

Interactive comment on “Observations of the effects of temperature on atmospheric HNO₃, ΣANs, ΣPNs, and NO_x: evidence for a temperature dependent HO_x source” by D. A. Day et al.

D. A. Day et al.

Received and published: 16 November 2007

Reply to comments of Referee 2

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

General comments:

This is an interesting paper which shows there are significant correlations between temperature and measurements of nitric acid, alkyl nitrates, peroxy acetyl nitrates and NO_x (and their ratios), and these observations are used to infer concentrations of OH

radicals.

The paper is certainly within the scope of ACP.

The results, although an indirect estimate, suggest that OH increases dramatically between 18 and 32 degrees Celsius. The conversion of NO₂ to form HNO₃ is controlled by OH, and so the ratio HNO₃/NO₂ can be used to calculate OH, if other quantities, e.g. boundary layer heights, deposition rates, rates of dilution and background (free tropospheric) concentrations and relevant kinetic data are either known or can be estimated.

The concentration inferred is consistent with measurement of some of the other species, whose budgets include reactions involving OH. Estimates of how OH may change with temperature in a forested environment are important for predicting future lifetimes of trace gas lifetimes, in particular climate-related gases. The speciation of NO_y, and how this changes with temperature, is also discussed together with modelling studies by other groups.

OH measurements, although becoming more common, are still relatively rare, and it is unusual for them to take place over long periods, where datasets can be built up as a function of temperature when other controlling parameters are relatively constant (here there is a single source region and observations are within a single season but with varying temperature). The Blodgett Forest site has been running now for quite a few years and long-term datasets of NO, NO₂ and NO_y species (the latter monitored by temperature controlled thermal dissociation to NO₂, with detection of NO₂ by LIF) are extremely valuable, with one use being the estimation of radical measurements as performed here. Of course, validation of this approach in the future via the direct measurement of OH in the forest is highly desirable, and having a wider suite of composition measurements (e.g. oxygenated VOCs etc.) will make the approach more robust.

The observations reported, although difficult, are of high quality (and novel, no one

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

has before performed such a comprehensive analysis with temperature), but the uncertainties in the approach (due to assumptions made about unmeasured physical and chemical parameters which are required in the analysis of the HNO₃/NO₂ ratio to get [OH]), propagate to a significant uncertainty in the inferred OH concentrations, resulting in a lower confidence in the validity of the conclusions, important as they are. However, the approach is novel and when applied to such an extensive dataset, is able to make justified comments on how radical concentrations ([OH] in this case) are changing with increasing temperature. The relationship is found to be linear.

Mostly the paper is very well written (see specific comments below). The approach is novel, and makes use of a considerable set of speciated NO_y measurements, and subject to some revisions, I recommend publication in ACP.

The paper concludes that additional HO_x sources are required beyond the understood ones in order to explain the inferred increase in OH with temperature. Recent work from several sources (including another paper from this group in ACPD) where HO_x is measured directly (or inferred from other measurements) have also suggested a similar conclusion that HO_x levels are underestimated by models in regions where isoprene concentrations are high, suggesting an as yet unidentified source of HO_x in forested areas which scales with isoprene. This could point to unknown chemical processes, or problems with the kinetics (e.g. OH yields from RO₂+HO₂ reactions where R comes from a biogenic VOC) or of course in the HO_x measurements themselves. OH lifetime measurements have also shown that OH sinks are underestimated in forested regions, and that the missing OH sink scales with temperature.

Specific points.

Page 7. The HNO₃ concentration is approximately described as a stationary state between chemical production and losses. Does this imply then that HNO₃ may not always be in steady state, or that some of the sources and sinks are not included in this expression?

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

We meant the first of the referees suggestions, that HNO₃ may not always be exactly in steady-state because the production and loss terms may be changing rapidly compared to the time required to reach steady-state. We do not believe we have omitted any important terms. Text has been added to the revised manuscript to clarify this point.

Page 7, -affected- rather than -effected- between equations (1) and (2)

This has been corrected in the revised manuscript.

Page 8. Why are the OH concentrations probably higher upwind? They are already quite high (1x10⁷10;7).

OH concentrations in the Sacramento plume transect (as modeled by Murphy et al. (2006)) were shown to be at a maximum at NO_x concentrations of 4 ppb, which is considerably upwind of the UC-BFRS (NO_x 0.5 - 1 ppb). This peak is due to an optimal balance between important production (HO₂+NO=>OH+NO₂) and loss (OH+NO₂=>HNO₃) terms of OH, or the transition from NO_x- to VOC-limited O₃ chemistry. At decreasing NO_x, HO_x-HO_x reactions constitute significant losses pathways for HO_x diminishing the recycling of HO_x back to OH.

In regards to the high OH referred to here, we used the value calculated by Dillon et al. (2002) for the average of the Sacramento plume as a demonstration of the approximate lifetimes of HNO₃ formation and losses as it is transported toward the UC-BFRS. In addition, this value is approximately the value predicted by Murphy et al. [2006] for NO_x = 2 ppb, which corresponds to an hour or two upwind of the UC BFRS where much of the locally observed HNO₃ is likely formed.

