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Atmospheric
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Discussions

Interactive comment on "Impacts of mechanistic changes on HO_x formation and recycling in the oxidation of isoprene" *by* A. T. Archibald et al.

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We thank referee 3 for providing a review of our paper. The referee is consistently negative about the value of the work we have presented, and raises a number of objections and issues. In most cases we strongly disagree with the opinions expressed by the referee, and are pleased to provide a detailed itemised series of responses to the comments made. In our opinion, many of the detailed points raised by the referee are either very minor, misleading or incorrect; or express subjective views for which the referee has not provided any support.

Ref 3: opening comment:

Archibald et al. focus on the sensitivity of HOx to a series of recently proposed mechanisms. A simplified mechanism is derived and implemented in a chemical transport model and the global impacts of such mechanistic changes are assessed. The authors conclude that the mechanism proposed by Peeters et al. could resolve the model/measurement inconsistency at low NOx.

In the present form and despite an interesting review of our present understanding of the isoprene photooxidation under low NOx, this study clearly lacks comparisons with fields or laboratory data to support its conclusion. This is crucial since there are many ways to "fix" OH in global models. The many studies which have investigated this topic prior to this work seem to suggest that a purely chemical "fix" may bring OH into closer agreement with the measurement but would result in inconsistencies with other VOC measurements (including isoprene) [1, 11, 6]. This in turn suggests other processes (such as dynamics) have to be accounted for in order to properly interpret field measurement. Surprisingly, this issue is not mentioned in this study.

Without a comparison with experimental data, the insights provided by this study into the isoprene - low NOx problem are not sufficient to warrant publication in ACP. However, I would strongly encourage the authors to incorporate their mechanism into a more complex box model to test it against results from field campaigns [11, 6].

Response to opening comment:

The referee raises a number of points in this opening comment, which we deal with in turn. The referee's opening paragraph does not accurately describe the scope and content of the paper. The mechanistic variations we test are not simply proposed, they are (with one exception) mechanisms which have either been determined from a consensus of laboratory study (which includes the corresponding author's own experimental results), or reported on the basis of detailed theoretical calculations by a long-established and highly-respected group. The impact on OH recycling of a suite of mechanisms with this level of experimental and theoretical support has not been tested in previous studies, and the conclusions we draw are certainly not limited to the vague statement made by the referee above (a more accurate summary of the new output and conclusions is given in our response to referee 1, and by referee 2).

We thank the referee for the complimentary remark about the review material, but strongly disagree that the paper needs to provide direct simulations of field observational data to be valid. As the referee points out repeatedly, simulation of field data requires a model which includes an appropriate description of a variety of processes (including correct representation of the strength and temporal variation of emissions, entrainment of background air, and deposition). The scope for systematic and compensating errors, and the ability to "fit" observations through tuning the strength of numerous processes, can therefore inhibit a true appraisal of a chemical mechanism. As a result, the systematic testing of chemical mechanisms over a range of conditions using box models is a long-established and informative activity, with numerous papers reported in ACP and elsewhere using this approach (e.g., Poechl et al., 2000; Kuhn et al., 1998; Emmerson and Evans, 2009; Archibald et al., 2009 and references therein). The present work therefore uses an appropriate method to analyse and report the sensitivity of the system to a series of changes to a detailed reference mechanism over a wide range of atmospherically-relevant conditions.

In practice (and as outlined in the "Introduction" to the paper and expanded upon in our response to referee 1), there is a clearly-defined traceable mechanistic link to reported model-measurement discrepancies in the field, via the pioneering studies of Lelieveld et al. (2008), Butler et al. (2008) and Kubistin et al. (2008). Those studies were able to develop empirical parameterised representations of OH recycling (referred to as a "fix" by the referee). Informed by the results of those studies, we are able to test the impacts of explicit, un-parameterised mechanisms for which there is firm experimental and theoretical support, and to illustrate the effects over a wide range of conditions.

We do not dispute that dynamics is one of many processes which plays an important role in interpreting field observations; and indeed this is one of the contributing difficulties in using fits to observational data alone to test and appraise chemical mechanisms.

