Anonymous Referee #1

Wang et al. report measurements of N_2O_5 and $ClNO_2$ at a mountain site on the North China Plain. The data contain occasional coal power plant plumes in which $ClNO_2$ mixing ratios were enhanced. N_2O_5 uptake parameters and $ClNO_2$ yields were calculated from a steady state model and found to be fast (i.e., large gamma and high phi) compared to other regions. Calculated uptake parameters were rationalized in terms of aerosol ionic composition (nitrate, chloride, and water calculated using a thermodynamic model). Overall the manuscript reads well and would be of interest to the community. Some of the methodology (such as the calculations of uptake parameters, equations 6 and 8,) require some clarification and may need refinement.

We thank the reviewer for the time spent with our manuscript and the constructive suggestions. We have revised the manuscript and clarified the methodology according to the reviewer's comments. Our responses, including changes made to the manuscript, are listed below.

Reviewer comments are in italics. Author responses are in plain face. Changes to the text are in blue.

Specific comments

1. *pg 3 line 11 Consider citing Tham, Y., C. Yan, L. Xue, Q. Zha, X. Wang, and T. Wang (2014), Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, Chin. Sci. Bull., 59(4), 356-359, doi: 10.1007/s11434- 013-0063-y.*

   pg 3, line 12 "such as Colorado, Hessen and Canada" Hessen and Colorado are States of Germany and of the U.S.A. To be consistent, please list the third one as Alberta (a province in Canada).

   pg, line 13. The Faxon et al 2015 study was in SE Texas and close to the coast and shouldn't be cited here. Instead consider citing Mielke, L. H., A. Furgeson, C. A. Odame-Ankrah, and H. D. Osthoff (2016), Ubiquity of $ClNO_2$ in the nocturnal boundary layer of Calgary, AB, Canada, Canadian Journal of Chemistry, 94(4), 414-423, doi: 10.1139/cjc-2015-0426.

   pg 3 line 14. Following " Anthropogenic sources of chlorine including coal combustion in power plants, industries, and biomass burning may potentially facilitate $ClNO_2$ production" cite Riedel, T. P., et al. (2013), Chlorine activation within urban or power plant plumes: Vertically resolved $ClNO_2$ and Cl_2 measurements from a tall tower in a polluted continental setting, J. Geophys. Res., 118(15), 8702-8715, doi: 10.1002/jgrd.50637.

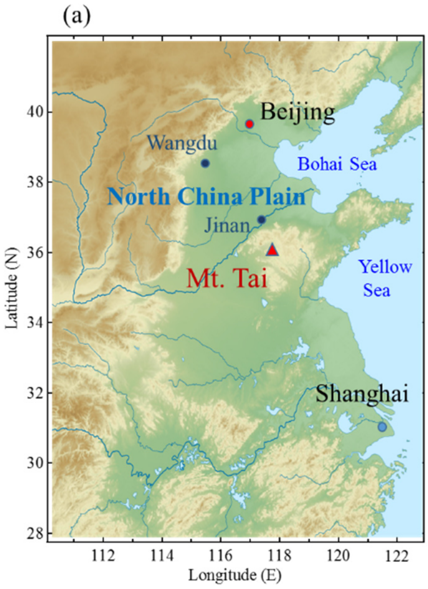
Response: The suggested references are added or changed according to the reviewer's suggestions.

2. *pg 3, line 15 Please state the uncertainty of this number (4.7 ppbv +/- ?)*

Response: This value was a 1-min averaged maximum concentration, with an uncertainty of ±0.8 ppbv. The information is clarified in the revised text.

3. *pg 3, line 26. For readers not familiar with the NCP – please indicate the relative locations of Wangdu and Jinan – perhaps as dots in Figure 1?*

Response: The locations of the Wangdu and Jinan are indicated in Figure 1, as shown below:



4. *pg 3, line 31 "In the present study, we measured the concentrations of N2O5, ClNO2, and related species at a mountaintop site in the NCP and characterized the nighttime nitrogen chemistry within the residual layer over a polluted region of northern China. " please state month or season and the year here as the season (i.e., temperatures) are relevant for N2O5 chemistry.*

Response: The information of the season and the year is added.

5. *pg 4 line 14 " the measurement site is located in an area that is not frequently visited and therefore, should not be significantly affected by local anthropogenic emissions" Since Mt. Tai has been the site of other studies, the data ought to exist to definitively say whether the site IS or IS NOT affected by local emissions.*

   pg 4, line 17. Along the same lines, since a dozen power plants are mentioned, do the data from the earlier suggest that the site is impact by coal power plant emissions (e.g., high SO2, black carbon, or sulfate levels)?

   Is this site sufficiently close or far enough to the coast to be impacted (or not) by sea salt aerosol?

Response: Yes, as the reviewer points out, previous studies and data had proven the site was not affected by local emissions. Previous studies had also observed occasional combustion plumes with high levels of SO_2 (>20ppbv), sulfate (>20 μg cm^{-3}) and black carbon (>5 μg cm^{-3}) at the summit of Mt. Tai (Zhou et al., 2009; Wang et al., 2011).

The mountain site is about 230 km from the Bohai Sea and the Yellow Sea as illustrated in Figure 1a, and is likely to receive minor influences from sea salt aerosol.

To clarify, we have updated the Figure 1a, and revised the text to include this information, as follows:
"Mt. Tai is 230 km away from the Bohai and Yellow Seas, and the cities of Tai'an and Jinan (the capital of Shandong Province) are located 15 km south and 60 km north of the measurement site, respectively."

"Previous studies at this site indicated that the site is regionally representative without significant local anthropogenic emissions, and affected by the regional aged air masses and occasional combustion plumes from fossil fuel or biomass in the region (e.g., Zhou et al., 2009; Wang et al., 2011, Guo et al., 2012)."

References:

Guo, J., Wang, Y., Shen, X., Wang, Z., Lee, T., Wang, X., Li, P., Sun, M., Collett Jr, J. L., Wang, W., and Wang, T.: Characterization of cloud water chemistry at Mount Tai, China: Seasonal variation, anthropogenic impact, and cloud processing, *Atmos. Environ.*, 60, 467-476, 2012.

Wang, Z., Wang, T., Gao, R., Xue, L., Guo, J., Zhou, Y., Nie, W., Wang, X., Xu, P., Gao, J., Zhou, X., Wang, W., and Zhang, Q.: Source and variation of carbonaceous aerosols at Mount Tai, North China: Results from a semi-continuous instrument, Atmospheric Environment, 45, 1655-1667, 2011.

Zhou, Y., Wang, T., Gao, X. M., Xue, L. K., Wang, X. F., Wang, Z., Gao, J. A., Zhang, Q. Z., and Wang, W. X.: Continuous observations of water-soluble ions in PM2.5 at Mount Tai (1534 ma.s.l.) in central-eastern China, Journal of Atmospheric Chemistry, 64, 107-127, 10.1007/s10874-010-9172-z, 2009.

6. *pg 4 line 24 " .... which was replaced daily and washed in the ultrasonic bath to minimize wall loss caused by deposited particles (Wang et al., 2016)." Was there any change in signal levels after the line was washed? What time of day was the tubing changed?*

   pg 4 line 27 "Manual calibrations of N2O5 and ClNO2 were conducted daily to monitor the instrument sensitivity and background." Please state what the CIMS response factors and associated uncertainties and background levels for each of the ions monitored were.

   pg 4, line 28 " The N2O5 standard was synthesized on-line from the reaction between NO2 and O3, and the ClNO2 was produced by passing a known concentration of N2O5 through a NaCl slurry " Please state how the N2O5 and ClNO2 concentrations of this source were quantified or what assumptions were made (e.g., ClNO2 yield from NaCl + N2O5).

Response: The detailed calibration, testing and uncertainties of the CIMS measurement have been described in our previous papers (Wang et al., 2016, Tham et al., 2016). The same configuration was used in the present study. For clarity, we have included more detailed information in the revised text, as follows,

"The inlet was installed ~ 1.5 m above the roof of a single-story building, and the sampling line was a 5.5 m PFA-Teflon tubing (1/4 in. o.d.) which was replaced daily in the afternoon before sunset and washed in the ultrasonic bath to minimize wall loss caused by deposited particles (Wang et al., 2016). A small proportion (1.7 SLPM) of total sampling flow (~ 11 SLPM) was diverted to the CIMS system, to reduce the residence time of the air samples in the sampling line. A standard addition of N_2O_5 into the ambient inlet was performed before and after the tubing replacement to monitor the transmission efficiency, and this practice limited the loss of N_2O_5 in the inlet to <10% in the 'clean' tubing and about 30% in the next afternoon. Manual calibrations of N_2O_5 and $ClNO_2$ were conducted daily to determine the instrument sensitivity, and the average of which during the observation period was 2.0 ± 0.6 for N_2O_5 and 2.2 ± 0.6 Hz pptv^{-1} for $ClNO_2$, respectively. The N_2O_5 standard was synthesized on-line from the reaction between NO_2 and O_3, and the produced N_2O_5 were determined from the decrease in NO_2 (Wang et al., 2014). This method has been validated with a Cavity Ring Down Spectrometer (CRDS) measurement in previous campaign (Wang et al., 2016). The $ClNO_2$ was produced by passing a known concentration of N_2O_5 through a NaCl slurry assuming unity conversion efficiency (Roberts et al., 2009) and negligible $ClNO_2$ loss in the system (Wang et al., 2016). The field background was determined by passing the ambient sample through a filter packed with activated carbon, with average levels of 7.8 ± 1.9 and 6.0 ± 1.6 Hz for N_2O_5 and $ClNO_2$, respectively. The reported concentrations were derived by subtracting the background levels. The detection limit was 4 pptv for both N_2O_5 and $ClNO_2$ (2σ, 1 min-averaged data), and the uncertainty of the nighttime measurement is estimated to be ± 25% (Tham et al., 2016)."

References:

Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A. R., Coffman, D., Quinn, P., and Bates, T.: Laboratory studies of products of N2O5 uptake on Cl− containing substrates, Geophys. Res. Lett., 36, 10.1029/2009gl040448, 2009.

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 2016.

Wang, X., Wang, T., Yan, C., Tham, Y. J., Xue, L., Xu, Z., and Zha, Q.: Large daytime signals of N2O5 and NO3 inferred at 62 amu in a TD-CIMS: chemical interference or a real atmospheric phenomenon?, Atmos. Meas. Tech., 7, 1-12, 10.5194/amt-7-1-2014, 2014.

Wang, T., Tham, Y. J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S. C. N., Dubé, W. P., Blake, D. R., Louie, P. K. K., Luk, C. W. Y., Tsui, W., and Brown, S. S.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res. -Atmos., 10.1002/2015jd024556, 10.1002/2015jd024556, 2016.

7. *pg 5, line 10 " Water soluble ionic compositions of PM2.5... were measured hourly..." It would be great to show a time series of these data. Were chloride concentrations higher in power plant plumes?*

Response: The time series of selected ionic species, including sulfate, nitrate and chloride are included in the revised Figure 2. The chloride concentrations in the coal-fired plumes are higher than the campaign average, and this information has been summarized in the revised Table 1. More description about the aerosol composition is also added in the revised text, as follows,

"During the campaign at Mt. Tai, the average concentrations of aerosol sulfate and nitrate were 14.8 ± 9.0 and 6.0 ± 4.7 μg m^{-3}, accounting for 29.5% and 12.0% of $PM_{2.5}$ mass, respectively. The aerosol organic-to-sulfate ratio, a parameter that potentially affects the uptake process (Bertram et al., 2009b), was 0.74 on average and much lower than those from studies mentioned above in Europe and US. Moreover, the nighttime averaged Cl^- concentration was 0.89 ± 0.86 μg cm^{-3}, and was an order of magnitude higher than Na^+, indicating abundant non-oceanic sources of chloride (e.g., from coal combustion and biomass burning in the NCP) (Tham et al., 2016), which could enhance the production of $ClNO_2$."

