

Interactive comment on “Measurements of tropospheric HO₂ and RO₂ by oxygen dilution modulation and chemical ionization mass spectrometry” by R. S. Hornbrook et al.

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We wish to thank both Referees for their very thoughtful reading of our manuscript and the valuable comments and suggestions made in their reviews. In light of both Referees making the recommendation that our manuscript would be better suited for AMT/AMTD, we have decided to withdraw our manuscript from ACP/ACPD and submit it to AMT/AMTD. Before doing so, however, we have taken into account the comments and suggestions made by the Referees, as outlined below. The version of the manuscript that will be submitted to AMTD will incorporate these modifications. We believe it will be a more concise and higher-quality work due in large part to the recom-

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mendations made by the Referees.

Response to Referee #1

Referee #1 Comment: The statement 'PeRCIMS is able . . . under the majority of tropospheric conditions' is not justified in the manuscript.

We have amended this statement to read: "A brief comparison of the peroxy radical measurements during these campaigns to a photochemical box model indicates good agreement under tropospheric conditions where NO_x (NO + NO₂) concentrations are lower than 0.5 ppbV (parts per billion by volume)."

Referee #1 Comment: The first paragraph is more-or-less textbook knowledge and should be cited from a book, if necessary.

We shortened the first paragraph of the introduction by eliminating a sentence regarding peroxy radical sources, and have included a second textbook reference for the paragraph at the end: Brasseur et al., 1999.

Referee #1 Comment: The abstract should provide more information about other instruments measuring HO₂ and RO₂. Are there reviews of the current instruments available? If yes, they should be cited. If not, the author might add a few lines about other instruments which use the same kind of conversion, e.g. FAGE-LIF.

The second paragraph of the Introduction has been reworded to highlight the different techniques used for RO₂ measurement. The reader is now directed to the review by Heard and Pilling (2003) and to Fuchs et al. (2008) for a more recent overview of the current peroxy radical measurement techniques.

Referee #1 Comment: The reason for the H₂ addition is the quenching of all OH to HO₂. That should be stated in line 23 page 22229. I also miss a number for the cleanliness of the used H₂.

The paragraph in question has been reworded to clarify that the H₂ is added so that all

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the OH is converted to HO₂, and the purity of the added H₂ has been included.

Referee #1 Comment: Section 4 on ambient measurements should be re-organized. The comparison of measurements with the model is the weakest part of the manuscript. For a technical paper like this manuscript the authors should select ONE day (i.e. 10-Mar-2006) as an example for a successful measurement using the newly proposed method. In my opinion the Figures 10a, 11, and 12 can merge into one figure with same time axis (19:30 – 22:00 might be sufficient). The discussion of the ambient measurement should then focus on the effect of the different RO₂ not on the agreement between a model and the measurements.

We have eliminated Fig. 10b, and combined Fig. 10a and 12 from the previous version (now Fig. 9), including the 1-minute average [NO] and the altitude on the upper plot. Figures 9 and 10 (previously Fig. 11) now have a uniform time axis (19:00 – 22:00).

Referee #1 Comment: In the discussion and conclusion the authors should explain how the detection of RO₂ in the HO₂ mode would influence their and other previously measured HO₂ data.

This was already partially addressed in the conclusions, but we have added addition text to both Sect. 4.2 and to the conclusions in this regard.

Referee #1 Technical Correction: The reactions R1-R9 are part of Scheme 1 and should not be repeated in the text.

Schemes 1 and 2 contain additional proposed reaction pathways (now in red), and the primary purpose for showing the reaction schemes in pictorial form is to show how these additional pathways fit in with the known tropospheric chemical reactions, R1-R9. For clarity, we have chosen to leave R1-R9 in the text, as these reactions are discussed in detail and we feel that referencing individual reactions or groups of reactions from those included in R1-R9 in the text is more straightforward than referencing Schemes 1 and 2 for specific chemical reactions.

