Referee 2

Comment:

This nicely and very clearly written paper describes measurements of nocturnal nitrogen oxides (NO, NO2, NO3, and N2O5) plus ozone, water vapour, and aerosol surface area at a mountainous location in the Taunus region near Frankfurt/Main. The major findings are significant in that include convincing evidence against the currently recommended rate coefficients for homogeneous hydrolysis of N2O5. I recommend acceptance of this paper after my (minor, I hope) comments below have been addressed.

Reply:

None required

Comment:

pg 1, lines 18-19. Replace "A steady-state lifetime analysis showed that the nocturnal NOx were generally dominated by reaction of NO3 with volatile organic compounds..." with "A steady-state lifetime analysis is consistent with the nocturnal NOx generally dominated by reaction of NO_3 with volatile organic compounds...". In my opinion, a steady state analysis cannot "show" a cause; it can only "show" magnitudes of loss rates, and be consistent with an explanation.

Reply:

Agreed. The text now reads "A steady-state lifetime analysis is consistent with the loss of nocturnal NO*x* being dominated by the reaction of NO_3 with volatile organic compounds in this forested region…."

Comment:

pg 1, line 28. "... which is absent (or present ...". Consider rephrasing. Presence and absence are like black and white or being pregnant – it either is or is not.

Reply:

The text now reads: "…..which is present at much reduced levels during the night."

Comment:

pg 2, lines 8-10. Please state what rate coefficients were used (i.e., NASA-JPL or IUPAC).

Reply:

At this stage of the discussion no rate coefficients are mentioned, the reactions are simply listed. No need to cite evaluations of kinetic data at this point.

Comment:

pg 2, line 24. Heterogeneous uptake of N2O5 not only produces nitrate but also $ClNO_2$ (Behnke, W., et al. (1997), Production and decay of $ClNO_2$, from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments, Journal of Geophysical Research-Atmospheres, 102(D3), 3795-3804, and Osthoff, H. D., et al. (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, Nature Geoscience, 1(5), 324-328). A fellow scientist, who is an expert on aerosol composition, transport and aging, told me at a conference that a group in Mainz claimed to have seen evidence for long-range transport of marine aerosol to the study region (near Mainz). I unfortunately do not remember who she had been talking to. Since I was born and grew up in Frankfurt/Main, I at first chuckled at the notion that the region would be strongly influenced by marine air, but then again, who is to argue with aerosol composition measurements. I was wondering what the authors' thoughts are on this, and if you could please add a short statement on whether the authors think chloride, from either marine or anthropogenic sources, could have been present in the aerosol phase at the Kleiner Feldberg location.

Reply:

The reviewer is probably referring to the work of Vester et al (Atmos. Env. 41, 2007, 6102-6115) who measured sea-salt in the coarse aerosol fraction (> 1 μm) in Mainz. That N_2O_5 can react with halide containing aqueous particles to release photochemically active halogens is indeed well known, having been first discovered in the laboratory more than two decades ago (Finlayson-Pitts et al., Nature 337, 241-244, 1989). The link to the present work seems, however, tenuous. Firstly, the fraction of aerosol above 1 μm was low (see text) and secondly, Hysplit back trajectories for the early part of the campaign suggest that the air mass spent about 5 days over land in the free troposphere (North-eastern Europe) before reaching the Kleiner Feldberg. It is unlikely that a significant fraction of (super-micron) sea-salt aerosol would survive transport over such a long period.

Comment:

line 27. "... partitioning ... between the NOx ... and NOy families ..." Consider rephrasing as what happens is not really partitioning between NOx and NOy (NOy includes NOx, so NOx can't partition to NOy); suggestion: partitioning between various forms of NOy, or NOx to NOz? Also, please define NOy, and see comment on page 21.

Reply:

The text has been modified and now defines NO*z* as NO*y* – NO*x*. "The sequential oxidation of NO to NO_2 to NO_3 to N_2O_5 and finally to particulate nitrate thus represents a change in the partitioning of nitrogen oxides between the NO*x* (NO + NO_2) and NOz families, where NOz is the sum of all nitrogen oxides (*NOy*) minus NO*x*. Note that N_2O_5 contributes twice to NO*y* as it contains two N-atoms. The heterogeneous loss of N_2O_5 or NO_3 also modifies the partitioning of NO*y* between the gas and particulate phases."

Comment:

pg 3, line 22. Give a reference for this equation. Suggestion: Fuchs, N. A., and A. G. Stugnin (1970), Highly Dispersed Aerosols, Ann Arbor, MI.

