Supplement of Atmos. Chem. Phys., 18, 9705–9721, 2018
https://doi.org/10.5194/acp-18-9705-2018-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Efficient N_2O_5 uptake and NO_3 oxidation in the outflow of urban Beijing

Haichao Wang et al.

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

List of the supplement information:

Text S1. Correction of nighttime NO_2 concentration

Figure S1. Correction factor of nighttime NO_2 in Changping site.

Figure S2. Backward trajectory calculations in Changping site.

Figure S3. The steady state lifetime estimation of NO_3 and N_2O_5 based on the box model.

Figure S4. The time series of N_2O_5 lifetime calculated by steady state method

Figure S5. Dependence of N_2O_5 lifetime on relative humidity.

Table S1. The statistical summary of the relevant parameters during the night time.

Table S2. List of the $\gamma \times f$ in this campaign.

Table S3. List of the observed $ClNO_2/N_2O_5$.

Text S1: Correction of NO_2 concentration.

Wangdu site is a semi-rural site in North China Plain and similar with the Changping site. During the 2014 Wangdu campaign (detailed in 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.

Figure S1(b) shows the profiles of the variation and mixing ratios of O_3 in the Wangdu and Changping 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 correction factor (0.6) used to be the averaged scaled value of the correction factors during nighttime, the nighttime correction factor is about 0.6 and was stable during the whole night. The standard deviation of the daytime correction factor for all the air masses experienced at Changping site was determined to be 0.27 (1σ), which extended to nighttime and result in an uncertainty of correction to be 45%. The uncertainty of NO_2 is therefore about 50% when further included the associated measurement uncertainty from calibrations.

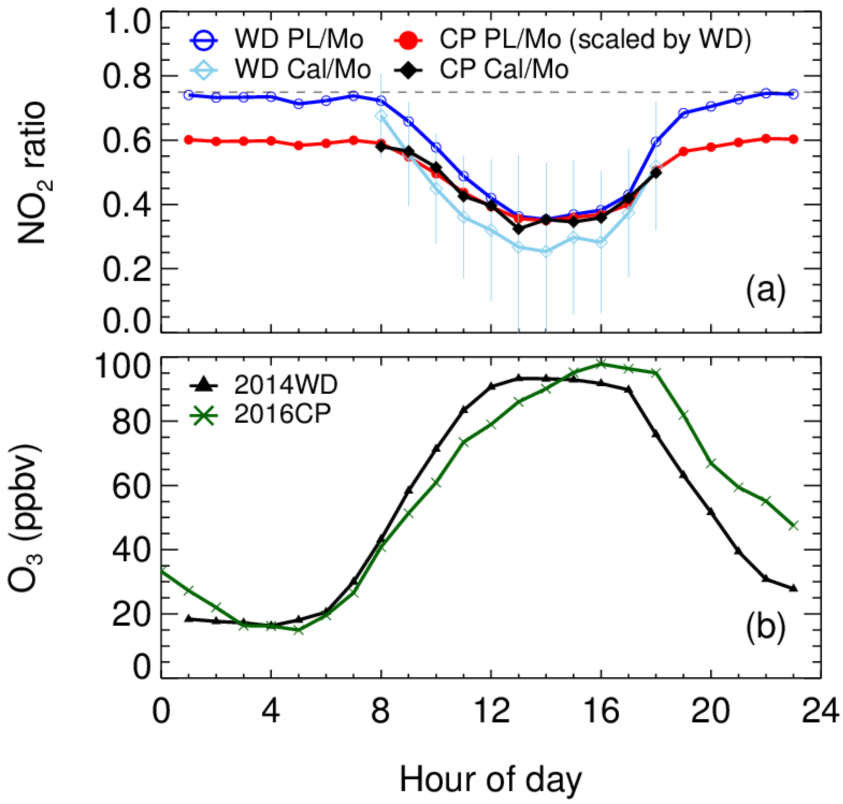

Figure S1. (a) The diurnal profiles of NO_2 ratio of PKU-PL, Cal (calculated by photo-stationary state method) to PKU-Mo measured in Wangdu and Changping. **(b)** The diurnal profile of O_3 during the Wangdu campaign and Changping campaign.

