

## ***Interactive comment on “The effects of isoprene and NO<sub>x</sub> on secondary organic aerosols formed through reversible and irreversible uptake to aerosol water” by Marwa M. H. El-Sayed et al.***

### **Anonymous Referee #3**

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#### Summary

This article examines the influence of NO<sub>x</sub> on the reversibility of aqueous SOA. The paper analyzed the irreversible and reversible water-soluble organic carbon (WSOC) in the particle phase, as well as WSOC in the gas phase from a site in the Eastern US. By correlating the gas phase and particle phase WSOC with isoprene concentration measured at a nearby site (~20 km away), the author believes that IEPOX uptake is responsible for the reversible aqueous SOA. By correlating the NO<sub>x</sub>/isoprene ratio vs. the percentage of reversible aqueous SOA of total particle phase WSOC, the author suggests that low NO<sub>x</sub>/isoprene ratios seem to enhance reversible aqueous SOA for-

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mation, which agrees with the author's assumption that IEPOX is the main reason for reversible aqSOA formed in late spring and summer.

This study provides a nice perspective of how reversible WSOC could affect the SOA budget and how drying the aerosol before performing field measurement could neglect reversible WSOC. The work performed to attribute the sources of such reversible WSOC by performing a time lag correlation on the isoprene concentration is interesting, but the lack of further analysis on the molecular composition of the gas and particle phase WSOC weakens the conclusion.

Overall, this article provides a unique perspective on the importance of WSOC in SOA with enough scientific content and novelty to be published in ACP. However, the conclusion that IEPOX is the likely cause of reversible WSOC in aqSOA is not strong enough and the logic between sentences in some paragraphs is not clear. The author needs to address the following issues and refine the wording before being published in ACP.

#### Major Comments

The sampling site of WSOC (Baltimore) is ~20 km away from the site sampling isoprene and NO<sub>x</sub> (Essex site), so whether the Essex site can be representative of the Baltimore site is a questionable part of this study, especially when the Baltimore site is heavily influenced by anthropogenic emissions and the author showed up to 11 hour lag comparison between the two sites. Back trajectory data would be better to use in this paper to justify the result, in order to (1) either prove that Baltimore is downwind of the Essex Site, (2) or to filter out those data when Baltimore is not downwind of the Essex site.

It is difficult to make a strong argument that IEPOX is the main reason for the reversible WSOC in the particle phase without chemical characterization. Other BVOCs (such as monoterpenes) can also form water soluble components that were shown to enhance SOA mass at high RH (Prisle et al., 2010), and their reaction mechanisms are also sensitive to NO<sub>x</sub> concentration (Wildt et al.). Even though IEPOX may seem to be a

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more likely compound for reversible aqSOA for this study, the author needs to provide stronger evidence to rule out other possibilities, such as a correlation plot between particle WSOC vs. time lagged monoterpene concentration.

Page 3, line 7, the author listed the ACP paper by Chan Miller et al. (2017) to show that glyoxal is formed in both low- and high- NO<sub>x</sub> pathways while IEPOX is mainly formed in the low NO<sub>x</sub> pathway. Therefore the author states that the correlation between NO<sub>x</sub>/isoprene can be attributed to IEPOX. But, the yield of glyoxal in high and low NO<sub>x</sub> conditions are different. Chan Miller et al. shows in his paper (Figure 2) that glyoxal formed from isoprene oxidation has a higher yield at low NO<sub>x</sub> condition compared with a high NO<sub>x</sub> condition. Therefore, I believe the increase of reversible aqSOA could be at least partially attributed to glyoxal. The author needs to specify all these possibilities in the paper rather than attributing the reversible aqSOA solely on IEPOX. The conclusion in the abstract as well as throughout the paper is too strong and needs to be revised.

Besides comparing WSOC<sub>p</sub>, dry/WSOC<sub>p</sub> with isoprene concentration, has the author studied the influence of ambient humidity on WSOC<sub>p</sub>, dry/WSOC<sub>p</sub>? Moreover, from Table S1, it seems that when ambient RH=80%, the RHs of the samples passed through the silica gel dryer were consistently higher in the summer time than in the winter time. What are the reasons and would that cause artifacts of the results?

