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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The effects of isoprene and NO_X on secondary organic aerosols formed through reversible and irreversible uptake to aerosol water" *by* Marwa M. H. El-Sayed et al.

Anonymous Referee #1

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Summary:

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 NOX 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

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Discussion paper

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 NOX) seem to suggest that low-NOX isoprene-derived aqSOA is more prone to reversibility than high-NOX 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:

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.

Furthermore, the Atmospheric Implications section and any discussion that follows lacks some key components. For example, peroxymethacryloyl nitrate (MPAN) is a known NOX reservoir formed through the photooxidation of biogenic hydrocarbons (Bertman and Roberts, 1991; Tuazon and Atkinson, 1990), yet it is not mentioned in any high-NOX 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 NOX influence on aqSOA appears shallow. Several times throughout the document the authors specify that low-NOX conditions are responsible for reversible aqSOA yet the only compounds mentioned are isoprene epoxydiol (IEPOX), glyoxal, methylglyoxal, and other low-NOX products. With the increase of anthropogenic activity, this may warrant further discussion.

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, NOX, and WSOC so that the data in this manuscript can come into context, e.g. Fig. 1. This timeseries 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.

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. 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.

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.

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 sub-section.

In the Conclusion section, the first paragraph reads: "Lower NOX 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 NOX 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.

A schematic / diagram of the setup is highly encouraged. This would help envision the split of WSOCp and WSOCg.

For my clarification, can the authors explicitly state the difference between aqSOA and WSOCp? I'm assuming a major difference is that WSOCp 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?

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

Minor Comments:

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).

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. 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.

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.

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.

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

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

Page 2 Line 37: Consider substituting ‘reaction’ with ‘oxidation’.

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.

Page 3 Line 5: Consider rewording “with our understanding” to “with the understanding”.

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

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

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.

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

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.

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?

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

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

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.

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.

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

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.

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 WSOCP,dry/WSOCP are from data collected for this manuscript, hence, would not be previously published.

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.

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?

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 WSOCg 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.

Page 6 Line 29: The authors suggest that the chain of reactions leading isoprene to be converted to WSOCg is $\sim$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? Is regional terpene, sesquiterpene, or agriculture emission chemistry considered? If it is beyond the scope of the article it should be stated.

Page 7 Lines 13-14: "Consistent with Fig. 3 and Fig. 4..." – I do not understand why WSOCg is strongly correlated with isoprene for lags of 3-5h (Fig. 3) whereas Evaporated WSOCp is correlated with isoprene for lags of 6-11 h? If evaporated WSOCp is an example of reversible aqSOA as is WSOCg 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.

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.

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.

Page 7 Line 34: Consider rephrasing.

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.".

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.

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

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

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.

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.?

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.

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

Page 10 Line 23: Consider an Oxford comma.

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

Page 11 Line 17: Remove first sentence.

Comments on Figures and Tables

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

timeseries 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).

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.

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.

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 WSOCg 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.

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.

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