

Authors' responses to referees' comments on: Jenkin et al., Atmos. Chem. Phys. Discuss., 12, 2891-2974, 2012

We are grateful to both referees for their generally supportive comments on this work, and for agreeing to review a particularly long and detailed manuscript. Each referee provides a few comments and technical corrections, which have been taken into full consideration when producing the revised version of manuscript. Responses to these comments are now provided.

Referee 1

Comment 1: This is a valuable paper that synthesizes current knowledge on the atmospheric chemistry of beta-caryophyllene and describes its implementation in the Master Chemical Mechanism which the authors make available to the community. Comparisons with measurements from chamber studies (including new and previously reported experiments) are interesting, as much for their agreements as for a few discrepancies.

Response: We are very grateful to the referee for recognising the value of this work, and for the supportive comments regarding the Master Chemical Mechanism and its evaluation using the new and previous chamber data, as described in this paper.

Comment 2: The model does reasonably well in many respects, including the prediction of [SOA] for a broad range of studies (last column of Table 1), the time evolution of betacaryophyllene, NO, NO₂ and O₃ (Fig. 11, 13), and many specific compounds predicted and observed by mass spectrometry, or at least associated to plausible fragments.

On the other hand, it is sobering to see that even first generation products are overpredicted by a factor of two (e.g. Fig. 15, top panels, noting that left and right scales differ). Many other comparisons (e.g. bottom of Fig. 15 and Figs. 16-19) only test the general shape of the time evolution, as model ppb are plotted alongside uncalibrated counts, and so are not quantitative.

Hence my only suggestion: To provide a summary of the model evaluation (beyond simply asserting that the model is generally acceptable, as now stated in the abstract), identifying major successes and discrepancies, somewhat along the lines of what I attempted to list above but that the authors could do much more thoughtfully. This could be done in the Discussion/Conclusion section, and it would also fit well in the Abstract, replacing the current wish list of future studies which seems a bit misplaced and arguable.

Response:

We understand and respect the general point the referee is making, and have included additional summary statements relating performance to specific observables in the revised manuscript. However, we would also maintain that the identified list of areas of uncertainty that we give (the "wish list") is our thoughtful summary of the results of the model evaluation that the referee seeks, and which also tries to reflect gaps in understanding that became apparent during the MCM construction process. It was decided to present the information in this way (in both Discussion/Conclusions and Abstract), because it is much more succinct than trying to list all areas of uncertainty and discrepancy in a complex system, which could be very long and (in our opinion) less helpful. In practice, it is also actually very difficult to identify what might be classed as "major successes and discrepancies", because the uncertainty bounds of model and measurement generally overlap. We return to some of the specifically-raised points below, but can explain our general thinking regarding the summary list as follows:

a) Species possessing the secondary ozonide functionality (which are comparatively volatile) are predicted to make major (but uncertain) contributions to the simulated first- and second-generation product distribution. This introduced uncertainty into several aspects of model performance, including the model-measurement comparisons of m/z 253 in the gas phase (i.e. the top panel of Fig. 15 commented on by the referee) and of the SOA profiles. These were therefore sensitive to the primary yield assigned to the secondary ozonide, and the extent to which this functionality is retained upon further oxidation. This is therefore identified as point (i) in Abstract (first bullet in Discussion/Conclusions), to reflect the level of success/discrepancy in simulating the observables identified above.

b) The formation mechanism for β -caryophyllinic acid (C137CO₂H) is currently not known, and the provisional representation used in the MCM is apparently unable to explain its observation in some reported studies. On the other hand, the formation of its isomer, β -caryophyllonic acid (C131CO₂H), seems almost inevitable as an important second-generation product of the further oxidation of β -caryophyllonic acid (C141CO₂H), although this has not been reported in some studies where its major formation is predicted by the MCM chemistry. These issues are therefore identified as points (ii) and (iii), to reflect the model-measurement successes/discrepancies in the various systems considered. (The referee's comment (3f) below would also appear to support inclusion of point (iii) in this way).

c) We found that to recreate the observed β -caryophyllene, ozone and NO_x profiles in the chamber photo-oxidation studies, it was necessary to change either or both of the primary OH yield from β -caryophyllene ozonolysis and the hydroxy nitrate yield from the OH-initiated chemistry within reported bounds – the simulations being very sensitive to these parameters. The need for improved quantification of these parameters is therefore identified as points (iv) and (v).

d) The simulated composition of SOA in the absence of NO_x invariably had major contributions from multifunctional species possessing hydroperoxide groups, although no such species have currently been reported in observational studies. This was therefore specifically identified in point (vi), as part of a more general statement about product identification and quantification in both SOA and gas phases.

