Support Information for

Efficient N_2O_5 Uptake and NO_3 Oxidation in the Outflow of Urban Beijing

Haichao Wang[1], Keding Lu[1*], Song Guo[1], Zhijun Wu[1], Dongjie Shang[1], Zhaofeng Tan[1], Yujue Wang[1], Michael Le Breton[2], Mingjin Tang[3], Yusheng Wu[1], Jing Zheng[1], Limin Zeng[1], Mattias Hallquist[2], Min Hu[1] and Yuanhang Zhang[1,4]

[1]State Key Joint Laboratory or Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China.

[2]Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden

[3]State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[4]CAS Center for Excellence in Regional Atmospheric Environment, Chinese Academy of Sciences, Xiamen, China

**Corresponding to*: Keding Lu (k.lu@pku.edu.cn)

List of the supplement information:

Text S1: Correction of NO_2 concentration.

During the 2014 Wangdu campaign (Tan et al., 2017), we used two Thermo Electron model 42i NO-NO_2-NOx analyzers to measure NO_2, one is PKU-PL equipped with a home-built photolytic converter, the other is equipped with a catalytic converter (PKU-Mo), the later one was used in this campaign. As the Figure S1(a) shows that the ratio of NO_2 measured by PKU-PL to that measured by PKU-Mo had clear diurnal profiles (in fact, the NO_2 ratio is a correction factor, here specifically defined as WD PL/Mo), which is about 0.75 and has small variation at nighttime, and drops to ~0.4 at noon. Additionally, based on the photo-stationary state method we calculated NO_2 (here defined as WD Cal) values by measured NO and $j(NO_2)$ according to Eq. (S1):

$$[\mathrm{NO_2}] = \frac{k_1[\mathrm{NO}][\mathrm{O_3}]}{j(\mathrm{NO_2})} \qquad \text{Eq. (S1)}$$

Here the k_1 is the reaction rate constant of NO with O_3. The WD Cal/Mo ratio keep reasonably consistent with the WD PL/Mo during the daytime.

Wangdu site is a semi-rural site in North China Plain and similar with the Changping site. Figure S1(b) shows the profiles of the variation and mixing ratios of O_3 in the two sites keep highly consistent. The ratio of the calculated NO_2 by the photo-stationary state method to PKU-Mo in Changping site also is the same tendency with that in Wangdu. For correcting the nighttime NO_2, we assumed that the NO_2 ratio of Changping is the same variation with that in Wangdu, and the calculated NO_2 by the photo-stationary state method is reliable. Then scaled the diurnal profile of WD PL/Mo with an offset to make the daytime ratio has the best fit with the daytime CP Cal/Mo (shown in the red line), here defined as CP PL/Mo (scaled by WD). After scaling, the nocturnal CP PL/Mo is an extended correction factor for the measured NO_2 by PKU-Mo. The nighttime correction factor is about 0.6 and was stable during the whole night.

