

## ***Interactive comment on “Characterizing source fingerprints and ageing processes in laboratory-generated secondary organic aerosols using proton-nuclear magnetic resonance (<sup>1</sup>H-NMR) analysis and HPLC HULIS determination” by Nicola Zanca et al.***

**Anonymous Referee #1**

Received and published: 14 March 2017

1. General comments: This article reports a very interesting study on the compositional features of secondary organic aerosol (SOA) samples generated using a Potential Aerosol Mass (PAM) oxidation flow reactor using organic precursors that are well-established source fingerprints: alpha-pinene (most studied biogenic VOC), naphthalene (proxy for anthropogenic aromatics), and isoprene (most abundant biogenic VOC). The generated SOA samples were characterized/analyzed by means of proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy and ion-exchange chromatogra-

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phy coupled to a UV detector (on-line) and a TOC analyzer (off-line). SOA is one of the least understood constituents of fine aerosol particles; current widely-used models cannot predict its atmospheric loadings, oxidation state, or even the nature of the atmospheric ageing processes. Understanding, characterize, and (semi-)quantify the effects of SOA formation and ageing is challenging because it requires a different framework to capture and describe the continuous evolution of the structural features of organic compounds. Nonetheless, if those aims are attained, the outcomes will be very important for the atmospheric chemistry modelling community. In this Reviewer opinion, the topic of this paper is relevant to the journal's interests and will be of interest to readers. Studies such as this one are needed to advance our understanding on SOA oxidative aging mechanisms at ambient conditions. All in all, the quality of the measurements is excellent and the presentation and discussion of data is good. Nevertheless, this Reviewer has identified some issues requiring further clarification from the Authors. I recommend publication of this study after the Authors consider the specific comments (below).

2. Specific comments: - Section 3.1.1, lines 198-200: Although there is a change in the intensity of NMR peaks between 1 and 3 ppm of alpha-pinene SOA with photochemical age, the <sup>1</sup>H NMR spectra of alpha-pinene SOA at medium ageing still exhibits resonance at the same chemical shift regions of alpha-pinene SOA with low oxidation level. Therefore, I do not think that there is a sharp change of NMR fingerprinting of alpha-pinene SOA already at medium ageing.

- Section 3.1.2, line 218: The Authors state that “moderately aged SOA show mainly the two singlets of phthalic acid” in the aromatic region. The singlets of phthalic acid should appear/resonate at approximately 8.1 ppm. This assignment is unclear in the spectra of naphthalene SOA (Figure 2) due to the presence of a broad resonance at approximately 7.2-8.3 ppm.

- Section 3.1.2, lines 218-221: Besides exhibiting NMR peaks between 3.5 and 6.0 ppm, all spectra also exhibit noticeable NMR peaks between 1 and 2 ppm. Could

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these NMR resonances be still a consequence of the presence of colloidal hydrophobic material in solution, or they could be attributed to aliphatic structures derived from the ageing process?

- Section 3.1.2, lines 224-229: In my opinion, the broad aromatic band between 6.5 and 8.5 ppm is totally indiscernible in the spectrum of the most aged naphthalene SOA sample. I am also compelled to disagree when the Authors conclude that “there is no clear trend in the formation/disappearance of aromatic and aliphatic bands with ageing”. In my opinion, the <sup>1</sup>H NMR spectrum of the most aged sample clearly indicate the disappearance of resonance in the aromatic region, whereas a few NMR peaks resonate in the aliphatic region (chemical shifts = 3.5 and 5.0 ppm). The Authors should include additional explanations to support their statement/conclusion.

- Section 3.2, lines 275-276: The chromatograms in Figure 5 suggest that the signal intensity of the chromatographic peaks corresponding to mono- and di-acids increases with increasing photochemical age, which seems to contradict the statement “that the TOC mass fraction of mono- and di-acids decreases from 33% to 18%” with increasing photochemical age. Besides, in lines 273-374, the Authors conclude that “a net increase in acidic compounds with photochemical age can be clearly observed”. Additional explanations should be provided to clarify these apparent conflicting conclusions.

- Section 3.2, line 282: the abbreviation “NC” for “neutral compounds” should have been previously defined in line 259.

- Section 4, lines 303-305: In Figure 7, it is unclear which marker correspond to ambient PEGASOS WSOC for the different oxidation levels.

- Section 4, lines 321-322: In the sentence “the H-NMR spectra of alpha-pinene SOA most closely mimic the functional group distributions of the ambient WSOC sample obtained in PEGASOS”, are the Authors referring to the spectrum in Figure S1? If so, please redirect the reader to Figure S1.

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- Section 4, lines 331-335: The Authors conclude that the correlation coefficients shown in Figure 7 for the NMR spectra of alpha-pinene vs. ambient WSOC are smaller than those between the HR-ToF-AMS spectra of PAM-generated SOA vs. ambient OOA reported in reference Lambe et al. (2011). Could this difference be explained by the fact that Lambe et al. (2011) is focusing on ambient OOA, which is a fraction of total organic aerosols (OA) and a proxy for SOA, whereas in this study the Authors are comparing the NMR spectra of alpha-pinene with those from the whole WSOC fraction which probably also includes a small fraction of primary OA? Secondly, I did not find Figure 9 in reference Lambe et al. (2011).

3. Technical corrections: - Section 2.1, Tables 1 and 2: There is some information missing from the “Oxidation Level” column for Pin#3 (Med.) and Pin#5 (Low) in Table 1, and for Iso#2 (med) in Table 2. Could you please also clarify the meaning of “f44” in these Tables? Is this corresponding to the m/z marker of COOH formation withdrawn from the AMS data? If so, this should be clarified in the manuscript.

- Section 2.2, line 144: Figure S1 shows the <sup>1</sup>H NMR spectrum of an ambient WSOC sample collected in San Pietro Capofiume and not the <sup>1</sup>H NMR spectra of methanol extracts from isoprene SOA samples. Instead, it could be Figure S2?

- Section 2.4, line 167: I did not find the full HPLC-UV-TOC analytical protocol in the Supplementary material.

4. References: Lambe A. T., Ahern A. T., Williams L. R., Slowik J. G., Wong J. P. S., Abbatt J. P. D., Brune W. H., Ng N. L., Wright J. P., Croasdale D. R., Worsnop D. R., Davidovits P., and Onasch T. B.: Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, *Atmos. Meas. Tech.*, 4, 445–461, 2011.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2017-91, 2017.

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