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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aircraft and ground-based measurements of hydroperoxides during the 2006 MILAGRO field campaign" *by* L. J. Nunnermacker et al.

L. J. Nunnermacker et al.

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We thank the two anonymous reviewers and Sasha Madronich for their thoughtful comments.

Reviewer #1

General comments

p8953/21. Comment that HNO_3 rather than NO_z should be used to judge NO_x or VOC limited O_3 production.

Text changed as suggested with an aside that HNO_3 is sometimes approximated by NO_z. The argument for VOC limited conditions still stands, as the reviewer supposes.

We are relying on the observation that H_2O_2 does not increase in plumes rather than any particular value of the ratio of H_2O_2 to NO_z or more properly HNO_3.

Specific comments

1. NO_z changed to HNO_3 as described above.

p 8961/15. dry deposition added as a loss mechanism

2. Question as to whether plumes the highest O_3 plumes show any increase in H_2O_2.

Text added to indicate that the 2 plumes with highest O_3 (179 and 116 ppbv) do not have increases in H_2O_2, and are accompanied by high NO_x (27 and 41 ppbv). Since high O_3 events are of particular importance this is a point worth making.

3. Details about other measurements, including peroxy radicals

The sum of peroxy radicals (HO_2 + RO_2) was measured at the Tecámac surface site, but not aboard the G1. We have added to Section 2.3 a reference describing the radical measurement technique, and a paragraph describing UV, rain and ozone measurements at the site.

4. and 5. Comments about the individual peroxides

The reviewer correctly notes inconsistencies in the description of speciated peroxides. The discussion has been clarified in several places. We have added a section in the introduction defining the individual peroxides, and briefly describing their sources. Sections 2.2 and 2.3, which give experimental details for the aircraft and ground-based measurements, now clearly specify which hydroperoxides were measured at each platform. Finally, we have changed the captions of Figure 8 and 11 to point readers to the text for clarification of the species measured.

6. Relation between O_3*H_2O and $2H_2O_2$+NO_z in polluted air masses.

We do not see a significant correlation between O_3*H_2O and $2H_2O_2$ + NO_z in more

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polluted conditions but do see a correlation (with a variable slope as given in Table 4 between O_3 and $2H_2O_2$ + NO_z. At the end of the paragraph we state with mild surprise that the relations predicted by Sillman (O_3 vs. $2H_2O_2$ + NO_z) occurs in Mexico City even though O_3 photolysis is not expected to be a dominant source of free radicals. In order to unravel these relations we would probably need to do process analysis on Eulerian model output. Lacking that we can offer a hypothesis that total radical production scales with O_3 (i.e. other radical sources are proportional to O_3) but total radical production in the polluted boundary layer does not scale with O_3 * H_2O. For this study we feel that it is worthwhile presenting an interesting observation even if we don't have the tools to give a complete explanation.

7. Abstract and conclusion states that H_2O_2 concentrations were about 1 ppb, lower than had been predicted from photochemical models based on the 2003 Mexico City study

These statement refer to a box model study by Madronich (2006). The citation was inadvertently omitted. There is a new Section 4.3, "Comparisons with calculations", which describes the box model calculations of Madronich (2006), Eulerian model results from Wenfang Lei and Xue Xi Tie (personal communications), and an analysis of weekday – weekend concentrations by Stephens et al (2008).

1. Do these measurements represent HO_2 alone or HO_2+RO_2? Also, please give a reference

Measurements are the sum of HO_2 and RO_2. We have clarified that in the text and in the captions to Figures 10 and 11. We have added to Section 2.3 a reference from Sjostedt at Georgia Tech (2007) describing the radical measurement technique.

9. Definition of OPE.

OPE in this paper is the slope of O_x (O_3 + NO_2) vs. NO_z. O_x is used instead of O_3 because it is not affected by titration of O_3 with NO – which can make a large

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difference under the high NO_x conditions in Mexico City. Text has been added making our definition explicit. Both O_3 and O_x have been used in previous studies. Often O_3 is used because NO_2 concentrations are low or because measurements of NO_2 are lacking. OPE as determined from measurements will be different from the true OPE because O_x (or O_3) and NO_z are not conservative. The usual problem is dry deposition of HNO_3 which should be minimized in Mexico City because of the very deep boundary layer and the limited age difference between morning and afternoon air masses.

10. What does r^2 refer to and is it useful for NO_x/NO_y.

Text added to notes below Table 5 stating that r^2 is the square of the correlation coefficient for O_3+NO_2 vs. NO_z and NO_x vs. NO_y. For the afternoon cases where NO_x/NO_y = 0.44 and 0.25, a high r^2 is not guaranteed if multiple plumes with different characteristics are sampled in a single transect. An r^2 near 1 is expected for the morning flights where most of the NO_y is NO_x. However, even for fresh emissions a high r^2 is not guaranteed as NO, NO_2, and NO_y are measured from separate channels in the "NO_x box".

