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Atmospheric
Chemistry
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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

Anonymous Referee #2

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General Comments:

The release of DMS has been recognized as the largest natural global source of sulphur into the atmosphere. DMS can be transferred into aqueous-phase aerosols or oxidized to several other gas-phase species which can contribute to aerosol formation and/or growth, e.g. SO2, H2SO4, DMSO, DSMO2, MSA, MSIA and MSEA. Therefore, it has been postulated that emission of DMS from the oceans can contribute to production of new condensation nuclei and eventually cloud condensation nuclei. Thus, DMS may have an influence on the Earth’s radiation budget. However, the understanding of the oxidation of DMS in the Remote Marine Boundary Layer (RMBL) is still highly uncertain. In the paper by Lucas and Prinn sensitivity of first, second and third order, and uncertainty analysis on the RMBL DMS chemistry are presented. For their study, Lucas and Prinn use a DMS mechanism that they developed (JGR. 107, 4201, 2002) (this paper will in the rest of the review be called Paper 1). Furthermore, the paper also presents a method comparison between the Direct Integration Method (DIM) and the Probabilistic Collocation Method (PCM) for sensitivity and uncertainty analysis.

It is of scientific interest to perform sensitivity and uncertainty analysis on chemical mechanisms in general and DMS mechanisms particular, because many aspects of DMS chemistry are unknown/uncertain. It is my personal opinion that sensitivity and uncertainty analysis should be applied much more on atmospheric chemical mechanisms than it is to day, because this can provide the scientific community with important information about these mechanisms use and limitations. Therefore, the paper addresses scientific questions within the scope of ACP.

However, it is of crucial importance that the mechanism and scenario which the sensitivity and uncertainly analyses are applied on are representative for the problem of focus. I have some concerns about the DMS mechanism and scenario used in the study (see below). However, when the authors have answered the questions/comments outlined below, I will recommend it for publication in ACP.

Specific Comments:

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.

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. Furthermore, I would like the authors of the paper to comments on the following 6 points about the used DMS mechanism:

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.

2: 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.

3: 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

perhaps also

SO2 + CH3O2 -> H2SO4 + Ě

CH3S + CH3O2 -> CH3SO + CH3O

CH3SO + CH3O2 -> CH3SO2 + CH3O

CH3SO2 + CH3O2 -> CH3SO3 + CH3O

Please explain why these reactions are not included.

4: 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.

5: 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:

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$CH_3OH \rightarrow CH_3SO \rightarrow CH_3SO_2 \rightarrow CH_3SO_3 \rightarrow MSA$

$CH_3S(O)OH \rightarrow CH_3SO_2 \rightarrow CH_3SO_3 \rightarrow MSA$

6: 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.

Additional Specific Comments:

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

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).

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

I will not repeat the concerns/comments outlined by A. Satelli, and anonymous referees #1 and #3. However, I recommend the authors to take these points into serious considerations, because I think they are very relevant.

Technical Corrections:

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.

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

Figure 3. Please add units to the axis.

Figure caption 6 and 7. Please change “sensitivities” to “normalized sensitivities”, and “sensitivity coefficients” to “normalized sensitivity coefficients”

Conclusion:

When the authors have included the answers to the questions/comments raised above

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and by the three other referees in their paper, I think it will be a very good scientific contribution to the understanding of the oxidation of DMS in the RMBL. Then I will highly recommend it for publication in ACP.

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