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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A three-dimensional model study of methanesulphonic acid to non sea salt sulphate ratio at mid and high-southern latitudes" *by* H. Castebrunet et al.

Anonymous Referee #2

Received and published: 7 September 2009

General comments

Castebrunet et al present a 3D model study of the sulphur cycle in the Southern hemisphere with a focus on Antarctica. They compare the model results for nss-SO_4^{2-} and MSA and their ratio with measurements to evaluate the model performance. I have to admit that I find the model performance rather poor and from the paper I gather that this is mainly due to missing processes or an incomplete description of these processes in the model. In their explanations for these discrepancies the authors seem to focus on unknowns in the chemical mechanism however the chemistry scheme that they use is very simplified and it is rather this simplicity that seems to be the problem. A number

of detailed (model) studies in the past have discussed uncertainties in the chemical mechanism in great detail (e.g. Barnes et al., 2006, Karl et al., 2007, Lucas and Prinn 2002, 2005, von Glasow and Crutzen, 2004) but none of them or their conclusions are cited/used in the current manuscript. An overall lack of understanding of the chemistry is certainly a severe restriction for model studies of this kind but my impression was that the current state of the art goes much further than what seems to be implemented in this model.

Major comments

Missing halogen chemistry: A decade of satellite observations of BrO has shown that during spring BrO is present all around the Antarctic continent at concentrations high enough to impact the oxidation of DMS. As most DMS is transported within the boundary layer, where the BrO is located, it has to be expected that this chemistry is of importance for all measurements of DMS and its oxidation products near the coast and in inland Antarctica in spring. Ignoring this with a mere reference to a lack of anti-correlation (p. 15002, l. 19/20) is not enough to explain why this chemistry has been ignored. Also: Why would you expect a clear anti-correlation of these two gases at a coastal site where several other oxidants? You should at least do a sensitivity study assuming a typical (based on measurements) BrO concentration to show what the potential impact of BrO were.

Incomplete model description: Important information about the model is missing. It is not even clear whether or not the model is run in a global or hemispheric setup. What data do you use for meteorology? Is this an online or a offline run? What year does your meteorology refer to? What model spin-up do you use, are the results from a single-year run or averages over a multiple-year run? How many model layers are within the boundary layer where most of the relevant chemistry and transport occurs? You mention that several species undergo dry deposition - how fast is this or how do you calculate the rates? Do you assume MSA and nss-SO_4^{2-} to be present in externally mixed aerosol and therefore having a different deposition velocity? What

are the anthropogenic sulphur sources based on that you use in one of the sensitivity studies? I couldn't find any explanation of the REF-ANTH scenario. Did you include volcanic sulphur sources? You might want to refer to Korhonen et al., JGR, 2008, who show that different sources cannot be assumed to add linearly and that therefore great care has to be used when interpreting these results. Their study is only for CCN but I would expect something very similar for chemistry as well. How did you implement the DMS + O_3 reaction in the model? The data set used for DMS fluxes is Kettle et al - there has been an update of that paper that was published in 2000 and in addition the data base at NOAA PMEL now has a much larger collection of data (they extended Kettle et al). By using offline oxidant concentrations you are assuming infinite supply of oxidants. Did you check whether this has any effect on your results? I was very surprised how simplistic the (uptake of) intermediate products of the DMS oxidation has been implemented - I'm not surprised that a major conclusion of your work seems to be that a better description of these processes is crucial - the question that remains is - why have you not improved this description in the model?

Model "validation": First I would suggest to rename this section to "Model evaluation", partly for slightly pedantic semantic reasons but mainly because you show a rather poor performance of the model. For several species the qualitative features of the measurements seem to be reproduced but the quantitative comparison shows mismatches of very often a factor of 2x or 3x but up to 6x. Nevertheless you use language in the text that suggests a much better performance. I was surprised how you describe all the potential short comings of trying to reproduce the Cape Grim conditions in the model; my impression was that this a station where the model results are closest to the data. When you refer to a "fairly well" reproduction (p. 15014, l. 10-13) of R at coastal sites - how many data points to you actually refer to? My impression was that there are only one, maybe two data points. Based on this section I would take all model results with a huge grain of salt! I also found it rather bold to use this model with all its limitations to try and model glacial cycles - what meteorology did you use for that and did you use modern day oxidant levels as well?

Specific comments

p. 14998, l. 13/14: This statement is somewhat unclear, please rephrase.

p. 14998, l. 14: Please change "dimension" to "dimensional"

p. 14999, l. 28: Please change "It is the.." to "This is the.."

p. 15000, l. 9: Please change "3 times more important" to "3 times higher" - if this is what you mean.

p. 15002, l. 4: Please change "If NO_3 .." to "As NO_3 .."

p. 15007, l. 2: Please explain what you mean with "mode nssSO_4".

p. 15007, l. 3: Please change "dispersed" to "variable" - if this is what you mean.

Section 4: Maybe use subscripts for R_{obs}, R_{sim}, R_{psim} to make it easier for the reader.

p. 15010, l. 9: Please insert "in" between "than fall"

p. 15010, l. 13: Isn't it surprising that the better correspondence to measured data for Rpsim only holds when the aqueous phase reaction of ozone with DMS is ignored? Other studies have shown this reaction to be rather important. Therefore it is really important to explain how you treat this reaction in the model.

p. 15011, l. 6-17: You explain that the potential reason for the lack of model skill in Gondwe et al is coarse model resolution. You stress that this is not the case in your model, yet the model-data comparison doesn't seem to be much better in your model, so the question arises what the reason for this misfit is in your results?

p. 15014, l. 19: Please change "linked with" to "linked to"

p. 15016, l. 4: "a decrease south of 40S" - this is in contrast to data yet you don't seem to explain why this is.

p. 15018, l. 4: Rpsim doesn't only "not improve" the results, it seems to deteriorate

them!

p. 15018, l. 13: Please change "twice larger than" to "twice as large as"

p. 15023: Is the PhD thesis of H. Castebrunet accessible?

Figures and Tables

Table 1: Please replace "Gaz" with "Gas" in the column header. Also please don't use dots in the rate coefficient expressions. What assumptions did you make on the acidity and liquid water content of the aqueous phase? How did you calculate the uptake rates? Typically "oxidation state" or "number" is used rather than "degree of oxidation"

Table 3: References b-d don't appear in the table, only in the caption.

Figure 2: The labels are by far too small and the caption seems incomplete.

Figure 3 and 5: the labels are too small.

Figure 8: Is there no variability/error in the Bates et al data? What years are the Cape Grim and Amsterdam island data from? What year does the model simulate?

Supplement

Please change "Supplement Material" to "Supplementary Material".

The affiliation of E. Cosme seems to be wrong.

Figure 1: The line for case REF-ANTH for MSA is missing.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 14995, 2009.