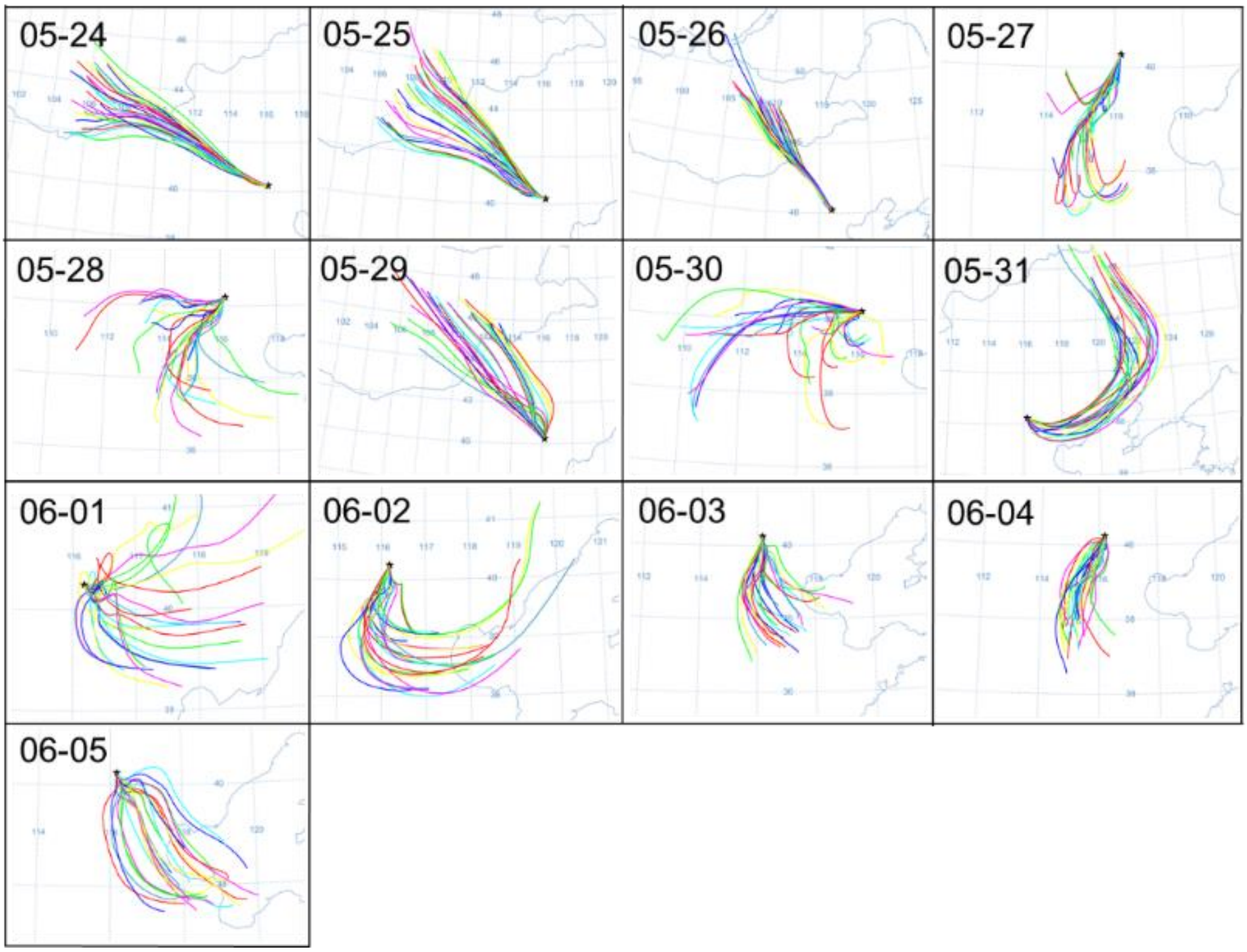

Figure S2. Backward trajectory calculations using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. The images depict a 24-h history of air masses arriving at the measurement site at 12:00 (CNST).

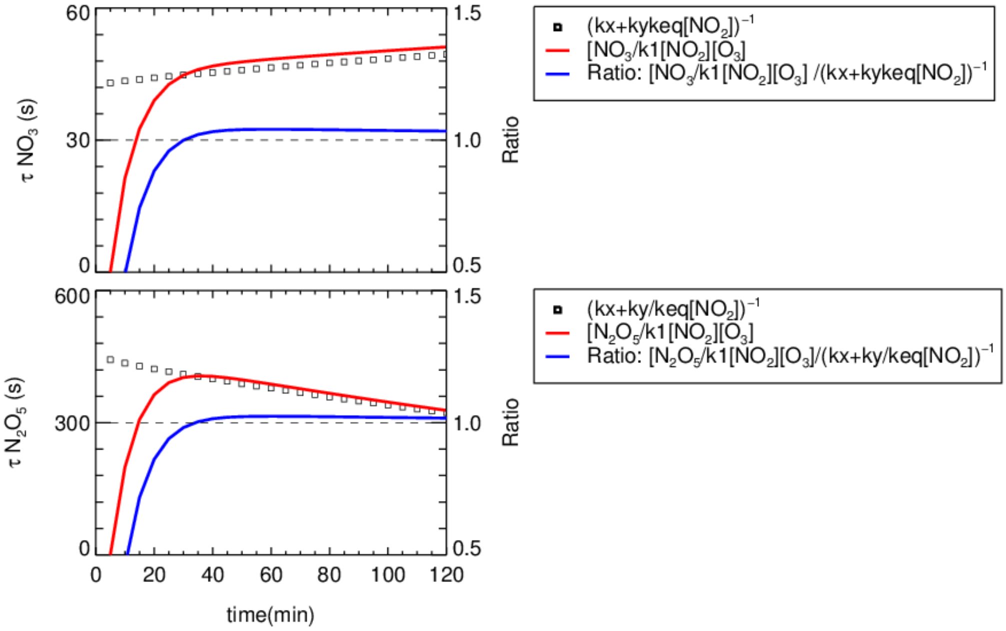

Figure S3. The estimated steady state time of NO_3 and N_2O_5 based on the box model simulation. The k_X and k_Y denotes the loss rate constants of NO_3 and N_2O_5, respectively. A box model was used to calculate the steady state lifetime of NO_3 and N_2O_5 after sunset during this campaign. The box 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.

