Replies to Referee 1's comments.

We thank the Referee for the through review. Below we copy his/her comments (in italics) and provide point-by-point replies.

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 (1H NMR) spectroscopy and ion-exchange chromatography 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 1H 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.

REPLY: There are indeed several specific resonances, some of which are known tracers of alpha-pinene oxidation, found in all alpha-pinene SOA samples, but their intensity decreases with ageing, especially between the fresh to the medium oxidation state samples. This shows up more clearly when using an y scale for Figure 1 illustrating the highest peaks (from pinic and pinonic acids in Pin#5 and Pin#6 samples) (see figure below). The integral of the resonance at 0.83 ppm arising from one of the two gem-methyls of pinonic acid changes from 2% and 3% of the total integral of the spectrum for samples Pin#5 and Pin#6, respectively, to 0.3% for all the other three samples. Therefore, the contribution of first generation oxidation products of alpha-pinene is one order of magnitude greater in fresh SOA than in the medium and high ageing state samples. This confirms that there is in fact a marked change in NMR fingerprinting already at medium ageing state. The figure below will be added in the Supplementary material. The text (lines 198-200 of the first submission) will be changed into:

"In the NMR spectra corresponding to a "medium" SOA oxidation level, the resonance at 0.83 ppm of chemical shift, arising from one of the two gem-methyls of pinonic acid, accounts for only 0.3% of the total integral of the spectrum, while it represented 2 – 3 % in the fresh SOA samples."
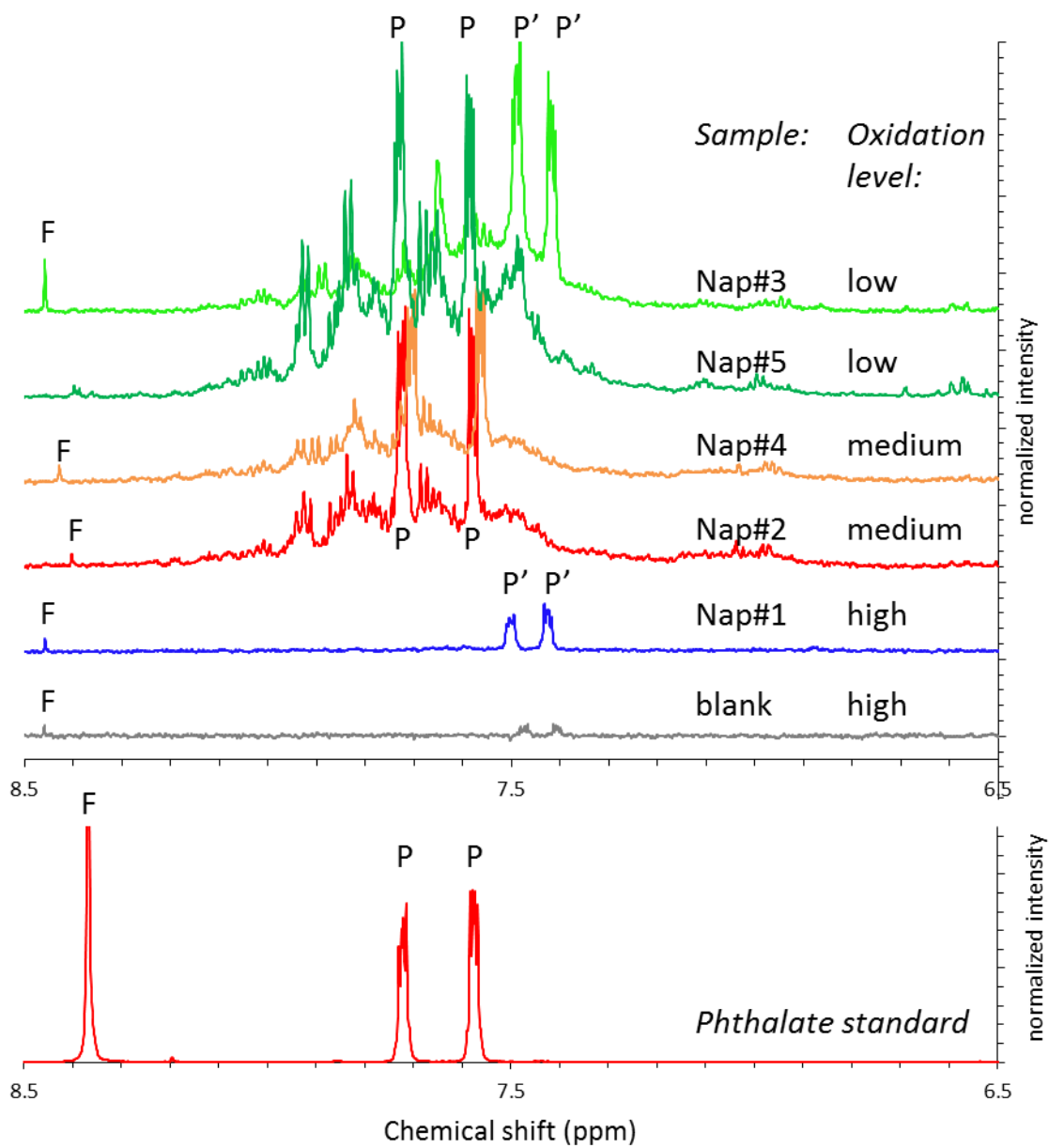
Chemical shift (ppm)
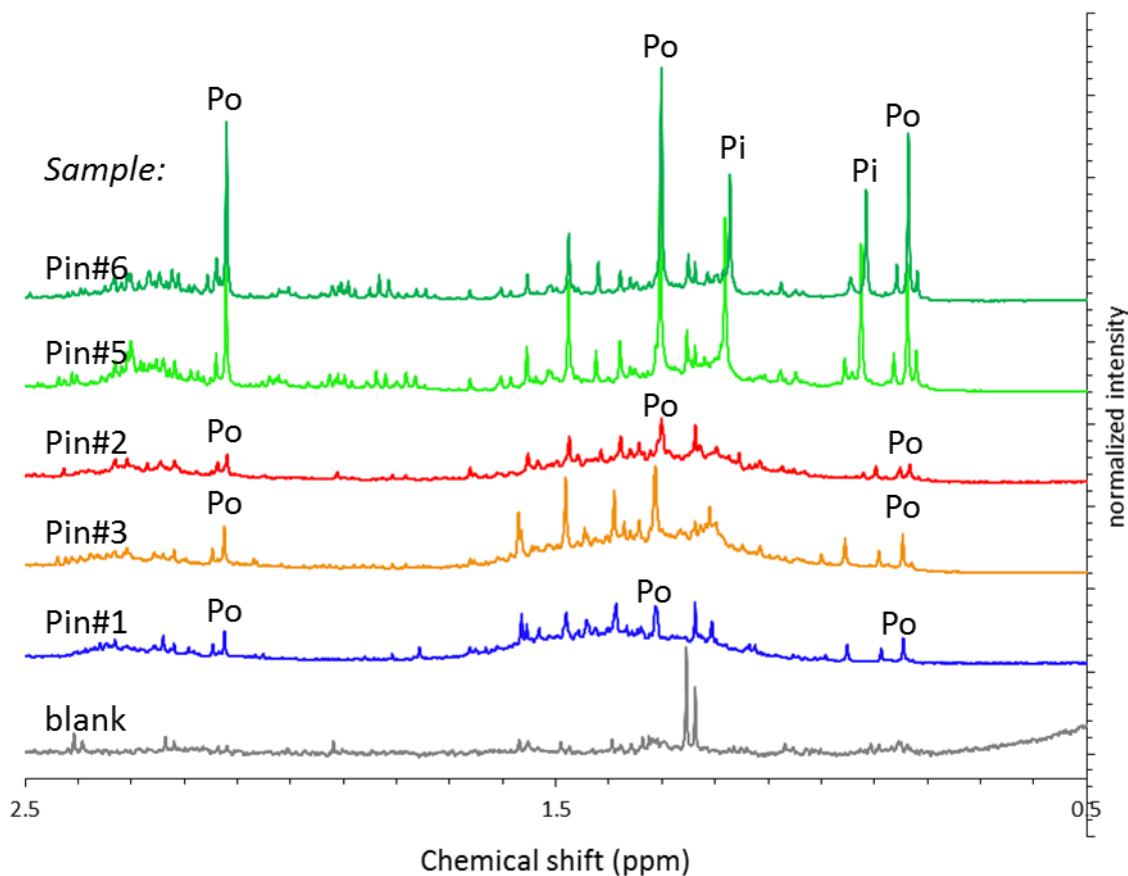
- *Section 3.1.2, line 218: The Authors state that "moderately aged SOA show mainly the two singlets of phthalic acid" in the aromatic region. The singlets of phthalic acid should appear/resonate at approximately 8.1 ppm. This assignment is unclear in the spectra of naphthalene SOA (Figure 2) due to the presence of a broad resonance at approximately 7.2-8.3 ppm.*

45

REPLY: Phthalic acid is a diprotic acid, and it can resonate in a range of chemical shifts depending on protonation sate, hence on pH of the aqueous solution. We have performed the NMR analysis of naphthalene SOA in unbuffered solution, therefore we expect the chemical shifts of carboxylic acids to differ to a certain

50 extent between samples. Below, we show a blow-up of Figure 2 of the original manuscript showing the aromatic region in more details. Most of the spectra show a very small singlet at 8.40 – 8.46 ppm which must be attributed to formate (marked with "F" in the figure). The 0.06 ppm difference in chemical shift between samples must be caused by pH differences in the solutions. At the bottom of the figure, we added the spectrum of a phthalic acid standard (potassium hydrogen phthalate) in buffered solution (a potassium deuterated

55 formate/formic acid buffer with pH~3.8, the same used for the isoprene experiments). The position of the formate peak indicates that the pH of the phthalic acid standard solution is approximately the same of sample Nap#2. Our test clearly indicates that the two complex resonances at 7.56 – 7.59 and 7.71-7.74 in sample Nap#2 - and of analogous peaks in samples Nap#4 and Nap#5 (marked with "P" in the figure) - must be attributed to phthalic acid. The other samples (Nap#1, Nap#3 and the blank) exhibit a system of peaks with

60 a fine structure similar to that of the standard of phthalic acid but resonating a lower chemical shifts (between 7.4 and 7.5 ppm) and marked "P' " in the figure. On the basis of the position of the formate peak, approaching 8.46 ppm, in these samples, the peak systems P' are presumably from phthalic acid, while in different pH conditions with respect to samples Nap#2, #4 and #5 and the phthalic acid standard solution.

65   Below, we present the same figure, with chemical shift range between 7.3 and 7.8 ppm enlarged, showing the fine structure of the phthalate resonances.
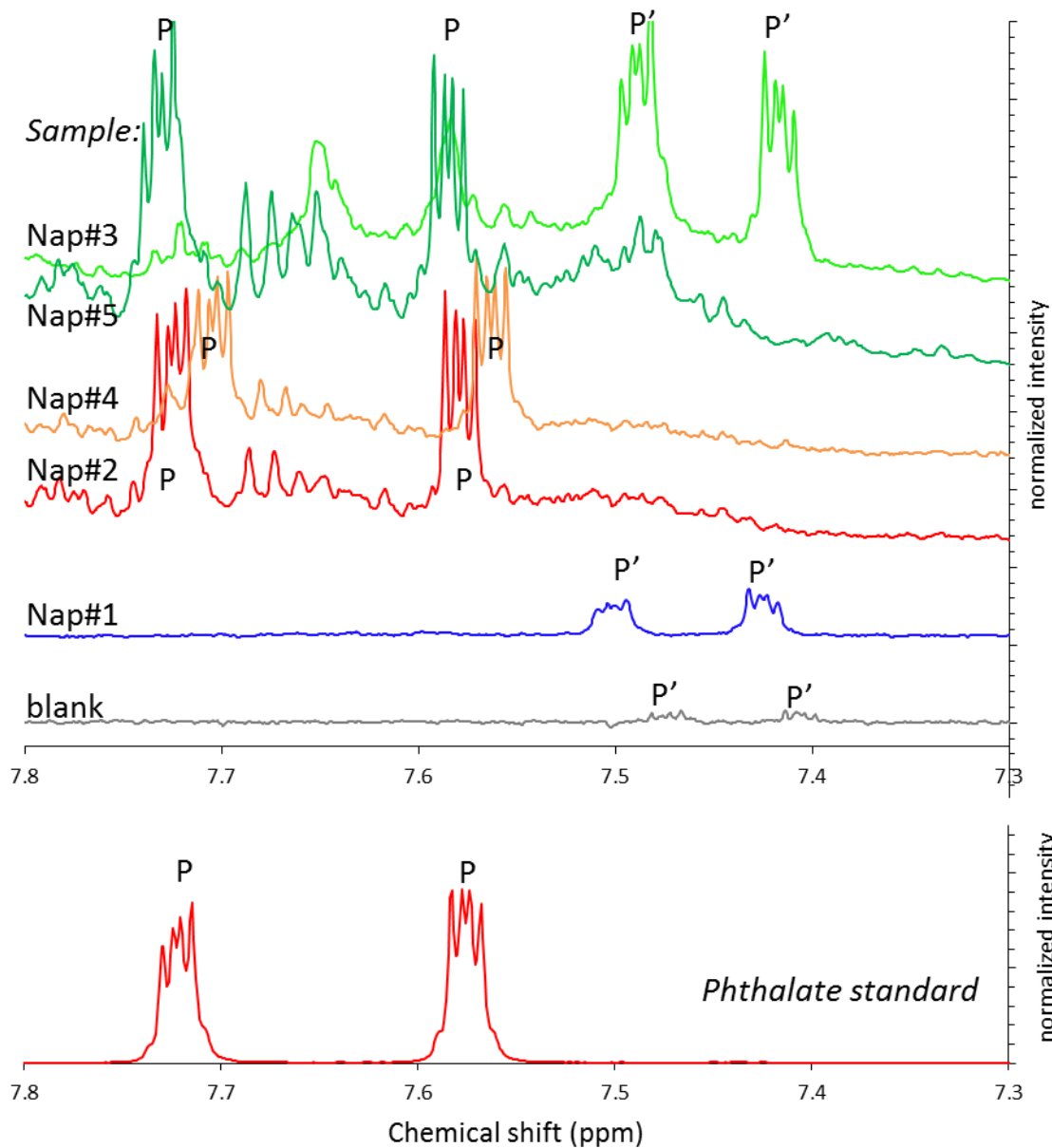
- Section 3.1.2, lines 218-221: *Besides exhibiting NMR peaks between 3.5 and 6.0 ppm, all spectra also exhibit noticeable NMR peaks between 1 and 2 ppm. Could these NMR resonances be still a consequence of the presence of colloidal hydrophobic material in solution, or they could be attributed to aliphatic structures derived from the ageing process?*

REPLY: The referee is right in pointing out the presence of multiple resonances between 1 and 2 ppm in the spectra of naphthalene SOA. It should be noted, however, that most of them are also found in the blank (spectrum in grey in the Figure 2). The inspection of such peaks in the blank suggests that α-pinene oxidation products, such as pinonic acid (peaks marked with "Po" in the figure below) and pinic acid (peaks marked with "Pi") together with other unidentified compounds (marked "X") from previous experiments have caused contaminations of the reactor during the naphthalene experiments (see figure below). Based on these results,

it is doubtful that any of the naphthalene SOA samples exhibited genuine resonances in the range between 1
and 2 ppm of chemical shift.
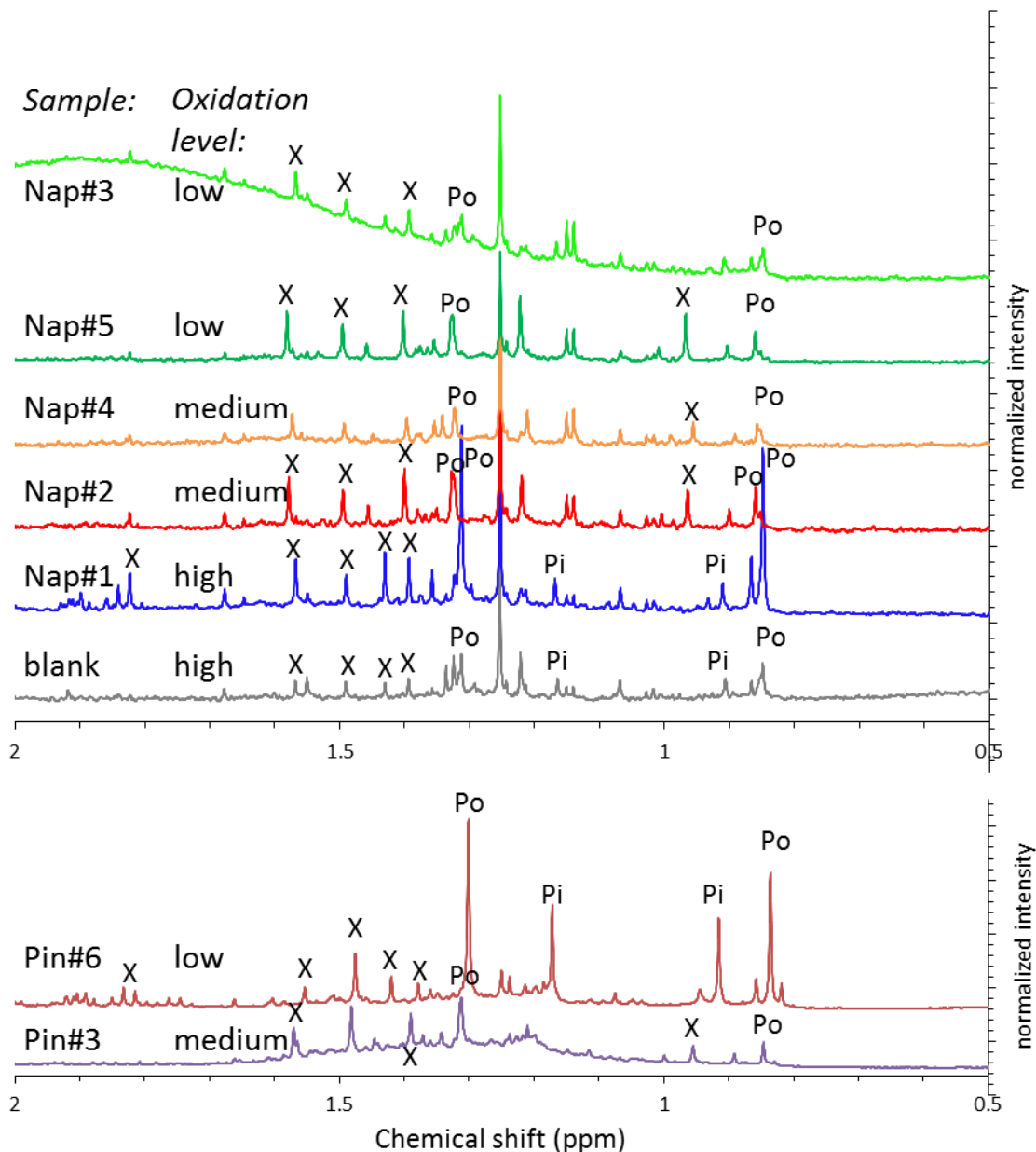
*- Section 3.1.2, lines 224-229: In my opinion, the broad aromatic band between 6.5 and 8.5 ppm is totally
indiscernible in the spectrum of the most aged naphthalene SOA sample. I am also compelled to disagree
when the Authors conclude that "there is no clear trend in the formation/disappearance of aromatic and
aliphatic bands with ageing". In my opinion, the 1H 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.*

REPLY: The inspection of the spectral feature of sample Nap#1 (the most aged naphthalene SOA sample)
is challenging due to the very small loadings and the interference from the reactor blank (see comment above).

