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

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. Longrunning 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 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?

Response: We have added the following text to Section 2.3: For typical nighttime conditions (60 ppb O3, 16 C) a sustained NO concentration of 20 ppt would result in production of $>$10 ppb NO2 during an 8-hour night. Such a large production rate of NO2 is unrealistic at this location.

and section 5.3: (note: Modeled midday [HO2 + RO2] values using lower NO concentrations corrected by the nighttime non-zero values from a possible leak (see Sect. 2.3) yields [HO2 + RO2] values of nearly double that shown in Fig. 6. Therefore, if anything, the uncertainty in NO is responsible for an underestimation of peroxy radical concentrations).

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

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arrival of the plume?

Response: This is true that deposition will affect the ratio of NOy to CO as we discuss below in Section 4.2. However, we suggest deposition may be, in part, the cause of an earlier NOy peak because the integrated effect of NOx => NOz photochemistry (and subsequent NOz deposition) on air reaching BF probably increases throughout the afternoon (offsetting increased transport), possibly peaking as late as the CO peak (~19h) which would represent air transported from Sacramento to BF during hours ~14-19. If changes in emissions were not important, then this balance appears to be established as early as hour 14 when NOy is observed to plateau.

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?

Response: It is true that the relative decreases of these two compounds toward their respective background concentrations should occur at the same rate due to dilution. However, in the case of NOx, daytime concentrations increase 3-fold above morning lows (and as much as 20-fold above FT background concentrations) as opposed to +30% (2-fold) for CO. Therefore dilution would cause a markedly faster relative decrease in NOx toward zero after the evening peaks.

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

Response: This has been corrected in the manuscript.

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.

Response: We think that this discussion is useful as it illustrates how using only midday concentrations from the diurnal cycles observed at BF combined with a simple steady-state approximation, OH concentration can be estimated. We calculate only one concentration. We discuss the limitations of this approximation and compare to two other more-detailed calculations of OH for this site.

6. Page 3455, line 7. Again, confusing OH estimates. The four fold reduction in OH is in reference to which calculation?

Response: We have added text to clarify this calculation and comparison. It now reads: If we invoke additional sources of PAN that are 3 times larger than the acetaldehyde source and repeat the calculation using equation 3 (see preceding paragraph), we calculate a 4-fold lower OH (3.8x106 molecules cm-3).

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?

We have added text in the preceding paragraph, where we first introduce this data: (data not shown, see Dreyfus et al. (2002) for similar summertime diurnal cycles at this location).

Later, on line 27, there is reference to 1% loss of PNs 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.

The 1% loss of PNs overnight is a lower limit of the chemical loss calculated by assuming that only PAi-PAi reactions (formed through R2) are responsible for permanent loss of PNs which is described in the preceding sentence. However, we added additional text here to clarify this calculation, provide context to the subsequent peroxy radical calculation and direct the reader to a later section where nighttime deposition is discussed.

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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?

Response: Particle numbers at Blodgett forest were measured from spring to early fall in 2002 (Lunden et al., 2004) and the calculated surface area was ˜200 micron2/cm3. An upper limit of 600 micron2/cm3 was used for this calculation. Biogenic VOC concentrations are referenced in the text. We have added text and a reference to provide details of this calculation.

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?

Response: Figure amended as suggested.

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.

Response: Yes, the 100 m boundary layer height is a generic number. It is not crucial to the calculation, since for a different BLH the deposition velocities will be scaled proportionally, but the chemistry will remain unchanged.

The 70% is a rough approximation in between the UC-BFRS concentrations and that calculated for the UC-BFRS concentrations diluted during the 2-hr transect from UC-BFRS to Big Hill with a dilution rate of ˜0.3 h-1 (50%). BVOC emissions are probably smaller upwind of UC-BFRS due to less vegetation and lower temperatures. We have added details to the text.

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?

Response: It was necessary to assume these yields to reproduce the observations with the model. These branching ratios are not from individual reactions but after multiple reactions after an 8 hour-night. We have added references on NO3-VOC chemistry.

Lastly, there is a reference to soil emissions. Please specify soil emission of what compound.

Clarified in text as NOx emissions.

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

Response: On average there is a subtle increase from ˜5:30 to 6:30 shown in Fig. 3. However as not to overemphasize this feature we have amended the text here to read: A similar peak was sometimes observed for CO which may be the result of more rapid soil emissions of CO following a nighttime build-up initiated by rising temperatures or increased sunlight photolyzing aldehydes that accumulated overnight.

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?

Response: The peroxy radical concentrations discussed in Section 5.1 and shown in Fig. 6 were calculated for instantaneous measurements (half-hour averages). The 68th percentile bounding lines shown in Fig. 6 represent the variability in the calculated concentrations resulting from atmospheric variability. We have added text to Section 5.1 to clarify this detail.

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?

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Response: We have added additional text to clarify this section as suggested.

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

Response: Yes. The equation has been corrected.

References

Lunden, M., Black, D., and Brown, N.: Characterizing the formation of secondary organic aerosols, Interim Report. Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory. eScholarship Repository, University of California, http://repositories.cdlib.org/lbnl/LBNL-54446, 2004.

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