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 #4

Received and published: 5 November 2004

Lucas and Prinn present a very detailed analysis of the gas phase reaction mechanism of DMS in the remote marine boundary layer, taking also (prescribed) emission, mixing with the free troposphere and some heterogeneous loss reactions into account. Using a photochemical box model, they employ 2 different methods, the "direct integration method" and the "probabilistic collocation method" to calculate both sensitivity and uncertainty coefficients. This is a very valuable approach which should be used more often in atmospheric chemistry.

Major comments

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.

There are a few reactions that are crucial for the determination of the final products of DMS oxidation, one of these is CH$_3$S(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 H$_2$SO$_4$, 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.

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.

**Minor comments**

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

p 6386, l. 21: difference between "structural" and "parametric"?
p 6388, l. 8: what is a "decoupled direct algorithm"?
p 6389, l 15: how good is this approximation for eta?
p 6389, l 18: "defined below" - where? I couldn’t find it

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.

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

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

section 6.2.4: I didn’t understand what "second-order coupling" means in this context.

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.

Table 3: caption unclear.

References mentioned in this review:


Kukui, A., Borissenko, D., Laverdet, G., and Bras, G. L.: Gas phase reactions of OH radicals with dimethyl sulfoxide and methane sulfonic acid using turbulent flow reactor

von Glasow, R., and Crutzen, P. J.: Model study of multiphase DMS oxidation with a focus on halogens, Atmos. Chem. Phys. 4, 589-608, 2004