Technical Corrections

p. 8955: Clarification of units for boundary layer heights

The text has been corrected to clarify that these are boundary layer *depths* in meters.

p. 8958: Clarification of units for altitude

We have added a statement to section 2.2 clarifying that all altitudes are mean sea level (MSL).

p. 8960: Clarify definition of free troposphere

We have removed the reference to the free troposphere, replacing it with "for altitudes $>$3500 m and [NO_y] $<$ 5 ppbv," as this represents air that has not been influenced recently by urban emissions.

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p. 8967: Origin of data for CSS measurements

Details of the CSS calculation, including the source of VOC and NO_x data, are now included in Section 4.1.

Table 3: Altitudes corresponding to mean temperatures

We have added the mean and maximum altitudes (MSL) to the G-1 summary statistics.

Figure 7. Clarifying the figure caption

The figure caption now describes clearly the meaning of the histogram

Figure 10 Normalized diurnal profiles

Diurnal profiles in the figure were normalized to more clearly show the relationship between different species, and the maximum values had been identified in the text (section 3.3.2). We have now added these maximum values to the figure caption as well.

Figure 16. Adding units in the figure caption

This has been corrected.

Reviewer #2

General comments

Observed levels of peroxides both in the air and on the ground near the source region were generally near 1 ppbv and much lower than that predicted by photochemical models based on the MCMA 2003 study. Were the levels of NO_x higher in 2006 compared to 2003? What factors could explain this discrepancy?

The model results are from Sasha Madronich (2006); citation inadvertently omitted. In his review of our manuscript, Sasha proposes that the discrepancy is due to NO_x concentrations in his calculation being a factor of 2 too low. This factor is not due to a change in NO_x emissions over 3 years. We have added a new section (4.3) with

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comparisons between the G-1 observations and model calculations.

Are the observed peroxide concentrations measured here consistent with the observed peroxy radical concentrations under low NO_x conditions?

The observed HO_2 radicals at T1 presented in Fig. 11 are consistent with the low concentrations and low formation rates observed from the G-1. Figure 11 indicates a typical daytime HO_2 maximum of 15 ppt. Adding together the bimolecular, 3 body, and H_2O-dependent (RH=25%) rate constants for forming H_2O_2, one obtains $P(H_2O_2)$ = 0.054 ppb/hour. Two days had a significantly higher maximum HO_2 concentration of 30 ppt which yields a $P(H_2O_2)$ of 0.22 ppb/hour.

Specific comments

1. Page 8956: The authors should provide a definition of HMHP.

The Introduction now includes a definition of Hydroxymethyl hydroperoxide (HMHP) and other hydroperoxides, as well as a discussion of their origins.

2. Page 8961: Instead of tabulating the relationship between O_3 and the sum of

NO_2+2H_2O_2, why not plot some of the data similar to Figure 3?

19 plots would be required to show all of the data. We felt that Table 4 contains a full description and we saved space by not showing examples.

3. Page 8964: Are there conditions where the surface peroxide concentrations correlate

with O_3xH_2O similar to the aircraft measurements shown in Figure 3?

This line of inquiry was not pursued. Our expectation is that there may be such periods but they would be hard to find in a polluted surface environment, and would be influenced by different surface loss rates of the species involved.

4. Similarly, are there conditions where the surface peroxide measurements correlate

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with NO_2+2H_2O_2 similar to the data shown in Table 4 for the aircraft measurements?

Unfortunately, there were no measurements of NO_2 or NO_y at the surface site, so this possibility could not be explored.

5. Page 8967: What are the inputs to the CSS model (specific VOCs, photolysis rates, etc.)?

A paragraph has been added to Section 4.1 describing the CSS model inputs.

6. What is the approximate value of NO_x when the CSS model predicts a net production of peroxides? What concentration of peroxides is predicted by the model?

There are some exceptions but peroxide formation is generally negative for $NO_x > 3$ ppb. We have stated this in Sec. 4.2. The CSS model does not predict, but rather uses peroxides as input, as now explained in Sec. 4.1.

7. If ozone photolysis is not the main radical source under these conditions, what are the dominant sources?

The fraction of radicals due to O_3 by region varies from 0.25 to 0.36 (Table 6). HCHO contributes a larger fraction than O_3. Text to this effect has been added to Sec. 4.2.

8. Page 8968, Table 6: If the authors are going to include the parameter "n" in Table 6, they should define it and discuss it the text.