Reply:

The equation referred to derives directly from simply gas-kinetic theory. Fuchs and Sutugin is usually cited in the context of their more complex expression which accounts for mass transport limitations to the uptake (which we ignore here).

Comment:

pg 3, line 24 - pg 4, line 5. Homogeneous reaction of N_2O_5 with water vapour. The magnitudes of the rate coefficients for this reaction have been called into question by several field studies, e.g., Brown, S. S., et al. (2009), Reactive uptake coefficients for N_2O_5 determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterisations, J. Geophys. Res., 114(D00), D00F10, doi:10.1029/2008JD011679, and Brown, S. S., et al. (2006), Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311(5757), 67-70. Results presented in these two studies suggest that the rate coefficients for homogeneous are likely too large (as was concluded later in this manuscript). Please add a comment to this effect in the introduction.

Reply:

The two Brown et al papers were already cited in this context. However, as requested, a comment has been added on page 3-4. "The available kinetic data (Atkinson, 2004) indicates a gas-phase reaction between N_2O_5 and H_2O which contains terms both linear and quadratic in H_2O concentration…….. Recent field measurements (Brown et al. 2006; Brown et al. 2009) have cast doubt on the accuracy of the laboratory studies, suggesting that the reaction proceeds significantly slower (see later).

Comment: :

pg 6, line 10. Please clarify what distance the 70 cm refers to (distance between ringdown mirrors, only the Teflon section, etc.).

Reply:

This was described in detail in Schuster et al. 70 cm refers to the distance between the mirrors. To avoid ambiguity we now write: The NO_3 cavity (PFA tubing, resonator length 70 cm, volume 79 cm^3) was operated close to ambient temperature, whereas the summed concentration of NO_3 + N_2O_5 was measured in a Teflon coated Pyrex cavity (resonator length 70 cm, volume 165 cm^3) heated to 80 °C…….

Comment:

pg 7, line 4 (and page 9, line 26). In the heated cell, N_2O_5 is measured as NO_3 at 85 C. Neither the Yokelson nor the Orphal study measured the NO_3 absorption cross-section in this temperature range. Please state what cross-section was used to determine N_2O_5. A useful reference might be Osthoff, H. D., et al. (2007), Temperature dependence of the NO_3 absorption cross-section above 298 K and determination of the equilibrium constant for NO_3 + NO_2 <-> N_2O_5 at atmospherically relevant conditions, Phys. Chem. Chem. Phys., 9(43), 5785-5793.

Reply:

True. In fact the cross-sections were taken from the parameters given by Orphal, which reproduce the temperature dependent datasets of Yokelson (200-298 K) and Osthoff (298 – 388 K). The value of the cross section used at 85 °C was 1.73×10^{-17} cm^2 $molecule^{-1}$, which agrees perfectly with the parameterisation given by Osthoff. The text now reads: Temperature dependent values of σ_{NO3} have been determined by Yokelson et al., (1994) and Osthoff et al., (2007). The parameterisations of Orphal et al., (2003) and Osthoff et al., (2007) both give a value of 1.73×10^{-17} cm^2 $molecule^{-1}$ at the peak of the 662 nm band at 85 °C. This value was convoluted with the laser emission profile to obtain effective cross sections as described previously (Schuster et al., 2009).

Comment:

page 10, lines 2-3. Can you please comment on whether the blue light converter converts either NO_3 or N_2O_5 to NO, and whether that constitutes an interference/bias in the NO_2 measurement?

Reply:

The blue light converter emits at wavelengths close to 395 nm where neither NO_3 nor N_2O_5 absorb light strongly. Based on known (IUPAC) relative cross sections for NO_2 and N_2O_5 (and the known conversion efficiency for NO_2) we can estimate that less than 0.1 % of any

N_2O_5 would be converted photolytically. For NO_3, the cross-section appears to be close to zero at 395 nm.

Comment:
page 11, lines 4-6. Please state what typical aerosol surface area densities were observed, as the area is the more critical parameter rather than particle count.
Reply:
This information is plotted in Figure 3. An indicatory value of 1×10^{-6} cm^2 cm^{-3} is mentioned at this position in the text. Typical night-time particle concentrations as measured by the SMPS were 2000-5000 particle cm^{-3} with a bi-modal distribution (maxima at ≈ 35 and 120 nm) with most surface area (typically 10^{-6} cm^2 cm^{-3}) contained in particles of radius ≈ 200-250 nm.

Comment:
page 15, line 24. Starting with: "poor agreement", consider starting a new subsection with a heading "inlet artifacts" or something similar.
Reply:
We consider it unnecessary to add an extra section to accommodate the single paragraph which follows.

