Atmos. Chem. Phys. Discuss., 8, S4295–S4300, 2008
www.atmos-chem-phys-discuss.net/8/S4295/2008/

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.

Anonymous Referee #1

Received and published: 30 June 2008

1. General comments

The paper presents a useful set of measurements for hydroperoxides in Mexico with analysis in relation to other measured species. The measurements are worth publishing for themselves, and the analysis adds useful concepts. I recommend publication. However, there are many places in the text where the details are vague, so that many minor corrections are needed.

The major conceptual theme of the paper is that peroxide measurements can provide evidence that identifies whether ozone production is NO_x-limited or VOC-limited. The authors' interpretation is reasonable and is probably correct. However, the text

sometimes misstates the relationship. The text (p. 8953, line 21) states that "ozone production is NO_x-limited or VOC-limited... according to whether peroxides or NO_z are the primary termination products." I believe the determining factor is the rate of production of peroxides relative to HNO_3, rather than relative to all NO_x reaction products. (This can be inferred from the Sillman and Kleinman references.)

In previous works this distinction was less important because HNO_3 was usually the dominant NO_x reaction product. However, the distinction may be important in Mexico City if PAN and other organic nitrates are the main components of NO_z.

This probably will not affect the conclusions of the manuscript, since the results show consistently low (1 ppb) and non-increasing H_2O_2 in the Mexico City plume and high (10 ppb) NO_z. However, there may still be some production of H_2O_2 in the Mexico plume (to compensate for removal due to chemistry and dry deposition), and the possibilty that the measured NO_z is mainly organic nitrates provides for some doubt. Minor changes to the text will address this issue.

2. Specific comments

1. Concerning the issue discussed above: I suggest modifying the statements on p. 8953, line 21 and on p 8960, line 26 so that the chemical trade-off is described as peroxides vs. HNO_3 rather than peroxides vs. NO_z.

Also, it is noteworthy that H_2O_2 remains constant in urban plumes but decreases in the power plant plumes (Section 3.2.2, p. 8961). This suggests that the urban plumes have some (small) photochemical production of H_2O_2 that does not occur (or is much smaller) in the power plant plumes. I suggest stating this in the text.

A minor detail: I suggest adding dry deposition as a loss mechanism for peroxides on p. 8961, line 15.

2. The results from Table 3 and Figure 2 show that O_3 was relatively low during most of the flights. The 95^{th} percentile O_3 is 90 ppb or below. However, peak O_3 reached

ACPD
8, S4295–S4300, 2008

179 ppb.

The text (Section 3.2.2, p. 8960-1) describes how must of the plume traverses show increased O_3 but no increase in H_2O_2. Figure 5 shows examples, both of which have O_3 lower than 100 ppb. It would be useful if the text could describe conditions associated with the absolute peak O_3 (179 ppb) and whether there was any increase in H_2O_2 for this case. (Also, what NO_x and NO_z correspond to the peak O_3?). Conditions for such high O_3 might be very different from conditions during more typical O_3. (It might be useful to add this to Figure 5 if the data is available.)

3. The results in the paper rely heavily on measurements from other research groups that are not described here, including VOC, NO_x, NO_y and peroxy radicals. The peroxy radicals in particular are a non-routine measurement. I suggest giving brief mention of these measurements and citing the research groups that provided them (p. 8955, bottom).

4. Many of the measurements consist of hydroxymethyl hydroperoxide (HMHP). It would be useful to add a brief description of this species and its main photochemical source. As currently written the text only describes formation of generic peroxides through the HO_2-RO_2 reaction (p. 8953, line 14). The most familiar organic peroxides are methyl peroxide (CH_3OOH) and similar species rather than hydroxy peroxides. I suggest adding a brief description of the formation of HMHP somewhere in the text.

5. The text sometimes confuses the terms hydroxymethyl hydroperoxide (HMHP), summed hydroperoxides and other related terms.

The abbreviation HMHP appears for the first time on p. 8956 (line 24) and is only defined in Table 2. A definition should be added on p. 8956.

The measurements appear to include both summed hydroperoxides (p. 8956, line 1 and Table 2) and hydroxymethyl hydroperoxide. The reported aircraft measurements are identified as HMHP (p. 8956, line 24). What about the surface measurements?

