

## ***Interactive comment on “Sensitivities in global scale modeling of isoprene” by R. von Kuhlmann et al.***

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### GENERAL COMMENTS

This paper investigates the representation of isoprene chemistry in global CTMŠs and the significance of various uncertain factors that are involved. The new and highly valuable contribution of this paper is that the differences between available chemical mechanisms have been studied using a global model. This allows a much better judgment of how relevant the uncertainties are for our understanding of tropospheric chemistry, as compared with the use of box models. In addition it allows a judgment of the relative importance of uncertainties in gas phase chemistry and the heterogeneous removal processes, which should help to put priorities for future research and to define defensible levels of chemical mechanism simplifications. In my view, however, there

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are several problems with the implementation of this approach and the inferences from it, as will be explained below. Some of these issues call for significant revisions of the manuscript, while others will hopefully trigger discussion. A number of corrections refer to rather ambiguous wording, which causes parts of this manuscript to be difficult to read.

1) What does the observational evidence tell us? This modeling study lacks links with the real world. This makes it difficult to tell realistic results from those that aren't. It is mentioned that the sensitivity tests have been chosen such that the parameters were varied within their uncertainty ranges. It is unclear, however, if the resulting concentrations are within the range of uncertainty of the measurements and what are the possible constraints on the uncertain processes that might follow from that. Measurements of O<sub>3</sub>, PAN, isoprene, NO<sub>x</sub>, etc. are available that could, and should in my opinion, be used for this purpose (LBA-CLAIRE?). If it is true, like it is suggested here, that measurements do not give substantial guidance yet, this would be a valuable recommendation.

2) Uncertain chemistry versus condensation error It should be explained what has guided the choice for the CBM and MOZART isoprene schemes. In fact, the choice for CBM does not seem quite appropriate if the aim of the comparison is to quantify how important uncertainties in isoprene chemistry are. CBM is a highly condensed scheme, which means that errors are accepted as long as they are within the expected errors of other uncertain processes (like emissions, heterogeneous removal etc.). This means that it does not reflect the state of the art of isoprene chemistry modelling, but the cheapest acceptable compromise given the overall uncertainty. The use of CBM would be relevant in a second stage, where the impact of chemical and non-chemical uncertainties have been assessed and we want to know if the applied level of simplification is still justified. The statement that 'no mechanism can be judged superior over the other schemes' seems to suggest that, sadly enough, it is.

3) How realistic is BASE? Because of the non-linear nature of photo-chemistry it is not

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clear what the results of sensitivity simulations mean, unless we know that the reference case (BASE) yields realistic results (which means we are "linearizing" around approximately the right point). The few tracers that are plotted in Figure 1 do not allow proper judgment of this. It is understandable that this number is minimized, nevertheless plots of isoprene and NO<sub>x</sub> in particular would greatly facilitate judgment of the general performance. In addition, a plot of BASE NO<sub>x</sub> helps interpreting the % changes in the next plots.

4) Definition of PAN The definition of PAN varies across chemical schemes. In CBM it represents the sum of all PAN-like compounds. Confusion should be avoided on this point, and it should be explained to what extent the different definitions may affect the PAN comparisons.

5) Vertical mixing It is unclear how relevant uncertainties in the vertical mixing over tropical rainforests are in comparison with the factors that have been tested in this study. The PBL is only mentioned once in a side remark. This should receive more attention. In addition, an indication is needed of how well vertical mixing and variations in PBL are represented in the CTM (LBA-CLAIRE?).

#### SPECIFIC COMMENTS

Abstract "The total tropospheric burden of O<sub>3</sub> ... from 273 to 299 Tg(O<sub>3</sub>). It is not clear what this difference refers to: methane only compared with what?"

Introduction "On the other hand Rosenthal et al ... increased CO<sub>2</sub> exposure" It is suggested that climate change is the only factor that might alter the future emission of isoprene. Land use change seems another obvious candidate that is missing here.

Model setup "The sensitivity simulations ... (archived mode)" Indicate what kind of parameters are involved

Model setup "In all simulations only the background ... Mim (Poschl et al, 2000) is included" This cannot be correct for the simulations that use alternative isoprene

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schemes.

Model setup Since other hydrocarbons ... in treating isoprene in global models  
The sensitivity of a global model to additional hydrocarbon input is, among other factors, determined by the N/C ratio (i.e. whether the chemistry is nitrogen or carbon limited). Neglecting hydrocarbons shifts this balance towards carbon limitation, which might overemphasize the importance of isoprene (which is not a baseline shift). The neglect of anthropogenic VOC seems justified. This might not hold, however, for the remaining 50% of biogenic emissions. It would not be fair to require that terpenes and the whole suit of other compounds are taken into account. However, the potential importance of this should be acknowledged.