Because IEPOX usually undergoes reactive uptake with high acidity aerosols (Gaston et al., 2014; Riedel et al., 2015), people have been assuming that isoprene-derived SOA is not very important in low acidity aerosols. However, the result presented in this study shows the importance of isoprene-derived SOA even for low acidity aerosol particles, especially when there is an amount of liquid water in the aerosol so IEPOX can have reversible partitioning. The author should probably talk about the importance of this aspect in the atmospheric implication section as well.

#### Minor Comments

Page 1, line 31. Oxford comma is recommended here after glyoxal.

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Page 2, line 1. Besides all the literature the author listed here, I believe Riedel et al., (ES&T Letters, 2015) should also be included as well when talking about reactive uptake of IEPOX.

Page 2, line 14. The author used an incorrect example here. Oligomerization is a non-reversible process, as also shown in De Haan et al. that the author cited.

Page 2, line 15. Oxford comma is recommended here after inorganics.

Page 3, line 25. Because the author performed the experiment using a home-built mist chamber, is there any characterization of this mist chamber, such as recovery efficiency of the gas phase species? Such information would help the reader in understanding the performance of the mist chamber and also error bar of the measurement.

Page 5, line 10. Has the author compared the ambient RH of summer and winter times? Does ambient RH have an effect on WSOC<sub>p</sub>, dry/WSOC<sub>p</sub>

Page 5, line 33-34. As previously mentioned, it would be better if the author could compare other BVOCs with WSOC obtained from this study to rule out the possibilities of other BVOCs producing WSOC.

Page 7, line 21. Has the author examined the relationship between ozone and WSOC<sub>p</sub>? If there is a correlation, then it means other BVOCs can also contribute to WSOC<sub>p</sub> as well.

Page 7, line 33-35. The sentence "If isoprene is indeed..." seems to be out of the place here because it does not go with the sentence below logically. The author can either elaborate more on this sentence or delete this sentence.

Page 8, line 22. AOD was not defined previously. Please define.

Page 8, line 23-line 36. This paragraph is pretty confusing because there are different concepts and ideas intertwined with each other. The author can talk about the results in Fig. 1 first, and then mention Liu et al. and Riva et al., and lastly talk about McNeil

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et al.

Page 8, line 32-line 33. What are the traditional SOA pathways? I would recommend specifying it more clearly because “uptake to aqueous particles” sounds like a traditional pathway of SOA formation to me as well.

Page 8, line 36. Perhaps I am missing something here. Why is the reversible aqSOA even higher given that ~10 to 15% of the total WSOCp evaporates?

Page 9, line 15. The reason that ambient IEPOX-SOA has a low volatility can additionally be attributed to the higher viscosity of SOA. If the viscosity of the SOA is higher, then it will be more difficult for the semi-volatile species to evaporate and escape from the particle phase within the timescale of the measurement, as discussed in Vaden et al. (2011) and Zhang et al. (2015). This can be another reason why some ambient aerosols do not show strong reversibility and the author should consider putting it in the discussion.

Page 10, line 13-line 21. This paragraph is confusing as well. At the beginning of the paragraph the author seems to believe the effect of ALW on WSOC is not as significant as OA concentration. By the end of the paragraph the author concludes that WSOC is not due to OA partitioning. Please revise this paragraph to give a clearer explanation.

Page 10, line 18. Please define LV-OOA and SV-OOA before using these two terms.

#### References

Prisle, N. L., Engelhart, G. J., Bilde, M. & Donahue, N. M. Humidity influence on gas-particle phase partitioning of  $\alpha$ -pinene + O<sub>3</sub> secondary organic aerosol. *Geophys Res Lett.* 37 (1), doi:10.1029/2009GL041402, (2010).

Wildt, J. et al. Suppression of new particle formation from monoterpene oxidation by NO<sub>x</sub>. *Atmos Chem Phys.* 14 (6), 2789-2804, doi:10.5194/acp-14-2789-2014, (2014).

Chan Miller, C. et al. Glyoxal yield from isoprene oxidation and relation to formalde-

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hyde: chemical mechanism, constraints from SENEX aircraft observations, and interpretation of OMI satellite data. *Atmos Chem Phys.* 17 (14), 8725-8738, doi:10.5194/acp-17-8725-2017, (2017).

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Vaden, T. D., Imre, D., Beránek, J., Shrivastava, M. & Zelenyuk, A. Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol. *Proc Natl Acad Sci USA.* 108 (6), 2190-2195, doi:10.1073/pnas.1013391108, (2011).

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A formatted version of the above comments is attached in the supplement.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-702/acp-2017-702-RC3-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-702>, 2017.

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