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Atmospheric
Chemistry
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Discussions

Interactive comment on "Inferring ozone production in an urban atmosphere using measurements of peroxynitric acid" *by* K. M. Spencer et al.

Anonymous Referee #1

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This paper describes measurements of peroxynitric acid (HO2NO2) made aboard the NCAR C-130 during the MILAGRO campaign of 2006. These measurements, in conjunction with measurements of NOx, are used to estimate the rate of O3 production in the Mexico City urban plume. Observations of HO2NO2 and the inferred ozone production rate are compared to the output of the NASA Langley photochemical box model. The model is found to underpredict HO2NO2 and thus ozone production and the modeled to measured disagreement is worst at high NOx. The authors conclude that the model and measurements can be brought into agreement by including the reaction of NO2* with H2O as a HOx source, reducing the rate of OH+NO2 or both.

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The paper presents an interesting use of measurements of HO2NO2 to probe our understanding of radical cycling and ozone production in an urban plume and should be published in ACP once the following issues are addressed:

1) Is the atmosphere at steady-state? (p. 2801) Comparing HO2NO2 calculated from the full diurnal equilibrium model to that calculated in steady state modeled HO2 and NO2 does not fully address the question of whether the sampled airmass is truly in steady state with respect to HOx sources and sinks. The fact that the slope of the correlation (Fig 3) is close to 1 indicates that the time constant for the box model to converge is primarily limited by the time required for HO2NO2 to reach steady state. However, the atmosphere might be out of steady-state with respect to HOx or NOx sources and sinks because the plume sampled is too close to the source and is still exhibiting effects of dilution and mixing? Other studies (e.g. Thornton et al 2002) have found the assumption of photostationary state at high NOx levels to be questionable because the parcels in question were still mixing into the background atmosphere. Presumably chemical processes (e.g HONO formation and photolysis) are also introducing effects that slow the approach to photochemical steady state. One partial test would be to evaluate whether there is a bias in the deviation of the NO:NO2 ratio from photostationary state at high NOx? If there is excess NO then it might indicate the measurements are too near the source. There are probably other steady-state relationships in the C-130 data set that could serve as additional checks.

2) Are the correlations among the major factors controlling HO2 (p. 2804 and Figure 8): While using CH2O as a proxy for HOx production is reasonable, it appears that CH2O and NOx are correlated and we presume that VOC reactivity is also strongly correlated with NOx. Given these correlations, it would be more straightforward to first indentify the size of an additional HOx source, the additional VOC reactivity or the excess HOx sink (presuming all are about equally correlated with NOx) and express each of these as a fraction of the total source/sink. It should also be confirmed that the analysis uses a VOC reactivity that is not averaged over a different time window than the HO2NO2.

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3) The Caltech group made important contributions to our understanding of the products of the OH+NO2 reaction. It is unclear how our understanding of the products affects the discussion about this rate in this paper. (p. 2806) It would help the reader who is more familiar with the primary literature than the JPL evaluations if the paper described the rates in the JPL evaluations and the assumed products with additional details, so that the reader can understand the arguments in question without going back to the two JPL reviews.

4) The paper should note that the problem with the HOx budget at high NOx appears to be distinct from the problem of excess HOx correlated with isoprene; although if the problem is a missing source molecule (and not excited state NO2) perhaps the issues are more related than has been described to date?

Figures:

Figure 7: It is not entirely clear what additional information the reader receives from this figure. It appears that perhaps the box model fails to capture the hot spots but the figure is never referenced in the text and could possibly be omitted without diminishing the discussion or conclusions.

Figure 8. The differences between the two panels are not readily apparent in the figure as presented. They seem to span the same range of pO3 and it is difficult to see whether or not the Langley model pO3 turns over more than the pO3 implied by the observations. Perhaps if you added a panel showing the ratio of the measured to modeled pO3?

Figure 9: This figure would be easier to read if it were reformulated so that agreement between a model and the observations gave a value of 1. Then the reader would be better able to judge whether the successive model changes make improvements to the analysis or not. The figure would be easier if the first panel showed the ratio of observed to model for the base model and then the next ones showed the other models, again as a ratio to the observations.

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