If we restrict our analysis to chemical shifts higher than 2.5 ppm – to get rid of most blank signals – and enlarge the y scale of the spectra, we can have closer inspection of the resonances in sample Naph#1 (see figure below). In spite of the poor signal-to-noise ratio of this spectrum, a very broad aromatic band between 6.7 and 8.2 ppm is still visible in Nap#1, whereas the baseline is completely flat in the blank spectrum. The aromatic band is actually structured into two sections, with one from phenolic compounds (from 6.7 to 7.2 ppm) and a second one arising from aromatic structures substituted with electron-withdrawing groups (from 7.2 to 8.2 ppm). The latter is relatively much less intense than in the other naphthalene SOA samples. In conclusion, the small sample amount for Nap#1 prevents an accurate quantification of aromatic compounds. The Referee is right in noticing that the aliphatic groups between 3.5 and 5 ppm are much more concentrated in this sample with respect to aromatics; however, it is not entirely true that aromatic groups have completely disappeared in this sample.
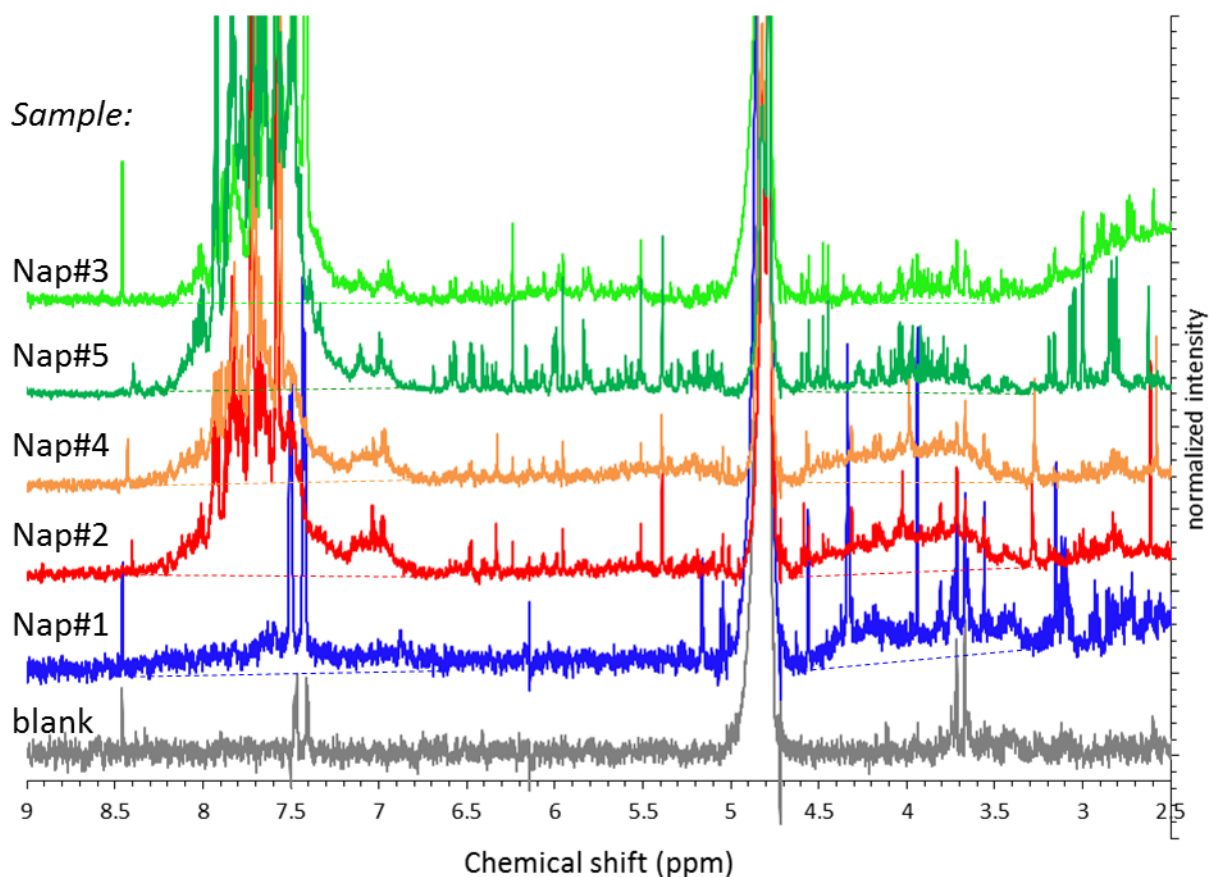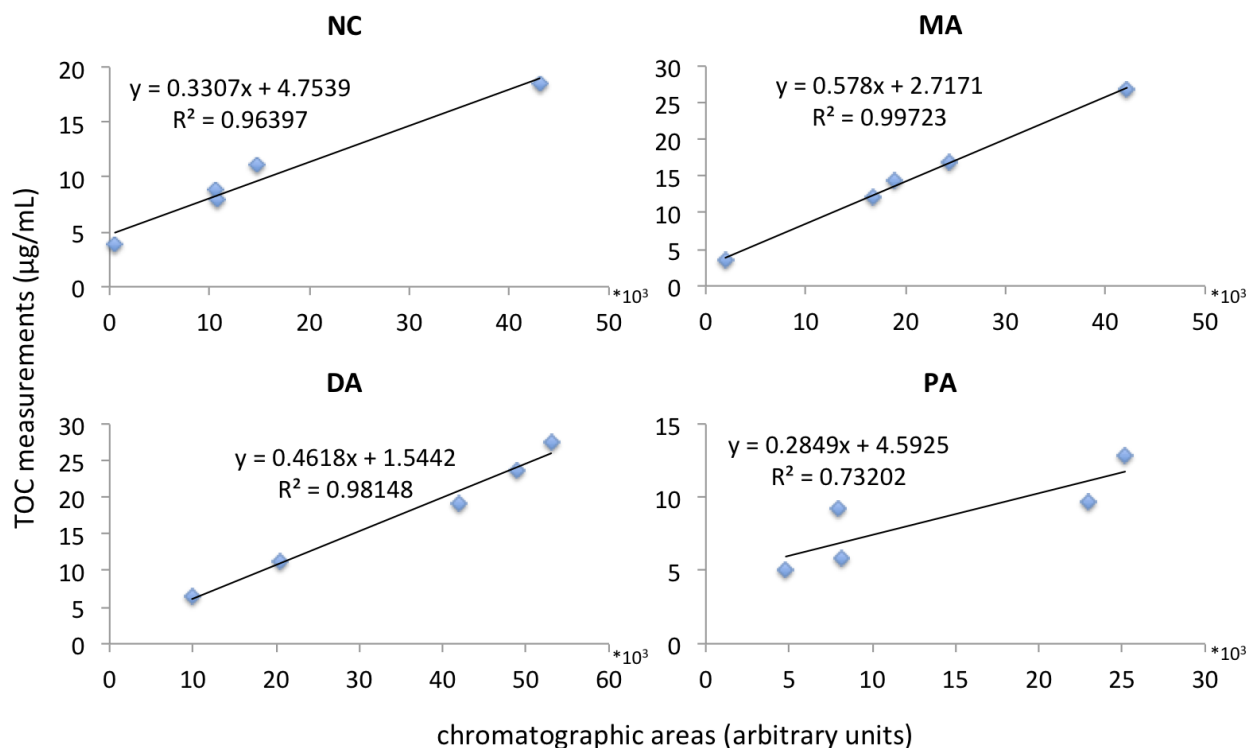

The text in the manuscript will be revised and implemented as follows:

"Despite the low naphthalene SOA concentration, a broad aromatic band between 6.5 and 8.5 ppm and the same signals found between 3.5 and 6.0 ppm seen in the samples with a medium O/C ratio are still visible in this most aged naphthalene SOA spectrum. However, the band from oxygenated functional groups between 3 and 4.5 ppm becomes relatively more intense with respect to aromatics compared to SOA samples of smaller ageing state. Compared to α-pinene SOA, the ^{1}H-NMR fingerprint of naphthalene SOA appears less sensitive to variations in the OH exposure between the low and the medium level of exposure. More substantial changes can be found for the most oxidized sample, which are only partly visible due the low signal-to-noise ratio of the spectrum."

- 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.

115

REPLY: There was a mistake in the text. The TOC mass fraction decreasing from 33% to 18% is only for

120 mono-acids, not for total mono-/di-acids. In fact, the fractional content of di-acids remained fairly stable during ageing in naphthalene SOA. The HPLC classes distributions for the naphthalene SOA samples are reported in Fig. S4 where the concentrations units are derived by the measured TOC content in the eluted chromatographic fractions instead of the integrals of chromatographic peaks. On the other hand, peak area and TOC content are clearly correlated for each HPLC fraction type (see figure below).

NC

$y = 0.3307x + 4.7539$
$R^2 = 0.96397$

MA

$y = 0.578x + 2.7171$
$R^2 = 0.99723$

DA

$y = 0.4618x + 1.5442$
$R^2 = 0.98148$

PA

$y = 0.2849x + 4.5925$
$R^2 = 0.73202$

TOC measurements (µg/mL)

chromatographic areas (arbitrary units)

125

The text will be revised as follows:

"However, the HULIS content, initially small, increases substantially and progressively with ageing. With increasing photochemical age, the TOC mass fraction of mono- and di-acids decreases from 33% to 18% and from 34% to 33% respectively, while the fraction of PA/HULIS increases from 11% to 30%".

130 Below we report Figure 5, reformatted also taking into account Referee 2's suggestions. We believe that the reduction of mono-acids and the relatively stable content of di-acids during ageing is clear from both the TOC measurements and the evolution of chromatographic peaks in Fig. 5.
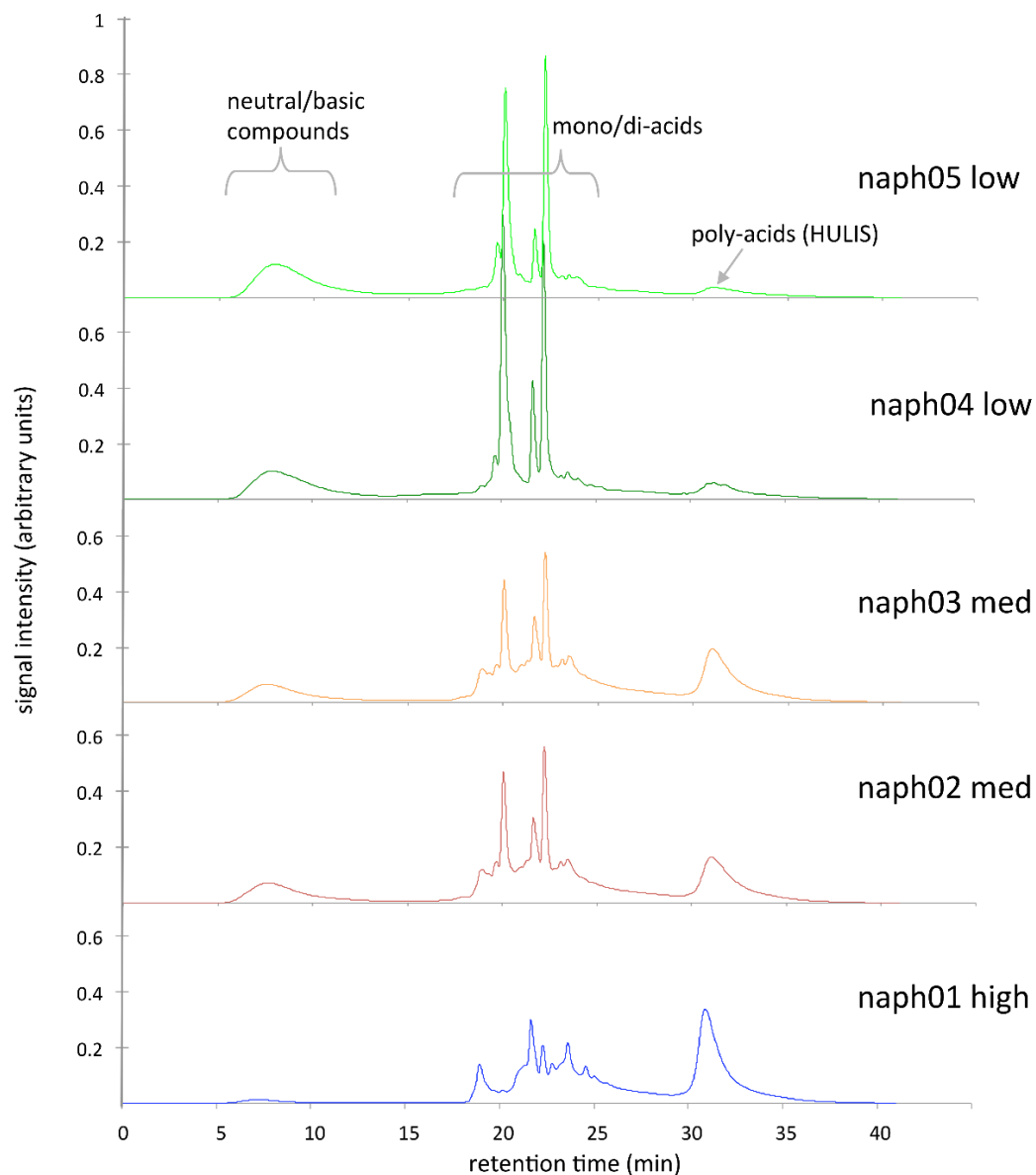
Figure 5.

135 Finally, we improved Section 3.2 with more clear references to the TOC data of the HPLC fractions presented in Figures S3 and S4 of the Supplementary. Additional observations on the distribution of HPLC classes is now reported at the end of Section 3.2.

- Section 3.2, line 282: the abbreviature "NC" for "neutral compounds" should have been previously defined
140 *in line 259.*

REPLY: It is in fact defined in the Methods section (2.4).

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

145 **REPLY:** The figure reports correlation coefficients. Each value (one point in the figure) represents the Pearson correlation coefficient for one individual SOA spectrum with respect to the reference spectrum for ambient WSOC (i.e., the same spectrum in Figure S1 upon binning). We have re-formatted the figure (taking into account also the comments by Referee 2):
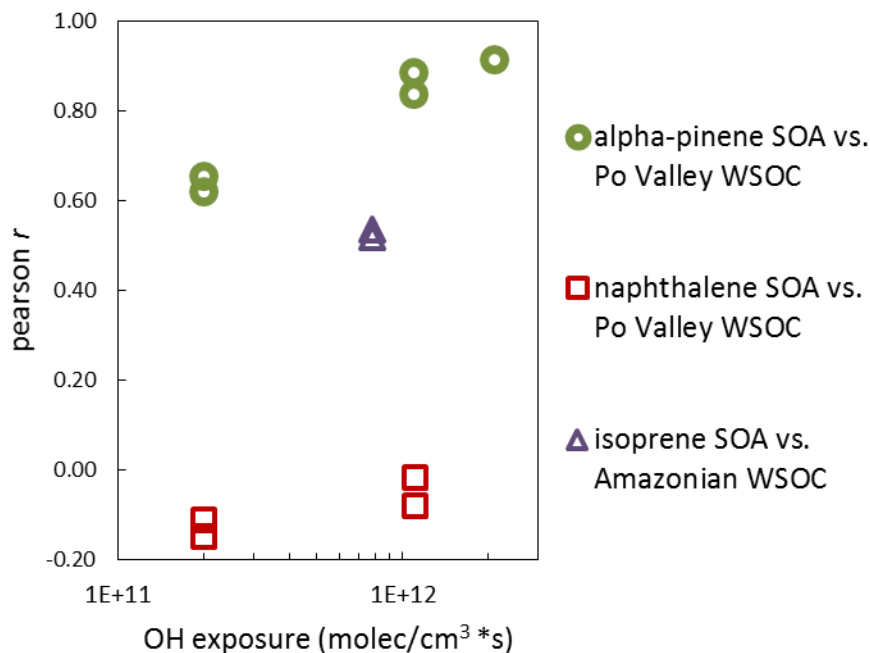
150 Figure 7.

- 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.

155 **REPLY:** True. We will correct the text.

- 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
160 *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).*

REPLY: The Referee is correct, the correlation coefficients between lab-generated SOA and ambient OOA
165 AMS were in fact reported in Fig. 5 in Lambe et al. (2011) not Fig. 9. We have changed the text. We acknowledge that the lack of full overlap between OOA and WSOC in ambient aerosol complicates the interpretation of the different results obtained in this study with respect to Lambe et al. (2011). Regarding the Referee's comment on the overlapping between OOA and WSOC, we have reasons to believe that OOA are not a subclass of WSOC: recent findings reported by Xu et al. (2017) indicate that ambient OOA can be fully

170　or only partially water-soluble depending on their oxidation degree. We will add a sentence in the text to make the reader more aware of the OOA vs. WSOC issue:

"It should be noted, finally, that a comparison of the AMS and NMR techniques with respect to their ability to trace chemical ageing in laboratory SOA and ambient oxidized aerosols is challenged by the incomplete overlap between the classes of organic compounds contributing to OOA and to WSOC (Xu et al., 2017)."

175

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

180　*from the AMS data? If so, this should be clarified in the manuscript.*

REPLY: "f44" refers to the fraction of the m/z 44 signal with respect to total OA in the AMS electron impact MS spectra. We will include a statement of explanation in Section 2.1:

"By varying the concentrations of OH inside the PAM reactor, SOA with different oxidation state could be obtained. For instance, the OH exposure varied from $2.0E11$ molec./cm^3*s to $2.1E12$ molec./cm^3*s between

185　the α-pinene experiments and the resulting SOA oxidation degree – traced by the "f44" parameter (i.e., the fraction of the m/z 44 signal with respect to the total OA) – increased from 0.05 to 0.24."

