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Interpretation of NO_3-N_2O_5 observation via steady state in high aerosol air mass: The impact of equilibrium coefficient in ambient conditions

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Abstract. Steady state approximation for interpreting NO_3 and N_2O_5 has large uncertainty under complicated ambient conditions and could even produces incorrect results unconsciously. To provide an assessment and solution to the dilemma, we formulate data sets based on in-situ observations to reassess the applicability of the method. In most of steady state cases, we find a prominent discrepancy between *K*eq (equilibrium coefficient for reversible reactions of NO_3 and N_2O_5) and correspondingly simulated $[N_2O_5]/([NO_2]\times[NO_3])$, especially in wintertime high aerosol conditions. This gap reveals the accuracy of Keq has a critical impact on the steady state analysis in polluted region. In addition, the accuracy of $\gamma(N_2O_5)$ derived by steady state fit depends closely on the reactivity of NO_3 ($k$$NO_3$) and N_2O_5 ($k$$N_2O_5$). Based on a complete set of simulations, air mass of $k$$NO_3$ less than 0.01 s^{-1} with high aerosol and temperature higher than 10℃ is suggested to be the best suited for steady state analysis of NO_3-N_2O_5 chemistry. Instead of confirming the validity of steady state by numerical modeling for every case, this work directly provides concentration ranges appropriate for accurate steady state approximation, with implications for choosing suited methods to interpret nighttime chemistry in high aerosol air mass.

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1 Introduction

Nitrate radical (NO_3), an extremely reactive species prone to build up at night, is an ideal candidate for steady state analysis in combine with dinitrogen pentoxide (N_2O_5) due to fast equilibrium reactions between them (R1).

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad \text{(R1a)}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \quad \text{(R1b)}$$

Numerous works have taken the advantage of the steady state calculation to quantify the total first-order loss rate for NO_3 or N_2O_5 such that they drew conclusions about the oxidation capacity and reactive nitrogen budgets contributed by this chemical system (Allan et al., 1999;Allan et al., 2000;Carslaw et al., 1997;Platt et al., 1984;Vrekoussis et al., 2007;Wang et al., 2013). Since the steady state approximation was extended to interpret atmospheric observation of NO_3-N_2O_5 by Brown et al. (2003), this method has been widely implemented to quantify N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) (Brown et al., 2009;Brown et al., 2003;Li et al., 2020;McDuffie et al., 2019;Phillips et al., 2016;Wang et al., 2017a;Wang et al., 2017c).

However, with the influence induced by complicated atmospheric conditions and emission, the steady state in ambient air mass will not always be the case (as illustrated in Text S1 and Figure S1). These situations are prevalent in nocturnal boundary layer (Phillips et al., 2016;Stutz et al., 2004;Wang et al., 2017a;Wang et al., 2017c) and therefore increase the difficulty of applying steady state directly on NO_3-N_2O_5 observation data, whereas few studies have systematically characterized the error source and application conditions of this method (Brown et al., 2009).

Due to faster approach to equilibrium than steady state, the application of equilibrium coefficient (*K*eq) in calculation steady state equations seems to be reasonable (Brown et al., 2003). For example, the ambient NO_3 concentration was usually calculated based on ambient N_2O_5 concentration with $K\text{eq}\times[NO_2]$ when determining their budgets or characterizing the lifetime or sink attribution of these two reactive nitrogen compounds (Brown et al., 2011;Osthoff et al., 2006;Wang et al., 2018b;Wang et al., 2017c;Wang et al., 2017d). In addition, the concentration conversion between NO_3 and N_2O_5 via *K*eq coefficient can simplified the calculation in the iterative box model, which is proposed to quantify $\gamma(N_2O_5)$ (Wagner et al., 2013). However, considerable uncertainty could be associated with the quantification of *K*eq and its different parameterizations (Cantrell et al., 1988;Pritchard, 1994). The impact of *K*eq value on steady state fit or concentration conversion have not been explored to date in the analysis of NO_3-N_2O_5 steady state.

