We thank Steven Brown for these constructive and helpful comments. Our replies (in blue/red) to each comment (in black) are listed below. Red text indicates changes to the manuscript.

Referee 1 (Steven Brown)

General Comment

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 NO_3 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.

We thank the reviewer for this positive assessment of our manuscript.

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.

As the Kleiner Feldberg is part of a mountain range, the altitude of the surrounding area depends on direction and distance from the summit.. The closest cities are at altitudes of about 120 ± 50 m. We add this information on page 4 and refer to a previous publication (Crowley et al, 2010) in which a topographical map was published.

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

There were, in total, six measurements of O_3. Some were research instruments and some were monitoring instruments with infrequent calibration and this may be the cause of some “disagreement”. We now suggest that the agreement was good, rather than excellent.

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

Yes, it should have been ethene. Corrected

Page 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?

We have added the text: Aerosol was sampled at ambient RH and no correction was applied 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.

Wind rose added in 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.

As expected, the data show that the high NO*x* from the urban sector was associated with the largest mixing ratios of anthrogogenic hydrocarbons. We now write:
High NO*x* levels measured in this sector were associated with the highest levels of anthropogenic hydrocarbons such as e.g. toluene.

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).

We now write: Precipitation periods were associated with [NO_3] and [N_2O_5] below the detection limit, which is likely a result of N_2O_5 uptake to droplets.

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.

This is true. We now write: During the period from 19:00 to 21:00 the lifetime of NO_3 attributable to reaction with NO, $\tau(NO)$, is greater than $\tau_{ss}(NO_3)$, which may be due both to non-acquisition of steady state (for the first hour or so) and a contribution of other loss processes.

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.

We agree. The text now reads: This expression is based on laboratory studies and results in a value at 283 K of ~2 × 10^{-2} which is larger than uptake coefficients obtained by analysis of both laboratory and field data in which the particle is not purely inorganic (Brown and Stutz, 2012). During periods when the NO_3 lifetime is long (e.g. $\tau_{ss}(NO_3) > 2000$ s or $L_{ss}(NO_3) < 5 \times 10^{-4}$ s^{-1}) as on the second period of the night of the 30.08 (lower panel), when using the γ parameterisation above, the losses of N_2O_5 to particles can account entirely for the observed lifetimes, or even exceed the steady state reactivity, which may be the result of using a high value for γ.

Page 14, 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?

The sentence was misleading and should have referred to the gradient in the NO3 lifetime rather than its variability. We now write:

Close examination of the NO_3 lifetime on these nights reveals an especially strong gradient, with $\tau_{ss}(NO_3)$ values increasing by e.g. 500 to 600 % over the course of an hour. Simultaneously, $\tau_{ss}(N_2O_5)$ values (not shown) increase by 200 %. The smaller increase in $\tau_{ss}(N_2O_5)$ is due to a simultaneous decrease of $[NO_2]$ by 50 % thus shifting the equilibrium towards NO_3. The large gradient in $\tau_{ss}(NO_3)$ cannot be attributed to a decrease in the mixing ratios of reactive trace gases, which were much less variable (see above). We therefore consider the possibility that the long lifetimes observed on these nights are related to sampling air masses from a low-lying residual layer (i.e. from above a particulary shallow nocturnal boundary layer) which, especially at low wind speeds, is decoupled from ground emissions of NOx and VOCs, allowing NO_3 and N_2O_5 to build up to higher levels and would also help to explain explain the lack of dependence on wind direction.

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?

The height difference between the summit of the mountain and the surrounding, countryside and cities is about 700m, i.e. higher than the nocturnal boundary layer of the surrounding areas. As the reviewer states, the NBL will follow, to some extent the topography so that a variable height NBL may be expected and which will depend on wind-flow and terrain structure. Essentially, the “low-lying residual layer” is a consequence of a very shallow NBL. We now qualify the statement related to sampling air from a low-lying residual layer in the following manner:

We therefore consider the possibility that the long lifetimes observed on these nights are related to sampling air masses from a low-lying residual layer (i.e. from above a particulary shallow nocturnal boundary layer) which, especially at low wind speeds, is decoupled from ground emissions of NOx and VOCs, allowing NO_3 and N_2O_5 to build up to higher levels and would also help to explain explain the lack of dependence on wind direction.

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

Yes. This has been corrected.

Page 15, line 32-33. Could the gradient be due to downward mixing of NO3 or N_2O_5 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.

This is true. However, as the NO3 production term does not change with height, changes in concentration are still related to the loss term for the sampled air-mass irrespective of whether the air sampled at any one DOAS light-path is influenced by mixing from above or not. i.e. if NO3 exists at further elevated concentrations above the highest DOAS light path, this is still a result of an extended lifetime aloft.

Page 16, lines 21-29. The argument regarding local BVOC emissions oxidized by NO_3 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?

There was no evidence of a significant reduction in NO3 to N2O5 ratio. However, the time required for NO2, NO3 and N2O5 to acquire equilibrium is the inverse sum of the forward and back, first-order rate constants i.e. 1/(kb + kf[NO2]). At 800 mbar and 285, kb is ~0.008 s-1 and kf ~ 1.2e-12. Taking a low value of [NO2] of 1 ppb then results in a relaxation time (to equilibrium) of 10 s. i.e. equilibrium is reached on a much shorter time scale than steady-state and will generally hold unless NO3 is lost very locally (e.g. in the inlet) or at low NO2 and low temperatures.