Interpretation of NO$_3$–N$_2$O$_5$ 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$_2$O$_5$ has large uncertainty under complicated ambient conditions and could even produce incorrect results unconsciously. To provide an assessment and solution to the dilemma, we formulate datasets 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$_2$O$_5$) and correspondingly simulated $[\text{N}_2\text{O}_5]/([\text{NO}_2] \times [\text{NO}_3])$, especially under high-aerosol conditions in winter. This gap reveals that the accuracy of $K_{eq}$ has a critical impact on the steady-state analysis in polluted regions. In addition, the accuracy of $\gamma$ (N$_2$O$_5$) derived by steady-state fit depends closely on the reactivity of NO$_3$ ($k_{\text{NO}_3}$) and N$_2$O$_5$ ($k_{\text{N}_2\text{O}_5}$). Based on a complete set of simulations, air mass of $k_{\text{NO}_3}$ less than 0.01 s$^{-1}$ with high aerosol and temperature higher than 10 °C is suggested to be the best suited for steady-state analysis of NO$_3$–N$_2$O$_5$ chemistry. Instead of confirming the validity of steady state by numerical modeling for every case, this work directly provides appropriate concentration ranges for accurate steady-state approximation, with implications for choosing suited methods to interpret nighttime chemistry in high-aerosol air mass.

1 Introduction

The nitrate radical (NO$_3$), an extremely reactive species prone to buildup at night, is an ideal candidate for steady-state analysis in combination with dinitrogen pentoxide (N$_2$O$_5$) due to fast equilibrium reactions between them (Reaction R1).

\begin{align*}
\text{NO}_2 + \text{NO}_3 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (\text{R1a}) \\
\text{N}_2\text{O}_5 + \text{M} & \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} \quad (\text{R1b})
\end{align*}

Under the steady-state condition, the lifetime of NO$_3$ (denoted as $\tau_{ss}(\text{NO}_3)$) can be calculated as the ratio of NO$_3$ concentration over the production rate ($k_{\text{NO}_3} + \text{O}_3[\text{NO}_2][\text{O}_3]$) or over the removal rate of both NO$_3$ and N$_2$O$_5$, as indicated in Eq. (1). A similar representation of N$_2$O$_5$ steady-state lifetime is also shown in Eq. (2). The loss frequencies of various sink pathways of NO$_3$ and N$_2$O$_5$ are integrated as total first order in the following equations, represented by the $k_{\text{NO}_3}$ and $k_{\text{N}_2\text{O}_5}$ terms. Briefly, $k_{\text{NO}_3}$ is contributed by the reaction of the NO$_3$ radical with NO and hydrocarbons and uptake on particles at night, ranging from hundredths of recip-
The application of ample, the ambient NO$_3$ method (Brown et al., 2009).

Numerous works have taken advantage of the steady-state approximation for the NO$_3$–N$_2$O$_5$ system is basically built on its chemical production and removal pathways, in case of extremely weak physical processes (e.g., transport, dilution, and deposition) relative to its chemical processes. With simultaneous measurements of NO$_3$, N$_2$O$_5$, and relevant precursor concentrations, the steady-state lifetime $\tau_{ss}$ (NO$_3$) and $\tau_{ss}$ (N$_2$O$_5$) can be quantified for a targeted period as shown in Eqs. (1) and (2). By substituting the $k$N$_2$O$_5$ with $0.25 \times c \times S_a \times \gamma$ (N$_2$O$_5$), the $\gamma$ (N$_2$O$_5$) and the reactivity of NO$_3$ (kNO$_3$, including the reactions of NO$_3$ with NO and hydrocarbons) can therefore be determined by Eqs. (4) and (5).

$$\tau_{ss}^{-1} (NO_3) \approx k_{NO_3} + 0.25c S_a K_{eq}[NO_2] \gamma (N_2O_5)$$

(4)

$$\gamma (N_2O_5) \approx k_{NO_3} \times (0.25c S_a K_{eq}[NO_2])^{-1}$$

(5)

Here $c$ represents the mean molecular velocity of N$_2$O$_5$, $S_a$ represents the aerosol surface area, and $K_{eq}$ is calculated from the rate constant of reversible Reactions (R1a).
(k_{R1a}) and (R1b) (k_{R1b}), which is a temperature-dependent parameter. It should be noted that the photolysis of NO₃ is not considered in the kNO₃ due to weak radiation at night, and the homogeneous hydrolysis was also ignored due to its small contribution in comparison to the heterogeneous pathway. A similar presumption was also implemented in previous studies (Brown et al., 2009; Mentel et al., 1996; Wahner et al., 1998). In the form of these two equations, the potential covariance between S₄ and NO₂ concentration can be avoided to decrease the uncertainty (Brown et al., 2009). By being fit to these two equations, γ (N₂O₅) can be directly derived from slope of the plot of τ_{eq}^{-1}(NO₃) against 0.25c_S₄K_{eq}[NO₂] or from the intercept of the plot of (0.25c_S₄τ_{eq}(N₂O₅))^{-1} against (0.25c_S₄K_{eq}[NO₂])^{-1} respectively. In the following analysis, the linear fit based on Eq. (5) is preferred in steady-state approximation.