We acknowledge, however, that we should have mentioned the potential contribution of dynamical effects in explaining the model-measurement discrepancies for OH (e.g. as covered in the ACP paper of Pugh et al., 2010), and this has been done in the "Introduction" in the revised manuscript. We strongly disagree, however, that initial testing of the impact of detailed chemical mechanisms needs to be carried out in a model with a more complex representation of dynamics. Surely the logical procedure is for the initial testing of dynamical effects to be tested in a model with a highly simplified representation of OH recycling (as done by Pugh et al., for example); and the initial testing of potentially contributory chemistry mechanisms to be tested in a simple box model (as done by us). The key results can then be taken forward into a model with intermediate representations of chemistry and dynamics, informed by the results of both approaches. The referee therefore seems to be arguing that it is acceptable to test dynamics with highly simplified chemistry and publish the results, but not vice-versa. We note that a main conclusion of the detailed study of Pugh et al. (2010) is that contributions from both dynamics and OH recycling are probably required to explain their observations. We are simply trying to provide a systematic assessment of the latter over a wide range of conditions to help inform future studies in the field; and indeed provide an optimised reduced representation of a highly detailed chemical mechanism to facilitate this.

The previous studies cited by the referee (all of which we also cite) are clearly extremely valuable and informative contributions to this subject area. However, we take some issue with the referee's inference that they all lead to consistent or foregone conclusions which somehow invalidate our work or render it unnecessary. The pioneering study of Butler et al. (2008) (referee's reference [1]) reports initial strong evidence for an isoprene-related model-measurement discrepancy, tests parameterised OH recycling mechanisms and discusses the potential role of segregation effects. It was, of course, unable to consider the more recently reported explicit chemistry, which we are able to assess in some detail. The study of Karl et al. (2009) (referee's reference [6]) does not set out to investigate OH recycling, and indeed uses observationallyconstrained concentrations of OH. It finds that inclusion of a representation of the HOx recycling mechanism of Peeters et al. (2009) suppresses the simulated concentrations of MACR+MVK away from their observed values, which are well-described by conventional chemistry. On the other hand, Pugh et al. (2010) (referee's reference [10]) find it difficult to implement any change in their model (including deposition and phenomenological adjustments to rate coefficients) which can address a large over-simulation of MACR+MVK with conventional chemistry, suggesting that their calculations would clearly benefit from this feature of the Peeters mechanism (which they could not easily test), and which would also provide the OH recycling that they conclude is required to supplement dynamical effects. We reiterate, therefore, that the outputs of our work provide a quantitative assessment of a series of mechanistic changes over a wide range of atmospherically-relevant conditions, which can help inform future studies which aim to build upon this previous work.

Ref 3: comment 1:

p5865: add reference to [13]

Response to comment 1:

In line with the referee's suggestion. reference to Thornton et al. (2002) has been added to the introduction in the revised manuscript.

Ref 3: comment 2:

p5870: the section on high NOx reaction of isoprene peroxy radical should be removed or made substantially shorter since no change in the standard MCM chemistry is made.

Response to comment 2:

We disagree with this suggestion. The aim of the section as a whole is to provide a reasonably comprehensive overview of the base mechanism, so that the implemented mechanistic changes can be put into context. These changes occur in competition with many aspects of the mechanism, including with the reactions of RO2 with NO.

In practice, the material which is specific to these reactions amounts to little more than statement of the reactions themselves (which would have to remain). This is because the oxy radical products are also formed in the absence of NOx. It is always a balance to know how much detail to include but, because previous overviews of the MCM isoprene mechanism have been selective in their coverage, we believe the balance is appropriate for the current paper. The complimentary remarks of referee 2 about the clarity of presentation would seem to support this.

Ref 3: comment 3:

p5870: I would not say there is a consensus on isoprene nitrates yield. Recent lab studies seem to suggest the yield could be relatively high [12, 7, 10] though a recent study using a chemical transport model concluded the yield of isoprene nitrates was likely small[4]. Pinho's reference is not the most appropriate (besides it is not found in the reference list).

