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Atmospheric
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Discussions

Interactive comment on “OH and HO_2 chemistry in clean marine air during SOAPEX-2” *by* R. Sommariva et al.

R. Sommariva et al.

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We thank the referees for their useful comments.

REFEREE #1

Comment: 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 cm-3 1-sigma, Creasey et al., 2003) of the measurements on February 7th (Fig.1). However, on February 8th significant

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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 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.

Response: We agree that the shape of the [OH] profile on February 8th and on February 16th is not well reproduced by the model and we propose to change the wording to say that the agreement is good in the middle of the day, but is less good in the early morning and in the evening. Thus we will change the wording in section 5.1 to reflect this comment. The tail on February 15th is discussed, but we will add some discussion on the different shapes on the profiles, although I am afraid that we will be able to do no more than to comment without explanation. Note that there is overlap of the uncertainties for most of the time, as shown in figures 13 and 14. The point at issue is that there is a consistent overestimation of the width of the profile.

Comment: 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 ($<$ 5 ppt). 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 occured 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.

Response: It is difficult to envisage a difference in NO concentrations at the two sampling points of this order of magnitude. The sampling points were about 20 metres apart, but the winds remained in the baseline sector during this period and the wind speeds were high (20-30 m s-1). There were only natural sources of NO in this wind sector and a localised source of this magnitude is difficult to envisage.

Comment: 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 HOx 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.

Response: We will add an appendix that includes the `simple' model mechanism.

Comment: Figs. 3, 4 and 6 show scatter plots and regression lines of measured vs. modeled HOx 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 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.

Response: We omitted data below the detection limits of FAGE for the correlation plots although they were included for the diurnal comparisons. A 1:1 line will be added to the correlation plots (figures 3, 4, 6) to emphasize the periods when the models overestimate the measurements and we will modify the text accordingly.

Minor Comments: 1. In the introduction or at the end of section 2.1 it should be pointed out that the complete set of HOx 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 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 9.7E+6 for the intercept in Fig.4 must be replaced by 9.7E+5. 9.

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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.

Responses: 1. The Creasey et al. (2003) paper is referenced, but we will make the reference on page 425 more transparent. 2. The sigma is the notation we have adopted before. It has the advantage that it is absolutely transparent. 3. We will add the rate coefficients to the text. 4. We have found an error in the macro used to average the input data for the `detailed' model. This has now been corrected. This error has no significant effect on the rest of the data. 5-6-7-8-9. The time zone will be included. The y-axes will be properly labelled. The tic marks and font sizes will be increased. The units will be included and the numbers corrected. 10. `std' will be defined (as standard deviation) in the figure caption.

REFEREE #2

Comment: The authors use a number of field measurements to constrain their model and to compare them with the model results. While the uncertainties of many of these measurements are listed somewhere in the paper, it would be very helpful if they could be shown in one central place, for example by expanding Table 1.

Response: We will put in an assessment of the uncertainties in each of the measurement techniques in Table 1.

Comment: It would be particularly helpful to include the errors of OH and HO2 in figures 1-6 and 8. The uncertainty should also be included in the discussion of the comparison.

Response: The experimental uncertainties are already shown together with the model uncertainties in figures 13-15. We don't think it would be particularly helpful to have them in the scatter plots.

Comment: Much of the manuscript is dedicated to the discussion of the role of HCHO as a major HO2 source. However, the approach taken by the authors constrains the HCHO in the model by the observations. At one point in the manuscript it is mentioned that if HCHO is not constrained the model calculates 50% lower HCHO concentrations. It would be interesting to know how the OH and HO2 levels change if HCHO is not constrained. In addition, the authors could consider what would happen if the measured HCHO concentration is indeed lower by the 50% inaccuracy that was mentioned for the HCHO measurement. This discussion would help in explaining how the conclusion that there are uncertainties in the chemical mechanism was reached.

Response: In response to referee #3 we have already removed our conclusions about the mechanistic uncertainties for HCHO. However we will discuss the effect of not constraining HCHO. There is very little effect on OH concentration (5-7%). The effect is greater for [HO2], but because the main source of HO2 is OH and the recycling from HO2 to OH is slow under these conditions, reducing HCHO by 50% only reduces [HO2] by 15-25%.

Comment: At various points in the manuscript the possibility that halogen chemistry may have an influence on the chemistry in the clean boundary layer is mentioned. Chlorine chemistry is included in the model. However, the heterogeneous release from sea salt, which has been considered as a major source of Cl at many occasions, is not considered as a source. It is thus likely that Cl levels at Cape Grim are higher than those in the models. Oxidation of methane and other hydrocarbons could have an influence on the radical cycle and the formation of HCHO even at Cl atom concentration of 1-5x10+4 atoms/cm3. There are also now various examples of measurements of BrO at levels of 1-2 ppt, and of IO at levels of 0.5-1 ppt in the marine boundary layer. While I agree with the authors that an accurate quantification of halogen chemistry is difficult, it is important to discuss the possibility that part of the HO2 discrepancy is due to halogen chemistry.

Response: As discussed in our response to referee #3, we will include an expanded discussion of IO and we will remove the section on Cl + organics in rural UK in the

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final version of the paper. The sources of chlorine in the `detailed' model are CH3Cl, CH2Cl2, CHCl3 and C2H2Cl4 as measured during the campaign. BrO was not measured during SOAPEX-2.

Minor/Technical Comments: Page 428 line 20: `..an aerosol..' should be `..on aerosol' Page 431 line 7 8: The authors should explain how OH concentration of 10+5 molec/cm3 could be observed if the detection limit is 1.4x10+5 molec/cm3. Page 434 line 2: Should `propagation/termination rates' be `propagation/termination ratios'? Page 441 line 20: `NO $<$ 4 ppt' instead of `NO $<$ 3 ppt'

Responses: The minor comments will be attended to. Rates should indeed be ratios.

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