Table 1: Chemical characteristics of coal-fired plumes exhibiting high levels of $ClNO_2$ observed at Mt. Tai during the summer of 2014

Date	Duration	N_2O_5 (pptv)		$ClNO_2$ (pptv)		O_3	NO_x	NO_x /NO_y	ΔSO_2 /ΔNO_y [a]	ΔCO /ΔNO_y [b]	Cl^- (μg cm^{-3})	t_{plume}	ϕ $_{ClNO2}$
		Mean	Maximum	Mean	Maximum								
30-31 Jul	23:40-0:45	5.9	14.2	528	1265	70	6.5	0.49	0.57	83	2.34	3.2	0.57
3-4 Aug	23:30-0:00	20.1	23.8	506	833	106	2.8	0.22	2.43	108	NA [c]	4.9	0.64
7 Aug	21:30-23:30	10.5	14.9	606	976	91	5.8	0.36	1.36	50	2.24	5.5	0.35 [d]
8 Aug	22:00-23:10	11.0	15.1	841	2065	76	8.5	0.45	0.65	45	NA	2.1	0.90
8-9 Aug	23:40-01:15	6.8	12.6	315	599	77	4.3	0.41	0.54	85	NA	4.4	0.23
10 Aug	0:00-2:00	10.5	15.5	692	1684	72	6.2	0.43	1.67	50	1.10	4.6	0.55
17-18 Aug	22:00-01:30	3.5	7.7	409	802	60	9.5	0.55	0.48	33	1.01	4.6	0.26 [d]
25-26 Aug	0:00-5:00	12.1	40.1	301	534	74	11.8	0.62	2.10	NA	1.88	3.0	0.20

[a] It represents the slope of SO_2 vs NO_y in plumes, and the overall slope for entire campaign was 0.31 with r^2 of 0.31.

[b] Same to above note with the campaign overall slope of 15.7 and r^2 of 0.23.

[c] Data not available in the case.

[d] For t_{plumes} longer than the nocturnal processing period since sunset, the time since sunset was used in the $ClNO_2$ yield calculation.

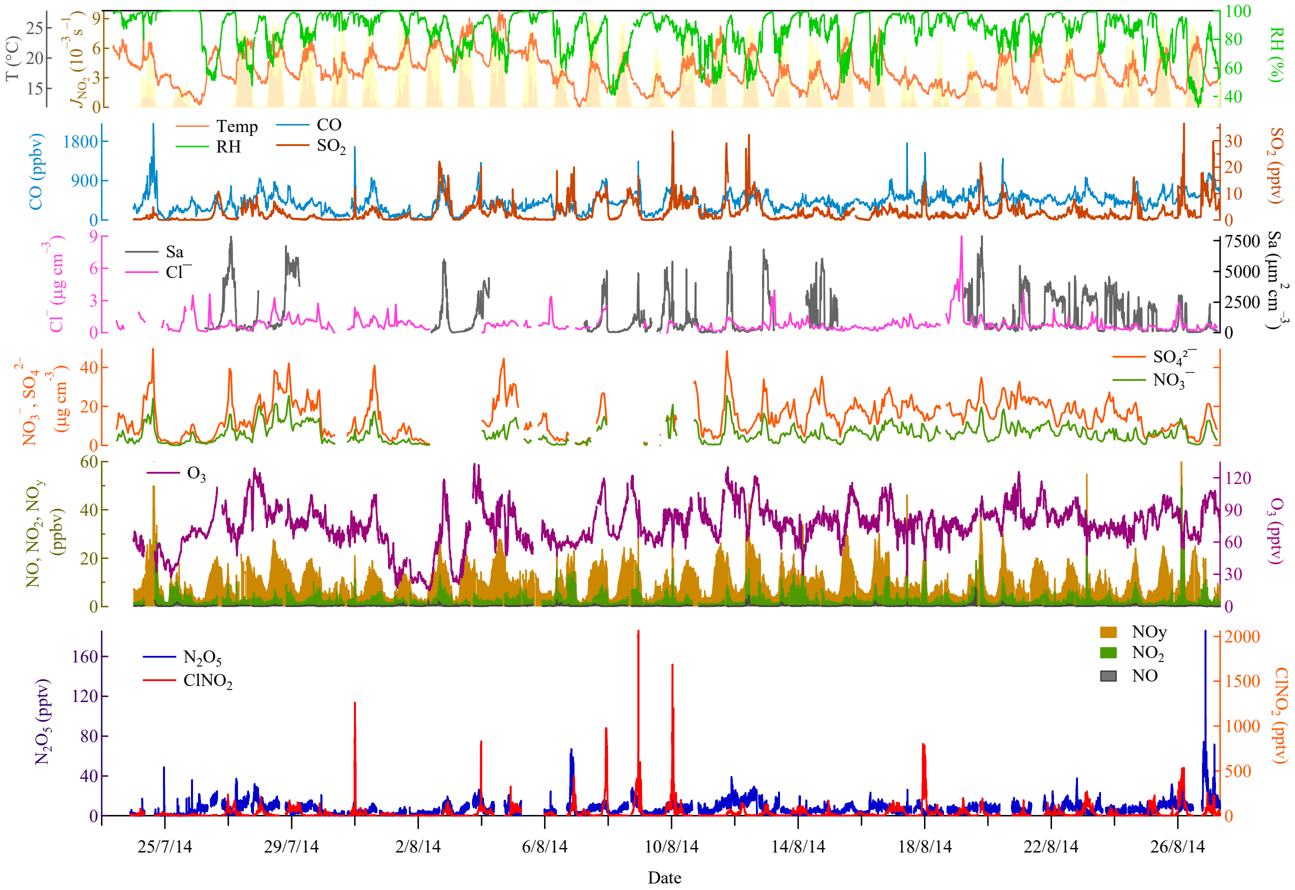


Figure 2 : Time series for N_2O_5, $ClNO_2$, related trace gases, aerosol properties, and meteorological data measured at Mt. Tai from July 24 to August 27, 2014.

References:

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 2016.

8. *pg 5 line 26 and Figure 2. There is a lot of sustained N2O5 during daytime which is unusual especially since temperatures frequently were >20C during the day. Is this a real signal? I am a bit doubtful. In any case, it warrants discussion that N2O5 at 3 pm was in greater abundance than at 3 am (Figure 3).*

   I am also suspicious about the relatively low levels at night. Was the N2O5 transmission efficiency monitored? If so, please show those data. If not, please state that it was not.

   It also looks like there is a hardly any NO during the day which is consistent with there being N2O5, but is strange also as NO2 should photo-dissociate and sustain NO. Perhaps the O3 levels are high enough and photolysis rates low enough for this to happen. In my opinion, this warrants a bit of analysis & discussion – are the levels consistent with a simple photostationary analysis, or is the pss severely perturbed (i.e., too much NO2 relative to NO)?

Response: We thank the reviewer for bringing the daytime N_2O_5 signals to our attention. According to the suggestions, we have further examined the daytime data. Because the daily maintenance and calibrations of CIMS were usually performed in the early afternoon, there were only a few cases with available afternoon data for analysis, which also accounts for the larger variability of N_2O_5 in the early afternoon. Using the photostationary analysis proposed by Brown et al (2005; 2016), we also calculated the daytime steady-state concentration of N_2O_5 for cases with daytime peaks. The predicted N_2O_5 concentrations showed an increasing trend in the afternoon, similar to the observation pattern for diurnal average, but the absolute values varied for different cases, as the examples shown in the below figure. The calculated N_2O_5 concentrations around 15:00 were much lower for a clean sky case with high photolysis rate (panel a in below figure), but were of the same magnitude as the observation for a reduced photolysis and foggy condition with higher NO_3 production rate (panel b in below figure). The limited daytime data do not allow us to perform further analysis to investigate the detailed reasons for this daytime phenomenon. Whether there were some interference signals or any other reasons still require additional studies.

To clarify, we have added the discussions in the revised text, and also included the comparison between steady-state predicted and observed N_2O_5 for two daytime cases in the supplement figure. In addition, as we described in the previous responses #6, the N_2O_5 transmission efficiency was monitored before and after the tubing replacement, and this information, as well as the uncertainties in the measurement, have been included in the revised text.

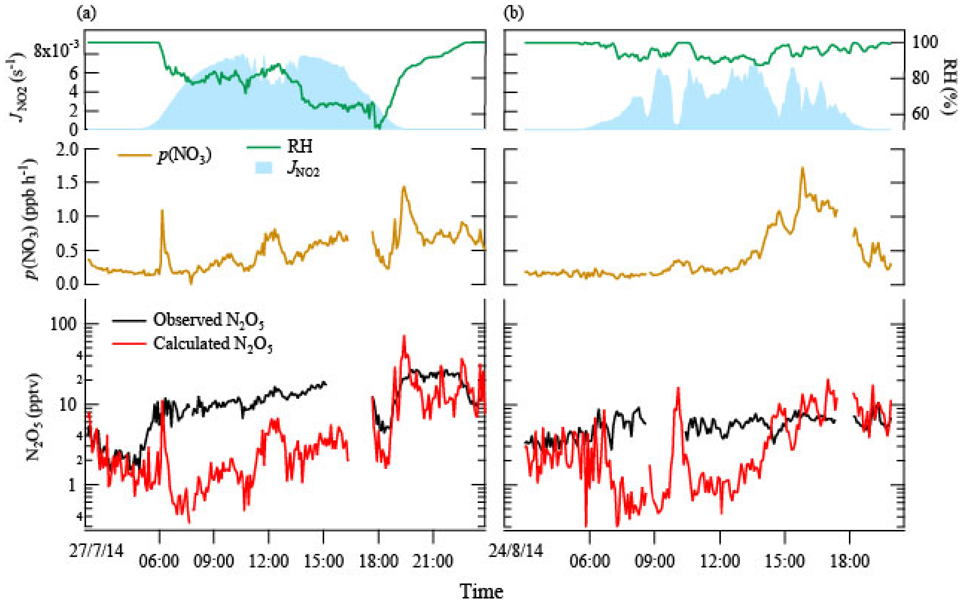


Figure S1: Observed and steady-state calculated daytime N_2O_5, nitrate radical production rate and meteorological parameters for the case of (a) 27 July and (b) 24 August, 2014.

The revised text reads,

"It was also noted that a small N_2O_5 peak (~10 pptv) with larger variability was present in the early afternoon. A simplified photostationary analysis following Brown et al. (2005; 2016) was performed to predict the daytime steady-state N_2O_5 concentrations for the few cases with daytime peaks. The predicted concentrations all showed increasing trends in the afternoon, similar to the observation pattern. However, for individual cases, the absolute values around 15:00 were much lower than observation under clean sky condition, but of the same magnitude as the observation for reduced photolysis and foggy conditions with higher NO_3 production rate (c.f. Figure S1 in the supplement). Daytime N_2O_5 signals with few pptv have also been observed by a CRDS at a mountain site in southern China (Brown et al., 2016), where the concentrations were in accord with steady state estimation in an average sense. Because daily maintenance and calibrations of the CIMS were usually performed during early afternoon periods, the limited daytime data in the present study was not sufficient to make clear whether there were any daytime interferences or sensitivity fluctuations. Thus additional studies are needed to validate the daytime phenomenon and examine the potential reasons, and the following analysis in the present work will mostly focus on nocturnal process."

