Referee 1

Comment:

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 N_2O_5 eqbm constant and the likely overestimate of the homogeneous rate of $N_2O_5 + H_2O$ are quite good. I recommend it be accepted when the following issues are addressed.

Reply:

None required

Comment:

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 (_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 NO_2 and O_3 concentrations). As for loss terms, it is hard to imagine that the spatial distribution of biogenic VOCs (inferred as the most important NO_3 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.

Reply:

This is all true. The short term variability is not caused by the source terms. It is likely caused by sampling of different air masses for which the sink term is variable due to e.g. different interaction with surrounding surfaces. The text on page 12 now reads "A major contributor to the variability is expected to be sampling of air masses that originate from different altitudes and which have experienced variable rates of loss to both gas-phase reactions and reactions with surfaces including vegetation and architecture between the emission region and the measurement site." The cause of the large variability is no longer mentioned in the abstract. An additional Figure (a 40 min section of NO_3 data) will be provided as supplementary information.

Comment:

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 N_2O_5 uptake as a potential cause of the reduction in reactivity during the night. N_2O_5 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.

Reply:

This is true. The fact is, however, that even with large uptake coefficients (as described in the paragraph above the one is question) the contribution of indirect (heterogeneous) loss is very small. The text has now been modified to accommodate the reviewers comment: "Unless the aerosol composition changes greatly during the night (being initially much more reactive than defined by the uptake coefficient above and subsequently becoming increasingly less reactive towards N_2O_5), indirect losses are unlikely to have caused the reduction in reactivity (factor of 10) observed after dusk."

Comment:

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, NO_3, N_2O_5, biogenic VOCs, etc are not known from the measurements, one can only conclude that *at the surface* the daytime and night-time rates of NOx oxidation are comparable. As for total NOx oxidation occurring 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 night-time chemistry given that surface measurements are less representative of the air than daytime surface measurements are.

Reply:

Whilst it is true that surface measurements of species such as NO_3 and N_2O_5 may not be representative of the entire boundary layer, the calculations of NOx loss involve only NO_2, O_3 and calculated OH (basically also dependent on O_3). Possibly only O_3 would be expected to have very strong vertical gradients. Nonetheless, we add the limiting statement "As vertical profiles of NO_2 / O_3 etc were not measured, our conclusion applies only to the surface."

Comment:

lines 20-24. Again, the authors' sentence is dead-on: Oxidation of biogenic VOCs by NO_3 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).

Reply:

None required

Minor Comment:

pg 5, line 10 – "fine" weather – meaning is not clear

Reply:

fine weather has been replaced with "warm, sunny periods…"

Minor Comment:

pg 5, line 26 – non-conductive tygon tubing was used? Usually metal tubing is used to eliminate electrostatic losses.

Reply:

Tygon is flexible, has a mean surface electric field close to zero and is commonly used for aerosol sampling.

Minor Comment:

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"?).

Reply:

Perhaps more important than the issues of broad-band or single–mode is the information that the coupling between the laser modes and the cavity modes is optimised by current modulation- The following text has been added. The laser current was modulated to broaden the laser-spectral bandwidth and improve the signal/noise ratio of the cavity emission, without loss of overlap with the broad NO_3 spectrum (Schuster et al. 2009).

Minor Comment:
pg 20, line 19-22- I don't understand this sentence.
Reply:
The sentence has been rewritten: R7b dominated the homogeneous gas-phase loss of N_2O_5 during the whole campaign with the ratio $k_{7b}[H_2O]^2$ / $k_{7a}[H_2O]$ as large as ≈ 2.5 at RH = 100 %. R7a is more important only when RH was less than ≈ 30 %.

Minor Comment:
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.

Reply:
The x-axes have been amended as suggested

Typographical Corrections:
pg 2 line 20: VOCs, not VOC   done
pg 2 line 31: remove "on"   done
pg 13, line 27 – 0.5 not 0,5   done
pg 16, line 21 – "reduce", not "reducing"   done
pg 16, line 23, rewrite as "…following sunset, however, does not …" done
pg 9, lines 26-27 – are these uncertainties 1 sigma or 2 sigma? information inserted
pg 10, lines 17-21 –detection limits defined – signal-to-noise = 2? The detection limits are based on reprodicibility of zero signals, hence quoting a S/N is not helpful. The text has been amended to reflect this.

pg 18, line 6 – maximum, not "max" done
pg 21, line 19 – rewrite as "…increases the NO2 oxidation rate".   done
pg 23, line 13 – rewrite as "…NO3 indicate an important…" (not "and") done
pg 24,line 1 – rewrite: not "…found to be direct…" but "…inferred to be direct". done