

Interactive comment on “Seasonal observations of OH and HO₂ in the remote tropical marine boundary layer” by S. Vaughan et al.

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Seasonal observations of OH and HO₂ in the remote tropical marine boundary layer

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Authors' Responses to Referees Comments

We thank the referees for their very careful reading of the manuscript. We address each of the comments/questions below.

Referee 1

Point 1. The units for alkenes are pptv as reported in the paper. The referee is right, C13439

the reported values (reported as an average) are sometimes below the quoted detection limit of the instrument (0.9 pptV for isoprene and toluene, 0.7 pptv for hexane). We will amend the concentrations to show that over the appropriate averaging period the detection limit represents the upper limit to the concentration. Even the peak values of the alkene species are only a few pptv for the campaigns, and so the HO₂ interference is very small. Calculations using the full Master Chemical Mechanism and constrained using the VOC measurements show that ~ 90% of the RO₂ species are HO₂ and CH₃O₂, with CH₃C(O)O₂ (5%) and C₂H₅O₂ (0.9%), all of which show no HO₂ interference. OHCH₂CH₂O₂ and HYPROPO₂ (derived from ethene and propene respectively) at 0.6% each of the total RO₂ are expected to provide some interference, but given that for the aircraft FAGE instrument the measured HO₂ interference for ethene RO₂ is 40%, the expected RO₂ interference for HO₂ is expected to be very small indeed. These details will be given in the revised paper.

2: In order to rule out any exhaust from FAGE providing a contamination of the NO_x instrument, the FAGE cylinder of NO was left closed on March 6, such that no measurements of HO₂ were possible. It was found that the levels of NO measured by the NO_x did not change, and so it was determined that the problem lay within the NO_x instrument, and thus there were no NO_x data (e.g. of NO) from March 6 as the instrument was repaired. Also, an instrument fault prohibited measurements of NO_x from 11th June during SOS2 and for the whole of SOS3.

3: We have agreed with one of the options of the referee, and will omit this figure.

4: With the unforced fits, the values of *b* are different, which consequently means that the units of *a* are different and hence there can be no critical comparison of the relative values of *a*. For example, in the fit of [OH] to P(OH)^{*b*} the units of *a* for OH are seconds when *b*=1. Using the unforced fits, the units of *a* for OH are molecule⁻¹·cm^{0.81}·s^{1.27} for SOS1, but would be molecule⁻¹·cm^{-0.33}·s^{0.89}. Thus, a comparison of the relative values of *a* for the unforced fits between campaigns would be impractical.

5. (a) The font sizes will be adjusted to make easier to read. (b) These references were in fact in a previous version of the manuscript, and for some reason are not included in this version, for which we apologise. (c) There is no appreciable tidal cycle over the 3 seasons at Cape Verde, and indeed this is one of the reasons that this site was chosen for a long-term monitoring station. There is significant discussion about seasonal cycles of trace gases, and regional effects, in a recently published overview of measurements taken at the Cape Verde site during the first 2-3 years of its operation (L.J. Carpenter et al., 2011). (reference below)

Referee 2

General comments

The referee asks about possible RO₂ interferences to HO₂ as reported by Fuchs et al. Please see the responses to Referee 1 above. We agree with the referee that although alkene concentrations are too low at Cape Verde to provide an interference (and will not influence the trend in P(OH)), this is not necessarily the case for other datasets from other environments (e.g. forested or urban environments). We will add this discussion in the revised MS.

We will expand the section on the variance analysis to provide some more background and more information on how the calculations are done. We prefer to put the main derivations in the appendix in order not to detract too much from the flow of the main paper. We will also redraft the Appendix bearing in mind these comments.

We agree with the referee and have already said in the paper that a more continuous dataset could provide more information on the source of the variability of [HO_x] over different timescales. The dataset obtained in 2007 and reported in Whalley et al. (2010) (reference below) contains only 5 additional days of OH measurements, and we feel that including this may not significantly add to the analysis, and may make any statistical interpretation difficult. Any combined dataset would then include a gap of about 20 months (June 2007–March 2009). The statistics of each campaign were analysed

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individually, but the variance analysis was not significantly different, but we will make some comment about this. The analysis of the 3 campaigns taken together will show whether the variance of [HO_x] was dependent on the variance of something else which may also be seasonal (V_{other}).

Specific and technical comments

We will try to use some compression to assist loading and printing the figures without losing quality. We will make more use of legends and insert more dates.