Page 11 : the inferred HO₂+RO₂ afternoon averages were 100-200 ppt (with a large uncertainty) from the deviation from photochemical steady state. These seem quite high, are there any HO₂+RO₂ measurements close to this sort of value in this environment? There is a difficulty with the deviation from steady state method as this relies on

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

the difference between 2 large numbers and [NO] is hard to measure at low levels.

We agree that better NO (and in situ actinic flux) would be desirable to better constrain calculations of HO₂+RO₂ at this site. Of course direct measurements of HO₂, OH and RO₂ would be even better. These values are at the high end but only by a factor of two or so compared to other results where midday peaks as high as 100 ppt have been described (Cantrell, et al., 1996a; Cantrell, et al., 1997; Cantrell, et al., 1996b; Hauglustaine, et al., 1996; Mihele and Hastie, 2003; Thornton, et al., 2002). We agree that the steady state usually relies on the difference between two large numbers, however, in this case the RO₂+HO₂ term is so large that it is equal to or greater than the O₃ term making the calculation more reliable than it usually is.

The max. predicted increase in HO₂+RO₂ with temperature is 50

We agree that conclusions based on our RO₂+HO₂ calculations are speculative. However, we do not have reason to believe that they would be systematically biased with temperature so the observations of the relative lack of correlation with temperature (within the stated certainty) is interesting and worth reporting alongside our OH increases inferred from our NO_y measurements.

We have added a passage to the revised manuscript explaining our assumptions for the relationship stated.

Page 11, it is square-root- rather than -route-

This has been corrected in the revised manuscript.

It is quite difficult to see if the current work and the modelling work of Sillman and Samson (1995) are consistent or not. Both sets of work use multiple assumptions and I was left wondering what the conclusions actually were regarding the comparison. The modelling study showed that in Michigan much of the increase in [OH] could be explained by higher ozone and water vapour. At the Blodgett site water vapour does not change, and considering the change in O₃ can only explain a small part of the

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

predicted increase in OH, implying that other HOx generating processes are needed (e.g. production of CH₂O).

One of the primary reasons for comparing to the Sillman and Samson (1995) paper was to compare to one of the only two papers that we are aware that explicitly discuss speciation of NO_y with temperature. It is true that direct comparison of their modeled results with our observations is difficult without knowing more details of their model.

In relation to a comparison of their modeled OH and our OH inferred from measurements, again, a direct comparison is difficult. We reference their work in this context to provide the reader with the most typical explanations for controls of OH. To this we compare our contrasting results that require other sources as stated (that may have some parallels to other more recent observations and models of HOx).

Notwithstanding the above comments, we do feel the same frustration as the reviewer, however, the Sillman and Samson paper is the first (and still the only) one to directly tackle the issue we discuss. We are in the process of developing a detailed model so that we can make a direct comparison for this site and not rely on the necessarily indirect comparisons to the pioneering calculations in the Sillman and Samson work.

References

Cantrell, C. A., Shetter, R. E., and Calvert, J.: Peroxy radical chemistry during FIELD-VOC 1993 in Brittany, France, Atmospheric Environment, 30, 3947-3957, 1996a

Cantrell, C. A., Shetter, R. E., Calvert, J. G., Eisele, F. L., Williams, E., Baumann, K., Brune, W. H., Stevens, P. S., and Mather, J. H.: Peroxy radicals from photostationary state deviations and steady state calculations during the Tropospheric OH Photochemistry Experiment at Idaho Hill, Colorado, 1993, Journal Of Geophysical Research-Atmospheres, 102, 6369-6378, 1997 Cantrell, C. A., Shetter, R. E., Gilpin, T. M., Calvert, J. G., Eisele, F. L., and Tanner, D. J.:

Peroxy radical concentrations measured and calculated from trace gas measurements

in the Mauna Loa observatory photochemistry experiment 2, Journal Of Geophysical Research-Atmospheres, 101, 14653-14664, 1996b

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

Hauglustaine, D. A., Madronich, S., Ridley, B. A., Walega, J. G., Cantrell, C. A., Shetter, R. E., and Hubler, G.: Observed and model-calculated photostationary state at Mauna Loa observatory during MLOPEX 2, Journal Of Geophysical Research-Atmospheres, 101, 14681-14696, 1996

Mihele, C. M. and Hastie, D. R.: Radical chemistry at a forested continental site: Results from the PROPHET 1997 campaign, Journal Geophysical Research, 108, 4450, 2003

Murphy, J. G., Day, D. A., Cleary, P. A., Wooldridge, P. J., Millet, D. B., Goldstein, A. H., and Cohen, R. C.: The weekend effect within and downwind of Sacramento: Part 2. Observational evidence for chemical and dynamical contributions, Atmos. Chem. Phys. Discuss., 6, 11971-12019, 2006

Sillman, S. and Samson, P. J.: Impact of Temperature On Oxidant Photochemistry in Urban, Polluted Rural and Remote Environments, J. Geophys. Res.-A., 100, 11497-11508, 1995

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 HO_x 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.

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper