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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nocturnal nitrogen oxides at a rural mountain-site in South-Western Germany" *by* J. N. Crowley et al.

Anonymous Referee #1

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General comments: The manuscript by Crowley et al describes high-quality measurements of NO3 and N2O5 at an interesting site in Germany. The results regarding the N2O5 eqbm constant and the likely overestimate of the homogeneous rate of N2O5+H2O are quite good. I recommend it be accepted when the following issues are addressed.

Specific comments: pg 12, line 17-20 – The discussion of the short term variability of the data would be greatly enhanced with a figure that shows a detailed section of the measurements ($\sim$5 min). Such a figure could appear in the Supporting Information. The answer given (mainly referencing the explanation of Brown et al 2003b) does not seem fully adequate. Regarding the chemical histories and loss processes encountered by the air masses, it is hard to see how the production term could be so

spatially inhomogeneous (and at the site, similar variability is not seen in the NO2 and O3 concentrations). As for loss terms, it is hard to imagine that the spatial distribution of biogenic VOCs (inferred as the most important NO3 loss process) should be able to cause the noise. Perhaps deposition to nearby surfaces (the ground, the container that houses the instruments) is very important? If that were the case, as small-scale mixing occasionally brings surface-exposed air to the inlet, lower concentrations would be observed. I do not know the true explanation of the variability, but think an improved approach is warranted.

pg 19, lines 19-21: that there is no trend in aerosol surface area at night is not enough to rule out changes in the rate of N2O5 uptake as a potential cause of the reduction in reactivity during the night. N2O5 uptake is determined by not just the surface area but also by the uptake coefficient (eq. 4), which depends on chemical composition and other factors.

pg 23, line 6-7: The authors' comment on differences in boundary layer height is a very, very important one! Since the vertical variation in NOx, NO3, N2O5, biogenic VOCs, etc are not known from the measurements, one can only conclude that *at the surface* the daytime and nighttime rates of NOx oxidation are comparable. As for total NOx oxidation occuring in the atmosphere above the measurement site, vertical data would be required. Of course this a limitation of all surface measurements, but it is particularly important for nighttime chemistry given that surface measurements are less representative of the air than daytime surface measurements are.

lines 20-24. Again, the authors' sentence is dead-on: Oxidation of biogenic VOCs by NO3 is only competitive with OH oxidation when considering the absolute concentrations of VOCs (mostly emitted during the day) and the total volume under which it is occurring (boundary layer height).

Minor comments: pg 2 line 20: VOCs, not VOC pg 2 line 31: remove "on" pg 5, line 10 – "fine" weather – meaning is not clear pg 5, line 26 – non-conductive tygon tubing

was used? Usually metal tubing is used to eliminate electrostatic losses... pg 6, line 19: I realize that the full description of the instrument was given in Schuster et al 2009, but a few words describing the laser would be helpful ("broadband"? "single-mode"?) pg 9, lines 26-27 – are these uncertainties 1 sigma or 2 sigma? pg 10, lines 17-21 – how are detection limits defined – signal-to-noise = 2? pg 13, line 27 – 0.5 not 0,5 pg 16, line 21 – "reduce", not "reducing" pg 16, line 23, rewrite as "...following sunset, however, does not ..." pg 18, line 6 – maximum, not "max" pg 20, line 19-22- I don't understand this sentence. pg 21, line 19 – rewrite as "...increases the NO2 oxidation rate" pg 23, line 13 – rewrite as "...NO3 indicate an important..." (not "and") pg 24, line 1 – important rewrite: not "...found to be direct..." but "...inferred to be direct". Without biogenic VOC measurements this is really an inference rather than a finding.

Figures 4,5,8,9,11: the x-axis tick labels are hard to read. There is no need to have the year written out for each tick mark. I recommend having only the time appear under the tick marks, and writing the dates only once. This would allow space for more ticks.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1309, 2010.