These points are explained in some detail in the Discussion/Conclusions, but are necessarily presented more briefly in the Abstract. We are reluctant to remove the list from the Abstract; however, as indicated above we have expanded the general statement about acceptable model performance in both Discussion/Conclusions and Abstract, by relating this to the specific observables, and by linking it to the summary list more clearly.

Concerning the referee's specific comment about the "sobering" factor of two model overestimation of the first-generation gas phase products in the top panel of Fig 15, we recognise that, at first sight, this might appear to be relatively poor agreement that may simply be accounted for by a yield error in the mechanism. However, we were actually delighted with this level of model-measurement agreement, which we think is fully acceptable given the uncertainties in mechanistic understanding, in vapour pressure estimation and in the calibration of the CIR-TOF-MS signals (indeed, this exemplifies why it is sometimes quite difficult to class such a result as either a "major success" or a "major discrepancy" in mechanistic evaluation studies, and why it can be more instructive to

highlight uncertainties and where future work is required). The discussion in section 6.3.1 indicates that the CIR-TOF-MS signals are uncertain to approximately +/- 40% and possibly miss additional contributions from small unspecific fragments. It also comments on the sensitivity of the gas phase simulations to the vapour pressure estimates, and (for m/z 253) the extent to which the more volatile secondary ozonide contributes to the signal. In view of the referee's comment, we have added a statement to the caption of Fig. 15 to refer the reader more directly to the discussion in section 6.3.1, thereby allowing the factor of two discrepancy in the Figure to be put into context.

The remaining comparisons (for both the new CIR-TOF-MS data and the previously reported PTR-MS data for Lee et al.) are semi-quantitative, with the relative magnitudes of the calibrated vs. uncalibrated signals giving an estimation of concentration (given knowledge of fragmentation behaviour), with PTR sensitivities being of similar orders of magnitude between structurally similar species. As recognised by the referee, the primary aim of these comparisons is, however, to compare the shapes of the various profiles, which allows valuable conclusions to be drawn concerning product identities, the oxidation generation in which they are formed and their lifetimes – and of course whether the mechanism/model is able to recreate the observation. Because of a lack of authentic standards, it was not possible to calibrate all the many detected signals, and focus was therefore placed on calculating the sensitivities for the species contributing to the major product families of m/z 253 and 237.

Comment 3: Technical suggestions:

a) "Fig. 5 caption (and other figures): "figures" -> "values" or "numbers"."

Response: We agree with the referee and have amended these terms accordingly in the revised manuscript.

b) "p.2902 and later: exocyclic need not be in quotes."

Response: When referring to the residual double bond in a given product in which the β -caryophyllene endocyclic double bond has previously been oxidised, we place the term "exocyclic" in quotes because the cycle to which the bond was originally exocyclic in β -caryophyllene no longer exists in many of the products. Thus, the bond is strictly not exocyclic, and the term is being used as a convenient label. The purpose of the quotes will be explained at first use in the revised manuscript. (Note that the same does not apply to the endocyclic bonds in products in which the β -caryophyllene exocyclic double bond has previously been oxidised, and the term endocyclic is therefore not placed in quotes).

c) p.2906/l.3: presumably mean $\text{CH}_3\text{C}(\text{O})\text{OO} =$ acetyl peroxy radical, not $\text{CH}_3(\text{O})\text{O}_2$
eq. 2 alignment

Response: The referee is correct, and we have amended this in the revised manuscript.

d) p.2911/15-20: The discussion of the source of NO is unclear, Do you mean "minimizing" rather than "optimizing"? Is "subtle" influence small but important, or small and not important? Also, it is well known that NO₂ will outgas from teflon surfaces. Are you sure the source was NO rather than NO₂?

Response: The simulations definitely required the source to be in the form of NO, which we agree is unusual and needed to be reported, even though we cannot explain its origin at this

stage. This is being investigated further as part of ongoing chamber evaluation, and chamber processes will be reported on more fully elsewhere. Inclusion of the source improved the quality of the comparison of the modelled and measured NO profiles, particularly in the early stages of the experiment. Its effect on the comparisons for β -caryophyllene, NO₂ and ozone was small and unimportant in improving model agreement. We have clarified this in the revised manuscript. It is also noted that the profiles for all these species were most sensitive to the gas phase chemistry initiated by NO₂ photolysis.

e) Table 1: [SOA] needs units.

