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

R. von Kuhlmann et al.

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First, we would like to thank the reviewer for his thorough review of our manuscript and for the constructive tone in which it is written. We discuss the general and specific comments in detail below. We have considered all specific and technical comments. The general comments have triggered a more carefull discussion on the use of observations in our study and also some clarification in the scope of the study.

GENERAL COMMENTS

1) + 3) It would certainly be desirable to discriminate one tested scenario over another based on available field campaign data. An attribution of improvements as well as deficiencies in a global 3D model to a certain process is, however, quite difficult and

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we now state clearly that experimental evidence does not give enough guidance for such strong statements. This is now also stated in the conclusions. Focussed field campaigns which focus on one aspect in connection with a 1D or box-model would probably be more suitable for this. Here, as stated also by the reviewer, we mainly try to give some guidance on which of the many uncertain aspects could deserve more attention.

We have, however, followed the advice of the reviewer to give better information on the base simulation and how it compares to observations. Thus, instead of only referring to the extensive evaluation in another study with model (von Kuhlmann et al., 2003b) we now added a section which gives a deeper discussion of some aspects especially important for this study. For example, due to the central role of isoprene the calculated levels are compared to a collection of observations in a newly added table, and we also discuss levels of nitrogen compounds at tropical locations. These findings better motivate some of the test scenarios and allow a better judgement of how important the effects found in the sensitivity runs are. We have also tried to relate the findings in the sensitivity runs more to the overall model performance, which can sometimes suggest a key reason for a model deficiency (e.g. too much lightning NO_x over the Amazon during the wet season) but cannot prove it.

2) Separating between the uncertainty in the detailed chemistry of isoprene and the additional uncertainty due to reduced chemical schemes was not the aim of this paper. A 3D model would not be the right tool to investigate this and an additional boxmodel evaluation of detailed isoprene chemistry would go far beyond the scope of this study, though it would be a highly valuable task to be tackled when new experimental data especially under lower NO_x conditions become available. However, in order to give a first estimation of the spread from the combined uncertainties in chemistry and its inevitable simplification in a 3D framework we have included 3 schemes that are in active use or have been recently published. There are apparently more published isoprene reaction schemes in use, but we have restricted our choice to 3 schemes for

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a good balance with the other sensitivity runs. Only schemes that were tested in the box-model study by Pöschl et al. (2000) were choosen in order to use the results found there in our interpretations. We have clarified the scope and limits of this study in the introduction.

4) It is true that "PAN" in the CBM scheme represents all PAN-type compounds, whereas in MOZART and MIM it only stand for peroxy acetylnitrate. However, because we excluded other NMHCs here these can only be isoprene-related PANs. These higher PANs will gererally have a much higher reactivity with OH (see e.g. Orlando et al., Atm. Env., 36(11), 1895–1990, 2002 for MPAN + OH) due to a remaining double bond and will thus not contribute much in long-range transport upon which we focus our discussion of this compound. From the most prominent PAN-type species included in the MIM scheme, MPAN, we can estimate the effect on the local comparison of the PAN species. We now mention this difference and discuss its impact in the revised manuscript.

5) Obviously, not all areas of uncertainty are or could principally be covered by our suite of sensitivity runs. We have therefore stated this subjectivity of the selection in the introduction. We agree that vertical mixing is a weak spot in our knowledge of current uncertainties in our model (and in general in global CTMs), but it goes beyond the scope of this study to also do a serious evaluation of different components contributing to this. It should be recognized that not only the PBL mixing scheme, but also the 2 components of our convection parameterization would be involved. In fact, we are currently looking into the model PBL scheme with sensitivity runs for a separate study. For the current manuscript, we now state the importance of further investigating this aspect in the introduction.

SPECIFIC COMMENTS

>Abstract: "The total tropospheric burden of O3 ... from 273 to 299 Tg(O3)." It is not clear what this difference refers to: methane only compared with what?

The second value is the mean burden of all sensitivity simulations (excluding the unrealistic VLOWDEP run). We now added this information in the abstract.

>Introduction: "On the other hand Rosenthiel et al ... increased CO2 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.

Yes, we agree and added this possible cause of future emission changes. Also, we worked in the first quantitative results from a recent study by Sanderson et al. 2003, who calculated anticipated isoprene emissions in a future climate with and without natural vegetation changes.

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

The parameters archived from the higher resolution run deal with PBL exchange (vertical diffusion diffusivity, counter-gradient term), convection (convective mass fluxes: entrainment, detrainment rates), and cloud physics (cloud fractions, condensation + evaporation rates, rain rates; each for convective and large scale clouds). However, we believe that this level of detail unnecessarily distracts the reader and we therefore refer to the paper describing in more details the meteorological component of MATCH.

>Model setup: "In all simulations only the background ... MIM (Pöschl et al, 2000) is included" This cannot be correct for the simulations that use alternative isoprene schemes.

True, the sentence was reworded to state that the background and isoprene chemistry was included.

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>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.

We agree that in general any deliberate model simplification but also any known or unknown model deficiency could not only result in a simple "baseline shift", and could thus affect the "local" (in parameter space) sensitivity of the system. Unfortunately, this is a problem inherent to all sensitivity studies with complex non-linear models. Nevertheless, we believe that it is beneficial to study the sensitivity of a particular process in the framework of a more complex model, because it attempts to consider more non-linear responses than in a study of the isolated process.

Concerning the other biogenic hydrocarbons we think that knowledge of the speciation (terpenes, sequiterpenes, other short lived compounds) and the source strengths and distributions is currently too uncertain to include them in this study. This would require a sensitivity study of its own.