We thank the Referee for pointing out missing f44 values from Table 1: Pin#3 oxidation level = med (f44 = 0.11), and Pin#5 oxidation level = low (f44 = 0.05). The AMS was instead not operative during experiment Iso#2 (Table 2).

190

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

REPLY: We apologize for the wrong reference and will correct it in the revised manuscript.

195

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

REPLY: The full description of the analytical protocol can be found in Mancinelli et al. (2007). We will change the sentence "The full HPLC-UV-TOC analytical protocol is reported in the Supplementary material"

200　into "The HPLC column and chromatographic conditions used in this study were the same as in Mancinelli et al. (2007)"

References:

Lambe, A. T., Chhabra, P. S., Onasch, T. B., Brune, W. H., Hunter, J. F., Kroll, J. H., Cummings, M. J.,
205　Brogan, J. F., Parmar, Y., Worsnop, D. R., Kolb, C. E. and Davidovits, P.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol chemical composition and yield, Atmos. Chem. Phys., 15, 3063–3075, 2015.

Xu L., Guo H., Weber R. J., Ng N. L.: Chemical characterization of water-soluble organic aerosol in contrasting rural and urban environments in the southeastern United States, Environ. Sci. Technol., 51,
210　78−88, 2017.

Replies to Referee 2's comments.

We thank the Referee for the very through review. Below we copy his/her comments (in italics) and provide point-by-point replies.

215

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,
220 *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*
225 *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
230 *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.*

235 **REPLY:** We thank the Referee for his/her through review. We agree on the fact that the correlation analysis between non-IEPOX isoprene SOA spectra and an ambient WSOC spectrum representing a polluted environment, where low-NOx chemistry is mostly suppressed, can be misleading. We have therefore revised Section 4 of the manuscript, by including a new comparison between the isoprene SOA spectral data and those from an ambient WSOC sample from a pristine continental environment. Such spectrum will be
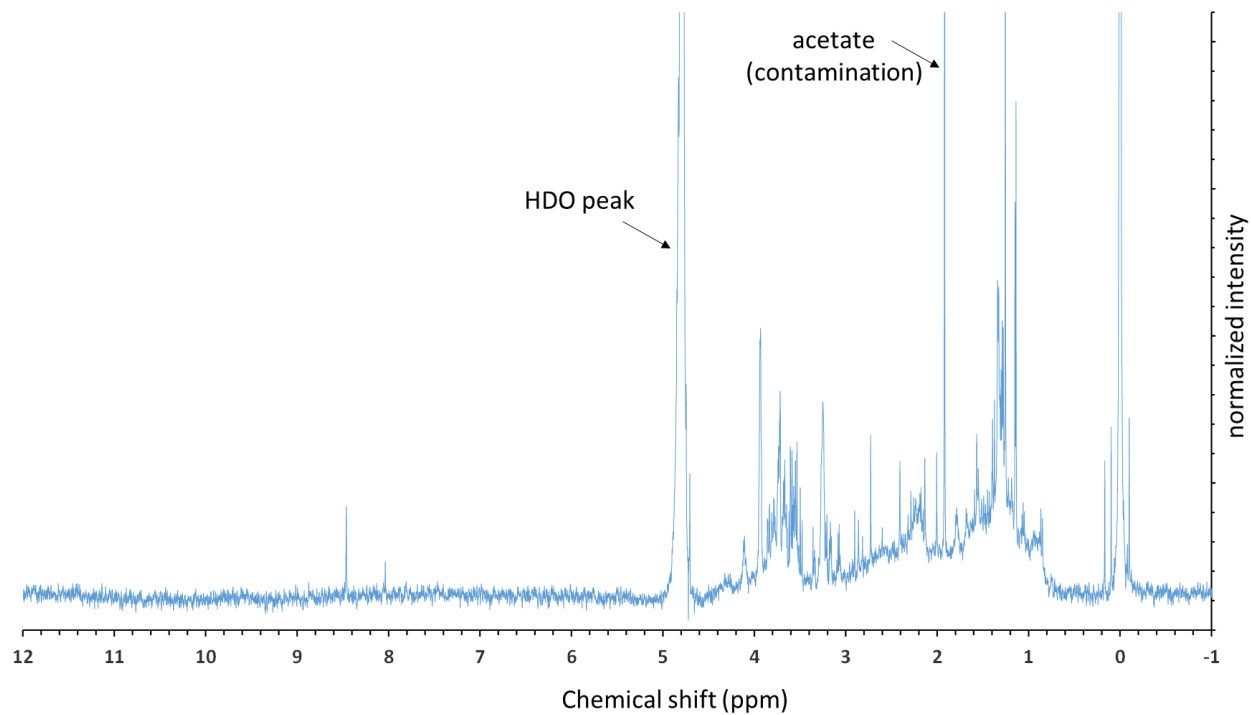240 reported as a new figure in the Supplementary Information:

Figure S1b.

The WSOC sample (PM1) considered for comparison with the isoprene SOA samples was collected at a pasture site in the Amazon basin (State of Rondônia, Brazil) from 12 to 14 November 2002. The sampling dates correspond to the beginning of the rainy season in this region of the tropics, when isoprene SOA formation from nearby forest emissions takes over local biomass burning sources (Decesari et al., 2006). Full documentation about the organic composition, including NMR data, of the aerosol samples collected during the 2002 field campaign in Brazil can be found in Tagliavini et al. (2005).

The results of the comparison between PAM-generated isoprene SOA samples and the Brazilian WSOC sample are reported in the new Figure 7 of the manuscript:
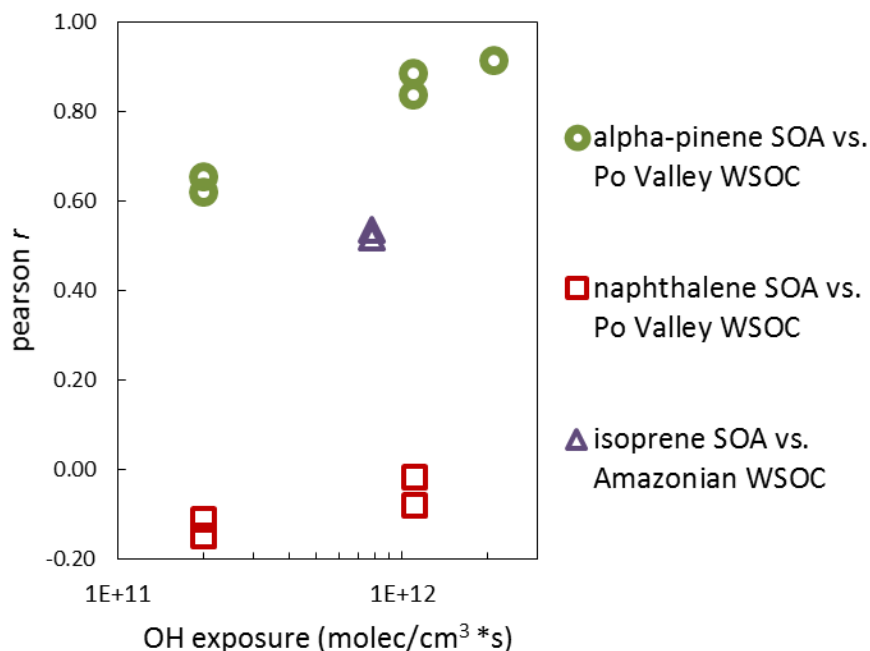
Figure 7.

The first paragraph of Section 4 of the manuscript will be changed as follows:

"In this section, the NMR and HPLC results obtained for the isoprene, α-pinene and naphthalene SOA
255 systems are compared with ambient OA samples. First, we investigated the similarity between the 1H-NMR
spectral profiles of SOA with those "typical" of ambient non-biomass-burning WSOC. For this purpose we
used one sample of PM1 collected during the 2012 PEGASOS field campaign (Sandrini et al., 2016) in the
rural Po Valley (Italy) which can be considered representative for a continental rural "near-city" site
(according to the criteria of Putaud et al., 2010). A second PM1 sample was collected at a rural site in the
260 State of Rondônia (Brazil) during the 2002 SMOCC field campaign, and, more precisely, during the early
rainy season, when local biomass burning sources had largely ceased and the organic composition of
submicron particles was dominated by biogenic emissions (Decesari et al. 2006). The ambient WSOC and
laboratory SOA spectra were binned to 400 points in order to remove the variability in chemical shifts due
to, e.g., different pH conditions during the analyses of the samples. Figure 7 shows the correlation between
265 the SOA spectra and the reference spectra of ambient WSOC: the α-pinene SOA and naphthalene SOA
spectra were compared to the Po Valley WSOC sample, while the isoprene SOA spectra were compared to
the Amazonian sample. There is good correlation ($0.62 < r < 0.92$) between the NMR spectra of α-pinene
SOA, at all oxidation levels, with the spectrum of the Po Valley PM1 sample. This finding is in line with
modelling results and previous experimental findings indicating that the organic composition in northern
270 Italy in the summertime is dominated by biogenic SOA (Bessagnet et al., 2008; Gilardoni et al., 2011). A
moderate positive correlation was also found between the spectra of isoprene SOA and of the PM1 sample
from rural Brazil ($r = 0.52, 0.54$). It should be noted that the relative humidity at this pasture site is variable
during the day and very high overnight during the rainy season, based on the meteorological data presented
by Betts et al. (2009). Therefore, biogenic aerosols are expected to include also isoprene SOA forming
275 through the IEPOX route (Hu et al., 2015), which is not accounted for by our laboratory experiments. Finally,
the naphthalene SOA spectra exhibit zero or negative correlations with the Po Valley WSOC spectrum (-0.15
$< r < -0.02$). […]"

We believe that the new version of the discussion section (containing the comparison with the ambient aerosol
data representative for an isoprene-dominated environment) supports the atmospheric relevance of the

280 isoprene SOA spectral data presented in this study. It should be noted, finally, that to our knowledge this is the first time that isoprene SOA NMR data - including the spectra of marker compounds (2-methyl-tetrols) and the spectral fingerprints for complex secondary organic compound mixtures generated in laboratory from isoprene photo-oxidation - are presented in the literature. We also modified Section 3.1.3 to highlight the implications of our NMR measurements of the isoprene SOA samples:

285 "The isoprene SOA 1H-NMR spectra profiles were all very similar (an example is provided in Figure 3). The comparison with literature data (Budisulistiorini et al. 2015) led to the unambiguous identification of 2-methyltetrols, clearly responsible for the two singlets at 1.12 ppm (methylic H atoms of methylerythritol) and 1.13 ppm (methylic H atoms of methylthreitol) and for a series of multiplets between 3.4 and 3.9 ppm. Methylerythritol is more abundant (60% of the sum of the two, as an average between two samples extracted
290 in water and three extracted in methanol) than methylthreitol. The spectra show the occurrence of only two diastereomers among the possible four ones (González et al. 2011), indicating that the formation of methyl-tetrols is stereoselective, as already proposed by Cash et al. (2016) on the basis of a theoretical analysis of the IEPOX chemistry, and in contrast with the conclusions of González et al. (2011) claiming that methyltetrols are produced in laboratory conditions only in racemic mixtures."

295 More implications of the NMR analysis of isoprene SOA will be presented in response to the Referee's 6th specific comment.

Specific comments:

1. Lines 31-32: Please clarify the definition of the maximum yield %'s listed. Are these yields mass of HULIS
300 *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)?*

REPLY: The yields refer to the fraction of WSOC (= organic carbon in HULIS with respect to the sum of neutral compounds and all acidic fractions). The sentence will be rephrased as follows:

305 "Over multiple days of equivalent OH exposure (30 atmospheric days), the formation of HULIS is observed in both α-pinene SOA and in naphthalene SOA (maximum yields: 16% and 30%, respectively, of total analyzed WSOC), providing evidence of the formation of humic-like polycarboxylic acids in unseeded SOA."

310 *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?*

315 The following text will be added to the end of Section 2.1 in the revised manuscript:

"To compare SOA formation processes occurring in oxidation flow reactors and in the atmosphere, two primary assumptions are required. First, we assume the kinetics of laboratory processes occurring at higher oxidant concentrations and shorter exposure times can be extrapolated to atmospheric processes occurring at lower oxidant concentrations and longer residence times. Second, we assume that the extent of nucleation or
320 phase partitioning of SOA is not limited by the shorter residence time in flow reactors. The first assumption is supported by Renbaum and Smith (2011), Bahreini et al. (2012), and Lambe et al. (2015). The second assumption may introduce uncertainty depending on the particle surface area available to promote condensation and the mass accommodation coefficient of the oxidized vapors (Lambe et al., 2015; Shantanu et al., 2017).

325

3. Line 73: Consider including these additional references in discussing vapor-phase wall losses:

(Matsunaga and Ziemann, 2010; Ye et al., 2016)

REPLY: Accepted. We thank the Referee for the useful references.

330 *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?*

335 **REPLY:** We agree. The sentence "The present study is the first application of 1H-NMR spectroscopy to SOA samples produced from the OH oxidation of biogenic and anthropogenic SOA" will be changed into "The present study is among the first applications of ^{1}H-NMR spectroscopy to SOA samples produced from the OH oxidation of biogenic and anthropogenic SOA in the laboratory". We included citations from relevant literature on laboratory experiments of SOA generation, while essentially ignoring the literature on NMR
340 aerosol field studies (except from a few papers which were cited here for reporting information on methodological aspects).

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?

345 **REPLY:** Not specifically for isoprene SOA samples. This is because the isoprene SOA samples were analyzed at a later time with respect to the alpha-pinene and naphthalene SOA ones, and in the meanwhile we realized that including a pH buffer led to a higher stability of chemical shifts.

6. Interpretation of isoprene results in Section 3.1.3 NMR fingerprints of non-IEPOX isoprene SOA: In light
350 *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-*
355 *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.*

REPLY: The two major compounds in our isoprene SOA samples are undoubtedly 2-methyl-tetrols. The
360 NMR resonances of these species are completely consistent with the spectra reported in Fig. S13 of the paper by Budisulistiorini et al. (2015) and with the chemical shift data reported for pure standards of 2-methyl-tetrols by González et al. (2011). On the basis of NMR spectra simulations performed using ACD/Labs software (Advanced Chemistry Development, Inc., 1D NMR Manager & NMR Predictor Suite v.12), the peroxide analogues of methyltetrols must exhibit some resonances above 4 ppm of chemical shift, because
365 hydroperoxyl groups are more electron-withdrawing than hydroxyl substituents. Most importantly, hydroperoxyl substituents can occur in variable number and at diverse positions in the molecules (Riva et al., 2016), resulting in rather complex NMR spectra, whereas our samples show clearly the occurrence of just two individual compounds, which we assign to the two major diastereomers of methyl-tetrols (2-methyl-

threitol and 2-methyl-erythritol). The reason why our samples of non-IEPOX SOA show prevalently 2-methyl-tetrols rather than their peroxide analogues, in contrast with the results of Krechmer et al. (2015) and of Riva et al. (2016), is unclear. We can speculate that peroxides self-reactions lead to the formation of alcohols (ROOH+ROOH => 2 ROH + H_2O_2) in the sample or on the filter surface. Considering that the discovery of non-IEPOX SOA is rather new and little is known about the stability of isoprene peroxides in aerosol samples, we can just acknowledge that more research must be carried out to clarify the discrepancy between our findings and the literature studies. We have included this specific issue in Section 3.1.3:

"The results of Liu et al. (2016), indicating that non-IEPOX isoprene SOA include peroxide-equivalents of methyltetrols, are in agreement with these findings. However, Riva et al. (2016) reported only peroxides for non-IEPOX SOA in unseeded experiments and no methyl-tetrols. It is possible that peroxides decomposed to tetrols in our filter samples during collection downstream the PAM or afterwards during storing. The actual stability of isoprene hydroperoxides in the aerosol itself is largely uncertain, therefore the discrepancy between the findings presented in this study and the results of Riva et al. (2016) cannot be clarified at this stage. In addition, neither Liu et al. (2016) and Riva et al. (2016) reported the presence of carboxylic or keto groups, while our data clearly indicate that these (and/or other acyl groups) are found in the unresolved mixtures of non-IEPOX isoprene SOA, and are responsible for the signal band between 2.0 and 2.6 ppm. Still, this band is much less intense than that of alcoxyls, which is opposite to what observed for α-pinene SOA where acyls are by far the main oxygenated aliphatic functional group. Thus, 1H-NMR spectroscopy provides distinct fingerprint for isoprene and monoterpene SOA."

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.

REPLY: We did not perform the water extraction in an inert atmosphere (e.g., under nitrogen flux), therefore, in principle, we cannot exclude the degradation of labile organic structures. These, however, must be extremely labile species and able to react with dissolved oxygen. The OH concentrations, instead, will be unrealistically too small in the sealed vials where the extraction was performed (the OH molecules in the few cubic centimeters of head space will be just some millions, while we can reach 1 µmol of organic carbon dissolved in the extract). We believe that the main effect of water extraction is the hydrolysis of anhydrides and acetals. It is largely recognized that several of the known types of oligomerization reactions deemed to occur in atmospheric organic particles are in fact reversible (Kroll and Seinfeld 2008). Such oligomers are not expected to survive the water extraction step of our analytical protocols, therefore, the HULIS determined in this study must be considered stable against hydrolysis. We will update the first paragraph of Section 3.2 to specify that:

"The HPLC analysis of fresh α-pinene SOA extracts shows the presence of compounds unretained by ion-exchange columns (neutral compounds) or weakly retained (mono- and di-acids) with a small contribution from compounds having a high retention factor (polyacids, PA, or HULIS), in agreement with previous results obtained from α-pinene SOA samples generated in environmental chamber experiments (unpublished data). It should be noted, however, that the chromatographic analysis of SOA compounds in water extracts generally does not allow to recover high-molecular weight organic oligomers susceptible to hydrolysis reactions (e.g., polyacetals, Kroll and Seinfeld 2008). The HULIS determined by our method are essentially only the non-hydrolyzable ones, stable in aqueous solutions."

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?