Chemical schemes In order to focus on mechanistic differences ... for all three mechanisms  
The disadvantage of highly tuned schemes like CBM, in comparison with mechanistic schemes, is that their performance should to be reevaluated after reaction rate updates. For the initial oxidation rates of isoprene this may not be so critical. For PAN chemistry, however, it is. An indication should be given of the importance of these adjustments and how these might influence the results.

Chemical schemes An exception to this ... in the CBM scheme  
This is not an exception since this acid is not involved in the first step of isoprene oxidation nor PAN chemistry.

Chemical schemes It is unclear why the number of isoprene related species and reactions is not given for CBM while it is for the others.

Emission strengths The decision for an increase ... agreement with observations  
It would help the reader to briefly summarize these findings as far as they are relevant to this work (and refer to von Kuhlmann 2003b for more details).

Sensitivity to the chemical scheme In the CBM mechanism ...35% is calculated  
It is unclear what is compared, and whether the numbers can in fact be compared. For

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CBM it refers to carbon loss in the first reaction of isoprene with OH. This cannot be compared with MIM and MOZART because the first reaction of CBM has no straightforward analog in these schemes. For example a comparison of isoprene CO yield for all schemes would make much more sense, since this would allow a clean comparison.

Sensitivity to the emission strengths A larger impact is predicted for PAN ... approximately linear An analysis of only two points of a relationship does not allow a statement about linearity.

Sensitivity to the emission strengths Clearly the overestimation of isoprene ... von Kuhlmann et al 2003 It is suggested that an overestimation of isoprene implies overestimation of the formation of its reaction products. If the isoprene lifetime, however, were the only factor to blame, then product formation would not be affected (in steady state).

Sensitivity of the emission strengths Thus, even when considering ... source in the region It should be mentioned how realistic a larger than 60% reduction in lightning NOx would be. The results suggest that lightning alone cannot explain a factor 10 difference between simulations and observations, although this is not explicitly mentioned.

Sensitivity to the fate of isoprene-nitrates More extreme assumptions ... deposition loss completely In CBM4 the heterogeneous removal of nitrates is treated like PAN. This implies that removal by dry deposition has been taken into account.

Sensitivity to deposition of intermediates We find that ... as a major contributor. It should be mentioned that acetone oxidation has not been accounted for, which may affect the additional impact of isoprene-derived peroxides on HOx.

## TECHNICAL CORRECTIONS

Introduction On the other hand ... necessary Use "number" instead of "amount"  
Emission strengths It is unclear whether ... cell of the model It is unclear what

is meant here by "loss processes". Presumably it refers to heterogeneous losses only. Change "processed" to "processes". The "first grid cell" is poorly defined (use "surface level" or so).

Emission strengths "The change in global source strength ..." Add "of NO<sub>2</sub>".

Sensitivity of the chemical scheme "Interestingly, for MOZART ... ((+40-60%)) ... as compared with BASE. "but the change" Replace "change" with "difference".

Sensitivity of the chemical scheme "These results are consistent ... low NO<sub>x</sub> scenarios" This sentence seems unnecessarily complicated, please rephrase.

Sensitivity to the chemical scheme "Significant deviations are also ... for the CBM simulation" Please explain what is meant by "each category".

Sensitivity to the chemical scheme "While in the base case ... of about 700-800 Tg/yr" More accurate wording should be used: "31 Tg(O<sub>3</sub>) is calculated " compared with "methane only",- this is only ... " for the other two schemes." "The gross production ... compared to an " average (?) " increase from the " methane only ".

Sensitivity to the emissions strengths "As discussed above ... strength is considered" This paragraph belongs to section 3.

Sensitivity to the emission strengths "The absolute difference ... last group of tests" Please explain what is meant.

Sensitivity to the emission strengths "This shows that the impact ... are slightly less affected" Slightly less affected by what?

Sensitivity to the fate of isoprene-nitrates "Studies investigating this product ... without releasing NO<sub>2</sub>" Replace "nitrogen is" by "nitrates are"

Sensitivity to deposition of intermediates "In the BASE case ... on the annual mean." Replace "which were" by "where"

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Sensitivity to deposition of intermediates ŠThus, other mechanistic ... Poschl et al (2000).Š Delete a Šfor theŠ

best regards, Sander Houweling

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