

Interactive comment on “Assessment of the NO-NO₂-O₃ photostationary state applicability on long-term measurements at the GAW global station Hohenpeissenberg, Germany” by K. Mannschreck et al.

Anonymous Referee #1

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General Comments

This paper describes the deviation of long-term measurements of NO, NO₂, O₃ and JNO₂ at Hohenpeissenberg from photostationary state, and explores the reasons for this deviation. The study indicates that photostationary state (as defined based on our current understanding of photochemistry) is not achieved about 70-85% of the time, and attributes some of this to local effects, largely connected with the location of the site and the proximity of the surrounding forest. The paper directly tackles an important issue noted in many previous photochemical studies - the deviation from photostationary state and consequent overestimation of peroxy radical concentrations

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(which highlights problems in our current understanding of tropospheric chemistry), describes an interesting and novel analysis of the discrepancies due to local impacts, and provides some valuable conclusions which should allow better determination of unknown oxidative processes in the troposphere in future.

The paper tackles important scientific issues within the scope of ACP, gives full credit to previous work in the field, and is generally well written and logically structured. The only significant recommendation I have for improvement would be the addition of a brief discussion of the implications of the findings here for analysis of measurement data using PSS techniques, and suggestions for siting measurement stations (or instrument inlets) to minimize possible problems associated with non-achievement of PSS conditions. I believe that this would provide valuable additional conclusions and would strengthen the paper significantly. After making these minor changes, I believe that the paper will be acceptable for publication.

Specific Comments

The authors might consider rearranging the title to "Assessment of the applicability of NO-NO₂-O₃ photostationary state to long-term measurements at the Hohenpeisenberg GAW station in Germany".

Page 2004, line 6: The abstract defines PSS as $\theta=1$, states that PSS was reached on 13-32% of cases, and then describes median values in the range 2.5-5.7. However, the 13-32% fraction is based on θ_{ext} , while the medians are based on θ . This is inconsistent, and is somewhat confusing - the θ and θ_{ext} terms are different for all cases where HO₂+RO₂ is greater than zero (i.e., all cases here). The abstract needs to be rephrased here, either to differentiate the terms clearly, or to remove direct references to θ (which is not defined until the main body of the text anyway).

Page 2005, line 17: "Theta is equal to 1 when...." it would be worth emphasizing immediately here that this is a relatively rare occurrence that may be limited to very polluted conditions; over most parts of the troposphere the θ_{ext} term, introduced on the

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next page, is generally more useful. A minor rearrangement of the last paragraph of page 2005 and first paragraph of page 2006 might help make this clearer.

Page 2006, line 13: The authors might also note a recent paper on this topic by Yang et al. [2004], which draws attention not only to the deviations from PSS, but to possible biases at low NO_x levels that may be relevant to the analysis on page 2015.

Page 2008: It would be helpful to include a small sketch or cartoon of the location of the old and new buildings with respect to the forest and slope. This would make interpretation of all the distance and angular information given much simpler.

Page 2012, line 4: Measurements of CO are not mentioned before this. It would be helpful either to describe the measurements (very briefly) in Section 2.2, or to point the reader to somewhere they are described in more detail (perhaps Handisides et al. [2003]?).

Page 2012, line 25: The discussion here (concerning Figs 3 and 4) changes quietly from θ to θ_{ext} . The two different approaches need to be more clearly distinguished here - both are useful, but they provide slightly different information. The former indicates all deviation from PSS, while the latter points to specific problems in our understanding - notably in chemistry and in local influences.

Page 2013, footnote: The origin of the linear dependence of RO₂ on JNO₂ isn't explained here (in clean conditions a square root dependence might be expected). It would be helpful to demonstrate that this is indeed the case, or to point the reader to somewhere this relationship is explored further (e.g., Zanis et al. [1999]).

Page 2015, line 2: The Sector A/Sector B analysis here is nice, but it would be helpful to indicate the sectors on Figures 4 and 6 so that readers can see clearly which is which. One way of doing this might be to highlight the outer circle in each polar plot with a bold line over the angular ranges of interest (other ways might also be acceptable).

Page 2016, line 1: A reference for the 60-80% NO₂ fraction would be useful.

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Page 2016: The possible contributions of biogenic hydrocarbons and aerosol from forest sources should also be acknowledged here. These may provide sinks of NO or O₃ which extend above the forest canopy, and which are thus less sensitive to sampling height or wind direction.

Page 2017, Section 4.1: It would be helpful to remind the reader again here that the forest is largely coniferous, and that little seasonal variation in the affect would be expected (at least, not from photolysis- reduction alone, though the time taken to restore PSS may still vary).

Page 2021: It would be very useful to conclude section 4 with a brief discussion of the further implications of these results, particularly regarding the local impacts on PSS. Could PSS box-model analyses of measurements be improved by taking these affects into account somehow? What are the authors recommendations regarding the selection of new measurement sites to minimize these local effects? The wider implications of the results are mentioned in a general way on Page 2018, lines 4-9, but specific suggestions would be very valuable.

Page 2029: The units of CO and NO_x should be stated in the caption (it would be helpful if they were both presented in ppb).

Page 1034: The "x-axis" is technically the "radial axis" on a polar plot.

Technical corrections

The English in the paper is generally good, but there are a few places where the phrasing is a little awkward. The following are suggestions for removing some of the more notable grammatical problems and typos.

Abstract, line 5: "In average PSS..." -> "On average, PSS..."

Abstract, line 19: "in a three week" -> "during a three-week"

Page 2007, line 3: "are" -> "have been"

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Page 2007, line 24: "elevates" -> "rises"; "over" -> "above"

Page 2007, line 25: "is operated" -> "has been operated"

Page 2008, line 2: "advected" -> "influenced" (or perhaps "affected"?)

Page 2008, line 14: "north-east" -> "the northeast"

Page 2008, line 15: "in 10 km"/"in 80 km" -> "at 10 km"/"at 80 km"

Page 2008, line 15: "1 Mio" -> "1 million"

Page 2009, line 2: "apart" -> "away"

Page 2009, line 6: "ground-based" -> "at the ground"

Page 2009, line 8: "on top" -> "at the top"

Page 2009, line 17: "in regular" -> "at regular"

Page 2009, line 25: "specifically" -> "quantitatively" (?)

Page 2012, line 17: "in a distance" -> "at a distance"

Page 2013, line 20: "Hauglustine" -> "Hauglustaine"

Page 2015, line 3: "intersections of" -> "common to" (?)

Page 2019, line 26: "so it can not" -> "and so cannot"

Page 2021, line 7: "which extent" -> "what extent"

Page 2021, line 20: "was higher" -> "were higher"

Page 2021, line 25: "of a four year period" -> "over a four-year period"

References

Yang, J., R. E. Honrath, M. C. Peterson, D. D. Parrish, and M. Warshawsky, Photostationary state deviation: Estimated peroxy radicals and their implications for HOx and

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ozone photochemistry at a remote northern Atlantic coastal site, J. Geophys. Res., 109, D02312, doi:10.1029/2003JD003983, 2004.

Zanis, P., P. S. Monks, E. Shuepbach, and S. A. Penkett, On the relationship of HO₂+RO₂ with J(O₁D) during the Free Tropospheric Experiment (FREETEX '96) at the Jungfraujoch Observatory (3580 m above sea level) in the Swiss Alps, J. Geophys. Res. 104, 26,913-26,925, 1999.

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