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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of the effects of temperature on atmospheric HNO_3, ΣANs, ΣPNs, and NO_x: evidence for a temperature dependent HO_x source" *by* D. A. Day et al.

Anonymous Referee #1

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Review of the manuscript "Observations of the effects of temperature on atmospheric HNO3, sum(ANs), sum(PNs), and NOx: evidence for a temperature dependent HOx source" by D. A. Day, P. J. Wooldridge, and R. C. Cohen.

General comments:

This paper describes measurements of total NOy and NOy composition, Ozone, NOx, and others, made in the summer at the UCBFR Station located northeast of the Sacramento urban area. The measurements are examined with regard to the temperature dependence of NOy partitioning, sequestration of NOx, ozone, and inferred radical concentrations.

The results presented in the paper are appropriate for the scope of ACP. The paper is clearly written and well structured. The title reflects well the content of the manuscript and so does the abstract. The data used is new and the conclusions are sufficiently substantial to warrant publication in ACP.

I recommend publishing the paper after careful consideration of the following:

Specific comments:

This is an interesting paper with important conclusions but in my opinion it is not very well supported by supplemental data. One wishes measurements of the PBL height, measurements of aldehydes, isoprene and its oxidation products, actinic fluxes, etc. would be available. While this of course cannot be held against the authors, it should be acknowledged that without some hard supporting data the conclusions are somewhat speculative.

Specifically, I would like to see a more thorough estimate of errors resulting from uncertainties in the PBL height. Reading the cited papers on the general meteorology in the area gave me the impression that PBL heights in the valley range from 400-800m (Seaman paper) which would imply an additional uncertainty of a factor of 2 which is presently not taken into account in the analysis. This could also be a systematic uncertainty as PBL height could be correlated with cloudiness (and actinic flux) or with the daily temperature rise.

Would it be possible to obtain information on the actual PBL heights from met radiosonde data which may be available in the area?

It might also be interesting to try and run a model with NMHC input from the Dillon paper and isoprene mixing ratios varied with temperature as derived from emission models and see whether the needed additional HOx sources could be explained this way. While it would certainly change the OH/HO2 ratio it is not immediately obvious that increased input of isoprene into the air mass would actually increase [OH].

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A main concern is the assumption of steady-state conditions for HNO3 and NO2 - especially with regard to deposition of HNO3 and the apparently significant soil emissions of NO2 along the transport path. Since deposition is highly variable depending on turbulence, soil and canopy conditions, and other factors, it is likely that the SS assumption is not valid. Similarly, if the soil emissions of NOx are as significant as described in section 3.5, they, too will not allow the system to reach steady-state with regard to HNO3.

Figure 2 shows a significant increase of NOx mixing ratios around 7 am. This is too early in the morning to be attributed to the Sacramento urban area (3-4 hr transport time). Are these emissions local? How do they impact the SS assumption?

The authors should re-examine all their assumptions and come up with a reasonable estimate of uncertainties for each aspect of their analytical approach. These combined uncertainties in the estimate of [OH] may well turn out to be large enough for the increase in primary production of OH from ozone to be statistically sufficient within the error bars of the increase calculated from the observations.

Minor comments:

The last paragraph of section 3.2 is confusing. I had to read it several times to understand it. It should be streamlined.

On page 11098, line 16 the authors state that the correlation between O3 and temperature is “strong”. A R^2 value of 0.43 is not my definition of a strong correlation. In fact, the considerable variability in the ozone vs. temperature makes me wonder whether the authors have tried to correlate this variability with other parameters like cloud cover, or humidity?

In section 3.2 the HNO3 background is estimated to be 200 pptv from “typical” free trop. values derived from measurements made high in the Sierra at a different time. Since the station is influenced by downslope winds at night I would think the nighttime

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HNO3 mixing ratios measured at UCBFRS would be similarly - if not more - justified to be used as a background value for the local air above the PBL. This value ranges from 400-500 pptv. What is the impact of using this value in equation (2) rather than 200 ppt?

Technical:

Page 11098, line 3 - fix formatting of “17th and 83rd”

Page 11100, line 16 - “effected” should read “affected”

References: Sillman and Sampson (1995), JAM 1995 Correct citation should be Sanford Sillman and Perry J. Samson, JGR 100, D6, 11479-11508, 1995 Please also note misspelled last name of second author - please correct throughout the manuscript.

Fig.1: The numbers on the x-axis are not the “Julian Day” numbers for this time period. Use “Day of Year” instead.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11091, 2007.