Atmos. Chem. Phys. Discuss., 14, C10637–C10640, 2015
www.atmos-chem-phys-discuss.net/14/C10637/2015/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hydrogen peroxide in the marine boundary layer over the southern Atlantic during the OOMPH cruise in March 2007" *by* H. Fischer et al.

Anonymous Referee #1

Received and published: 1 January 2015

Review of Fischer et al.

Summary

The authors present an analysis of H2O2 (HP) and CH3OOH (MHP) during the OOMPH cruise in the S. Atlantic. They compare the results to model output and make inferences regarding the model representation of HP & MHP sinks.

Their chemical transport model has a tendency to underestimate the observed HP during the first part of the campaign, but not the second part, while overestimating MHP throughout. The authors argue that the model HP underestimate is unlikely to

reflect sources, and instead indicates that HP sinks in the model are too strong – and in particular dry deposition. A sensitivity simulation in which they impose a lower deposition velocity improves agreement for HP, while not affecting MHP much because of the lower solubility.

They point out that the MHP overestimate in the model could reflect a number of factors, including the collection efficiency, which was not quantified but estimated at 60%, as well as chemical reactions (i.e. CH3O2 + OH) that were not included in their baseline simulation.

The argument that the model H2O2 bias arises from dry deposition is plausible but far from definitive. In my opinion they need to do more quantitative analysis to justify this assessment. They state that the model accurately simulates HO2, and that therefore the discrepancy is unlikely due to misrepresentation of the H2O2 source. But specifically, how good is the agreement for HO2, and how does that error propagate onto the predicted H2O2? Measurements of HO2 are themselves far from perfect, and in at least some FAGE measurements include an interference from some RO2. Is that an issue here? Once you consider both measurement and model uncertainty in terms of HO2, what is the resulting error bar imparted to the H2O2 predictions that is associated with the sources? Does the model prediction of H2O2 and CH3OOH depend on NO being accurately simulated? Is it?

Are there any other HP sinks to be considered, such as uptake to aqueous aerosols, that could have an impact? What about aerosol uptake of HO2?

Overall, the attribution of HP model bias to dry deposition relies too much on hand-waving. The paper needs a more quantitative consideration of the other budget terms, and a propagation of those uncertainties (or envelope of sensitivity runs) to the predicted HP. If the model-measurement discrepancy is larger than can reasonably be accommodated by those other terms, then it becomes reasonable to invoke dry deposition. It may well be that this is the case, but not enough has been done to establish

it.

It's hard to know what to make of the MHP analysis, since the authors don't seem to know how much to trust the measurements. The sampling efficiency of 60% was not measured but calculated based on a previous study, and MHP was assumed to be the dominant peroxide (the technique measures the sum). For this portion of the paper to be useful, we need a quantitative treatment of what the authors consider to be the uncertainties on the measured concentrations, and to see to what degree these are smaller than the model-measurement differences.

Specific comments:

30557, 22-26: "As shown by Hosaynali Beygi et al. (2011), EMAC reproduces observed HO2 levels during the whole campaign and indicates similar levels for HO2 and CH3O2, the precursors of CH3OOH. Given that the precursor levels are simulated realistically by EMAC, it is very unlikely that an underestimation of the peroxide production is responsible for the H2O2 underestimation during the first half of the campaign."

Perhaps I missed it, but I don't see in the Hosaynali Beygi paper where they directly evaluate the EMAC simulation of HO2. Same goes for OH, which is referred to later ("the model also reproduces OH concentrations"). There is an evaluation of a constrained box model (their Fig 9), but that is not the same thing.

Fig 4, why do the model H2O2 concentrations become negative early on March 14?

Since the second channel is MHP + all other peroxides, wouldn't it make more sense to compare with the same model quantity rather than just the model MHP?

30557, 18: "hence the main problem seems to be that the model underestimates H2O2 during the early phase of the campaign" . . . not sure I follow. Isn't the fact that CH3OOH is overestimated throughout also a problem?

30551, 25-27: doesn't catalase react to some degree with MHP also? Please provide some quantitative information on how specific this is.

30552, 15: does the 25 ppt detection limit apply to MHP as well as H2O2?

30555, 18: "measured and observed H2O2" . . . should be "measured and modeled", I guess

30557, 13 and Fig 6: please discuss what we learn from the ratio of the two that wasn't already apparent from the plots of the species individually

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30547, 2014.