REPLY: We do not claim that our laboratory study is comprehensive with respect to simulating the full range of possible atmospheric conditions conditioning SOA formation. We just specified that the SOA chemical composition data presented in this study are more representative for the low relative humidity (RH) conditions. This is often the case, for instance, of Mediterranean climates in summertime (the average RH corresponding to the Po Valley sample in Fig. S1 was 35%), but it is also common for continental sites in temperate climates during a high-pressure anomaly, like in the case of the May 2008 field campaign in Cabauw (RH ~ 30% to 50% in the first 2 km of atmosphere, according to Derksen et al., 2011). The other ambient sample considered in this study is the Amazonian PM1 sample from Rondônia (Brazil) introduced for comparison with the isoprene SOA sample (see above). We could not find meteorological data for the collection time of this last sample, therefore we must refer to climatological data for Rondônia, presented by Betts et al. (2009). Note that the sampling location was a deforested pasture site, where water vapor mixing ratio is normally lower than at forest sites in the same region. Our sample was collected at the very beginning of the rainy season, just after the end of the transition period (i.e., the transition between the dry and the wet season). On the basis of the temperature and water mixing ratio data presented by Betts et al. (2009), we can calculate a maximum relative humidity (RH) of 90 – 92% (night-time and early morning hours) and a minimum RH of 65 – 77% in afternoon hours, when the atmospheric mixing layer reaches its maximum thickness. We can conclude that, during the collection time of the PM1 WSOC sample considered in this study (12 – 14 Nov 2002), the aerosol particles were fully deliquesced overnight, while the liquid water content in daytime was quite variable and certainly not always high, considered the weak hygroscopicity of the particles measured at the pasture site (hygroscopic growth factor < 1.1 at 80% RH, according to Rissler et al., 2006). Therefore, although an IEPOX route of formation of isoprene SOA is widely recognized as a very significant source of organic aerosols in the Amazon basin (Hu et al., 2015), it is not clear whether this is really prevalent respect to non-IEPOX SOA formed at lower RH values at the deforested pasture site considered here.

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.

REPLY: The Referee is right. However, as we noted in the same section, "naphthalene and other polyaromatic hydrocarbons are co-emitted with many other anthropogenic IVOCs and VOCs including aliphatic compounds in the real atmosphere". We can speculate that aliphatic IVOCs have much lower HULIS formation yields than aromatic ones, therefore the HULIS fraction in fresh anthropogenic emissions must be smaller than the 11% observed for pure naphthalene. The same is valid for anthropogenic SOA in aged plumes: the overall HULIS fraction would be much smaller than the 30% found for pure naphthalene, and becoming more comparable with the 12% observed in the field at a rural site. This is just a hypothesis, but we would like to stress the fact that the HULIS yield of aromatic compounds like naphthalene is probably greater than for other IVOCs (as aromatic compounds undergo oxidative carbon-carbon bond cleavage with much smaller molecular fragmentation than aliphatics) and that consequently the HULIS fraction of both fresh and aged naphthalene SOA must be higher compared to a more complex mixture of IVOCs.

The text in the paper will be revised as follows: "The α-pinene SOA generated in the PAM reactor at high photochemical age and the fresh naphthalene SOA are characterized by a HULIS amount similar to that of Cabauw samples, while the polyacidic content of aged naphthalene SOA is higher than in the ambient samples. In the real atmosphere, naphthalene is co-emitted with many other reactive VOC and IVOC with potentially very diverse HULIS formation yields, therefore the results presented in Figure 8 do not necessarily mean that the chemical composition of ambient OA in Cabauw is better described by the monoterpene chemistry rather than by anthropogenic IVOC oxidation. On the other hand, these results demonstrate that laboratory experiments of SOA formation can generate complex mixtures of products with the same

chromatographic properties of HULIS provided a sufficient extent of photochemical aging using the PAM reactor or related techniques".

465 Finally, we omitted the pie chart of isoprene SOA from Figure 8, because it cannot be considered representative for the HPLC composition of a polluted site (Cabauw) (see reply to the Referee's first major comment).

10. Please provide additional context for the ambient samples from Cabauw and Po Valley. Are the
470 *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.

REPLY: According to the definition of "sites' catchments" by Henne et al. (2010) ("area in which surface fluxes are expected to create a detectable and significant signal at the receptor sites"), the Cabauw site is affected by aerosol sources from a vast region in north-west Europe, while the station of Ispra in the Po
475 Valley receives contributions from a more confined area in northern Italy and the great Alpine region. In both areas, the most common land types are managed agricultural land and deciduous forests, the latter being active sources of monoterpenes. In addition, both stations were clustered among the most impacted ones from urban emissions, which include emissions of intermediate volatility aromatic hydrocarbons. We can therefore conclude that monoterpenes and anthropogenic VOCs are expected to impact ambient SOA both in the rural
480 Netherlands (Cabauw) and in the Po Valley (S. Pietro Capofiume, not considered in Henne et al. (2010) is similar to Ispra, though more rural).

Information on sources of SOA in the Po Valley and at the rural site of Brazil has already been included into the revised paragraph of Section 4 upgraded in response of the Referee's first comment. Here we report the new text to integrate into the 3rd paragraph of the same section for introducing the ambient samples from
485 Cabauw:

"The distribution of neutral vs. acidic classes of compounds in ambient WSOC refers to the average of the samples collected at the rural background station of Cabauw in the Netherlands (Paglione et al. 2014b). The station is located downwind from anthropogenic sources and biogenic emissions (terpenes from deciduous forests) over a large sector of north-west Europe (Henne et al., 2010). The HULIS contribution in these
490 samples varied between 15 and 20%, […]."

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.

495 **REPLY:** Below are the new versions of Figures 1, 2 and 3 with highlighted the spectral regions characteristic of functional groups.
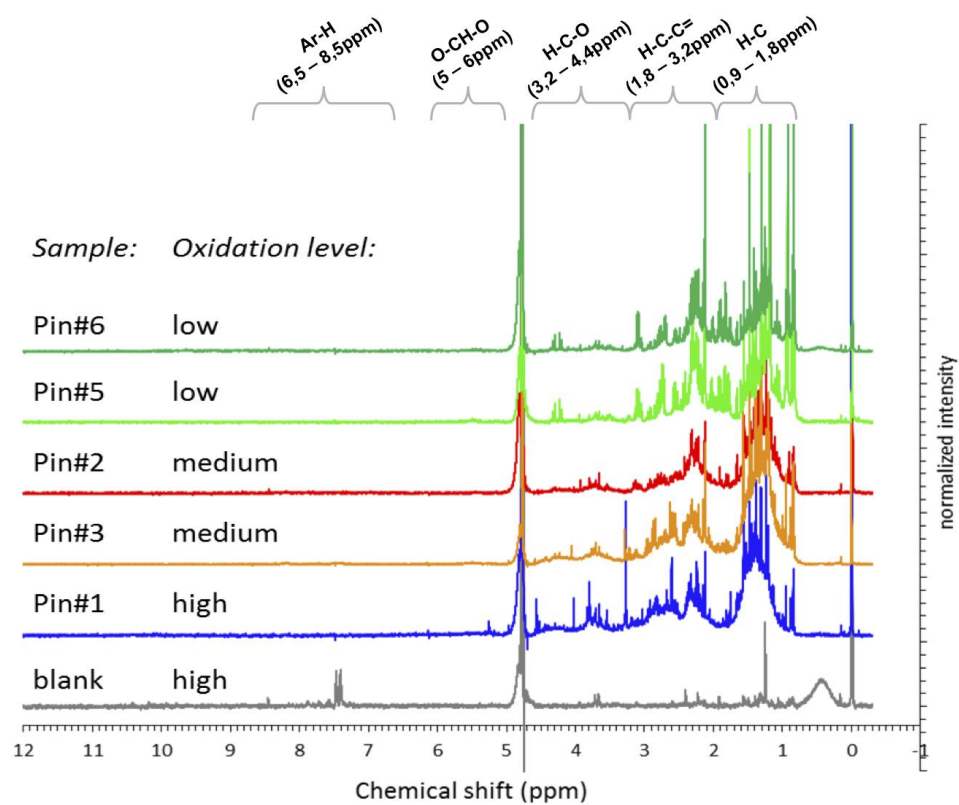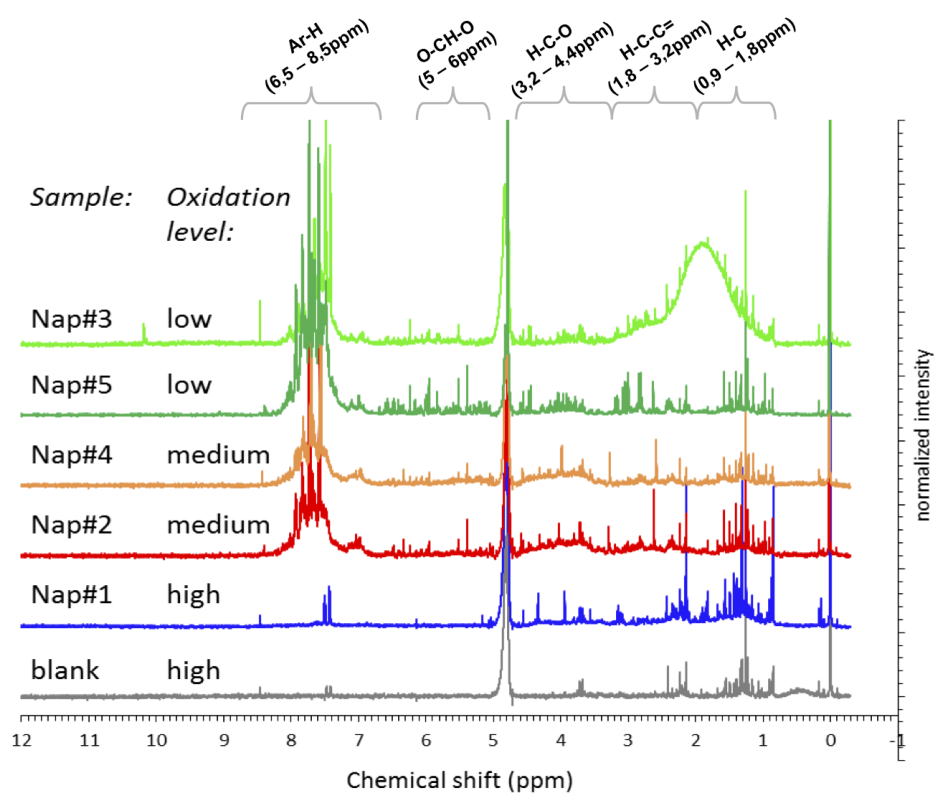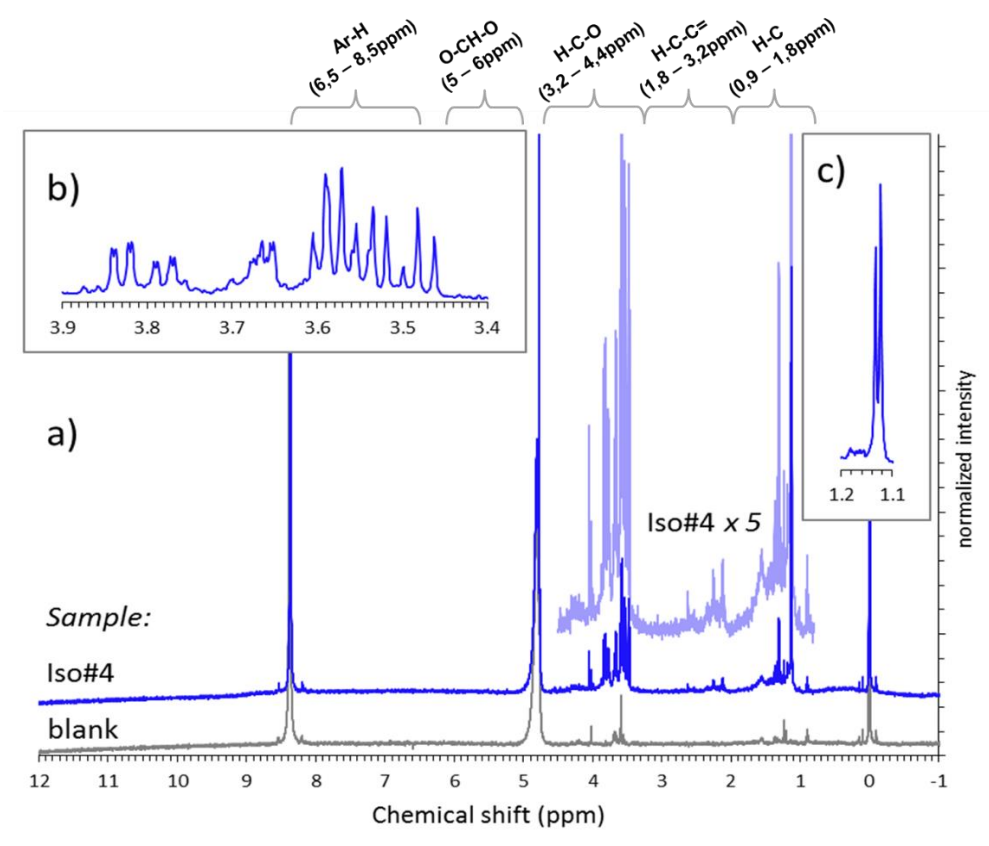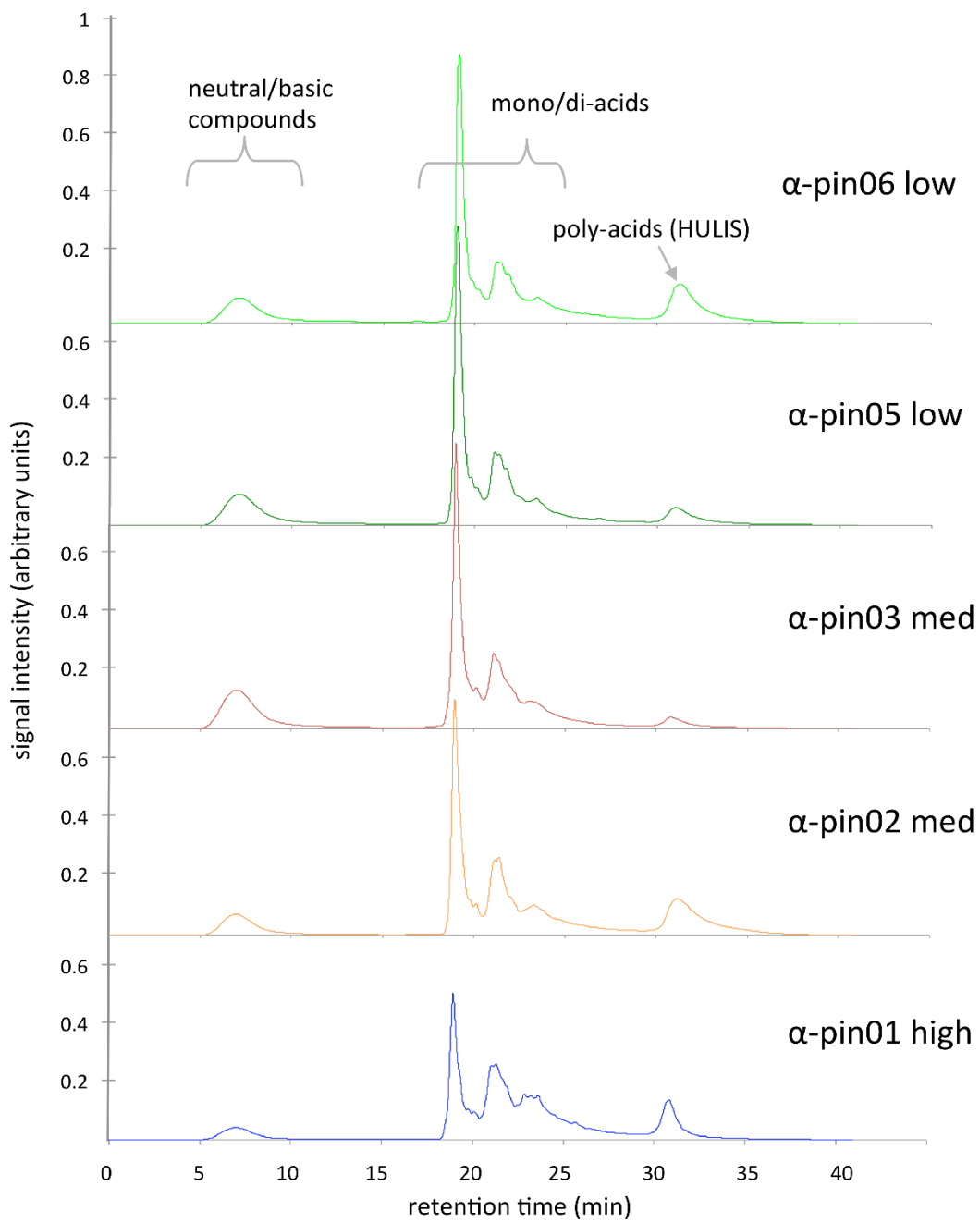
Figure 1

500   Figure 2.

Figure 3.

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?*

REPLY: NMR spectra are often normalized so that the intensity of the most intense peaks is 100%, but the sets of spectra reported here have very variable contributions from intense individual resonances, preventing a clear visualization of the differences in the background resonances between spectra. We believe the current figures are a reasonable compromise in showing the main spectral features accompanying chemical ageing of SOA. Nevertheless, we agree with the Referee on the fact that the current visualization of the NMR spectra does not allow to look into the details. We have therefore produced zoomed-in versions on specific spectral regions and report them in the Supplementary Information (new Figures S5 and S6).