References:

Brown, S. S., Osthoff, H. D., Stark, H., Dubé, W. P., Ryerson, T. B., Warneke, C., de Gouw, J. A., Wollny, A. G., Parrish, D. D., and Fehsenfeld, F. C.: Aircraft observations of daytime NO 3 and N 2 O 5 and their implications for tropospheric chemistry, Journal of Photochemistry and Photobiology A: Chemistry, 176, 270-278, 2005.

Brown, S. S., Dubé, W. P., Tham, Y. J., Zha, Q., Xue, L., Poon, S., Wang, Z., Blake, D. R., Tsui, W., Parrish, D. D., and Wang, T.: Nighttime Chemistry at a High Altitude Site Above Hong Kong, J. Geophys. Res. - Atmos., 10.1002/2015jd024566, 10.1002/2015jd024566, 2016.

9. *pg 6 "The elevated ClNO2 levels observed at Mt. Tai are similar to recent measurements at a surface rural site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016), but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world." This is an interesting comparison though more information is needed to put this particular study site and the above comparisons in context. Is the study site affected by sea salt aerosol from the Pacific Ocean? Based on that information, what levels of ClNO2 would have been expected?*

Response: As stated in previous response #5, the mountain site is about 230 km from the Bohai Sea and the Yellow Sea as illustrated in Figure 1a, and is likely to receive minor influences from sea salt aerosol. This information has been included in the revised text.

In our previous measurement in the NCP, unexpected abundant fine chloride aerosols were observed, and further chemical analysis suggested the non-oceanic Cl^- sources dominantly from coal-fired power plants with additional contribution from biomass burning (Tham et al., 2016). More discussion of the aerosol composition is added here to aid the comparison, as stated in the response #7:

"The elevated $ClNO_2$ levels observed at Mt. Tai are similar to recent measurements at a rural surface site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016), but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world. During the campaign at Mt. Tai, the average concentrations of aerosol sulfate and nitrate were 14.8 ± 9.0 and 6.0 ± 4.7 μg m^{-3}, accounting for 29.5% and 12.0% of $PM_{2.5}$ mass, respectively. The aerosol organic-to-sulfate ratio, a parameter that potentially affects the uptake process (Bertram et al., 2009b), was 0.74 on average and much lower than those from studies mentioned above in Europe and US. Moreover, the nighttime averaged Cl^- concentration was 0.89 ± 0.86 μg cm^{-3}, and was an order of magnitude higher than Na^+, indicating abundant non-oceanic sources of chloride (e.g., from coal combustion and biomass burning in the NCP) (Tham et al., 2016), which could enhance the production of $ClNO_2$."

References:

Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K., and Coffman, D. J.: Direct observations of N2O5 reactivity on ambient aerosol particles, Geophys. Res. Lett., 36, 10.1029/2009GL040248, 2009.

10. *pg 6 line 13 "88.6 ppbv" and "24.4 ppbv" - are these averages? If so, also state the range of values (or standard error).*

    pg 6, line 16 "16.4 ppbv" same comment as above

Response: These are averages, and the standard errors are included in the revised text.

11. *pg 6, line 23 – section 3.2 This plume is very interesting. It may be that all the SO2 has generated enough sulfate to make the aerosol quite acidic. Was Cl2 monitored by any chance?*

Response: Increases of sulfate aerosol (SO_4^{2-}) were observed in the plumes, with average concentrations ranging from 11.0 to 19.2 µg m^{-3}. The aerosol acidity can be roughly estimated from aerosol neutralization degree, defined as the mole concentration ratio of NH_4^+ to ($2\times SO_4^{2-}$ +NO_3^-). The determined ratios were mostly close to or slightly higher than 1.0 for these plumes, suggesting that the aerosols within the plume were neutralized or slightly basic.

We did not monitor the Cl_2 during the measurement. Although the CIMS used here could detect the signals of $I(Cl_2)^-$, but no calibration of Cl_2 was conducted in the present study. Now our group is developing and testing the calibration method for Cl_2, and hopefully we can have this useful information in the future studies.

12. *pg 8, line 20 " Because of the lack of concurrent VOCs measurements in the present study, we used the average VOC speciations measured before sunrise and in the evening at Mt. Tai during our previous study in 2007 ". Would these VOC levels be sustained in the power plant plume, where the P(NO3) is greater than in surrounding air? Consider adding a statement that this estimate is likely an upper limit.*

Response: We agree with the reviewer that VOC levels in the power plant plumes would be lower compared to other periods with regional diffuse pollution condition, and the estimated nighttime $k(NO_3)$ would be an upper limit. We have clarified this in the revised text, as follows,

"The estimated $k(NO_3)$ could be considered as an upper limit for coal-fired plumes because of potential lower biogenic VOC levels within the plumes. The estimation here does not account for the VOC changes between years and the night to night variability, which may result in uncertainties. The $k(NO_3)$ derived by another approach, i.e., from the nighttime steady state fits, provides a consistency check and evaluation of the errors, as described below."

13. *pg 9, lines 19-20. "the observed values in the present study are significantly higher". This could also be indicative of a measurement bias such as N2O5 inlet losses (see earlier comment). Considering that the authors claim very large gamma values, attention should be paid to biases introduced by measurement uncertainties. Please add a couple of sentences about this potential issue to the manuscript.*

Response: We thank the reviewer's suggestion. As stated in the above response #6, the information on the inlet loss and measurement uncertainty has been added in Section 2.2 in the revised text.

14. *pg 10, line 1. There a multiple versions of the E-AIM model. Please be specific as to what was used (inputs & model).*

Response: The model version is added in the revised text, as follows, "For comparison, γ values were calculated using this parameterization based on the measured aerosol composition and molarity of water determined from the thermodynamic model with inputs of NH_4^+, Na^+, SO_4^{2-}, NO_3^- and Cl^- (E-AIM model IV, http://www.aim.env.uea.ac.uk/aim/model4/model4a.php) (Wexler and Clegg, 2002)."

15. *pg 10, line 21 "nitrate can suppress the N2O5 uptake (Bertram and Thornton, 2009)" The nitrate effect is well documented and goes back to Mentel, T. F., M. Sohn, and A. Wahner (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1(24), 5451-5457, doi: 10.1039/a905338g, and not Bertram and Thornton. In general, gamma scales inversely with nitrate as the reaction of NO2+ with nitrate reverses N2O5 uptake and is consistent with Figure S1 shows. The paragraph on lines 17-25 is unnecessarily confusing in that the discussion here neglects the simultaneous effects of other ions (e.g., chloride – discussed in next paragraph). Consider tightening this paragraph.*

Response: We agree with the reviewer's comments on the 'nitrate suppress effect'. We have corrected the reference and condensed the discussion here by eliminating the confusing statements in Line 20-25. The revised text reads,

"A moderate negative dependence ($r = 0.54$) of determined γ on aerosol nitrate concentration can be inferred, with lower values of γ associated with higher nitrate content (cf. Figure S2a). This pattern is consistent with the nitrate suppress effect on N_2O_5 uptake identified from previous laboratory studies (Mentel et al., 1999), and also similar to the anti-correlation of γ and nitrate from tower measurements in the USA and aircraft measurements over the UK (Wagner et al., 2013; Morgan et al., 2015). The relationship between the γ with the aerosol water to nitrate ratio also exhibits consistent trend with the previous observations and parameterizations (e.g., Bertram and Thornton, 2009; Morgan et al., 2015), with increasing uptake as the ratio increases (Figure S2b)."

References:

Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Physical Chemistry Chemical Physics, 1, 5451-5457, 1999.

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 2009.

16. *pg 11, equation 6. The math here is not sound – it should not be dN2O5/dt in the denominator (if N2O5 achieves steady state, as argued earlier, this quantity would be zero). Please remove the first 2 terms.*

    The assumption here is that ClNO2 is conserved and is not produced by other sources (such as Cl + NO2) – please state these assumptions.

    The paragraph that follows equation 6 does not provide enough information. How was the yield of ClNO2 actually calculated? Was the N2O5 uptake loss truly integrated using a time-integrated box-model? Or was it approximated using the ratio of observed mixing ratios (as suggested by the first term in eqn 6)? Note that rates change from the point of emission to the point of observation.

Response: We thank the reviewer for the valuable suggestion. The equation has been revised and the first two terms have been removed. The description on $ClNO_2$ yield calculation is clarified, and assumptions made in the estimation are included in the revised text, as follows:

"For regional diffuse pollution cases, the ϕ defined in R3 can be estimated from the ratio between $ClNO_2$ production rate and N_2O_5 loss rate, as the first term in below equation:

$$\phi = \frac{d\mathrm{ClNO_2}/dt}{k(\mathrm{N_2O_5})_{\mathrm{het}}[\mathrm{N_2O_5}]} = \frac{[\mathrm{ClNO_2}]}{\int k(\mathrm{N_2O_5})_{\mathrm{het}}[\mathrm{N_2O_5}]\,dt} \qquad (6)$$

$k(N_2O_5)$ values can be determined using the inverse steady-state lifetime analysis described above in Eq. 3, and the production rate of $ClNO_2$ can be derived from the near-linear increase in $ClNO_2$ mixing ratio observed during a period, when the related species (e.g., NO_x, SO_2) and environmental variables (e.g., temperature, RH) were roughly constant. The approach here assumes that the relevant properties of the nocturnal air mass are conserved, and neglects other possible sources and sinks of $ClNO_2$ in the air mass history. For the intercepted coal-fired plumes exhibiting sharp $ClNO_2$ peaks, the $ClNO_2$ yield can be estimated from the ratio of the observed $ClNO_2$ mixing ratio to the integrated N_2O_5 uptake loss over the plume age (i.e., the second term in Eq. 6). The analysis assumes that no $ClNO_2$ was present at the point of plume emission from the combustion sources and no $ClNO_2$ formation before sunset, and that the γ and ϕ within the plumes did not change during the transport from the source to the measurement site. The potential variability in these quantities likely bias the estimates, but these assumptions are a necessary simplification to represent the averaged values that best describe the observations. It should be noted that the steady-state N_2O_5 loss rate is crucial in the yield estimation, which could be underestimated by potentially overestimating the loss rate in some cases with large uncertainties in N_2O_5 measurement and NO_3 reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the $ClNO_2$ yield from the ratio of enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- + HNO_3) in the cases. Given the low time resolution of nitrate data that could potentially introduce large uncertainties, this approach will only be used as a reference to validate the former analysis based on Eq. 6. "

References:

Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., Bahreini, R., VandenBoer, T. C., Wolfe, D. E., Williams, E. J., Roberts, J. M., Brown, S. S., and Thornton, J. A.: Chlorine activation within urban or power plant plumes: Vertically resolved ClNO2 and Cl2 measurements from a tall tower in a polluted continental setting, J. Geophys. Res. -Atmos., 118, 8702-8715, 10.1002/jgrd.50637, 2013.

17. *pg 12, line 5 "The parameterized ϕ values exhibit positive dependence on the aerosol chloride concentration and the Cl-/H2O ratio. " I am assuming this is based on the colors shown in Figure 10? How good is the water estimate?*

Also, if concentrations of N2O5 are underestimated due to a measurement bias and real concentrations of N2O5 were higher, things fall into place ... (see earlier comments)

pg 12, line 2. Please state that the chloride concentration was measured and the water content is based on a thermodynamical model and perform an error estimate (so that appropriate error bars can be added to Figure 10).

