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Comment on acp-2021-886

Anonymous Referee #2

Referee comment on "Interpretation of NO_3 - N_2O_5 observation via steady state in high-aerosol air mass: the impact of equilibrium coefficient in ambient conditions" by Xiaorui Chen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-886-RC2>, 2021

General comments:

Chen *et al.* analyze the steady state approximation in the interpretation of observations of NO_3 and N_2O_5 mixing ratios in ambient air with a focus on the potential error arising from the deviations in the equilibrium constant, and the resulting potential sensitivity of N_2O_5 uptake coefficients derived from this method. They use data from two recent ground-based field campaigns in and near Beijing. Of particular value is the assessment of the equilibrium constant to the actual reaction quotient (i.e., K_{eq} compared to $[\text{N}_2\text{O}_5]/([\text{NO}_2][\text{NO}_3])$). This effect results from the competition between reactive uptake for N_2O_5 and thermal dissociation of N_2O_5 in the equilibrium, and should be described as such (see comments below). The variation in equilibrium constants from different databases or reaction mechanisms is also particularly valuable, and does not appear elsewhere in the literature to my knowledge.

The analysis will be of interest to the atmospheric chemistry community generally and those who study nighttime chemistry specifically. I recommend publication after attention to the following comments.

The most general overall comment for this manuscript is clarity. This is true in a number of places. For example, equations (1) and (2) define the equations used in the analysis, but the equations themselves are not derived, their assumptions not justified, and the chemistry that underlies them not defined. The introduction should presume the reader do not have an intimate familiarity with nighttime chemistry and should take the time to define assumptions and chemistry. For example, what exactly is k_{NO_3} , what controls it and what values should it have? The oxidation chemistry that leads to this loss rate constants should be described, at least briefly.

Other examples are given in the specific comments below.

Specific comments:

Line 39: The steady state approximation dates well before Brown 2003, to the early work of Platt and coworkers, e.g. Platt, U., D. Perner, J. Schröder, C. Kessler, and A. Toennissen, *The Diurnal Variation of NO₃*. J. Geophys. Res., 1981. **86**(C12): p. 11965-11970.

Line 45: Text S1 and Figure S1 are referenced at this point, although the methods used in here have not yet been introduced. For example, the scatter plots at the bottom of Figure S1 have rather complicated axes, and the slopes are stated as being a measure of the N₂O₅ uptake coefficient. Equations describing these relationships should precede their presentation in a figure.

Line 57: Reference to iterative box model is not defined. Those who have worked with such a model will understand this statement, but it will not be clear to most readers.

Line 62: The phrase "half artificial" is not defined. A reference to the following sections (e.g., "see below") is needed at a minimum.

Line 64: Linear fit between which variables? Does this refer to equations 1 and 2 that follow? Specify if this is the case.

Line 72: "steady" rather than "stead". This error appears in multiple places. Authors should search on "stead" and replace with "steady".

Line 73: Does weak physical processes mean transport and boundary layer dynamics or something else? Specify.

Line 78-79, equations 1 and 2: These equations are complicated and lack a statement of assumptions or a derivation. The text should provide these.

Line 100-107: The description of the artificial data set is not clear. First, the justification

for the term “half artificial” is not clearly defined – i.e, what about this is only half artificial (or half real) rather than completely artificial or real? Second, it seems that the authors are applying a test for the validity of steady state and then excluding data points that do not meet a steady state criterion (itself not defined ... is this agreement of model with observed NO_3 or N_2O_5 to within the stated limits, or is this just model to model?). The text reads, however, as though large amounts of data are simply being excluded from the analysis or replaced with artificial data (as stated further down in the paragraph) if they do not fit the model, which would be neither scientifically rigorous nor consistent with what is shown in the figures. Possibly the issue here is with the text-based description. The authors should read this carefully to be sure that it means what they intend.

Line 108: 5 ppbv NO is very large indeed, and is equivalent to an NO_3 loss rate coefficient of approximately 3 s^{-1} , likely much larger than rate coefficients associated with N_2O_5 uptake or NO_3 -VOC reactions. Is this a sufficient filter for assessing NO_3 chemistry that is not attributable to NO reaction?

Figure 1: What starting mixing ratios of NO_2 and O_3 are used in this simulation? Are these held constant? Are the results different if these are initialized and then allowed to vary? The N_2O_5 loss rate constant is given in the figure, but should be compared explicitly to the thermal lifetime (thermal dissociation rate constant) of N_2O_5 in the equilibrium. Does this ratio match that of the incomplete equilibrium shown in panel D?

