

# ***Interactive comment on “Chemical and meteorological influences on the lifetime of NO<sub>3</sub> at a semirural mountain site during “PARADE”” by N. Sobanski et al.***

## **Anonymous Referee #2**

Received and published: 26 February 2016

### General comments:

This well written manuscript by Sobanski et al. outlines a comprehensive study of NO<sub>3</sub> mixing ratios and lifetimes in the context of a field campaign (referred to by the acronym PARADE) in the German mountain region, Taunus, during Summer 2011. The campaign was equipped with a broad range of instrumentation to detect most atmospheric species (as well as meteorological data) that are relevant for NO<sub>3</sub> generation and destruction in order to interpret the key findings, which included unusually large and also highly variable NO<sub>3</sub> mixing ratios, and long lifetimes (up to 1 hr and more). The general discussion uses a steady state model which is based on the most relevant NO<sub>3</sub> production reaction at nighttime (NO<sub>2</sub> + O<sub>3</sub>). The manuscript also considered none-

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steady state conditions and contains novel aspects such as the influence of Criegee intermediates on the NO<sub>3</sub> production rates through reactions with NO<sub>2</sub>; also the reaction of OH and HNO<sub>3</sub> was considered. Loss mechanisms of NO<sub>3</sub> are discussed based on reaction with NO and volatile organic compounds (VOC, biogenic and anthropogenic). Data are additionally interpreted on basis of meteorological conditions and in this context it is argued that the high NO<sub>3</sub> concentration on some occasions are likely to be due to a “low lying residual layer” over the boundary layer with a significant positive NO<sub>3</sub> concentration altitude gradient.

Key instruments are (i) a cavity ring down spectrometer (CRDS) for the detection of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (in a heated channel) as well as (ii) a 4-beam long-path differential optical absorption spectrometer (LP-DOAS). A comparison of the corresponding data is also included in the paper mostly to argue for the residual layer hypothesis.

Generally, the manuscript is well structured and there is a good flow of the text. The discussion of data dwells on the most significant events and atmospheric scenarios during the 3 week campaign and the items that require discussion and explanation have been carefully selected. Based on the methodology the data inspire confidence and the majority of conclusions are supported by arguments that are anchored in the data, however some discrepancies remain.

This manuscript clearly merits publication in ACP, however, it is recommended that the comments and minor corrections listed below are considered prior to acceptance.

Specific comments and observations:

Section 1: Page 1&2: The introduction is giving a good overview of the most relevant atmospheric reactions that influence the NO<sub>3</sub> concentration. This part of the manuscript would however benefit from more quantitative data on the reaction rates as they are known in the literature (IUPAC and Atkinson et al.). Reaction rates could be incorporated in the R-equations or presented in form of a table and would provide the reader with kinetic information on the relevance of each reaction for the NO<sub>3</sub> chemistry.

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Section 2: The information on the instrumentation specification is brief, as most of the experimental setup utilized during PARADE have been published before. However, the reader would benefit from some more information on the key instruments. Page 5: What zeroing/calibration procedures for the CRDS instruments were applied? Page 5: The description of the NO<sub>2</sub> instrument (Page 5) is particularly short (Thieser et al. 2015).

Page 5 & 6: The literature used for the cross-sections for NO<sub>3</sub> and NO<sub>2</sub> does not seem to be mentioned (neither for the CRDS nor the LP-DOAS setups).

Page 5, Line 24: What does “quasi online” mean?

Page 6: An overall uncertainty of the LP-DOAS setup of 10% for NO<sub>3</sub> is stated. The cross-section uncertainty is of that order. The error evaluation seems to be too optimistic.

Section 3: Page 9: Please check (Eq4). If L is a loss rate constant in units of [s<sup>-1</sup>] the power of “-1” seems out of place.

Page 9, Line24: What does the index ‘DER’ stand for?

Page 9, Line30: Why is it meaningful to state an average value of the steady state lifetime, if the night to night variability is high? What is meant by values (plural)?

Page 10, Line 8: “Because the error made by assuming steady state is generally small . . .”, can this be quantified?

Page 11, Line 26: What is meant by “weaker day/night cycle”?

Page 12, Line25: What is meant by “these time scales”?

Page 13: The arguments in Section 3.3.4 are well laid out and appear conclusive; nevertheless the section would benefit from explicit mentioning of reaction rates (e.g. for sCl +NO<sub>2</sub>; also see comment above).

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Page 13 (bottom part): Even though sCI mixing ratios of  $\sim 4$  pptv seem clearly too high, the authors outline an interesting hypothesis that merits further research.

Page 14: What is meant by “low-lying residual layer”? What constitutes this layer and how is it contrasted to the boundary layer, as the measurements were taken at some height of 825 m ASL.

Page 15: Fig. S2 in the main text would be really helpful for the discussion of the observed NO<sub>3</sub> vertical concentration gradient. The altitudes of the sender/receiver units and retro-reflectors of the LP-DOAS setups in comparison to the altitude of the CRDS instrument should be repeated here for the benefit of the reader.

Page 15: Is there any evidence for mixing of the layers when comparing the four DOAS directions and different heights probed during the measurements?

Page 16, Line 16: How can be assumed that there are no significant NO<sub>3</sub> gradients in the proposed “residual layer”. Again, is there evidence for mixing owing to convective currents in the time series of the data on the relevant days?

Page 16, Line 7-9: Does Fig 12 (left panel) really allow this statement? Can the statement be underpinned by quantitative information on altitude dependence, and the term “closer” through R-values for example.

Page 16: The last paragraph in section 3.3.6 seems to be better placed in the previous section on the discussion of the residual layer and not in the comparison of CRDS and LP-DOAS.

Generally, some material from the supplementary material would have been helpful in the main text; notably Fig S1, S2, S4 and S8. S1 and S2 are important to get an idea of the topography in the vicinity of the measurement site. Especially in the context of section 3.3.5 and 3.3.6 these figures are helpful.

Technical corrections:

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In many places mixing ratios are not expressed by volume. Examples are: P5,L23,L26,L27; P8, L15;P14,L19; P16,L4,L11.

Page 3, Line 23: State the month(s) in 2011 explicitly here.

Page 4, Line 13: "Fig. S1" should be highlighted.

Page 6, Line 7: "broadbanding"? Is that the term to use? Moreover, the information in this line is redundant and was mentioned before on page 3.

Page 9, L26: In Eq 5 the minus signs in the denominator are hardly discernible.

Page 11, Line 6: IUPAC should get a reference.

Page 11, Line 29: "Fig. 7" should be highlighted.

Fig. 1 & 2: There is a discrepancy on the third cold front arrival time (third blue vertical line). It may be better to merge Figs. 1 & 2 into one figure with six panels. If this could be done without loss of plot quality, this would help the reader.

Fig. 5 Units of seconds are missing on the vertical axis of the upper panel.

Fig 6. The red and black trace refer to the left axis and radiation (in yellow) to the right axis. This is confusing, as the other panels are colour coded.

Fig 7. The lower panel does not seem to show LSUM, LNO. The stated time grid appears inconsistent with the dots in the figure (e.g. 30 min for LVOCS).

Page 22, Lines 2&3: "...of 4 the..." and "...at the 5 Großer Feldberg."?

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