

Interactive comment on “OH and HO₂ chemistry in clean marine air during SOAPEX-2” by R. Sommariva et al.

Anonymous Referee #1

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Review of Paper OH and HO₂ chemistry in clean marine air during SOAPEX-2 by R. Sommariva, A.-L. Haggerstone, L. J. Carpenter, N. Carslaw, D. J. Creasey, D. E. Heard, J. D. Lee, A. C. Lewis, M. J. Pilling, and J. Zador

This paper presents data for OH and HO₂ radicals that have been measured on four days in extremely clean marine air during the SOAPEX-2 field campaign in Tasmania. The measurements are used for a detailed test of box-models that are assumed to represent the current knowledge of atmospheric chemistry under baseline conditions. One strength of the mostly well written paper is the careful uncertainty analysis of the model that takes into account the uncertainties of the kinetic rate coefficients and the measured input data. For HO₂ the model is found to significantly overestimate the measurements in most cases. The paper presents some interesting analysis indicating that heterogenous losses of HO₂ could play a more important role in marine air than

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is estimated from laboratory measurements. My concern about the paper is that for OH it claims a much better agreement between the model and the observations than is supported by the data. If this concern and the other comments listed below are sufficiently addressed, the paper is suitable for publication in ACP.

MAJOR COMMENTS

1. In section 5.1 the authors report the results of the measured to modeled OH comparison. They come to the conclusion that "the agreement is quite good" with model overestimates of less than 10% on the first two days (February 7th and 8th) and less than 30% on the other two days (February 15th and 16th). In the abstract and conclusions the deviations are specified to be even less than 20% on the last two days. In my opinion these conclusions are not justified as they are not supported by the data presented in the paper. I agree that the measured and modeled OH data are in good agreement within the precision ($2E+5 \text{ cm}^{-3}$ 1-sigma, Creasey et al., 2003) of the measurements on February 7th (Fig.1). However, on February 8th significant systematic deviations between measurements and model results can be seen. In the morning the modeled OH concentrations rise about 1 hour earlier than the experimental data. Conversely, the modeled OH decreases about 1 hour later in the afternoon than measured. As a consequence the modeled OH data are about a factor 2 higher than the measurements during the morning and afternoon, whereas at noon there is quite good agreement. It means that the modeled diurnal variation behaves substantially different from the observations. The different behaviour can neither be explained by the relative small statistical noise of the measured OH data, nor by the accuracy of the OH calibration (26% 1-sigma, Creasey et al, 2003) assuming that it remained constant throughout the day. The model error (15-20% 1-sigma) that is well discussed in section 5.5 is of statistical nature and cannot explain the systematic discrepancies between the modeled and measured diurnal profiles. A similar picture can be seen on February 16th (Fig.2) where the modeled diurnal profile is again much broader than in the measurements. Also on February 15th the modeled OH seems to rise earlier in the

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morning than the corresponding measurements. This time however the measured OH shows an unusual slow decay that extends beyond sunset and is also not reproduced by the model. In my opinion the deviations between model results and observations seen on the four days cannot simply be summarized as good agreement within 10–20%, but imply that the baseline chemistry is not as simple as often assumed and/or some components or physical parameters that have a strong influence on OH were not measured. This important result should be given attention and further discussed by the authors.

2. The paper reports an evening tail in measured OH and HO₂ on February 15th that looks similar for both species. The authors argue that the source of the evening OH cannot be explained by the reaction of HO₂ with NO, because NO was too low (< 5ppt). I estimate that NO of the order of 50 ppt would possibly be sufficient to explain the observed OH tail for the given HO₂. Is it possible that some local NO contamination occurred at the measurement site that could have affected the FAGE measurements without being noticed by the NO measurement instrument? Of course this would not explain the source of the relative high HO₂ concentrations .

3. The paper explains in detail how the Master Chemical Mechanism MCM 3.0 with more than ten thousand reactions was first reduced to a detailed chemical mechanism of 2085 relevant reactions, and then, by omission of the oxidation schemes of the NMHCs, to a simple mechanism of only 75 gas-phase reactions. Both the simple and the more detailed model results agree well with each other, but do not agree well with the HO_x measurements. In order to understand which gas-phase reactions were finally included in the simple model, I suggest to list the relative short mechanism in a table, rather than to let the reader try to reconstruct the mechanism from the MCM along the intricate guide line given in this and the referenced papers.

4. Figs. 3, 4 and 6 show scatter plots and regression lines of measured vs. modeled HO_x concentrations. Apparently only subsets of the available data (presented in Figs. 1, 2, and 5) are shown in the correlation plots, neglecting for example the measured

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OH data with values less than $7E5$ cm⁻³. The reason for this selection should be explained. In case of differently behaving measured and modeled diurnal profiles no linear relationship is expected for the data and it may not be reasonable to apply a linear fit to the scatter plots. It is then perhaps more reasonable to compare the data to a 1:1 line representing the case of an ideal agreement. However, if a linear regression is justified, the 1-sigma errors of the fitting parameters should also be given. In that case the slopes and non-zero intercepts should be discussed with respect to their statistical significance and meaning.

MINOR COMMENTS

1. In the introduction or at the end of section 2.1 it should be pointed out that the complete set of HO_x data measured during the SOAPEX-2 field campaign has already been presented before by Creasey et al. (2003).
2. I suggest to use the term 'HO₂+RO₂' for the sum of all peroxy radicals (i.e. without the Greek Sigma) as RO₂ denotes the class of all organic peroxy radicals.
3. The comparison of the model calculations using old and new recommendations for the rate coefficients of OH with CO and NO₂ is quite interesting. Please specify explicitly the numbers for the old and the new recommended rate coefficients used in the calculations.
4. Figure 1: what is the reason for the large spike in the modeled OH (simple model, blue curve) on February 8th at noon and why does the spike not appear in the more detailed model?
5. The time zone used in the paper should be specified in the labels of the time axis of the figures.
6. The y-axis of Figs. 1, 2, 5, 8, 13, 14, 15 should be properly labelled, i.e. [OH] or OH concentration, [HO₂] or HO₂ concentration etc.
7. Figures: tic marks on the axis can hardly be seen; a larger font size for the labels

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would improve the readability.

8. In the captions of Figs. 3-6 the units of the calculated intercepts should be given. I assume the number $9.7\text{E}+6$ for the intercept in Fig.4 must be replaced by $9.7\text{E}+5$.

9. Figs. 9, 10, 11, 12: the overhead titles should be deleted and the information moved into the figure captions; what is the meaning of J38 ?

10. Figs. 11, 12: the abbreviation 'std' is unusual and should be defined.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 419, 2004.

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