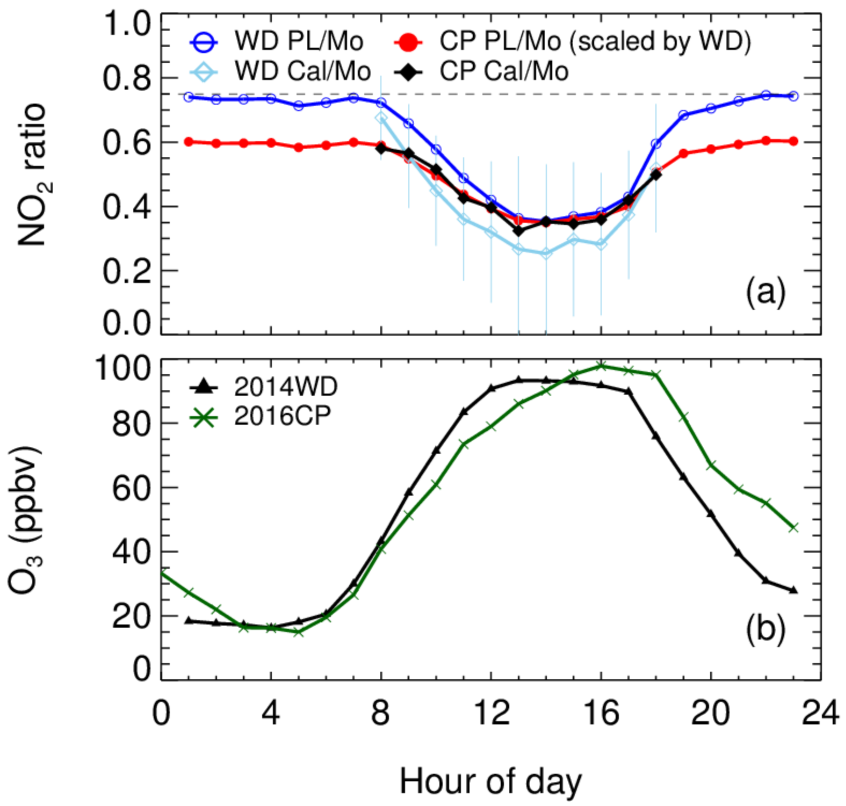

Figure S1. (a) The diurnal profiles of NO_2 ratio of PKU-PL, Cal (calculated by photo-stationary state method) to PKU-Mo measured in Wangdu and Changping. **(b)** The diurnal profile of O_3 during the Wangdu campaign and Changping campaign.

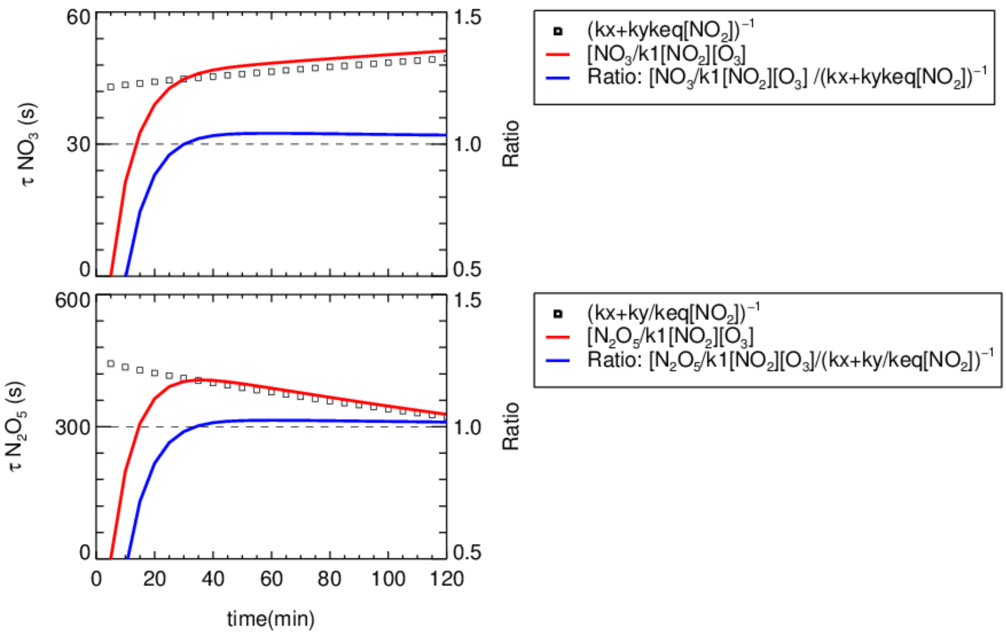

Figure S2. The estimated steady state time of NO_3 and N_2O_5 based on the box model simulation. The k_X and k_Y denotes the loss rate constants of NO_3 and N_2O_5, respectively. A box model was used to calculate the steady state lifetime of NO_3 and N_2O_5 after sunset during this campaign. The box model used the chemical mechanism Regional Atmospheric Chemical Mechanism version 2 included the N_2O_5 heterogeneous hydrolysis processes. The initial concentrations of NO_3 and N_2O_5 were set to zero. The initial concentrations of NO_2 and O_3 were set to the typical values of 15 ppbv and 90 ppbv, respectively. The model was constrained to typical VOCs reactivity toward NO_3 (0.015 s^{-1}) and heterogeneous uptake rate (0.0008 s^{-1}) in this site.