2.2 Steady-state model and half-artificial datasets

The steady-state model is reformulated from a zero-dimensional box model to produce NO₃ and N₂O₅, which are in steady state as far as possible. It is constrained by measurements of NO, NO₂, O₃, CO, CH₄, VOCs, HCHO, S₄, relative humidity (RH), temperature (T), and pressure, coupled with the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2). Each data point is treated as an independent air mass, aging 10 h and keeping input constraint unchanged. As NO₃–N₂O₅ chemistry, the interest of this work, usually shows marked impacts during the night, only the time periods with negligible photolysis frequency are under consideration. In the standard simulation (herein referred to as Mod0), the uptake coefficient of N₂O₅ is set to 0.02, as a reasonable value of literature (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).

Two half-artificial datasets are derived from PKU2017 and TZ2018 field campaigns (see Sect. S2) based on the steady-state model for analysis in the following sections. The simulated NO₃ and N₂O₅ and other observed values used for the constraints of the steady-state model jointly formulate these half-artificial datasets. Specifically, the NO₃ and N₂O₅ concentrations in this dataset are output of the steady-state model simulation and guaranteed to be in steady state with respect to other observed precursors. To verify the steady state of NO₃ and N₂O₅ for each data point, we filtered the dataset according to the deviation between the steady-state lifetime of N₂O₅ (τ_{ss}(N₂O₅) = \frac{K_{NO₂}[NO₂]}{k_{R1b}[NO₂][O₃]}) and calculated lifetime of N₂O₅ (τ_{calc}(N₂O₅) = \frac{k_{R1b}[NO₂][O₃]}{K_{eq}[NO₂]-1}). If the deviation exceeds 10% for a data point, it will be excluded from the following analysis. We presume that if any data point output from the model is still out of steady state in terms of NO₃ and N₂O₅, the sink rate constant of air mass represented by this data point should be too weak for steady-state analysis within a reasonable timescale. In addition, the data higher than 5 ppbv NO are filtered out in the following calculation, since the resulting large variation in kNO₃ can bias the linear fit even though NO₃ and N₂O₅ approach steady state rapidly under high NO (discussed in Sect. 3.2). The fraction of excluded data is less than 8%, and they are expected to have little influence on our results. The calculated nighttime loss fraction accounted for by NO₃ and N₂O₅ show large discrepancy (see Sect. S3 and Fig. S2) between these two half-artificial datasets, which provide us a good opportunity to investigate the factors impacting steady-state approximation across different conditions.

Rather than using observation data directly, a half-artificial dataset can provide a larger amount of valid data for steady-state analysis with a known γ (N₂O₅) value. In addition, this method avoids the impacts from steady-state deviation, which helps to analyze the factors influencing γ (N₂O₅) quantification via steady-state approximation backwards from a known steady-state condition.

3 Results and discussion

3.1 Varying equilibrium coefficient under steady state

The rates of NO₃–N₂O₅ 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 Reactions (R1a) and (R1b) or the ratio of [N₂O₅]/([NO₂] × [NO₃]). Although this approach is reasonable under ideal conditions, the exact 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 NO₃–N₂O₅ is not negligible, especially under the high-aerosol-loading condition. NO₃ and N₂O₅ achieve a steady state after 1.5 h evolution, when concentration and rates remain constant (Fig. 1). In this simulation, the starting mixing ratios of NO₂ and O₃ are 10 and 23 ppbv, respectively, which is the average level for the nighttime conditions in PKU2017. The concentrations of these two precursors are held constant in the simulation to better illustrate the influence of removal rates. This result will stay almost the same no matter whether these starting values are initialized to be constant or allowed to vary. Under steady state, the net equilibrium reaction rate in Fig. 1b and c stays negative and positive for NO₃ and N₂O₅, respectively. In addition, the absolute values and difference of the forward and backward reaction rates remain unchanged after achieving steady state. This result is similar to a previous numerical calculation study (Brown et al., 2003), while the deviation between reversible reaction rates becomes larger in our case.