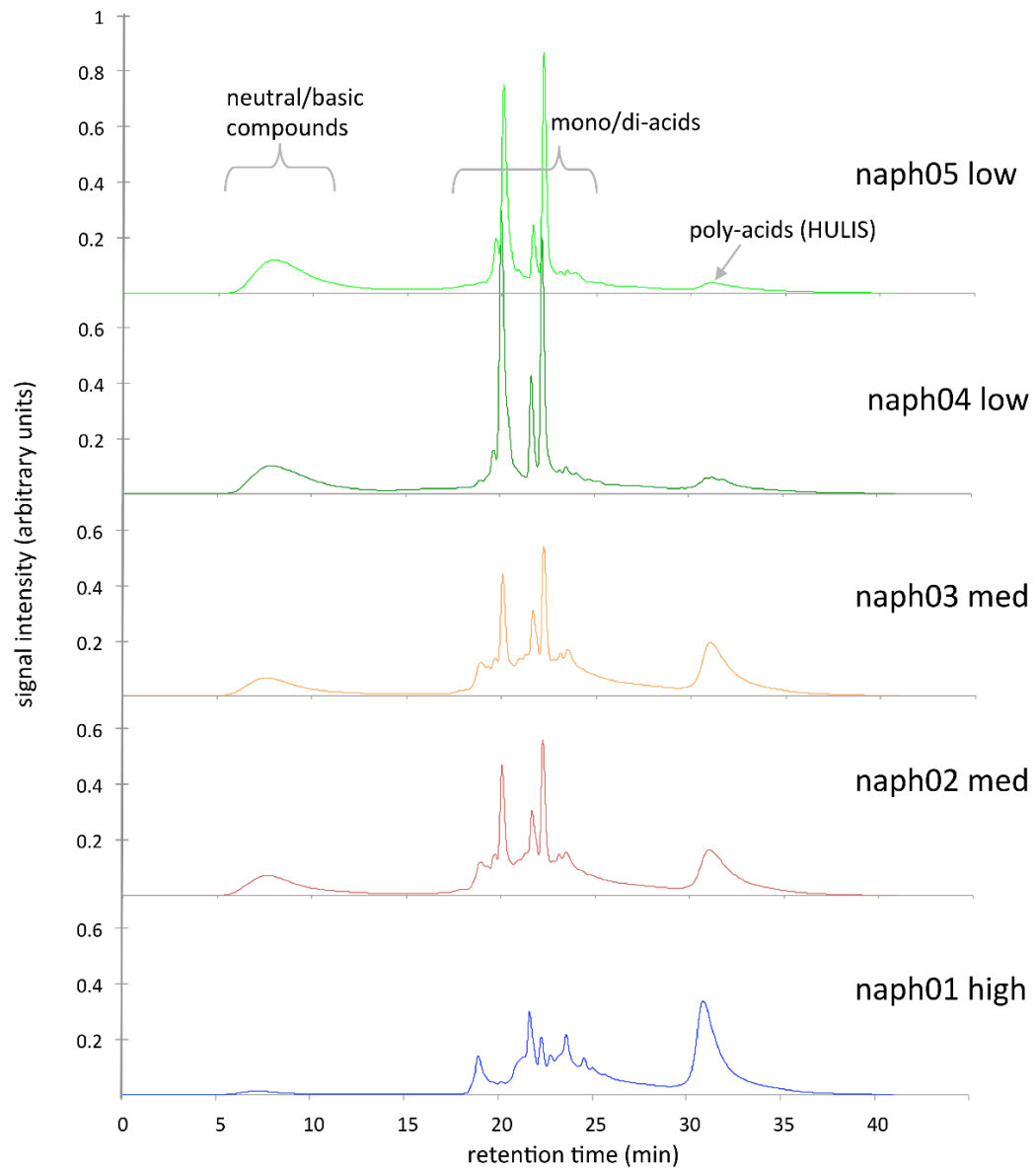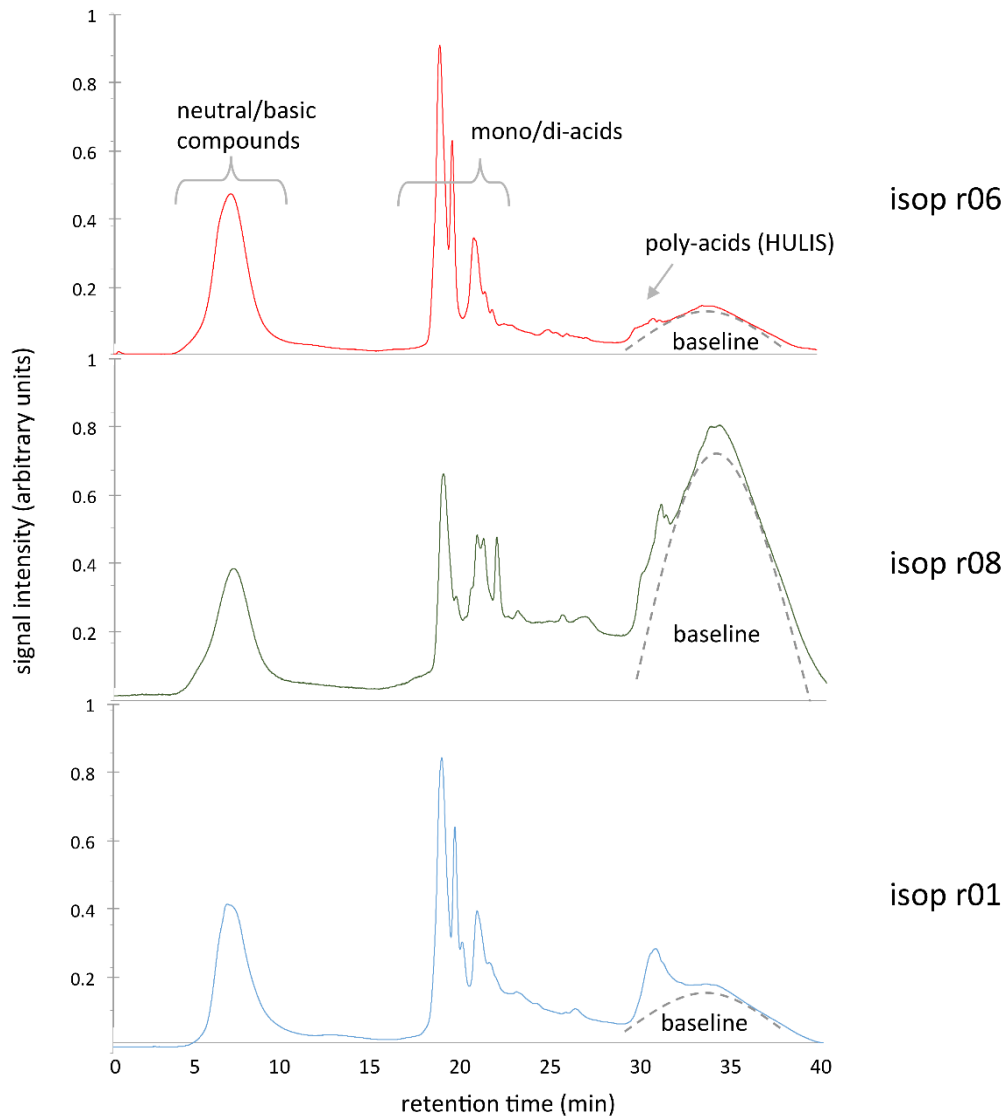Finally, please find below the updated HPLC figures with tick marks on the y axis.

515

Figure 4

Figure 5

neutral/basic compounds

mono/di-acids

isop r06

poly-acids (HULIS)

baseline

isop r08

baseline

isop r01

baseline

retention time (min)

signal intensity (arbitrary units)

520   Figure 6.

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.

525   The measured f43 is, in general, not well correlated with photochemical age, and is highly precursor-specific (e.g. Ng et al, ACP, 2010, 2011; Lambe et al., ACP, 2011). For the most part, f44 is a better measurable surrogate for the photochemical age and is less precursor-specific. Thus, we feel f44 is the best available metric with which to compare the formation processes of HULIS as a function of photochemical age in the laboratory and field studies described here.

530

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".

REPLY: All corrections have been made. We thank the Referee for the help in editing the text.

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

610

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Abstract. The study of secondary organic aerosol (SOA) in laboratory settings has greatly increased our
625 knowledge of the diverse chemical processes and environmental conditions responsible for the formation of particulate matter starting from biogenic and anthropogenic volatile compounds. However, characteristics of the different experimental setups and the way they impact the composition and the timescale of formation of SOA are still subject to debate. In this study, SOA samples were generated using a Potential Aerosol Mass (PAM) oxidation flow reactor using α-pinene, naphthalene and isoprene as precursors. The PAM reactor
630 facilitated exploration of SOA composition over atmospherically-relevant photochemical aging time scales that are unattainable in environmental chambers. The SOA samples were analyzed using two state-of-the-art analytical techniques for SOA characterization - proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy and HPLC determination of humic-like substances (HULIS). Results were compared with previous Aerodyne aerosol mass spectrometer (AMS) measurements. The combined ^{1}H-NMR, HPLC, and AMS datasets show
635 that the composition of the studied SOA systems tend to converge to highly oxidized organic compounds upon prolonged OH exposures. Further, our ^{1}H-NMR findings show that only α-pinene SOA acquire spectroscopic features comparable to those of ambient OA when exposed to at least $1*10^{12}$ molec OH /cm^3*s OH exposure, or multiple days of equivalent atmospheric OH oxidation. Over multiple days of equivalent OH exposure, the formation of HULIS is observed in both α-pinene SOA and in naphthalene SOA (maximum
640 yields: 16% and 30%, respectively, of total analyzed WSOC), providing evidence of the formation of humic-like polycarboxylic acids in unseeded SOA.

1 Introduction

Organic aerosol (OA) constitutes a large proportion of ambient particulate matter, affecting the Earth's
645 radiation balance, cloud formation and human health (Hallquist et al., 2009). Understanding and simulating

the concentration and composition of OA particles is one of the major challenges of modern atmospheric chemistry. In the mid 2000's the discovery that oxidized organic compounds dominate in concentration compared to that of primary organic compounds outside urban areas (Zhang et al., 2007; Jimenez et al., 2009), together with the understanding that the ambient organic aerosol concentrations were systematically under-predicted by existing chemical transport models (Heald et al., 2005), led to a reevaluation of the treatment of secondary organic aerosol (SOA) formation processes in chemistry and climate models. Since the model-measurement gap is mostly overcome by subjecting the particles to "oxidative aging", understanding the nature of ageing processes has become a primary objective of new generation SOA studies. Experimental findings showing the existence of highly-oxidized SOA molecular tracers with a high oxygen-to-carbon (O/C) ratio (Szmigielski et al., 2007) and molecular structures that are chemically distinct from 1st and 2nd generation oxidation products of the same precursors (Jenkin et al., 2000) provided indirect confirmation of still unknown chemical processes forming highly oxidized, low-volatility compounds.

The first formulations of SOA ageing into models were based on the chemistry of saturated hydrocarbon oxidation by OH, for which a step-by-step process with a slow, progressive increase of the oxidation state, along with a decrease in volatility, can be proposed (Robinson et al., 2007). The duration of such processes clearly exceeds the residence time of SOA in traditional environmental chamber experiments with equivalent atmospheric ageing times of less than 1 day. These limitations led to the emergence of oxidation flow reactors that are capable of higher integrated oxidant exposures, including the Potential Aerosol Mass (PAM) oxidation flow reactor (Kang et al., 2007; Lambe et al., 2011) and related techniques (Hall IV et al., 2013; Keller and Burtscher, 2012; Slowik et al., 2012). Recent studies suggest that flow reactor-generated SOA particles have similar composition to SOA generated in chambers (Lambe et al., 2015; Bruns et al., 2015). Modeling work further suggests that flow reactors simulate tropospheric oxidation reactions with minimal experimental artifacts (Li et al., 2015; Peng et al., 2015, 2016). Recent applications of oxidation flow reactors in field measurements showed that the maximum yields of SOA were attained at approximately 2-3 days of equivalent atmospheric OH oxidation; at higher photochemical age, SOA yields decrease substantially (Tkacik et al., 2014; Ortega et al., 2016; Palm et al., 2016). Such observations demonstrate the influence of fragmentation reactions in which oxidation leads to C-C bond cleavage with the production of highly volatile products (Kroll et al., 2009; Chacon-Madrid and Donahue 2011; Lambe et al., 2012).

The idea of a slow, multi-generation SOA ageing was recently challenged by recent findings from reaction chamber experiments employing modern chemical ionization mass spectrometric methods. For example, it was found that oxidized gaseous compounds with O/C > 0.7 form readily upon VOC oxidation (Ehn et al., 2012, 2014; Krechmer et al., 2015; Rissanen et al., 2014) and that even the chemical tracers of "aged" SOA can be in fact produced among 2nd generation oxidation products (Müller et al., 2012). The quantification of highly oxidized SOA compounds in reaction chambers is challenging because of significant vapor and particle wall losses (Matsunaga and Ziemann, 2010; Zhang et al., 2014; Krechmer et al., 2016; Ye et al., 2016), but these findings suggest that SOA ageing can be much faster than previously thought (Hodzic et al., 2016). As a result of the diverse implementations of SOA schemes in models, the quantification of SOA production and concentration in the atmosphere is still highly uncertain: a recent intercomparison between 20 state-of-the-art global models showed that the estimated SOA annual production rates differ of one order of magnitude (Tsigaridis et al., 2014). These results call for more experimental observations for constraining the existing SOA parameterizations.

The present study focuses on laboratory production of SOA from three different precursors using a PAM reactor. The novel feature of this work is our application of two off-line analytical techniques that provide valuable insight in regards to SOA composition yet are rarely employed for SOA characterization. The first technique, ^{1}H-NMR spectroscopy, is a universal technique in organic chemistry. It was used to confirm the molecular structures of many SOA tracers (Finessi et al., 2014) or for following SOA reaction products in aqueous solution (Yu et al., 2011). The few examples of ^{1}H-NMR spectroscopy on SOA complex mixtures (Cavalli et al., 2006; Baltensperger et al, 2008; Bones et al., 2010; White et al. 2014) indicate that the technique can be very specific for distinguishing different biogenic and anthropogenic SOA systems. The present study is among the first applications of ^{1}H-NMR spectroscopy to SOA samples produced from the

OH oxidation of biogenic and anthropogenic SOA in the laboratory. The acquisition of NMR fingerprints for fresh and aged biogenic and anthropogenic SOA can be useful also for interpreting factor analysis results obtained on a timeline of NMR spectra of ambient aerosol extracts (e.g., Paglione et al. 2014a). The second technique is a HPLC set-up for the determination of humic-like substances (HULIS). HULIS have been observed in ambient organic aerosol for nearly two decades (Havers et al., 1998; Limbeck et al., 2003), but their formation pathways aside from production in biomass burning plumes remain unclear (Graber and Rudich 2006). It is well-known that high-molecular weight oxygenated organic compounds readily form by heterogeneous reactions (Limbeck et al., 2003) or by gas-to-particle conversion (Kalberer et al., 2006), but there is little evidence for their identification with HULIS in ambient aerosols (especially if we base the definition on the chromatographic behavior, as in Baduel et al., 2009).

Here we focus on SOA systems generated from three distinct precursors: isoprene, α-pinene and naphthalene. Naphthalene is used as proxy for anthropogenic aromatic intermediate volatility organic compounds (IVOCs). Alpha-pinene is the most studied biogenic monoterpene due to its global importance as a biogenic SOA precursor (e.g. Pye et al., 2010), while isoprene is the most abundant biogenic VOC, accounting for 44% of global emissions (Guenter et al., 1995). The discovery of isoprene SOA is relatively recent (Claeys et al. 2004). In the presence of acidic wet aerosols, SOA originates from the heterogeneous uptake of isoprene epoxides ("IEPOX channel", Lin et al., 2012). Since aerosol water and acidity are primarily determined by anthropogenic mineral acids, the formation of SOA from isoprene appears to be very much controlled by anthropogenic emissions. On the other hand, recent experiments conducted at very low nitrogen oxide (NO) concentrations, and in the absence of seed aerosols, showed that SOA can still form from isoprene ("non-IEPOX" SOA, Krechmer et al., 2015). Such aerosols are more representative of the preindustrial world and their characterization is of paramount importance for understanding the climate radiative forcing of SOA at the global scale. Our results, obtained in the PAM reactors in absence of NOx, are representative for non-IEPOX isoprene SOA.

2 Experimental methods

2.1 PAM oxidation flow reactor

The PAM oxidation flow reactor is a horizontal 13L glass cylindrical chamber that is 46 cm long x 22 cm ID. Carrier gas flows of 8.5 liter per minute (lpm) N_2 and 0.5 lpm O_2 were used, with 8.5 lpm of flow pulled through the reactor and 0.5 lpm of excess flow removed prior to the reactor. Other experimental details are fully described in Lambe et al. (2011). In this study, the PAM reactor was connected to a Scanning Mobility Particle Sizer (SMPS), an Aerodyne time-of-flight aerosol mass spectrometer (AMS), and a filter holder equipped with 47 mm (prebaked) quartz-fiber filters. SOA concentrations calculated from SMPS and/or AMS measurements averaged over filter collection times provided an estimate of the organic matter loading on the filters.

During the first set of experiments involving α-pinene and naphthalene as SOA precursors, by varying the concentrations of OH inside the PAM reactor, SOA with different oxidation state could be obtained. For instance, the OH exposure varied from $2.0x10^{11}$ molec./cm^3*s to $2.1x10^{12}$ molec./cm^3*s between the α-pinene experiments and the resulting SOA oxidation degree – traced by the "f44" parameter (i.e., the fraction of the m/z 44 signal with respect to the total OA) – increased from 0.05 to 0.24. A total of five α-pinene and five naphthalene SOA samples were obtained (collection time between 3 and 20 h), with integrated OH exposures varying between $2x10^{11}$ and $2x10^{12}$ molecules/cm^3*s, corresponding to a photochemical age of 1.5 to 15 days assuming a 24-hour average OH concentration of $1.5*10^6$ molec cm^{-3} (Mao et al., 2009).

During the second set of experiments, isoprene SOA samples were generated in the reactor (Table 2). Due to the lower yields of SOA produced by isoprene oxidation, samples were collected at OH exposure of approximately $8*10^{11}$ molec cm^{-3} sec (corresponding to a photochemical age of 6 days) at which the maximum SOA yield is obtained (Lambe et al., 2015). The collection time was varied between 2 and 18 h.

To compare SOA formation processes occurring in oxidation flow reactors and in the atmosphere, two primary assumptions are required. First, we assume the kinetics of laboratory processes occurring at higher oxidant concentrations and shorter exposure times can be extrapolated to atmospheric processes occurring at lower oxidant concentrations and longer residence times. Second, we assume that the extent of nucleation or phase partitioning of SOA is not limited by the shorter residence time in flow reactors. The first assumption is supported by Renbaum and Smith (2011), Bahreini et al. (2012), and Lambe et al. (2015). The second assumption may introduce uncertainty depending on the particle surface area available to promote condensation and the mass accommodation coefficient of the oxidized vapors (Lambe et al., 2015; Shantanu et al., 2017).

2.2 Extraction and off-line sample characterization

Each filter was extracted with 5 mL of deionized ultra-pure water (Milli-Q) in a mechanical shaker for 1 h and the water extract was filtered on PTFE membranes (pore size: 0.45 μm) in order to remove suspended particles. The water extracts were dried by rotary evaporator and were then re-dissolved in 2.15mL of D_2O: 0.65mL for proton-nuclear magnetic resonance (^{1}H-NMR) characterization (Decesari et al., 2000), and 1.5mL for HPLC analysis and total organic carbon (TOC) analysis (Mancinelli et al., 2007). Tests of extraction using methanol instead of water were carried out on three isoprene SOA samples. The ^{1}H-NMR spectra of methanol extracts were completely consistent with those obtained for the other three analyzed in deuterated water (Fig. S2), indicating that there were no specific classes of water-insoluble compounds in the isoprene SOA under the conditions used in this study. The following discussion will focus on the water-soluble fraction for which spectroscopic and chromatographic data were obtained for all three SOA systems.

