Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Chemical and meteorological influences on the lifetime of NO$_3$ at a semirural mountain site during "PARADE"" *by* N. Sobanski et al.

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General Comments:

This paper analyzes the lifetimes of NO3 and N2O5 based on measurements from a mountaintop site in west central Germany during late summer 2011. The data include both in-situ measurements from a CRDS instrument and vertically resolved measurements from a long path DOAS instrument. Additional supporting measurements of NOx, O3, aerosols and VOCs are available for a reasonably complete assessment of both the production and loss processes for the NO3 and N2O5 reactive intermediates. A key observation is that the steady state lifetimes for NO3 are at times considerably greater than would be calculated from the loss of NO3 to VOCs, particularly biogenics.

The attempt to explain this observation leads to two key results.

The first is a consideration of the potential NO3 source from the oxidation of NO2 by stabilized Criegee intermediates (sCI) produced in the ozonolysis of alkenes. This production has not to my knowledge been considered in the context of field data previously. Although the effect is not large enough to explain the observed discrepancies in NO3 lifetimes, the thorough estimations of the range of sCI concentrations and associated rate coefficients for reactions with NO2 are a highly valuable contribution to the literature. The analysis shows in particular that there may be situations where this reaction is non-negligible in comparison to the conventional NO3 source from the reaction of NO2 with O3.

The second is an analysis of mixing effects between different altitudes within the nocturnal boundary layer / residual layer structure. The combination of CRDS and DOAS measurements provides a convincing data set to demonstrate the important role that mixing can play in determining NO3 concentrations and apparent lifetimes. While these effects have been considered previously (e.g., Stutz 2004), the analysis here provides a compelling example.

The paper is a valuable contribution to the literature and should be published in ACP subject to consideration of the list of minor comments below.

Specific Comments:

Page 4, line 4. Site altitude is given in meters above sea level. What is the altitude of the surrounding area? How far above ground level is this site? This is important in understanding whether the site should be in the broader nocturnal boundary layer or the residual layer.

Page 4, line 32. Suggest using a different description than "excellent" for the instrument agreement, since 10% is not especially good agreement for O3.

Page 5, line 26. "Ethane" is repeated. Possibly "ethene" is meant?

Line 6, section 2.25. Were particle surface areas measured at dry or ambient RH, or at some intermediate RH, and was there a need to correct surface areas for hygroscopic growth?

Page 8, line 3-6. A more traditional wind rose is described in the text but not shown in figure 3. This would be helpful alongside the existing figure 3.

Page 8, line 8-9. Statement that air masses from local urban area are expected to have higher aerosol and VOC implies that such measurements were not available. Suggest removing the word "expected" in favor of a quantitative statement about the wind direction dependence of the available aerosol and VOC data.

Page 8, line 12. Suggest inserting the word "likely" since there is no quantitative assessment of the droplet surface area or heterogenous uptake rates. Could also include a standard citation for this effect if desired (e.g., Leliveld & Crtuzen, 1990).

Page 10, line 28-30. Statement is not consistent. The 2 hour approach to steady state cited in section 3.3 and figure S3 uses LVOCs (here equivalent to LNO) of 2.5e-3 s-1, not 0.01 s-1 as shown in figure 6. Disagreement between calculated and observed NO3 lifetimes would seem to be less likely due to lack of steady state than shown by the supplemental figure.

Page 11, line 6. A gamma value of 0.02 may be consistent with recommendations but lies on the high end of the range of the values determined in both laboratory and field studies, which show values as low as 1e-4 (e.g., Brown & Stutz, Chem. Soc. Rev., 41, 6405-6447, 2012). The comparison between the calculated heterogeneous loss and the observed lifetimes thus represents something close to an upper limit of the former to the latter. Lower gamma would explain why heterogeneous loss sometimes exceeds the calculated lifetimes. The possibility of much lower uptake coefficients should be referenced in this discussion.

Page 13, line 4-8. The factor of 5-6 variability in tau(NO3) is an overstatement of

the actual variability in the loss of the sum of NO3 and N2O5, as indicated by the concurrent change in tau(N2O5). What is the variability in P(NO3) during this time?

Page 14, line 9 and following discussion. What is meant by the term "low-lying residual layer". The measurement site is already at some altitude above ground level (see comment above) and may already be above what would normally be considered the height of the nocturnal boundary layer. Is this mountaintop site not already in the residual layer, or are the local boundary layer dynamics influenced by the terrain so as to create some sort of local nocturnal boundary layer effect?

Page 14, line 28. Should "above the residual layer" be "above the nocturnal boundary layer" ?

Page 15, line 32-33. Could the gradient be due to downward mixing of NO3 or N2O5 from altitudes not sampled by the DOAS – i.e., presumably the measured gradient does not end at the highest DOAS level, so the observed change could be due more to mixing than to variation in the loss term.

Page 16, lines 21-29. The argument regarding local BVOC emissions oxidized by NO3 within a gradient is quite plausible and likely the best explanation of the observations. However, should it also be accompanied by a shift in the equilibrium ratio of N2O5 to NO3? In other words, if the NO3 were lost to BVOC reactions near the observatory, the N2O5 to NO3 ratio would possibly not respond as quickly, leading to a larger observed ratio of N2O5 to NO3 than that predicted by equilibrium. Can the authors comment on the potential magnitude of this effect, for example using the NO3-BVOC rate constant compared to the N2O5 thermal dissociation rate constant? If so, is there any evidence from the N2O5 to NO3 ratio so support this hypothesis?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-38, 2016.