Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "Observations of the effects of temperature on atmospheric HNO$_3$, ΣANs, ΣPNs, and NO$_\mathrm{x}$: evidence for a temperature dependent HO$_\mathrm{x}$ source" *by* D. A. Day et al.

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Reply to comments of Referee 1

Observations of the effects of temperature on atmospheric HNO3, SigmaANs, SigmaPNs, and NOx: evidence for a temperature dependent HOx source; by D. A. Day et al.

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

General comments:

This paper describes measurements of total NOy and NOy composition, Ozone, NOx,

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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.

In the revised manuscript we will clarify those aspects of the manuscript that are somewhat speculative because of the absence of the correlative measurements referred to by the referee. Some of the measurements listed above do exist and have been described in other manuscripts. These manuscripts provide supporting context for the meteorological variability in the region, the variation in isoprene and other biogenic VOC, the variation of weekdays vs. weekends and the spatial evolution of the plume. Other desirable measurements are not available.

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.

We added the following text:

First, we do not believe there is a large change of mixed layer height that is correlated with temperature in this region because the PBL height is more strongly defined by the dynamical forcing of the large scale circulation and the Sierra Nevada Mountains than it is by surface heating. Also the PBL is less driven by latent heat than in other regions because of this dynamical effect and the low humidity in the region. Furthermore, the overall cloudiness in the region during the summer is so low that variations in clouds (or actinic flux) are unimportant. Data from 7 days of flights over this region of the Sierra Nevadas during summertime showed no correlation between afternoon mixing layer heights and surface temperatures (Carroll and Dixon, 1998). In that study afternoon surface temperatures varied by 10C and the lack of correlation was observed for the three surface elevations reported in their transect (150 masl, 550 masl, and 1250 masl), roughly along the transect from the Sacramento Valley to our observation site. Although mixed layer heights did not correlate with temperature they were observed to vary substantially (660-1250 magl at the highest elevation location, 1250 masl) but on average only increasing from 800 magl above the city of Sacramento to 1000 magl at the highest elevation where the ground was 1250 masl.

Although we do not believe this to be the case, it is possible to assume the mixed layer height is correlated with temperature and then evaluate how this correlation affects the NO2/HNO3 ratio (and consequently the calculated OH). Assuming that HML grows lineary from 530 to 1070 m from 15-29C and inserting these values into Eq. (2) results in a smaller relative change in the calculated OH over this temperature range. With this assumption, we calculate a 2.3-fold increase with T from 15-29C compared to the 3.2 fold increase assuming a constant mixed layer height. With the varying boundary layer

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height we calculate 30

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

There is some wind profiler data in the region but it would be a significant new research project to evaluate the temperature dependence of the boundary layer height from that data. Other measurements indicate that the variation will be small or uncorrelated (Carroll and Dixon, 1998)

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].

We are in the process of building and testing such a model using chemistry from the MCM (Perez and Cohen, in preparation). However, not surprisingly given other recent model-measurement comparisons for HOx in regions of high isoprene (Ren, et al., 2007; Tan, et al., 2001; Thornton, et al., 2002) , the standard model severely underestimates OH. Our basis for associating the temperature dependent increase of OH with isoprene is not a model calculation but rather these other field measurements that show that models are either missing a large HOx source or overestimating a sink in the presence of isoprene (Farmer and Cohen, 2007; Kuhn, et al., 2007; Ren, et al., 2007; Thornton, et al., 2002).

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

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regard to HNO3.

The steady-state time scale is short enough (2.5 hours) that our approximate discussion will hold even in the face of variations among the parameters listed by the referee. The time scales in question are similar to those discussed in our recent analysis of peroxynitrates chemistry where we showed that the steady-state equations are within 30-50

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?

We believe the concentration increase in the early morning results from mixing of air in the residual and nocturnal layers with air that has been trapped in the surface layer, where the layers are as defined in Brown et al. (2007). We speculate that air in the nocturnal surface layer has reduced NO2 because of removal via production of NO3 and subsequent reaction of NO3 with biogenic VOC. These VOC are not available in the residual layer and thus at sunrise most NO3 and N2O5 in this layer is returned to the NOx pool.

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.

In a revised manuscript we examine all of the key assumptions in more detail. We still find that the hypothesis that the only change in the OH source is increased photolysis of O3 fails to explain the observations, However, we discuss how much other factors would have to change for the data to be consistent with that assumption.

Minor comments: The last paragraph of section 3.2 is confusing. I had to read it several

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times to understand it. It should be streamlined.

The paragraph has been revised as follows:

We expect that the OH concentrations predicted using the local NO2 and HNO3 concentrations in the steady-state calculation are an overestimate of the OH responsible for producing the observed HNO3 due to elevated NO2 levels upwind. Without a more detailed model, estimating the effective NO2 for use in Eqs. 1 and 2 is difficult. To bracket the amount of NO2 and thus the absolute value of OH we use a three-fold larger value of NO2 resulting in calculated OH of 2.7 x 10^6 and 8 x 10^6 molecules per cm^3 for the two temperature extremes. Despite lowering the OH by a factor of three, the trend with temperature is still large, increasing approximately three-fold. These calculations using the different NO2 concentrations both produce OH estimates in the range of the average OH concentration in the Sacramento plume (0.6-1.6 x 10^7 molecules/cm3) that Dillon et al. (2002) calculated using a Lagrangian model and VOC measurements for the five-hour transect from Folsom, CA to the UC-BFRS. That model represented a single average daily maximum temperature of 25C

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?

