

Interactive comment on “Distribution of gaseous and particulate organic composition during dark α -pinene ozonolysis” by M. Camredon et al.

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We thank the two anonymous referees for their suggestions for improvements to the manuscript, and Drs. Compernelle and Barley for their comments regarding the vapour pressure estimation methods adopted here and elsewhere. In this response we first address the issue of vapour pressure estimation methodology and model uncertainty, and then consider the other comments and points raised by the referees.

Choice / impacts of vapour pressure estimation method:

We adopted the Myrdal and Yalkowsky (1997) approach, coupled with the Joback method for boiling points (e.g. Reid et al., 1986) as it has previously been shown to perform well in reproducing experimental data (e.g. Camredon et al., 2006). Sub-

Full Screen / Esc

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Discussion Paper



sequently the study of Barley et al. (2010) amongst others has indicated that this approach may systematically underestimate the SVOC vapour pressures. If this is the case the agreement with observed mass in our experiments may indicate mechanistic shortcomings in the gas-phase MCM α -pinene mechanism and/or effects of accretion reactions in the condensed phase or involving heterogeneous uptake of gaseous species. Barley et al. show that the Nannoolal methods (Nannoolal et al., 2004; 2008) perform significantly better than Myrdal and Yalkowsky coupled with Joback (referred to as P_{vap}M&Y,J) against experimental data for a range of atmospherically relevant functionalised organic compounds typical of SOA components.

We have extended the sensitivity study reported in the paper to reflect this issue. We have recalculated the 298 K vapour pressures for the "top ten" species simulated to be the major contributors to the α -pinene ozonolysis SOA mass using the Nannoolal methods (referred to as P_{vap}N,N) and compared the results with the other methods. For these species, P_{vap}N,N are systematically higher than P_{vap}M&Y,J, with divergences varying between a factor of 10.9 and 94.4 (see figure 4, revised manuscript). We have therefore recalculated the simulated SOA mass with vapour pressures for all species (P_{vap}M&Y,J) multiplied by factors of 10 and 100, representative of the range of increase in vapour pressure obtained with the Nannoolal method. This leads to a reduction in the maximum SOA mass of factors of 2 and 6 respectively compared with that obtained with P_{vap}M&Y,J for the α -pinene + O₃ experiment, and by factors of 8 and 30 respectively for the α -pinene + O₃ + CO experiment, in all cases now substantially below the experimentally observed value. Inclusion of condensed-phase reactivity for non-volatile products on timescales of 60, 30 and 5 minutes increases the simulated mass to the envelope of the observed values. In the case of the α -pinene + O₃ experiment, a condensed phase lifetime of SVOC of the order of 5 minutes increases the simulated SOA mass by less than a factor of 3, using the P_{vap}M&Y,J or P_{vap}M&Y,J multiplied by factors of 10 or 100. In the case of the α -pinene + O₃ + CO experiment, the simulated results show a greater sensitivity to vapour pressure estimates. In this experiment, the formation of SOA comes from first generation oxidation products from

α -pinene ozonolysis, as OH radicals are scavenged by CO. The simulated SOA formation is therefore very sensitive to the vapour pressure of these compounds. These results are shown in the revised manuscript, figure 5.

Although it provides a comprehensive detailed description of the tropospheric chemistry currently available, the MCM is not (through necessity) fully explicit: Systematic approximations include the pooling of organic peroxy radicals to simplify the representation of their self and cross-reactions, and omission of minor channels in the VOC degradation mechanisms (as outlined in the latest protocol (Saunders et al., 2003)), in particular for larger species such as α -pinene. Significant uncertainties exist in the degradation mechanisms of (large) bi- and multi-functional organics owing to a lack of laboratory experimental data. Much of the chemistry in the MCM is based on analogy to similar (smaller) species and structure activity relationships (SARs), defined using simplified datasets of reactions of a smaller subset of similar organics. Much of the testing and evaluation of the MCM chemistry has focused upon gas-phase degradation, and in particular correct simulation of ozone production during photo-smog experiments (e.g. Pinho et al., 2007 and references therein). Given the system complexity, manually constructed degradation mechanisms for sizeable VOCs are unlikely to include all observed processes (see comments below), and we might anticipate that minor channels are omitted so that SOA mass calculated from such mechanisms could therefore underestimate that observed (all other factors, e.g. vapour pressures, being equal). In the case of α -pinene, specific examples not included in the MCM mechanism used here include the OH-initiated oxidation pathways identified by Peeters et al. (2001) / Vereecken et al. (2007) (discussed further below).

It may therefore be that the relatively good agreement obtained between the measured and simulated aerosol mass reflects a combination of underestimated vapour pressures, and underprediction of low-volatility products within the MCM mechanism. If the Nannoolal methods are adopted, the lower mass (compared with experiment) predicted by our sensitivity study may indicate that either (i) chemical channels missing

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from the MCM comprise a significant proportion of the SVOC pool or (ii) condensed phase reactions forming lower volatility products, and/or heterogeneous reactions of VOCs increasing SOA mass, are significant and occur rapidly, although a number of other uncertainties also exist, including the assumed density of the aerosol particles, measurement uncertainty (parent reactants, SMPS measurements, contributions from particles below the monitored size range) and model approach (assumption of thermodynamic equilibrium without explicit treatment of micro-physical processes). While a number of α -pinene degradation products have been identified which are not included in the MCM, the qualitatively good agreement for the observed and simulated mass distribution reported here suggests that the model simulates the major contributors to the observed SOA composition (with the exceptions of the m/z 225 and 241 peaks discussed below). Although as many minor channels will produce species isobaric with those included in the model, with low resolution mass spectra such as those recorded in this work, substantial fragmentation occurring and in the absence of individual species' instrument response factors, caution is needed regarding this inference.

Substantial oligomer formation within SOA is well established, and indeed some form of condensed-phase reaction is clearly necessary to explain the ESI-MS mass spectra reported here. If the lower vapour pressure estimations suggested by the Barley et al. study are adopted (Nannoolal), and noting the other limitations mentioned above, the condensed phase reactivity tests performed here suggest that the lifetime of condensed SVOC may be short (of the order of a few minutes) to reproduce the observed SOA mass. It would be interesting to perform time-resolved measurements of aerosol composition in future experiments to investigate this point.

While the original manuscript noted the importance of and dependence upon vapour pressure estimation methodology, including reference to the Barley et al. study, we have now modified the body of the manuscript and its figures to extend this discussion in line with the points raised above, particularly regarding vapour pressure estimates and the potential for counteracting model errors and omissions. We have modified

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Figure 4 to include the Nannoolal vapour pressure calculations, added a further figure (5a/b) to illustrate the effect their adoption would have upon the calculated SOA mass. We have also included these points in the summary of the paper and noted them in the abstract, as suggested by the referees / comment authors.

Further points - Referee 1:

"....page 27847, where it is indicated that the theoretical studies of Peeters and co-workers have identified possible alternative pathways which may have a significant impact. Given the nature of the pathways generally involves isomerisations to give products with a larger number of polar substituents, this would presumably tend to make the product distribution less volatile. Does the model-measurement comparison allow any view to be formed in relation to the importance of these omitted pathways through identification (or not) of the masses corresponding to the postulated products? It would be good to be able to either confirm or refute the pathways (e.g., in section 5.1 or section 5.2)."

Peeters et al. (2001) and Vereecken et al. (2007) have identified alternative OH-initiated oxidation pathways of α -pinene, such as isomerisation of the peroxy radical PROH3 by 1,6-H shift or ring closure and of the alkoxy radical AROH3 by 1,5-H shift or ring closure. These pathways would lead to the formation of multi-oxygenated secondary species, and thus species having a low volatility. First generation products formed according to these additional oxidation pathways are listed in the revised manuscript (table 6). In the case of the gas-phase composition / mass spectra, the peaks which are observed but not simulated (principally, at m/z 149 and m/z 165) do not correspond to any of the first generation products formed by the alternative OH-initiated oxidation pathways of α -pinene suggested by Peeters et al. (2001), Fantechi et al. (2002), Vereecken and Peeters (2004) or Vereecken et al. (2007) (revised manuscript, section 5.1.3). In terms of the condensed phase composition however, all of these additional species have a molar mass that corresponds to a peak present in the positive ESI-MS mass spectrum. Species having a molecular mass of 184, 186

or 200 g.mol⁻¹ would contribute to the peaks at the [R+Na]⁺ adduct of m/z 207, 209 and 223 respectively, in addition to the other species already present in the simulation. Species having a molecular mass of 202 and 218 g.mol⁻¹ would explain the missing simulated m/z peak of two of the major ESI-MS peaks in the positive spectrum at the [R+Na]⁺ adducts of m/z 225 and m/z 241. The difficulty in definitively demonstrating their presence is then that we do not know the absolute sensitivity of the analysis to the various specific compounds; however our condensed phase data are certainly consistent with the occurrence of these pathways (or of others forming products at the same m/z). We note that these additional first generation products still do not account for the unobserved masses between 240 and 280 Da, which could arise from further (gaseous or condensed phase) oxidation of species not explicitly described in the MCMv3.1. We have revised the manuscript to include this discussion in sections 5.1 and 5.2, and added table 6 to explicitly consider these additional pathways and identify the candidate species and masses considered.

-"... page 27848, where it is commented that "No chemical reactions were implemented in the condensed phase." The possible impact of this omission is then considered Section 4.1, through parameterised formation of non volatile products of condensed phase reactions impact of including the condensed phase chemistry would no doubt be much greater if one of the alternative methods of vapour pressure estimation (yielding systematically higher vapour pressures) had been used in the base case simulations ... It would therefore seem important to point out that the perceived impact of the condensed phase chemistry is sensitive to the applied vapour pressure estimation method, and probably to demonstrate this."

This point is addressed in the comments & revisions described above in response to the comments of Drs Compernelle & Barley.

-"I also note that the mass distribution presented in Figure 6 seems to suggest that the mass contribution of the detected dimers is somewhat greater than that of the detected monomers, such that the importance of the condensed phase chemistry is greater than

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the sensitivity test in section 4.1 implies."

Figure 6 certainly indicates that more dimer than monomer species are detected in the condensed phase, although given that the sensitivity of the ESI-MS will vary with compound identity and potentially with size, this does not demonstrate that the concentration of dimers is higher. If future experiments are able to place an absolute scale on the mass spectra observed (for the condensed phase species), the relative contribution may be directly assessed, but this is not possible with our current data for which only the relative experimental signal is determined. Sensitivity studies on the condensed phase reactivity have been performed for various lifetime of condensed SVOC in section 4.1. For the lifetimes of 60, 30 and 5 minutes, and for all the vapour pressure estimates, the non-volatile species represent the major fraction of the simulated mass at the end of the experiment, in agreement with the large proportion of dimers detected by ESI-MS. For the example of the α -pinene + O₃ experiment simulated with the use of PvpMY,J, the non-volatile species contributes about 75, 95 and 100 % to the total simulated SOA mass after 2h for lifetimes of condensed SVOC of 60, 30 and 5 minutes respectively.

"On page 27865, it is commented that hemiacetals and peroxyhemiacetals might be converted back to monomers during ESI-MS analysis. Can the authors comment further on this, or provide a reference or supporting material? It would seem to be a very important point, not only for quantification of the role of these reactions, but also because the decomposition might lead to different monomers via a concerted rearrangement."

Peroxyhemiacetals are indeed likely to be thermally labile and unstable compounds (Jang et al., 2002; Surratt et al., 2006). During ESI, samples are subjected to temperatures of up to 350 C within the ion source; any thermally labile groups may therefore fragment during analysis. For example, we have run many standards of peroxides using this technique and found that they undergo fragmentation by loss of water within the ion source. The fragmentation of dimers back to monomers (or to different monomers)

Full Screen / Esc

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Discussion Paper



is indeed a possibility, and this may account for some of the low molecular weight peaks observed that are not predicted from our mechanisms, however to our knowledge no experimental evidence of this has yet been published. We have extended the discussion of this possibility within the revised manuscript (section 5.3.2)

-"Page 27844, line 23: An upper limit mixing ratio for NO is provided in support of the statement about NO_x-free conditions. Owing to the presence of 100 ppb ozone, and absence of light, NO_x would be expected to be entirely NO₂. A quantification of NO₂ should therefore more appropriately be provided."

An upper limit for NO₂ has been added in the revised paper.

-"Figure 6, lower panel: the ESI-MS intensity scale appears to have a typo."

The intensity scale has been corrected in the revised manuscript.

Further points - Referee 2:

-"As the authors point out, the choice of vapor pressure estimation method is a critical determinant of calculated SOA loading. As discussed by other reviewers, the method chosen (and used to obtain the results shown in Fig 3) may substantially underestimate SVOC vapor pressures; this would have the effect of masking other deficiencies in the model. An investigation into possible offsetting factors would seem to be warranted. Examples include the formation of low-volatility species (such as acids) via unidentified mechanisms, or accretion reactions involving the heterogeneous uptake of gas-phase species. In the current study, oligomer formation only occurs by reaction of particulate SVOCs, so relatively volatile species could not be incorporated into the aerosol (which is believed to happen for molecules such as glyoxal). On the other hand, the model does not include the loss of SVOCs to the chamber walls, which might significantly lower predicted loading (Hildebrant et al., 2009). It would be helpful to include these in the model, or at least discuss what effects these processes might have on modelled results."

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The vapour pressure estimate impacts, and model uncertainties, are discussed above in response to the points raised by other contributors to the discussion. In terms of wall loss, this was directly determined for the aerosol via the observed evolution of SOA mass after the (near-)completion of the α -pinene oxidation, while dilution losses of gaseous compounds were accounted for via monitoring the removal of an SF₆ dilution tracer. No correction for wall loss of SVOC was applied to our simulations. As the referee points out, in principle such losses will occur, and will reduce the SVOC loading and hence SOA formation in comparison with that modelled. Hildebrant et al. (2009) quantified potential upper and lower limits to this effect, which they assumed to result from SVOC interactions with particles previously deposited to the chamber walls, for toluene photooxidation in a moderate volume chamber (12 m³) and found an upper limit for the difference in aerosol mass to be up to 50% at the end of a three-hour experiment. We anticipate the effect to be less than this upper limit for our experiments, carried out in the much larger EUPHORE chamber (200 m³ volume; surface:volume ratio ca. 0.75 m⁻¹) and over a shorter timescale (faster reacting system). Wall loss has not been noted for VOCs in past studies of aromatic systems in EUPHORE (e.g. Bloss et al., 2005). We have modified the manuscript to note that this effect is not included in our simulations (section 3.3), although the vapour pressure issues discussed above would have a much more significant impact upon the modelled SOA.

