

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.

Anonymous Referee #2

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Review of Day et al.

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

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by OH, and so the ratio HNO_3/NO_2 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, NO_2 and NO_y species (the latter monitored by temperature controlled thermal dissociation to NO_2 , with detection of NO_2 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 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 HNO_3/NO_2 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

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justified comments on how radical concentrations ($[\text{OH}]$ 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 $\text{RO}_2 + \text{HO}_2$ 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 HNO_3 concentration is approximately described as a stationary state between chemical production and losses. Does this imply then that HNO_3 may not always be in steady state, or that some of the sources and sinks are not included in this expression? Page 7, -affected- rather than -effected- between equations (1) and (2) Page 8. Why are the OH concentrations probably higher upwind? They are already quite high (1×10^7). Page 11 : the inferred $\text{HO}_2 + \text{RO}_2$ afternoon averages were 100–200 ppt (with a large uncertainty) from the deviation from photochemical steady state. These seem quite high, are there any $\text{HO}_2 + \text{RO}_2$ 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 the difference between 2 large numbers and $[\text{NO}]$ is hard to

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measure at low levels.

The max. predicted increase in HO₂+RO₂ with temperature is ~ 50%, quite a bit less than the factor of 2-3 increase in OH with T that is predicted. The conclusion is that the increase HO₂+RO₂ would be expected to be quite a bit higher than 50% (making assumptions about the relationship between OH and HO₂+RO₂, perhaps these could be expanded upon), with the conclusion that the increase in OH and HO₂+RO₂ occur in different places, or that a chemical process can alter the HO₂+RO₂/OH ratio. These must remain speculative given the uncertainty in estimating the peroxy radical concentration?

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

It is quite difficult to see if the current work and the modelling work of Sillman and Sampson (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 predicted increase in OH, implying that other HO_x generating processes are needed (e.g. production of CH₂O).

The figures and captions are clear.

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

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