Diagrams are encouraged.

We added the comma, as suggested. In terms of more details on the MC, including a diagram, this MC (or one quite similar) has been described in many prior publications (e.g., (Anderson et al., 2008a; 2008b; Ervens et al., 2011; Hennigan et al., 2008; 2009; Sareen et al., 2016; Spaulding et al., 2002; Zhang et al., 2012) including by our group (El-Sayed et al., 2016; 2015). See our reply to comments #10 and #55, as well.

26. Page 3 Line 27: Outline the model before explaining what mode it was operated in.

We have made the suggested change.

27. Page 3 Line 28: Why is ‘dried’ in quotes? Given the brief description and lack of diagram, it can be hard for the reader to put words into context.

This keeps with the convention in our prior publications. We have added the following for clarification: “**Note that the WSOC_{p,dry} channel has not been designed to dry particles completely to efflorescence (El-Sayed et al., 2016).**”

See also our response to comment #55 below.

28. Page 3 Line 31: Brand (if any, or if custom made) and dimensions of the parallel plate denuder? What flows can it handle? The gas-phase interferences are not necessarily limited to isoprene oxidation products, is that correct?

We have added (Sunset Laboratories) to indicate the manufacturer. The Referee is correct that the potential gas-phase interferences would not be limited to isoprene oxidation products; however, we note that such interferences in the PILS have been investigated and are minor, even without the denuder (see Sullivan et al. (2004)).

29. Page 4 Line 26: The first paragraph of the Results section. . . is it common to take measurements so infrequently? What does the literature recommend?

Is the Referee suggesting that ~4 weeks of semi-continuous measurements carried out continuously in each season is infrequent? This represents thousands of WSOC_p, WSOC_{p,dry}, and WSOC_g measurements within each season. The timing is also highly consistent with intensive atmospheric chemistry field campaigns.

30. Page 4 Line 29: “. . . WSOC_p measurements has been. . .” was it one measurement or multiple? Ensure verb matches the subject of the sentence. If plural, then correct to

“...WSOC_p measurements have been...”, whereas if singular, correct to “...WSOC_p measurement has been...”.

We changed “has” to “have”.

31. Page 4 Line 31: Consider removing sentence “In this regard...was formed.” as it doesn’t add critical information sandwiched between two sentences that by themselves give enough information.

We agree, and have removed this sentence.

32. Page 4 Line 34: Consider having that formula as an equation with a designated equation number. Also, it appears the subscript ‘P’ is Italicized outside of the bracket, but not inside, and could be corrected. Also, there appears to be a formatting issue with this paragraph in general.

We have corrected the formatting issues with the paragraph, and the italicized ‘p’. For such a simple formula, whose elements have been clearly defined and discussed prior to this point, it is probably not necessary to designate this as an equation.

33. First two paragraphs of Section 3: Consider merging first two paragraphs in one.

This was a formatting mistake – it has been corrected.

34. Page 5 Line 5: Sentence starts with “Figure 1...”, yet in Line 8 of the same page, sentence starts with “Fig. 1...”. The authors are invited to check for consistency and formatting guidelines of the journal. This may apply for more than one instance.

“Fig.” changed to “Figure”.

35. Page 5 Line 16: I don’t understand the citation to El-Sayed et al., 2016. My understanding is that the values 0.92 and 0.87 for mean WSOC_{p,dry}/WSOC_p are from data collected for this manuscript, hence, would not be previously published.

The mean WSOC_{p,dry}/WSOC_p ratio of 0.87 for the summertime data was published in El-Sayed et al. (2016). Likewise, the WSOC_{p,dry}/WSOC_p ratio for the fall was published in El-Sayed et al. (2015). The previously unpublished data are those from the winter and spring. Additionally, all of the analyses (e.g., with isoprene) into the factors that affect the WSOC_{p,dry}/WSOC_p ratio are new in this manuscript.

36. Page 5 Line 19: I don't think this sentence belongs here. Aside from this point being stressed before, it is out of place in this paragraph / section. Statements like these should go at the end of the introduction, and they are already included.

We have changed the sentence so that it now reads: “**In the following sections, we characterize the reasons underlying the seasonal differences in $WSOC_{p,dry}/WSOC_p$ shown in Fig. 1.**”

37. Page 5 Line 34: The authors could take more care with outlining the Aerosol Mass Spectrometer (AMS) rather than introducing an undefined acronym. In that regard, what is an 'IEPOX factor' and how does it relate to source apportionment techniques/AMS?