Response: The reviewer's observation is correct; the dependence of parameterized ϕ on Cl^-/H_2O is derived from the color code in the Figure 10a. We have made this clear in the revised text, as follows,

"The parameterized ϕ values exhibit positive dependence on the aerosol chloride concentration and the Cl^-/H_2O ratio, as shown by the color code in Fig 10a."

The method for calculating the water content is also clarified in the revised text. For the error in water content calculation, sensitivity tests showed that a 3% change in RH implied an uncertainty in the particle liquid water content of ~5%. Thus we included this error information and the overall uncertainty estimation in the revised text, and added the error bars in the revised Fig 8 and Fig 10.

In addition, as described in previous comments, the measurement uncertainty of N_2O_5 is included in the revised text, and the propagated uncertainty of estimated uptake coefficients (γ) and yield (ϕ) accounting for errors associated with the measurements and statistical uncertainty in the calculations, are also added in the revised text and figures.

The clarified and revised text reads,

"An error estimation showed that a 3% change in RH implies an uncertainty in the particle liquid water content of ~5%. In the calculation, mean values of *V*/*S* (64.8 - 77.2 nm) measured in the present study instead of empirical pre-factor *A* were used, and the reaction rate coefficients were employed as the empirical values suggested by Bertram and Thornton (2009)."

"We compared the field-derived values to the parameterization for cases with available aerosol compositions, using an empirical k' of 1/450, as recommended by Roberts et al. (2009). The particle liquid water content $[H_2O]$ was calculated from the thermodynamic model (E-AIM model IV) based on measured aerosols composition, as described above."

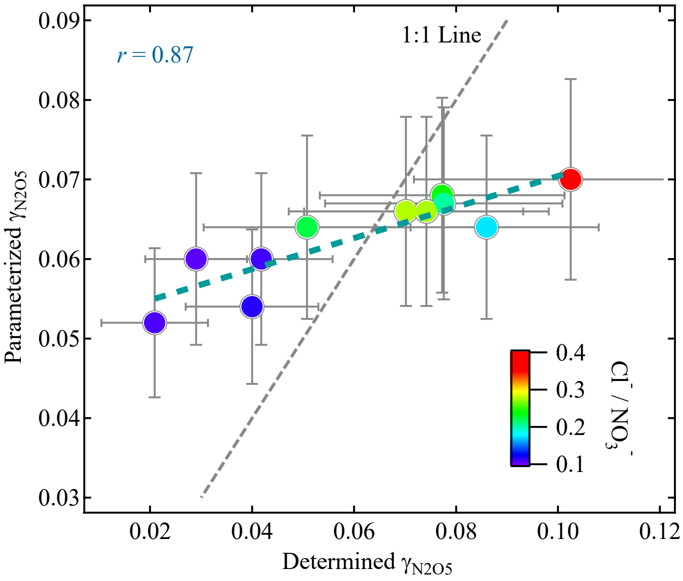


Figure 8: Comparison of field-determined γ with that derived from the parameterization of Bertram and Thornton, (2009). The colors of the markers indicate the corresponding concentrations ratio of particulate chloride to nitrate. The error bars represent the total aggregate uncertainty associated with measurement and derivation.

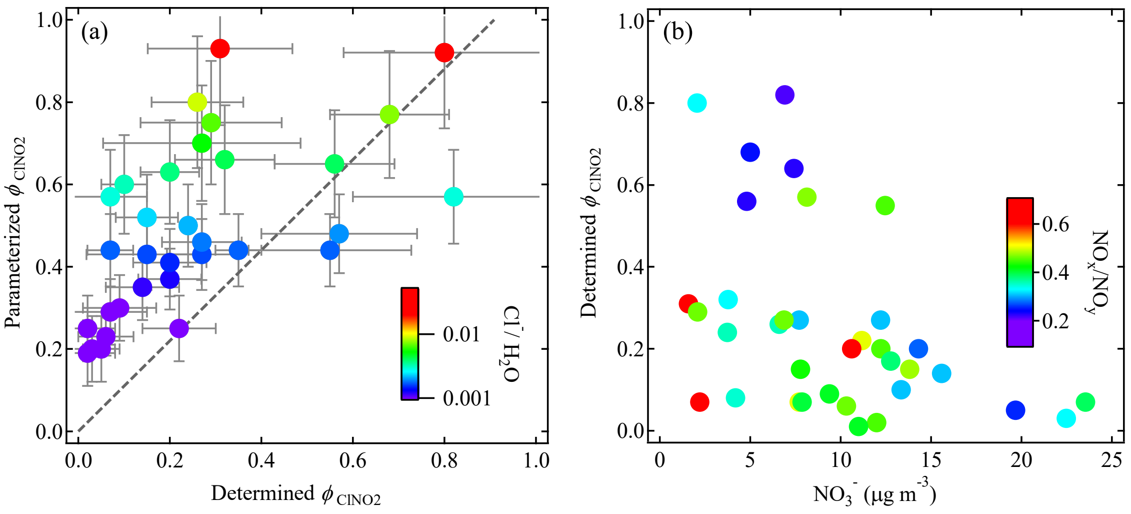


Figure 10: (a) Comparison of field-determined ϕ with that derived from parameterization (Eq. 7), and the colors of the markers represent the corresponding Cl^-/H_2O ratio; (b) relationship between field-determined ϕ and measure nitrate concentrations in aerosols, and colors of markers represent the corresponding NO_x/NO_y ratio. The error bars represent the total aggregate uncertainty as similar as Figure 8.

18. *pg 12, eqn 8. This equation is not correct. It ought to be the loss rate of N2O5, not its rate of change (d[N2O5]/dt) which would be zero at steady state. There are major assumptions made here – that aerosol nitrate is conserved, i.e., absence of aerosol deposition and volatilization via NH4NO3 formation etc. These assumptions should be clearly stated.*

   pg 12, line 31. "The NO3 formation was predicted by integrating each derived formation rate over the corresponding ..." the formation rate of nitrate changes from the point emission to the point of observation, which was not taken into account here.

Response: We thank the reviewer's helpful suggestions. The equation has been corrected by removing the first term. We also clarified the definition of nitrate formation rate here as the nitrate exclusively produced from N_2O_5 reactions. The assumptions made for estimating the formation rate and production of nitrate are now included and clarified in the revised text, as follows,

"Based on the reactions described above, the formation rate of soluble nitrate from N_2O_5 reactions, $p(NO_3^-)$, can be determined from the $ClNO_2$ yield and N_2O_5 heterogeneous loss rate as follows:

$$p(NO_3^-) = (2-\phi)k_{N_2O_5}[N_2O_5] \qquad (8)$$

The $p(NO_3^-)$ values obtained for the select cases during the study period ranged from 0.02 to 0.62 ppt s^{-1}, with a mean value of 0.29 ± 0.18 ppt s^{-1}, corresponding to 0.2- 4.8 μg m^{-3} hr^{-1} and 2.2 ± 1.4 μg m^{-3} hr^{-1} (Table 2). The derived rates are comparable to the observed increases in nitrate concentrations (2-5 μg m^{-3} h^{-1}) during haze episodes in summer nights at a rural site in the NCP (Wen et al., 2015). By assuming that produced nitrate is conserved and neglecting the deposition and volatilization loss (e.g., via ammonium nitrate), the in-situ NO_3^- formation could be predicted by integrating each derived formation rate over the corresponding analysis period. Similar to N_2O_5 uptake coefficient and $ClNO_2$ yield determination above, the nitrate formation estimation here assumes a conserved air mass with a constant formation rate over the study period. For coal-fired plumes, we equated the measured nitrate concentrations with the increases by assuming that no aerosol nitrate was directly emitted from the nocturnal point sources."

19. *pg 13, line 16. Wang et al., 2016 is not the best reference. Please cite Behnke, W., C. George, V. Scheer, and C. Zetzsch (1997), Production and decay of ClNO2, from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments, J. Geophys. Res., 102(D3), 3795-3804, doi: 10.1029/96JD03057 instead.*

Response: The reference is changed according to the reviewer's suggestion.

20. *pg 13, lines 16/17 "For simplicity, the reactions of NO3 with VOCs can be assumed to result in the complete removal of reactive nitrogen (Wagner et al., 2013)". This is likely not true in this study, where NO3 primarily reacts with terpenes. Wangberg et al. (1997), Product and mechanistic study of the reaction of NO3 radicals with alphapinene, Environm. Sci. Technol., 31(7), 2130-2135, and others since have showed that a significant fraction of NO2 is ultimately released again.*

Response: We thank the reviewer for pointing out this issue. We have revised the text to include this information and also added the caveat that possible overestimation on NO_x loss because of NO_2 recycling from NO_3-VOC reactions. The revised text reads,

"$ClNO_2$ mainly functions as a reservoir of NO_x, rather than as a sink, because the formation of $ClNO_2$ throughout the night with subsequent morning photolysis recycles NO_2 (Behnke et al., 1997). The reactions of NO_3 with VOCs would predominantly produce organic nitrate products (Brown and Stutz, 2012 and references therein), but some fraction of NO_2 can be regenerated in the NO_3 reactions (i.e., with terpenes) (e.g., Wangberg et al., 1997) or released from the decomposition of organic nitrate during the transport (e.g., Francisco and Krylowski, 2005). For simplicity, we neglect the recycling of NO_2 from NO_3-VOC reactions by assuming the complete removal of reactive nitrogen (Wagner et al., 2013). This would overestimate the NO_x loss since the monoterpenes contribute to around half of NO_3 reactivity at the present study, but this assumption does not significantly affect the conclusion because NO_3 loss with VOCs was the minor path comparing to N_2O_5 heterogeneous loss. Thus, the nocturnal NO_x loss rate can be quantified by the following equation:"

Added references:

Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO2 from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments, J. Geophys. Res. -Atmos., 102, 3795-3804, 10.1029/96JD03057, 1997.

Brown, S. S., and Stutz, J.: Nighttime radical observations and chemistry, Chem. Soc. Rev., 41, 6405-6447, 10.1039/C2CS35181A, 2012.

Wängberg, I., Barnes, I., and Becker, K. H.: Product and Mechanistic Study of the Reaction of NO3 Radicals with α-Pinene, Environ. Sci. Technol., 31, 2130-2135, 10.1021/es960958n, 1997.

Francisco, M. A., and Krylowski, J.: Chemistry of Organic Nitrates: Thermal Chemistry of Linear and Branched Organic Nitrates, Industrial & Engineering Chemistry Research, 44, 5439-5446, 10.1021/ie049380d, 2005.

21. *pg 13, line 22. "The NOx removal rate varied from 0.19 to 2.34 ppb h-1, with a mean of 1.12 ± 0.63 ppb h-1. This loss rate is higher than that determined from tower measurements during wintertime in Colorado, with integrated nocturnal NO2 loss ranging from 2.2 to 4.4 ppbv (Wagner et al., 2013)" Comparing absolute loss rates may not be meaningful since the overall NOx levels may be different – consider normalizing, for example, through division of average nocturnal NOx mixing ratios at both locations to derive a pseudo-first order loss rate coefficient.*

Response: We have included the normalized loss rate coefficient of NO_x in the revised text according to the suggestion. Wagner et al. (2013) did not provide the loss rate or loss rate coefficient in their work, so we have updated the comparison with other references. The revised text reads:

"Using the coefficients described above, we calculated the nocturnal loss rate of NO_x for each case, as summarized in Table 2. The NO_x removal rate varied from 0.19 to 2.34 ppb h^{-1}, with a mean of 1.12 ± 0.63 ppb h^{-1}, which corresponds to a pseudo-first order loss rate coefficient of 0.24 ± 0.08 h^{-1} in average for the studied cases. This loss rate is higher than that determined from a mountain site measurement in Taunus, Germany (~0.2 ppb h^{-1} with typical NO_2 level of 1-2 ppb) (Crowley et al., 2010), and the results from aircraft measurements in US over Ohio and Pennsylvania and downwind region of New York (90% and 50% NO_x loss in a 10-hour night, respectively) (Brown et al., 2006). For reference, this nocturnal average loss rate is approximately equivalent to NO_2 loss via reaction with OH at afternoon condition assuming OH concentration around 2×10^6 molecules cm^{-3}, indicating the importance of nocturnal heterogeneous reactions on NO_x processing and budget."

