

## ***Interactive comment on “The chemistry of OH and HO<sub>2</sub> radicals in the boundary layer over the tropical Atlantic Ocean” by L. K. Whalley et al.***

**Anonymous Referee #1**

Received and published: 19 September 2009

The authors present and discuss observations of OH and HO<sub>2</sub> in the tropical marine boundary layer and analyze them with the help of a box-model based upon the Master Chemical Mechanism. The results presented in this work expand the sparse database of HO<sub>x</sub> measurements in the most photochemically active region of the lower atmosphere and are, therefore, appropriate for publication in ACP. However, before final publication is considered, the authors should address the concerns and problems discussed hereafter.

### **General Comments**

The manuscript could benefit from some reorganization and simplification. For example, the model-measurements comparison is spread over three subsections (3.1, 3.3 and 3.5) and the sensitivity analysis is divided between subsection 3.4 and 3.5. This

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causes repetitions, unnecessary wordiness and sometimes confuses the discussion. I strongly suggest the authors consider consolidating the various subsections into just three (daytime and nighttime model-measurements comparisons and sensitivity analysis) in addition to the rate of production and destruction analysis subsection. As a minor, but related, point the manuscript requires more attention to the english to avoid non-scientific/rigorous terms and definitions and/or colloquial expressions (e.g., "its presence being felt", "oxidative degradation", "manifested through" and such).

The description of the model needs several corrections and clarifications. The MCM contains 135 VOC (not 125) and it does not use the latest kinetic data. In fact, the latest release was in 2003. If parts of the MCM included in the model used in this work were updated, the authors should say which ones and give the appropriate references. It should be stated more clearly which VOC were in the model (those listed in table 1?) and that the constraints were averaged as indicated in table 1 (if this is the case). Indicating HCHO as a measured constraint is misleading, because later on it is stated that 500 ppt is a typical value. So HCHO was estimated, not unlike H<sub>2</sub>. Also, from section 2.3 it seems that the base model included both deposition and heterogeneous uptake, but in the following sections it seems that these processes were included only in the test models discussed with the sensitivity analysis.

The comparison between the model and the measurements and the sensitivity analysis need to address the differences between the two broad scenarios of the campaign. It appears that, not only HO<sub>2</sub> was higher in the first part of the campaign, but also that the model underestimated it, while the opposite was true for the second part of the campaign. Therefore, in trying to improve the agreement between the model and the measurements different approaches should have been used and the two cases should have been treated separately. In addition, the authors speculate -correctly- about the role of HCHO, which was not measured. However, it seems the model was run only using lower [HCHO], but not higher, although the authors cite previous works suggesting up to 1 ppb of HCHO. Also, it seems that the model was constrained to

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very long averages (1 h) of NO<sub>x</sub>: the authors should comment on the impact of NO<sub>x</sub> variability on the model calculations and on the agreement with the measurements.

In section 3.2, the role of HOI and HOBr as sources and sinks of HO<sub>x</sub> is discussed. A brief comparison with similar previous works (e.g. the NAMBLEX campaign) could add context to the numbers given here. It is also mentioned that different results were achieved depending on the uptake coefficient used for HO<sub>x</sub>. But this test - and the effect on the model-measurement comparison - is not mentioned in the sensitivity analysis section. The role of halogen oxides in reducing/increasing OH is also much discussed, but only in reference to the perturbation of NO<sub>x</sub> and there is no mention to the potential role of XNO<sub>y</sub>. It should also be clarified whether the calculations discussed on page 15980 come from the model or not, and in the latter case, whether the hypothesis was checked using the model.

In the sensitivity analysis section, the discussion of the role of HO<sub>2</sub> heterogeneous uptake is a little confused. It is stated that it is needed an uptake coefficient of 0.4 with a representative surface area of 1e-6 cm<sup>2</sup> cm<sup>-3</sup> or, alternatively, a more realistic uptake coefficient of 0.1 with a surface area of 4e-6 cm<sup>2</sup> cm<sup>-3</sup>. But the calculation in the first paragraph of page 15983 suggest a correction factor for the surface area of 2. This means a corrected surface area of 2e-6 not 4e-6 cm<sup>2</sup> cm<sup>-3</sup>: could this please be clarified. Some comment about the composition of the particles should also be added, as the Thornton (2008) paper suggest that the HO<sub>2</sub> uptake coefficient is dependent on this parameter.

In section 4, the removal processes of ozone are discussed. It should be clarified how these numbers were obtained, because, since the MCM model is constrained to measured ozone, it would not make sense to use its results to calculate ozone losses. It also appear that ozone deposition has been neglected: it is not indicated in Figure 1 (and neither HO<sub>2</sub> sinks other than peroxides) and it is not mentioned in section 2.3. This should be explained.

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#### Specific/Technical Comments

in abstract and conclusions and in sec 3.1: please state explicitly the level of agreement for HO<sub>2</sub> in percent (possibly for the two regimes).

page 15961, line 1: this sentence is inexact. OH is the dominant oxidant in the troposphere under most, but not all conditions.

page 15961, line 10-14: this paragraph should be rephrased to clarify its meaning ("disproportionately" with respect to what?); a verb is missing in the last sentence.

page 15963, line 1: remove fullstop before parenthesis.

page 15963, line 27-29: "fairly flat diurnal profiles"? please explain. The observations of IO and BrO suggest that these species are relevant on a global scale, but they are not "evidence". Also: "is thought to be representative", please give reference or rephrase.

page 15964, lines 7-14: the conditions encountered during the campaign were mostly low NO<sub>x</sub>, therefore it would be better to have here the equations relevant for those conditions, rather than the equation for high NO<sub>x</sub> conditions.

page 15966, line 5: "located"

page 15972, line 1: "H<sub>2</sub>O vapour"? please use either just "H<sub>2</sub>O" or "water vapor"

page 15972, line 17: "constrained to"

page 15974, line 4: "scenarios"

page 15977, line 21: "visa versa"?

page 15977, line 25-28: please rephrase. There is some verb missing and species "reach" steady state not "run to". Besides, unless the model is also run constrained to peroxides this happens in every model run (if not so, please add explanation in sec. 2.3).

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page 15978, line 19: delete "from"

page 15983: line 20: please indicate the lifetime with respect to surface deposition

page 15988 line 9-10: "additional" instead of "added"

page 15989 line 2: please be quantitative

table 2: what do the asterisks mean?

figures 3, 5, 8, 9: the colors are all similar and difficult to distinguish. In figure 3, in particular CO does not appear to be blue, nor NO green.

figure 6 caption: "diurnal"

figure 7: please add an horizontal line at 1 (as in figure 8) to the lower panels.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15959, 2009.