For remote environments containing low concentrations of alkenes and other non-methane hydrocarbons, the production of OH from the reaction of O(1D) atoms with water vapour has been shown to dominate the production of OH. Whalley et al (2010) performed a rate of production analysis for OH and showed for this site that P(OH) is at least 75% of the rate of production of OH. For the HO₂ steady-state derivation, the rate of CH₃O₂+CH₃O₂ is significantly less than the production rate of RO₂ from OH reacting with methane and other VOCs. This section will be expanded to cover this discussion.

From equation (4), the parameterised form of OH is $[OH] = a J(O1D)$ (i.e. $b=1$ and $c=0$), where a is a constant which depends upon details of ozone, water vapour, VOCs that react with OH and rate constants. Equation (5) is a more general parameterised form of equation (4), except that the parameter c allows for OH to be present when $J(O1D)=0$, and the power b allows for a non-linear dependence of OH on $J(O1D)$, which may come from recycling of HO₂ to OH, or from other photolytic sources of OH which are not linear in $J(O1D)$.

Changes in Relative Humidity. Looking at the percentage contributions of the sampled air from airmasses from different source regions, there is considerable variability over the whole of SOS3. The RH does sometimes change quite suddenly throughout the 3 SOSs. For SOS3 there was indeed a change of air mass 10-12 September (a lot more European air masses and less coastal African, but also more open Atlantic) and the RH

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did drop during this period and rise up again when the air veered back to the traditional coastal African air mass. We will make a statement in the text about the changes in RH during the SOS campaigns. We have figures which also show the change in RH together with the contributions of the various airmasses for the 3 campaigns, and will consider modifying figure 4-6 to incorporate this, whilst checking that the plots are not too congested.

R2 values – we will be more specific on the values of r2 in the text.

HO2 production – yes, it is made from OH + HCHO (but this is quite small compared to OH+CO, 20-25% was found by Whalley et al. (2010)).

Please use a different verb than “yields”. We will use “provides” to avoid confusion. HO2/(RO2+HO2) ratio. We are not able to explain the disagreement during SOS1, and so we will remove the section comparing the calculated ratio to the measured values during SOS1 and SOS2.

p.21450: no contradiction here. [HOx] concentrations follow the diurnal trends in P(OH). However, the relative changes in P(OH) between campaigns are not reflected by comparable changes in the levels of [OH] and [HO2]. For example, peak P(OH) actually decreases from SOS1 to SOS2/3, but peak [OH] is observed to increase from SOS1 to SOS2/3. The contributions of the loss of OH through reaction with CO and CH4 are easy to calculate, and will be given in the paper, except there are no CO data for SOS3.

p.21452: The average midday value of J(O1D) for RHaMBLe was about 2.9 E-5 s-1 as compared to 3.7 E-5 s-1 for SOS1-3, but the relative levels of ozone mean that P(OH) was slightly higher during RHaMBLe than SOS.

p.21453: During this study the slopes were close to 0.5, and will be stated in the paper. This agrees well with the SOAPEX and some other low NOx marine environments.

p.21454: We will be consistent with units – in some places it may be appropriate to vie

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the equivalence (10 pptv = 2.5×10^8 molecule cm-3)

p.21455: Ozonolysis is indeed insignificant here – so this sentence will be removed.

Table 2: Instrument problems with some of the supporting measurements led to significant gaps in the data for SOS3 when there were simultaneous OH and HO2 measurements. As stated clearly in the paper, there were no NOx and CO measurements during SOS3. However J(O1D) measurements were available in SOS3 and limited O3 and H2O vapour. (SOS3 is described in section 3.1.3).

Tables 3, 4: This is explained on p.21438 (line 4): the NO is added 60 seconds after the laser is tuned onto the OH resonance and so only 4 minutes of HO2 data are recorded instead of 5 minutes for OH. There is no difference in R2 for forced and unforced fits. Errors are only quoted for unforced fits to demonstrate how close to agreement there is with the predictions (i.e. b=1 and 0.5 for OH and HO2, respectively). The errors for the forced fits have been omitted for clarity and it has already been stated that p.21449 line 3-4 that the values of a do not agree within the standard errors on the fit (which are not shown for clarity).

Figure 2: No NO data are available during those particular generator events. But the HO2 clearly show the impact of this. The wind direction was coming from the appropriate direction (ocean clean sector or generator direction) for the two plots.

