



Supplement of

Interpretation of $\text{NO}_3\text{--N}_2\text{O}_5$ observation via steady state in high-aerosol air mass: the impact of equilibrium coefficient in ambient conditions

Xiaorui Chen et al.

Correspondence to: Haichao Wang (wanghch27@mail.sysu.edu.cn) and Keding Lu (k.lu@pku.edu.cn)

The copyright of individual parts of the supplement might differ from the article licence.

1	Contents
2	<i>Supplementary Text:</i>
3	Text S1. Ambient case invalid for NO ₃ -N ₂ O ₅ steady state analysis
4	Text S2. Observation datasets from field campaigns 2017PKU and 2018TZ
5	Text S3. Characteristic of nighttime NO ₃ -N ₂ O ₅ loss pathway in half-artificial dataset
6	Text S4. Parameterization of Keq coefficient in different databases
7	Text S5. Sensitivity tests of time to approach steady state
8	Text S6. The impacts of k_{NO_3} and $k_{\text{N}_2\text{O}_5}$ levels on $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$
9	
10	<i>Supplementary Figures:</i> Figure S1 to Figure S10
11	
12	<i>Supplementary Tables:</i> Table S1 to Table S4
13	
14	<i>References</i>
15	
16	
17	

18 **S1. Ambient case invalid for NO₃-N₂O₅ steady state analysis**

19 Take two typical cases in winter and summer respectively for example to illustrate the
20 conditions under which steady state analysis is invalid for interpreting NO₃-N₂O₅
21 observation and deriving $\gamma(\text{N}_2\text{O}_5)$. Over the period of wintertime case shown in Figure S1,
22 the NO_x and Sa concentration were low, indicating a clean episode. The $\gamma(\text{N}_2\text{O}_5)$ and $k\text{NO}_3$
23 can be determined from the intercept and slope respectively by linear fit based on steady
24 state equation Eq. (5). The details and derivation of this approach are provided in
25 introduction and method section. Albeit the correlation coefficient for deriving $\gamma(\text{N}_2\text{O}_5)$ by
26 steady state approximation appears to be high, an unreasonably negative $k\text{NO}_3$ value derived
27 during this analysis period (Figure S1d) indicates that the steady state in this case still
28 requires much longer induction time due to low strength of NO₃-N₂O₅ sink. In summertime
29 case, although large sink rate contributed to fast approach of steady state, frequent injection
30 of NO_x emission could significantly modify the air mass condition. The time for mixing and
31 reacting was still less than enough as emissions deviates the air mass from steady state
32 (Figure S1e-S1g), leading to weak correlation factors (Figure S1h).

33

34 **S2. Observation datasets from field campaigns 2017PKU and 2018TZ**

35 The datasets used for analysis in this study were obtained from two field campaigns with
36 different ambient conditions. The PKU2017 winter campaign took place from mid-November
37 to late-December 2017 in the campus of Peking University, which is at urban area of Beijing,
38 China. And the other one TZ2018 summer campaign took place from late-May to mid-June
39 2018 at a suburban supersite, Taizhou, China. More specific information about these two
40 campaigns can be referred to our previous studies (Ma et al., 2019; Wang et al., 2020), while
41 only basic background of site location and analysis-relevant instrumentation are provided
42 below.

43 During the PKU2017 campaign, all instruments were applied on the roof of building in
44 the campus of Peking University, which was about 100 m west to the major roads with strong
45 influence of vehicle emissions. Each sampling inlet was distributed at least 20 m above the
46 ground. The strong northerly winds with dry and clean air mass during the winter would
47 periodically transport to this site, bring in fresh O₃ at night. The TZ2018 site is surrounded by
48 agricultural land and fishponds, resulted in strong influence of biogenic emissions and
49 occasional biomass burning. Each sampling inlet was distributed about 5 m above the ground.
50 It should be noted that low concentration level of NO was frequently observed at this site due
51 to a major highway within 0.5 km.

52 Same instrumentation was implemented in these two campaigns, and the related
53 information are given in Table S1. We adjusted the nighttime NO concentration near the
54 detection limit to zero during the periods with O₃ concentration higher than 25 ppbv, as the
55 lifetime of NO would be extremely short at night under this condition and the NO
56 measurement at the low level usually has large uncertainty.

57

58 S3. Characteristic of nighttime NO₃-N₂O₅ loss pathway in half-artificial dataset

59 The validity of NO₃-N₂O₅ steady state depends on their atmospheric lifetime, in other
60 words their loss rate constants (Brown et al., 2003). In different seasons or areas, variations of
61 emission, temperature, and other relevant factors can sufficiently change the sink strength of
62 ambient NO₃ and N₂O₅ and thus relative occupations of these pathways. As half-artificial
63 datasets (detailed in Methods) indicated, the average nighttime loss rate of NO₃ and N₂O₅ at
64 PKU site in winter were 41 pptv h⁻¹ and 195 pptv h⁻¹, whereas much higher rates were obtained
65 at TZ2018 campaign with 451 pptv h⁻¹ for NO₃ and 390 pptv h⁻¹ for N₂O₅. Distinguished from
66 a dominant sink rate of N₂O₅ in winter, total sink rate attribution shifted to NO₃ side in summer
67 with significant larger sink strength than that in winter. The average proportions of NO₃ and
68 N₂O₅ removal in each night is shown in Figure S2, where the nights with missing data
69 represents that there is less than 15% valid data. Under the condition of approximate steady
70 state, the sink flux contributed through N₂O₅ reaches up to 55~95% in wintertime campaign
71 2017PKU with an average higher than 80%, whilst it turns out to be less than 50%, even 5%,
72 in 2018TZ summer campaign. Besides the different emission compositions at these two sites
73 leading to significant distinction of removal attribution (strong biogenic emission at TZ site
74 and high anthropogenic emission at PKU site), high temperature during summer facilitates the
75 equilibrium in reactions R1 shifting to NO₃, further increasing the sink flux of NO₃. The
76 attribution of removal pathways among NO₃ and N₂O₅ directly determines the weights of two
77 terms on the right side of steady state expressions Eq. (4) and Eq. (5), contributing to assessing
78 the impacts of several variables on steady state fitting among different reactivity conditions.