We have reworded the phrasing. We agree the correlation is not strong, but it is visible to the eye.

We have not identified a single primary variable that provides a stronger correlation than temperature, although we note the work of Dreyfus et al. (2002) showing that the increase depends quite strongly on isoprene emission and oxidation rates (which are of course dependent on temperature and NOx). Cloud cover and humidity do not vary enough in this region during the time period in question to affect O3 production rates.

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Text to this effect has been added to the revised manuscript.

In section 3.2 the HNO3 background is estimated to be 200 pptv from typical free troposperic 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 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?

In our opinion, our observations in the nocturnal boundary layer are affected by near surface chemistry with production from reactions of NO3 and N2O5 at night. In the revised manuscript we will include the calculation suggested by the referee, along with this caveat explaining why the lower value seems more likely to us. The result of using 400 pptv rather than 200 pptv background HNO3 is an increase in OH of 2.5 x 10^6 molecules/cm3 nearly invariant with temperature which represents a 4.3-fold increase in calculated OH (compared to 3.2 for using 200pptv) over the temperature range.

Technical:

The revised manuscript includes changes for all of the technical notes of the referee.

References

Brown, S. S., Dube, W. P., Osthoff, H. D., Wolfe, D. E., Angevine, W. M., and Ravishankara, A. R.: High resolution vertical distributions of NO3 and N2O5 through the nocturnal boundary layer, Atmospheric Chemistry and Physics, 7, 139-149, 2007

Carroll, J. J. and Dixon, A. J.: Tracking the Sacramento pollutant plume over the western Sierra Nevada. Final Report to California Air Resources board under Interagency Agreement 94-334. 26 pages plus appendicies., http://www.arb.ca.gov/research/apr/past/atmospheric.htm, 1998

Cleary, P. A., Wooldridge, P. J., Millet, D. B., McKay, M., Goldstein, A. H., and Cohen, R.

C.: Observations of total peroxy nitrates and aldehydes: measurement interpretation and inference of OH radical concentrations, Atmos. Chem. Phys., 7, 1947-1960, 2007

Dillon, M. B., Lamanna, M. S., Schade, G. W., Goldstein, A. H., and Cohen, R. C.: Chemical evolution of the Sacramento urban plume: Transport and oxidation, J. Geophys. Res.-A., 107, 4045, 10.1029/2001JD000969, 2002

Dreyfus, G. B., Schade, G. W., and Goldstein, A. H.: Observational constraints on the contribution of isoprene oxidation to ozone production on the western slope of the Sierra Nevada, CA, J. Geophys. Res.-A., 107, 4365, doi:10.1029/2001JD001490, 2002

Farmer, D. K. and Cohen, R. C.: Observations of HNO3, SAN an SPN and NO2 fluxes: Evidence for rapid HOx chemistry within a pine forest canopy, Atmospheric Chemistry and Physics Discussions, 7, 7087-7136, 2007

Johnston, H. S., Miller, C. E., Oh, B. Y., Patten, K. O., and Sisk, W. N.: Internal Energy Distributions From Nitrogen Dioxide Fluorescence .1. Cumulative Sum Method, Journal of Physical Chemistry, 97, 9890-9903, 1993

Kuhn, U., Andreae, M. O., Ammann, C., Araújo, A. C., Brancaleoni, E., Ciccioli, P., Dindorf, T., Frattoni, M., Gatti, L. V., Ganzeveld, L., Kruijt, B., Lelieveld, J., Lloyd, J., Meixner, F. X., Nobre, A. D., Pöschl, U., Spirig, C., Stefani, P., Thielmann, A., Valentini, R., and Kesselmeier, J.: Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget, Atmos. Chem. and Phys., 7, 2855-2879, 2007

Ren, X., Olson, J. R., Crawford, J. H., Brune, W. H., Mao, J., Long, R. B., Chen, G., Avery, M. A., Sachse, G. W., Barrick, J. D., Diskin, G., Huey, L. G., Fried, A., Cohen, R. C., Heikes, B., Wennberg, P. O., Singh, H. B., Blake, D. R., and Shetter, R. E.: HOx observations and model comparison during INTEX-A 2004, submitted to J. Geophys. Res.-A., 2007

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Tan, D., Faloona, I., Simpas, J. B., Brune, W., Shepson, P. B., Couch, T. L., Sumner, A. L., Carroll, M. A., Thornberry, T., Apel, E., Riemer, D., and Stockwell, W.: HOx budgets in a deciduous forest: Results from the PROPHET summer 1998 campaign, Journal of Geophysical Research-Atmospheres, 106, 24407-24427, 2001

Thornton, J. A., Wooldridge, P. J., Cohen, R. C., Martinez, M., Harder, H., Brune, W. H., Williams, E. J., Fehsenfeld, F. C., Hall, S. R., Shetter, R. E., Wert, B. P., and Fried, A.: Observations of ozone production rates as a function of NO2 abundances and HOx production rates in the Nashville urban plume, J. Geophys. Res., 107, 4146, doi:10.1029/2001JD000932, 2002

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

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