

We thank the review 1 for this positive appraisal of our manuscript. Each comment made (black) and our response (blue) is listed below. Red text indicates where changes to the manuscript have been made.

This manuscript reports estimates of uptake coefficients of N_2O_5 and yields of ClNO_2 based on measured data of the major nitrogen oxides species, NO_3 , N_2O_5 and ClNO_2 , 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_2 and particulate nitrate, the second one on the steady state life time of NO_3 . 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 parameterizations either by the IUPAC evaluation or by Bertram and Thornton. The fractional ClNO_2 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_2O_5 are found, this work is a very valuable and timely contribution, since the heterogeneous fate of N_2O_5 and its impact on NO_x , O_3 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_3 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.

[We thank the reviewer for this very positive overall assessment of the paper.](#)

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.

The suggested changes to Figure 1 have been made and the aqueous phase chemistry is now illustrated in more detail.

2) page 8, lines 24 and below: the degassing of HNO_3 following uptake of N_2O_5 and nitrate formation via uptake of HNO_3 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_2O_5 uptake. If HNO_3 in the gas phase is not partitioning to the aerosol phase, HNO_3 deriving from N_2O_5 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.

[We have indicated how the degassing of particulate nitrate as \$\text{HNO}_3\$ and the nighttime uptake of \$\text{HNO}_3\$ would affect our results. Based on measurements during a subsequent campaign we find no strong indication that our calculations are strongly biased, but, in the absence of simultaneous gas-phase \$\text{HNO}_3\$ measurements cannot prove this. The lengthy discussion is an honest airing of these issues which we prefer not to understate.](#)

3) page 12, around line 28: are VOC data available that could help explaining the variability of the NO₃ lifetime? A note on this is mentioned at the end of section 4.3

As is generally the case, the VOC measurements (GC) were generally made at low time resolution and do not shed light on this issue.

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.

We agree and the sequence has been changed so that section 4.4 (now 4.6) has been moved after sections 4.5 (now 4.4) and section 4.6 (now 4.5).

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 consistency could be emphasized more.

This section and this statement has now been moved to the end of the document, just before the conclusions. Whilst we indicate that some ambient datasets confirm the laboratory observation of γ suppression by organics and/or nitrate, others do not. We also do not know what drives the high variability in the ambient measurements of gamma. Clearly, more ambient datasets are urgently required before we can conclude that we have reached a level of understanding that enables prediction of N₂O₅ uptake coefficients in different environments. We have added a sentence to the conclusions to indicate this “There is an urgent need for further laboratory work on synthetic aerosols and more field measurements that investigate the uptake of N₂O₅ in different “real-world” environment, especially chemically complex ones as found in the continental boundary layer.”

6) page 15, line 5: low f values may also result from the presence of organics nitrated by nitronium, in spite of the presence of chloride.

Agreed. We now write: “We thus expect f to be largest in polluted coastal regions (unless there is a large organic content that can react with H₂NO₃⁺) and lowest (or zero) in continental regions with no marine influence or anthropogenic chlorine emissions.”

7) page 16, description of parameterization: it is not explicitly stated how [H₂O] was derived for the IUPAC parameterization; this is only mentioned for the Bertram and Thornton parameterization further below.

We now mention how liquid water constant was also calculated for the IUPAC parameterisation.: “IUPAC preferred values are listed (for ammonium sulphate) as $\alpha_b = 0.03$, $k_{H_2O} = 1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $D_1 = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $H = 2 \text{ M atm}^{-1}$. Particle liquid water content [H₂O(l)], was calculated with the E-AIM model (<http://www.aim.env.uea.ac.uk/aim/model3/model3a.php>) (Clegg et al., 1998; Wexler and Clegg, 2002) using particulate nitrate, sulphate and ammonium concentrations measured by the AMS and the relative humidity.”

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.

We have added text to highlight this point and provide a potential explanation:

“..... the BT- parameterisation lies at the upper range of the measurements for relative humidities between 65 and 75 % and at the lower end for the highest relative humidities encountered, which may indicate a positive dependence of measured γ on RH which is not predicted by the parameterisations. As the particles during PARADE have significant organic content (see Fig. 2) this may reflect the fact that the organic suppression of γ is reduced at high relative humidity as reported by (Gaston et al., 2014). We note however that the values of γ measured at large RH are larger than most measurements on pure laboratory samples, which may indicate a measurement bias under some conditions.

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.

We now write: “As discussed by Gaston et al. (2014) and Grzinic et al. (2015), the effect of organic content in a particle will depend on the amount and oxidation state of the organics, with both solubility and viscosity impacting on the response of γ to changes in relative humidity.”

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.

We have now added the sentence: as discussed by Grzinic et al. (2015), the increasing viscosity driven by the presence of oxidized organics may lead to a reduction in diffusive transport into the particle.

11) Figure 9: would it be helpful to add aerosol surface to volume ratio to the plots to make the correlation of the NO₃ lifetime with A versus that with NO₂ apparent in the data plots a), c) and e)?

In plot e), add symbols for NO₂ or remove them in the other plots as well to make consistent among all.

The aerosol surface area does not change much over these periods. To preserve clarity of presentation, we prefer not to add more detail to these plots.

We have made the representation of the NO₂ data consistent (with symbols).

Technical comments

Page 9, line 10: as N₂O₅ and HNO₃ have completely different

Correction made

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

Correction made

Page 13, line 3: upper case K in Keq

Correction made

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

We now write: “as Wagner et al. (2013) point out”

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

To remove ambiguity we now write: values reported in the present work were derived...

Page 15, line 20: sentence needs revision; largely based on the relationship of ClNO₂ with air mass origin?

We now write: “which is largely based on the dependence of ClNO₂ on air mass origin...”

Page 18, line 8: setting f to one

Correction made