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

Anonymous Referee #3

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This paper presents a modelling study, in which explicit chemical mechanisms are used, in conjunction with measurements of a number of atmospheric species, to investigate the chemical processes controlling the ambient levels of OH and HO2 radicals in the coastal boundary layer in Tasmania. The HOx radical concentrations have also been measured by these authors, using the FAGE technique.

The paper provides valuable insights into the sources, sinks and extent of recycling of HOx radicals at very low NOx levels, with the employed chemical description (based on the Master Chemical Mechanism) generally leading to a reasonable description of the observations. Detailed sensitivity and uncertainty analyses are included which assess the relative importance of the processes controlling the free radical concentrations, and those parameters and processes which may contribute to the observed model-measurement discrepancies. The paper is clearly written and makes a valuable

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contribution to the literature in this area. It should certainly proceed to full publication in ACP. However, there are two points on which the analysis and discussion appears to fall below the generally high standard of the paper, as outlined below. The authors should consider improvements in these areas in the production of the finished article.

Comment 1: HCHO and peroxides: The abstract makes the definitive statement that a poor model-measurement comparison for HCHO 'suggests that there are significant uncertainties in the chemical mechanism', and this is also amplified in the summary and conclusions section. However, the discussion of this topic within the body of the paper, in addition to not being entirely clear, does not really seem to reach this conclusion. First, large uncertainties (50%) in the measured HCHO concentrations are quoted, which could presumably go a long way to explaining the discrepancy. Secondly, it is stated on page 8, that the zero-dimensional modelling method is not in any case appropriate for calculating background HCHO concentrations, due to its lifetime (I fully agree with this). It is therefore not clear how the statements in the abstract and summary are reached.

In fact, some attempt could and should be made to estimate what the concentration of HCHO should be, and this should contribute to the discussion. This could involve running the box model over several diurnal cycles. On the basis of a steady state back-of-the-envelope calculation carried out by this referee, methane oxidation should lead to a concentration of HCHO of about 150 ppt, which is about a factor of two lower than the presented observations. This calculation is based the assumption that the oxidation of one molecule of CH4 ultimately generates one molecule of HCHO, and that [OH] is about 10+6 molecule cm-3 and j-HCHO is about 5 x 10-5 s-1 (these are not incompatible with the presented data). The generation of HCHO is either direct, or via CH3OOH or CH3OH. For the low NOx conditions of the present study, oxidation via CH3OOH is particularly important. The timescale for HCHO to reach steady state is therefore also governed by the lifetime of CH3OOH, which is of the order of 1 day. However, the apparent lifetime is even longer, because OH+CH3OOH largely generates CH3O2, which partially reforms CH3OOH. Therefore modelling the steady state background concentration of HCHO, and indeed CH3OOH, requires a modelling timescale of at least several days (and much more if CH3OH is a significant intermediate product).

This indicates that the model applied in the present paper should really also be initialised with compatible background concentrations of CH3OOH. The fluxes in Figure 7 clearly demonstrate that the production of CH3OOH (4.54 x 10+5 molecule cm-3 s-1) significantly exceeds is removal (0.58 x 10+5 and 0.86 x 10+5 molecule cm-3 s-1, by photolysis and OH reaction respectively), indicating that the CH3OOH concentration was not initialised at a compatible figure. Based on information in the paper, I do acknowledge that this concentration is likely to be significantly greater than the observations, although no quantitative comments on the uncertainty in the measurements of CH3OOH are made.

In addition to the above appraisal of HCHO formation from methane, it is also possible that the higher hydrocarbons and other unmeasured organics could contribute. On page 3, it is demonstrated that the other measured species account for about 10% of OH reaction, relative to CH4. The oxidation of one molecule of a Cn hydrocarbon can lead to the formation of up to Cn molecules of HCHO, provided there is sufficient time for breakdown of intermediate products. The minor hydrocarbons (up to C7) therefore provide the possibility of additional HCHO formation which is not insignificant compared with that derived from CH4 (again, calculations over several diurnal cycles might be informative). It is likely, therefore, that the HCHO concentrations calculated on the basis of understanding of tropospheric organic chemistry (as presumably adequately represented in the Master Chemical Mechanism) would be well within the quoted factor of two uncertainty in the HCHO measurements. In contrast to the statements in the abstract and summary, it could be that the model-measurement discrepancy for HCHO is mainly due to limitations in the modelling method and uncertainties in the ambient measurements.

Comment 2: iodine chemistry: At several points in the paper, the topic of iodine chemistry is raised, but then almost immediately dropped. In each case, the justification for this is not fully satisfying. On page 4, it is stated that detectable levels of CH3I can have at least some effect of HOx. Therefore undetectable levels of much more reactive species such as CH2I2 can also have an effect. The fact that they were not detected is not, in itself, enough justification for not considering iodine chemistry. On page 9, a brief statement is made about observed levels of IO, but the reason for not considering it further is given as 'the HOI photolysis rate could not be modelled'. Data readily available in relevant evaluations demonstrate that HOI photolysis is rapid (typically occurring in a few minutes), such that its lifetime is probably comparable with the resolution of the presented free radical data. Given that the modelling is based on observational constraints, surely the impact of IO could be provisionally assessed by simply including one extra reaction: HO2+IO = OH (+ I), where HOI photolysis is assumed to be instantaneous. If this has a negligible effect, then the omission of iodine chemistry can be properly justified. However, I suspect the problem for the authors is that it is not insignificant. Based on the maximum IO and HO2 concentrations for 15th February given (about 2 x 10+7 and 2 x 10+8 molecule cm-3), and a rate coefficient of about 9 x 10-11 cm3 molecule s-1, a maximum reaction flux of about 4 x 10+5 molecule cm-3 s-1 can be calculated. Inspection of Figure 7 reveals that this is clearly significant.

Other comments

Page 1, line 4 of introduction: When referring to the 1 s lifetime for OH, this should perhaps be identified as the 'boundary layer lifetime', because the lifetime increases at higher altitude.

Page 2, paragraph before reaction (7): 'branching ration' should be 'branching ratio'.

Page 3, line 9 of section 4.1: I think '1%' should be '0.1%'.

Page 4: The justification for the treatment of Cl atom chemistry is not well supported by reference to conditions and calculations relevant to southern England. Data for organics are presented in this paper, and can be used to demonstrate briefly whether they compete favourably for Cl in comparison with ozone. The associated comment about the ClOx-O3-NOx null cycle is invalid at the low levels of NOx in the present study, because the reaction of ClO with HO2 will compete.

Page 5, sentence starting on line 24 of section 5.1: The modelled concentrations are exceeded by the measurements on occasions other than the evening of 15th (e.g. 7th, middle of day). This statement is therefore incorrect.

Page 6, comparison with Chen et al. in section 5.3: Because the list of OH contributions from the two studies were not carried out with the same model and assumptions, it should be made clearer that this is a comparison of the reported results of two studies. Otherwise the differences might be interpreted differences between the impact of the chemistry at two locations.

Page 7, penultimate paragraph of section 5.4: In relation to the influence of the higher reaction probability, the statement 'it is clear that the modelled concentrations are much closer to the measurements' is not true for the overnight levels.

Page 8, discussion of Figure 9: The fact that the sensitivity index of HCHO swings between positive and negative values could be worthy of comment.

Page 19, Figure 7: The formation of CH3OOH from CH3O2 and HO2 is represented twice. One of these could be replaced by formation of H2O2 from the HO2 self reaction.

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

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