References:

Crowley, J. N., Schuster, G., Pouvesle, N., Parchatka, U., Fischer, H., Bonn, B., Bingemer, H., and Lelieveld, J.: Nocturnal nitrogen oxides at a rural mountain-site in south-western Germany, Atmos. Chem. Phys., 10, 2795-2812, 10.5194/acp-10-2795-2010, 2010.

Brown, S., Ryerson, T., Wollny, A., Brock, C., Peltier, R., Sullivan, A., Weber, R., Dube, W., Trainer, M., and Meagher, J.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-70, 2006.

22. *pg 14, line 21 " The results demonstrate the significance of heterogeneous N2O5- ClNO2 chemistry in the polluted residual layer over the NCP, ..." Are these rates significant? Perhaps. The question is: significant in what sense or compared to what? Consider adding more context (e.g., daytime nitrate formation rates, rates of other locations, etc.)*

Response: This paragraph has been revised and improved, as follows:

"Fast heterogeneous N_2O_5 uptake dominated and accounted for a mean of 87% of the regional nocturnal NO_x loss in the NCP. The estimated nocturnal loss rate of NO_x is higher than that previously observed in US and Europe, with averaged loss rate and rate coefficient of 1.12 ± 0.63 ppb h^{-1} and 0.24 ± 0.08 h^{-1}, respectively. Moreover, heterogeneous reactions contributed to substantial nitrate production up to 17 μg m^{-3}, with a mean nocturnal formation rate of 2.2 ± 1.4 μg m^{-3} h^{-1}, and in-situ production could account for 32 ± 27% of the observed nitrate concentrations in the studied cases. The results may help explain the previously observed rapid nighttime growth of fine nitrate aerosols in the NCP, and demonstrate the importance of heterogeneous N_2O_5-$ClNO_2$ chemistry on NO_x and aerosol budgets in the polluted residual layer over the NCP, which underpins the need for further studies regarding their roles in the formation of complex haze pollution in northern China."

23. *pg 19, Figure 1. Please indicate the scales of Fig. 1a (lat/long) and 1b (km/km)*

    pg 19, Figure 2 Please give a vertical scale for jNO2

    pg 21 Figure 4c – is the triangle the measurement location? If so, indicate in the caption.

Response: We have updated the figures and captions according to the review's suggestion.

24. *Figure 4b and 5b – state the fit uncertainties (-1.77+/-?; -1.44+/-?) on the figure*

    pg 22 Figure 7 - state the fit uncertainties (0.011+/-? and 0.040+/-?) on the figure

Response: The fit uncertainties are included in the revised figures.

25. *pg 22 Figure 8 – show the error bars for the experimental values*

Response: As shown in the previous responses #17, the error bars are included in the revised figures.

26. *pg 24 Figure 10 is there a difference between phi(N2O5) in Figure 10a and phi(ClNO2) in Figure 10b (and Tables 1 and 2)? The main manuscript defines only phi without subscript.*

Response: It should be ϕ_{ClNO2} in the y-axis of Figure 10a, and the typo was corrected in the revised figure.

Anonymous Referee #2

The paper reports on measurements of N2O5 and ClNO2 on a mountain top site in the North China Plane (NCP), and examines the chemistry of N2O5 to ClNO2 conversion in power plant plumes that were observed during the project. This study is a very useful addition to the growing literature on this important chlorine activation pathway. In general the paper is clear and very well written and should be publishable pending the handling of the following comments and questions.

We thank the reviewer for the valuable feedback, and we have revised the manuscript according to the comments. Our responses, including changes made to the manuscript, are listed below.

Reviewer comments are in italics. Author responses are in plain face. Changes to the text are in blue.

General Comments

1. *I would like to see a better description of the aerosol particle characteristics and chemistry. For example, surface area, organic fraction, in addition to nitrate and chloride could be included in Figure 1. This would be particularly useful since this is likely the major difference between the environment in this study relative to the studies in Europe or North America.*

Response: We thank the reviewer for the valuable suggestion. Additional description and discussion of the aerosol characteristic are included in the revised text. The time series of measured aerosol nitrate, sulfate, chloride and surface area was also added in the revised Figure 2, as follows:

"The average nighttime mixing ratios of O_3 and NO_2 were 77 and 3.0 ppbv, respectively, with an average nitrate radical production rate $p(NO_3)$ of 0.45 ± 0.40 ppb h^{-1}, which is indicative of potentially active NO_3 and N_2O_5 chemistry during the study period. However, the low N_2O_5 mixing ratios observed during most of the nights suggest a rapid loss of N_2O_5, which is consistent with the observed high aerosol surface area (Sa), varied from ~100 to 7800 μm^2 cm^{-3} with a mean value of 1440 μm^2 cm^{-3}."

"The elevated $ClNO_2$ levels observed at Mt. Tai are similar to recent measurements at a surface rural site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016), but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world. During the campaign at Mt. Tai, the average concentrations of aerosol sulfate and nitrate were 14.8 ± 9.0 and 6.0 ± 4.7 µg m^{-3}, accounting for 29.5% and 12.0% of $PM_{2.5}$ mass, respectively. The aerosol organic-to-sulfate ratio, a parameter that potentially affects the uptake process (Bertram et al., 2009b), was 0.74 on average and much lower than those from studies mentioned above in Europe and US. Moreover, the nighttime averaged Cl^- concentration was 0.89 ± 0.86 µg cm^{-3}, and was an order of magnitude higher than Na^+, indicating abundant non-oceanic sources of chloride (e.g., from coal combustion and biomass burning in the NCP) (Tham et al., 2016), which could enhance the production of $ClNO_2$."

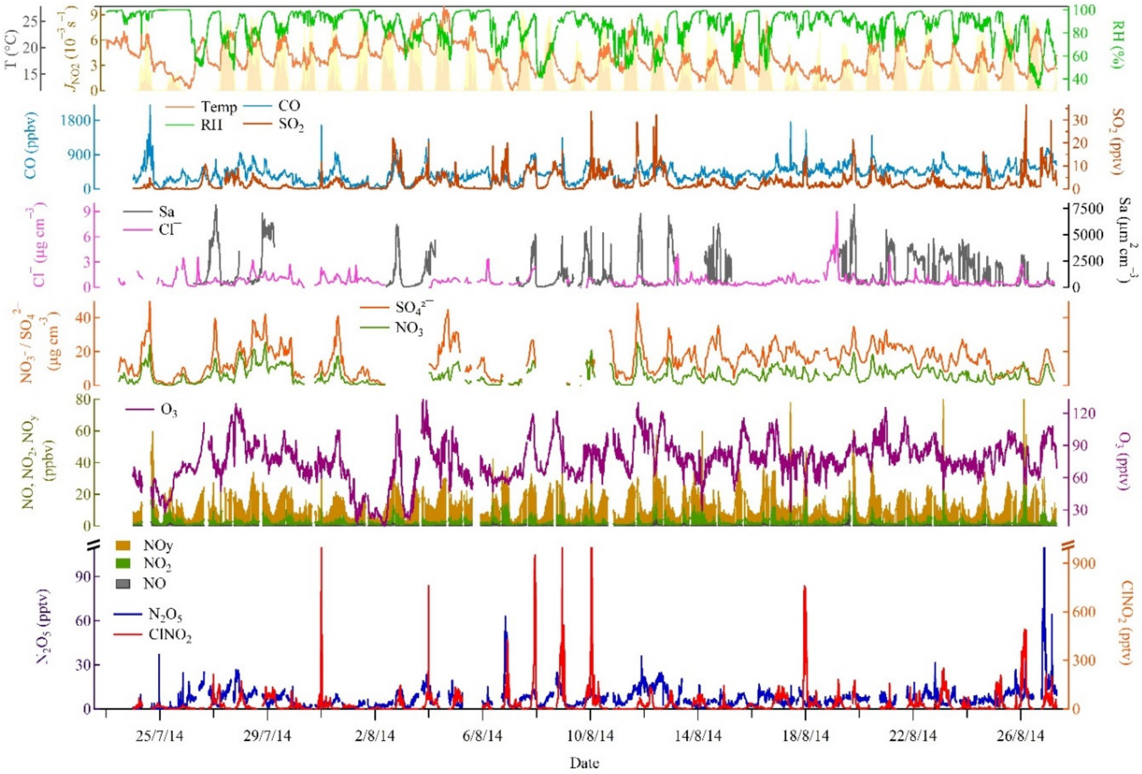


Figure 2 : Time series for N_2O_5, $ClNO_2$, related trace gases, aerosol properties, and meteorological data measured at Mt. Tai from July 24 to August 27, 2014.

References:

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 2016.

2. *It would also be helpful if instead of mass concentration, some of the correlations in figures (Figure 11, Figure S1) could be also done with molar concentration, which is how the lab studies (Bertram and Thornton,2009, Roberts et al, 2009) were parameterized.*

Response: We changed the aerosol nitrate and chloride concentrations in the supplement figures to molar concentrations, as shown below. For the Figure 11, it was intended to compare the predicted nitrate concentration with the measured increase of nitrate concentration, so we think the comparison in mass concentration is straightforward and just keep it as before.

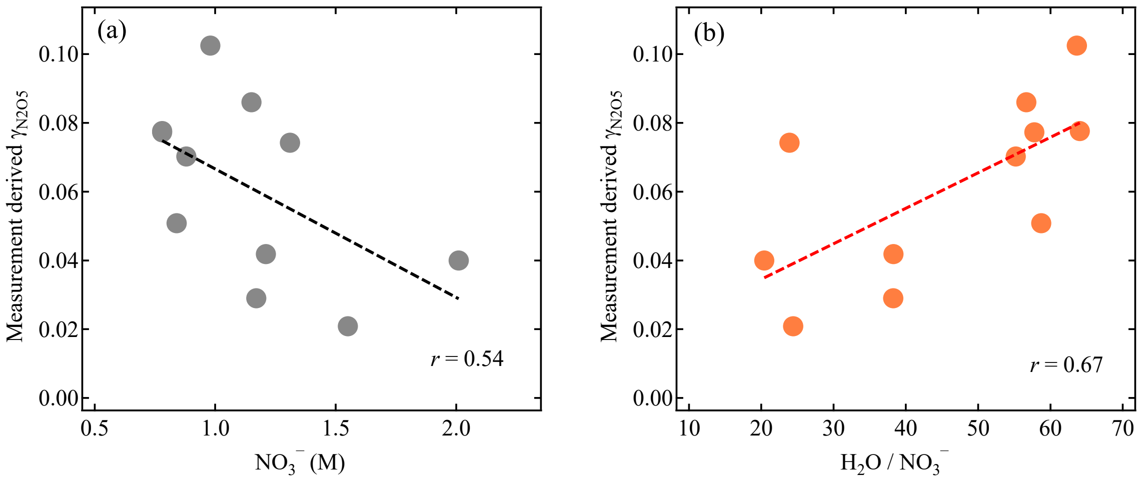


Figure S2: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol nitrate and (b) the molar ratio of aerosol water to nitrate during the study period.