79 Taking two typical cases from these two datasets for example, the N₂O₅ lifetime was about
80 20 minutes in winter (Figure S3(a)), while was largely reduced to 100 seconds for summertime
81 case (Figure S3(c)). The steady state lifetime of N₂O₅ ($\tau_{ss}(N_2O_5) = \frac{[N_2O_5]}{k_{R1}[NO_2][O_3]}$) and
82 calculated lifetime of N₂O₅ ($\tau_{calc}(N_2O_5) = (k_{N_2O_5} + \frac{k_{NO_3}}{K_{eq}[NO_2]})^{-1}$) were used for determine
83 whether the situation had satisfied steady state (see details in methods section). Significantly
84 different atmospheric lifetime for these two cases was majorly resulted from varying uptake

85 removal pathways instead of $k\text{NO}_3$ from gas-phase reactions. Higher humidity at TZ site
86 during nights facilitated hygroscopic growth of particles, the Sa concentration of which usually
87 increased up to thousands of $\mu\text{m}^2 \text{cm}^{-3}$ promoting the uptake reactions of NO_3 and N_2O_5 ,
88 whereas Sa in the PKU site case become lower than $500 \mu\text{m}^2 \text{cm}^{-3}$ under the impact of clean
89 and dry air mass. The steady state lifetime denoted by blue dash line in Figure S3(a)&(c),
90 shows good agreement with atmospheric lifetime in both of cases, indicating that the NO_3 -
91 N_2O_5 chemical system simulated by steady state model is validated to be approximate steady
92 state (deviation $<5\%$). However, even in these cases, the derived uptake coefficient of N_2O_5 ,
93 $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$, through steady state fitting (Figure S3(b)&(d)) still have a significant bias ($>20\%$)
94 from the setting values 0.02. Furthermore, we found that unexpected difference between
95 $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ fitting results and $\gamma(\text{N}_2\text{O}_5)$ setting values is common for all selected steady state
96 periods in datasets. Since the influence of covariance of Sa and $K_{\text{eq}} \times [\text{NO}_2]$ has been avoided
97 by applying Eq. (5) (Brown et al., 2009), the bias of $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ presented in the above fitting
98 calculation could be produced by interaction between equilibrium and steady state, variation
99 of relevant parameters in the fitting equations (such as $k\text{NO}_3$, $k\text{N}_2\text{O}_5$, etc), which are discussed
100 in the main text.

101

102 **S4. Parameterization of Keq coefficient in different databases**

103 Keq of NO₃-N₂O₅ system is a temperature dependent parameter, which has been
 104 extensively quantified in the laboratory (Pritchard, 1994). According to simultaneous
 105 measurements of N₂O₅, NO₃ and NO₂ concentration in a reaction chamber, the Keq can be
 106 directly calculated (Cantrell et al., 1988;Graham and Johnston, 1978;Osthoff et al., 2007),
 107 while the measurements of k_{R1a} and k_{R1b} or other accompanied parameters provides indirect
 108 ways to quantify Keq (Cantrell et al., 1993;Kircher et al., 1984;Smith and Ravishankara, 1985).
 109 However, distinct differences arise from these Keq results, which might be ascribed to the
 110 calibration uncertainty of absorption cross sections of NO₃ and NO₂ molecule (Osthoff et al.,
 111 2007). Jet Propulsion Laboratory (JPL) database provides an empirical formula, similar with
 112 Arrhenius formula, to calculate Keq in a simple way:

$$113 \quad K_{eq}(JPL) = A \times \exp(B/T), \quad (S1)$$

114 Here T denotes ambient temperature, and coefficients A and B are empirical parameter derived
 115 from laboratory works. Nevertheless, only parameterizations of k_{R1a} and k_{R1b} based on fall-off
 116 curve are described in IUPAC database and most of chemical mechanisms, without a direct
 117 formula to estimate Keq value. To our best knowledge, only one previous study compared two
 118 of these parameterizations in terms of temperature dependence (Chang et al., 2011).

119 Here, a set of uniform formulas are applied to describing k_{R1a} and k_{R1b}, capable of
 120 reproducing the preferred values given by several popular atmospheric chemistry mechanisms
 121 (Mozart, CB05, Saprc07, RACM2 and kinetic databases JPL2015 as well as IUPAC2017) and
 122 finally calculating Keq. As shown in Eq. (S2) and Eq. (S3):

$$123 \quad k_{R1a}([M], T) = \left(\frac{k_o(T)[M]}{1 + \frac{k_o(T)[M]}{k_{\infty}(T)}} \right) \times F \left(\left\{ 1 + \left[\frac{\log_{10} \left(\frac{k_o(T)[M]}{k_{\infty}(T)} \right)}{g} \right]^2 \right\}^{-1} \right), \quad (S2)$$

$$k_{R1b}([M], T) = \left(\frac{\frac{k_o(T)[M]e^{-\frac{-B1}{T}}}{A}}{1 + \frac{k_o(T)[M]e^{-\frac{-B1}{T}}}{k_\infty(T)e^{-\frac{-B2}{T}}}} \right) \times F \left(\left[1 + \frac{\log_{10} \left(\frac{k_o(T)[M]e^{-\frac{-B1}{T}}}{k_\infty(T)e^{-\frac{-B2}{T}}} \right)}{g} \right]^2 \right)^{-1}, \quad (S3)$$

125 The parameter [M] represent molecular density in ambient air. $k_o(T)$ and $k_\infty(T)$ are rate
 126 coefficients of third-body reactions under low and high pressure respectively, which over
 127 different temperatures can be extrapolated by Eq. (S4) and Eq. (S5) based on 300 K
 128 measurement or simulation results:

$$129 \quad k_o(T) = k_o^{300} \left(\frac{T}{300} \right)^{-n}, \quad (S4)$$

$$130 \quad k_\infty(T) = k_\infty^{300} \left(\frac{T}{300} \right)^{-m}, \quad (S5)$$

131 All parameters in the above formulas are summarized in Table S3 and Table S4, which
 132 can be applied to calculating Keq coefficient via k_{R1a}/k_{R1b} . We found that there are significant
 133 differences among the parameters from these chemical mechanisms and databases, with a
 134 maximum discrepancy of 63% propagating to Keq at 298 K.

135

136 S5. Sensitivity tests of time to approach steady state

137 In Figure S8 and Figure S9, a series of sensitivity test provide an assessment of the time
138 a valid steady state needs under several conditions. The most sensitive variables to the time to
139 reach a valid steady state are $k\text{N}_2\text{O}_5$, $k\text{NO}_3$ and T, the enhancement of which reduces the
140 induction time, facilitating the approach to valid steady state of $\text{NO}_3\text{-N}_2\text{O}_5$ system. The time
141 for a simulation of a particular case, starting from initialized conditions to meet the steady
142 state criterion (detailed in the methods section), is defined as the time to reach a valid steady
143 state. In the case of increasing $k\text{N}_2\text{O}_5$ and $k\text{NO}_3$, the fast approaching to steady state is accounted
144 by lower concentration of NO_3 and N_2O_5 when the steady state is valid. By comparing the
145 sensitivity tests based on summertime (Figure S8(a)) and wintertime (Figure S8(b)) conditions,
146 the impacts of $k\text{N}_2\text{O}_5$ on approaching steady state is found to be more efficient than that of
147 $k\text{NO}_3$ in winter, while both contribute similarly in summer.

