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Atmospheric
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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: "I find it reasonable that the authors only perform sensitivity and uncertainty analyses on the scenario presented in this paper. However, the RMBL can vary a lot depend on the location and time of the year, e.g. in the paper by Capeldo and Pandis (JGR. 102, 23251, 1997) the emission of DMS vary from 0.025 to 0.345 ppt/min. The authors should therefore discuss how representative the used scenario is for the RMBL, and compare the scenario with RMBL conditions in general. Points to address concerning the scenario compare with the general RMBL should be, how representative are the meteorological conditions, the concentration levels of the chemical compounds, the used aerosols conditions, the cloud formation frequency etc. Such a description is very important because, according to the paper, the non-gas-phase processes seem to be very important processes in the performed sensitivity and uncertain study."

Reply to Comment 1: We agree with the reviewer's concerns about using a single scenario for our model simulations. Rather than carrying out simulations across many scenarios, we focused on a detailed analysis for a single scenario. This scenario is not arbitrary but follows from the observational constraints applied in Lucas and Prinn (2002), which is a good, but not ubiquitous, representation of the DMS cycle in the RMBL under stable mixing conditions. We emphasize these limitations more clearly in many places in our revised manuscript (e.g. the abstract, introduction, and especially the end of Sect. 2.2).

It is also important to keep in mind that, given the stochastic nature of our uncertainty study, we do not run a single case, but thousands of cases. In this sense, therefore, the random variations in some of our model parameters could be viewed as arising from variable RMBL conditions. Accordingly, we have increased the uncertainties of most of our model parameters (from factors of 2.5 to 3.5) to compensate for the highly variable conditions within the RMBL. The new 2-σ uncertainty range for the DMS emission rate in our model (7.8×10^3 to 1.2×10^6 molec/cm^3/s) is now much wider than the range considered in Capaldo and Pandis.

Comment 2: "I find the description of DMS chemistry and the used DMS mechanism in the paper too sparse, this should be improved. The authors should give a more detailed description of the present knowledge of the oxidation of DMS in the RMBL, because the main purpose of the paper is to understand the sensitivities and uncertainties related to one specific DMS mechanism."

Reply to Comment 2: See reply to Comment 2 by Referee 1.

Comment 3: "1: According to Paper 1 Lucas and Prinn use the recommendation from DeMore et al. (1997) as rate constant for the abstraction channel of DMSOH + OH, and the recommendation from Atkinson et al. (1997) for the addition channel. This seems to be inconsistent. Please explain why this choice has been made."

Reply to Comment 3: We used the JPL Evaluation rate constant recommendations for as many of the DMS reactions as possible. Assuming the reviewer is referring to the DMS+OH reaction (instead of DMSOH+OH), the JPL Evaluation recommends a rate constant for DMS+OH abstraction, but not DMS+OH addition. We therefore turned to Atkinson et al. for this addition rate constant, which we modified using measurements of the temperature dependent reversible addition of OH to DMS (Barone et al. 1996). Considering the uncertainties we assign for these reactions, the DMS+OH abstraction and addition branching in our scheme is consistent with other studies.

Comment 4: "For reaction: CH3SO3 -> CH3 + SO3, the authors use the recommended rate from Yin et al. (JAS. 11, 309, 1990) while Saltelli and Hjorth (JAS, 21, 187, 1995) argued, based on results from Barnes, that this rate should be lower. Therefore, Saltelli and Hjorth decreased the rate by a factor of 133. Can the authors please explain why this argument has not been considered in their mechanism? May be this could also change the conclusion about the CH3SO3 dissociation described in the last paragraph on page 10."

Reply to Comment 4: The dissociation of CH_3SO_3 serves as a branching point between H_2SO_4 and MSA formation, and decreasing this dissociation will increase the production of MSA. A complementary way of increasing MSA production through this route is by increasing the burden of CH_3SO_3, which we did in Lucas and Prinn (2002). We argued in that paper that increasing the production of MSA through CH_3SO_3 is not statistically sufficient to explain the time-dependent MSA observations we analyzed. On this basis, therefore, we have not altered the dissociation rate constant as was done in Saltelli and Hjorth (1995).

We also note that decreasing the mean value of this dissociation rate constant by a factor of 100 has a small, but noticeable impact on the results. The major conclusions are not changed though, because MSA in our model is also efficiently produced through non-CH_3SO_3 routes.