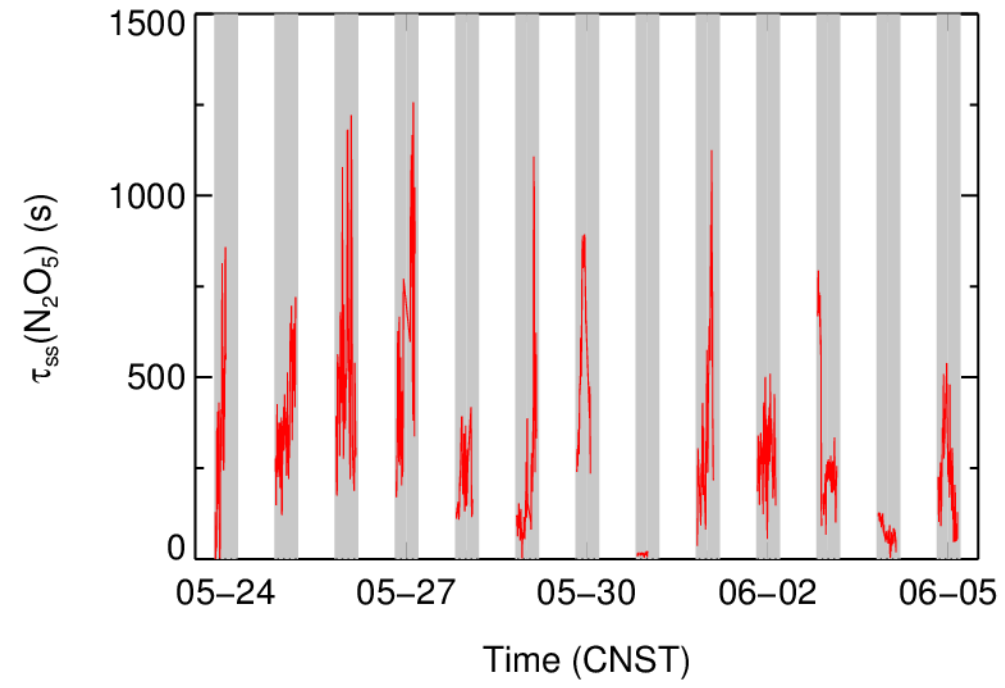

Figure S3. The time series of N_2O_5 lifetime calculated by steady state method.