Response to comment 3:

We thank the referee for pointing out the omission of the Pinho reference from the list, which has been included in the revised manuscript. For clarification, it is:

“Pinho, P.G., Pio, C.A., Jenkin, M.E.: Evaluation of isoprene degradation in the detailed tropospheric chemical mechanism, MCM v3, using environmental chamber data. Atmos. Environ. 39, 1303–1322 (2005).”

It is actually an appropriate reference, as it comments on the range of isoprene nitrate yields reported in the literature when the mechanism was developed (which was from about 4% to 14%), which included that from Sprengnether et al. (2002) (referee's reference [12]). It reports the effect of varying the yield over that range in relation to SAPRC chamber data, leading to support for the value of 10% applied in the MCM. The majority of the values reported in laboratory studies agree with this, within the experimental uncertainties, and this is why we used the expression “a consensus of reported yields”.

In view of the referee's comment, we have changed this to "an evaluation of reported yields". The recent value of Paulot et al. (2009a) (referee's reference [7]) is (12 +/- 3)%, and therefore is in agreement. The referee's reference [10] does not appear to report a value for the nitrate yield from the relevant reaction, but focuses on NO3-initiated chemistry.

The chemical transport model study of Horowitz et al. (2007) (referee's reference [4]) supports the lowest reported value of 4% on the basis of observational constraints, a conclusion which (although very important feedback) disagrees with the majority of laboratory determinations of the parameter. This is actually a very good illustration of the difficulties in optimising mechanistic parameters by simulating field observations alone, and why it is important also to use complementary approaches, such as that we apply in the present paper. One would normally expect a near-consensus of laboratory determinations of a specific parameter to be more reliable than one optimised from constraints to field observations.

Taking this further, the results of Horowitz et al. (2007) may instead be indicative of a more fundamental shortcoming in the current representation of isoprene oxidation in atmospheric models, rather than simply an error in a specific reaction branching ratio. In particular, the existence of isomerisations for isoprene-derived RO2 radicals (e.g., as represented in the Peeters mechanism) would have the effect of lowering the isoprene nitrate yield through providing competing reactions for the RO2 + NO reaction. This point is returned to in our response to comment 9 below.

Ref 3: comment 4:

p5873: How was the rate of (R13a) estimated ?

Response to comment 4:

Because the methodology for assigning parameters is given in the referenced MCM construction protocol papers (Jenkin et al., 1997; Saunders et al., 2003), we chose

not to provide this level of detailed information in this overview. The rate coefficient for abstraction of the hydroperoxy H atom (3.6 x 10-12 cm3 molecule-1 s-1 at 298K) is based on the results of Vaghjiani and Ravishankara (1989) for CH3OOH, which formed the basis of the IUPAC recommendation (Atkinson et al., 2006).

Ref 3: comment 5:

p5874: I do not understand why the authors chose to drive their models with varying emissions of NO and isoprene. This greatly complicates the comparisons of the different chemistries since after two days the chemistry hasn't reached steady state (especially since there is no deposition in the model). At the same time, it misses (as noted by the authors) a lot of important processes to properly model boundary layer conditions (which makes me wonder how robust is the comparison with the study of Karl et al.). As many previous studies suggested deposition and chemical segregation can greatly affect the resulting OH. In particular, deposition of ISOPOOH has been suggested to be very fast [5] and the deposition of MVK and MACR substantially underestimated[11]. This would affect the conclusions of the authors which are looking for a purely chemical "fix". Reduction of the effective reaction rate between ISOP and OH should also be considered (but would require a more complex model).

Response to comment 5:

We do not understand why the referee has such objections to an emissions-driven box model, or why he/she thinks it complicates the comparison. It is a very widely used methodology, as is the procedure of allowing an initial diurnal cycle of "spin-up" before analysing the results. The previous mechanism intercomparison paper of Archibald et al. (2009) (e.g., Figure 4 of that paper) using the same model demonstrated that the diurnal concentration cycles of free radicals and intermediate oxidation products are reproducible after the first day.

Concerning the impacts of including product deposition, these have at most only a very minor impact on our results and on the comparison with the results of Karl et al. (2009).