In this study, we formulate a half artificial dataset with expected properties based on field

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63 campaigns. With the dataset, we illustrate the reasons for *K*eq values distinct from
64 parameterization in ambient conditions, the possible uncertainties of linear fit resulted from
65 different *K*eq, and the influence of other atmospheric variables on $\gamma(N_2O_5)$ derivation via
66 steady state method. Furthermore, a series of ambient condition tests specify the exact ranges
67 suited for steady state analysis according to not only the validity of steady state but also *K*eq
68 values, which optimizes the validity check by numerical modeling in previous research
69 (Brown et al., 2009;Brown et al., 2003) and develops complete standard for data filtering.

70 ## 2 Methods

71 ### 2.1 $\gamma(N_2O_5)$ derivation by steady state approximation

72 The framework of stead state calculation for NO_3-N_2O_5 system is basically built on its
73 chemical production and removal pathways, in the case of extremely weak physical processes
74 relative to its chemical processes. With simultaneous measurements of NO_3, N_2O_5 and relevant
75 precursor concentrations, the steady state lifetime $\tau_{ss}(NO_3)$ and $\tau_{ss}(N_2O_5)$ can be
76 quantified for a given analysis period, and yield $\gamma(N_2O_5)$ and the reactivity of NO_3 (kNO_3,
77 including the reactions of NO_3 with NO and hydrocarbons) based on Eq. (1) and Eq. (2).

78 $$\tau_{ss}{}^{-1}(NO_3) \approx k_{NO_3} + \ 0.25cS_aK_{eq}[NO_2]\gamma(N_2O_5), \quad (1)$$

79 $$\left(0.25cS_a\tau_{ss}(N_2O_5)\right)^{-1} \approx \gamma(N_2O_5) + \ k_{NO_3}\left(0.25cS_aK_{eq}[NO_2]\right)^{-1}, \quad (2)$$

80 Here *c* represents the mean molecular velocity of N_2O_5, Sa represents the aerosol surface area
81 and the *K*eq is calculated from the rate constant of reversible reactions R1a (k_{R1a}) and R1b
82 (k_{R1b}), which is a temperature-dependent parameter. In the form of these two equations, the
83 potential covariance between Sa and NO_2 concentration can be avoided to decrease the
84 uncertainty (Brown et al., 2009). By fit to these two equations, $\gamma(N_2O_5)$ can be directly derived
85 from slope of the plot of $\tau_{ss}{}^{-1}(NO_3)$ against $0.25cS_aK_{eq}[NO_2]$ or from intercept of the plot
86 of $\left(0.25cS_a\tau_{ss}(N_2O_5)\right)^{-1}$ against $\left(0.25cS_aK_{eq}[NO_2]\right)^{-1}$ respectively. In the following
87 analysis, the linear fitting based on Eq. (2) is preferred in steady state approximation.

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2.2 Steady state model and half-artificial datasets

A half-artificial dataset can be provided by a steady state framework model, extended from 0-dimension box model, where steady state of NO_3 and N_2O_5 is valid for each data point. As NO_3-N_2O_5 chemistry, the interest of this work, usually shows marked impacts during the night, the data set includes only the time periods when photolysis rates are negligible. The model runs are constrained by measurements of NO, NO_2, O_3, CO, CH_4, VOCs, HCHO, Sa, relative humidity (RH), temperature (T), pressure, coupled with Regional Atmospheric Chemistry Mechanism, version 2 (RACM2). Other details on the species surrogates and deposition rates can be referred to previous study (Chen et al., 2019;Wang et al., 2018a).