148 The different sensitivities to their reactivity in different seasons could be determined by
149 the weights of loss pathways (Text S3). During the winter, such as the condition of PKU2017,
150 the N_2O_5 usually accounted by over 80% of the overall loss frequency of $\text{NO}_3\text{-N}_2\text{O}_5$ system,
151 leading to high sensitivity to $k\text{N}_2\text{O}_5$, while comparable loss frequency was occupied by both
152 of NO_3 and N_2O_5 during the summer. As for the temperature, lower temperature shifts the
153 equilibrium in R1 to N_2O_5 side, which delay the time for developing equilibrium. By contrast,
154 enhanced loss through NO_3 with higher ambient temperature decreases the influence of
155 equilibrium, boosting the approach to steady state. Moreover, Figure S9 shows relatively weak
156 sensitivity of NO_2 and O_3 concentration to steady state approach. While changing O_3
157 concentration barely contribute to promote a valid steady state in the scenario of this analysis,
158 the NO_2 concentration shows a positive sensitivity in some cases. Like the ambient
159 temperature, changing NO_2 concentration could shift the ratio of $\text{N}_2\text{O}_5/\text{NO}_3$ when steady state
160 is valid and thus the time it requires. Especially under the condition of low ratio of NO_2 to O_3 ,
161 like that in TZ2018, the enhancement of NO_2 concentration shift NO_3 to N_2O_5 production and
162 amplify the influence of equilibrium reactions. Instead, with a sufficiently high ratio of NO_2/O_3 ,
163 the loss associated with $\text{NO}_3\text{-N}_2\text{O}_5$ system has been already dominated by N_2O_5 removal,

164 eliminating the influence of NO₂ increase on delaying steady state. Previous research has also
165 found similar trends of time to develop steady state according to simple scenarios simulated
166 by box model (Brown et al., 2003).

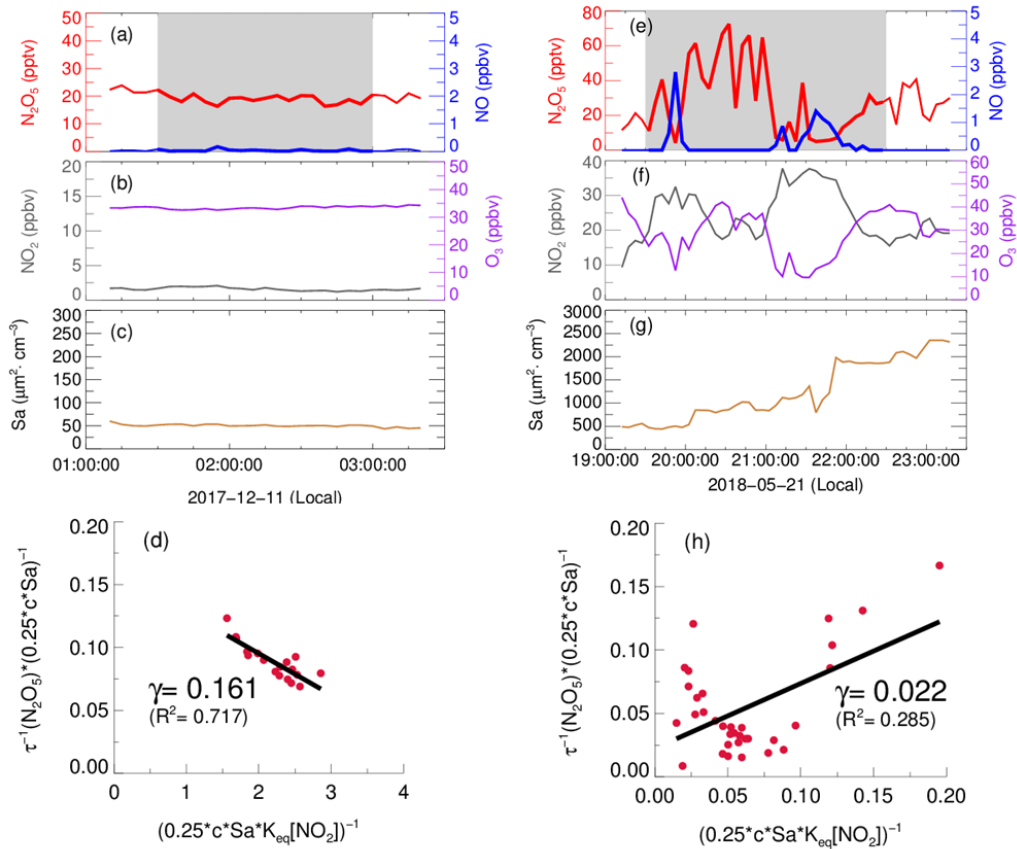
167

168 **S6. The impacts of $k\text{NO}_3$ and $k\text{N}_2\text{O}_5$ levels on $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$**

169 In order to demonstrate the impacts of $k\text{NO}_3$ level on deriving $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$, another three
170 half artificial data set are formulated through steady state model also based on the same
171 observational constraints with $k\text{NO}_3$ levels increased to 3 times (Mod1), 6 times (Mod2) and
172 10 times (Mod3) respectively, while other parameters remained unchanged. Similarly, the
173 steady state fitting is used to obtain $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ for each 2-hour time-period as Mod0. The mean
174 discrepancy from complete steady state of these time periods and the median deviation of
175 derived $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ from pre-set $\gamma(\text{N}_2\text{O}_5)$ are shown as solid circles and triangles in Figure S9.
176 With the enhancement of $k\text{NO}_3$ constraints, $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ deviation from true value increase
177 dramatically, though the $\text{NO}_3\text{-N}_2\text{O}_5$ system behave generally closer to steady state. A larger
178 deviation of $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ will be yielded from linear fit at a higher $k\text{NO}_3$ level, while the relative
179 varieties of $k\text{NO}_3$ stay the same. It indicates that the region with strong biogenic emissions is
180 not suited to steady state fitting, such as TZ site, neither are the time periods with NO injection
181 due to the resulted high reactivity and fast variation. Therefore, air mass with medium to low
182 level of $k\text{NO}_3$ is required to produce accurate $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ when applying steady state to analysis,
183 like data sets of airborne or residual measurements (Brown et al., 2009; Brown et al.,
184 2006; Morgan et al., 2015).

