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Atmospheric
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Discussions

Interactive comment on "Seasonal observations of OH and HO_2 in the remote tropical marine boundary layer" *by* S. Vaughan et al.

Anonymous Referee #3

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General comments:

The authors present OH and HO2 measurement results at the Cape Verde Atmospheric Observatory during three distinct periods in different seasons in 2009. The dependence on J(O1D) and P(OH) is the main focus. They include studies on variances of OH and HO2 with different time scales. This manuscript is new in that (1) the OH and HO2 concentrations in different seasons under the unpolluted tropical marine conditions (and without forest influence) are reported and (2) HO2 variance is studied. The paper is basically well organized, logic is clearly presented. But additional clarification and justification are necessary, especially with respect to the calibration details and possible influence of heterogeneous loss and/or halogen chemistry on the OH (or HO2) vs. J(O1D) (or P(OH)) analyses. In the three "seasons", J(O1D) values did not change largely under this tropical conditions; I am not sure if it is adequate to mention "seasonal" observations (e.g., in title and elsewhere). The seasonal component of variance (OH) is thus smaller than Rohrer and Berresheim. Overall, I recommend publication after revision with respect to the specific points below:

Specific comments: 1. Abstract, line 11. Late February and March

2. page 21434, line 19. third most abundant greenhouse gas after H2O and CO2? Add Forster et al. (2007) in the reference list.

3. page 21435, line 26 and Fig. 1. The major processes which become important under the influence of forests and pollutions are also included in Fig. 1. (e.g., OH + RH, RO2 + NO etc.)

4. page 21438, line 3. Do the authors mean the measurement cycle is 360 sec?

5. page 21438, lines 13 and 16, page 21447, line 16 and at many other places (including texts and equations of Appendix A): The authors use "HOx" meaning either HO2 or OH. The readers might produce wrong impression if they perceive "HOx" as the sum of OH and HO2 at these equations. Do the authors take into account T_HO2 as a different value from T_OH?

6. page 21439, line 22. Not only for alkene-derived peroxy radicals but also for aromatics-derived ones

7. page 21440, line 23-25. Is there any influence of possible heterogeneous loss of the radicals on the surface of the black nylon tube?

8. page 21440 and 21450. I guess OH and HO2 calibrations were made frequently (e.g., every day). How large was the temporal variation of the calibration constant? This might be important for the discussion of the small seasonal difference in OH and HO2.

9. page 21442, lines 5-7. How much percentages of data were discarded according to

the wind direction criteria?

10. page 21443, line 5. Ryall et al., 2001 (not 2011)

11. page 21445, line 21. OH exceeding 10**8 cm**-3 is not usually observed under open ambient air conditions even with strong NO spikes. Please check the concentration again.

12. page 21447, lines 18 and 19. Equations (4) and (7) should be mentioned here to explain why the authors chose b = 1 (for OH) and b = 0.5 (for HO2).

13. page 21447 and Tables 3 and 4. Why "a" values in parentheses are missing?

14. page 21448, line 8. Not only HO2 self reaction but also the HO2 + RO2 (CH3O2) reaction should contribute.

15. page 21448, line 12. Here equation (7) should be reminded again.

16. page 21448, from line 16. Can the lower R2 values for OH than HO2 be simply explained by relatively larger uncertainty in OH? (because of lower concentrations of OH than HO2)

17. page 21449, line 8. Can the observed species listed in Table 2 (and CH4) explain the OH lifetime of 0.45 s? Can HCHO be present at relatively high concentrations?

18. page 21449, line 21. I do not understand what is meant by "the total peroxy budget" Are they concentrations, although the values in line 22 (5.4 and 8.5 x 10**6) would be too small as concentrations of total peroxy radicals?

19. pages 21450-21451. If heterogeneous loss of HO2 on aerosol surfaces and/or HOx loss related to halogen chemistry are important as discussed, “b” values for HO2 should be different from 0.5 in the unforced fit, because the relative importance of HO2 self-reaction (or cross reaction with CH3O2) is reduced. But this is not the case.

20. page 21452, line 14. Were the NO concentrations similar for SOS2 and RHaMBLe?

21. page 21454, line 22. It seems too much to say that nighttime HO2 persists throughout the year, from very limited observations.

22. page 21454, line 27. ppbv

23. page 21455, line 5. Remove "at night"

24. page 21455-21456, Fig. 12. It is not adequate that x-axis extends to 365 days, because the total measurement period (for three distinctive periods) covers only 7 months or less. What do the increases in the variances from 100 days to 365 days, found for many cases in Fig. 12, mean? What do the step-like increases in HO2 variances at 2 or 3 days (in x axis) mean?

25. Caption for Fig. 11. The S/N ratio used for the LOD estimation should be specified.

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