In the standard simulation (herein referred as Mod0), the uptake coefficient of N_2O_5 is set to 0.02, as a reasonable value of literatures (Brown et al., 2006;Chen et al., 2020;McDuffie et al., 2018;Morgan et al., 2015;Phillips et al., 2016;Wagner et al., 2013;Wang et al., 2017c;Yu et al., 2020). Each data point is treated as an independent air mass, aging 10 hours without illumination and keeping input constraint unchanged. The simulation results of these two half-artificial datasets based on PKU2017 and TZ2018 field campaigns (see Text S2) show a large variability of nocturnal air masses (see Text. S3 and Figure S2). We presume that if any data point outputted from this model is still invalid for steady state, the sink rate constant of air mass represented by this data point should be too weak for steady state analysis in ambient conditions within a reasonable timescale. Data filtering according to Eq. (1) and Eq. (2) restricts available data points not to deviate from steady state more than 10%. In addition, the data higher than 5 ppbv NO is filtered out in the following calculation, since the resulting large variation of $k$$NO_3$ can break the fitting even under the steady state (discussed in 3.2). Rather than using observation data directly, replacing with half-artificial dataset can provide larger amount of valid data for steady state analysis with known $\gamma(N_2O_5)$ value and avoid the impacts from steady state deviation, which helps to analyze the factors influencing $\gamma(N_2O_5)$ quantification via steady state approximation backwards from a known steady state condition.

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3 Results and discussion

3.1 Varying equilibrium coefficient under steady state

The rates of NO_3-N_2O_5 reversible reactions are expected to be equal for the steady state case, so that the equilibrium coefficient *K*eq can be determined from either the rate constant ratio of R1a and R1b or the ratio of $[N_2O_5]/([NO_2]\times[NO_3])$. Although this approach is reasonable under ideal conditions, the exactly same rates between reversible reactions and the following calculation based on *K*eq scaling are not so appropriate for ambient atmosphere where the removal pathway for NO_3-N_2O_5 are not negligible, especially under the high aerosol loading condition. The NO_3-N_2O_5 achieves steady state after 1.5-hours evolution, when concentration and rates remain constant (Figure 1). Under steady state, the net equilibrium reaction rate in Figure 1(b)&(c) stays negative and positive for NO_3 and N_2O_5 respectively. Besides, the absolute values and difference of the forward and backward reaction rates remain unchanged after achieving steady state. This result is similar with a previous numerical calculation study (Brown et al., 2003), while the deviation between reversible reaction rates becomes larger in our case.

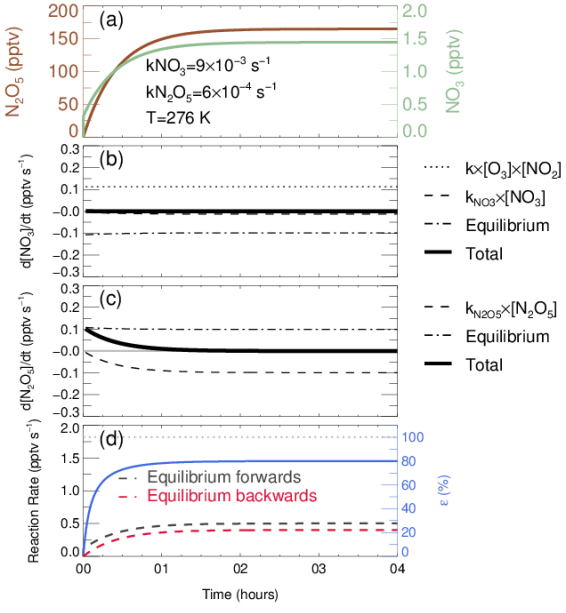

Figure 1. Evolution of NO_3-N_2O_5 system simulated by steady state model for an average case. (a) Temporal profiles of N_2O_5 and NO_3, the constraint of simulation is displayed as the text; (b) Evolution of $d[NO_3]/dt$ calculated from source of $k_{O3+NO2}\times[O_3]\times[NO_2]$, sink of $kNO_3\times[NO_3]$ and equilibrium terms, detailed in the text; (c) Evolution of $d[N_2O_5]/dt$ calculated from equilibrium terms, sink of $kN_2O_5\times[N_2O_5]$; (d) Forward (N_2O_5 formation) and backward (N_2O_5 decomposition) equilibrium rate are represented as black and red

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dash lines, the equilibrium completeness ε is calculated by the ratio of backward rate over forward rate, shown as blue full line.