185 Similarly, the influence of different levels of $k\text{N}_2\text{O}_5$ is also explored by adjusting the pre-
186 set $\gamma(\text{N}_2\text{O}_5)$ or the Sa concentration constraint in the steady state model, as presented in the
187 Figure S10(c)&(d). With the enhancement of $k\text{N}_2\text{O}_5$ level up to 5 times (Mod4), 12.5 times
188 (Mod5) and 25 times (Mod6) of that in Mod0, the steady state approach can provide more
189 reliable results of $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$, especially in the summer data set. This is because a large $k\text{N}_2\text{O}_5$
190 level contributes to approaching steady state, which instinctively attenuates the deviation of
191 fitting results produced by the small difference between both sides of Eq. (5).

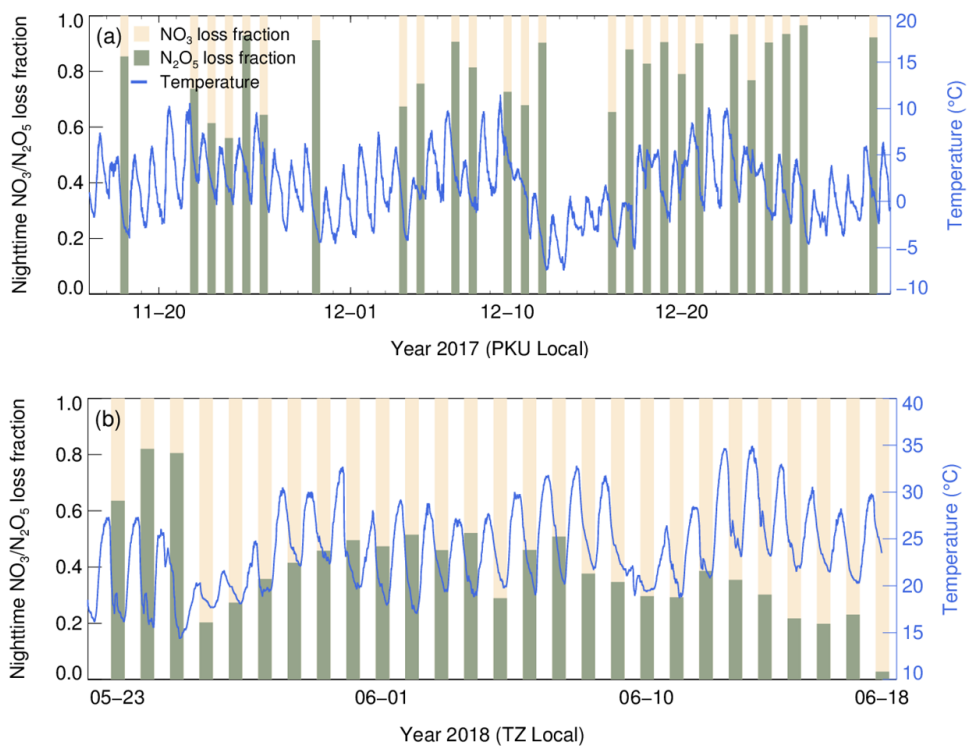
192



193

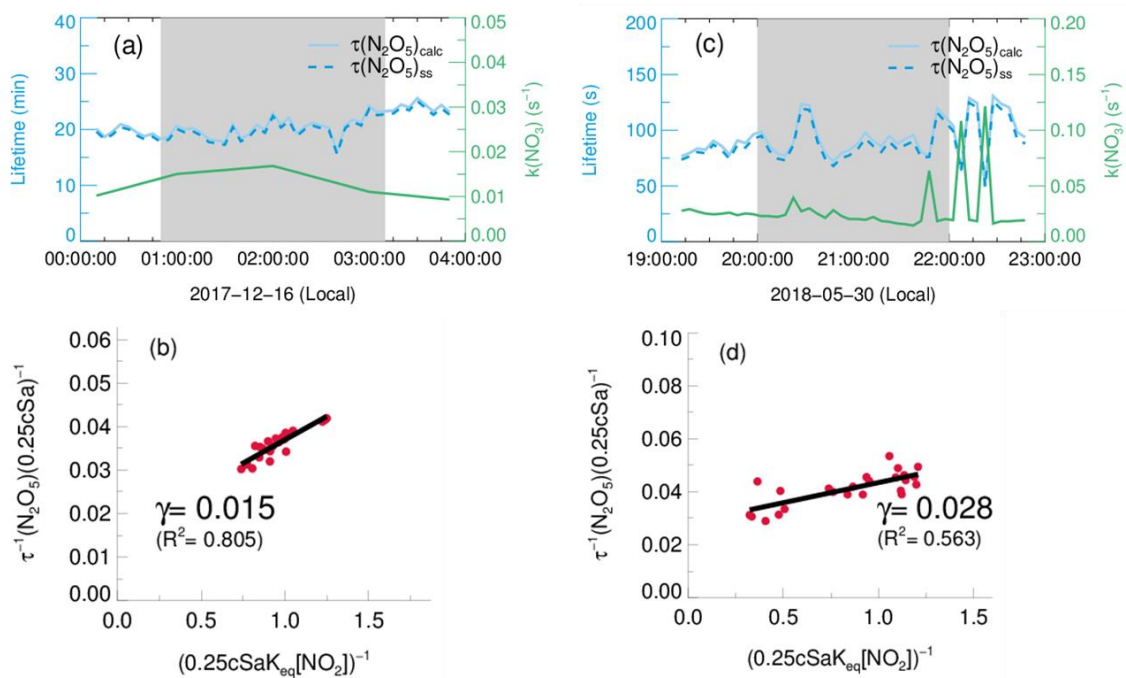
194 **Figure S1.** Exemplary steady state fit and the variations of relevant parameters in ambient conditions of
 195 (a)&(b)&(c)&(d) PKU site and (e)&(f)&(g)&(h) TZ site. The red dots in (d)&(h) represent the correlation plot
 196 between $(0.25cS_a\tau_{ss}(N_2O_5))^{-1}$ and $(0.25cS_aK_{eq}[NO_2])^{-1}$ used for deriving $\gamma(N_2O_5)$ and kNO_3 as illustrated
 197 in the method. The text on the plot gives the best fit results of $\gamma(N_2O_5)$ and correlation coefficient.