AMS has been defined.

38. Page 6 Line 29: The authors suggest their diel profile in Fig. S2 is consistent with their data in Figure 3. I would argue that, 3h lag considered, there ought to be an inflection point during the diurnal morning when as $WSOC_g$ increases, isoprene decreases. The authors need to address why that inflection in Fig. S2 is not reflected in Fig. 3, arguably indicating the importance of confidence intervals / error bars during the summertime.

We agree with the Referee's point of adding confidence intervals and/or error bars to several of the Figures (see our response to comment #1 above). However, with regards to this comment, we disagree with the Referee's suggestion that there should be an inflection point in the $WSOC_g$ (time lagged) diurnal profile. In the morning, isoprene emissions and OH radical generation both ramp up, and the boundary layer (BL) undergoes rapid expansion. At some times (07:00 – 10:00 am, local time), isoprene oxidation and BL dilution combine to exceed the effects of fresh isoprene emissions, leading to a decrease in isoprene concentrations. The inflection point at 10:00 am (local time) comes from a transition where isoprene emissions exceed the loss from oxidation and the effect of dilution, leading to an increase in isoprene concentrations. There is a fundamental difference in $WSOC_g$; however, in that OH radical oxidation is generally not a loss for most $WSOC_g$ in the same way that it is for isoprene. $WSOC_g$ is not chemically specific – it is likely made up of hundreds (or more) of different oxygenated organic gases. Therefore, while oxidation may transform many of the individual $WSOC_g$ compounds, many of these transformations will convert one water-soluble organic gas into another (see (Hodzic et al., 2014)). Losses of $WSOC_g$ include dry deposition and transformation into SOA, but we do not necessarily expect these losses to exceed $WSOC_g$ production at the same time as isoprene experiences the transition shown in Fig. S2.

39. Page 6 Line 29: The authors suggest that the chain of reactions leading isoprene to be converted to $WSOC_g$ is ~3-5h. While the data is convincing, without air mass trajectories or insolation data, incorporated with statistics, this assertion is slightly weak. Could other VOC or VOC oxidation mechanisms explain $WSOC_g$? Is regional terpene, sesquiterpene, or agriculture emission chemistry considered? If it is beyond the scope of the article it should be stated.

The Referee brings up an excellent point (also made by Referee 3). We have added an explanation for why monoterpene oxidation is not likely contributing to our observations of evaporated WSOC_p. The following paragraph is now at the beginning of section 3.3: “During the late spring, the onset of reversible aqSOA formation corresponds to the dramatic increase in isoprene concentrations (Fig. 2). Observations of the Aerodyne aerosol mass spectrometer (AMS) IEPOX factor (Budisulistiorini et al., 2016) and chemical markers for isoprene SOA (Kleindienst et al., 2007) show similarly sharp transitions in the spring and fall in the southeastern U.S. The highest reversible aqSOA levels were observed during the summer when isoprene emissions were at their maximum. Other VOCs, such as monoterpenes, also contribute to SOA in the eastern U.S. (Xu et al., 2015), but monoterpene and isoprene SOA tracers show distinctly different temporal patterns in the eastern U.S. Isoprene SOA peaks during summer, but monoterpene SOA tracers exhibit similar (or lower) concentrations in the summer compared to other seasons (Ding et al., 2008; Kleindienst et al., 2007). Further, monoterpene SOA is typically associated with semi-volatile and less-oxidized OA factors in the AMS analysis (Jimenez et al., 2009; Xu et al., 2015), but WSOC_p is poorly correlated with these factors (Timonen et al., 2013; Xu et al., 2016). On the basis of these prior studies, and the results in Figures 1 and 2, we attribute the reversible aqSOA in Baltimore to isoprene.”

