

***Interactive comment on “Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM<sub>2.5</sub> collected from the Birmingham, Alabama ground site during the 2013 Southern Oxidant and Aerosol Study” by W. Rattanavaraha et al.***

**Anonymous Referee #4**

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This paper presents novel data from solvent-extracted filter-collected aerosol in the southeastern United States during the SOAS campaign in summer 2013, which has been analyzed to understand the distribution of isoprene oxidation products, as well as correlated against other measurements to elucidate formation mechanisms of these species. This is a good contribution to understanding of anthropogenic effects on SOA formation from isoprene, and I recommend publication after minor corrections & consideration of a few questions.

C1

Questions:

1) On p. 16 you describe the slightly lower contribution of the low-NO<sub>x</sub> pathway tracers at your BHM urban site – 93% compared to 97-98% at the more rural sites. Do I understand this contribution analysis correctly to imply that at all 3 sites the overwhelming majority of isoprene SOA tracers are from the “low-NO<sub>x</sub>” pathway? Given that your site is urban, does this suggest that a rethink of the “high-NO<sub>x</sub>” / “low-NO<sub>x</sub>” split of these tracers is in order? Or, how do you understand the fact that in an urban center with 3-15 ppb NO<sub>x</sub>, only 7% of the isoprene SOA tracers appear to be “high-NO<sub>x</sub>” products?

2) The lack of diurnal variation between avg daytime and nighttime concentrations of isop-SOA tracers is interesting. Do you think this is mainly because they are long-lived and formed upwind? Or do you think there might be some offsetting daytime higher source strength and nighttime temperature-driven higher particle partitioning? Maybe add a bit of discussion of this around line 374. As I mention later, I also think the diurnal cycle/day-night comparison supplemental figures should go in the main paper.

3) Couldn't the NO<sub>x</sub>/NO<sub>y</sub> plume age correlation with O<sub>3</sub> you mention at the beginning of 3.3.1 be just be a consequence of the relative diurnal variations you mentioned previously in NO<sub>x</sub> and O<sub>3</sub>? Thus, plume age could be actually not changing much... suggest thinking about this in your discussion. Related question pertaining to the negative correlation of plume age and 2-MG mentioned at the top of page 19: do you see a typical diurnal cycle of “plume age”, or is the variation mostly in the day to day differences? (also related: are we looking at intensives data here or just day/night samples?) I'm wondering if this could just be saying that 2-MG has a pretty consistent diurnal cycle, with a peak in the afternoon after NO<sub>x</sub> has decreased.

4) Towards the middle and bottom of p. 19 you are talking about both NO<sub>2</sub> and NO<sub>3</sub> enhanced MAE/HMML derived SOA formation. You seem to be assuming that these might have similar structures – my first question: is there a known mechanism for MAE/HMML from NO<sub>3</sub> + isoprene? Because usually NO<sub>3</sub> initiated chemistry retains

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the NO<sub>3</sub> group, I would expect it to make different products than these. Further down in that paragraph that goes onto the next page: I don't think it's at all obvious that high-NO<sub>x</sub> SOA tracers would be the same as NO<sub>3</sub> chemistry tracers – the nitrate group is at a different position in the molecule when formed via isopRO<sub>2</sub>+NO vs. NO<sub>3</sub>+isoprene chemistry.

Minor suggestions/edits:

- 1) line 52: "indicates that" => "is consistent with the observation that"
- 2) line 54: "the reports" => "previous studies suggesting"?
- 3) line 61: remove "potential"?
- 4) lines 72-73: add mention of biogenic sources of VOCs here too
- 5) line 90-91: phrase "isomeric isoprene epoxydiols" is a bit confusing – maybe "multiple isomers of isoprene epoxydiols"?
- 6) line 111: "considerable" doesn't sound quantitative– maybe "large"?
- 7) line 120: "estimates" => "estimated"
- 8) lines 122-123: I think it hadn't yet been stated that IEPOX is necessarily formed in the particle phase – a brief explanation somewhere before this conclusive statement would be good.
- 9) around lines 129-130: does this addition only increase accuracy of isoprene SOA prediction, or total SOA prediction more generally?
- 10) lines 133-136: a little unclear – I think what you mean to say here is in order to develop feasible control strategies, not in order to understand?
- 11) line 145: mention here that you're talking about filter collected also in BHM (right?), not just as part of SOAS.
- 12) lines 146-148: you've already introduced these acronyms, so I think you can just

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use the abbreviations here

- 13) line 188: suggest to add a bit more details here which (relevant) trace gases were measured, and that they were measured continuous as well
- 14) Around line 199: suggest adding a brief discussion here of the target functional group of the derivatization – what chemical conversion are you doing, and what class of compounds does it enable quantifying?
- 15) Around line 220-221: Are you analyzing derivatized or not in this case? It's unclear from the way you reference section 2.2.1. Also I think you mean to refer to section 2.2.2.
- 16) line 290: omit "°" in front of temperature
- 17) line 299: do you mean to again compare intensive days to regular days with the "lower"? if so, I recommend mentioned also the averages for intensive days, with parallel structure to the sentence above: "on intensive days, compared to ..., ... and ... on regular sampling days." Or, if you actually meant to compare to the concentration of O<sub>3</sub> itself, I don't understand why.
- 18) line 307-308: don't you have a direct measurement of OC that you could also compare to the Budis and Hu 2015 references' values to confirm your hypothesis here?
- 19) Line 312: remove hyphen in "High-NO<sub>x</sub>" since it's not used as an adjective here.
- 20) line 313: "most likely in conjunction with rising O<sub>3</sub> levels": what does this mean? are you suggesting the major NO<sub>x</sub> loss is to reaction with O<sub>3</sub>? I think rather you're making RONO<sub>2</sub>/ROONO<sub>2</sub>/HNO<sub>3</sub> and also the BL height is increasing - and NO<sub>x</sub> emissions peak at rush hour, while O<sub>3</sub> production cranks along all day driven by radiation. So, NO<sub>2</sub> goes down while O<sub>3</sub> goes up, but in my opinion, "in conjunction with" suggests a direct chemical connection that isn't likely the major reason they show the opposite trend