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Referee #1 Technical Correction: The statements in lines 8-12 page 22223 need references.

The details in lines 8-12 are based on the Edwards et al. paper, and the reference is given at the beginning of the paragraph.

Referee #1 Technical Correction: Eq. 3 can be deleted since it is repeated in Eq. 4.

The more specific Eq. (3) has been deleted, and the general Eq. (4) is now Eq. (3).

Referee #1 Technical Correction: Figure 9 and Table 5 provide identical information. Please delete Figure 9.

Figure 9 has been deleted.

Response to Referee #2

Referee #2 Comment: In my opinion this manuscript it would be well suited for submission to AMT and leave only one atmospheric science example in the paper, probably Figure 10. Then Fig. 11 and 12 should be removed and used in one of the future papers.

As discussed previously, Fig. 10b has been eliminated, and Fig. 10a and 12 have been combined into a single figure (now Fig. 9). We feel that the inclusion of Fig. 9 and 10 (previously Fig. 11), is useful for investigating the impact of the ratio of non-CH₃O₂/RO₂ on the separation between HO₂ and HO₂ + RO₂.

Referee #2 Comment: A presentation of the intercomparison to the HO_x measurement in the DC-8 from INTEX-B is critical and will broaden the scope of this paper. What do these comparisons say about radical measurement techniques and what is the benefit of the PeRCIMS application?

We agree that the intercomparison between these two techniques should be addressed and plan to do so in a future paper.

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Referee #2 Comment: In Figure 12, a comparison to OH measurements (as opposed to only acetaldehyde), will be valuable for examination of model constraints. Using acetaldehyde model discrepancy is only justified if the authors' measurements are used to better constrain the model. I suggest using the HO₂ and HO₂ + RO₂ measurements to further develop the model and present those results.

Unfortunately, there are no C-130 OH measurements available for this flight. We feel that the comparison of acetaldehyde measurements to the model acetaldehyde does contribute to the paper, and have chosen to leave it in.

Referee #2 Technical Correction: Schemes 1 & 2: Please revise these schemes to be more understandable, in particular explaining in the captions why pathways are bold, gray, etc.

The schemes have been revised and now have captions defining the colors. Bolded text and arrows have been eliminated.

Referee #2 Technical Correction: The manuscript refers to the 'neutral chemistry' and 'dilution' regions of the inlet but those regions aren't specified in the figure, add these labels.

These regions have been labeled in the figure, along with the "Ion Reaction Region".

Referee #2 Technical Correction: Table 6: "RO₂ Measured?" as a column heading is misleading. This wording assumes the functional group is directly measured by the PeRCIMS.

This column header has been changed to "PeRCIMS sensitive to RO₂ group", and a footnote has been added to the column header explaining the data in the column.

Referee #2 Technical Correction: Section 1, Introduction: Line 13, page 22221: "presently-available techniques... do not provide speciated measurements of individual RO₂, but rather a sum of RO₂"... However, in this manuscript, the modified instrument can only separate out HO₂ and HO₂+RO₂, and cannot provide speciated

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RO2.

It was not our intention to imply that the PeRCIMS is capable of speciated RO2 measurements, rather to explain that no speciated RO2 measurements are currently available. Thus, in addition to modifying this paragraph as per Referee #1's comment, we have clarified that the method presented in this paper is also a technique that observes a "sum" of RO2. The emphasis in the paragraph was that although speciation of RO2 is not yet possible, separation between HO2 and HO2 + RO2 under photochemical timescales is useful and worthwhile.

Referee #2 Technical Correction: Line 3, page 22224: "...simultaneously provides better measurement sensitivity and separation than with dilution alone" there is no evidence (numbers) backing up this claim.

We have reworded the text to "provides better measurement separation than with dilution alone", and have explained that this is due to being able to generate more widely separated [NO]/[O2] ratios.