In this case, the original equilibrium is imperfect reached (the original equilibrium condition is perfect reached as *K*eq and the ratio of $[N_2O_5]/([NO_2]\times[NO_3])$ are equivalent), leading to errors on projection of NO_3 and N_2O_5 concentration via $K\text{eq}\times[NO_2]$. In fact, we note that a new equilibrium between NO_3 and N_2O_5 is developed with constant but unequal rates. Under this new equilibrium condition, the ratio of R1b reaction rate (the red dash line in Figure1(d)) over R1a reaction rate (the black dash line in Figure1(d)) can be regarded as the degree of approaching original equilibrium (the blue line in Figure1(d)). In addition, this value is also the ratio of $[N_2O_5]/([NO_2]\times[NO_3])$ against original *K*eq, therefore we defined this ratio as a correction factor ε, implemented to calculate accurate $[N_2O_5]/([NO_2]\times[NO_3])$ with significant NO_3-N_2O_5 removal pathways. The value of *K*eq after scaled by ε can be used for converting the concentration of NO_3 and N_2O_5 via Eq. (3):

$$\varepsilon \times K_{eq} = \varepsilon \times \frac{k_{R1a}}{k_{R1b}} = \frac{[N_2O_5]}{[NO_2][NO_3]}, \quad (3)$$

Sensitivity tests are conducted to demonstrate the dependence of ε on relevant variables based on steady state model. The average ambient conditions observed at wintertime PKU site and summertime TZ site are taken as basic constraint for sensitivity tests (Table S2), respectively. By separately altering variables, such as NO_2, O_3, kN_2O_5, kNO_3 and T, the sensitivity of ε value can be obtained as shown in Figure 2 and Figure S4. The ε value depends primarily on kN_2O_5 and T in both scenarios, where ε increases with T (approaching 1 under relatively high T) and decreases with kN_2O_5. In comparison, the ε value behaves insensitive to kNO_3 as well as NO_2 and O_3 concentration, at least within the range of reasonable ambient conditions. High kN_2O_5 is resulted from high aerosol events, usually occur in winter accompanied with low temperature and high relative humidity in some populated areas (Baasandorj et al., 2017;Huang et al., 2014;Wang et al., 2017b;Wang et al., 2014), further decreasing the accuracy of original *K*eq values. It can be inferred that in order to accurately interpreting relationship of NO_3 and N_2O_5, calculation relying on equilibrium equation and steady state approximation should consider the dependence of ε on ambient conditions.

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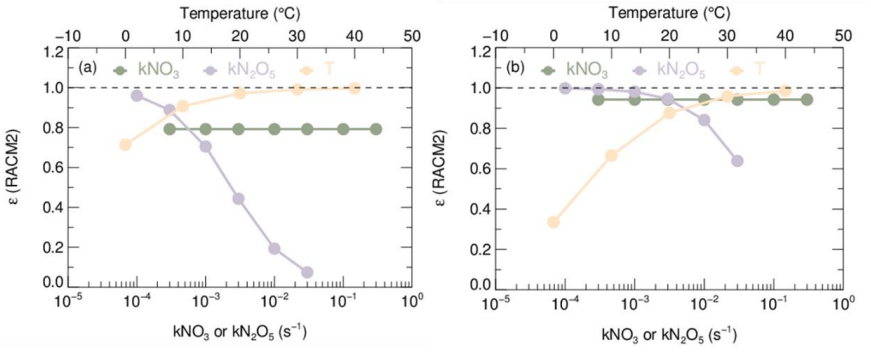

Figure 2. Sensitivity plot of $k\mathrm{NO_3}$, $k\mathrm{N_2O_5}$ and Temperature (T) against coefficient ε. (a) Basic model constraint is according to typical winter condition of PKU2017; (b) Basic model constraint is according to typical summer condition of TZ2018. It should be noted that the provided ranges of each factor do not exactly equal to but encompass the ambient conditions encountered during the two campaigns.