2.3 NMR spectroscopy

The ^{1}H-NMR spectra were acquired at 600MHz with a Varian 600 spectrometer in a 5mm probe with 0.65mL of each sample re-dessolved in D_2O. Sodium 3-trimethylsilyl-(2,2,3,3-d4) propionate (TSP-d_4) was used as the referred internal standard. A buffer of potassium deuterated formate/formic acid (pH~3.8) was used in the second series of experiments (isoprene SOA) to stabilize the chemical shift of hydrogen atoms in acyl functional groups, while the extracts obtained during the first experiments (α-pinene and naphthalene) were analyzed unbuffered. ^{1}H-NMR spectroscopy of low-concentration samples in protic solvents provides the speciation of hydrogen atoms bound to carbon atoms (H-C). On the basis of the range of frequency shifts (the chemical shift, in ppm) in which the NMR resonances occur, they can be attributed to different H-C containing functional groups (Paglione et al. 2014a).

2.4 HPLC-UV-TOC method

HULIS were determined using the ion exchange chromatographic method described by Mancinelli et al. (2007). A HPLC system (Agilent Model 1100) with gradient elution was used. The subsequent elution of chemical compounds bearing zero, one, two or more than two ionized groups per molecule (mainly carboxylate ions at pH 7) is monitored by an UV detector at 260 nm. Downstream of the detector, a fraction collector is programmed to sample separately "neutral compounds" (NC), "monocarboxylic acids" (MA), "dicarboxylic acids" (DA), and "polycarboxylic acids" (PA) or HULIS. The amount of WSOC recovered in each fraction is determined off-line by TOC analysis using an Analytik-Jena multi analyzer N/C (model 2100). The HPLC column and chromatographic conditions used in this study were the same as in Mancinelli et al. (2007). Further information on the nature of the chemical classes separated by the HPLC method based on elution tests of standard compounds, including discussion of possible misclassification, is reported by Decesari et al. (2005).

3.1 Results: ^{1}H-NMR results

3.1.1 NMR fingerprints of fresh and aged α-pinene SOA

Figure 1 shows the ^{1}H-NMR spectra of α-pinene SOA with increasing photochemical age. The first spectrum corresponding to a "low" SOA oxidation level is similar to reported NMR spectra of environmental chamber-generated α-pinene ozonolysis (Cavalli et al., 2006). However, the NMR fingerprint of α-pinene SOA evolves rapidly with further oxidation steps. A clear, progressive disappearing of 1st generation oxidation products (pinic and pinonic acid) with increasing O/C ratio can be observed. In the NMR spectra corresponding to a "medium" SOA oxidation level, the resonance at 0.83 ppm of chemical shift, arising from one of the two gem-methyls of pinonic acid, accounts for only 0.3% of the total integral of the spectrum, while it represented 2 – 3 % in the fresh SOA samples. This indicates that α-pinene SOA composition evolves rapidly towards more highly-oxidized molecular structures with little resemblance to 1st generation oxidation products. At "medium" and "high" oxidation levels, the unsubstituted alkyl groups of the SOA mixture give rise to a broad Gaussian band between 1.1 and 1.8 ppm of chemical shift with a maximum at 1.4 – 1.5 ppm. The middle point position showing a slight deshielding with respect to a purely alkylic chain (∼ 1.3 ppm for fatty acids) indicates the presence of electronegative groups (such as oxygen atoms) in beta or gamma position with respect to these alkyl groups. The band between 1.9 and 3 ppm, attributable to C-H groups of acyl groups (HC-C=O), also shows a transition towards structures containing more deshielded H atoms. In all cases, the most conspicuous band in this spectral region is found at 2.2 – 2.3 ppm of chemical shift, which corresponds to acetyl and acyl groups of aliphatic compounds with a low O/C ratio, like pinonic acid (R-CH$_2$-C=O and CH$_3$-(C=O)-R, where R is mainly a C$_x$H$_{2x+1}$ radical). Such band persists in all SOA samples, but an additional band between 2.5 and 2.9 ppm is observed in the two samples with the highest O/C ratio, indicating that the aliphatic groups become more and more substituted by electronegative groups: the keto and carboxylic groups become spaced by no more than two methylene (or methyns) groups (x(C=O)-CH-CH-(C=O)X, where X is a generic substituent). Finally, the NMR resonances in the third important aliphatic region of alcoxyl groups (CH-O), between 3.3 and 4.2 ppm of chemical shift, are always relatively small, with peak intensity at intermediate photochemical age. SOA species that contribute to NMR resonance in this region may be correlated with semivolatile, highly functionalized species that contribute to maximum SOA yields observed at intermediate OH exposures (Lambe et al., 2015).

Overall, the NMR fingerprint of α-pinene SOA is highly dependent on photochemical age, with a sharp change already at medium ageing. The most oxidized samples show spectral features that have lost any clear similarity with those of SOA sampled in reaction chambers experiments without ageing (Cavalli et al., 2006).

3.1.2 NMR fingerprints of fresh and aged naphthalene SOA

The ^{1}HNMR spectra of naphthalene SOA samples with increasing O/C ratio are presented in Figure 2. The extract of the least-oxidized sample (on the top) shows broad resonances between 0 and 3 ppm probably due to the effect of colloidal hydrophobic material in solution. Despite such artifact, all spectra of fresh and moderately aged SOA show clear signals from aromatic structures (region at chemical shift from 6.5 to 8.5 ppm) and alkenes (approximately between 5 and 7 ppm). The HNMR spectra of naphthalene SOA are very different than HNMR spectra of SOA produced from the OH oxidation of one-ring aromatic VOCs (Baltensperger et al., 2008), which have mostly aliphatic groups originating from ring opening reactions. Our data are in agreement with molecular speciation studies (Lee and Lane 2009), indicating that naphathalene is oxidized to form 1- or 2-ring aromatic compounds such as naphthol, and substituted benzoquinones, cinnamic acid, and phthalic acid (Chhabra et al., 2015). The chemical shift range of the main aromatic band, between 7.4 and 8.1 ppm, indicates that aromatic rings are substituted prevalently by electron-withdrawing groups, such as carbonyl and carboxyls. At moderate ageing states, a small band at 6.9 – 7.1 ppm indicates the formation of phenolic structures. The HNMR spectra of fresh naphthalene SOA show several singlets in the aromatic region, indicating a diversity of individual compounds occurring in relatively high concentrations,

while moderately aged SOA show mainly the two singlets of phthalic acid. All spectra contain signals at lower chemical shifts with respect to the aromatics, mainly between 3.5 and 6.0 ppm (with the interference of the partly suppressed peak of water in the middle): several functional groups can give rise to these bands, including alkoxy-, peroxy-, esters, hemiacetals and acetals, and vinyls.

The spectrum of the most aged sample (NAPTH 1), which is also the one with the lowest SOA concentration, shows an interference from α-pinene SOA in the aliphatic region. This feature is likely due to experimental setting contamination from a previous α-pinene SOA experiment. Despite the low naphthalene SOA concentration, a broad aromatic band between 6.5 and 8.5 ppm and the same signals found between 3.5 and 6.0 ppm seen in the samples with a medium O/C ratio are still visible in this most aged naphthalene SOA spectrum. However, the band from oxygenated functional groups between 3 and 4.5 ppm becomes relatively more intense with respect to aromatics compared to SOA samples of smaller ageing state. Compared to α-pinene SOA, the ^{1}H-NMR fingerprint of naphthalene SOA appears less sensitive to variations in the OH exposure between the low and the medium level of exposure. More substantial changes can be found for the most oxidized sample, which are only partly visible due the low signal-to-noise ratio of the spectrum.

3.1.3 NMR fingerprints of non-IEPOX isoprene SOA

The samples of isoprene SOA were obtained from the same OH exposure (corresponding approximately to a "medium" exposure in the α-pinene and naphthalene experiments) and differed only for collection time and sample quantity loaded on the filter. The isoprene SOA ^{1}H-NMR spectra profiles were all very similar (an example is provided in Figure 3). The comparison with literature data (Budisulistiorini et al. 2015) led to the unambiguous identification of 2-methyltetrols, clearly responsible for the two singlets at 1.12 ppm (methylic H atoms of methylerythritol) and 1.13 ppm (methylic H atoms of methylthreitol) and for a series of multiplets between 3.4 and 3.9 ppm. Methylerythritol is more abundant (60% of the sum of the two, as an average between two samples extracted in water and three extracted in methanol) than methylthreitol. The spectra show the occurrence of only two diastereomers among the possible four ones (González et al. 2011), indicating that the formation of methyl-tetrols is stereoselective, as already proposed by Cash et al. (2016) on the basis of a theoretical analysis of the IEPOX chemistry, and in contrast with the conclusions of González et al. (2011) claiming that methyltetrols are produced in laboratory conditions only in racemic mixtures. The two methyltetrols account for 65% of the total ^{1}H-NMR signal, the rest being characterized by broad background signal with very few sharp resonances, indicating that the isoprene SOA samples are composed mainly of methyl-tetrols together with a significant amount of mass composed of a very complex mixture of products. The unresolved background resonances are located below the peaks of the methyltetrols, suggesting that the complex mixtures (which can include also oligomeric species) encompass molecular species (or monomers) similar to methyltetrols (at least in their C-H backbone). However, the range of chemical shifts of the background bands characterize molecular species with more electronegative groups (leading to more de-shielded H atoms) than methyltetrols: the band of methylic protons extends to 1.7 ppm (respect to 1.12-1.13 of methyltetrols) and the band of alcoxyl groups (HC-O) extends to 4.3 ppm. The results of Liu et al. (2016), indicating that non-IEPOX isoprene SOA include peroxide-equivalents of methyltetrols, are in agreement with these findings. However, Riva et al. (2016) reported only peroxides for non-IEPOX SOA in unseeded experiments and no methyl-tetrols. It is possible that peroxides decomposed to tetrols in our filter samples during collection downstream the PAM or afterwards during storing. The actual stability of isoprene hydroperoxides in the aerosol itself is largely uncertain, therefore the discrepancy between the findings presented in this study and the results of Riva et al. (2016) cannot be clarified at this stage. In addition, neither Liu et al. (2016) and Riva et al. (2016) reported the presence of carboxylic or keto groups, while our data clearly indicate that these (and/or other acyl groups) are found in the unresolved mixtures of non-IEPOX isoprene SOA, and are responsible for the signal band between 2.0 and 2.6 ppm. Still, this band is much less intense than that of alcoxyls, which is opposite to what observed for α-pinene SOA where acyls are by far

the main oxygenated aliphatic functional group. Thus, ^{1}H-NMR spectroscopy provides distinct fingerprint for isoprene and monoterpene SOA.

3.2 HPLC results

890 The HPLC analysis of fresh α-pinene SOA extracts shows the presence of compounds unretained by ion-exchange columns (neutral compounds) or weakly retained (mono- and di-acids) with a small contribution from compounds having a high retention factor (polyacids, PA, or HULIS), in agreement with previous results obtained from α-pinene SOA samples generated in environmental chamber experiments (unpublished data). It should be noted, however, that the chromatographic analysis of SOA compounds in water extracts

895 generally does not allow to recover high-molecular weight organic oligomers susceptible to hydrolysis reactions (e.g., polyacetals, Kroll and Seinfeld 2008). The HULIS determined by our method are essentially only the non-hydrolyzable ones, stable in aqueous solutions. The HULIS content increases only moderately with ageing, while the yield/fraction of di-acids increases significantly with respect to mono-acids and neutral/basic compounds (Figure 4). With increasing photochemical age, the total organic carbon (TOC) mass

900 fractions of mono-acids, di-acids and HULIS increase from 20% to 34% and 7% to 16%, respectively, whereas the mass fraction of neutral compounds decreases from 19% to 9% (Figure S3). These results are in qualitative agreement with the known chemistry of α-pinene SOA, in which mono- and dicarboxylic acids are the most characteristic condensable 1st generation products (Jenkin et al., 2000; Jaoui and Kamens 2001) while tricarboxylic acids such as 3-methyl-1,2,3-butanetricarboxylic acid or pinyl-diaterpenyl ester

905 (Szmigielski et al., 2007; Yasmeen et al., 2010) are present in lesser amounts and can contribute the observed concentrations of HULIS in this study.

The HPLC fractionation of naphthalene SOA (Figure 5) shows that fresh samples are characterized by a mixture of neutral compounds and mono- and di-acids, completely consistent with the molecular compositions reported in the literature (Lee and Lane 2009). However, a net increase in acidic compounds

910 with photochemical age can be clearly observed. However, the HULIS content, initially small, increases substantially and progressively with ageing. With increasing photochemical age, the TOC mass fraction of mono- and di-acids decreases from 33% to 18% and from 34% to 33% respectively, while the fraction of PA/HULIS increases from 11% to 30% (Figure S4). This is the first evidence of HULIS formation (determined with the ion-exchange method) in laboratory-generated SOA. The formation of polyacidic

915 molecules with three or more carboxylic groups implies the opening of the second aromatic ring in the naphthalene precursor backbone, and/or oligomerization reactions. In both cases, products of such oxidation reactions cannot be explained by current naphthalene SOA molecular speciation studies (e.g. Kautzman et al., 2010).

Finally, the HPLC analysis of isoprene SOA shows that neutral compounds (NC) were dominant in all sample

920 extracts (Figure 6). NC accounted for 59% of the TOC content of the sum of the HPLC fractions. The second most abundant fraction (34%) are the mono-acids, while diacids accounted for a much smaller fraction of TOC, and polyacids were almost absent (ca. 1% of the TOC). The dominance of NC is consistent with the high yield methyltetrols and their analogues (see Section 3.1.3). Assuming that the distribution of NMR functional groups approximately reflects their carbon content, methyltetrols (accounting for 65% of the total

925 NMR signal) can account for the whole of the HPLC neutral compounds, and, as a corollary, the complex mixtures of products detected by unresolved bands by NMR spectroscopy correspond to the mono- and di-acids in HPLC. As already noticed in the previous section, the NMR analysis shows indeed the occurrence of acyl groups which indicate/support the presence of carboxylic acids. We cannot exclude, however, possible misclassification of some neutral compounds into the monoacid fraction, as already observed for some

930 dicarbonyls (Decesari et al. 2005). It is worthwhile to clarify that the definition of chemical classes is based uniquely on the retention factor on the anion-exchange, and therefore sensitive to chromatographic secondary interactions and to chromatographic conditions. Such (unwanted) effects can explain the difference in speciation between samples Pin#2 and Pin#3, both obtained at medium oxidation state (Figure S3). Pin#3

935 was injected at significantly higher concentrations than the other samples (about 3 times than Pin#2), which can have caused the elution of some acidic compounds along with the unretained NC fraction. The results of HPLC analysis of this particular sample are therefore excluded from the following discussion.

4 Discussion and conclusions

In this section, the NMR and HPLC results obtained for the isoprene, α-pinene and naphthalene SOA systems
940 are compared with ambient OA samples. First, we investigated the similarity between the ^{1}H-NMR spectral profiles of SOA with those "typical" of ambient non-biomass-burning WSOC. For this purpose we used one sample of PM1 collected during the 2012 PEGASOS field campaign (Sandrini et al., 2016) in the rural Po Valley (Italy) which can be considered representative for a continental rural "near-city" site (according to the criteria of Putaud et al., 2010). A second PM1 sample was collected at a rural site in the State of Rondônia
945 (Brazil) during the 2002 SMOCC field campaign, and, more precisely, during the early rainy season, when local biomass burning sources had largely ceased and the organic composition of submicron particles was dominated by biogenic emissions (Decesari et al. 2006; Tagliavini et al., 2006). The ambient WSOC and laboratory SOA spectra were binned to 400 points in order to remove the variability in chemical shifts due to, e.g., different pH conditions during the analyses of the samples. Figure 7 shows the correlation between
950 the SOA spectra and the reference spectra of ambient WSOC: the α-pinene SOA and naphthalene SOA spectra were compared to the Po Valley WSOC sample, while the isoprene SOA spectra were compared to the Amazonian sample. There is good correlation ($0.62 < r < 0.92$) between the NMR spectra of α-pinene SOA, at all oxidation levels, with the spectrum of the Po Valley PM1 sample. This finding is in line with modelling results and previous experimental findings indicating that the organic composition in northern
955 Italy in the summertime is dominated by biogenic SOA (Bessagnet et al., 2008; Gilardoni et al., 2011). A moderate positive correlation was also found between the spectra of isoprene SOA and of the PM1 sample from rural Brazil ($r = 0.52, 0.54$). It should be noted that the relative humidity at this pasture site is variable during the day and very high overnight during the rainy season, based on the meteorological data presented by Betts et al. (2009). Therefore, biogenic aerosols are expected to include also isoprene SOA forming
960 through the IEPOX route (Hu et al., 2015), which is not accounted for by our laboratory experiments. Finally, the naphthalene SOA spectra exhibit zero or negative correlations with the Po Valley WSOC spectrum ($-0.15 < r < -0.02$). This result is somewhat expected if we consider that ambient water-soluble aerosols are characterized by acyl functional groups (HC-C=O) in higher concentrations with respect to alcoxyl groups (HC-O) and by a smaller aromatic content (Decesari et al., 2007), with a functional group pattern that is well
965 reproduced by α-pinene SOA and not by naphthalene SOA. Clearly, naphthalene SOA *alone*, with hydrogen-to-carbon (H/C) ratio less than 0.9 due to relatively high aromatic content (Lambe et al. 2011, 2015), does not mimic ambient OA *bulk* composition. It should be noted, however, that naphthalene and other polyaromatic hydrocarbons are co-emitted with many other anthropogenic IVOCs and VOCs including aliphatic compounds in the real atmosphere; therefore the contribution of naphthalene SOA could be simply
970 masked by the contribution of aliphatic IVOC SOA in the ^{1}H-NMR spectra of ambient WSOC. When limiting the correlation analysis of Figure 7 to the aromatic and vinyl region of the spectra (> 6 ppm), Pearson r coefficients of 0.49 to 0.58 are found between the naphthalene SOA and the ambient WSOC spectra, while small values (between -0.2 and 0.4) are found for the α-pinene and isoprene SOA. This result suggests that SOA produced from naphthalene or similar precursors, including many other ring-retaining oxidation
975 products (Section 3.1.2) can explain the presence of aromatic moieties in ambient water-soluble aerosols in areas not affected by biomass burning emissions.