In this case, the original equilibrium is imperfectly realized (a perfect realization of the original equilibrium condition is that K_{eq} and the ratio of [N₂O₅]/([NO₂] × [NO₃]) are equivalent as in Eq. 6), leading to errors on the projection of NO₃ and N₂O₅ concentration via K_{eq} × [NO₂]. In fact, we note that a new equilibrium between NO₃ and
N$_2$O$_3$ is developed with constant but unequal rates. Under this new equilibrium condition, the ratio of (R1b) reaction rate (the red dashed line in Fig. 1d) over (R1a) reaction rate (the black dashed line in Fig. 1d) can be regarded as the degree of approaching original equilibrium (the blue line in Fig. 1d). In addition, this value is also the ratio of [N$_2$O$_3$]/([NO$_2$] × [NO$_3$]) against original $K_{eq}$; therefore we defined this ratio as a correction factor $\epsilon$, implemented to calculate accurate [N$_2$O$_3$]/([NO$_2$] × [NO$_3$]) with significant N$_2$O$_3$ removal pathways. The value of $K_{eq}$ after scaled by $\epsilon$ can be used for converting the concentration of NO$_3$ and N$_2$O$_3$ via Eq. (6):

$$\epsilon \times K_{eq} = \epsilon \times \frac{k_{R1a}}{k_{R1b}} = \frac{[N_2O_3]}{[NO_2][NO_3]}.$$  

Sensitivity tests are conducted to demonstrate the dependence of $\epsilon$ on relevant variables based on the steady-state model. The averages ambient conditions observed at the wintertime Peking University (PKU) site and summertime Tai Zhou (TZ) site are taken as two basic constraints for sensitivity tests (Table S2 in the Suppement). By separately altering variables, such as NO$_2$, O$_3$, kNO$_2$, kNNO$_3$, and $T$, the sensitivity of the $\epsilon$ value can be obtained as shown in Figs. S2 and S4. The $\epsilon$ value depends primarily on kN$_2$O$_3$ and $T$ in both scenarios, where $\epsilon$ increases with $T$ (approaching 1 under relatively high $T$) and decreases with kN$_2$O$_3$. In comparison, the $\epsilon$ value behaves insensitively to kNO$_3$ as well as NO$_2$ and O$_3$ concentration, at least within the range of reasonable ambient conditions. High kN$_2$O$_3$ results from high-aerosol events, usually occurring in winter accompanied by low temperature and high relative humidity in some populated areas (Baasandorj et al., 2017; Huang et al., 2014; Wang et al., 2017b, 2014), further decreasing the accuracy of original $K_{eq}$ values. It can be inferred that in order to accurately interpret the relationship of NO$_3$ and N$_2$O$_3$, calculation relying on the equilibrium equation and steady-state approximation should consider the dependence of $\epsilon$ on ambient conditions.

Even if the $K_{eq}$ value serves as a good representation of the ratio of [N$_2$O$_3$]/([NO$_2$] × [NO$_3$]) or $\epsilon$ can be readily quantified in the field, the discrepancy among different databases in calculating $K_{eq}$ still increases the uncertainties of NO$_3$–N$_2$O$_3$ calculation through steady-state approximation or equilibrium, which has not been carefully considered. Here, we apply a set of uniform formulas to describe $K_{R1a}$ and $K_{R1b}$ (see Sect. 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 Figs. S5 and S6, $K_{eq}$ variations derived from these six different databases reflect considerable discrepancy from each other, especially in colder conditions. Because parameterized $K_{eq}$ values are only dependent on ambient temperature, they continuously increase with time due to the decrease in temperature. In addition to the discrepancy between different $K_{eq}$ parameterizations, the $\epsilon$ 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 an existing database would fail to reproduce an accurate relationship between NO$_3$ and N$_2$O$_3$.

To further elucidate the impact of $K_{eq}$ on deriving $\gamma$ (N$_2$O$_3$) via steady-state approximation (hereafter defined as $\gamma_{ss}$ (N$_2$O$_3$)), Fig. S6 shows the steady-state fit based on all six database-derived $K_{eq}$ values and in the same time periods as Fig. S5 through Eqs. (4) and (5), respectively (both equations can derive a pair of $\gamma_{ss}$ (N$_2$O$_3$) and kN$_2$O$_3$). $K_{eq}$ (corrected with $\epsilon$) is calculated with NO$_3$ and N$_2$O$_3$ concentration simulated based on RACM2. Fits based on Eq. (4) could lead to 11%–46% underestimation of $\gamma_{ss}$ (N$_2$O$_3$), as indicated by varying slopes in Fig. S7b and d, when using the database-derived $K_{eq}$. Conversely, fit by Eq. (5) (shown in Fig. S7a and c) biases the result of kN$_2$O$_3$ as the slopes without much influence on $\gamma_{ss}$ (N$_2$O$_3$) as the intercept. Previous research ascribed inconsistent fit results between two equations to measurement uncertainty (Brown et al., 2009, 2006). However, fit with the original $K_{eq}$ might be the primary reason for such inconsistent results and even differentiates the derived $\gamma_{ss}$ (N$_2$O$_3$) and kNNO$_3$ from true values. Therefore,
steady-state fit based on Eq. (5) might be the best choice for $\gamma$ ($N_2O_5$) derivation via steady-state approximation. Similarly, Eq. (4) is preferred to be applied when $kNO_3$ is the final objective.