Even if *K*eq value serves as a good representation of the ratio of $[\mathrm{N_2O_5}]/([\mathrm{NO_2}]\times[\mathrm{NO_3}])$ or ε can be readily quantified on field, the discrepancy among different database in calculating *K*eq still increase the uncertainties of $\mathrm{NO_3}$-$\mathrm{N_2O_5}$ calculation through steady state approximation or equilibrium, which has not been carefully considered to date. Here, we apply a set of uniform formulas to describing k_{R1a} and k_{R1b} (see Text. S4) from preferred values of several popular atmospheric chemistry mechanisms (Mozart, CB05, Saprc07, RACM2 and kinetic databases JPL2015 as well as IUPAC2017) and finally calculating *K*eq. As is shown in Figure S5, *K*eq variations derived from these six different databases reflect considerable discrepancy from each other, though they vary with consistent tendency. Because original *K*eq values are only dependent on ambient temperature, they continuously increase with time due to the decrease of temperature. In addition to discrepancy between different *K*eq parameterizations, ε value varies dissimilarly with each *K*eq, ranging from 70% to 90%. All these results demonstrate that, in most cases, *K*eq values simply derived from existing database would fail to reproduce accurate relationship between $\mathrm{NO_3}$ and $\mathrm{N_2O_5}$.

To further elucidate the impact of *K*eq on deriving $\gamma(\mathrm{N_2O_5})$ via steady state approximation (hereafter defined as $\gamma_{ss}(\mathrm{N_2O_5})$), Figure S6 shows the steady state fit based on all six database-derived *K*eq and in the same time periods as Figure S5 through Eq. (1) and Eq. (2) respectively (both of equations can derive a pair of $\gamma_{ss}(\mathrm{N_2O_5})$ and $k\mathrm{NO_3}$). The *K*eq (corrected with ε) is calculated with $\mathrm{NO_3}$ and $\mathrm{N_2O_5}$ concentration simulated based on RACM2. Fit based on Eq. (1) could lead to 11~46% underestimation of $\gamma_{ss}(\mathrm{N_2O_5})$, as indicated by varying slopes in Figure S6(b)&(d), when using the database-derived *K*eq. Conversely, fit by Eq. (2) (shown in Figure S6(a)&(c)) bias the result of $k\mathrm{NO_3}$ served as the slopes without much influence on $\gamma_{ss}(\mathrm{N_2O_5})$

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served as the intercept. Previous research ascribed inconsistent fit results between two equations to measurements uncertainty (Brown et al., 2009;Brown et al., 2006). However, fit with original *K*eq might be the primary reasons for such inconsistent results, and even deviates the derived $\gamma_{ss}(N_2O_5)$ and kNO$_3$ from true values. Therefore, steady state fit based on Eq. (2) might be the best choice for $\gamma(N_2O_5)$ derivation via steady state approximation. Similarly, Eq. (1) is preferred to be applied when kNO$_3$ is the final objective.

3.2 Impacts of NO_3-N_2O_5 reactivity on steady state

In order to further explore the impacting factors on steady state fit method, $\gamma_{ss}(N_2O_5)$ results are derived for each 2-hour time period of PKU2017 and TZ2018 dataset based on output from steady state model. Since the pre-set $\gamma(N_2O_5)$ in this model is 0.02, the degree of deviation from this value is supposed to reflect the accuracy of the fitted result.

It can be noticed from Eq. (2) that the variability of kNO$_3$ during the same time period leads data points to scatter on lines with different slopes, which could bias the resulted $\gamma_{ss}(N_2O_5)$ from model pre-set value. As is shown in Figure 3, the absolute percentages of $\gamma_{ss}(N_2O_5)$ deviation grow dramatically with the increase of relative standard deviation of kNO$_3$ (kNO$_3$ RSD) in both of winter and summer data sets. The positive correlation even gives rise to extreme deviation in summer data set with up to almost 10 times of model setting $\gamma(N_2O_5)$. In fact, there remains accurate $\gamma_{ss}(N_2O_5)$ values derived in each range of kNO$_3$ RSD, indicating a not strictly positive correlation between $\gamma_{ss}(N_2O_5)$ deviation and kNO$_3$ RSD. It implies that large variation of kNO$_3$ only enhance the possibilities of inaccurate results from steady state fit rather than hinder the $\gamma_{ss}(N_2O_5)$ quantification all the time. This phenomenon can only be accounted by the distribution of kNO$_3$ values point by point.