Comment:
page 19, line 11. Please replace the word "figure" with "number" (I was wondering for a moment why the graph would shrink ...).
Reply:
We figure that's why Figures have large Fs and numbers are figures with small Fs. We'll change figure to number !

Comment:
page 21, lines 15 and 17 (E12). This definition of NOx is inconsistent with the definition of NOx on page 2, line 27. Consider labelling the "NOx" on page 21 as "Nocturnal NOx" and the NOx on page 2 as "daytime NOx". Also, why are PAN and $ClNO_2$ not included in F(NOx)?
Reply:
This has been tidied up and we not longer refer to NO*x*. Halogenated nitrogen oxides are unlikely to be significant at this site, PAN was not measured. The sentence now reads: In the absence of NO, the fraction of nitrogen oxides (*F*), which is present in reactive form (i.e. as NO_3 or N_2O_5) at night can be simply expressed as……..(E12)……..This expression ignores longer lived NO*x* reservoir species such as HNO_3, PAN or halogenated nitrogen oxides, which, unlike NO_3 and N_2O_5 are not in rapid equilibrium with NO_2. The contribution of NO_3 and N_2O_5 to NO*y* (which would include trace gases such as HNO_3 and PAN) is, of course smaller.

Comment:
line 27. There is also a minor NO_3 photolysis channel to NO. Orlando, J. J., et al. (1993), Quantum Yields for NO_3 Photolysis between 570 and 635 nm, J. Phys. Chem., 97(42), 10996-11000. Please change “back to NO_2” to “back to NO_2 and NO”.
Reply:
The sentence has been changed to read “NO_3 and N_2O_5 remaining at the end of the night are rapidly converted photolytically / thermally back to NO_2 (and, less importantly NO) at dawn, hence the rapid reduction in *F* at circa 06:00 on the 14th.”

Comment:
pg 25 line 29. article number is missing from this citation.
pg 26, line 28. article number is missing from this citation.
pg 27, line 13. article number is missing from this citation.
Reply:
Corrections made

Comment:
pg 28, lines 14-23. I am not sure where/why evaluation #14 was cited. Please update and cite only #15.
Reply:
The 2003 and 2006 JPL documents recommend slightly different values even though the same kinetic database was available (see text on page 14/15).

Comment:
line 25. Add subscripts to NO_3 and N_2O_5.
Reply:
Will be done.

Comment:
pg 31, Figure 2 caption. Looking at the Figure, it is unclear where the sample flow exits the sample cavities. Please add a sentence to the caption, or modify the Figure.
Reply:
The caption has been modified: Gas was sampled from the centre of the tube to the NO_3 / N_2O_5 and NO / NO_2 / O_3 instruments and exits close to the cavity mirrors as described in detail by Schuster et al (2009).

Comment:
pg 33, Figure 4. [NO_2] increases by about 500 ppt after sunrise; before sunrise, there were 60 ppt of N2O5 and 20 ppt of NO3, which would yield about _140 ppt of NOx. Can you please comment in the text (e.g., at the bottom of page 12) as to where you think the extra NOx came from? The constant ozone mixing ratio suggests that boundary layer mixing / vertical transport at that time would have been minimal.

Reply:
This phenomenon (a greater increase in NO_2 after sunrise that explicable by the photolysis induced conversion of NO_3 and N_2O_5 at dawn) was observed on several (but not all) mornings. The following text has been offered as an explanation. “The direct photolysis of NO_3 depletes N_2O_5 via the equilibrium (R2, R-2) and also releases NO to further remove NO_3. NO is also generated in the photolysis of NO_2 at roughly the same time, and both NO_3 and N_2O_5 return to below detection limit within 1 hour. During this period, NO_2 and NO are observed to increase by 450 ppt and 20 ppt, respectively. The amount of NO_2 released from the degradation of NO_3 and N_2O_5 can be estimated as 2 x $[N_2O_5]$ + $[NO_3]$, which, for the data in Figure 4, amounts to ~ 140 ppt. This accounts for only ~ 30 % of the total increase in NO*x* directly after sunrise. The extra NO_x observed cannot be from degradation of the expected major long lived reservoir species (e.g. HNO_3 and PAN). HONO photolysis may however play a role. Assuming 300 ppt HONO at dawn and an approximate, average value of J-HONO ~ 1×10^{-4} s^{-1} over a 40 minute period (Kraus and Hofzumahaus, 1998) would result in the release of ~ 70 ppt of NO. A further possibility is upslope winds (caused by warming of the easterly side of the mountain as the sun rose) bringing fresh NO*x* to the site. On one morning (10th of May) an excess release of NO*x* was not observed, and the generated amounts of NO and NO_2 agreed with that released from NO_3 and N_2O_5. As the 10th of May 2008 was a Saturday, this may indicate a weekend effect, with upslope winds bringing less locally emitted pollution from early morning commuter traffic.”