Comment 5: "When the focus is on the RMBL then the CH3O2 and HOx chemistry should be important. Therefore, I believe that the following reactions, may be, should have been included in the mechanism:"
CH3SCH2OO + CH3O2 ->
MSEA + HO2 -> CH3SO + H2O2
MSEA + CH3O2 -> CH3SO + CH3OOH
MSIA + HO2 -> CH3SO2 + H2O2
MSIA + CH3O2 -> CH3SO2 + CH3OOH
SO2 + CH3O2 -> H2SO4 +
CH3S + CH3O2 -> CH3SO + CH3O
CH3SO + CH3O2 -> CH3SO2 + CH3O
CH3SO2 + CH3O2 -> CH3SO3 + CH3O

Reply to Comment 5: The reviewer's concerns about the absence of certain HO_2 and CH_3O_2 reactions are warranted, as the estimated rate constants for some of the above reactions are relatively large. We note, however, that the corresponding reactions in our scheme have faster rates than the above cited reactions, typically by an order of magnitude or more. For this reason, we have not included these reactions. Two exceptions are the MSEA oxidation reactions with HO_2 and CH_3O_2, which are nearly as fast as our MSEA+OH reaction. We now include these reactions in our scheme. A quantitative comparison of the reaction rates is given below using the maximum oxidant concentrations occuring in our model and rate constants in our model and Yin et al.

$[oxidant]_{max}$ (molecules/cm^3): $[OH]=3.5 \times 10^6$, $[HO_2]=1.5 \times 10^8$, $[O_3]=4.9 \times 10^{11}$, $[NO]=2.5 \times 10^7$, $[NO_2]=3.7 \times 10^8$, $[CH_3O_2]=1.3 \times 10^8$

Reaction	rateconst $*$ [oxidant]	$=$ lossrate(molec/cm^3/s)
$CH_3SCH_2OO + CH_3O_2$	$1.8 \times 10^{-13} *$ [CH3O2]	$= 2.3 \times 10^{-5}$
$CH_3SCH_2OO + NO$	$1.2 \times 10^{-11} *$ [NO]	$= 3.0 \times 10^{-4}$
$MSEA + HO_2$	$8.5 \times 10^{-13} *$ [HO2]	$= 1.3 \times 10^{-4}$
$MSEA + CH_3O_2$	$8.5 \times 10^{-13} *$ [CH3O2]	$= 1.1 \times 10^{-4}$
$MSEA + OH$	$5.0 \times 10^{-11} *$ [OH]	$= 1.8 \times 10^{-4}$
$MSIA + HO_2$	$1.0 \times 10^{-15} *$ [HO2]	$= 1.5 \times 10^{-7}$
$MSIA + CH_3O_2$	$1.0 \times 10^{-15} *$ [CH3O2]	$= 1.3 \times 10^{-7}$
$MSIA + OH$	$9.0 \times 10^{-11} *$ [OH]	$= 3.2 \times 10^{-4}$
$SO_2 + CH_3O_2$	$5.0 \times 10^{-17} *$ [CH3O2]	$= 6.5 \times 10^{-9}$
$SO_2 + OH$	$9.2 \times 10^{-13} *$ [OH]	$= 3.2 \times 10^{-6}$
$CH_3S + CH_3O_2$	$6.1 \times 10^{-11} *$ [CH3O2]	$= 7.9 \times 10^{-3}$
$CH_3S + O_3$	$5.5 \times 10^{-12} *$ [O3]	$= 2.7 \times 10^{0}$
$CH_3SO + CH_3O_2$	$3.0 \times 10^{-12} *$ [CH3O2]	$= 3.9 \times 10^{-4}$
$CH_3SO + O_3$	$6.0 \times 10^{-13} *$ [O3]	$= 2.9 \times 10^{-1}$
$CH_3SO_2 + CH_3O_2$	$2.5 \times 10^{-13} *$ [CH3O2]	$= 3.2 \times 10^{-5}$
$CH_3SO_2 + O_3$	$5.0 \times 10^{-15} *$ [O3]	$= 2.4 \times 10^{-3}$

Comment 6: "Recently Le Bras group has realised that the fate of DMSO + OH is MSIA + CH3 (rate constant 8.70E-11 cm3/s at room temperature). For the mechanism used in the paper the following reaction sequence is suggested:
DMS + OH -> DMSO + HO2
DMSO + OH -> DMS(O)(OH)
DMS(O)(OH) + O2 -> DMSO2 + HO2
DMS(O)(OH) -> MSIA + CH3
i.e. an indirect formation of DMSO2 which Le Bras does not observe. Please comment."