3.2 Impacts of NO$_3$–N$_2$O$_5$ reactivity on steady state

In order to further explore the impacting factors on the steady-state fit method, $\gamma_{ss}$ ($N_2O_5$) results are derived for each 2 h time period of the PKU2017 and TZ2018 datasets based on output from the steady-state model. Since the preset $\gamma$ ($N_2O_5$) 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. (5) 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 $\gamma_{ss}$ ($N_2O_5$) deviation dramatically with the increase in relative standard deviation of $kNO_3$ ($kNO_3$ RSD) in both winter and summer datasets. The positive correlation even gives rise to extreme deviation in the summer dataset, with up to almost 10 times of model setting $\gamma_{ss}$ ($N_2O_5$). In fact, there remain 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. This implies that large variation in $kNO_3$ only enhances the possibilities of inaccurate results from steady-state fit rather than hinder the $\gamma_{ss}$ ($N_2O_5$) quantification all the time.

In addition to the large variation in $kNO_3$ in a short time period, the absolute level of $kNO_3$ and $kN_2O_5$ could influence the possibilities of inaccurate results from steady-state fit due to the high $kNO_3$. Therefore, a trade-off between the variation in $kNO_3$ and the high level of $kNO_3$ (fast approach to steady state) should be made when deriving $\gamma_{ss}$ ($N_2O_5$).

 boosts the approach to steady state (Sect. S5 and Fig. S8), higher levels of $kNO_3$ amplify the bias of $\gamma_{ss}$ ($N_2O_5$), contrary to $kN_2O_5$, with the same relative variation in $kNO_3$ (Sect. S6 and Fig. S10). This indicates that the region with plural emissions (e.g., strong biogenic or vehicular emission) might not be suited for steady-state fit due to the high $kNO_3$. Therefore, a trade-off between the variation in $kNO_3$ and the high level of $kNO_3$ (fast approach to steady state) should be made when deriving $\gamma_{ss}$ ($N_2O_5$).
3.3 Implication for accurate steady-state analysis of NO$_3$–N$_2$O$_5$

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

Here almost 20,000 simulations are displayed in the parallel plot of Fig. 4, where each line connects five constraint parameters to the calculated steady-state time and $\varepsilon$ (the correction factor for $K_{eq}$ parameterization to match the exact ratio of $[N_2O_5]/([NO_2] \times [NO_3])$, detailed in Eq. 6). The gray traces represent the simulations that could not match steady state within 600 s and were defined as less valid cases here. By this definition, we intend to indicate that it is also viable to apply steady-state approximation on air mass, which requires more than 600 s to match steady state, whereas the uncertainty caused therefrom could increase to some extent.

The pink and blue traces together represent the simulations that could match valid steady state within 600 s without consideration of $K_{eq}$ deviation (in other words the value of $\varepsilon$). Furthermore, the criteria to apply steady-state approximation appropriately is approach to steady state within 600 s and $\varepsilon$ larger than 0.9, which are indicated as pink traces. While the levels of $T$, NO$_2$, and O$_3$ have a minor effect on the approach to steady state, simultaneous low kN$_2$O$_5$ (indicated as low $S_a$ 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 $S_a$ increases to at least 3000 µm$^2$ cm$^{-3}$ with $\gamma$ (N$_2$O$_5$) of 0.02. This implies that clean air mass is not suited for steady state in any cases, whereas the high-aerosol condition provides more possibilities to approach steady state even with low kNO$_3$. However, in order to interpret NO$_3$–N$_2$O$_5$ chemistry with an accurate $K_{eq}$ coefficient, the $\varepsilon$ 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 $[N_2O_5]/([NO_2] \times [NO_3])$ from original $K_{eq}$ (also indicated in Fig. 2), leading to inaccurate results of calculation based on $K_{eq}$.

4 Conclusions

In this study, 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, $\varepsilon$, is relatively sensitive to N$_2$O$_5$ 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 a high level of kNO₃ might amplify the bias of γₛₛ (N₂O₅) yield from steady-state fit and appears to be accompanied by fast variations, air mass of kNO₃ less than 0.01 s⁻¹1 with high aerosol and T higher than 10 °C are therefore the best suited for steady-state analysis of NO₃−N₂O₅ 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 winter conditions will also be applicable. Our results provide an insight into improving the accuracy of the steady-state approximation method and finding suited areas to interpret nighttime chemistry. Further improvement of in situ NO₃−N₂O₅ budget quantification might rely on the direct measurements via flow tube system or machine learning prediction based on ancillary parameters.

**Code and 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).

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