Response: This has been amended in the revised manuscript.

f) p. 2916/17-22: It's unfortunate that the main SOA product, C₁₃CO₂H, was not seen by Li et al. But the MCM prediction should help motivate its future detection.

Response: We agree, and hope that our work will help inform and motivate future investigations.

Referee 2

Comment 1: The authors present in this manuscript a “detailed” degradation mechanism for one of the most important sesquiterpene emitted to ambient atmosphere: beta-caryophyllene. The authors use the MCM mechanism that is build using solid knowledge of kinetic degradation of b-caryophyllene as well as its degradation products. The performance of the MCM mechanism was evaluated using a series of experimental data obtained either from the literature or originated directly from smog chamber experiments conducted by the authors. The experimental data comprises a wide variety of conditions: e.g. ozonolysis, photooxidation in the presence of NO_x etc: : Although the model is very complex (280 multi-functional compounds) and is based on a variety of assumptions as well as its combination with chamber auxiliary mechanism developed using another smog chamber (wall chemistry), the model seems to produce a reasonably well picture of the SOA as well as products distribution either in the gas or in the particle phases.

Response: We are very grateful to the referee for recognising the value of this work.

Comment 2: As mentioned by the authors, the mechanism is based on a detailed degradation of b-caryophyllene that is expensive and time consuming to be implemented directly in applications requiring great computational efficiency. It will be suitable if the authors provide to the scientific community a condensed mechanism for b-caryophyllene to be implemented in air quality models focusing on the main products that lead to ambient SOA formation from b-caryophyllene (e.g. b-caryophyllinic acid that was detected in ambient aerosol).

Response: We agree with the referee that the generation of traceable reduced mechanisms is the ultimate goal, and is something we are considering in ongoing studies. We also hope that making the present β -caryophyllene scheme freely available will help such activities in the wider community.

Comment 3: It's clear to me that the paper is long however it provides useful and needed informations for b-caryophyllene that its chemistry is still difficult to understand.

Response: We are very grateful to the referee for this supportive comment.

Comment 4: The auxiliary chemistry is not discussed appropriately to reflect the importance of wall chemistry! Mainly when using wall chemistry to characterize a chamber that was not used to generate the experimental data set used for the evaluation of the MCM mechanism! This becomes more complicated when using data from a series of smog chambers that their experimental characterization is not available/associated with the set of data used for the mechanism! Does the wall chemistry is dependent on the history of each chamber? Comment(s)!

Response: We agree that it is important to consider the impacts of chamber walls, and to use or characterise an appropriate auxiliary mechanism, when interpreting hydrocarbon/NO_x photo-oxidation experiments. The present work includes a level of auxiliary mechanism development and characterisation of chamber processes (particularly for the wall partitioning of oxygenated organic products), and further evaluation of the Manchester chamber is ongoing, and will be reported elsewhere.

As described in section 4.1 of the manuscript, the representation of conventional chamber processes was taken from that reported for the PSI chamber. This covers a conventional description of wall sources of radicals, the reactivity of background organics, and adsorption or desorption of oxidised nitrogen species. Inevitably, the auxiliary mechanism has a greater impact in some chemical systems than it does in others, with the greatest importance being for systems that do not have an intrinsic gas phase process to initiate the chemistry, as is the case for systems such as photo-oxidation of alkane/NO_x or aromatic hydrocarbon/NO_x mixtures, which take some time to get going. For the current system, the simulations were found to be very insensitive to inclusion of the auxiliary mechanism (i.e. it could actually have been left out altogether without changing the main conclusions of the study), as also commented on in section 4.1. The reason for this is that the chemistry is rapidly initiated by the ozonolysis of β -caryophyllene, following NO₂ photolysis, with secondary removal from the OH (and other) radicals that the ozonolysis generates. The gas phase chemistry therefore completely dominates the observed time dependence for NO_x, ozone and β -caryophyllene, as described in section 6.1. As a result we feel the discussion of the conventional auxiliary chemistry already given is commensurate with its importance in this study.

Comment 5: The paper need to be edited carefully for errors. Mainly the authors need to check the reference section: there are references missing from the reference section! Years are not accurately reported for some references etc...

Response: We are very grateful to the referee for pointing this out. These errors and omissions have been corrected in the revised manuscript.

Comment 6: The topic of this manuscript is of great interest and appropriate to ACP. The paper should be published after the authors address the comments raised above.

Response: We thank the referee for this supportive comment.