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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Parametric sensitivity and uncertainty analysis of dimethylsulfide oxidation in the remote marine boundary layer" *by* D. D. Lucas and R. G. Prinn

**D. D. Lucas and R. G. Prinn**

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Comment 1: "The conclusions only hold for the analyzed conditions, most importantly: cloud-free RMBL, summer mid lat; even though the temperature dependence of the chemistry was investigated, important seasonal changes do occur (see eg results from Cape Grim and related modeling studies (Ayers et al, 1996, Koga and Tanaka, 1996, von Glasow and Crutzen, 2004)). Furthermore, the chemistry of sulfur in the RMBL is clearly very strongly dependent on the respective conditions, so "typical conditions" can hardly be simulated when only using input from one flight of the ACE-1 campaign. This should be stated more clearly in the text and the abstract."

Reply to Comment 1: We agree and have made appropriate modifications. See our reply to Comment 1 by Referee #2 for details.

Comment 2: "There are a few reactions that are crucial for the determination of the final products of DMS oxidation, one of these is CH3S(O)OH + OH, which has recently been investigated in the lab by Kukui et al, 2003 and shown to be roughly 100 times faster than assumed by Lucas and Prinn. Von Glasow and Crutzen (2004) investigated the impact of this reaction on the final products using a 1D model and found significant changes under cloud-free conditions when compared to the rate coefficient estimated by Lucas and Prinn. This single reaction has the potential to drastically change the conclusions of Lucas and Prinn regarding the gas phase production of MSA and H2SO4, ie one of the major conclusion of this manuscript. If at all possible the analysis should be rerun with the new, measured, rate coefficient. Note that the assumed uncertainty for this reaction in the study of Lucas and Prinn is only a factor of 2.5, so that their results do not cover the actual rate coefficient."

Reply to Comment 2: We first note that this rate constant was not initially identified as an important parameter in our original analysis (i.e. parameter 10 does not appear in Figs. 4 or 9 in the original ACPD paper). The reviewer's recommendation falls outside of our 2-$\sigma$ range, however. We have therefore changed the mean value for this rate constant from $1 \times 10^{-12}$ to $9 \times 10^{-11}$ cm$^3$/molec/s, increased the uncertainty to a factor of 3.5, and re-ran our analysis.

We find that our major conclusions are not altered with the new rate constant value. Although this may seem surprising, it is not. MSA in our model is directly produced by reactions involving MSIA, MSEA, and $CH_3SO_3$, with the latter two routes being relatively more important in these simulations. Without the MSIA and MSEA routes, our MSA concentrations would be too low and have an excessively large diurnal amplitude as noted in Lucas and Prinn (2002).

As for the discrepancy with the von Glasow and Crutzen study, we note that their mech-



**ACPD**

4, S3944–S3948, 2004

Interactive Comment

anism did not include pathways to and from MSEA, so the $CH_3S(O)OH$ + OH reaction played a more important role in their study than in ours.

Comment 3: "A very useful result from this paper would be a "to do" list for the kinetic community. Some of the information is already included in the text, however, it would be good if the reactions that most urgently need (re-)evaluation in the lab were listed explicitly. This is a result that is a direct product of the approach employed and should be used."

Reply to Comment 3: We agree that a "to do" list is important for the kinetic community, though our results indicate that the largest sources of uncertainty are from non-photochemical processes. To better emphasize the targets for reducing the DMS-related uncertainties, we have highlighted the major conclusions from Fig. 10 in Section 4.3.2 of the revised paper in the form of a bullet point list. We also now specifically mention in the abstract and conclusion that the rate constants for reactions involving $CH_3SO_3$ and $CH_3S(O)OO$ require future attention.

Comment 4: "The derivation/explanation of the different sensitivity approaches is written in a sometimes very compact way and sometimes very hard to follow for the non-specialist. Please try to improve the readability esp. around equations 8, 9, 11 - 15"

Reply to Comment 4: We have made an effort to improve the mathematical nomenclature and derivations in the revised manuscript.

Comment 5: "p 6386, l. 21: difference between "structural" and "parametric"?"

Reply to Comment 5: In the revised manuscript, the third paragraph of the Introduction and the beginning of Section 2.3 now provide better descriptions of the differences between structural and parametric uncertainty in the context of this study.

Comment 6: "p 6388, l. 8: what is a "decoupled direct algorithm"?"

Reply to Comment 6: This phrase is not necessary, so we have removed it from the manuscript to avoid confusion.



**ACPD**

4, S3944–S3948, 2004

Interactive Comment

Comment 7: "p 6389, l 15: how good is this approximation for eta?"

Reply to Comment 7: The "goodness" of the approximations (i.e. $\hat{\eta}$) are quantified in Fig. 4 of the revised manuscript. As shown in the figure, all of the fits have $R^2$>0.84, and the fits hold over many orders of magnitude.

Comment 8: "p 6389, l 18: "defined below" - where? I couldn t find it"

Reply to Comment 8: For clarity, the definition of $\xi$ (i.e. the standard normal random variable) has been moved to the beginning of Section 3.2.1 in the revised manuscript.

Comment 9: "section 6.2.1: discussion of DMS + NO3: Koga and Tanaka, 1996 and von Glasow and Crutzen, 2004 found this reaction to be very important in winter, so the statement about the negligible importance of this reaction should be weakened by adding that this has been investigated for summer conditions only."

Reply to Comment 9: We agree. Our estimates for concentrations of $NO_3$ are now diagnosed from steady state chemistry instead of being assumed. $H_2SO_4$ is now highly sensitive to the DMS+$NO_3$ reaction rate constant at night. This result is noted in the Abstract, Conclusions, and Section 4.2.1 in the revised manuscript.

Comment 10: "p 6401, l 7/8: please add the reaction numbers"

Reply to Comment 10: The reactions corresponding to the non-$CH_3SO_2$ pathway for producing $H_2SO_4$ are described more thoroughly in Section 2.1.1 in the revised manuscript.

Comment 11: "p 6401, l 13-18: this is a very important conclusion which should be stressed a bit more and maybe mentioned in the abstract."

Reply to Comment 11: We also believe this to be an important conclusion, and have improved its discussion in the abstract. We have also tried to better emphasize this point in the last paragraph of Section 4.2.1 and in the Conclusions of the revised manuscript.

Comment 12: "section 6.2.4: I didn't understand what "second-order coupling" means



**ACPD**

4, S3944–S3948, 2004

Interactive Comment

in this context."

Reply to Comment 12: We now provide an explicit example of a higher-order effect in Section 4.2.4 of the revised manuscript.

Comment 13: "Some of the reactions in the mechanism used by L+P have been assumed by them in a previous publication (Lucas and Prinn, 2002). To my knowledge there is no experimental evidence yet. Please mention whether or not the overall results are (strongly) dependent on these reactions to point to potential lab studies necessary in this field."

Reply to Comment 13: Reactions 46-49 in Table 1 of the revised manuscript are assumed reactions from our previous publication. Three of these impact our results, and these reactions are now described in more detail in Section 2.1.1. The impacts of these reactions on the results are also noted throughout the text (abstract, conclusions, and other relevant sections).

Comment 14: "Table 3: caption unclear."

Reply to Comment 14: The caption for Table 3 has been clarified.

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6379, 2004.