

Interactive comment on “The chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic Ocean” by L. K. Whalley et al.

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Many thanks to the reviewer for helpful comments to improve the paper. The specific comments of the reviewer are addressed below:

Referee comment: 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 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.

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Author reply: The manuscript's results sections are now organised as suggested by the referee:

3.1 Daytime measured and modelled OH and HO₂

3.2 Nighttime measured and modelled HO₂

3.3 Rate of production and destruction analysis

3.4 Sensitivity analysis of modelled OH and HO₂ concentrations

The discussion on the sensitivity of the model to various parameters ([HCHO], halogen chemistry, NO_x and heterogeneous loss processes) is now limited to section 3.4 and, as such, avoids repetitions. An additional figure has been included in section 3.2 to highlight the change in modelled [HO₂] during the nighttime with and without 100 pptv of PAN.

Referee comment: 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).

Author reply: These terms have been removed/reworded.

Referee comment: 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.

Author reply: The model was run with kinetic data taken straight from the MCM v 3.1; the kinetic data was not updated. The description of the model in the manuscript has been re-worded as follows: 'A box model was used to calculate OH and HO₂ concentrations, and contained a near explicit chemical scheme for the oxidative degradation

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of C1 – C5 hydrocarbons, extracted from the Master Chemical Mechanism (MCM) version 3.1 (Saunders et al., 2003). The entire MCM treats the degradation of 135 VOCs and considers oxidation by OH, O₃ and NO₃. The degradation continues until CO₂ and H₂O vapour form as the final oxidation products. Complete details of the kinetic and photochemical data used in the mechanism are available at the MCM website (MCM, <http://mcm.leeds.ac.uk/MCM/home>).

Referee comment: 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).

Author reply: The VOC used in the model are those listed in table 1, typical 24 hr averages of the VOC were also given in table 1. This may have caused confusion; the model was constrained with the hourly measurements of the VOC (not the 24 hr values). The ROPA and RODA pie charts (figure 6, (was figure 5 in the original manuscript)) relate to parameter concentrations / levels between 12:00:00 and 13:00:00 and so we feel it will be more useful to provide typical levels of the model constraints for this hour, rather than a 24 hr average. To further avoid confusion, the description of model constraints in the manuscript now reads: 'The model was constrained to hourly measurements of a number of VOCs (listed explicitly in Table 1), NO_x, O₃, CO, CH₄, j(O₁D) and meteorological parameters. The midday concentrations/values of these model constraints are given in Table 1 for information; there are, however, some deviations from these typical values in the hourly measurements that are used as model inputs.'

Referee comment: 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 H₂.

Author reply: Since submission of the manuscript further analyses of the HCHO LP-DOAS data have been performed, the mean [HCHO] measured during May (coinciding with the RHaMBLe intensive) was 328 ± 100 pptv. This has been used to constrain the

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base-case model scenario. Elevated [HCHO] ~ 2 ppbv were observed during RHaMBLe and correspond to days when elevated [HO₂] were observed. These elevated episodes have been removed when calculating the mean [HCHO] for May so as not to skew the background [HCHO] level used to constrain the model. The HCHO model constraint is discussed as follows in the manuscript: 'A constant HCHO concentration of 328 pptv was assumed in the base-case model scenario, based on average [HCHO] measured by LP-DOAS during May at the observatory. Deviations from this background [HCHO] used (and the impact upon HO_x levels) are considered in section 3.4.'

Referee comment: 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.

Author reply: As a consequence of the rearrangement of the manuscript the base-case model now includes deposition and heterogeneous uptake (this wasn't the case in the original manuscript). A full description of the heterogeneous processes included in the model is found in the experimental section (2.3). The sensitivity of the modelled HO_x to these heterogeneous loss terms is discussed in section 3.4.

Referee comment: 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 HO₂ 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. Author reply: The difference between the two broad scenarios encountered are briefly introduced in section 3.1 Daytime mea-

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sured and modelled OH and HO₂. A full discussion on possible changes in chemistry that could account for the different [HO₂] observed during both scenarios is now found in section 3.4 Sensitivity analysis of modelled OH and HO₂ concentrations. As suggested in the original manuscript the elevated HO₂ during the first half of the campaign could be due to elevated [HCHO] during this period. HCHO was measured periodically during the campaign by the LP-DOAS (whenever the LP-DOAS was tuned to the appropriate spectral region). Recent analysis of the HCHO data that exists shows that on the 23rd/24th May [HCHO] were extremely elevated ~ 2 ppbv (relative to the [HCHO] of 328 pptv used to constrain the model) – a model run, in which the [HCHO] is constrained at 2 ppbv is now shown in figure 9 (was figure 8 in the original manuscript) in section 3.4 and is discussed in relation to the elevated [HO₂] observed in section 3.4. Another potential cause for the difference in HO₂ concentrations during the two scenarios is a change in the HO₂ sinks (halogen oxides / aerosol uptake). As suggested by the referee (and discussed by Thornton (2008)) a change in aerosol composition may change the uptake coefficient of HO₂ – this is discussed in relation to the change in air-mass types (long-range transport of US air vs marine air) in section 3.4 of the manuscript. The sensitivity of HO₂ to changes in halogen oxide concentrations is also discussed.

