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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone production in remote oceanic and industrial areas derived from ship based measurements of peroxy radicals during TexAQS 2006" *by* R. Sommariva et al.

Anonymous Referee #1

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This paper describes shipboard total peroxy radical measurements and analysis using other measured quantities during TEXAQS 2006. The route of the ship allowed observations off the eastern US, around Florida, within the Gulf of Mexico, and in the immediate vicinity of Houston, Texas. These data allowed comparison of the relatively clean oceanic observations with those from the more polluted Houston regions. Ozone production and loss were calculated from the observations and were compared for the various measurement regions. The paper is generally well-written and follows a logical path of presentation. This reviewer has a few suggestions and questions that perhaps could make some of the points of the paper clearer.

Page 23112, lines 8-9. Isn't ozone destroyed at low NOx because the rates of HO2+O3, and O3 photolysis to O(1D) followed by reaction with water vapor become larger than the rate of HO2+NO plus RO2+NO? While radical-radical reactions become relatively more important at low NOx, they aren't the cause of net ozone loss.

Page 23114, line 8. Suggest adding references to Andres-Hernandez and Cantrell regarding dual channel chemical amplifiers.

Page 23114, line 21. Just a comment on the "absolute" nature of CRDS. The technique does determine the absolute amount of an absorber in the laser beam path, but issues such as inlet losses, artifacts (such as from NO+O3 in ambient air), and interfering absorbers require careful assessment. Regarding the comparison, Iam surprised by the degree of scatter. You should discuss the relative uncertainties in the two measurements and assess whether the amount of scatter is what would be expected. Also, is the 9% slope within the expected uncertainties?

Page 23115. This paragraph discusses the calibration of the chemical amplifier (chain length) and issues related to the observation of the peroxy radicals. I suggest actually give the chain length or range of chain lengths used during the study. Line 20-21. The agreement between the two calibration methods does not demonstrate that the data does not require a humidity correction. The agreement could be entirely fortuitous. The argument needs more information. For example, based on previous studies, what is the expected humidity correction? Likely it is at least a factor of 2 for the humid marine boundary layer. This casts a big question over the absolute amounts of peroxy radicals from this study. In the future, I suggest using the method of standard addition of radicals to ambient air to overcome this problem. It does appear that perhaps there are discrepancies between the reported laboratory studies of the humidity effect and what is actually observed in ambient air studies. Thank you for pointing out the impact of humidity on the NO2 measurement itself. What does this imply for the comparison with the CRDS discussed earlier? Lines 27-29. In discussing the total uncertainty, do the values refer to 2-sigma uncertainties (or something else). The uncertainty interval

should be stated. The integration time affects these values, so it would be good to state it here as well (even if it is stated elsewhere in the paper).

Page 23116. Other measurements aboard the ship are discussed. Again, integration times and uncertainty intervals should be included in the discussion. The words “accuracy” and “uncertainty” appear to be used interchangeably. Just make sure all is clear to the reader.

Page 23119, lines 4-6. This statement implies something about the dependence of the total peroxy radical amount on the amount of VOC and NOx. It would be helpful to the reader if this discussion was more specific as to what is meant. The argument that values are higher in the most polluted regions does not appear to be supported by the average values presented in Figure 6. Does this statement refer to the mean or median values, or to the outliers? Line 9. The range of times included in “daytime” data should be spelled out. Lines 15-17. It would be helpful if NOx values were given for these conditions in support of this statement. Lines 18-26. This nighttime observations are interesting and this reviewer would like to see discussed more. On the night of 7 September, what were the NOx and O3 levels. NO3 reacts with aldehydes and alkenes, while O3 only reacts with alkenes. Is there enough information, perhaps including some modeling to say what reactions lead to the high peroxy radical levels? Were there NO3 measurements anywhere in the region that can be used to give an indication of its importance?

Summary statistics of the observations appear to be given for some of the regions, but not all. I suggest a table summarizing (mean and/ or median, standard deviation, 95% range, numbers) the daytime and nighttime values observed for each of the 5 regions (filtering by some criteria as appropriate), and also including statistics for NOx and some measure of the VOC impact (e.g. total OH reactivity or some other measure) to go along with Figure 5. This would help the reader understand the changing environments and the resulting change in peroxy radical amounts.