ACPD

8, S4295–S4300, 2008

These are just described as 'hydroperoxide' (p. 8957, line 5). Are they equivalent to the aircraft measurement of HMHP?

The caption to Figure 8 describes the measurement as 'total peroxide', but the line in the figure is labeled 'total hydroperoxide' and the axis is labeled 'hydroperoxide'. Can this be clarified? If the figure represents total hydroperoxide, does this refer to the sum MHP+HMHP as suggested by Table 2?

These terms should be clarified, possibly in combination with a brief discussion of the sources of HMHP and MHP as suggested above.

6. Section 3.2.3 (p. 8961-2) describes O_3 versus the sum $2H_2O_2$+NO_z and notes that the slope between the two is lower when relative humidity is high. The explanation in the text (that radical production increases with O_3 and radical losses are represented by $2H_2O_2$+NO_z) is similar to the relation in the free troposphere illustrated in Figure 3. In the free troposphere H_2O_2 increases with the radical source, represented by O_3*H_2O.

The chemistry in polluted regions is more complicated but it would be interesting to show whether there is a similar relation between O_3*H_2O and $2H_2O_2$+NO_z in polluted regions.

7. The abstract states that 'peroxide mixing ratios near the ground were generally ner 1 ppb, lower than had been predicted from photochemical models based on the 2003 Mexico City study'. A similar statement appears in the conclusion. However, the body of the paper never identifies peroxide mixing ratios from models and does not give a reference for model results. The paper should provide this information.

8. Section 3.3.2 and Figure 10 show measurements of peroxy radicals. Do these measurements represent HO_2 alone or HO_2+RO_2? Also, please give a reference for the source of the measurements. Peroxy radical measurements in particular are not routine and the text should refer to the group that made the measurements.

ACPD

8, S4295–S4300, 2008

9. The text refers to ozone production efficiency (OPE) (p. 8968, line 11 and Table 5). I suspect that the authors are actually referring to the measured slope between O_3 and NO_z. This slope has been interpreted as the ozone production efficiency (Trainer et al., 1993, and since), but the true OPE (defined as the ratio of production of ozone to production of NO_z) is often lower than the O_3-NO_z slope (e.g. Sillman et al., 1998). Please change the wording to say exactly what the values represent.

10. Table 5 gives values for r^2 associated with OPE and with NO_x/NO_y. It is not clear what these refer to. The r^2 for OPE probably refers to the correlation between O_3 and NO_z, as discussed just above. (Please clarify in the text.) What does r^2 mean for NO_x/NO_y?

The r^2 might refer to the correlation between NO_x and NO_y, but if this is the case I suggest removing it from the table. The NO_y includes NO_x as a major component (and the actual measured NO_y consists mostly of NO_x). A correlation coefficient between these does not make any sense.

3. Technical corrections

p. 8955: 'Boundary layer behavior and heights appeared to be similar at T1 and T2 (i.e., 1000–3500 m a.g.l. from 11:00–15:00 LST, respectively).' This is confusing as written. Does it mean that the boundary layer height increased from approximately 1000 m a.g.l. at 11:00 LST to 3500 m a.g.l. at 15:00 LST, and that the heights and increase were similar at T1 and T2 and over all days of the study? Please clarify in the text.

Section 3.2 (p. 8958-8959). Are the altitudes given here mean sea level or above ground level? They are probably msl, but it would help to identify it in the text.

p. 8960 (line 4): Altitudes above 3500 m (a.g.l.) are identified as 'free troposphere'. This is confusing because 3500 m a.g.l. would not be in the free troposphere in Mexico City. Please clarify.

ACPD
8, S4295–S4300, 2008

p. 8967, bottom: The constrained steady state model requires measured speciated VOC and NO_x. The text should state where these measurements came from.

Table 3: What altitude does the temperature correspond to? Perhaps mean flight altitude can be given in the table (assuming that the temperature corresponds to the aircraft elevation). The temperatures are only meaningful if altitudes are given.

Figure7: The caption needs to state exactly what the figure represents. The text describes this (p. 8963, line 8), but the figure caption should also give this information.

Figure 10: it appears that the diurnal profile of each species was normalized so that the maximum value is equal to one. I suggest stating this explicitly in the caption and, if possible, giving the values that correspond to the diurnal maxima.

Figure 16: The caption needs to give the units for the rate of production of peroxide.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8951, 2008.