40. Page 7 Lines 13-14: “Consistent with Fig. 3 and Fig. 4. . .” – I do not understand why WSOC_g is strongly correlated with isoprene for lags of 3-5h (Fig. 3) whereas Evaporated WSOC_p is correlated with isoprene for lags of 6-11 h? If evaporated WSOC_p is an example of reversible aqSOA as is WSOC_g by proxy, then if they are produced by the same pathway in the same parcel of air, wouldn't they require the same lag time? If not, and they are two different generation isoprene oxidation products, then why is there a relationship in Fig. S4? This is not clear to me, though perhaps I'm missing something. The following sentence “The above observations suggest that isoprene is strongly linked with the formation of reversible aqSOA in the eastern U.S” therefore does not speak to me.

Once IEPOX forms from isoprene oxidation, there is still additional time required to form aqSOA. Budisulistiorini et al. (2017) simulate 6- and 12-h processing times for aqSOA to form from IEPOX. We have clarified our discussion about this study so that it now reads: “The (6 to 11) h time lag between isoprene and the evaporated WSOC_p is consistent with the predicted kinetics of IEPOX SOA formation in the eastern U. S. (Budisulistiorini et al., 2017).”

41. Page 7 Line 20: A simple phrase at the beginning or end of the sentence explaining why the 9h lag was chosen would be helpful. Even though Fig. 4 can by itself be sufficient for an inference, a verbal explanation is helpful.

We have added the following to the end of this sentence: “since this timing corresponded to the maximum evaporated WSOC_p.”

42. Page 7 Line 22: “. . .it is clear. . .” – as per my comment on Fig. 5, without box-and-whiskers, the ‘dramatic’ decrease is not clear. Upon initial inspection, it would appear most of the data does not exceed 1 ug/m3, thus invalidating the ‘dramatic’ decrease.

We have added box-and-whiskers to Fig. 5. The average difference in evaporated WSOC_p between the lowest and highest bins in Fig. 5 exceeds 1 μg m⁻³. In Maryland, where the average annual PM_{2.5} concentration is less than 12 μg m⁻³ and the average annual OA concentration is ≈4 μg m⁻³, a difference greater than 1 μg m⁻³ is substantial. We have changed this sentence to read: **“Figure 5 shows that the amount of evaporated WSOC_p decreased substantially with an increase in the NO_x/isoprene ratio.”**

43. Page 7 Line 34: Consider rephrasing.

We have switched the order of the two sentences at the beginning of this paragraph to improve clarity.

44. Page 8 Line 15: Awkward phrase: “These results represent, to our knowledge, the first observations to characterize the seasonal occurrence of. . .” consider revising to, e.g., “To the best of our knowledge, observations of seasonal dependence of reversible aqSOA are reported for the first time in this work.”.

We have removed the phrase “to our knowledge”.

45. Page 8 Line 16: “important implications” has been used 2 out of 3 times in this document at this point. I wonder if it becomes a redundancy. Consider substituting with, e.g., “affect measurement techniques” or something less vague.

We have changed the sentence to: **“The results suggest an important effect on aerosol measurements that implement drying, which may not measure (or may incompletely measure) reversible aqSOA.”**

46. Page 8 Line 21: Consider removing “. . .to confirm this hypothesis.”

We have changed “confirm” to “test.”

47. Page 8 Line 22: I don’t believe the acronym ‘AOD’ has been defined before by the authors.

Acronym has been defined.

48. Page 9 Line 7: The last sentence is very vague by itself. The paragraph, in general, appears out of place. It is a good point by the authors, but does not seem fit between discussion of aqSOA reversibility on model prediction and discussion of their observations; rather, it can be moved to the end as an anecdotal sentence, or, if elaborated, a paragraph on its own.

We have replaced this sentence with: “Thus, accounting for the reversible partitioning of water-soluble organic gases to aerosol water would likely improve model predictions of these compounds.”

49. Page 10 Line 14: If the effect of ALW is more pronounced at low organic concentrations, why is there no discussion about salting out effects, Raoult’s law, etc.?

In this case, we are discussing the effect of ALW on gas-particle partitioning according to Raoult’s law (that is what serves as the basis for Pankow’s partitioning theory, and the reference cited in this sentence). Salting in/out would be an effect on aqSOA, which is not the subject of this paragraph.

50. Page 10 Line 16: “Our observations show. . .” – if the authors cite their previous publication, I would recommend revising the sentence to “Previous results from our group show. . .” or words to that effect.

We have made the suggested change.

51. Page 10 Line 18: The authors have not defined neither LVOOA nor SVOOA before, unless I missed it.

Acronyms have been defined.