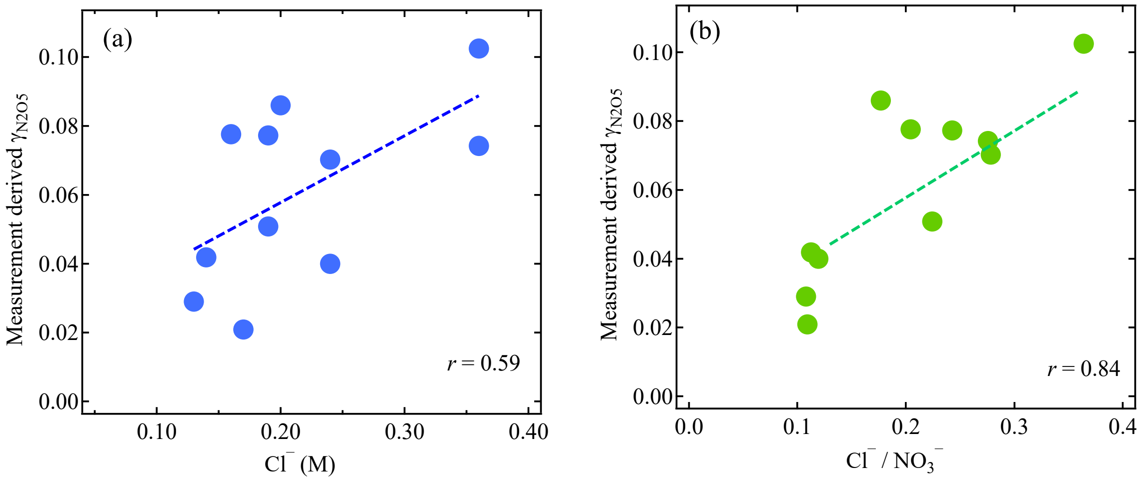


Figure S3: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol chloride and (b) the molar ratio of aerosol chloride to nitrate during the study period.

Specific Comments

3. *Abstract, Line 12. I know what you mean when you say effect the next day's photochemistry, but someone not familiar with ClNO2 would first need to know that it photolyzes to yield chlorine atoms, so some additional explanation would be good here.*

Response: We revised the abstract to clarify the effects as follows:

"Dinitrogen pentoxide (N_2O_5) and nitryl chloride ($ClNO_2$) are key species in nocturnal tropospheric chemistry, and have significant effects on particulate nitrate formation and the following day's photochemistry through chlorine radical production and NO_x recycling upon photolysis of $ClNO_2$."

4. *Abstract Line 18. A brief phrase describing how you got the uptake coefficient and yield would be good here.*

Response: As the reviewer suggested, we added the methodology information in the abstract to clarify it as follows:

"The heterogeneous N_2O_5 uptake coefficient (γ) and $ClNO_2$ yield (ϕ) were estimated from steady-state analysis and observed growth rate of $ClNO_2$. The derived γ and ϕ exhibited high variability, with means of 0.061 ± 0.025 and 0.27 ± 0.24, respectively."

5. *Abstract, Line 22. When you use the word "determined" it sounds like a measurement. It would more accurate to say 'estimated' or 'modeled'.*

Response: We changed the word of 'determined' to 'estimated'.

6. *Page 3, Line 2. Not sure what is meant when you say "the field determination of (phi) is limited". Do you mean that there are not very many reported determinations of (phi) from field measurements?*

Response: The reviewer's understanding is correct. To clarify, we revised the text as follows:

"There are only a few studies on the determination of ϕ from field measurement, and the possible effects of real atmospheric aerosols (including organic composition, mixing state, and chloride partitioning between particle sizes, etc.) have not been well characterized (Mielke et al., 2013; Phillips et al., 2016)."

7. *Page 3, Line 13. The Thornton et al., 2010 reference should be included in this list.*

Response: The suggested reference is added to the list.

8. *Page 4, Line 19. It would be more proper to say 'iodide ion chemical ionization mass spectrometry with a quadrupole mass spectrometer'.*

Response: We corrected it according to the suggestion.

9. *Page 11, Eq. 6. The term dN2O5/dt should really be the loss rate of N2O5, which are corrected shown in the next two terms in the equation.*

Response: We agree with the reviewer's suggestion, and the equation was corrected by removing the first two terms.

10. *Page 11, Lines 15-20. The big problem with this analysis is that it assumes that the growth rates that are inferred from Figure 9 correspond to the actual kinetic time within the plume. There is no way to know if that is true. The features in Figure 9 could be due to something completely different, e.g. a gradual shift in wind direction so that the plume as gradually influencing the site, starting with the dilute edge. There is simply no way to know what the*

physical circumstances were, with the evidence at hand. Another approach needs to be found, or the analysis should be abandoned.

Response: We agree with the reviewer that the growth rate estimation could be biased due to the potential variation of the plume, and simplified estimation would result in some uncertainties. We were aware of these limitations in the estimation, and therefore had carefully inspected the time series to choose the data during a period when related parameters in the air mass were relatively constant. It is likely that the assumptions are reasonable during the short time periods, usually around 2 to 3 hours. In addition, we have applied an alternative approach to derive the $ClNO_2$ yields from the ratio of observed enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- and HNO_3), according to the method suggested by Riedel et al. (2013). The derived ϕ values from this approach exhibit reasonable agreement with the original analysis, and most of the differences between two groups of data are within 40% (see figure below). Although either approach requires assumptions and would introduce some uncertainties, the general consistency can serve as a check to corroborate the yield analysis.

To clarify, we have revised the text by elaborating these assumptions in the estimation and the criteria for selecting cases, and also added the comparison results between two different approaches in the revised version, as follows:

"For regional diffuse pollution cases, the ϕ defined in R3 can be estimated from the ratio between $ClNO_2$ production rate and N_2O_5 loss rate, as the first term in below equation:

$$\phi = \frac{d\mathrm{ClNO_2}/dt}{k(\mathrm{N_2O_5})_{\mathrm{het}}[\mathrm{N_2O_5}]} = \frac{[\mathrm{ClNO_2}]}{\int k(\mathrm{N_2O_5})_{\mathrm{het}}[\mathrm{N_2O_5}]\,dt} \qquad (6)$$

$k(N_2O_5)$ values can be determined using the inverse steady-state lifetime analysis described above in Eq. 3, and the production rate of $ClNO_2$ can be derived from the near-linear increase in $ClNO_2$ mixing ratio observed during a period, when the related species (e.g., NO_x, SO_2) and environmental variables (e.g., temperature, RH) were roughly constant. The approach here assumes that the relevant properties of the nocturnal air mass are conserved, and neglects other possible sources and sinks of $ClNO_2$ in the air mass history. For the intercepted coal-fired plumes exhibiting sharp $ClNO_2$ peaks, the $ClNO_2$ yield can be estimated from the ratio of the observed $ClNO_2$ mixing ratio to the integrated N_2O_5 uptake loss over the plume age (i.e., the second term in Eq. 6). The analysis assumes that no $ClNO_2$ was present at the point of plume emission from the combustion sources and no $ClNO_2$ formation before sunset, and that the γ and ϕ within the plumes did not change during the transport from the source to the measurement site. The potential variability in these quantities likely bias the estimates, but these assumptions are a necessary simplification to represent the averaged values that best describe the observations. It should be noted that the steady-state N_2O_5 loss rate is crucial in the yield estimation, which could be underestimated by potentially overestimating the loss rate in some cases with large uncertainties in N_2O_5 measurement and NO_3 reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the $ClNO_2$ yield from the ratio of enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- + HNO_3) in the cases. Given the low time resolution of nitrate data that could potentially introduce large uncertainties, this approach will only be used as a reference to validate the former analysis based on Eq. 6."

“The determined ϕ for the seven coal-fired plumes are also listed in Table 1. During the measurement period, ϕ varied from 0.02 to 0.90, with an average of 0.28 ± 0.24 and a median of 0.22. In comparison, the ϕ derived from the production ratio approach showed comparable results with an average of 0.25 ± 0.17, and the ϕ values from two different approaches match reasonably well with a Reduced Major Axis Regression (RMA) slope of 0.78 ± 0.08 and r^2 of 0.73 (cf Figure S4), which corroborates the yield analysis and indicates that the differences are within the overall uncertainty of 40%.”

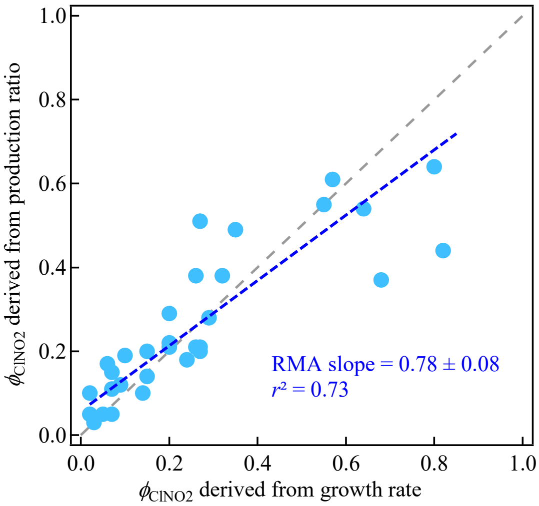


Figure S4: Comparison of estimated $ClNO_2$ yields from two different approaches: approach A using the ratio of the observed $ClNO_2$ growth rate to steady-state N_2O_5 loss rate based on Eq. 6; approach B using the production ratio of observed enhancements of $ClNO_2$ and total nitrate, $\phi = 2/(\Delta NO_3^-/\Delta ClNO_2 + 1)$ according to Riedel et al., 2013.

References:

Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., Bahreini, R., VandenBoer, T. C., Wolfe, D. E., Williams, E. J., Roberts, J. M., Brown, S. S., and Thornton, J. A.: Chlorine activation within urban or power plant plumes: Vertically resolved ClNO2 and Cl2 measurements from a tall tower in a polluted continental setting, J. Geophys. Res. -Atmos., 118, 8702-8715, 10.1002/jgrd.50637, 2013.

11. Page 11-12, Eq.7 and Lines 1-2. With the equation written as is, k' would then be 1/450, not 450 as stated, to match the parameterization of Roberts et al., 2009. I believe the correct expression was used to generate the points in Figure 10a since Eq. 7 as written would generate phi's that were quite a bit <1.

Response: We corrected the typo in the revised version.

12. Page 12, Eq. 8. Same problem as Eq. 6, dN2O5/dt is not the proper term here.

Response: The equation is corrected by removing the first term.

Anonymous Referee #3

General comments:

This paper presents measurement of N2O5 and ClNO2 from a polluted mountaintop site in the North China Plain during summer 2014. Measurements of these nighttime reactive nitrogen species in the polluted residual layer of China are novel and a valuable contribution to the literature. The authors attribute several of the plumes encountered at the mountaintop site to emissions from regional coal fired power plants. They further use several standard analysis metrics to interpret the data and provide estimates of N2O5 uptake coefficients and ClNO2 yields, along with the overall influence of nighttime chemistry on aerosol nitrate formation in the region. Results for N2O5 uptake coefficients are generally larger and ClNO2 yields are generally smaller than previous literature determinations. These observations may not be unrelated. If the analysis method biases the N2O5 uptake coefficient to large values, then the same analysis will tend to predict lower ClNO2 yields. The authors should be careful to consider uncertainties that could lead to such a bias, especially in the aerosol size distribution measurement and in the assessment of NO3-VOC reactivity. Alternatively, the very high relative humidity at this site could lead to exactly the effect that is found here, producing faster N2O5 reactivity but also a larger fraction tending toward HNO3 rather than ClNO2. The paper could make this point explicitly in its comparison to previous work (e.g. Phillips, et al., Wagner et al.). The paper should be published subject to these comments and the minor comments below.