Referee #2 Technical Correction: Section 3, Instrument Characterization: Line 5-8 page 22237: How is the inlet pressure reduced to 100 Torr? Pumping activated by a computer controlled sensor?

The text has been modified to include the detail that the inlet pressure is computer-controlled to the lower pressure, and that ambient pressure is monitored. The details regarding the scroll pump and pressure controller that together control the inlet at a constant pressure are in Sect. 2.3, and are still true for this case.

Referee #2 Technical Correction: Line 16-20 page 22240: "Overall, due to the differences in sensitivity of the PeRCIMS to different RO2 radicals, reported measurements of ambient HO2+RO2 and HO2 must account for the relative reactivity of RO2 precursors in the air masses being studied" Why and how? This claim is not justified without more discussion or a reference.

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It is actually not the measurements that must account for the different RO₂ sensitivities, but the HO₂ measurement uncertainties. The text has been changed to reflect this, both in the text in question, and in the discussion regarding the uncertainties in Sect. 4.2.

Referee #2 Technical Correction: Line 8, page 22242: “We found it not possible to explain our laboratory observations of the sensitivity of RO₂ radicals in our instrument.” This is in conflict with the statement above (Line 16-20 page 22240).

These are two separate issues and are not contradictory. In the former (p. 22240), the relative reactivity of RO₂ precursors directly affects the relative ratio of non-CH₃O₂ to CH₃O₂ radicals in a given air mass. In this situation, the uncertainty of the reported ratio of HO₂/HO₂+RO₂ is affected, as many non-CH₃O₂ have alpha-RO₂ values that are different from CH₃O₂. In the latter (p. 22242), the inability “to explain our laboratory observations of the sensitivity of the RO₂ radicals in our instrument” refers to our inability to justify alpha values greater than unity based on standard tropospheric chemistry. However, we propose that, based on the conditions of the inlet (reduced pressure, high O₂, high SO₂, high NO_x, etc. compared to ambient atmosphere), additional chemical reactions occur in which RO₂ are chemically converted into H₂SO₄ directly without being first converted to HO₂. We have added “Using the above chemistry,” to line 8 on p. 22242 for clarification and to justify exploring other inlet chemistry to explain the instrument sensitivity to RO₂ radicals.

Referee #2 Technical Correction: Section 4, Measurement: Line 17, page 22244: “The rate coefficients for the RO + O₂ were set to their recommended values (1 × 10⁻¹⁴ for primary RO and 8 × 10⁻¹⁵ for secondary RO), and to zero for tertiary RO.” Need reference.

References have been included.

Referee #2 Technical Correction: Line 5, page 22249: “Excluding data points with measured or modeled peroxy mixing ratios < 2 pptv as well as those with correspond-

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ing 1-min average [NO] > 0.5 ppbV...” What is the justification for excluding these observed ranges?

The values < 2 pptV were excluded to avoid including extreme measurement/model ratios from small values near the measurement detection limit. Text explaining this has been added to the sentence in question.

As alluded to in the previous paragraph in the text, there is generally poor agreement between photochemical models and measurements when [NO] > 0.5 ppbV. We have added text to the previous paragraph explaining that for this reason, the analysis in question will only include measurements when [NO] < 0.5 ppbV. Although we do plan to investigate the discrepancy between measured and modeled peroxy radicals in high NO_x environments, this is not within the scope of this paper. However, since this issue is something that has been noted in the literature, we do not consider the discrepancy grounds to question the methodology being presented here. As discussed in the text, the measurement/model discrepancy is something that we plan to address in another paper.

Referee #2 Technical Correction: Line 15, page 22249: “O-D” photochemical models”. I think this should be “0-D” (with a zero and not a capital “o”). The concept of 0-D was not defined in this paper. Either explain 0-D or revise sentence to say LaRC box model.

The text was changed to read “comparison to photochemical box models”, as it is not just to the LaRC box model that the data can be compared.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22219, 2010.

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