Reply to Comment 6: First, we note that our mechanism does not have "DMS + OH -> DMSO + HO2" as suggested by the reviewer. Instead, we form the DMS-OH adduct, which then reacts with O_2 to produce DMSO.

Second, the lack of an O_2 influence on the DMSO + OH reaction in the recent experiments of the Le Bras group (Kukui et al., JPC 2003) is intriguing and requires future attention. We will update our mechanism as more evidence becomes available concerning the formation of $DMSO_2$. In the meantime, the DMSO-OH + $O_2 \rightarrow DMSO_2$ + HO_2 reaction in our study is not without precedent. It follows from Yin et al. and other studies. The same reaction, for example, appears in Aresene et al. (Atmos. Environ., 2001) and as reaction 8 in Gross et al. (JPC, 2004).

Third, our mechanism is not inconsistent with the finding by the Le Bras group that MSIA is the major sulfur product of DMSO + OH. At the mean values of the rate constants in our mechanism, MSIA is produced with a yield of 80%, compared to 90% noted in the abstract of Kukui et al. (JPC, 2003). Moreover, considering our large uncertainties, our uncertainty analysis covers cases in which MSIA goes from being the minor product to essentially the only product.

Fourth, $DMSO_2$ and DMSO are not species of focus in our paper, and modifying the formation pathway for $DMSO_2$ will have only a minor impact on our overall results.

Comment 7: "The authors should explain the following two reactions in the DMS mechanism:
CH3SOH -> CH3SO3H
CH3S(O)OH -> CH3SO3H
I have never seen these two reactions in a DMS mechanism. Usually MSA is formed from:
CH3OH -> CH3SO -> CH3SO2 -> CH3SO3 -> MSA
CH3S(O)OH -> CH3SO2 -> CH3SO3 -> MSA"

Reply to Comment 7: We apologize for our lack of clarity. These two reactions (46 and 47 in discussion paper, 48 and 49 in revision) are parameterized versions of two of the MSA production pathways tested in Lucas and Prinn (2002). The MSA production pathways in the reviewer's comment involve the CH_3SO_3 radical, which also rapidly dissociates to form H_2SO_4. An important conclusion in Lucas and Prinn (2002) was the requirement for an efficient MSA production path involving MSEA and/or MSIA, but not CH_3SO_3. Without knowledge of the specific mechanism involved, we decided to use parameterized reactions to provide a means to achieve this MSA production. We have clarified this point in the text and Table 1. We also note that similar, non-CH_3SO_3 MSA production routes are found in previous studies (Hatakeyama and Akimoto, Koga and Tanaka).

Comment 8: "The authors should also note that in a resent ab initio/density function theory study by Gross et al. (JPC. A, 108, 8659, 2004) the addition path way of DMS + OH was discussed. This is to my knowledge the first study where the rate constants of DMSOH+O2-> have been theoretical determined. Their main results were:"
DMSOH + O2 -> DMSO + HO2 (channel 1, dominant channel)
DMSOH + O2 -> DMS(OH)(OO) (channel 2, minor channel)
DMSOH + O2 -> CH3SOH + CH3O2 (channel 3, do not occur)
"however, the study concluded that channel 2 could contribute from 0% to 50% compared with channel 1 (channel 2 is not included in Lucas and Prinn s DMS mechanism). Furthermore, the Gross et al. study describe the following reaction path of DMSOH + O2 (which is not included in Lucas and Prinn's DMS mechanism):"
DMSO + HO -> DMS(OH)(OO)
DMS(OH)(OO) + NO -> DMS(OH)(O) + NO2
"the last reaction can be important even under very low NOx concentrations."

Reply to Comment 8: We thank the reviewer for highlighting this recent publication. The reviewer is correct in noting that channel 2 above is not contained in our current box model mechanism. This channel was, however, included in our previous study (reaction R3 in Lucas and Prinn, 2002), where it participated in MSA production. The fate of the DMS(OH)(OO) adduct is still uncertain, but may play a role in MSA and $DMSO_2$ formation. Given this uncertainty and the better fit we achieved in Lucas and

Prinn (2002) using the oxidation of MSIA (reaction R8), we opted to exclude channel 2 above.