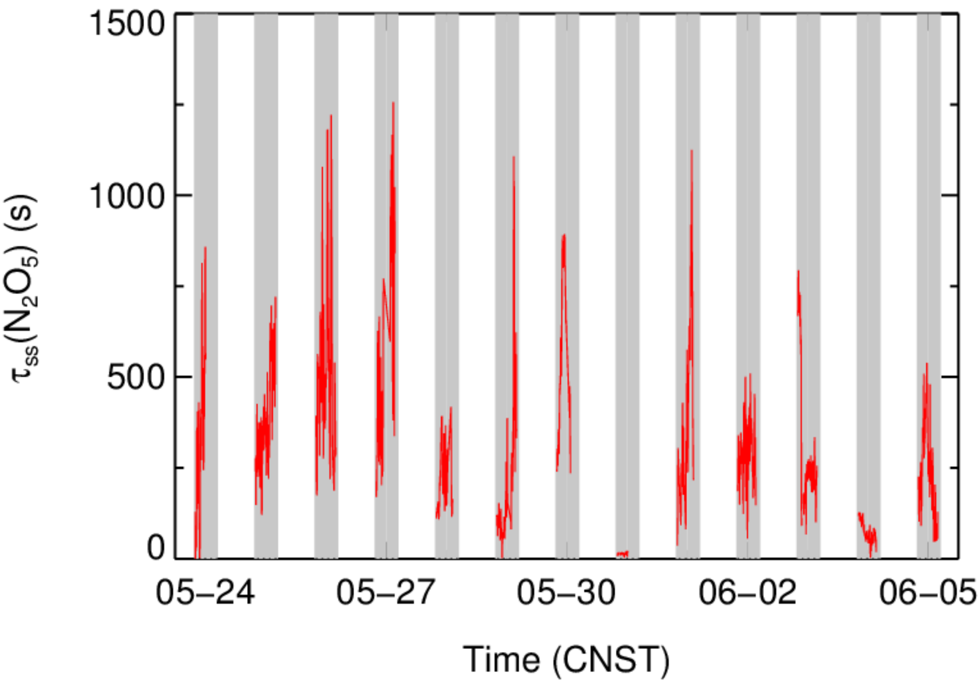

Figure S4. The time series of N_2O_5 lifetime calculated by the steady state method.

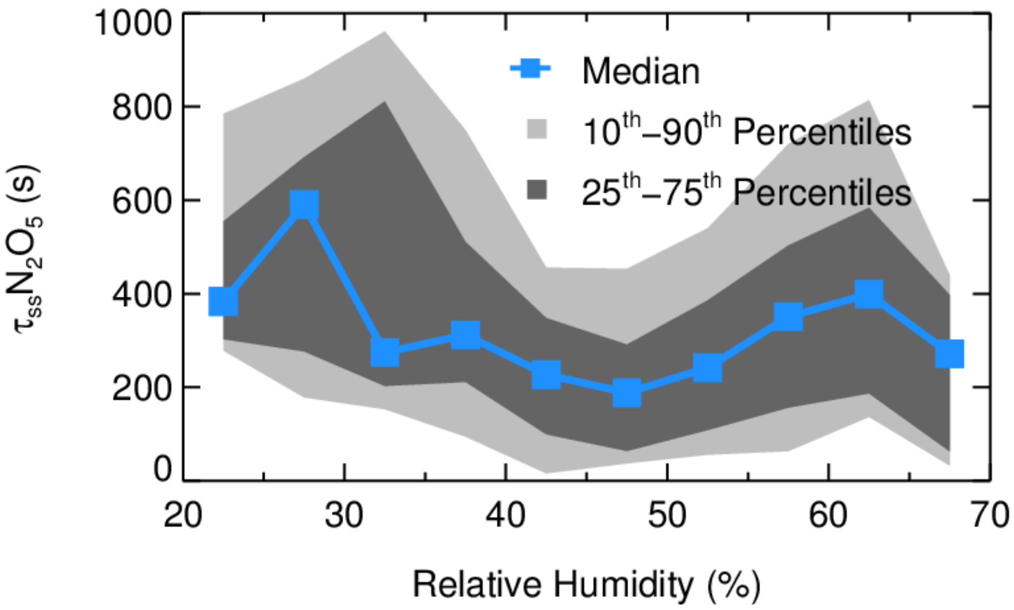

Figure S5. Dependence of N_2O_5 lifetime on relative humidity, data was selected from 20:00 to 04:00. Data are shown as medians, 25-75th percentile ranges, and 10-90th percentile ranges, as shown in the legend.

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 $\gamma \times f$ during the campaign

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