C4

- 21) line 323: the referred to AMS here was at CTR, correct? Suggest you say so.
- 22) line 354: suggest “ranging up to”
- 23) line 359: “was” => “were”
- 24) line 360: “an increased” => “a larger”
- 25) line 365-366: “of that . . . OM mass.” awkward phrasing – suggest rewording.
- 26) line 367: start a new paragraph at “Levogluconan. . .”?
- 27) line 369-370: more BB influence at the urban site! This surprises me – why do you think this would be the case? Is there any other confirmatory evidence of this? Or are there other possible sources in an urban area? I would have thought rural areas would have more BB contributions, because of regional crop burning. . .
- 28) line 375: remove “also”
- 29) line 378: now you are talking about there BEING some diurnal variation, where the beginning of this paragraph talks about no difference day/night. I suggest reworking the text to clarify – I guess you’re looking at different sets of samples, but it’s confusing as written.
- 30) line 379: do you mean no stat. sig. DIFFERENCE between periods? And, do you mean between different times of day within the intensives, or between different 2-day intensive sampling periods? (I have the same question in some of the SI captions)
- 31) line 393: first report of an “r” instead of  $r^2$  . . . makes comparisons tricky. Maybe just keep as  $r^2$  but mention the correlation is negative?
- 32) line 404: concentration would only increase with lowering PBL height if isoprene continues to be emitted at night . is it?
- 33) line 406: if MPAN oxidation is responsible for 2-MG formation, you’d need to see the NO<sub>2</sub> correlation, which you don’t, correct?

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- 34) line 419: “initiated” (spelling error)
- 35) lines 424-428: this isn’t super clear : are you saying that Ng 2008 didn’t see this correlation because they didn’t have RO<sub>2</sub>+HO<sub>2</sub> reactions, and you’re attributing your observation of a weak correlation to those RO<sub>2</sub>+HO<sub>2</sub> rxns and not RO<sub>2</sub>+RO<sub>2</sub> or RO<sub>2</sub>+NO<sub>3</sub>, which Ng would have observed exclusively? Suggesting reworking the text.
- 36) line 452: suggest “putative” => “potential”
- 37) line 475: briefly explain “salting-in” chemistry
- 38) lines 485-486: “may stem from. . . campaign”: add, or the fact that it was always plenty acidic and thus not at all pH-limited! (not just that it was relatively constant)
- 39) lines 498/499: depending on how you end up discussing this high-NO<sub>x</sub>/low-NO<sub>x</sub> idea, consider reminding the reader here of which products correspond to which NO<sub>x</sub> regime.
- 40) line 504: you mean specifically, without the intermediate of IEPOX, right? If so, say so.
- 41) line 522: “effect” => “affect”
- 42) lines 534-536: “in addition . . . regimes.” seems to be introducing some new ideas – be sure you say something about this above in the main text.
- 43) lines 439-545: “In this study . . . (Riva et al., 2015).” I think the bulk of this text should go above in 3.3.2. with just a summary here - seems like you’re presenting some new correlations here in the conclusions section.
- 44) lines 555-556: again, nearly invariant and ALWAYS very acidic is the key I think you’re trying to present here.
- 45) line 560: “since urban emissions are directly present” => “ in the presence of fresh urban emissions”

C6

46) Table 1: the periods for the intensive aren't clear to me - the 4 sampling periods suggest coverage of 2 days, but these periods list 3 days - ?

47) in table 4: I assume the bold lines are aggregated tracers for MAE/HMML vs. IEPOX? Explain in the caption

48) Table 5: "average amount detected tracers" => "average fraction of detected tracers"

49) Fig. 2: Looks like NO<sub>x</sub> peaks are mostly during fires, based on CO spikes concurrent? Does this affect any of the plume age analysis?

It's quite hard to discern any day/night patterns here - maybe average day & night values, with SD bars, for some key metrics would be a good figure to include in the main body text? Also, add your plume age calc here to the time series? I'm curious how much it varies over the campaign vs. has a typical diurnal pattern.

50) In caption of Fig. 4: say something about this being a smaller fraction than Fig. 3 – because significantly weaker correlation.

SI: I would put S5-S7 in the main body of the paper. Also, in those captions, when you say there is "no significant variation was observed amongst intensive samples", do you mean to compare different date periods where you did the 4 time chunks, or do you mean between the 4 time chunks over all of the date periods where you did that finer time resolution, or both? please clarify

An SI figure with a couple key structures & corresponding acronyms would be nice (MAE, HMML, etc.)

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