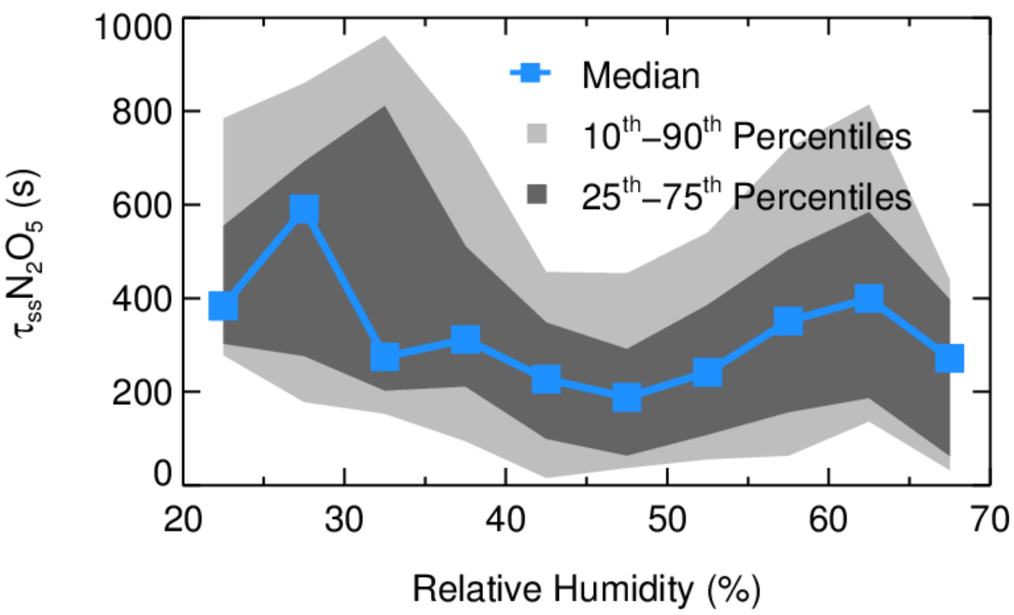

Figure S4. Dependence of N_2O_5 lifetime on relative humidity, data was selected from 20:00 to 04:00. Data are shown as medians, 25-75^{th} percentile ranges, and 10-90^{th} percentile ranges, as shown in the legend.

Table S1. The statistical results of the relevant parameters in this study (19:30-05:00).

Parameters	Minimum	Maximum	Mean	SD
RH (5min)	12%	76%	44%	12%
Temp (5min, ^{o}C)	9.8	30.5	20.5	4.0
NO_2 (5min, ppbv)	0.7	69.2	14.4	10.1
O_3 (5min, ppbv)	0.5	156.1	40.8	31.2
$PM_{2.5}$ (5min, μg m^{-3})	<LOD[a]	92	26	21
S_a (5min, μm^2 m^{-3})	33	1457	562	338
N_2O_5 (1min, pptv)	<LOD[a]	937	73	90
$ClNO_2$ (1min, pptv)	<LOD[a]	2480	382	337
NO_3 (1min, pptv)[b]	0	133	8	12

Note: [a] Limit of the detection; [b] calculated by the measured N_2O_5, NO_2 and ambient temperature.

Table S2. Lists of the observed $ClNO_2/N_2O_5$ (1 min average, from 19:30 to 05:00)

Date	Nighttime (average)			Nighttime (maximum)		
	$ClNO_2$	N_2O_5	$ClNO_2:N_2O_5$	$ClNO_2$	N_2O_5	$ClNO_2:N_2O_5$
05/23-24	31	14	2.3	129	132	0.9
05/24-25	98	60	1.6	401	255	1.5
05/25-26	118	89	1.3	405	513	0.7
05/26-27	58	83	0.7	173	272	0.6
05/27-28	425	56	7.7	1002	197	4.7
05/28-29	327	50	6.5	1428	466	2.8
05/29-30	306	134	2.3	923	436	2.0
05/30-31	504	13	42.0	1243	132	8.8
05/31-06/01	300	48	6.3	848	230	3.4
06/01-02	770	106	7.3	1602	300	5.0
06/02-03	852	148	5.8	1425	937	1.4
06/04-05	1172	129	9.0	2450	356	6.4
Average	414	73	6.0	-	-	-

Table S3. Lists of the daily yield of $ClNO_2$ times N_2O_5 uptake coefficients ($\gamma \times f$)

Start time	End time	$\gamma \times f$
05/23 19:00	05/24 00:00	0.035±0.005
05/24 23:50	05/25 04:00	0.027±0.002
05/25 19:00	05/25 23:00	0.010±0.003
05/26 18:00	05/26 21:00	0.008±0.004
05/27 19:00	05/27 22:00	0.020±0.003
05/28 19:00	05/28 23:00	0.017±0.003
05/29 19:00	05/29 23:00	0.009±0.001
05/30 21:00	05/31 03:00	0.030±0.005
05/31 21:00	06/01 01:00	0.031±0.005
06/01 18:00	06/02 03:00	0.014±0.003
06/02 18:00	06/02 20:30	0.013±0.002
06/04 19:20	06/05 00:00	0.016±0.002
average ± standard deviation		0.019±0.009