Karl et al. (2009) estimate deposition loss rates of MVK and MACR to be more than an order of magnitude slower than the chemical loss rates, and deposition does not seem to be represented in their calculations either. In practice, product deposition would have little effect on the magnitude of the OH-recycling mechanisms considered here, since much of the key chemistry occurs prior to first generation product formation. The only exceptions potentially relate to the isoprene hydroperoxides, and the hydroperoxymethyl butenal(s) (HPC4CHO). In both cases, gas phase oxidation almost certainly dominates over deposition, particularly for HPC4CHO for which rapid photolysis is even estimated to dominate over reaction with OH (photolysis lifetime 30 minutes). In the case of the hydroperoxides, even if some deposition does occur, it is simply substituting one OH-neutral process with another.

Ref 3: comment 6:

p5874: Wouldn't the epoxide mechanism also apply to ISOPBOOH ?

Response to comment 6:

The epoxide mechanism reported by Paulot et al. (2009b) applies to all the isoprene hydroperoxides. Because our work was completed prior to publication of the Paulot study, we were unable to consider an explicit representation of their mechanism. Unfortunately, this tends to be inevitable in a rapidly evolving subject area such as isoprene oxidation. However, we make a point of discussing the implications of the Paulot study in relation to our results (this is commented on further in the response to comment 8).

Ref 3: comment 7:

p5875: The specific conclusion that chemical mechanisms (or chemical transport models) are unable to capture OH concentration under low NOx was reached by multiple investigations prior to the authors' work (Archibald 2009). This should be properly reflected in the text.

Response to comment 7:

We feel this is a very unnecessary and misrepresentative comment. The "Introduction" to the paper and numerous discussion points refer to the multiple prior investigations (and we note that referee 2 actually states that "careful attention is given to the previously published literature"). The section referee 3 is commenting on is discussing the model set up, and is one of the first references to our previous mechanism intercomparison (Archibald et al., 2009) which used the same model. We are simply pointing out that that study confirmed suppression of OH levels at low NOx for all the considered mechanisms in the intercomparison exercise, including MCM v3.1; and therefore its appropriateness to use as a base case mechanism against which to test the mechanistic variations we consider.

Ref 3: comment 8:

p5878: I do not think the epoxide chemistry [8] is equivalent to the mechanism depicted in Fig. 4. ISOPBOOH reaction with OH has been shown not to yield a dihydroxydihydroperoxide as suggested by the authors. The mechanism shown in Fig 4 results in the loss of two HOx in the formation of dihydroxydihydroperoxide while the formation of IEPOX is HOx neutral. This is a pretty significant difference. Furthermore the chemistry of the epoxide is likely significantly different from the dihydroxydihydroperoxide.

Response to comment 8:

As indicated above, we were unable to consider an explicit representation of the Paulot et al. (2009b) epoxide mechanism, but discuss the implications of that study in relation to our results. An important point (given on page 5873) is that the reactions of OH with three of the four isoprene hydroperoxides in MCM v3.1 are OH neutral, and therefore have the same first order impact as the Paulot epoxide mechanism. It is important to note that it is very well established that the reaction of OH with hydroperoxides can propagate OH (i.e., since the pioneering work of Vaghjiani and Ravishankara, 1989 on CH3OOH), and this has formed the basis for many of the generic OH + hydroperoxide reactions in the MCM ever since its inception in 1996.

In the case of ISOPBOOH, an updated explicit mechanism based on conventional chemistry (Figure 4) is implemented to replace an MCM simplification for tertiary hydroperoxides. We do not claim this is equivalent to the epoxide mechanism, but it does allow a first order indication of the impact of increased associated OH propagation. The mechanism allows a proportion of direct OH propagation when the product RO2 radical reacts by propagating channels (i.e., with NO or RO2). Reaction with HO2, in particular, does lead to termination (i.e. OH loss) with the hydroperoxide group retained in the organic product. In this case, the OH-neutral step is delayed to the next generation of oxidation, as the hydroperoxide group is effectively "latent OH". In the epoxide mechanism, the first step is OH neutral and the second removes OH.