We thank the reviewer for the valuable suggestions. We are aware of the uncertainties in the measurement and analysis that could potentially bias the results. In the revised text, we have included a more detailed description of the measurement uncertainty in the methodology part, including N_2O_5 transmission efficiency, calibrations and surface area calculation. We have also clarified the assumptions and uncertainties in the NO_3 reactivity estimation and determination of uptake coefficient and yield. Additional approach for yield estimation is also applied as a check to corroborate the analysis and results. More discussions on the observed high uptake coefficient and the possible effects of high humidity and aerosol characteristics comparing to previous studies are also added in the revised text.

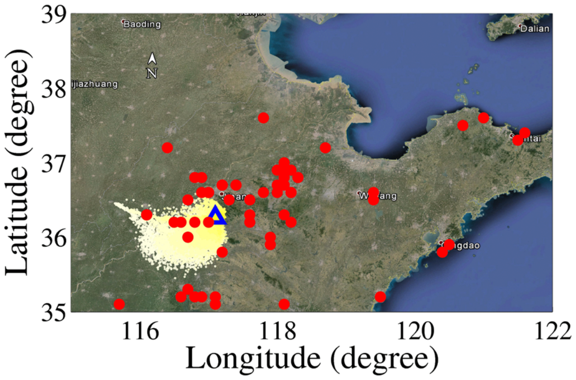
Our responses to the comments, including changes made to the manuscript, are listed point-by-point below.

Reviewer comments are in italics. Author responses are in plain face. Changes to the text are in blue.

Specific comments.

1. *Page 4, line 16-17. Is there a database showing the location of major coal fired power plants that could be included with the map in Figure 1? This would help to clarify the number of sources and their distance from the observatory.*

Response: The location information of major coal-fired facilities in the industry (cement and steel production) and power plants in the region is included in the maps in Figure 4c and 5c, to aid the discussion in the section of coal-fired plumes (section 3.2). Figure 4c is shown below for reference:



2. *Page 4, line 27. What were the results of the manual calibrations for N2O5 and ClNO2? Give some sense for reproducibility, and lack of either N2O5 loss or ClNO2 generation on the inlets.*

Response: To clarify, we added a more detailed description of the N_2O_5/$ClNO_2$ measurement, including transmission efficiency, calibrations and the uncertainties in the methodology part. The revised text reads,

"The inlet was installed ~ 1.5 m above the roof of a single-story building, and the sampling line was a 5.5 m PFA-Teflon tubing (1/4 in. o.d.) which was replaced daily in the afternoon before sunset and washed in the ultrasonic bath to minimize wall loss caused by deposited particles (Wang et al., 2016). A small proportion (1.7 SLPM) of total sampling flow (~ 11 SLPM) was diverted to the CIMS system, to reduce the residence time of the air samples in the sampling line. A standard addition of N_2O_5 into the ambient inlet was performed before and after the tubing replacement to monitor the transmission efficiency, and this practice limited the loss of N_2O_5 in the inlet to <10% in the 'clean' tubing and about 30% in the next afternoon. Manual calibrations of N_2O_5 and $ClNO_2$ were conducted daily to determine the instrument sensitivity, and the average of which during the observation period was 2.0 ± 0.6 for N_2O_5 and 2.2 ± 0.6 Hz $pptv^{-1}$ for $ClNO_2$, respectively. The N_2O_5 standard was synthesized on-line from the reaction between NO_2 and O_3, and the produced N_2O_5 were determined from the decrease in NO_2 (Wang et al., 2014). This method has been validated with a Cavity Ring Down Spectrometer (CRDS) measurement in previous campaign (Wang et al., 2016). The $ClNO_2$ was produced by passing a known concentration of N_2O_5 through a NaCl slurry assuming unity conversion efficiency (Roberts et al., 2009) and negligible $ClNO_2$ loss in the system (Wang et al., 2016). The field background was determined by passing the ambient sample through a filter packed with activated carbon, with average levels of 7.8 ± 1.9 and 6.0 ± 1.6 Hz for N_2O_5 and $ClNO_2$, respectively. The reported concentrations were derived by subtracting the background levels. The detection limit was 4 pptv for both N_2O_5 and $ClNO_2$ (2σ, 1 min-averaged data), and the uncertainty of the nighttime measurement is estimated to be ± 25% (Tham et al., 2016)."

References:

Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A. R., Coffman, D., Quinn, P., and Bates, T.: Laboratory studies of products of N2O5 uptake on Cl− containing substrates, Geophys. Res. Lett., 36, 10.1029/2009gl040448, 2009.

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 2016.

Wang, X., Wang, T., Yan, C., Tham, Y. J., Xue, L., Xu, Z., and Zha, Q.: Large daytime signals of N2O5 and NO3 inferred at 62 amu in a TD-CIMS: chemical interference or a real atmospheric phenomenon?, Atmos. Meas. Tech., 7, 1-12, 10.5194/amt-7-1-2014, 2014.

Wang, T., Tham, Y. J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S. C. N., Dubé, W. P., Blake, D. R., Louie, P. K. K., Luk, C. W. Y., Tsui, W., and Brown, S. S.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res. -Atmos., 10.1002/2015jd024556, 10.1002/2015jd024556, 2016.

3. *Page 6, line 5. Elevated CO is not normally associated with coal fired power plant emissions, at least in the U.S and Europe.*

Response: The reviewer makes an excellent point here. In north China, the industry sector, including the cement kilns, iron and steel industry, etc., contributes the largest portion of CO emission, whereas the power plants are the fourth contributor to CO emission because of the better combustion efficiency (Streets et al., 2006; Zhang et al., 2009; Saikawa et al., 2017). For both SO_2 and NO_x emissions, the power plants and industry are the two largest source sectors. Therefore, from the measurement results, we can certainly attribute the plumes with a steep increase of SO_2 to coal combustion origin, and the ratio of CO to SO_2 or NO_y may give some indications of its source from power plants or industrial plants.

To clarify, we changed the definition of the high $ClNO_2$ plume from 'power plant plumes' to 'coal-fired plumes', and revised the manuscript title as "Fast heterogeneous N_2O_5 uptake and $ClNO_2$ production in coal-fired plumes observed in the nocturnal residual layer over the North China Plain". The relevant description in the text was also revised accordingly.

References:

Saikawa, E., Kim, H., Zhong, M., Avramov, A., Zhao, Y., Janssens-Maenhout, G., Kurokawa, J. I., Klimont, Z., Wagner, F., Naik, V., Horowitz, L. W., and Zhang, Q.: Comparison of emissions inventories of anthropogenic air pollutants and greenhouse gases in China, Atmos. Chem. Phys., 17, 6393-6421, 10.5194/acp-17-6393-2017, 2017.

Streets, D. G., Zhang, Q., Wang, L., He, K., Hao, J., Wu, Y., Tang, Y., and Carmichael, G. R.: Revisiting China's CO emissions after the Transport and Chemical Evolution over the Pacific (TRACE-P) mission: Synthesis of inventories, atmospheric modeling, and observations, Journal of Geophysical Research: Atmospheres, 111, 10.1029/2006JD007118, 2006.

Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in 2006 for the NASA INTEX-B mission, Atmos. Chem. Phys., 9, 5131-5153, 10.5194/acp-9-5131-2009, 2009.

4. *Page 6, line 26. What are the slopes of correlation plots of SO2 vs NOy, SO2 vs CO and CO vs NOy? This information is important in the attribution of this plume to a coal fired plant, since coal typically has larger SO2/NOy and lower CO/NOy than that from urban emission. These values could be included in Table 1.*

   For comparison, what was the overall relationship between CO and NOy or SO2 and NOy for the entire campaign? If most of the NOy is urban, then the global relationships might define the urban numbers so that the power plants could be more easily distinguished.

Response: We appreciate the reviewer's helpful suggestions. We examined the correlations among SO_2, NO_y and CO in these cases to figure out the source information. The slopes of SO_2 vs NO_y in these cases ranged from 0.48 to 2.43, and were all higher than the overall slope of 0.31 for the entire campaign, indicating the coal combustion source of these plumes. The slope of CO vs NO_y varied from 33 to 108, and was also higher than the campaign global slope of 15.7. As we stated in the previous response, both high SO_2/NO_y and CO/NO_y slopes (and ratios) suggest that the plumes were likely originated from coal-fired facilities in industrial plants, whereas high SO_2/NO_y with relatively lower CO/NO_y possibly suggest the source from power plants.

In the revised version, we added the derived slopes of SO_2 vs NO_y and CO vs NO_y in Table 1, and also included the ratios of SO_2/NO_y and CO/NO_y in Figure 4a and 5a. The text and discussions are also clarified and revised to match these changes, as follows,

"As described above, several plumes with elevated $ClNO_2$ concentrations (> 500 pptv) were observed during the measurement period. Figure 4a illustrates the high $ClNO_2$ case observed during the night of July 30-31, 2014. The $ClNO_2$ concentration peaked sharply at 1265 pptv, which was accompanied by a steep rise in the concentrations of SO_2, NO_x and CO. The SO_2/NO_y ratio increased from ~0.1 to 0.6 in the plume center, with a $\Delta SO_2/\Delta NO_y$ slope of 0.57, indicating the coal combustion source of the plume. The coincident increase in CO/NO_y ratio from ~30 to 90 suggests that it was likely originated from coal-fired industry facilities, such as cement and steel production plants, which is the largest emitting sector of CO in north China (Streets et al., 2006; Zhang et al., 2009). The 12-h backward particle dispersion trajectories calculated from the HYSPLIT model revealed that the air masses mostly moved slowly from the west, and passed over the region with cement and steel production industry and power plants before arriving at the measurement site. Figure 5a shows the highest $ClNO_2$ case (2065 ppbv) observed on the night of August 8, 2014. The simultaneous increases in SO_2, NO_x and CO concentrations, together with the higher SO_2/NO_y ratio (~0.5) comparing to that outside of plume (~0.1) and the campaign average (0.24), again indicate the coal combustion origin of the plume. The relatively lower CO/NO_y ratio of ~50 possibly suggests the plume affected by power plant emission, as shown by the derived backward particle dispersion trajectories. Table 1 summarizes the chemical characteristics of the eight cases of high-$ClNO_2$ coal-fired plumes during the study period. In these cases, the average SO_2 mixing ratios ranged from 2.3 to 18.7 ppbv, and the maximum $ClNO_2$ and N_2O_5 mixing ratios ranged from 534 to 2065 ppbv and 7.3 to 40.1 ppbv, respectively, with corresponding $ClNO_2/N_2O_5$ ratios of 25 to 118. The mixing ratios for O_3 and NO_2 ranged from 60 to 106 ppbv and 2.8 to 11.8 ppbv, respectively, resulting in high $p(NO_3)$ values of 0.60 to 1.59 ppbv h^{-1}. The aerosol chloride concentration ranged from 1.01 to 2.34 µg cm^{-3}, which was higher than the nighttime average (0.89 µg cm^{-3}) and conducive to $ClNO_2$ production from R3."