Page 2312, line 12. Suggest changing “in the Ocean” to “observations in the Ocean category” or something similar. This paragraph discusses the sources of peroxy radicals from reactions of OH. What is the relative importance of these reactions compared to direct formation, say from oxygenated VOC photolysis? In other words, a budget of HOx+RO2 would be instructive for the reader.

Page 23121, line 24. This statement appears to contradict the one on page 23119, line 4-6. Suggest clarifying and/or making the discussion consistent.

Page 23122, lines 2-14. This discussion of the total peroxy radical amount versus NOx is interesting. In lines 7-9, I think you mean that the “average” levels were more influenced by outliers. Since you have calculated the expected peroxy radical levels, a plot of the observed to calculated ratios versus NOx would also be interesting. This would tell us whether we understand peroxy radical chemistry at high NOx, something that has been questioned in the literature.

Page 23122, lines 19-20. Add the word “rate” or “rates” several times, for example after the words “photochemical ozone formation” and “photochemical production and loss”, but also in several other places throughout the paper. Line 23. The loss rate of ozone “includes” the rate of the reaction of O(1D) with water vapor, but is also destroyed by HO2+O3. In very polluted regions (such as studied near Houston), the loss of NO2 (reaction with OH or other processes) results in loss of Ox which is effectively loss ofO3.

Page 23123, equation 5. While the quenching of O(1D) is due to all molecules in the air (primarily N2 and O2), there is no rate coefficient for O(1D)+M! You, of course, mean the weighted average of the quenching rate coefficients for the two processes. It should be stated as such.

Several places (including lines 13-14) calculations from a box model based upon the MCM are mentioned. I suggest describing the calculations earlier in the paper, including the actual mechanism used, how the model was initialized, and what times

calculated values were extracted to compare with the observations and used in calculations such as discussed here (essentially moving the discussion at the end of the paragraph and expanding upon it).

Page 23124, line 4-13. In these calculations, surely the mean values (about which the changes are made) affect the sensitivity. For example, the sensitivity to NO might be very different at 1 pptv compared to 100 ppbv. Line 12-13. The statements appears to say that the sensitivity of the Net O3 production rate to the total peroxy radical level is 1.0, but Table 1 gives a value of 0.9. This should be made consistent.

Lines 13-22. The discussion makes it sound like no rate coefficients for organic peroxy radical reactions with NO have been measured. There are recommendations at least for CH3O2, C2H5O2, CH3C(O)O2, and CH3C(O)CH2O2, and there are data for many more. Generic values are only used for very large or multiply substituted R-groups. It would still be useful to estimate and present weighted values (likely different for the different VOC regimes encountered) for the RO2+NO rate coefficient since they are so important.

Page 23125, line 1. I'm not sure "diurnal" is the correct word here (applying to a 24 hour period), since the values are only shown for daytime hours. Perhaps just say that the figure shows the variation of the values versus time of day. Lines 11-12. This statement does not appear to agree with the values shown in 5, where peroxy radicals change greatly over the course of the day, and NOx appears relatively constant.

Page 23129, lines 21-25. I definitely do not like the way the data are presented in Figure 10. The size of the data points and the presentation of concentration versus NOx makes it very difficult to assess how well the observations and models agree, and how well the observations from the two time periods agree. It would be helpful, for example to bin the data based on NOx level, and to show measurement-model ratios rather than absolute amounts. I find the statement that the "agreement..was very good" completely unsatisfying and unacceptable. If a comparison is to be made, provide quantitative

statistics on the agreement (e.g. mean measured and modeled ratios averages 1.xx with a standard deviation of yy). Then discuss the differences given the measurement and model uncertainties. On page 23130, line 5, the term "remarkable agreement" is used. Please be quantitative about the level of agreement. In the Summary and Conclusions section (Page 23131, lines 19-25), the terms "quantitatively compared" and "agreed reasonably well" are used. I would not say that the two datasets have been compared quantitatively, or at least that the quantitative comparisons are not given. The term reasonably well is subjective and tells the reader little about how they really agreed or disagreed.

All in all, this paper presents some interesting results that should be published. I suggest that the authors clarify these points for the reader and the paper will be even better.

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