Ref 3: comment 9:

p5881: The authors state that half of the OH increase is related to NO, which makes me wonder if the model is properly set up to adequately compare the different mechanism (see also comment on p5874). Shouldn't the authors use a constant value of NOy instead (from field values maybe) letting the model partition between the different members of NOy [2]. That would make the comparisons between the mechanisms more consistent. This also suggests that similar conclusions could be reached if the consumption of NOx in the model was reduced. What would be the effect of a reduction of the isopn yield to 4% for instance, change in their deposition or oxidation rate or even changes in the night time chemistry ....

Response to comment 9:

Each calculation at a given NO emission rate has the same NOy burden, such that the tests do exactly what the referee is suggesting, i.e., they let the model species partition between the different members of the NOy family. When a mechanistic change is implemented, this invariably results in a (comparatively small) shift in the partitioning between NOx and NOz, but the NOy remains the same (where NOy = NOx + NOz). Thus, even using a value of NOy constrained to a field observation (as the referee

suggests) would lead to compensating changes in NOx and NOz upon implementation of a mechanistic change – and would only be considering one value rather than a range of relevant values, as done in our paper. Because the concentration of OH depends strongly on NOx, it can have a direct change which is related directly to the modification to the organic mechanism (i.e. OH recycling), and an indirect change which is related to the impact the mechanistic change has on NOx. In the particular case the referee comments upon (initial implementation of the RO2 isomerisation reactions according to Peeters, denoted Mechanism 3a), the direct and indirect effects on increasing OH are comparable (each about 10-15% at the lowest NOx), and this was therefore worthy of comment.

As we state at the relevant point, the NOx increase is mainly due to a reduction in the formation of isoprene nitrates, resulting from the RO2 isomerisation reactions being able to compete with the reactions with NO; with this effect logically becoming more significant as NOx is lowered. This is actually an illustration of the point we raised above in the response to comment 3, related to accounting for discrepancies between laboratory isoprene nitrate yields, and those derived from constraining to field data. At about 1 ppb NOx, the production of isoprene nitrates is reduced by about 30% in our calculations, with this increasing at the low end of the NOx range (about 30 ppt) to about a factor of 3 reduction. Thus, the reduction is typically of the order of a factor of 2 over the intermediate atmospheric range, which could be regarded as a comparable effect to reducing the branching ratio for nitrate formation from the RO2+NO reaction from 10% to about 5%. This phenomenological reduction is therefore of about the correct magnitude to reconcile the laboratory determinations of the parameter with that obtained through optimising this aspect of a conventional mechanism on the basis of field observations (e.g., Horowitz et al., 2007), confirming that the Peeters mechanism could also help resolve this conundrum. We have included a brief discussion of this point in the revised manuscript.

In a highly detailed mechanism, such as MCM v3.1, it is of course possible to list hundreds of alternative tests which could be carried out, including those identified by the referee (although we note that including isoprene nitrate deposition would not allow NOy to be constrained, unless an artificial balancing source of an NOy species is applied). The paper deliberately focuses on chemical mechanistic changes for which there is reported experimental or theoretical support, rather than performing a global parameter sensitivity test. In practice, the range of isoprene mechanisms currently applied in atmospheric models contain some variability in parameter values (including isoprene nitrate yields) but all show broadly the same trait in relation to OH suppression at low NOx (e.g., Archibald et al., 2009). To illustrate this, we have run a sensitivity test in which the MCM v3.1 RO2+NO isoprene nitrate yield has been lowered from 10% to 4% (see Figure 1). This confirms that the change leads to a small NOx-increasing repartitioning of NOy, but that the simulated OH essentially remains on the same trend line, i.e., only what we refer to above as the “indirect effect” occurs. At the lowest NOx input rate, this results in an associated 11% increase in OH, which is indeed similar to the indirect effect obtained upon initial implementation of the RO2 isomerisation reactions in Mechanism 3a. Ongoing work is considering the impacts of a wider series of mechanistic changes related to oxidised nitrogen chemistry, and these will be reported at a later date.

Ref 3: comment 10:

p5882: The rate of HPCH4CHO photolysis should be given in the text, especially given its uncertainty. Since this is by far the largest source of OH in the mechanism, I think it crucially demands some experimental validation.