198



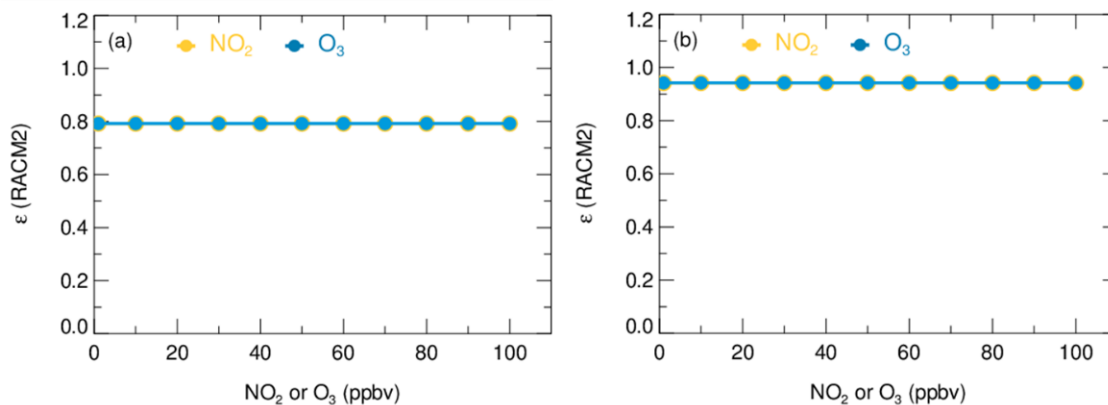
199
 200 **Figure S2.** Timeseries of each night ($\text{SZA} > 90^{\circ}$) mean $\text{NO}_3/\text{N}_2\text{O}_5$ loss pathways fractions calculated from steady
 201 state model and ambient temperature in (a) PKU2017 winter campaign and (b) TZ2018 summer campaign.

202



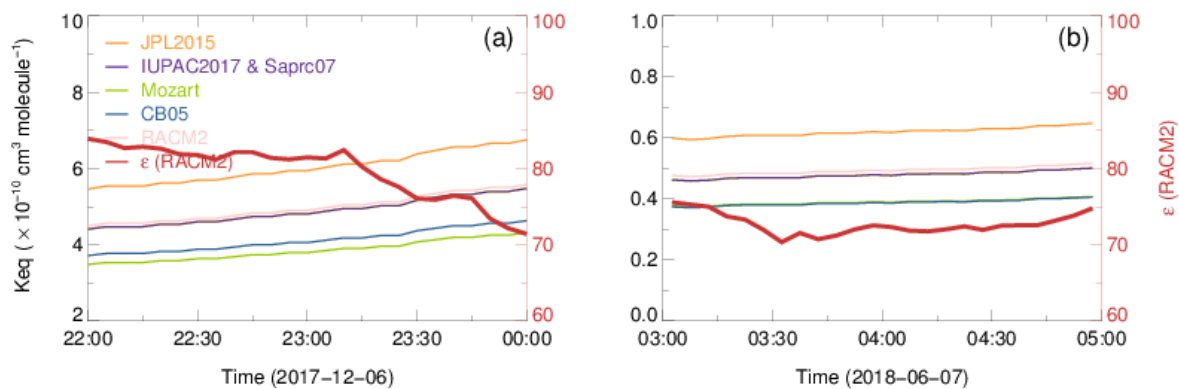
203
 204
 205
 206
 207
 208
 209
 210

Figure S3. Example analysis of N_2O_5 lifetime and $\gamma_{ss}(N_2O_5)$ derivation through steady state fitting for (a)&(b) PKU2017 case in winter and (c)&(d) TZ2018 case in summer. The steady state lifetime and calculated atmospheric lifetime are shown as blue dash line and full line respectively. The green line is lumped NO_3 loss frequency. The red dots in (b)&(d) represent data points in the shadow area, used for steady state fit (black line) by the plot of $(0.25cS_a\tau_{ss}(N_2O_5))^{-1}$ against $(0.25cS_aK_{eq}[NO_2])^{-1}$. The text on the plot gives the best fit results of $\gamma_{ss}(N_2O_5)$ and correlation coefficient.



211
212 **Figure S4.** Sensitivity plot of NO_2 and O_3 concentration against coefficient ϵ calculated based on rate constants
213 from RACM2. (a) Initial model constraint is according to winter condition of PKU2017; (b) Initial model
214 constraint is according to summer condition of TZ2018.

215



216

217

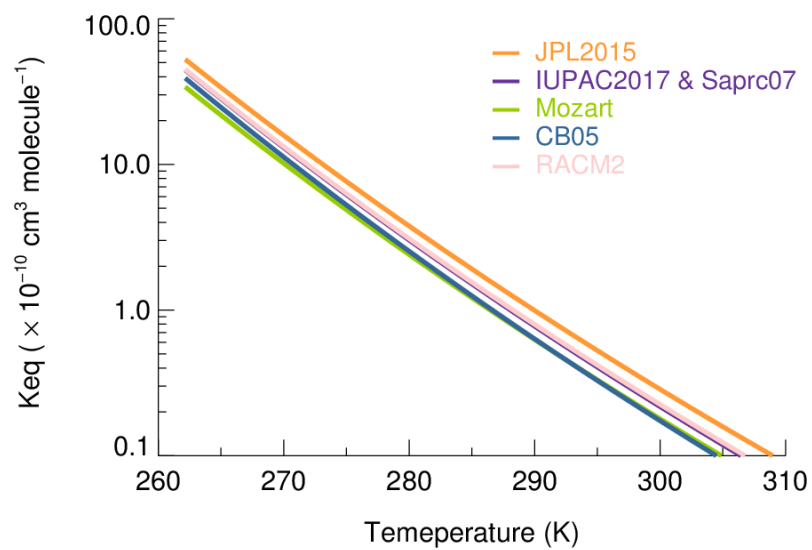
218

219

220

221

Figure S5. Exemplary comparison of K_{eq} parameterization in (a) 2017-12-06 of PKU2017 dataset and (b) 2018-06-07 of TZ2018 dataset, using parameters from JPL2015 (orange), IUPAC2017&Saprc07 (purple), Mozart (green), CB05 (blue) and RACM2 (pink). It should be noted that the databases of Saprc07 and IUPAC2017 have the exactly same parameters, K_{eq} derived from which are thus both denoted as purple line. The ϵ value calculated based on RACM2 is shown as red line.