Entry in Table 6 changed to indicate that n is the number of calculations

9. Page 8969: Are there other sources of hydroxymethyl hydroperoxides besides biogenic alkenes? What level of biogenics were measured during the flights and at T1? A

brief description of the mechanism of formation of HMHP somewhere in the manuscript

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Interactive Comment

would be useful.

Hydroxymethyl hydroperoxide can also be a termination product of HO2 and HOCH2OO radicals (Qui et al., 1999). This reference has been added to the new paragraph in the Introduction, where HMHP is defined. Sections 2.2 and 2.3, which give experimental details for the aircraft and ground-based measurements, now clearly specify which hydroperoxides were measured at each platform. Section 3.1.1 now includes a summary of the observed HMHP and its relationship to measured concentrations of isoprene.

Reviewer 3, Sasha Madronich

General comments

1. First, a bit more detailed description is needed for the Constrained Steady State (CSS) model, especially the inputs (concentrations, environmental parameters) used to constrain it.

A paragraph has been added to Section 4.1 providing this information.

2. Second, it may be useful to compare with some earlier models. For example, a box model study (Madronich, 2006) predicted first-day production of several hundred ppb O_3 and ca. 5 ppb H_2O_2, which is far more than observed during MILAGRO. That model was initialized with 80 ppb of NO, while urban monitoring stations show a long term average of 140 ppb NO_x during the morning rush hour (e.g. Fig. 1 of Stephens et al., 2008). The higher NOx levels would be expected to decrease both H_2O_2 and O_3 (by NO titration and NO_x termination of radicals).

A new section 4.3 “Comparisons with calculations” has been added. We include a discussion of results from Madronich (2006) and Stephens et al (2008) that follows the above comments. The citation for Madronich (2006) was inadvertently omitted in the ACPD text. That has been corrected.

3. It may also be useful to compare the peroxide measurements to three-dimensional

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model results (e.g. Lei et al., 2007; Tie et al., 2007); while peroxide concentrations are not explicitly reported in those publications, the results should be available from the authors.

As suggested, we contacted Wenfang Lie and Xue Xi Tie who graciously gave us unpublished Eulerian model results for H_2O_2. General features (i.e. $\sim$ 1ppb H_2O_2 in the Mexico City urban area) and specific features for the 18 March flight compared very well with our observations. This is part of the new Section 4.3.

4. Third, it may be interesting to do some sensitivity calculations with the CSS model. Of special interest may be variations in the VOC/NO_x ratio (and possibly the relative humidity), to assess the robustness of the conclusion that the chemical regime is VOC-limited.

This is a task better suited to a CTM. We have in the past looked at the effects of small (10%) changes in precursors but that was only for the purpose of testing the Ln/Q formulas.

Minor comments

8952/19-21: Delete "facing many urban areas" since only talking about megacities.

This has been corrected.

8955/6: Comma after "flights".

This has been corrected.

8955/21: Should specify in the text that legs L1 and L2 are in the vicinity of ground sites T1 and T2.

Text to this effect has been added.

8958/19: A mean CO concentration of 284 ppb seems high for background air.

“Background” was the wrong word. We have added text to section 3.1.1 to say that

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measurements on leg 5 were significantly lower than the other legs.

8959/1-2: Second half of sentence is missing a verb.

This has been corrected.

8961/15-16: Losses of H_2O_2 by photolysis and OH have a time scale of several days, so why should they cause low H_2O_2 in Tula plumes?

The time scale for loss of 0.6 ppb H_2O_2 by photolysis, OH, and dry deposition is on the order of 1 day. There may be some production occurring outside of the plume which could reduce the time required for an apparent loss of 0.6 ppb. Still as noted these times are longer than the transport time from Tula to the G-1. We have added to the text two possibilities for the observations: loss of H_2O_2 on aerosols and inlet losses due to reaction of H_2O_2 with SO_2. Peroxide decomposition on aerosol surfaces may be efficient if transition metals are present. We have conducted laboratory studies that rule out artifact loss of peroxide up to an SO_2 concentration of 200 ppb. However, instantaneous concentration of SO_2 may have exceeded this value in some passages through the Tula plume.

8968/5: ppb/hr not ppb/min.

This has been corrected.

8968/20: Use hyphen for median-constrained.

This sentence has been clarified.

8968/22,23: Should mention use of hydrocarbons earlier (e.g. 8967/26) as they are mentioned in relation to Fig. 16.

The text has been changed so that a description of the inputs to CSS model are now discussed before model results.

Table 1: For 18 March, should say "no a.m. flight".

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This has been corrected.

Table 6: Percent O_3 or fraction O_3?

This quantity is the fraction of O_3. The table entry has been corrected.

Also, define n.

n = number of calculations. This has been added to the table.

Fig. 16: Would be useful to mark T0, T1, T2. Also needs units.

Locations of the surface sites and units have been added to the figure

List of references

All added.

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