When considering the full spectral range, the H-NMR spectra of α-pinene SOA most closely mimic the functional group distributions of the ambient WSOC sample obtained in PEGASOS (Fig. S1). Interestingly, similarity between H-NMR spectra of α-pinene SOA and Po Valley WSOC increases with increasing
980 photochemical age. For the most oxidized α-pinene SOA samples, the functional group composition, characterized by polysubstituted aliphatic compounds rich of acyls (carboxylic or keto groups), overlaps well with that of ambient WSOC. A good fit between α-pinene SOA and ambient WSOC mass spectral features

is already achieved at medium oxidation conditions, in agreement with the results of Lambe et al. (2011) showing that the correlation between the AMS spectra of PAM-generated α-pinene SOA with the spectra of ambient OOA increases up to an exposure of 1 x 10^{12} OH molec cm^{-3}*s and remains rather stable afterwards. These results suggest that NMR-traced ageing processes reflect the same chemical mechanisms already studied using high-resolution AMS techniques. However, the correlation coefficients shown in Figure 7 for the NMR spectra of α-pinene vs. ambient WSOC (r^2 = 0.39 to 0.84) are smaller than those between the HR-ToF-AMS spectra of PAM-generated SOA vs. ambient OOA (r^2 = 0.7 to 0.9) (Fig. 9 in Lambe et al., 2011). Apparently, the AMS features of ambient OA are more easily reproduced by PAM experiments than the NMR composition, or, in other words, NMR spectroscopy exhibits a greater selectivity for the OA components than AMS. Specifically, ^{1}H-NMR spectroscopy was able to resolve significant changes in composition of α-pinene SOA with photochemical ageing in great detail, especially at an OH exposure of ~1.1 * 10^{12} molec OH /cm^3 s equivalent to multiple days of atmospheric ageing. It should be noted, finally, that a comparison of the AMS and NMR techniques with respect to their ability to trace chemical ageing in laboratory SOA and ambient oxidized aerosols is challenged by the incomplete overlap between the classes of organic compounds contributing to OOA and to WSOC (Xu et al., 2017).

A comparison of fresh and aged SOA with ambient WSOC samples with respect to the HPLC fraction distributions is reported in Figure 8. The distribution of neutral vs. acidic classes of compounds in ambient WSOC refers to the average of the samples collected at the rural background station of Cabauw in the Netherlands (Paglione et al. 2014b). The station is located downwind from anthropogenic sources and biogenic emissions (terpenes from deciduous forests) over a large sector of north-west Europe (Henne et al., 2010). The HULIS contribution in these samples varied between 15 and 20%, in line with previous results obtained in the Po Valley (Mancinelli et al., 2007), but lower than in biomass burning aerosol samples (Decesari et al., 2006). The α-pinene SOA generated in the PAM reactor at high photochemical age and the fresh naphthalene SOA are characterized by a HULIS amount similar to that of Cabauw samples, while the polyacidic content of aged naphthalene SOA is higher than in the ambient samples. In the real atmosphere, naphthalene is co-emitted with many other reactive VOC and IVOC with potentially very diverse HULIS formation yields, therefore the results presented in Figure 8 do not necessarily mean that the chemical composition of ambient OA in Cabauw is better described by the monoterpene chemistry rather than by anthropogenic IVOC oxidation. On the other hand, these results demonstrate that laboratory experiments of SOA formation can generate complex mixtures of products with the same chromatographic properties of HULIS provided a sufficient extent of photochemical aging using the PAM reactor or related techniques. The HULIS fraction of WSOC is in fact proportional to the AMS f44 for SOA (integrated over the filter sampling times) (Figure 9) irrespectively of precursor type. Therefore, the formation of polycarboxylic acids determined by the HPLC technique follows the same positive trend in concentrations of the AMS proxy for C(O)OH groups with increasing OH exposure. This is in contrast with the numerous observations of rapid formation of SOA oligomers during reaction chamber experiments (Kalberer et al., 2006; Reemtsma et al., 2006), indicating that oligomers do not account for chromatographically-defined HULIS. A survey of the laboratory studies on the formation of humic material in secondary aerosol shows that evidence for the formation of polycarboxylic acids comes from the reaction of phenolic compounds in the presence of particulate water (Hoffer et al., 2004), while little is known for unseeded, dry gas-to-particle formation experiments. With the exception of the very preliminary data reported by Baltensperger et al. (2008), our results – to our best knowledge – are the first showing the occurrence of HULIS *sensu strictu* in monoterpene and aromatic hydrocarbon SOA, and these HULIS are clearly shown to be a product of photochemical ageing.

In conclusion, we observed that OA ageing reactions in the PAM reactor produces water-soluble compounds of high complexity but with spectroscopic and chromatographic properties that converge towards those characteristic of ambient OA. Specifically, a good correlation between ambient HPLC/HNMR samples and aged α-pinene SOA was observed in respect to HULIS content and NMR functional group distribution, while aged aromatic IVOC SOA show clear potential for HULIS formation. The isoprene SOA samples do not show compositional features with a clear overlap with those of ambient WSOC obtained in the Cabauw and

Po Valley samples that are representative of continental polluted atmospheres, but should serve as useful reference spectra for future studies/environments impacted by non-IEPOX isoprene SOA.

1035 ## Acknowledgements

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Tables

Sample	Oxidation level	PAM Lamp voltage (V)	OH Exposure (molec/cm^3*s)	Collection Time (h)	average AMS OM concentration (RIE*CE=1.4) (μg/m^3)	OM on filter based on AMS (RIE*CE=1.4) (μg)
α-pinene						
Pin#1	High (f44 = 0.24)	110	2.10x10^{12}	18.5	46.1	384
Pin#2	Med. (f44 = 0.11)	75	1.10x10^{12}	3.2	151.6	221
Pin#3	Med. (f44 = 0.11)	75	1.10x10^{12}	20.2	14.1	129
Pin#5	Low (f44 = 0.05)	30	2.00x10^{11}	20.5	7.5	69
Pin#6	Low (f44 = 0.05)	30	2.00x10^{11}	7.1	50.3	161
Naphthalene						
Nap#1	High f44 = 0.30)	110	2.10x10^{12}	19.7	31.3	277
Nap#2	Med. (f44 = 0.19)	75	1.10x10^{12}	7	55.3	174
Nap#3	Low (f44=0.084)	30	2.00x10^{11}	6.6	16.9	50
Nap#4	Med (f44 = 0.20)	75	1.10x10^{12}	6.6	42.9	127
Nap#5	Low (f44 = 0.074)	30	2.00x10^{11}	15.8	34.7	246
blanks						
Blk#1		110	2.10x10^{12}	6.1	0	0
Blk#2		110	2.10x10^{12}	23.2	0	0
Blk#3		110	2.10x10^{12}	6.1	0	0

Table 1. PAM experimental conditions for naphthalene and α-pinene SOA ageing studies.

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Sample	Oxidation level	PAM Lamp voltage (V)	OH Exposure (molec/cm^3*s)	Collection Time (h)	average AMS OM concentration (RIE*CE=1.4) (µg/m^3)	OM on filter based on AMS (RIE*CE=1.4) (µg)
Isoprene						
Iso#1	Med (f44 = 0.046)	60	7.8*10^{11}	3.7	409	651
Iso#2	Med (f44 = N.A.)	60	7.8*10^{11}	2.8	575	700
Iso#3	Med (f44 = 0.039)	60	7.8*10^{11}	2.2	678	656
Iso#4	Med (f44 = 0.037)	60	7.8*10^{11}	2.9	551	684
Iso#5	Med (f44 = 0.040)	60	7.8*10^{11}	16.1	685	4959
Iso#6	Med (f44 = 0.066)	60	7.8*10^{11}	3.9	767	1280
Iso#7	Med (f44 = 0.059)	60	7.8*10^{11}	3.8	593	986
Blanks						
Blk#1		60	7.8*10^{11}	15.9	0	0
Blk#2		60	7.8*10^{11}	3.1	0	0
Blk#3		60	7.8*10^{11}	16.3	0	0

**Table 2 PAM experimental conditions for isoprene SOA ageing studies.**

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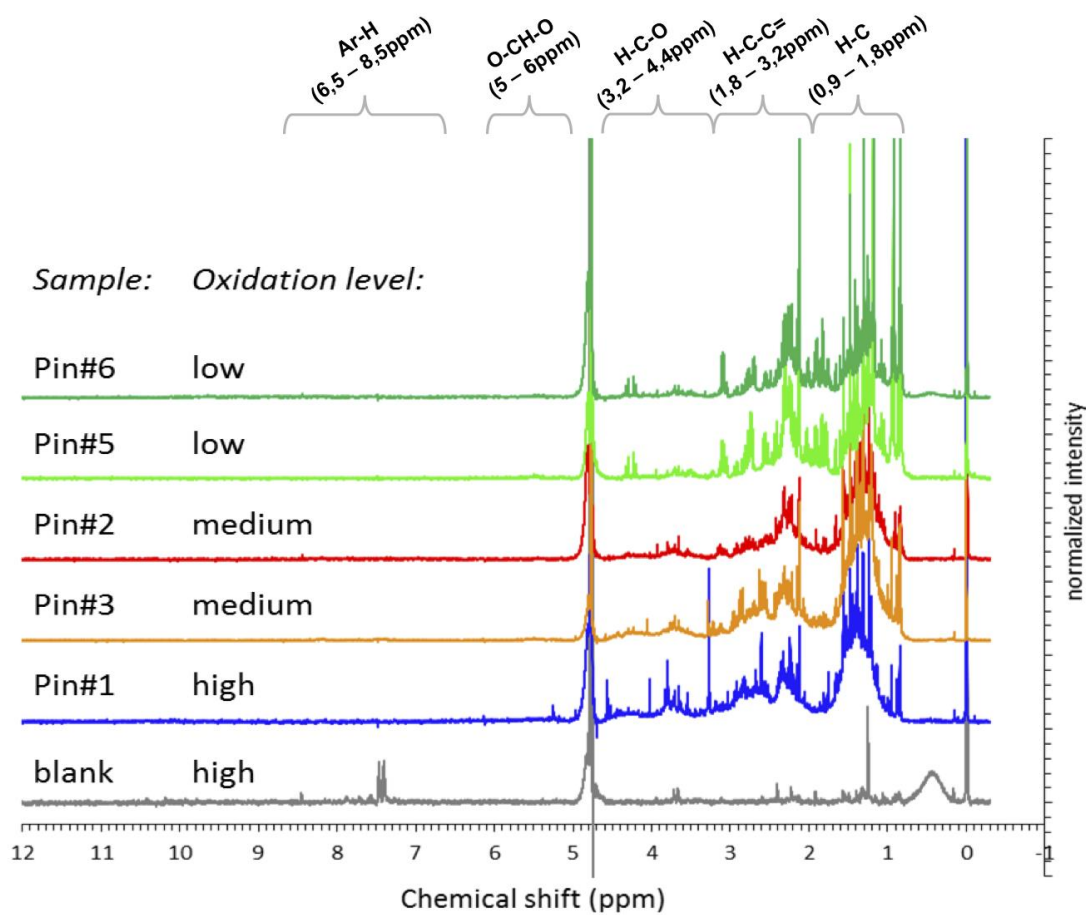
Figure 1. **¹H-NMR spectra of α-pinene SOA as a function of increasing photochemical age in the Potential Aerosol Mass (PAM) oxidation flow reactor. The sharp singlet at zero ppm represents the internal standard (Tsp-d4), while the broad peak at 4.8 ppm is the – partly instrumentally suppressed – HDO peak. The sharp singlets between 0.9 and 2.2 ppm in the fresh SOA samples (Pin#5 and Pin#6) are genuine bands of the samples and were identified as methyl groups of pinic and pinonic acid.**

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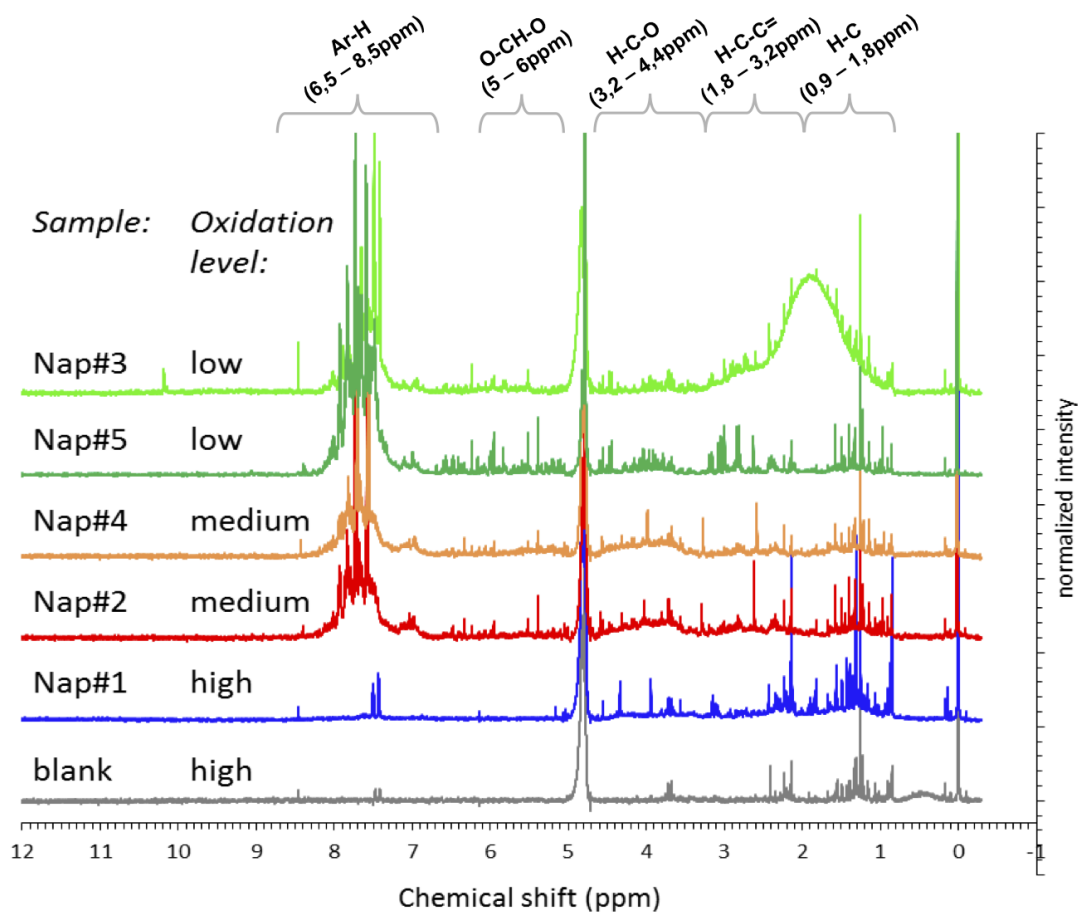
1440

Figure 2. ^{1}H-NMR spectra of naphthalene SOA as a function of increasing photochemical age in the PAM reactor. The sharp singlet at zero ppm represents the internal standard (Tsp-d4), while the broad peak at 4.8 ppm is the – partly instrumentally suppressed – HDO peak.
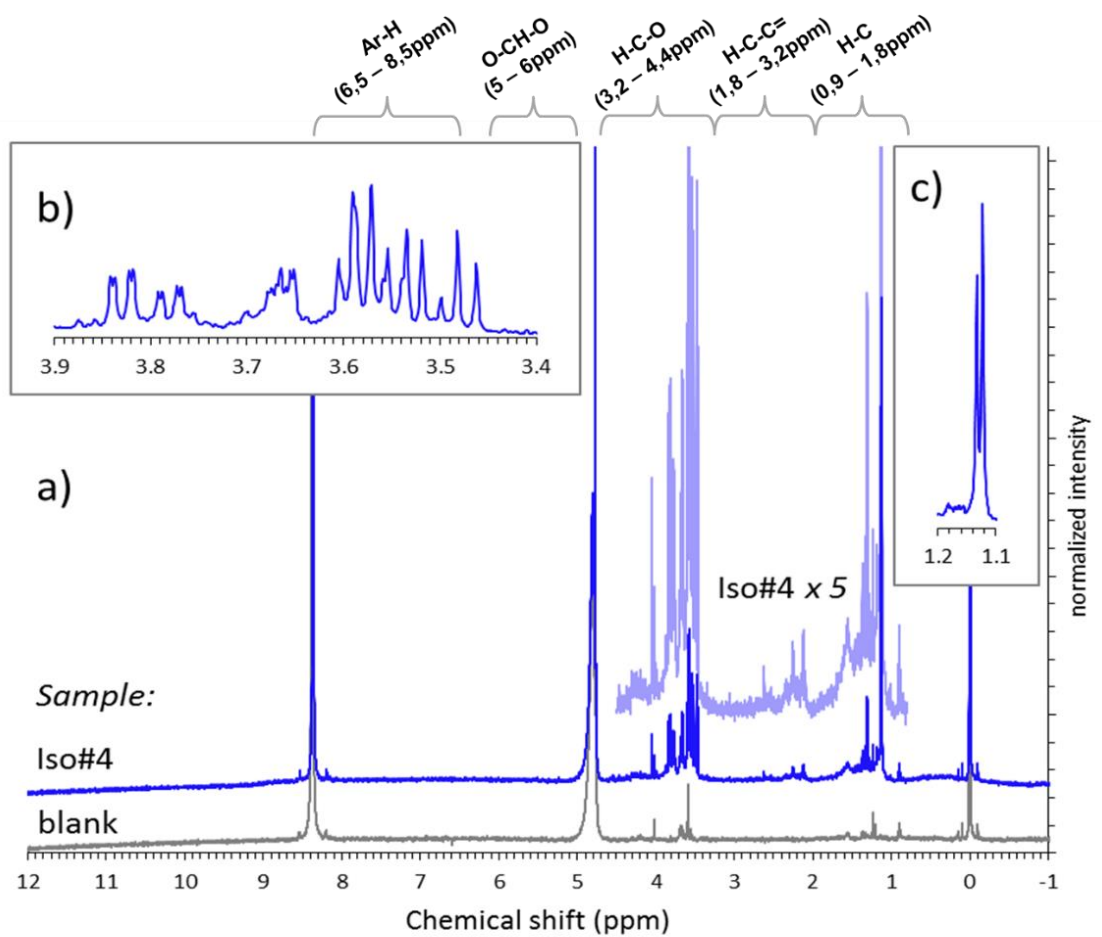
1445