Line 146: Losses for NO_3 and N_2O_5 are generally not equal in creating a deviation from equilibrium. Large NO_3 loss rate constants normally do not lead to a deviation from equilibrium, whereas even relatively modest N_2O_5 rate constants can easily lead to large deviations from equilibrium. This is the result of competition between N_2O_5 loss through aerosol uptake and thermal dissociation, where the thermal dissociation rate constant is slow at colder temperatures and therefore is subject to competition reactions. Rapid reaction of NO_3 , by contrast, generally does not compete with the rapid forward reaction. Suggest removing the reference to NO_3 loss here.

Figure 2: The relationship of the top and bottom axes are not clear. One would expect that the change in k_{NO_3} or $k_{\text{N}_2\text{O}_5}$ would correspond directly to the change in temperature on the top axis, but this appears not to be the case. Therefore, it is not clear what the lines on the plot are showing – i.e., the influence of temperature or the rate constants. Possibly different traces are plotted against different axes, but this is not specified anywhere in the text. Clarify the description or separate these plots into two different sets. Also, as per the previous comment, any dependence of the deviation from equilibrium on either temperature or N_2O_5 loss rate constant would co-vary, so the condition chosen for either T or $k_{\text{N}_2\text{O}_5}$ in the complementary plot needs to be specified. This is not specified in the text or the figure caption.

Line 183, Figure S6: Give the values of the derived $\gamma_{\text{N}_2\text{O}_5}$ – one can see the differences in the slopes of the lines in the figures, but the quantitative values should also be given on the figures or in a separate table.

Line 230-244 and Figure 4: The parallel axis plot in Figure 4 is visually appealing, but difficult to interpret. What is plotted along the bottom of the figure, and why do lines connecting each of the axes have curvature along the bottom axis? Is each line simply a collection of simulations associated with a given parameter in each axis but different parameters in the other axes? It is not clear from the text exactly how this plot has been constructed.

What is clear is that the grey lines indicate invalid steady state, defined as an approach time greater than 600 s. This appears arbitrary, as observed NO_3 and N_2O_5 are often much more aged than 10 minutes from the point of emission of NO_x or the time since sunset. The authors may want to consider a different definition with a longer time horizon, or if not, the statement about 600 s should not be simply “invalid” but rather described as an arbitrary threshold.

Supplement

Lines 62-65: NO values near the detection limit are corrected. What is this correction? Does this mean the data were arbitrarily adjusted to zero during periods when it is anticipated that they would be zero?

Line 88-90 and Figure S3: What is $\text{Tau}(\text{N}_2\text{O}_5)\text{SS}$ and $\text{Tau}(\text{N}_2\text{O}_5)\text{Calc}$? These quantities are not defined in the figure caption, the supplement text or the main text. It is difficult to understand what is being compared here, especially given the remarkable agreement between what appears to be an observational and model quantity.

Figure S5 and Tables S3, S4: The comparison of equilibrium constants based on different mechanism is an important contribution from this paper. Suggest a figure that makes a comparison between the parameterizations of K_{eq} , either calculated from parameters as in JPL, or from the ratio of $k_{\text{forward}}/k_{\text{reverse}}$ as in the other parameterizations, to show the variability that is used in the current literature. Figure S5 is useful for specific in-field data, but only shows variation as a function of time without a clear T dependence. A separate T dependence would clarify this figure.

This section could make reference to the review article of Chang *et al.*, who consider the T-dependence of two parameterizations (JPL and IUPAC). Chang, W.L., P.V. Bhave, S.S. Brown, N. Riemer, J. Stutz, and D. Dabdub, *Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N_2O_5 : A Review*. *Aerosol Science and Technology*, 2011. **45**: p. 655-685.

Also, in Figure S5, why is the particular time period chosen out of each campaign? In each case, this is 2 hours of data out of several weeks of measurement.

Line 142-143: Specify how the time to reach a valid steady state is defined. Model mixing ratios equal to some fraction of observed ones, for example?

Figure S7: Same comment as above – the top and bottom axes apparently have no correspondence to each other, which is confusing.

Line 182-187 and Figure S9: What is the mechanism that leads to incorrect determination of $\gamma_{\text{N}_2\text{O}_5}$ at increasing k_{NO_3} ? Perhaps a plot to demonstrate why the slope or intercept changes by such a large amount would be helpful.

The right axis in Figure S9a also does not match the tick marks on the right axis in panel b, which shows the values on this axis.