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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.

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This paper describes measurements of peroxides in and near Mexico City during the MILAGRO field campaign. Such measurements are an important contribution to the integrated data set, and also provide insight on the VOC- or NOx- sensitivity of ozone production in and downwind of the city. A central result is that net peroxide production is small (perhaps even negative) in the city and increases only slightly in the immediate surroundings (near the T1 and T2 sites). On this basis, it is concluded that oxidant formation in Mexico City is VOC-limited. The manuscript is suitable for publication in ACP, with consideration of some suggestions.

Some value could be added to the paper by enhancing the modeling part. 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. 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 O3 and ca. 5 ppb H2O2, 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 NOx during the morning rush hour (e.g. Fig. 1 of Stephens et al., 2008). The higher NOx levels would be expected to decrease both H2O2 and O3 (by NO titration and NOx termination of radicals). It may also be useful to compare the peroxide measurements to three-dimensional 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. Third, it may be interesting to do some sensitivity calculations with the CSS model. Of special interest may be variations in the VOC/NOx ratio (and possibly the relative humidity), to assess the robustness of the conclusion that the chemical regime is VOC-limited.

Minor comments: 8952/19-21: Delete "facing many urban areas" since only talking about megacities. 8955/6: Comma after "flights". 8955/21: Should specify in the text that legs L1 and L2 are in the vicinity of ground sites T1 and T2. 8958/19: A mean CO concentration of 284 ppb seems high for background air. 8959/1-2: Second half of sentence is missing a verb. 8961/15-16: Losses of H2O2 by photolysis and OH have a time scale of several days, so why should they cause low H2O2 in Tula plumes? 8968/5: ppb/hr not ppb/min. 8968/20: Use hyphen for median-constrained. 8968/22,23: Should mention use of hydrocarbons earlier (e.g. 8967/26) as they are mentioned in relation to Fig. 16. Table 1: For 18 March, should say "no a.m. flight". Table 6: % O3 or fraction O3? Also, define n. Fig. 16: Would be useful to mark T0, T1, T2. Also needs units.

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