Figure 3. Panel a: ^{1}H-NMR spectrum of isoprene SOA generated in the PAM reactor at an OH exposure of $8*10^{11}$ molec cm^{-3} sec. The bottom trace shows the same spectrum with enlarged the broad background bands. Panel b and c show the methyltetrols resonances between 3.4 and 3.9 ppm and 1.12-1.13 ppm, respectively
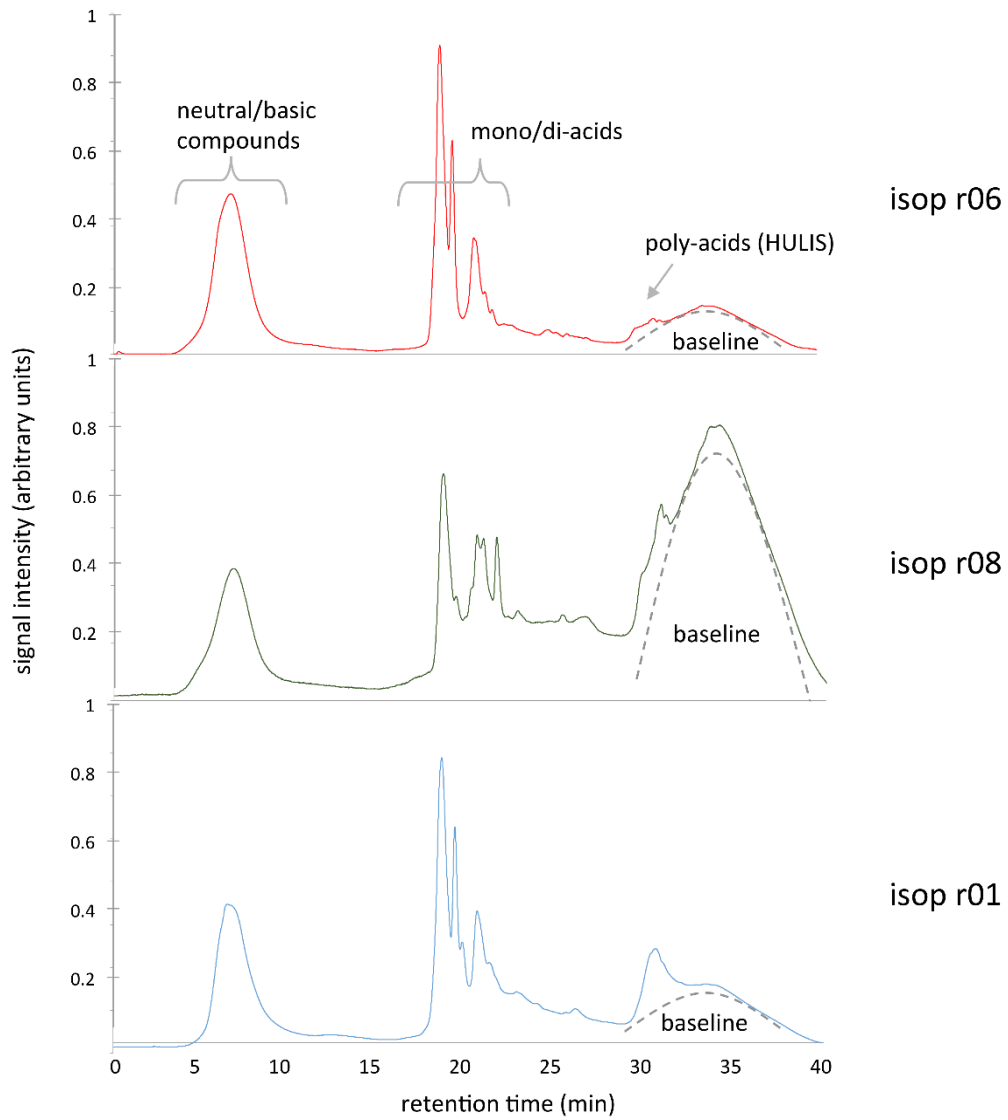
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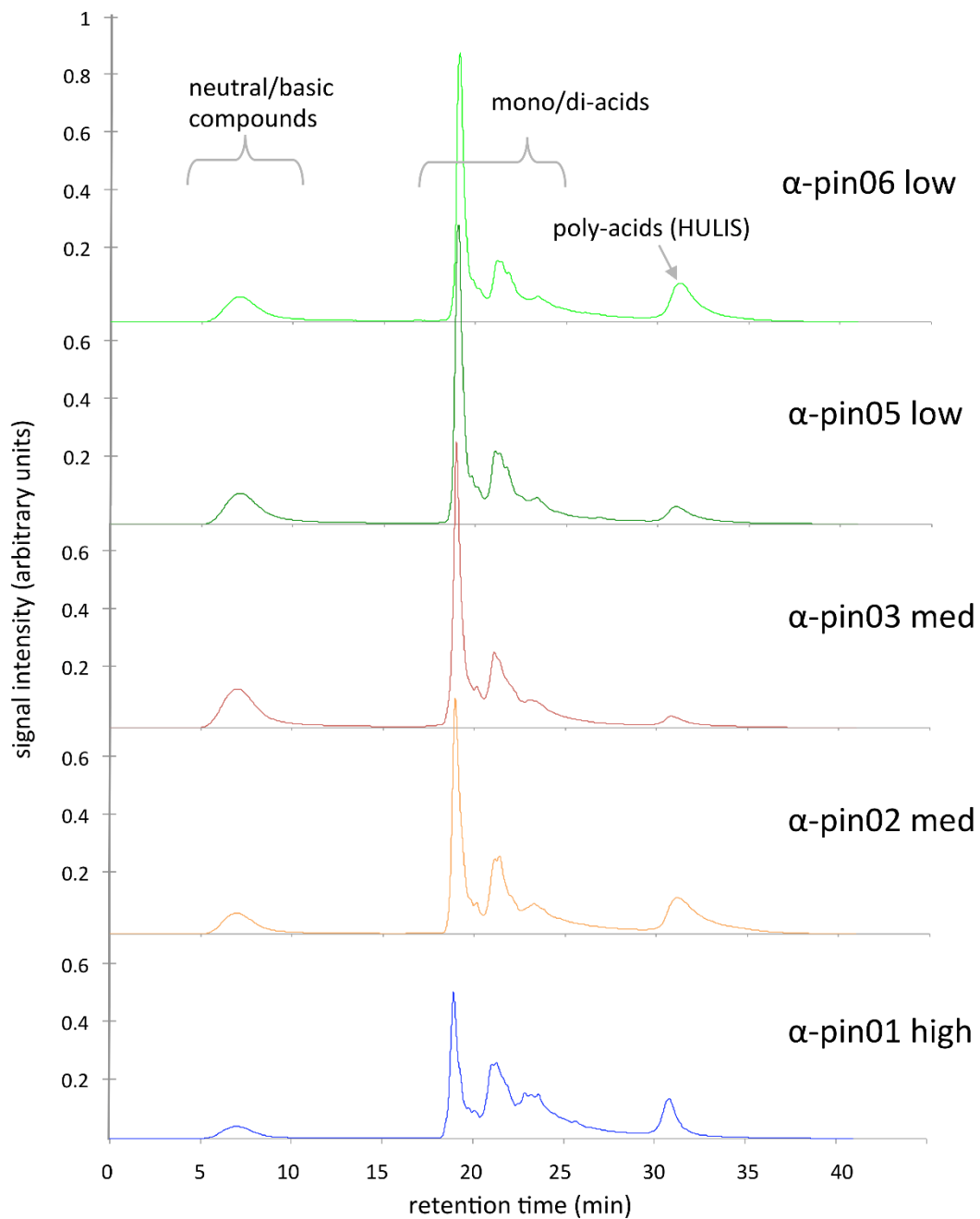
Figure 4. HPLC chromatograms of α-pinene SOA water extracts. Chromatographic features are grouped into neutral, mono-/di-carboxylic acid, and polycarboxylic acid classes based on their affinity for the column phase. Sample identifications are provided in Table 1.
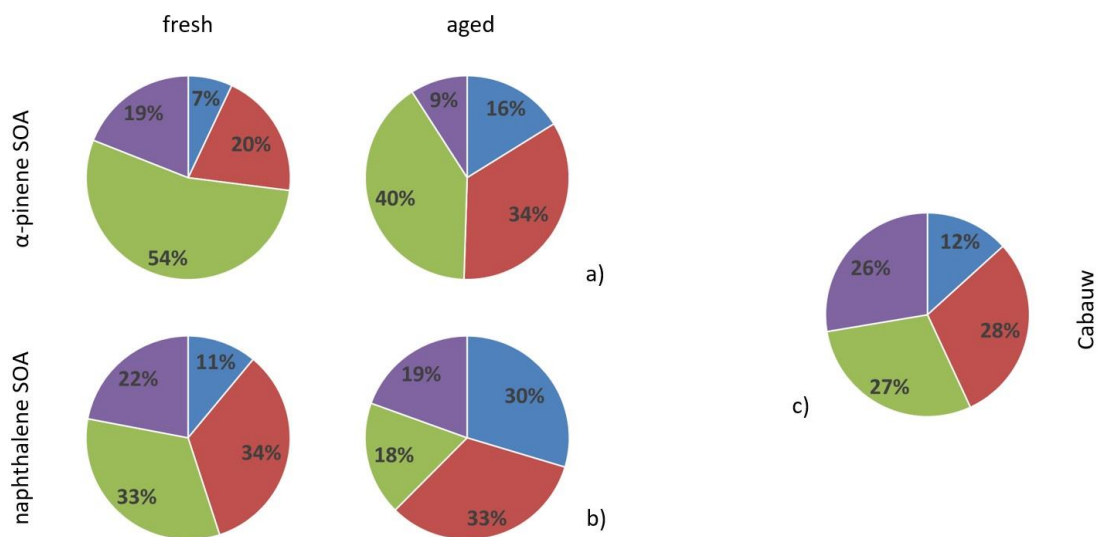
1455
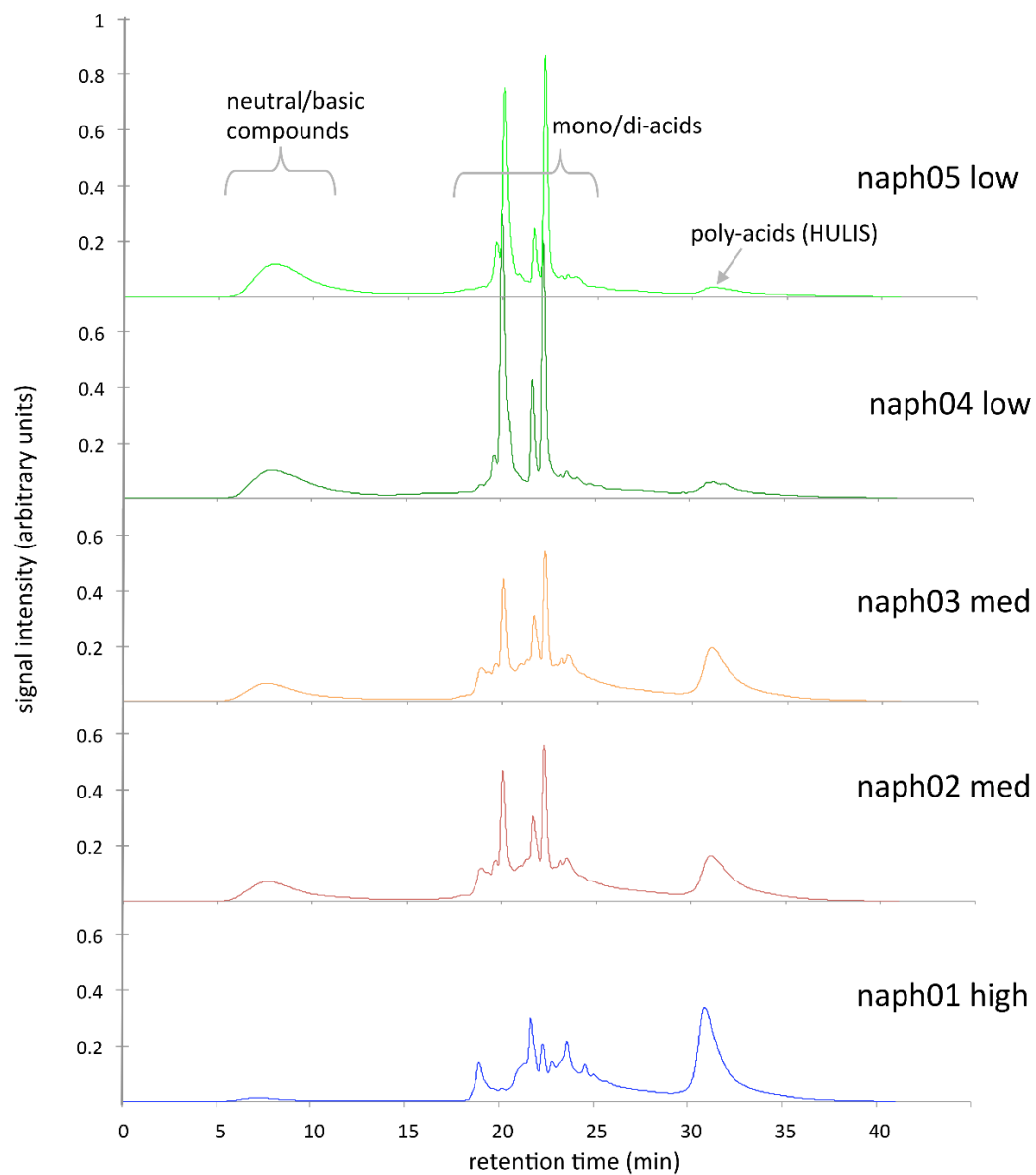
Figure 5. HPLC chromatograms of naphthalene SOA water extracts. Chromatographic features are grouped into neutral, mono-/di-carboxylic acid, and polycarboxylic acid classes based on their affinity for the column phase. Sample identifications are provided in Table 1.

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Figure 6. HPLC chromatograms of isoprene SOA water extracts. Chromatographic features are grouped into neutral, mono-/di-carboxylic acid, and polycarboxylic acid classes based on their affinity for the column phase. Sample identifications are provided in Table 2.

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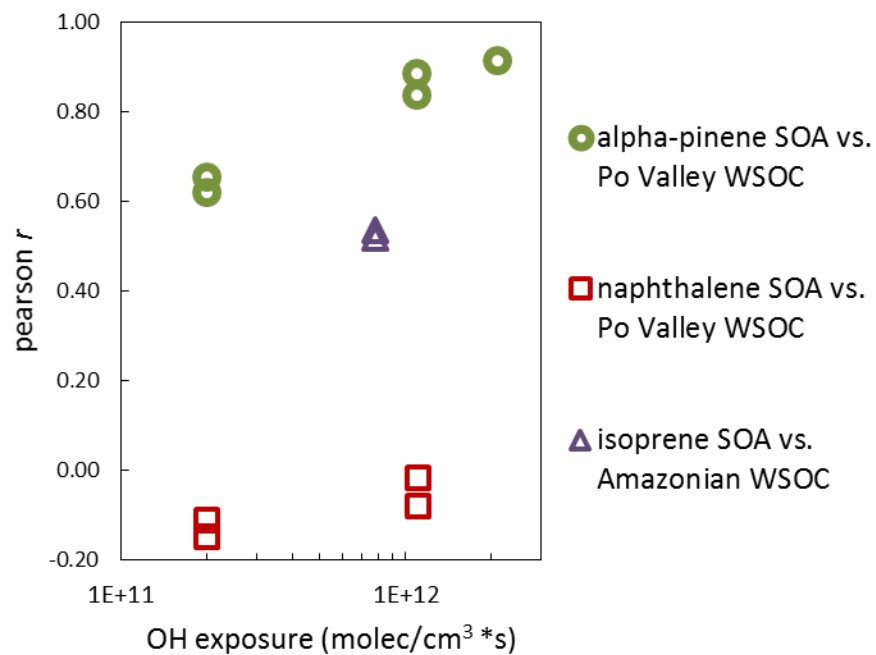
Figure 7. Pearson correlation coefficient between H-NMR spectra of PAM-generated SOA and ambient PEGASOS WSOC.

fresh **aged**

α-pinene SOA

7% / 20% / 54% / 19% (fresh)

9% / 16% / 34% / 40% (aged)

a)

naphthalene SOA

11% / 34% / 33% / 22% (fresh)

30% / 33% / 18% / 19% (aged)

b)

Cabauw

12% / 28% / 27% / 26%

c)

1470

Figure 8. Distribution of HPLC fractions (total recovered TOC content = 100%) for α-pinene SOA (panel a), naphthalene (panel b), isoprene (panel c), and for ambient OA sampled in Cabauw, Netherlands (panel d).
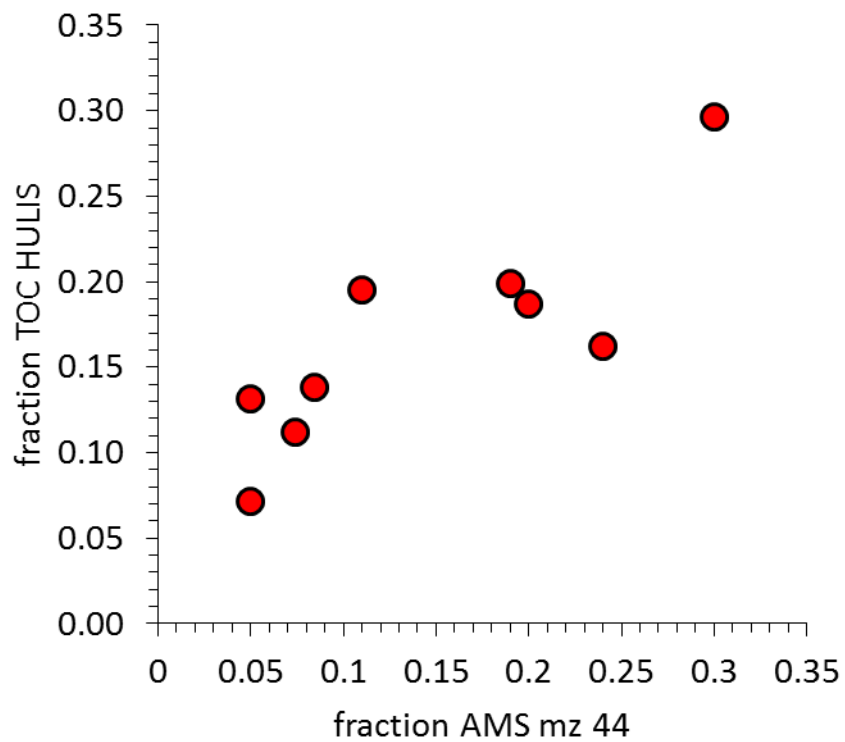
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Figure 9. Correlation plot between the AMS f44 of SOA and the HULIS fraction of HPLC-eluted WSOC.