As for the "DMSO + HO -> DMS(OH)(OO)" reaction commented on above, we believe the reviewer instead meant the channel 2 reaction.

For the DMS(OH)(OO) + NO reaction, it is an interesting, alternative path leading to DMSO-OH. To clarify, Gross et al. do not state that this path is important under low NO_x conditions. Also, as noted in Gross et al., this reaction with NO is based on the chamber study of Arsene et al. (Atmos. Environ. 2001). We find it difficult to extend the Arsene et al. results to our model conditions, however, because the initial NO_x levels in their chamber (>569 ppb) are at least 35000 times larger than our NO_x levels (2-16 ppt). We anticipate that neglecting this reaction with NO will not affect our results.

Comment 9: "Page 6, second column, line 40: We evaluate the expression for |psi| =< 1. Please explain why."

Reply to Comment 9: We assume that the reviewer is referring to our choice to evaluate Eq. 8 in the discussion paper (Eq. 10 in the revision) over the range $|\xi| \leq 1$. This range was chosen because it corresponds to the conventional range of mean value +/- one standard deviation.

Comment 10: "Page 8, Section 6 it is written that The model is integrated until a repetitive diurnal cycle is achieved for all the gas-phase DMS-related species. I would like the authors to comment on the following two questions: How many days is the model integrated before the DMS-related species have a repetitive diurnal cycle? And which gas-phase species are defined as DMS-related? (SO2? H2SO4? MSA? MSEA? MSIA?) Because the loss of SO2, H2SO4, MSA, MSEA and MSIA in the model depend on the non-gas phase processes. Therefore, these species very easily can be accumulated/loosed in the model (i.e. never reach a respective diurnal cycle) if the non-gas-phase processes are not tuned. If these non-gas-phase processes are tuned, how representative are they then for the RMBL? (note the non-gas-phase processes are crucial in this study)."

Reply to Comment 10: We integrate the model for 10 days, after which the cycles of all species are repetitive (i.e., the concentrations at 0 and 24 hours local time are equal). These cycles are independent of the initial concentrations. We define "DMS-related species" as all species that contain sulfur. Our model is an "open system" in which all of the sulfur-containing species have at least one source and sink. This implies that there is no net monotonic build-up (i.e., accumulation) or depletion once the repetitive cycles are established. The model includes non-gas-phase sources and sinks (i.e., DMS emissions, scavenging by aerosols, and entrainment into and out of the boundary layer). The values of the parameters for the non-gas-phase processes are mainly determined from aircraft observations during ACE-1 as noted in the text.

Comment 11: "Figure 4, page 11: How is the term most important sensitivity coefficient defined?"

Reply to Comment 11: In general, the "most important sensitivity coefficients" are those with large magnitudes. More specifically, they have magnitudes within a defined percentage of the largest occurring value for a given species at any time. For DMS, SO_2, MSA, and H_2SO_4, respectively, they fall within 5%, 35%, 28%, and 35% of the largest value at any instant in the diurnal cycle. We have included these threshold values in the caption of Figure 4.

Comment 12: "It will be more convient for the reader if only one type of units is used to describe the concentrations of the gas-phase compounds. The paper mix between ppb and ppt, and molecules/cm3."

Reply to Comment 12: We apologize for the change in units. We have modified the text to make the concentration units more consistent. Now, all of the concentrations have units of molecules/cm^3, except for O_3 and NO in Table 2.

Comment 13: "Page 7, second column, line 10: For the independent random variables x and y, and constant a, following properties are used: E[x+y] “ E.. . Using these should be changed to The expression of E (see Table caption 3) obey: E[x+y] “ E.. . Using these ."

Reply to Comment 13: This discussion has been clarified extensively in response to this comment (see Eq. 13 in revision).

Comment 14: "Figure 3. Please add units to the axis."

Reply to Comment 14: We have clarified the units in the figure.

Comment 15: "Figure caption 6 and 7. Please change sensitivities to normalized sensitivities, and sensitivity coefficients to normalized sensitivity coefficients."

Reply to Comment 15: The figure captions have been changed accordingly.

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