-"the doubling of SOA mass when condensed-phase reactions (forming NVOCs) are assumed to occur rapidly suggests that the average SVOC initially formed from α -pinene ozonolysis is partitioned between the gas and particle phases roughly equally. Is there any experimental evidence for this? Some comparison of the gas-phase (CI) and condensed-phase (ESI) chemical composition measurements would seem to be worthwhile. I do not see any obvious correspondence between the two (Figures 5 and 6). This could be a result of oligomer-forming reactions having gone to completion; but in that case, the aerosol would no longer be composed of semivolatile organics."

The implementation of condensed phase reactivity leading to non-volatile organic com-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

pounds is expected to increase the simulated SOA mass considering that (i) the loss of a SVOC in the condensed phase shifts its gas/particle equilibrium towards the condensed phase and (ii) the transformation of this SVOC in a non volatile organic compound prevents any re-volatilisation in the gaseous phase as gas phase oxidation proceeds. A further indirect impact comes from the global increase in the organic aerosol mass that also enhances the uptake of all SVOC. In addition, the influence of gas phase reactivity on SOA mass is dependent upon the vapour pressure estimation method used as shown in figure 5 of the revised manuscript. Therefore the predicted SOA mass responds to the condensed phase reactivity and assumed condense-phase lifetime in a complex manner. The inferred "approximate doubling" – presumably the approximate increase between the solid red and large-dashed black lines on figure 3 of the original manuscript, corresponding to no condensed phase reactivity and a condensed phase lifetime of 5 minutes respectively – is probably due to a combination of all the consequences of condensed phase reactivity on the absorption of SVOC listed above. In terms of comparison between the gaseous and condensed-phase spectra, this is complicated as the response and fragmentation of the two instruments differ. In addition, the ESI-MS has been optimised for a target mass of 200 Da, so there may be higher levels of small volatile species than the mass spectrum indicates. These will not be major peaks as they would still show up but calibration for ESI sensitivity would be required for a direct comparison. We have added a figure comparing the mass spectra directly (Supplementary figure S3 of the revised manuscript); only a small overlap between m/z signals is observed. If the caveats over the observational limitations may be disregarded, this would further indicate that condensed phase reactions and/or processing are very significant. However without fully characterising the CIR-TOF-MS and ESI-MS response factors and fragmentation it is hard to draw such a conclusion definitively. Again it would be interesting to acquire time-resolved composition data to explore this behaviour.

-"there is little discussion of the time dependence of individual species (mass spectro-metric peaks) in the gas phase. (Time-dependent measurements cannot be made of

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the particulate organics, given that only one filter sample is made per experiment.) If different peaks in the CI measurements or simulated CI mass spectra exhibit significant differences in their time evolution, the model-measurement comparisons for these species would provide a powerful test of the MCM description of α -pinene ozonolysis."

Time-evolution of the evolving chemical composition is of course of interest and was omitted in part in consideration of the length of the manuscript, and in part due to the data quality. We have compared the observed and predicted evolution of the major m/z peaks in Supplementary figures S1 and S2, discussed in the revised manuscript (section 5.3.1). The CIR-TOF-MS signal for many of the larger SVOC (Fig. S2) is low and the temporal evolution at a given m/z therefore somewhat noisy. The simulated results show a good agreement with the data for the smaller species (Fig. S1). For the larger species (Fig. S2) the model is comparable to the observed temporal evolution from the CIR-TOF-MS measurements except for m/z 147, although the quality of the data is such that definitive conclusions are hard to draw. In the case of m/z 147, the significant difference probably indicates that the main contributor to the observed peak is not represented in the model (the simulated concentration at m/z 147, C614OH (2,3-oxo-5,6-hydroxy hexane) is small). The observed signal could be explained by the formation of species not included in the MCMv3.1 or could arise from fragmentation of analytes during the CIR-TOF-MS analysis. See also comments above to the related point raised by Referee 1 over evidence for additional (non-MCM) product channels.

"p. 27858, 1st paragraph: It would seem that a third possibility is that these compounds simply are not formed, contrary to the model predictions."

We agree this is an alternative possibility. We have modified the manuscript to note this further possibility in section 5.1.3, and in the extended discussion of model uncertainties, section 4.

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Full Screen / Esc

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