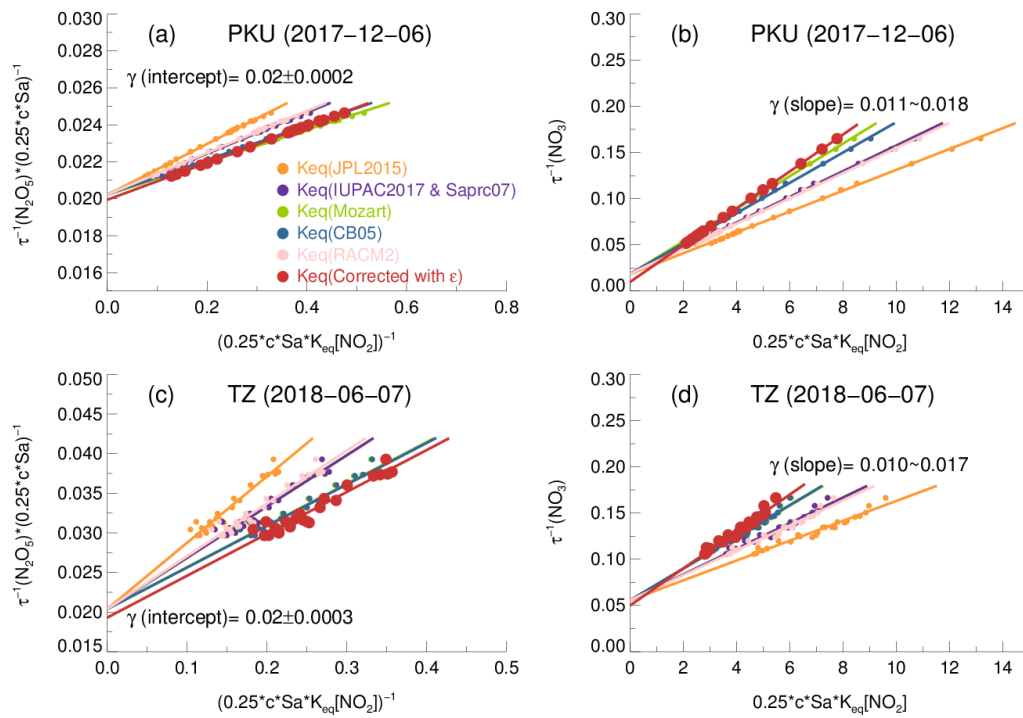


222

223

Figure S6. The dependence of different K_{eq} parameterizations on temperature.

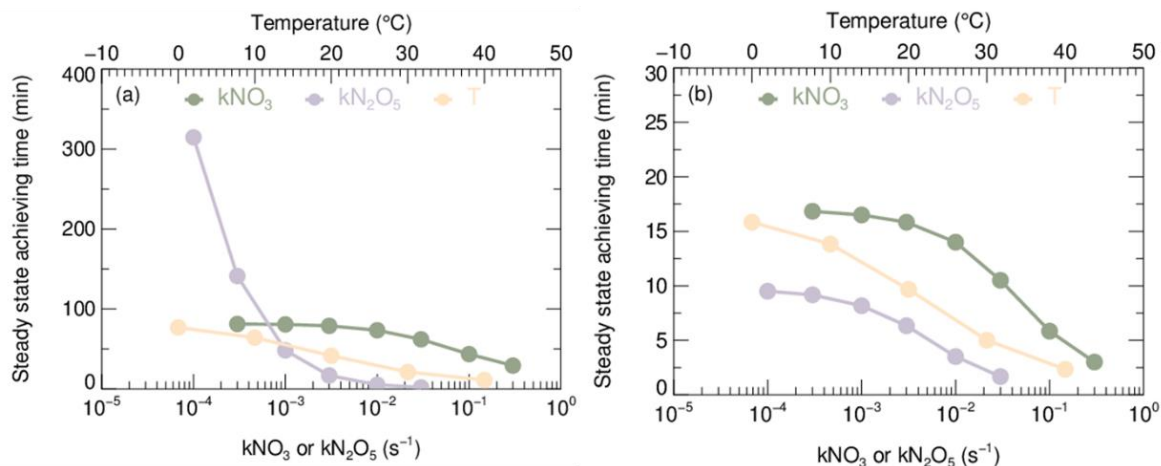
224



225

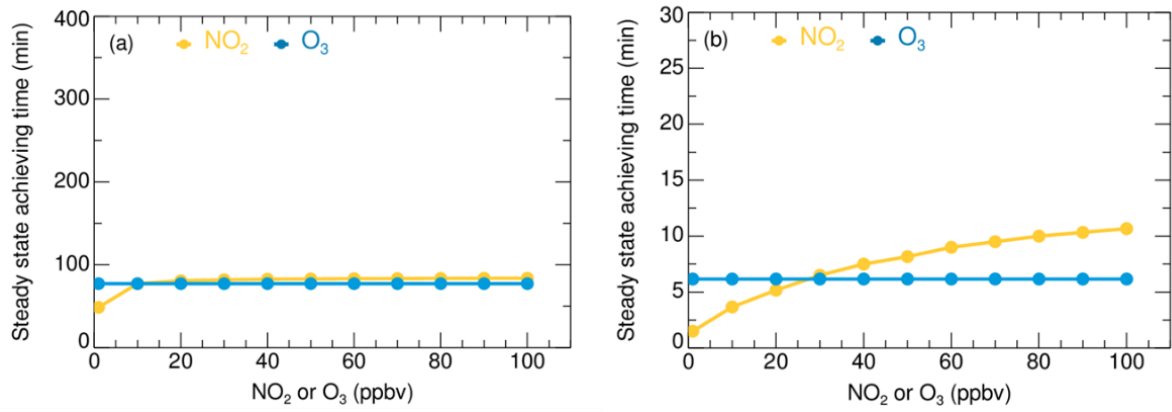
226 **Figure S7.** Exemplary fitting plot according to steady state approximation Eq. (1) (a)&(c) and Eq. (2) (b)&(d),
 227 using Keq parameterization of JPL2015 (orange), IUPAC2017&Saprc07 (purple), Mozart (green), CB05 (blue)
 228 and RACM2 (pink). The Keq (corrected by ϵ) is derived from output of steady state model coupled with RACM2.
 229 The values of derived $\gamma(N_2O_5)$ by intercept or slope are shown in text in the figures.

230



231
 232 **Figure S8.** Sensitivity plot of $k\text{NO}_3$, $k\text{N}_2\text{O}_5$ and T against steady state achieving time of $\text{NO}_3\text{-N}_2\text{O}_5$ system. The
 233 trace of T is plotted against the upper horizontal axis and the traces of the other two parameters are plotted
 234 against the lower horizontal axis. (a) Initial model constraint is according to winter condition of PKU2017; (b)
 235 Initial model constraint is according to summer condition of TZ2018.

