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Atmospheric Chemistry and Physics Discussions

Interactive comment on "OH and HO_2 chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake" *by* R. Sommariva et al.

Anonymous Referee #1

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This manuscript describes a comparison between OH/HO_2 measurements and steady state model calculations which were constrained with a large suite of measurements at Mace Head, Ireland. The basic model run showed an agreement, within the uncertainty of the OH measurements, between modeled and measured OH. However, HO_2, was overestimated. While the inclusion of oxygenated hydrocarbons lead to an improvement, the largest factor in reducing the discrepancies was found to be halogen compounds, which were also measured. The manuscript shows convincingly that these species have to be included in chemical models of coastal areas to accurately describe HO_x chemistry. I recommend the publication of the manuscript after revisions,

which will be outlined in the following detailed comments:

Page 10953, line 2: I have my doubts that the NO/NO_2 ratio is a good indicator for long chemical processing time, in particular if halogens are present. I am sure there are better indicators to make a statement on chemical processing time. If not, please explain why the NO/NO_2 ratio is advantageous.

Page 10955, line 18: How reasonable is it to constrain a model with NO and NO_2 values, while leaving out chemistry such as the various IO reactions that can change the NO/NO_2 ratio? Omitting the influence of IO, which is present at high enough concentrations to impact the NO/NO_2 ratio considerably, could lead to erroneous OH and HO_2 levels. Please comment on this question in the manuscript.

Page 10954, line 19: It would be helpful to give the accuracy of the photolysis estimates for those days without spectral radiometer data. The statement, that the agreement between measured and estimated photolysis rates was better than 50

Page 10956, top Table 1: Please specify which of the HCHO data listed in Table 1 sets have been used to constrain the model. Why was one chosen over the other?

Page 10957, line 17: Please specify the accuracy (including the uncertainty of the calibration) of the OH and HO_2 measurement. Citing standard deviations gives the impression of a statistical error, which is not the case for the influence of calibration uncertainties on the field observations. In the text, please use statements such as "agreement within the error of the measurements". For example, statements such as that on page 10958 that the agreement was better than 10

Page 10957, line 15: I would like to applaud the authors for giving a "model uncertainty". However, I do not believe that this uncertainty was actually used in the manuscript. At least in the figures, the model data does not have uncertainties. The authors may consider the bold step of putting error bars on model results. Page 10981, line 21: One expects the concentration of halogen oxides to be lower at higher NO_x.

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The omission of XO in the model would therefore have a smaller influence at higher NO_x.

Page 10967, lines 2 4: Figure 9 should be Figure 5

Page 10970: It is becoming increasingly clear that IO is indeed spatially unevenly distributed, as discussed at the beginning of this page. Therefore, the question arises whether using the DOAS IO measurements is the correct approach to constrain the model. One could argue that the DOAS measurements are only a lower limit for the IO concentrations, and that the impact of IO is larger than described in most of the manuscript, or that the averaged DOAS values are not necessarily representative for the local observations at the Mace Head observatory. It appears that for days such as 18 August the agreement between measurements and model with 50ppt of IO is quite good. It would improve the manuscript if this point would be discussed in more detail.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 10947, 2005.