52. Page 10 Line 23: Consider an Oxford comma.

We have made the suggested change.

53. Page 10 Line 25: “They dealt with this problem by. . .” sounds too colloquial. Consider revising.

We changed “dealt with” to “addressed.”

54. Page 11 Line 17: Remove first sentence.

We have made the suggested change.

Comments on Figures and Tables

55. Table S1: Along the same lines of my comments for Page 3 Line 28, this table is not very helpful. It takes a while to understand it. Are the standard deviations for the duration of the study? How often were these measurements made? Would a time series help? Why was the diffusion drier not sized to handle a 90% RH stream and reducing it to <20% RH? What were the dimensions? These details could go in the Supplement (in my opinion).

We understand the Referee's comment, which is in line with other comments suggesting more experimental details be added to the Methods section and the Supplement (e.g., Comments #10, #27, and #28). We appreciate the sentiment of having experimental details presented in this paper, reducing the need to refer back to prior papers. However, we also need to be cognizant of avoiding repetition of descriptions (and in some cases figures) presented in our prior work. El-Sayed et al. (2016; 2015) present a detailed discussion of the methods we use in this work (both present instrument schematics), including discussions relevant to this Referee comment. For example, the 2nd paragraph of the "Materials and Methods" section of El-Sayed et al. (2016) includes:

"The goal for the $WSOC_{p,dry}$ measurement was not to remove all particle bound water, but rather to approximate the lowest RH that particles may be exposed to in ambient air during the study period to simulate "natural" drying processes (Supporting Information Figure S2). The dried channel included a silica gel diffusion dryer, which was made in-house similar to commercial models (e.g., TSI model 3062). $WSOC_p$ losses through the 3-way valve and through the dried channel were evaluated prior to the start of the sampling period and were found to be negligible (Supporting Information Figure S3). The dryer was replaced daily and its efficiency was checked with an orange silica gel color-indicator as well as an RH sensor (Omega, RHUSB) that measured the RH of air exiting the dryer."

56. Figure 1: With the understanding that the authors composed a box-and-whiskers diagram to visualize their data, can something be done about the x-axis potentially misleading a reader that all five data are not evenly spaced across the year? If not, that is OK in my view, but if the data can be displayed with the x-axis being more akin to DateTime, it would better visualize (in my opinion) the seasonal cycles the authors wish to present.

Table 1 presents the dates that correspond to the seasonal labels in Figure 1. In the final version of the published paper, we will request that Table 1 and Figure 1 appear on the same page so that readers can easily locate these dates.

57. Figure 2: Upon reading the caption, this is an annual profile averaged across 5 years. I would request the data be replotted using markers and lines, at least, and ideally with some form of confidence intervals to reflect the averaged data. While the point of the authors is that

isoprene is high during the summer months, the data can be presented with a little more rigor and care. If data from MDE comes like this, the authors can state it.

We agree with the Referee's suggestion, and have updated Figure 2 accordingly.

58. Figure 3: If the authors claim that their calculation (or rather, literature review) of isoprene lifetime to OH oxidation is on the order of 1-2h, then this figure really requires at least vertical error bars. While the median WSOC_g does correlate with isoprene mixing ratios at lag times between 3-5 h, other types of statistics are encouraged for the argument to be valid.

We have added a supplemental figure to support Figure 3 that shows the individual data points and box and whiskers for one of the lag times. We also point the Referee to our extensive discussion this figure in Section 3.3, especially: “Overall, this suggests that fresh isoprene emissions take about (3 to 5) h to form WSOC_g in an urban environment during typical summertime conditions. Note that the measurement of WSOC_g only includes compounds with effective Henry's law constants above $\sim 10^3$ M/atm (Spaulding et al., 2002), so the MC does not efficiently sample many first-generation isoprene oxidation products, such as methacrolein ($K_H = 4 \times 10^0$ M/atm) or methyl vinyl ketone ($K_H = 4 \times 10^1$ M/atm) (Sander, 2015).”

59. Figure 5: Consider visuals, at least on the x-axis, to show regime of polluted vs clean air (low values on the x-axis are clean; high values are polluted). Also, if formatting permits, vertical box plots could help visualize the binning. In my opinion, the graph is very misleading otherwise.

We have added box plots to Figure 5.

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