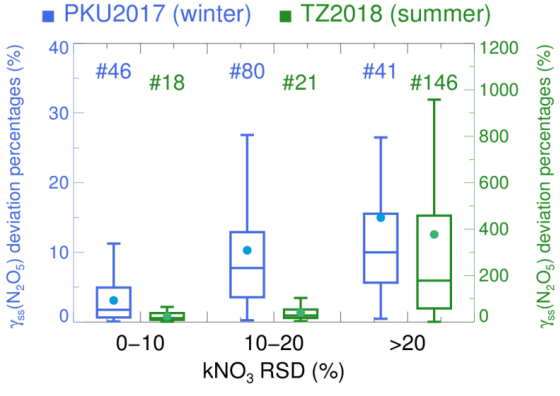

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Figure 3. Relationship between $\gamma(N_2O_5)$ derivation through steady state approximation and kNO$_3$ relative standard deviation (RSD) in box whisker plot. The blue and green color represent dataset from PKU2017 and TZ2018 respectively, binned according to kNO$_3$ RSD. The dots are the mean deviation of $\gamma_{ss}(N_2O_5)$. The number above the box whisker represents the valid data points in each bin.

Besides the large variation of kNO$_3$ in short time period, the absolute level of kNO$_3$ and kN$_2$O$_5$ could influence the possibilities of inaccurate $\gamma_{ss}(N_2O_5)$ from different aspects. Although the enhancement of kNO$_3$ and kN$_2$O$_5$ boost the approach to steady state (Text. S5 and Figure S7), higher levels of kNO$_3$ amplify the bias of $\gamma_{ss}(N_2O_5)$, contrary to kN$_2$O$_5$, with the same relative variation of kNO$_3$ (Text. S6 and Figure S9). It indicates that the region with plural emissions might not be suited for steady state fit due to the high kNO$_3$. Therefore, a trade-off between the variation of kNO$_3$ and the high level of kNO$_3$ (fast approach to steady state) should be made when derive $\gamma_{ss}(N_2O_5)$.

3.3 Implication for accurate steady state analysis of NO$_3$-N$_2$O$_5$

While a few previous researches have examined the validity of steady state under certain conditions via numerical modeling when interpreted the ambient data (Brown et al., 2009; Brown et al., 2003), a clear range well suited to steady state analysis of NO$_3$-N$_2$O$_5$, taking both Keq and validity of steady state into consideration, has not been determined to date.

Almost 20000 simulations are displayed in the parallel plot of Figure 4, where each line connects 5 constraint parameters to the calculated steady state time and ε. The steady state is validated by the approach to steady state within 600 s and the accurate Keq coefficient is defined as ε larger than 0.9. The pink and blue lines together represent the conditions valid for steady state without consideration of accurate Keq. While the level of T, NO$_2$ and O$_3$ have minor effect on the approach to steady state, simultaneous low kN$_2$O$_5$ (indicated as low Sa in the plot) and kNO$_3$ prevent the NO$_3$-N$_2$O$_5$ system from developing steady state. For example, when kNO$_3$ is lower than 0.01 s^{-1}, the air mass will be valid only if Sa increases to at least 3000 μm^2 cm^{-3} with $\gamma(N_2O_5)$ of 0.02. It implies that clean air mass is not suited for steady state in any cases, whereas high aerosol condition provides more possibilities to approach steady state even with low kNO$_3$. However, in order to interpreting NO$_3$-N$_2$O$_5$ chemistry with accurate Keq coefficient, the ε larger than 0.9 is additionally taken into consideration, which excludes 50% of valid steady state cases mainly with high aerosol and lower than 10°C. These cases could bias [N$_2$O$_5$]/([NO$_2$]×[NO$_3$]) from original Keq (also indicated in Figure 2), leading to inaccurate results of calculation based on Keq.