Referee comment: Also, it seems that the model was constrained to very long averages (1 h) of NO_x: the authors should comment on the impact of NO_x variability on the model calculations and on the agreement with the measurements.

Author reply: The ambient NO_x concentrations are extremely low at the site and as such are close to the limit of detection of the NO_x analyser – as highlighted in table 1 the LOD for NO for a 1 hr average is 1.5 pptv, similar to the ambient concentrations at times. We require 1 hr averages, therefore, to observe a signal above the noise of the instrument and have confidence in the NO_x data used to constrain the model. We have now included a discussion on the sensitivity of HO_x concentrations to NO_x in section 3.4, extending from the discussion of how halogen oxides can accelerate

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NO_x oxidation: ‘The difference between the two model scenarios in which halogen chemistry is switched off and NO_x chemistry is (a) constrained to observations and (b) is doubled, allows the impact of variable [NO_x] upon [OH] and [HO₂] to be assessed. On average, modelled [OH] and [HO₂] increase by $\sim 4\%$ and $\sim 8\%$ respectively via increases in R10 and R11 when [NO_x] was set to twice the observations.’

Referee comment: In section 3.2, the role of HOI and HOBr as sources and sinks of HO_x is discussed. A brief comparison with similar previous works (e.g. the NAMBLEX campaign) could add context to the numbers given here.

Author reply: A discussion of the NAMBLEX work in relation to the effect of halogen oxides upon HO_x levels is now provided: ‘The inclusion of a halogen scheme has been shown to improve the HO₂ modelled to measured agreement at a number of marine locations (Bloss et al., 2005b; Smith et al., 2006; Sommariva et al., 2006; Kanaya et al., 2007). Sommeriva et al., (2006) report that combined, IO and BrO accounted for $\sim 30\%$ of the HO₂ loss term during the NAMBLEX campaign at [IO] = 4 pptv and [BrO] = 6.5 pptv. Switching the halogen chemistry off in the Cape Verde model serves to increase [HO₂] by $\sim 12\%$ during the daytime and $\sim 2\%$ during the night. [OH] decrease by $\sim 12\%$. Sommeriva et al., (2006) found that the modelled to measured HO₂ agreement could be improved further during the NAMBLEX campaign by making the assumption that the source of IO was not evenly distributed over the DOAS light-path, rather it was concentrated by the shore close to the HO₂ FAGE measurements, and as a consequence [IO] were ~ 10 times higher by the FAGE inlet. There are no macro-algae beds around the Cape Verde islands unlike Mace Head that could be acting as a source of IO and so it is unlikely that there is a hotspot of IO production by the CVAO; this is supported by the good modelled to measured HO₂ agreement that exists when it is assumed that the [IO] is evenly distributed throughout the DOAS lightpath, representative of a oceanic source.’

Referee comment: It is also mentioned that different results were achieved depending on the uptake coefficient used for HO_x. But this test - and the effect on the model-

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measurement comparison - is not mentioned in the sensitivity analysis section.

Author reply: The discussion on changing the HOX uptake coefficient has been moved to section 3.4 Sensitivity analysis of modelled OH and HO₂ concentrations, the effect of changing this parameter is included in table 2 also.

Referee comment: The role of halogen oxides in reducing/increasing OH is also much discussed, but only in reference to the perturbation of NO_x and there is no mention to the potential role of XNO_y. 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.

