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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.

Anonymous Referee #2

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1. General comments

This paper presents aircraft and ground-based measurements of hydrogen peroxides during the MILAGRO field campaign. Measurements of hydrogen peroxides provide an important constraint on models of ozone production, as hydrogen peroxides are produced from radical termination reactions under NOx-limiting conditions. As mentioned in the paper, it is important for photochemical models to accurately reproduce the chemical pathways associated with both VOC and NOx limiting conditions, and measurements and models of hydrogen peroxides can help to distinguish between these two regimes. As a result, the measurements in this paper can be used to im-

prove our understanding of ozone production in Mexico City and should be published. Unfortunately, the paper mainly presents general relationships of the observations, and only presents limited tests of photochemical models.

The authors state in the abstract that the 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. However, there is no further discussion of this issue in the rest of the manuscript. What factors could explain this discrepancy? Were the levels of NOx higher in 2006 compared to 2003? Are the observed peroxide concentrations measured here consistent with the observed peroxy radical concentrations under low NOx conditions?

The conclusion of the paper also states that the observed peroxide levels were lower than that predicted by several models, yet there is no discussion in the paper about these models and what could be the source of the discrepancy. Overall, this is an interesting paper, but the manuscript would benefit from a more detailed discussion of whether the observed peroxide concentrations are consistent with model predictions.

2. Specific comments

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

2) Page 8961: Instead of tabulating the relationship between O3 and the sum of NO2+2H2O2, why not plot some of the data similar to Figure 3?

3) Page 8964: Are there conditions where the surface peroxide concentrations correlate with O3*H2O similar to the aircraft measurements shown in Figure 3?

4) Similarly, are there conditions where the surface peroxide measurements correlate with NO2+2H2O2 similar to the data shown in Table 4 for the aircraft measurements?

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

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

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

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.

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 would be useful.

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

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Interactive Comment