Comment:
pg 35, Figure 6. Please state in the Figure caption what the dashed and solid black lines are conveying.
Reply:
The following text has been added to the caption: “The solid black lines represent the expected slopes (calculated using literature values for K_2) at the extremes of the small temperature range covered, and should therefore encompass all the data. The dotted black lines use the values of K_2 at the outer bounds of the recommended uncertainty in this parameter.”
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Comment:
pg 38, Figure 9. The red and blue line are identified as homogeneous and heterogeneous loss of N2O5, but are defined differently in the text (page 18, line 21).
Reply:
The text on page 18, line 21 was incorrect. The blue line represents heterogeneous loss.

Comment:
The lifetime of NO_3 approaches the rate of photolysis after sunrise. Perhaps photolysis could be added to the figure?
Reply:
Adding photolysis (presumably as J-NO_3) to the picture would not help very much. The NO_3 loss rate is determined also by the rate at which N_2O_5 thermally dissociates to NO_2 and NO_3 at the prevalent temperatures and not only with it’s own J-value.

Comment:
On the y-axis, please use U.S. notation (decimals and commas).
Reply:
Figure 9 has been corrected (as have Figures 10 and 11 for the same reason)

Comment:
I am not sure I "buy" the explanation of the gray trace. Consider rephrasing the explanation in the main text. At the levels of NO3 observed here, both pinene and isoprene are rapidly oxidized by ozone and NO3. Unless there was a continuous weak nocturnal source of these compounds (I don't think there is), I'd expect their concentrations to approach zero rapidly. A more likely explanation is that there are other, unsaturated, hydrocarbons present that react with NO3 and ozone more sluggishly than either alpha-pinene or isoprene. The net result would then be a curve similar to the grey line shown.
Reply:
As stated in the text, previous measurements of biogenics at this site showed that both isoprene and terpene concentrations decreased slowly after sundown, only returning to baseline levels in the early hours of the next morning. In the absence of other measurements, we cannot rule out that other (less reactive) hydrocarbons are present and contribute to NO_3 removal. We have added the text: "In the absence of simultaneous measurements of biogenics or other reactive traces gases (e.g. unsaturated hydrocarbons) that could react with NO_3, the above discussion about the main NO_3 loss reactions remains speculative."

Comment:
pg 39, Figure 10. I believe the y-axis title is incorrect (should it be lifetime, or "tau" ?). Also, the labels for the blue and black line are unnecessarily confusing as one has to read the text on page 20 to understand the rationale behind those numbers. Since there is plenty of white space available on the Figure, consider labeling the blue line with something like "khomo based on Wahner et al., 1998". I am also not sure what the blue line is supposed to represent – is equivalency justified? Consider removing the blue line, as I find it very confusing.
Reply:
Sometimes the y-axis is labelled 1/tau in this kind of analysis. This is the same as *f*ss as described by equation E11. Some text has been added to the figure caption which hopefully helps explain what the blue and red lines represent.:"The blue line represents equivalency of the direct and indirect losses of NO_3 (intercept = slope = 1.6×10^{-3} s^{-1}). The difference in slope between this and the red line serves to indicate the dominance of direct loss over indirect loss.

Comment:
Figure 11. If one integrates $k[NO_2][O_3]$, one can estimate F(NOx) plus the products of NO_3 and N_2O_5 reactions (presumably mostly HNO3, but also organic nitrates). Consider adding integral $k[NO_2][O_3]dt$ to (at least) the top panel.
Reply:
Done. The results show that circa 1.5 ppb of NO*x* are consumed by $NO_2 + O_3$ during the night. Text has been added to describe this: The integrated loss of NO_2 (calculated from the NO_2 and O_3 concentrations and the rate coefficient k_1) is also displayed for the night of 13th-14th May in this Figure. By the end of the night, about 1.5 ppb of NO_2 have been converted via NO_3 and N_2O_5 to gas-phase and particle phase products.

Comment:
Figure 12. The title of this Figure is misleading as I was expecting loss rates, not mixing ratios, to be shown. Since [OH] was calculated using Ehhalt's parameterization, consider plotting k8[NO_2][OH] and the results of (E13) instead of showing the mixing ratios of NO_2 and N_2O_5.

Reply:
This part has been rewritten. OH is now calculated at each time step and the flux of NO_2 (in ppb /s) via the daytime and night-time loss reactions is plotted over a several day period of the campaign.