Atmos. Chem. Phys. Discuss., 9, S1030–S1033, 2009
www.atmos-chem-phys-discuss.net/9/S1030/2009/

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.

Anonymous Referee #1

Received and published: 24 March 2009

General comments:

This paper presents an analysis of diurnal cycles in several components of reactive nitrogen at a forested site in the foothills of the Sierra Nevada mountains, up the slope from the Sacramento area and impacted by urban emissions from this region. Long-running measurements at that site have been described in several previous publications, and these are appropriately cited and reviewed here. The relevant aspects of related analyses from other locations are comprehensively reviewed as well. The focus of this analysis is on the diurnal cycles for summertime, weekday measurements at this location. Data are presented for representative time traces during summer and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

other seasons, though the bulk of the analysis is on diurnally averaged data. Analysis is done in terms of time of day trends in emissions, transport, process chemistry and deposition. In that sense the paper is a comprehensive look at sources, sinks and transformations of reactive nitrogen species in a diurnally forced flow pattern and in complex terrain. It draws conclusions regarding the production and loss of NOx, PAN compounds, alkyl nitrates and HNO3 for both daytime and nighttime regimes.

While at times qualitative and in a few cases speculative, the analysis is a new look at existing data and presents interesting results for reactive nitrogen chemistry and transport. The paper should be published in ACPD subject to consideration of the following comments.

Specific comments

1. Section 2.3, NO data. A bias in the NO measurements is identified in this section, but not referenced later during the analysis that utilize this measurement. How much does the bias affect the following analyses? Some sense of the resulting error bars in the derived quantities would be useful. Is the 20 ppt positive NO at night definitely a bias, or possibly the result of soil NOx emissions?

2. Page 3447, line 28-30. Not clear why deposition would cause NOy to peak earlier than CO. This would change the ratio of NOy to CO, but not the relative timing in the arrival of the plume?

3. Page 3449, line 10-12. If NOx decreases more rapidly than its tracer, CO, then the difference must be due entirely to chemistry, not dilution?

4. Page 3451, line 4. Referencing of the two Munger papers is formatted incorrectly.

5. Page 3451. Discussion of OH derived from equation (1) is confusing, as three separate numbers are given. It seems the conclusion is that the equation cannot be used to predict OH, and that a calculation from a separate paper must be used? If so, the content of the paragraph could be significantly shortened or omitted.

6. Page 3455, line 7. Again, confusing OH estimates. The four fold reduction in OH is in reference to which calculation? Later on line 22, references to decreases for isoprene, MVK and MACR are made, though these data are not shown? Are these data for the same year as the reactive nitrogen analysis? Later, on line 27, there is reference to 1% loss of PN's overnight, but it is not clear which reaction is responsible for this? There is a subsequent derivation of a peroxy radical concentration that is more consistent with the data. How reasonable is this peroxy radical level? Is it justifiable at night? How do the losses of PN to reaction with soil NO and deposition affect these calculations? The discussion is somewhat confusing at this point and should be clarified.

7. Page 3459, line 24. Aerosol surface areas at UC-BFRS are not sufficient to compete with NO3-VOC reactions. What is the aerosol surface area that is typical, and how was it measured? What levels of biogenic VOC are referenced in comparison to this aerosol surface area?

8. Page 3460, line 11. The Big Hill site is 20 km upwind, at night, from UC-BFRS. This is presumably to the East. Can this be indicated on the map in Figure 1?

9. Page 3460, line 17. Nocturnal boundary layer 100 m deep. Is this number generic, or taken from measurements near the site. How appropriate is this number for complex terrain with slope flows? Also not clear why the choice of 70% for a concentration difference between Big Hill and UC-BFRS.

10. Page 3461, 1st paragraph. Should make some reference to literature on NO3-VOC reactions. Why assume a 5% yield of NO2 from reaction of NO3 with aldehydes? Can the branching that produces 45% HNO3 from NO3 with biogenic VOC be justified? Is this a secondary reaction with an aldehyde product? Lastly, there is a reference to soil emissions. Please specify soil emission of what compound.

11. Page 3462, line 27. Early morning peak for CO not obvious from the data in Figure 3.

12. Section 5.1, general comment. How well can the photostationary state be applied to averaged, rather than instantaneous data. Are there any non-linearities that would prevent this? If not, should include some comment to this effect. Could such an analysis affect the conclusion that peroxy radicals are very high at this site in summer?

13. Page 3463, equation (5). Should state or show more explicitly how this is used. Is the quantity a ratio of perturbed to unperturbed stationary state?

14. Page 3464. Please check equation (6). Should the quantity in parentheses be in the numerator rather than the denominator?

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