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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 referee for his useful comments.

Comment: [...] 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. [...]

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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 (4.54x10+5 molecule cm-3 s-1) significantly exceeds is removal (0.58x10+5 and 0.86x10+5 molecule cm-3 s-1, by photolysis and OH reaction respectively), indicating that the CH3OOH concentration was not initialised at a compatible figure. [...] 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.

Response: The box models which we ran to simulate [HCHO] and the hydroperoxide concentrations were run iteratively for seven identically constrained days to initialize their concentrations in the final run. While this approach provides a reasonably realistic method, we accept that substantial uncertainties remain in the calculated concentrations of these species. A much more detailed model evaluation is needed to justify our assertion that the models underestimate [HCHO] and overestimate [CH3OOH]/[H2O2].

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Such an evaluation is not the main focus of this paper and so we have decided to withdraw these sections from the final version of the paper: Page 421, lines 1-4 (in the Abstract). Page 439, line 24 - page 440 line 6 (in the Uncertainty Analysis Section). Page 442 lines 20-25 (in the Conclusions).

Comment: 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 2x10+7 and 2x10+8 molecule cm-3), and a rate coefficient of about 9x10-11 cm3 molecule s-1, a maximum reaction flux of about 4x10+5 molecule cm-3 s-1 can be calculated. Inspection of Figure 7 reveals that this is clearly significant.

Response: We agree with the referee that the fact that CH2I2 was not detected is not enough to exclude iodine chemistry from the model. Moreover, a recently published report from McFiggans et al. (ACPD, 4, 9393-967, 2004) shows that molecular iodine may be a more significant source of I than CH2I2 in the marine boundary layer. Unfortunately HO2 data for February 7th were not available, but working from figure 7,

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the flux through HO2 + HO2 we can estimate a [HO2] of about 4x10+8. This is actually rather higher than the value the referee used to calculate the IO + HO2 flux. The `simple' model was run with a basic IO mechanism (IO + HO2, HOI photolysis, HOI heterogeneous loss, with a maximum [IO] = 0.8 ppt) using estimated photolysis rates and simple heterogeneous uptake of HOI (k=ACg/4). The effect is that OH increases by ˜10% and HO2 decreases by ˜10%. However proper calculation requires accurate photolysis rates and aerosol uptake rates. This rough calculation shows that the effect of IO is significant and is being considered in more detail in the NAMBLEX campaign (where [IO] was generally higher). The paragraph on iodine chemistry in the Model Description Section (Page 428, lines 1-9) will be deleted in the final version of the paper and the above comment will be added to the paragraph at the end of the Uncertainty Analysis Section (page 440).

Comment: 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 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 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.

Response: We agree on these points. They will be corrected in the final version of the paper.

Comment: 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.

Response: We agree on this point. Lines 21-24 on page 427 will be deleted in the final version of the paper.

Comment: 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.

Response: Chen et al. used a model with a vertical transport component. The following sentence will be added to the paragraph at the end of the comparison (page 434, line 21): It should be noted that Chen et al. used a model with a vertical transport component and they do not specify which height the fluxes they report refer to.

Comment: 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.

Response: The OH sensitivity to HCHO is positive during the early morning-late afternoon and negative in the central part of the day. This is due to the relative importance of HCHO as OH sink and radical source. In the early morning OH + HCHO is comparable to OH + CH3OOH and less than OH + H2 (at 10:00 fluxes are: 1.6, 1.7 and 2.4x10+5 molecule cm-3 s-1, respectively), but in the middle of the day OH + HCHO becomes more important than OH + CH3OOH and as important as OH + H2 (at 14:00 fluxes are: 4.0, 3.4 and 3.8x10+5 molecule cm-3 s-1, respectively). On the other hand j(HCHO) is broader than j(O1D): in the early morning production of HO2 by this route becomes the major radical production reaction. In addition since ozone photolysis is slow, HO2 + O3 is a significant source of OH. So in the early morning late afternoon perturbing HCHO affects OH production from HCHO through HO2 more than OH loss, thus giving a positive SI. The above comment will be added to the Sensitivity Analysis paragraph, after line 20 at page 438.

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.

Response: The plot reports radical fluxes, so one is the flux of HO2 to CH3OOH and the other is the flux of CH3O2 to CH3OOH. The reaction CH3OOH + OH -> HCHO + OH is not shown because it does not affect OH. The HO2 self-reaction is already represented. In the caption we can specify that the figures refer only to the radical fluxes.

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