Author reply: Both reaction R7 and R17 would reduce OH formation from R10 so, as pointed out by the referee, the formation of XNO_y species can also reduce OH formation. Both these reactions are now included in the discussion, in section 3.4, of the interaction of XO and NO_x and the potential effect on HO_x. These reactions were present in the model, however, (see supplementary information) as was the thermal decomposition of XNO_y and so will have contributed to the reduction in [OH] between runs 'halogen chemistry switched off' and 'halogen chemistry switched off and NO_x doubled'. The differences between the model runs are highlighted in figure 9 (was figure 8 in the original manuscript) and also in table 2. $\text{XO} + \text{NO} \rightarrow \text{NO}_2 + \text{X}$ (R7) $\text{XO} + \text{NO}_2 + \text{M} \rightarrow \text{XONO}_2 + \text{M}$ (R17) $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ (R10) To clarify, ClO chemistry has not been included in any model runs, (no ClO measurements were made during RHAMBLE and so the impact of this chemistry cannot be satisfactorily assessed by the model) rather the rate coefficients of the reaction of ClO with NO and HO₂ relative to the rate coefficients of IO with NO and HO₂ have been compared. The [HO₂] was slightly higher than [NO] at the CVAO (midday [HO₂] ~ 12 ppt, [NO] ~ 4 pptv), under these conditions the overall rate of ClO + NO will be comparable to ClO + HO₂, whilst IO + NO will be much slower than IO + HO₂. As pointed out by the referee, the formation of XNO_y species can remove additional NO_x from the system (which may reduce OH formation via R10 further) and so overall we would expect under CVAO conditions that

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the presence of ClO would reduce OH formation. Two model runs have been performed to assess the impact of IO and BrO on HO_x, taking into account that IO and BrO can accelerate the oxidation of NO_x and, as discussed in the manuscript, under conditions encountered at the CVAO we find that the presence of IO and BrO lead to an increase in [OH] overall.

Referee comment: In the sensitivity analysis section, the discussion of the role of HO₂ 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 cm² cm⁻³ or, alternatively, a more realistic uptake coefficient of 0.1 with a surface area of 4e-6 cm² cm⁻³. 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 cm² cm⁻³: 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 HO₂ uptake coefficient is dependent on this parameter.

Author reply: The heterogeneous loss schemes included in the model (and choice of aerosol surface area and uptake coefficient) are now discussed in the experimental section 2.3. The discussion on the choice of aerosol surface area used in the model has been re-worded in the manuscript, in an attempt to avoid confusion, as follows: 'The particle radius and number population, used to determine the aerosol surface area, were measured with a Scanning Mobility Particle Sizer (SMPS) (0 – 1 μm) and a Aerosol Particle Sizer (APS) (1 – 10 μm) (Allan et al., 2009) at a height of 30 m. The average aerosol surface area observed at the CVAO at this height during the project was ~ 1 10⁻⁶ cm² cm⁻³. For particles of 0 – 1 μm diameter (which encompasses the bulk of the aerosols at the site) a dry aerosol distribution was determined. At an average ambient humidity of ~80% the radius of sea-salt aerosols are expected to grow by a factor of ~1.4 (Allan et al., 2009), leading to an ambient aerosol surface area of roughly a factor of 2 (radius²) larger for this size range. A strong gradient in the aerosol surface area at the ground to a height of ~12 m has recently been recorded at

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the site (von Glasow, 2009). It is estimated from these gradient measurements that the aerosol surface area is approximately a factor of 2 greater at the height of the FAGE nozzle (~3.5 m) compared with the aerosol surface area at 30 m. To account for the difference in sampling height and aerosol growth factors an aerosol surface area of $4 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ was used in model calculations. An uptake coefficient (γ) of 0.1 was used based on recent recommendations (Taketani et al., 2008).'

Referee comment: 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 HO₂ sinks other than peroxides) and it is not mentioned in section 2.3. This should be explained.

Author reply: The relative contribution of the chemical removal processes of ozone, discussed in section 4, were determined by calculating the overall rate of the rate determining reactions that leads to a loss in O₃ – these are listed in table 3. The model has not been used to determine O₃ loss. The purpose of this calculation was to determine whether increases in [HO₂] away from the surface could balance the loss of [IO] away from the surface, so only chemical loss processes were considered. To clarify this in the manuscript the following paragraph has been included: 'Although these analyses only consider the chemical processes that lead to a loss in O₃ and neglect physical processes, such as surface deposition and entrainment of O₃, which can modify the overall O₃ destruction, this work demonstrates the increase in HO₂ and BrO concentrations is sufficient to compensate for the loss of IO at the higher altitudes.' The purpose of figure 1 was to show pictorially the sources and sinks of O₃, OH and HO₂. Owing to comments by referee 1 and 2 we have decided to redraw figure 1 and focus just on OH and HO₂ and their relevant formation and loss pathways for simplicity. The ozone destruction reactions (including surface deposition) are now listed in the introduction section of the manuscript instead.

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Referee comment: Specific/Technical Comments in abstract and conclusions and in sec 3.1: please state explicitly the level of agreement for HO₂ 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_x, therefore it would be better to have here the equations relevant for those conditions, rather than the equation for high NO_x conditions. page 15966, line 5: "located" page 15972, line 1: "H₂O vapour"? please use either just "H₂O" 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). 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.

Author reply: All Specific/Technical Comments raised by the referee have been addressed

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