

Interactive  
Comment

***Interactive comment on “Observations of NO<sub>x</sub>,  
ΣPNs, ΣANs, and HNO<sub>3</sub> at a rural site in the  
California Sierra Nevada Mountains: summertime  
diurnal cycles” by D. A. Day et al.***

**D. A. Day et al.**

Received and published: 23 June 2009

We thank the referee for his/her constructive suggestions for improving the paper. In the following the reviewer comments are repeated followed by our response.

General comments:

This paper presents an analysis of measurements of a variety of nitrogen compounds, including NO<sub>x</sub>, 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 NO<sub>y</sub> budget, and as a result this

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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 NO<sub>x</sub> and O<sub>3</sub> in the calculation, but do not describe how they estimated the value of j<sub>12</sub>.

Response: A description of the method for estimating j<sub>12</sub> has been added to the text.

It is also not clear whether the uncertainty in their estimation of j<sub>12</sub> is taken into account in the uncertainty in the HO<sub>2</sub> + RO<sub>2</sub> 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 [HO<sub>2</sub> + RO<sub>2</sub>] for j<sub>12</sub> values ranging from +/-30% of the calculated values in order to provide a liberal range in uncertainty of [HO<sub>2</sub> + RO<sub>2</sub>] that may result from uncertainty in determination of the photolytic rate constant of NO<sub>2</sub>. 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. See revised figure below.

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 briefly. The manuscript would benefit from an expanded discussion of the steady-state calculation analysis, perhaps including a simple radical budget analysis which

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 3435, 2009.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