Response to comment 10:

The photolysis lifetime of HPC4CHO (30 minutes) is actually given in the text on page 5885, in relation to the formation timescale of hydroxyacetone and other secondary products from photolysis of one of the HPC4CHO isomers. In view of the referee’s comment, we have also added this as a photolysis rate (5 x 10-4 s-1) at the appropriate

point on page 5882.

We could not agree more that it is very important that the photolysis rate of HPC4CHO is validated experimentally. This is why we state repeatedly that it is critical that the details of the Peeters mechanism are either confirmed or refuted by laboratory study. That the referee has also reached this conclusion having read our paper, illustrates perfectly the value and purpose of carrying out a chemical mechanism sensitivity test of the type we have, i.e., to help guide and inform future work.

Ref 3: comment 11:

p5883: What is the yield of HPCH4CHO with the slow Peeters’ mechanism ? What is the yield of MVK and MACR (normal and slow Peeters’ chemistry) ? What is the yield of the isoprene hydroxyperoxide (normal and slow Peeters’ chemistry) ? How does it compare with previous studies ?

Response to comment 11:

There have currently been no experimental studies carried out under the conditions necessary to evaluate the Peeters mechanism in this way, i.e., there are no yields with which to compare. As we discuss in some detail in the paper, the previous studies have generally employed levels of NOx or peroxy radicals which are too high to allow the RO2 isomerisation reactions to compete. The only exception to this is the recent study of Paulot et al. (2009b) which reports evidence for trace amounts of the hydromethylbutenal product(s) under NOx-free conditions. This is why one of our main conclusions is that it is imperative that the details of the Peeters mechanism are either confirmed or refuted by laboratory studies employing appropriate conditions to allow it to be tested (i.e., those more relevant to the atmosphere). As we comment below, this is also actually required to validate all isoprene mechanisms currently in use.

Ref 3: comment 12:

p5883: Shouldn’t the radical originating from HPCH4CHO photolysis isomerize to make an acid ? This would considerably reduce the hydroxyacetone yield. Under low NOx condition, one would also expect reaction with HO2 to dominate which would reduce the yield of hydroxyacetone.

Response to comment 12:

The first point is incorrect. A radical isomerisation has to make another radical, and cannot form a closed-shell product. It is also not at all clear why the referee thinks it could make an acid; or why he/she regards it as acceptable to make such review statements completely unsupported by information or reference. As we state in the text on page 5885, the radical is most likely to undergo a 1,5 H shift isomerisation, involving transfer of the labile aldehydic H atom. This produces an acyl radical which will add O2 to generate HOCH2C(CH3)=CHC(O)O2.

We take the referee's second point to be that this radical will mainly react with HO2, thereby inhibiting hydroxyacetone formation (certainly the initially formed radical cannot possibly react competitively with HO2). In practice, HOCH2C(CH3)=CHC(O)O2 will likely react about equally with both HO2 and RO2 at very low NOx. Noting that this is an acyl peroxy radical, both these reactions are likely to have significant propagating channels which will allow generation of hydroxyacetone from the subsequent radical-propagated reaction sequence. The proportion forming terminating products will not form hydroxyacetone directly, but will almost certainly form it with high yield (with some delay) upon further reaction.

Ref 3: comment 13:

p5892: Given the very large uncertainties in the chemistry presented in this study and the lack of new evidence supporting this scheme, the authors should be a lot more cautious with the reported increase of OH (two significant digits !). Another illustration of this very large uncertainty is the recent study of Ghosh et al. [3] which suggests that the branching ratio between the E and Z isomer is 1:1. This is at odds with the theoretical study of Peeters et al. [9]. How would it affect the authors' conclusions ?

Response to comment 13:

Because some of the sensitivity tests have very small effects, we have tended to present the results of all tests at the percentage level. The referee's point is well taken for the larger changes, although it should be noted that we are more approximate in the presentation of the figures at other places in the manuscript (for example, in the Abstract). We have considered this carefully in the revised manuscript, and reduced the number of significant figures, where appropriate.

