

## ***Interactive comment on “Estimating N<sub>2</sub>O<sub>5</sub> uptake coefficients using ambient measurements of NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub> and particle-phase nitrate” by G. J. Phillips et al.***

**Anonymous Referee #1**

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### General comments

This manuscript reports estimates of uptake coefficients of N<sub>2</sub>O<sub>5</sub> and yields of ClNO<sub>2</sub> based on measured data of the major nitrogen oxides species, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub>, as well as of important aerosol characteristics, including nitrate (but unfortunately not chloride) content, from Kleiner Feldberg observatory, Germany, during the 2011 PARADE campaign. Two methods were employed to derive heterogeneous reaction rates: the first one relied on the formation rates of ClNO<sub>2</sub> and particulate nitrate, the second one on the steady state life time of NO<sub>3</sub>. The results for the uptake coefficients turn out to be in good agreement with uptake coefficients as derived from laboratory experiments and taking into account nitrate and estimated chloride contents and using

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parameterizations either by the IUPAC evaluation or by Bertram and Thornton. The fractional ClNO<sub>2</sub> yields are consistent with the highly variable (and usually low) particulate chloride contents at this site.

In spite of the fact that no surprises with respect to the multiphase chemistry of N<sub>2</sub>O<sub>5</sub> are found, this work is a very valuable and timely contribution, since the heterogeneous fate of N<sub>2</sub>O<sub>5</sub> and its impact on NO<sub>x</sub>, O<sub>3</sub> and partially the halogen budgets is poorly constrained. While laboratory studies on this subject provide important cornerstones on kinetics and yields for model systems, the complexity of particulate matter and feedbacks with gas phase cycles, including uncertainties related to NO<sub>3</sub> sinks in the gas phase, render it very important to analyze measured field data to test the hypotheses established based on laboratory studies. The manuscript is a very detailed account of a rigorous and careful analysis of the PARADE data that includes also thoughtful consideration of the uncertainties related to complex meteorology and air mass histories. The manuscript is overall well written and structured; in parts the reader may get lost in the details of the analysis and would appreciate some help to get back on the storyline. The specific comments below are of minor concern, but could help to polish and streamline the manuscript.

1) Figure 1, shown in the context of the introduction, could be more specific in the particulate phase chemical reactions, i.e., include R1-R3; maybe then also the parameter  $f$  could be indicated where water and chloride compete for nitronium ion. If the figure is in one-column width, this would still fit within the same size of particle.

2) page 8, lines 24 and below: the degassing of HNO<sub>3</sub> following uptake of N<sub>2</sub>O<sub>5</sub> and nitrate formation via uptake of HNO<sub>3</sub> from the gas phase are strongly linked to the aerosol pH, which is influenced by both air mass history longer back as well as recent N<sub>2</sub>O<sub>5</sub> uptake. If HNO<sub>3</sub> in the gas phase is not partitioning to the aerosol phase, HNO<sub>3</sub> deriving from N<sub>2</sub>O<sub>5</sub> would also be likely be degassed. The rather lengthy discussion of the two assumptions continuing on the next page is not really coming back to this point.

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- 3) page 12, around line 28: are VOC data available that could help explaining the variability of the NO<sub>3</sub> lifetime? A note on this is mentioned at the end of section 4.3
- 4) section 4.4 appears partly repetitive, since to some degree most of the issues are already addressed in the detailed discussion of the different analysis methods. To this reviewer, this section is interrupting a bit the sequence of sections 4.1, 4.2., then continued in sections 4.5 and 4.6. The authors could consider integrating the additional aspects into the sections before or after to improve overall text flow.
- 5) page 14, line 30: this first summary statement could be expressed in a more positive mood. It is a substantial result that consistency with lab observation is achieved! So, the value of finding this consistence could be emphasized more.
- 6) page 15, line 5: low *f* values may also result from the presence organics nitrated by nitronium, in spite of the presence of chloride.
- 7) page 16, description of parameterization: it is not explicitly stated how [H<sub>2</sub>O] was derived for the IUPAC parameterization; this is only mentioned for the Bertram and Thornton parameterization further below.
- 8) page 17 (and elsewhere), discussion of Figure 8: the data derived from this study show (to the eye) a trend of  $\gamma$  increasing with humidity. Is this trend significant? The same trend is not apparent from the accepted parameterizations. This could maybe be addressed in a short discussion.
- 9) page 17, line 23: Grzinic et al. (2015) should be added here in addition to mention that it is not just the oxidation state and reduced water concentration but also the higher viscosity (coming along with that) leading to lower uptake coefficients.
- 10) page 18, line 11 and below: As shown by Grzinic et al. (2015), the (volume) reaction limited regime may not be appropriate, since the increasing viscosity driven by oxidized organics leads rather to a decrease of the reacto-diffusive length.
- 11) Figure 9: would it be helpful to add aerosol surface to volume ratio to the plots to

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make the correlation of the NO<sub>3</sub> lifetime with A versus that with NO<sub>2</sub> apparent in the data plots a), c) and e)? In plot e), add symbols for NO<sub>2</sub> or remove them in the other plots as well to make consistent among all.

Technical comments

Page 9, line 10: ...as N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> have completely different. . .

Page 12, line 13: ...of this night and may also be. . .

Page 13, line 3: upper case K in *K<sub>eq</sub>*

Page 13, line 14: 'As the authors point out', maybe reiterate Wagner et al. (2013), since their mentioning is quite a few lines back

Page 14, line 21: ...values reported here. . ., check: here or there (CalNex)

Page 15, line 20: sentence needs revision; ... largely based on the relationship of CINO<sub>2</sub> with air mass origin?

Page 18, line 8: ...setting *f* to one,. . .

References

Gržinić, G., Bartels-Rausch, T., Berkemeier, T., Türler, A., and Ammann, M.: Viscosity controls humidity dependence of N<sub>2</sub>O<sub>5</sub> uptake to citric acid aerosol, *Atmos. Chem. Phys.*, 15, 13615-13625, 2015

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