

Interactive comment on “Heterogeneous N₂O₅ uptake coefficient and production yield of ClNO₂ in polluted northern China: Roles of aerosol water content and chemical composition” by Yee Jun Tham et al.

Anonymous Referee #2

Received and published: 26 May 2018

General Comments:

This paper reports an analysis of N₂O₅ uptake coefficients and ClNO₂ yields from a polluted site in the North China Plain during a summer 2014 field intensive. The analysis finds variation of N₂O₅ uptake coefficients that is characteristic of data sets in other parts of the world. Comparisons between field determinations and laboratory based parameterizations, and between the determined uptake coefficients and other variables, shows that aerosol liquid water / relative humidity is a determining factor. This finding is in contrast to field studies in the U.S. and Europe.

C1

ClNO₂ yields are shown to be lower than current parameterizations based on the competition between chloride and liquid water, consistent with findings from other regions. The authors suggest ClNO₂ suppression on biomass burning derived particles despite higher chloride content in these aerosol.

Overall, the paper adds to the growing database of these analysis and will be a valuable contribution to the literature. Publication is recommended after the authors address the following comments.

Specific comments:

Page 2, line 4: “yielding N₂O₅” rather than “yielding a N₂O₅”.

Page 3, line 20: Also add Morgan et al., 2015 and McDuffie et al., 2018, to this list.

Page 3, line 22: sentence not clear. Does “laboratory parameterizations can be over-estimated” mean that the observations are higher than or lower then the parameterizations?

Page 3, line 32: “NO₃- aerosol downwind of” rather than “NO₃- aerosol in downwind of”

Page 4, line 8: Is the quoted N₂O₅ a maximum or an average? Please specify.

Page 5, lines 25-26: Are the quoted average production rates of NO₃ for nighttime only for for nighttime and daytime?

Page 5, equation 4: The method of Phillips et al. (2016) is referenced, but the method for calculating the production rates in the numerator in the right hand side of the equation is not specified for the data here. How are these quantities (pClNO₂ and pNO₃-) determined?

Page 5, line 33: Define “most nights” – how many nights had $r^2 > 0.6$ for the stated correlation?

C2

Page 6, line 14-15: Assumption 3 is not reasonable. HNO₃ is in equilibrium with aerosols regardless of how it is produced. That is, HNO₃ equilibration and N₂O₅ uptake are not separate processes, but tightly coupled ones. The assumption is more likely intended to state that N₂O₅ heterogeneous uptake during the night of observations is a larger source of total soluble nitrate (HNO₃ plus NO₃⁻) than soluble nitrate production from the preceding day, or that the correlation with ClNO₂ is determined by the nighttime produced nitrate rather than the background that was present at sunset.

Page 6, line 19: remove the word “have”

Page 6, line 22: Is there a quantitative definition of “drastic changes” here? In other words, is the data filtering arbitrary, or done in a well-defined manner using characteristics of time rates of change.

Page 6, lines 26-28: See comment above. The partitioning of total nitrate between gas and particle phase is an important limitation, and it would be useful to define any quantitative information, such as an aerosol thermodynamic model, that would indicate where this partitioning is. The photochemical soluble nitrate production should be in the background of the correlation (i.e., the intercept) and so might not affect the results.

Text on pages 6-7 and Figure 3: Explain why there is significant OH + NO₂ during the night. Explain how particulate NO₃⁻ production from NO₃ + VOC is calculated. Many NO₃ + VOC reactions produce organic nitrates rather than HNO₃, so it is not clear how this source of HNO₃ has been calculated based on the information given. The total production rate of NO₃⁻ is also referenced in the text but not shown in the figure. The differentiation between day and night in Figure 3 is not clear. Presumably the time axis is local time, not UTC? Please specify for clarity. The times of day and night should be shown, preferably with a shaded region to indicate night. Data for gas phase HNO₃ are presented here for the first time. Why in the preceding analysis was ClNO₂ only correlated against particulate phase NO₃⁻ if gas phase HNO₃ is also available? The analysis should be done from the correlation between ClNO₂ and total nitrate (HNO₃

C3

+ NO₃⁻) since the two are in rapid equilibrium on the time scale of ClNO₂ production through N₂O₅ uptake.

Page 7, line 22: “The question that arises” rather than “The question arises”

Page 7, line 33: “coefficients” rather than “coefficient”

Page 8, line 21: Figure 5 would be clearer if the field data were on the y-axis and the parameterization on the x-axis.

Page 9, line 22: “to changes in RH” rather than “on the changes in RH”

Page 9, lines 25-30: Is [H₂O]/V/S_a really independent of aerosol water itself? It seems that the effects discussed here and on the rest of page 9 can be determined from laboratory experiments under controlled conditions but not easily determined from field data. The authors should be careful to phrase this argument as consistent with laboratory data rather than a determination of these effects from field measurements.

Page 9, first paragraph: The major conclusion is that RH, and by extension the calculation of aerosol liquid water, was the determining factor for N₂O₅ uptake. In this context, it will be helpful to say more about the measurement of the wet aerosol surface area and its associated uncertainties, since wet aerosol surface area is often a difficult quantity to measure, and the measurement or calculation can itself introduce an RH dependence to the aerosol surface area measurement. The description in the methods section (Page 5, lines 7-9) is brief. A more comprehensive description of this measurement and statement of its potential dependence on RH, along with the uncertainty in the aerosol surface area, is needed.

Page 10, line 22, Figure 7a: As for figure 5, this would be clearer with the field data on the y-axis. All other plots in figure 7 have field data on the y-axis, and the same should be done for figure 7.

Page 10, line 24: remove the word “in”. Also “Such a discrepancy” rather than “Such discrepancy”.

C4

Page 10, line 29: What is meant by “from quadratic fitting”? Is there a polynomial fit that should appear in Figure 7?

Page 10, line 33: Remove the word “good” or else replace by something more specific, such as “statistically significant”, if appropriate. Also, the term “quadratic data fitting” appears again here without explanation or a displayed fit.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-313>, 2018.