The referee comments that the lack of new evidence implies uncertainty in the results. In practice, some of the sensitivity tests we consider in the manuscript are already very well supported by existing experimental study, in particular the inclusion of the propagating channels for the reactions of HO2 with acyl and beta-oxo peroxy radicals.

Assuming the referee is specifically referring to the tests involving the Peeters mechanism, it is very important to note that it is also broadly supported by existing laboratory and chamber results, and therefore equally as valid as the more conventional mechanisms which have been validated on the basis of laboratory and chamber data. The important deviations in mechanism performance occur under conditions which have generally not been accessed in laboratory study, but which are highly relevant to atmospheric conditions. It is therefore imperative that experimental data is obtained under more atmospherically-relevant conditions, not only to evaluate the Peeters mechanism, but also to evaluate all the other isoprene mechanisms used by everyone which are claimed to be supported by experimental study. It therefore seems to be an extremely narrow viewpoint for the referee to single out the Peeters mechanism alone as requiring this new evidence, when it is a more general issue, particularly as the novel features of the Peeters mechanism can apparently help to reconcile some model-measurement discrepancies under atmospheric conditions. We have made this point in the revised manuscript.

It should also be noted that we make a point of presenting some supporting evidence for the Peeters mechanism, which has invariably been overlooked in previous discussions of the mechanism. In particular, we refer to, and discuss the implications of, the kinetics studies of Perrin et al. (1998) and Jorand et at. (2003), which report clear experimental evidence for isomerisations of delta-hydroxy peroxy radicals formed in alkane systems. On the basis of these results it is actually possible to argue that mechanisms which omit isomerisations of delta-hydroxy peroxy radicals (i.e., all mechanisms currently in use) are not supported by existing experimental evidence.

Finally, it should be noted that the referee's above comment actually misrepresents the output of the recent experimental study of Ghosh et al. (2010), which selectively studies the further chemistry of the 1-hydroxy-2-methyl OH-isoprene adduct in the presence of O2 and very high NO. Ghosh et al. (2010) were able to report a yield of the E delta-peroxy radical isomer of (10 +/or – 3)%, but with the remainder attributed to the sum of the Z delta-peroxy radical isomer and the beta-peroxy radical isomer. To further their analysis, they assumed a 1:1 E:Z ratio, based on the results of an earlier theoretical study of Dibble (2002). In fact, the parameters calculated by Peeters et al. (2009) indicate a yield of the E delta-peroxy radical isomer of 8.3%, when back decomposition of the peroxy radical is precluded by the presence of very high NO. This is in excellent agreement with the experimental observation of Ghosh et al. (2010), which is therefore another piece of experimental evidence which, contrary to the referee's assertion, actually quantitatively supports the Peeters mechanism.

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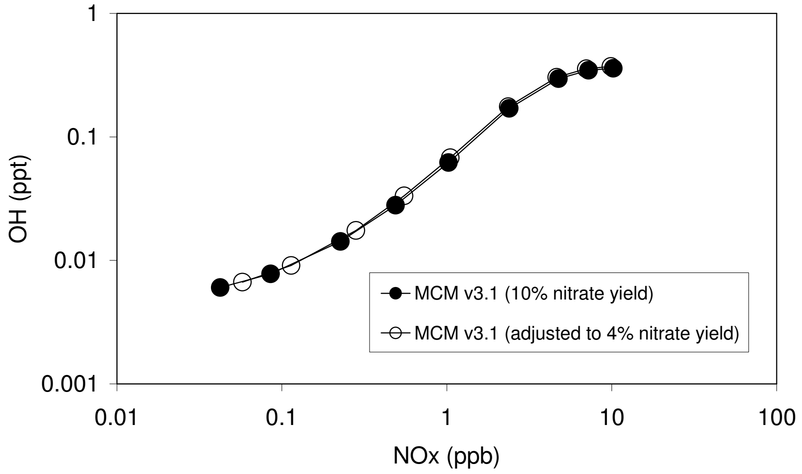

Fig. 1. Simulated impact of changing the isoprene nitrate yield from RO2+NO reactions from 10% to 4%.