236



237

238

Figure S9. Sensitivity plot of NO₂ and O₃ concentration against steady state achieving time of NO₃-N₂O₅ system.

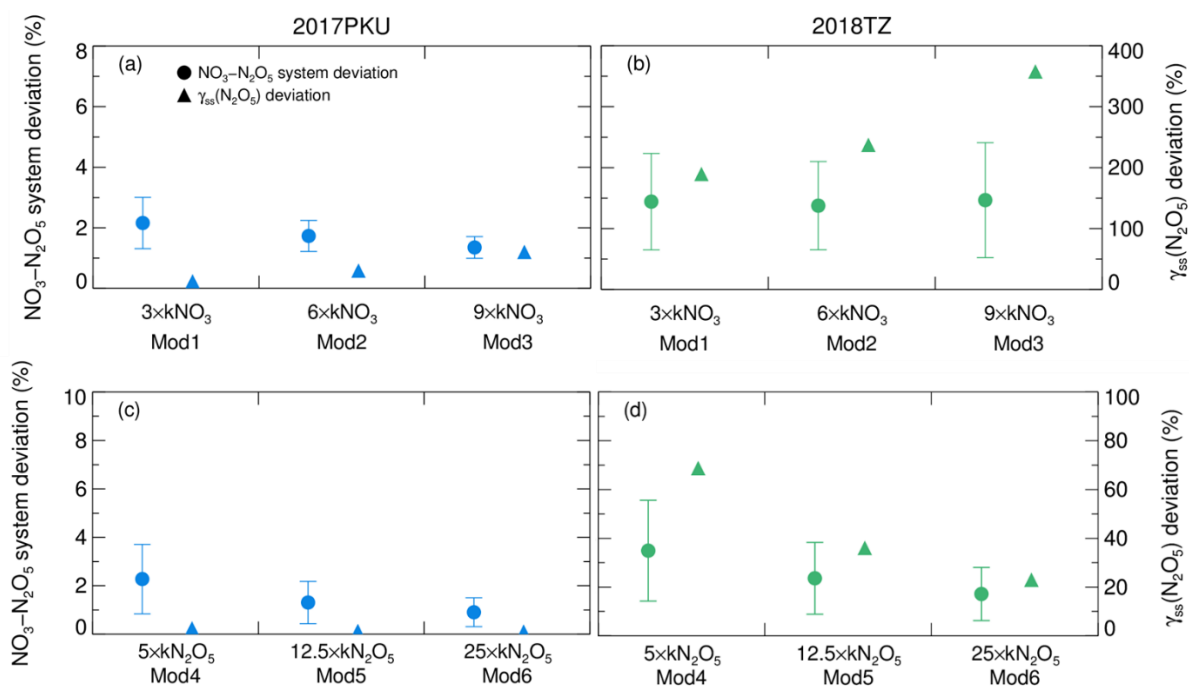
239

(a) Initial model constraint is according to winter condition of PKU2017; (b) Initial model constraint is according

240

to summer condition of TZ2018.

241



242

243

244

245

246

247

248

249

Figure S10. The average of $\text{NO}_3\text{-N}_2\text{O}_5$ system deviating from steady state and the median value of $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$ deviating from true value determined from different model constraints based on (a)&(c) PKU2017 dataset in blue and (b)&(d) TZ2018 dataset in green. The full circles represent the average of $\text{NO}_3\text{-N}_2\text{O}_5$ system deviating from steady state and the triangles represent the median deviation of $\gamma_{\text{ss}}(\text{N}_2\text{O}_5)$. As indicated in the text, the $k\text{NO}_3$ of Mod1, Mod2 and Mod3 are multiplied by 3,6 and 10 respectively against Mod0, and the $k\text{N}_2\text{O}_5$ of Mod4, Mod5 and Mod6 are multiplied by 5, 12.5 and 25 respectively against Mod0.

250 **Table S1.** Principal parameters and performance of related instruments.

Parameter	Technique	Time resolution	Detection Limit(1 σ)	Accuracy
NO	Chemiluminescence ^a	1 min	200 pptv	$\pm 20\%$
NO ₂	Chemiluminescence	1 min	300 pptv	$\pm 20\%$
O ₃	UV photometry	1 min	500 pptv	$\pm 5\%$
VOCs	GC-MS/FID ^b	60 min	20-300 pptv	$\pm 15\%$
Monoterpene	PTR-MS ^c	10 s	20 ppbv	$\pm 15\%$
Sa	Nano SMPS, SMPS, APS	5 min	-	$\pm 10\%$

251 ^a Photolytic conversion to NO through blue light before detection; ^b Gas chromatography equipped with a mass spectrometer and a flame
 252 ionization detector; ^c Monoterpene was only measured in TZ2018.

253

254 **Table S2.** Parameters of initial model constraint for sensitivity test.

Parameters	NO ₂ /ppbv	O ₃ /ppbv	T/K	Sa/ $\mu\text{m}^2 \cdot \text{cm}^{-3}$	$\gamma(\text{N}_2\text{O}_5)^{\text{a}}$	$k\text{NO}_3/\text{s}^{-1}$
Winter case	10	23	276	540	0.02	9×10^{-3}
Summer case	27	49	300	2670	0.02	9×10^{-2}

255 ^{a.} With the Sa, T and $\gamma(\text{N}_2\text{O}_5)$, the constraint of $k\text{N}_2\text{O}_5$ can be calculated as $6 \times 10^{-4} \text{s}^{-1}$ for winter case and $3 \times 10^{-3} \text{s}^{-1}$ for summer case.

256

257 **Table S3.** Summary of parameters for calculating rate constant of k_{R1a} .

Source	k_0^{300}	n	k_∞^{300}	m	F	g
JPL2015	2.4×10^{-30}	3.0	1.6×10^{-12}	-0.1	0.6	1.0
Mozart	2.0×10^{-30}	4.4	1.4×10^{-12}	0.7	0.6	1.0
CB05	2.0×10^{-30}	4.4	1.4×10^{-12}	0.7	0.6	1.0
Saprc07	3.6×10^{-30}	4.1	1.9×10^{-12}	-0.2	0.35	$0.75-1.27 \times \log_{10} 0.35$
RACM2	2.0×10^{-30}	4.4	1.4×10^{-12}	0.7	0.6	1.0
IUPAC2017	3.6×10^{-30}	4.1	1.9×10^{-12}	-0.2	0.35	$0.75-1.27 \times \log_{10} 0.35$

258

259

260 **Table S4.** Summary of parameters for calculating rate constant of k_{R1b} .