Figure 11: The RHaMBLe 2007 night-time data could be shown but we feel that this would confuse the plot. The values from the 2007 study are stated in the text (p21454).

Referee 3

1: OK – this will be changed.

2: Forster (2007) was on the list of references in an earlier version, but somehow is not on this one, and will be added.

3: Figure 1 is being removed and so the text will be modified accordingly to incorporate

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this comment.

4: The overall measurement cycle, including finding the wavelength which corresponds to the peak of the OH transition, was actually about 8 minutes. The measurement cycle was typically (for OH) broken into finding the peak transition (2 minutes), making online measurements (5 minutes) and making offline measurements (1 minute). This will be made clear.

5: We will make very clear whether it is OH or HO₂ that is being referred to throughout the paper.

6: We will insert that aromatic-derived peroxy radicals can also cause this.

7: The calibrations were performed with exactly the same set-up as the sampling, so the calibration factor includes any potential effects of heterogeneous losses of radicals on the tube. We cannot say for sure whether there is any loss or not on this tube (but it is not necessary to know this as long as the calibration is undertaken under the field sampling conditions).

8: Calibrations were performed as often as possible (typically every 1-2 days), with the exception of SOS2. Only 1 calibration was possible during SOS2 due to failures in both the hygrometer and penray lamp, but this calibration was close to that undertaken at the end of SOS1 and also at the start of SOS3. How the calibration factor varied through the campaigns is detailed on p.21439 lines 13-20. The calibration-to-calibration variability was typically about 10%.

9: 8% of the available measurements were excluded due to meteorological conditions, mostly in SOS3.

10: We will change this.

11: Although most unusual values, we have checked, and during some of the generator events on this day, this was the value which the instrument measured.

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12: Yes, we will insert that.

13: Please see comments for Referee 2 where this is addressed.

14: Yes, we will insert this into the text.

15: Yes, we will insert this into the text.

16: The larger relative uncertainty in the measurement of OH will play some part, but the fact that increasing the averaging time does not increase R² that much, as stated on lines 18-24, we think suggests that there are other factors influencing the quality of the fit.

17: No, the concentrations do not explain the short lifetime of OH, so the reason for this low value is not clear at this point. An average peak [HCHO] of 328 pptv was measured at this site in May-June 2007 by Mahajan et al. (2011) (reference below), and cannot explain this lifetime.

18: It should be 108 molecule cm⁻³ (apologies)

19: There will be some deviation from the square-root relationship, as this is derived without taking into these (and other) loss processes for HO₂ which only involve one HO₂ molecule. However, there will also be a significant influence on the magnitude of the value of a in the power expression (as the concentration of HO₂ will be reduced by these processes), which could mask this in the fitting.

20: The typical values of NO during RHAMBLE were 1.9 pptv. The levels of NO_x during 2008 and 2009 were higher than in 2007 (Carpenter et al., 2011). Reference will be made to this in the paper.

21. This statement is based on the evidence from both the SOS campaigns and RHAMBLE, but we agree with the referee that the data are too limited and so modify the statement.

22: We will change pbv for ppbv

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23: We will remove “at night”

24: We will change to the actual number if necessary (198 days). The increase from 100 to 365 days (or 198) may suggest an additional contribution to the variance from seasonal factors, although a fuller dataset would be required to confirm this. The jumps at 2-3 days reflect a greater variance in [OH] and [HO₂] measurements between timebins of 2-3 days (i.e. the variance over 3 days is larger than the variance of 1 day) than there is variance on a day-to-day basis. The jump may also be a result of the non-continuous dataset and the use of a timebin length of 1.5 days – it should be remembered that measurements were typically only possible from 6 am to 9 pm. We will add comments to the text to make this clearer.

25: S/N=1. This will be added to the caption for figure 11.

References.

L. K. Whalley et al., “The chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic Ocean”, *Atm. Chem. Phys.*, 10, 1555, 2010.

L.J. Carpenter et al., “Seasonal characteristics of tropical marine boundary layer air measured at the cape verde atmospheric observatory”, *J. Atm. Chem.*, in press, 2011.

A. Mahajan et al., “DOAS observations of formaldehyde and its impact on the HO_x balance in the tropical Atlantic marine boundary layer”, *J. Atm. Chem.*, 66, 167, 2011.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 21429, 2011.