Review of “Characterizing source fingerprints and ageing processes in laboratory-generated secondary organic aerosols using proton-nuclear magnetic resonance (1H-NMR) analysis and HPLC-HULIS determination.”

General Comments:

This manuscript describes the chemical analysis of laboratory-generated secondary organic aerosol (SOA) from isoprene, alpha-pinene, and naphthalene precursors. The authors generate SOA within a Potential Aerosol Mass (PAM) oxidation flow reactor, varying actinic flux to achieve various overall OH exposures, collect SOA on quartz fiber-filters, and then extract water soluble organics for analysis using 1H-NMR and HPLC. The authors find that with increased OH exposure 1H-NMR analysis shows further oxidized organic material being generated, consistent with spectroscopic features of known oxidation products from the studied systems. In comparison to 1H-NMR and HPLC analysis of ambient samples taken from the Po Valley, Italy, and Cabauw, Netherlands, the authors find that highly-oxidized alpha-pinene SOA 1H-NMR spectroscopic features and HULIS chromatographic features from similarly aged alpha-pinene and naphthalene most resemble that of the ambient samples.

Overall the manuscript is clearly written and the experimental setup and analysis straight forward. The results have potential to be of interest to ACP readers, though I think improvements are needed in discussing and considering the true atmospheric relevance of the current work. In particular, the inclusion of the isoprene results seem superfluous and of confusing atmospheric relevance because of potentially contradictory experimental conditions used and results obtained, and also because the selected ambient samples were not taken from areas notable for isoprene-dominated chemistry. Additional experimental methodology should be clarified as well. After specific and technical comments are addressed below, this manuscript may be suitable for publication in ACP.

Specific comments:

1. Lines 31-32: Please clarify the definition of the maximum yield %’s listed. Are these yields mass of HULIS generated per mass of precursor reacted away, similar to an SOA yield? If so, please provide quantification/calibration information. Rather, are they fraction of WSOC that is designated as HULIS (as presented in SI Figs. S3, S4)?
2. Lines 50-79: In light of the discussion here, the authors should provide additional context about the major SOA formation processes governing their particular experiment. Since the experiments are unseeded, what is the relative importance and timescale of nucleation, heterogeneous oxidation, and gas-particle partitioning in generating the characterized SOA? And how do these processes and timescales differ with ambient timescales even if similar total OH exposure is achieved?
3. Line 73: Consider including these additional references in discussing vapor-phase wall losses: (Matsunaga and Ziemann, 2010; Ye et al., 2016)
4. Lines 87-89: This statement does not seem fair or accurately written considering the authors cite work of Cavalli et al., 2006 later for comparing alpha-pinene SOA and plenty of 1H-NMR spectroscopy has been performed on SOA samples from urban areas e.g. (Cleveland et al., 2012). Do the authors want to reword the sentence to specify something specific about novelty of applying the technique to *laboratory-generated* SOA from known biogenic and anthropogenic SOA precursors?

5. Lines 151-153: Can the authors clarify if this choice in using the buffer has to do with the specific products expected from non-IEPOX isoprene chemistry that may be subject to chemical shift of the hydrogen atoms?
6. Interpretation of isoprene results in Section 3.1.3 NMR fingerprints of non-IEPOX isoprene SOA: In light of the experimental conditions being dry (according to lines 117) and unseeded, why do the authors attribute the spectroscopic features to 2-methyl tetrols as products in their experiments? These are typically observed as particle-phase products resulting from IEPOX route of SOA formation from isoprene, but the authors claim their conditions may resemble more of non-IEPOX route of SOA formation according to Krechmer et al., 2015 in lines 107-112 and Liu et al., 2016 in lines 249-250. Do the authors suggest that peroxide-equivalents of 2-methyl tetrols (formed via nucleation under their experimental conditions?) would have the exact same NMR fingerprint as 2-methyl tetrols? If so, this really weakens the use of NMR fingerprints with true molecular-level mechanistic understanding. The authors should reconcile their measurements and the mechanism more clearly.
7. Lines 279-281, Lines 355-361: The authors should clarify if water extraction methods of the organic material from filters can lead to aqueous processing and artificial formation of HULIS.
8. Line 298: The experimental setup is dry. How can the authors be certain that they are generating the same compounds in SOA formation/mimicking atmospherically relevant mechanisms from their chosen precursors and then comparing to WSOC from atmospheric samples?
9. Lines 346-349: While this may be true, Figure 8 seems to suggest that even just fresh naphthalene SOA has the closest WSOC breakdown of HPLC fractions with the ambient OA sample. This suggests that the experimental results are getting the right HPLC fractions, but not necessarily for the right composition/same mechanisms and for that matter the same oxidative aging. Considering the ambient sample is from a rural site, it also seems odd that the naphthalene WSOC breakdown is so close to that observed.
10. Please provide additional context for the ambient samples from Cabauw and Po Valley. Are the campaigns noted to be regions of high monoterpene emissions and anthropogenic (aromatic) emissions? They are both described as be rural sites, yet see comment 9 above.
11. Figures 1-3: Similar to the regions pointed out in HPLC results for neutral, mono/di-acids, HULIS, it would be helpful if there were similar labels pointing out characteristic bond features associated with the chemical shifts in the 1H-NMR spectra.
12. Figures 1-6: As plotted, it is sometimes difficult to really compare the intensities along an arbitrary y-axis with no units to compare peak heights and especially with peaks that extend into another sample's y-axis. Consider individual y-axes for each sample with relevant ticks or overlaying some samples' spectra?
13. Figure 9: Seems like the range of f44 is in quite good agreement with HULIS as shown in triangle plot of (Ng et al., 2011). What about f43? This would strengthen argument of associated HULIS with photochemical age and atmospheric relevance.

Technical comments:

1. Lines 39-40: Sentence is awkwardly worded. Please revise, e.g. “In the mid 2000’s the discovery that oxidized organic compounds dominate in concentration compared to that of primary organic compounds outside urban areas…”
2. Line 186: Spelling on “twards”
3. Line 296: Missing alpha symbol for alpha-pinene
4. Line 329: Insert “to” after “up”.

References:

Cleveland, M. J., Ziemba, L. D., Griffin, R. J., Dibb, J. E., Anderson, C. H., Lefer, B. and Rappenglück, B.: Characterization of urban aerosol using aerosol mass spectrometry and proton nuclear magnetic resonance spectroscopy, Atmos. Environ., 54, 511–518, doi:10.1016/j.atmosenv.2012.02.074, 2012.

Matsunaga, A. and Ziemann, P. J.: Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements, Aerosol Sci. Technol., 44(10), 881–892, doi:10.1080/02786826.2010.501044, 2010.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H. and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11(13), 6465–6474, doi:10.5194/acp-11-6465-2011, 2011.

Ye, P., Ding, X., Hakala, J., Hofbauer, V., Robinson, E. S. and Donahue, N. M.: Vapor wall loss of semi-volatile organic compounds in a Teflon chamber, Aerosol Sci. Technol., doi:10.1080/02786826.2016.1195905, 2016.