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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of NO_x, ΣPNs, ΣANs, and HNO_3 at a rural site in the California Sierra Nevada Mountains: summertime diurnal cycles" *by* D. A. Day et al.

D. A. Day et al.

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The earlier version of this reply was mistakenly truncated because we attempted to include a figure.

We thank the referee for his/her constructive suggestions for improving the paper.

General comments:

This paper presents an analysis of measurements of a variety of nitrogen compounds, including NOx, alkyl nitrates (ANs) and peroxy nitrates (PNs) at the Blodgett forest site, focusing on measurements of the diurnal variations of these compounds to evaluate the current understanding of the chemical and dynamical processes controlling their

production and fate. There is still some uncertainty associated with the chemistry of these compounds and the partitioning of the total NOy budget, and as a result this paper provides some new information through qualitative and quantitative analysis of the diurnal cycles of these compounds measured during the summer. In addition, the authors attempt to estimate the total peroxy radical concentration at this site through calculations of the deviation from the photostationary state relation. These latter results suggest that the concentration of peroxy radicals may be larger than previously measured under similar conditions. The paper is generally well written, and the results are worthy of publication in ACP.

My main concern is with the calculation of the total peroxy radical concentration using deviations from the photostationary state. As discussed in Cantrell et al. [1997], this method for estimating peroxy radical concentrations is highly uncertain even with reasonably accurate input values. The authors use their measured values of NOx and O3 in the calculation, but do not describe how they estimated the value of j12.

Response: A description of the method for estimating j12 has been added to the text.

It is also not clear whether the uncertainty in their estimation of j12 is taken into account in the uncertainty in the HO2 + RO2 calculated concentrations shown in Figure 6. These issues should be clarified in the revised manuscript.

Response: We have added a calculation of the average diurnal cycle of [HO2 + RO2] for j12 values ranging from +/-30% of the calculated values in order to provide a liberal range in uncertainty of [HO2 + RO2] that may result from uncertainty in determination of the photolytic rate constant of NO2. Average mid-day values for these limits range from ˜80-100 ppt to ˜240-280 ppt. The lower limit is still at the high end of previous observations. Revised Figure 6 shows these limits.

A better approach is to use a steady-state analysis to estimate the total peroxy radical concentrations which the authors appear to have done for mid-afternoon conditions based on the discussion on page 3464. However, these calculations are only discussed

ACPD

9, S2623–S2626, 2009

Interactive Comment

briefly. The manuscript would benefit from an expanded discussion of the steady-state calculation analysis, perhaps including a simple radical budget analysis which could give additional insights into what appears to be high HOx concentrations in this environment.

Response: The apparent high HOx concentrations at this site and their unusual sources have been the subject of several previous manuscripts (Dillon et al., 2002; Farmer and Cohen, 2008; Holzinger et al., 2005; Kurpius and Goldstein, 2003). These papers collectively indicate the subject is more complex than we can do justice to within this manuscript and with the available data. To remedy this we have organized a large field campaign that includes comprehensive VOC, NOx, HOx and aerosol observations: BEARPEX. Results from that experiment should appear in this special issue of ACP alongside the present manuscript soon. The manuscript submitted by LaFranchi et al. (2009) does support the conclusions about HOx described here.

We recognize the reader could use more information. In the revised manuscript, we mention that the model we use is described in detail in Farmer and Cohen (2008). We also have added text to emphasize the point that the HOx-NOx chemistry described here is consistent when viewed from several different perspectives.

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ACPD

9, S2623–S2626, 2009

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