Source	k_0^{300}	n	k_∞^{300}	m	F	g	A	B ₁	B ₂
JPL2015 ^a	2.4×10^{-30}	3.0	1.6×10^{-12}	-0.1	0.6	1.0	5.8×10^{-27}	10840	10840
Mozart	2.2×10^{-30}	4.4	1.4×10^{-12}	0.7	0.6	1.0	3.0×10^{-27}	10900	10900
CB05 ^b	$k_0^{300}/A = 1.0 \times 10^{-3}$	3.5	$k_\infty^{300}/A = 9.7 \times 10^{14}$	-0.1	0.45	1.0	-	11000	11080
Saprc07 ^b	$k_0^{300}/A = 1.3 \times 10^{-3}$	3.5	$k_\infty^{300}/A = 9.7 \times 10^{14}$	-0.1	0.35	0.75- $1.27 \times \log_{10} 0.35$	-	11000	11080
RACM2	2.2×10^{-30}	4.4	1.4×10^{-12}	0.7	0.6	1.0	2.7×10^{-27}	11000	11000
IUPAC20 17 ^b	$k_0^{300}/A = 1.3 \times 10^{-3}$	3.5	$k_\infty^{300}/A = 9.7 \times 10^{14}$	-0.1	0.35	0.75- $1.27 \times \log_{10} 0.35$	-	11000	11080

261 a. This rate constant expression is reformed from k_{R1a}/K_{eq} as defined in JPL2015, where the k_{R1a} and K_{eq} are calculated with values
 262 recommended by JPL2015;

263 b. The k_0^{300}/A and k_∞^{300}/A are given in the form of ratio instead of separately.

264

265 **References:**

- 266 Brown, S. S., Stark, H., and Ravishankara, A. R.: Applicability of the steady state approximation to the
267 interpretation of atmospheric observations of NO₃ and N₂O₅, *J. Geophys. Res.- Atmos.*, 108,
268 10.1029/2003jd003407, 2003.
- 269 Brown, S. S., Ryerson, T. B., Wollny, A. G., Brock, C. A., Peltier, R., Sullivan, A. P., Weber, R. J., Dube, W. P.,
270 Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen oxide
271 processing and its role in regional air quality, *Science*, 311, 67-70, 10.1126/science.1120120, 2006.
- 272 Brown, S. S., Dube, W. P., Fuchs, H., Ryerson, T. B., Wollny, A. G., Brock, C. A., Bahreini, R., Middlebrook, A.
273 M., Neuman, J. A., Atlas, E., Roberts, J. M., Osthoff, H. D., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A.
274 R.: Reactive uptake coefficients for N₂O₅ determined from aircraft measurements during the Second Texas Air
275 Quality Study: Comparison to current model parameterizations, *J. Geophys. Res.- Atmos.*, 114, D00F10(01-16),
276 Artn D00f10
277 10.1029/2008jd011679, 2009.
- 278 Cantrell, C., Davidson, J., McDaniel, A., Shetter, R., and Calvert, J.: The equilibrium constant for N₂O₅ = NO₂
279 + NO₃ - Absolute determination by direct measurement from 243 to 397 K, *The Journal of Chemical Physics*,
280 88, 10.1063/1.454679, 1988.
- 281 Cantrell, C., Shetter, R., Calvert, J., Tyndall, G., and Orlando, J.: Measurement of rate coefficients for the
282 unimolecular decomposition of N₂O₅, *The Journal of Physical Chemistry*, 97, 10.1021/j100138a013, 1993.
- 283 Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous Atmospheric
284 Chemistry, Ambient Measurements, and Model Calculations of N₂O₅: A Review, *Aerosol Sci. Technol.*, 45, 665-
285 695, 10.1080/02786826.2010.551672, 2011.
- 286 Graham, R., and Johnston, H.: The photochemistry of the nitrate radical and the kinetics of the nitrogen
287 pentoxide-ozone system, *The Journal of Physical Chemistry*, 82, 10.1021/j100492a002, 1978.
- 288 Kircher, C., Margitan, J., and Sander, S.: Pressure and temperature dependence of the reaction nitrogen dioxide
289 + nitrogen trioxide + M .fwdarw. nitrogen pentoxide (N₂O₅) + M, *The Journal of Physical Chemistry*, 88,
290 10.1021/j150663a037, 1984.
- 291 Ma, X., Tan, Z., Lu, K., Yang, X., Liu, Y., Li, S., Li, X., Chen, S., Novelli, A., Cho, C., Zeng, L., Wahner, A., and
292 Zhang, Y.: Winter photochemistry in Beijing: Observation and model simulation of OH and HO₂ radicals at an
293 urban site, *Sci. Total Environ.*, 685, 85-95, <https://doi.org/10.1016/j.scitotenv.2019.05.329>, 2019.
- 294 Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J.,
295 Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical
296 composition on N₂O₅ uptake: airborne regional measurements in northwestern Europe, *Atmos. Chem. Phys.*, 15,
297 973-990, 10.5194/acp-15-973-2015, 2015.
- 298 Osthoff, H., Pilling, M., Ravishankara, A. R., and Brown, S.: Temperature Dependence of the NO₃ Absorption
299 Cross-section Above 298 K and Determination of the Equilibrium Constant for NO₃ + NO₂ ⇌ N₂O₅ at
300 Atmospherically Relevant Conditions, *Physical chemistry chemical physics : PCCP*, 9, 5785-5793,
301 10.1039/B709193A, 2007.
- 302 Pritchard, H.: The nitrogen pentoxide dissociation equilibrium, *Int. J. Chem. Kinet.*, 26, 61-71,
303 10.1002/kin.550260108, 1994.
- 304 Smith, C., and Ravishankara, A. R.: Kinetics of the reaction nitrogen dioxide + nitrogen trioxide + M at low
305 pressures and 298 K, *The Journal of Physical Chemistry*, 89, 10.1021/j100254a024, 1985.

306 Wang, H., Chen, X., Lu, K., Tan, Z., Ma, X., Wu, Z., Li, X., Liu, Y., Shang, D., Wu, Y., Zeng, L., Hu, M., Schmitt,
307 S., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Wintertime N₂O₅ uptake coefficients over the North China
308 Plain, *Science Bulletin*, 65, 765-774, <https://doi.org/10.1016/j.scib.2020.02.006>, 2020.
309