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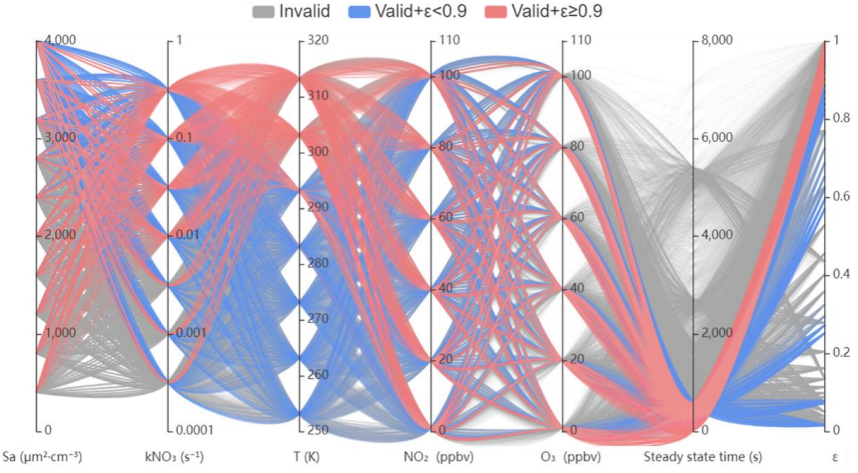

Figure 4. Numerical simulations for determining conditions available for steady state approximation method in a parallel axis plot. The first five axes from the left represent initial variables used for constraining the simulations respectively. The last two axes represent the time required for achieving steady state and the ε value calculated from the simulated results. The gray lines show cases unable approach steady state within 600 s. The blue lines show valid steady state cases with ε less than 0.9, which is also inappropriate for steady state analysis. The pink lines show valid steady state cases with ε higher than 0.9, which is suited for steady state analysis.

In summary, we found that the parameterized *K*eq coefficient deviates much from the ratio of $[N_2O_5]/([NO_2]\times[NO_3])$ in some cases where steady state is valid. The indicator of the deviation, ε, is relatively sensitive to N_2O_5 reactivity and ambient temperature. It implies that conditions suited for steady state analysis should be determined according to not only the validity of steady state but also *K*eq especially under high aerosol conditions, like some regions in India, China, Europe and the US (Baasandorj et al., 2017;Cesari et al., 2018;Huang et al., 2014;Mogno et al., 2021;Petit et al., 2017;Wang et al., 2017b). Considering that high level of kNO_3 might amplify the bias of $\gamma_{ss}(N_2O_5)$ yield from steady state fit and appears to be accompanied with fast variations, air mass of kNO_3 less than 0.01 s^{-1} with high aerosol and T higher than 10°C is therefore the best suited for steady state analysis of NO_3-N_2O_5 chemistry, which indicates that this method would be more applicable in polluted regions with high aerosol loading during summertime. If the restriction of ε is relaxed to 30%, some of winter conditions will also be applicable. Our results provide an insight to improve the accuracy of steady state approximation method and find suited areas to interpret nighttime chemistry. Further improvement of in-situ NO_3-N_2O_5 budgets quantification relies on the direct measurements via flow tube system or machine learning prediction based on ancillary parameters.

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Supporting Information: The Supporting Information is available on line. Description of the invalid ambient case for NO_3-N_2O_5 steady state analysis (Text S1), description of observation datasets from field campaigns 2017PKU and 2018TZ (Text S2), description of nighttime NO_3-N_2O_5 loss pathway two half-artificial dataset (Text S3), parameterization of Keq coefficient in different databases (Text S4), sensitivity tests of time to approach steady state (Text S5), description of the impacts of $k$$NO_3$ and $k$$N_2O_5$ levels on $\gamma_{ss}(N_2O_5)$ (Text S6), related Figures and Tables support the analysis in the text.

Code/Data availability. The datasets used in this study are available from the corresponding author upon request (wanghch27@mail.sysu.edu.cn; k.lu@pku.edu.cn).

Author contributions. K.D.L. and H.C.W. designed the study. X.R.C and H.C.W. analyzed the data and wrote the paper with input from K.D.L.

Competing interests. The authors declare that they have no conflicts of interest.

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