We have revised our statement now more cautiously pointing out possible limitations. The possibility of overemphasizing the importance of isoprene by omitting other NMVOCs (biogenic and anthropogenic) is also included. However, our use of a lower isoprene emission rate compared to Guenther et al. (350 Tg-C/yr vs. 500 Tg-C/yr) works against this notion.

>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.

A reevaluation or retuning of the CBM version has not been done here, but in the study by Zaveri and Peters (J. Geophys. Res., 104, 30387–30415, 1999) a comparison of an updated version of the original CBM-IV, called CBM-Z, to smog chamber results and to a partially revised version (CBM-IV(R)) and the original CBM-IV was presented. The reaction rates in that study rely on more recent evaluations (DeMore et al., 1997, JPL) which are very similar to those used in our study. Zaveri and Peters (1999) found that mostly CBM-IV(R) performed better (also with respect to PAN) as CBM-IV, and CBM-Z performed somewhat better than CBM-IV(R).

Generally, we expect that the un-harmonized schemes would tend to deviate more from each other. The results of Zaveri and Peters (1999) would indicate that an un-harmonized version of the CBM would yield lower PAN results and lower O3 in source regions than the version used here. Thus, giving worse agreement in the smog-chamber simulation, but applied in the 3D model bringing PAN levels closer to field campaign data in the remote troposphere. A similar estimate can be made from inspecting the rate reaction directly affecting PAN in our version and the CBM version in Houweling et al. (1998) (H98 hereafter): While the thermal equilibrium rates are quite similar, in H98 a faster rate is used for the reaction of the peroxyacetyl radical (PA) with NO. This would also result in lower PAN production. We also note that Zaveri and Peters (1999) and also Duncan and Chameides (1998) use in their modifications of the CBM-IV scheme reaction rates for PA (C2O3 in their notations) representative for peroxyacetyl radical (CH3(O)O2), although in principle this compound can also represent radicals formed from higher aldehyde compounds. This practice is justified by the notion that CH3(O)O2 will generally be the dominating species in this group. This would also support our practice to further update these rates for use in our study besides the

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general benefit of a harmonized set of reactions.

Given that only a vague discussion of the effects can be made and that favouring one approach or version of the scheme over the other is difficult we have decided not to included this lengthy discussion in the revised manuscript (though it is available to the interested readership here), but plainly state that the versions of the scheme will be slightly different than in the original publications.

>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.

Peroxy-acetic acid (CHC(O)O2H) is formed from PA + HO2. Upon photolysis or deposition this would be a way to by-pass PAN formation. The effect of this was, however, found to be very small so that we have decided to remove this detail in the revised manuscript.

>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.

We agree and have removed this inconsistency. It was originally left out because many reactions in the CBM are not uniquely isoprene related We now give number of species and reactions for each chemical scheme.

>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).

We have now included some more discussion of the performance of the base simulation and the findings from von Kuhlmann (2003b) in a separate paragraph. Thus, this sentence reworded and shortened accordingly.

>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.

This is a misunderstanding of our wording: the two numbers given were not meant to be comparable. We agree that only the overall CO yield would be comparable. We have done this calculation for the three schemes and added a discussion of the results, which show that in CBM and even more so in the MOZART run the yield of CO from isoprene is lower than for the MIM scheme.

>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.

For the response of PAN to the isoprene emissions we actually have three test runs: The base run (CH4) with zero isoprene and thus zero isoprene related PAN, the BASE simulation and a run with a 50% reduced isoprene emissions. The fact that in the latter run results in roughly a 50% reduction in PAN in the upper troposphere thus suggests approximate linearity in the response. We have reformulated this part for greater clarity.

>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).

Yes, but too high isoprene emissions and its photochemical lifetime in the PBL are strongly coupled. This is because OH concentrations which represents the dominant photochemical sink of isoprene are strongly influenced by isoprene concentrations in the boundary layer over the Amazon (e.g. Crutzen et al., Atm. Env., 34, 1161–1165, 2000). Thus, it is hardly possible to separate cause and consequence in this case.

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If neglected non-chemical sinks would be the cause of the overestimate of isoprene concentrations our arguments would still hold and less oxidation products (including PAN) would be formed. We agree that in case the overstimate of isoprene is due to an underestimated chemical sink which is independent of the isoprene emission strength, e.g. through underestimated secondary HO_x production, our argument would not hold. We have revised our statement accordingly.

>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.

This is in fact an interesting and much more complicated point than we previously anticipated. In a separate study we are investigating more thoroughly the performance of the lightning parameterization used in MATCH using satellite data of flash frequencies. There are additional issues to consider in this comparison, such as the viewing time of the GOME instrument (about 10:30 local time). In the comparison of NO_2 mentioned we used the 24h-mean values from MATCH corrected by a constant factor of 0.7 accounting for a generic diurnal cycle in NO_2, which we have now shown are reasonable as an average but have a considerable spatial and temporal variablility (Kunhikrishnan et al., Atm. Env., in press, 2003).

We have therefore toned down this point now stating only qualitatively that the comparison to GOME-NO_2 indicates an overestimate of NO_x during this time and mention that other options (biomass burning, soil-NO_x emissions, too long NO_x lifetime) could also play a role.

>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.

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Corrected, we now state that only wet deposition has been neglected and a slower dry deposition is taken into account in CBM. We also checked again that this was also done in our implementation of the CBM scheme. These assumptions still imply a lower deposition than in any of our test runs. E.g. in our standard case dry deposition of isoprene nitrates is about 2 times faster than for PAN.

>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.

This is now stated in the revised text.

TECHNICAL CORRECTIONS

All technical corrections have been considered in the revised manuscript leading to significantly improved clarity of the formulation. Thanks for pointing these out.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3095, 2003.

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