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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous N_2O_5 uptake coefficient and production yield of $ClNO_2$ in polluted northern China: Roles of aerosol water content and chemical composition" *by* Yee Jun Tham et al.

Anonymous Referee #1

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Tham et al report N2O5 uptake coefficients and ClNO2 yields based on measurements of N2O5, ClNO2, and PM2.5 aerosol size distribution and composition at Wangdu in the summer 2014. The N2O5 uptake coefficients and ClNO2 yields were estimated based on observed production of ClNO2, (bulk) particulate nitrate, and in situ N2O5 concentration and aerosol surface area. These observed values are compared with predictions from several literature parameterizations. The authors show that γ(N2O5) increases with relative humidity (and aerosol liquid water content) and decreases with increasing particulate nitrate content. ClNO2 yields were variable and appeared to

show a decreasing trend in the presence of BB aerosol.

The paper is written well and will be a useful addition to the literature once the authors have satisfactorily addressed the comments below.

Major comments 1) Bulk aerosol properties are used in the analysis to calculate, for example, aerosol liquid water content at equilibrium, N2O5 uptake, and ClNO2 yield. In reality, however, the aerosol will consist of particles that have varying degrees of external (and internal) mixing. This may be particularly important for N2O5 to ClNO2 conversion, which takes place very efficiently on (supermicron) sea salt derived aerosol or in certain power plant plumes, but hardly at all on secondary aerosol that contains little chloride. Furthermore, the conversion of N2O5 to ClNO2 occurs mainly on the aerosol surface and not in the bulk. The authors should add more discussion on the limitations arising from the use of bulk aerosol properties in their analysis.

2) A major limitation, which unfortunately has become quite common in the literature, is to perform analysis with in situ variables (i.e., ClNO2 and N2O5 concentrations) and with variables that will integrate over the air mass's history, such as aerosol nitrate, and then to assume that upwind conditions were similar. This is a major assumption, of course, and many preceding papers spent a lot of time justifying it. It may be useful to add more discussion on what the upwind air masses typically would experience prior to observation (e.g., absence/presence of local sources etc.) at Wangdu.

3) In part because of (2), data were selected in the analysis. While the selection criteria are stated, it is in principle worrisome and may lead to selection bias. Can anything be said about the data that were excluded from analysis? For example, what fraction of the data were excluded, and can you give an indication as to what happens in terms of N2O5 to ClNO2 conversion during those periods - were the mixing ratios of ClNO2 high or low, and was the uptake of N2O5 fast or slow? Could these data be analyzed and added with a lighter shade to some of the Figures?

4) The conversion of N2O5 to ClNO2 is often stratified vertically, with usually rapid

N2O5 losses at the surface, and higher ClNO2 production rates aloft. How does stratification / vertical mixing affect the analysis?

Minor comments

page 1 / line 19 - replace "10" with "ten"; state on what basis cases were selected and how the N2O5 uptake coefficients and ClNO2 yields were estimated

line 21 - grammar: "an average", but then two values (one for N2O5 and one for ClNO2) are given; formatting for the ranges given in brackets is not consistent; The authors should state their estimated errors of the "observed" N2O5 and ClNO2 uptake parameters here.

line 25 - "by the amount of water in the aerosol, a phenomenon that differs from other field observations". Most models and the Bertram/Thornton parameterization (Eq 3) that contains a water term and would have been included in other field studies. Is the author's statement then really true?

line 26 - "Laboratory-derived parameterization also overestimated the ClNO2 yield." Please correct the grammar here.

pg 3/ line 11 - "450" Roberts et al. Geophys. Res. Lett., 36, L20808, 10.1029/2009GL040448, 2009 give a much larger value here; consider adding a second set of ÏŢparm calculations with the Roberts et al. value and add to Figure 7a.

page 4 / line 11 "We first derive values for γ(N2O5) and ÏŢ with the measurement data". Please state briefly here how this is done.

page 5. Please add a table summarizing the various measurements made. Without one, statements such as "Volatile organic compounds including methane, C2-C10 hydrocarbons, formaldehyde, and oxygenated hydrocarbons and acetonitrile (CH3CN) were measured with a cavity ring–down spectroscopy technique instrument, an online gas chromatograph equipped with a mass spectrometer and a ïňĆame ionization detector, a Hantzsch ïňĆuorimetric monitor, and a proton-transfer-reaction mass spec-

trometer, respectively" are unnecessarily confusing.

line 28 - "steady-state" Brown et al. (J. Geophys. Res., 108, 4539, 10.1029/2003JD003407, 2003) showed that the time to achieve a steady state can be substantial, especially in polluted conditions. Have the authors verified (e.g., through box model simulations) that the steady-state approximation is valid?

page 7 / line 23 "what drive" Grammar (either "what drives" or "what factors drive")

page 8 / the "observed" γ(N2O5) is really an aggregate vale for N2O5 uptake on the entire aerosol distribution

line 2 - [H2O], [NO3-], and [Cl-] will likely be functions of aerosol size; please add a disclaimer that this calculation assumes that they are not, and that the predicted gamma values may be biased as a result.

Out of curiosity - is it possible that ClNO2 is produced mainly on sea salt aerosol at Wangdu?

line 4 - the E-AIM allows for inclusion of organics, which would alter the liquid water content (maybe). Has this been considered

line 12 what values of Rc and Rp were used in the B&T+org calculation, and are these values realistic for this comparison? (see also major comment 2).

pg 9 / line 16 - sulfate should be doubly charged

pg 10 / factors that affect ClNO2 yield - this is an interesting paragraph, but I am a bit skeptical about what appear to be low field yields.

Have the authors considered that the lack of agreement may be due to breakdown of the assumptions going into the calculation (uneven distribution of chloride throughout the aerosol, for example)?

page 22 - Please increase the font size on figures 2a and 2c (they are too small).

In Figures 2b and 2d, do the axis intercepts allow an assessment of how much aerosol nitrate is derived from daytime vs nighttime chemistry?

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