Table 2: Chemical characteristics of coal-fired plumes exhibiting high levels of $ClNO_2$ observed at Mt. Tai during the summer of 2014

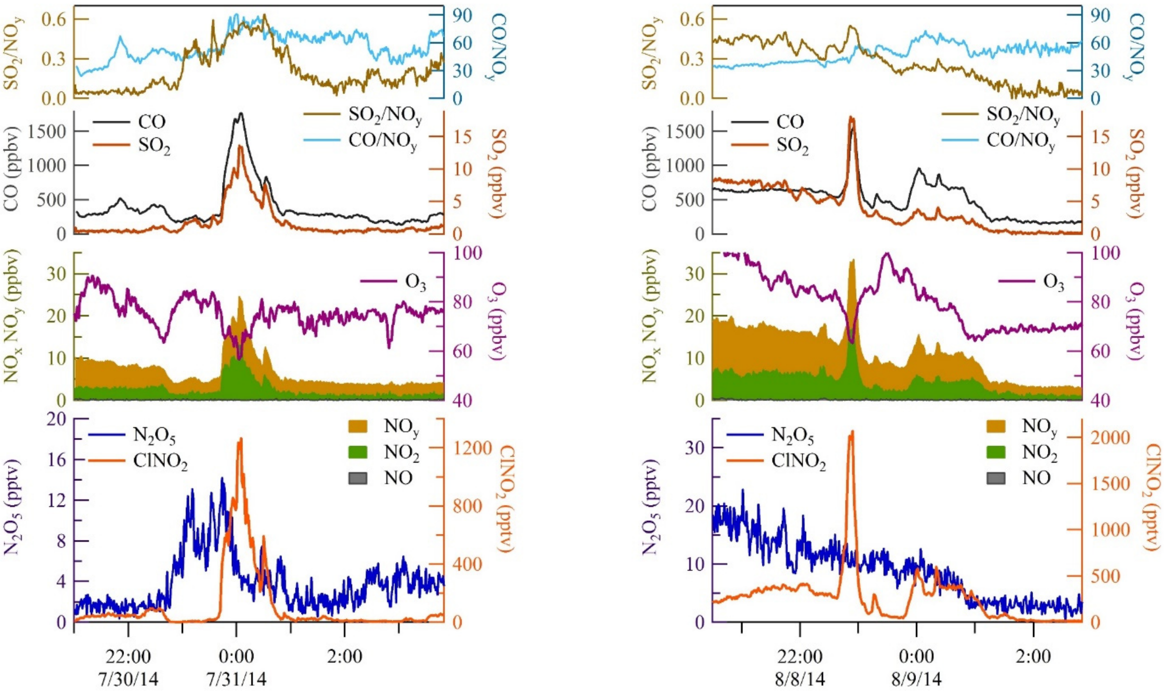
Date	Duration	N_2O_5 (pptv) Mean	N_2O_5 (pptv) Maximum	$ClNO_2$ (pptv) Mean	$ClNO_2$ (pptv) Maximum	O_3	NO_x	NO_x /NO_y	ΔSO_2 /ΔNO_y [a]	ΔCO /ΔNO_y [b]	Cl- (μg cm^{-3})	t_{plume}	ϕ $_{ClNO2}$
30-31 Jul	23:40-0:45	5.9	14.2	528	1265	70	6.5	0.49	0.57	83	2.34	3.2	0.57
3-4 Aug	23:30-0:00	20.1	23.8	506	833	106	2.8	0.22	2.43	108	NA [c]	4.9	0.64
7 Aug	21:30-23:30	10.5	14.9	606	976	91	5.8	0.36	1.36	50	2.24	5.5	0.35 [d]
8 Aug	22:00-23:10	11.0	15.1	841	2065	76	8.5	0.45	0.65	45	NA	2.1	0.90
8-9 Aug	23:40-01:15	6.8	12.6	315	599	77	4.3	0.41	0.54	85	NA	4.4	0.23
10 Aug	0:00-2:00	10.5	15.5	692	1684	72	6.2	0.43	1.67	50	1.10	4.6	0.55
17-18 Aug	22:00-01:30	3.5	7.7	409	802	60	9.5	0.55	0.48	33	1.01	4.6	0.26 [d]
25-26 Aug	0:00-5:00	12.1	40.1	301	534	74	11.8	0.62	2.10	NA	1.88	3.0	0.20

[a] It represents the slope of SO_2 vs NO_y in plumes, and the overall slope for entire campaign was 0.31 with r^2 of 0.31.

[b] Same to above note with the campaign overall slope of 15.7 and r^2 of 0.23.

[c] Data not available in the case.

[d] For t_{plumes} longer than the nocturnal processing period since sunset, the time since sunset was used in the $ClNO_2$ yield calculation.



Revised Figure 4a and Figure 5a: Time series for $ClNO_2$, N_2O_5, and related trace gases observed within the high-$ClNO_2$ coal-fired plume during the nights of July 30-31, 2014 (left panel) and August 8-9, 2014 (right panel)

5. Page 7, line 17. Authors probably mean a slope steeper than -1 (rather than +1).

Response: The typo is corrected in the revised text.

6. *Page 8, line 25. The determination of N2O5 reactivity is not quite clear. Text implies that equation 3 is used, and that k(NO3)/Keq[NO2] is subtracted from this number based on the measured VOCs from a different year. Correct? If so, this should be stated explicitly, possibly with an equation.*

   If the above is correct, then for the sake of clarity, the NO3 loss rates quoted in line 23 should be divided by Keq[NO2] to make it obvious how the budget was done.

   What is not given here is a sense for the uncertainty (e.g., N2O5 contributions of 80% and 71% given to two significant figures with no uncertainty). Since VOC measurements from a separate year are used, and since the NO3 reactivity is dominated by reaction with monoterpenes, which are variable and quite temperature dependent, there could be substantial year to year variability and thus considerable uncertainty in this budget. At the very least, this uncertainty should be qualitatively noted. If the authors have data that would quantify year to year or night to night variability in the NO3 losses, then those numbers should be used to formulate a quantitative error budget.

Response: We thank the reviewer for the comments on the uncertainty and pointing out the unclear description. In the revised version, we have clarified the description of the determination of N_2O_5 reactivity, and also added more statement on the uncertainty of NO_3 relativity estimation. Moreover, we also changed the text to avoid using the exact number of 80% and 71%, but reported the results in range to reflect the potential uncertainty.

The clarified and revised text reads:

"The determined nighttime $k(NO_3)$ was 1.33×10^{-2} s^{-1} for the first half of the night and 1.07×10^{-2} s^{-1} for the period after midnight, which is equivalent to an NO_3 lifetime of approximately 1.5 min. The estimated $k(NO_3)$ could be considered as an upper limit for coal-fired plumes because of potential lower biogenic VOC levels within the plumes. The estimation here does not account for the VOC changes between years and the night to night variability, which may result in uncertainties. The $k(NO_3)$ derived by another approach, i.e., from the nighttime steady state fits, provides a consistency check and evaluation of the errors, as described below.

The heterogeneous loss rate, $k(N_2O_5)_{het}$, can be obtained by subtracting the $k(NO_3)/K_{eq}[NO_2]$ from the determined $\tau(N_2O_5)^{-1}$ in Eq.3. Figure 6a shows the averaged total N_2O_5 reactivity and fractions of N_2O_5 loss via NO_3 ($k(NO_3)/K_{eq}[NO_2]$) and heterogeneous N_2O_5 loss during the study period. As shown, the heterogeneous loss was dominant, accounting for 70-80% of total N_2O_5 reactivity with higher fraction before midnight. Figure 6b shows the contribution of different VOC categories to the average first-order NO_3 loss rate coefficients, $k(NO_3)$. Biogenic monoterpenes accounted for more than half of the NO_3 reactivity, followed by anthropogenic alkenes (such as butene), isoprene and dimethyl sulfide (DMS). Aromatics and alkanes made small contributions (<1%) to the total NO_3 reactivity. Although some unmeasured organic species (e.g., peroxy radicals) could also contribute to a small fraction of NO_3 loss (Brown et al., 2011; Edwards, et al., 2017), the dominant NO_3 reactivity by biogenic VOCs is similar to that observed at a mountain site in southern China (Brown et al., 2016) and aircraft measurement in residual layer in southeast US (Edwards, et al., 2017), whereas the anthropogenic contribution is much higher in the present study. The estimated

NO_3 activity is slightly lower than that obtained from surface site measurements in the NCP (Tham et al., 2016; Wang et al., 2017b), which is in line with the higher abundances of VOCs in the polluted boundary layer."

"The average $k(NO_3)$ derived from the steady state fits is 0.015 ± 0.010 s^{-1}, which is comparable to that predicted from the VOC concentrations described above, indicating that the estimated results in the present study are reliable and likely representative of averaged conditions in the region. The agreement between these two methods also corroborates the determination of the uptake coefficient from steady state analysis. The estimated uncertainty in each individual determination varied from 35 to 100%, including statistical errors and uncertainty associated with measurements of gaseous and aerosol species (Tham et al., 2016)."

References:

Brown, S. S., Dubé, W. P., Peischl, J., Ryerson, T. B., Atlas, E., Warneke, C., de Gouw, J. A., te Lintel Hekkert, S., Brock, C. A., Flocke, F., Trainer, M., Parrish, D. D., Feshenfeld, F. C., and Ravishankara, A. R.: Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study, J. Geophys. Res. -Atmos., 116, 10.1029/2011JD016544, 2011.

Edwards, P. M., Aikin, K. C., Dube, W. P., Fry, J. L., Gilman, J. B., de Gouw, J. A., Graus, M. G., Hanisco, T. F., Holloway, J., Hubler, G., Kaiser, J., Keutsch, F. N., Lerner, B. M., Neuman, J. A., Parrish, D. D., Peischl, J., Pollack, I. B., Ravishankara, A. R., Roberts, J. M., Ryerson, T. B., Trainer, M., Veres, P. R., Wolfe, G. M., Warneke, C., and Brown, S. S.: Transition from high- to low-NOx control of night-time oxidation in the southeastern US, Nature Geosci, 10, 490-495, 10.1038/ngeo2976, 2017.

7. *Is there any potential for unmeasured VOC that contributes more to the NO3 reactivity budget? Have the authors considered reaction of NO3 with peroxy radicals?*

Response: The peroxy radicals were not measured at Mt. Tai and therefore were not considered in the NO_3 reactivity estimation. The VOC species used for NO_3 reactivity estimation in the present work were chosen based on the results of previous literature (e.g., Brown et al., 2011; Brown et al., 2016; Tham et al., 2016). We agree with the reviewer that there are some unmeasured organic species that could also contribute to the NO_3 reactivity, as listed in the review work by Atkinson and Arey (2013); but in most of the previous work, the reported NO_3-VOC reactivity was dominated by biogenic VOCs, especially the monoterpenes and isoprene, followed by anthropogenic alkenes, whereas the contribution of peroxy radicals was very small (e.g., Brown et al., 2011; Brown et al, 2016; Edwards, et al., 2017). The results here show similar pattern dominated by BVOC and alkenes categories; therefore, we consider the underestimation of NO_3 reactivity from the unmeasured species should be within the overall analysis uncertainty. Moreover, the comparison of NO_3 reactivity estimated from VOC concentrations to that from steady-state analysis also provides a consistency check on the determined values.

To clarify, we have included this information in the revised text, as shown in the previous responses to comment #6.

References:

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem. Rev., 103, 4605-4638, 2003.

Brown, S. S., Dubé, W. P., Peischl, J., Ryerson, T. B., Atlas, E., Warneke, C., de Gouw, J. A., te Lintel Hekkert, S., Brock, C. A., Flocke, F., Trainer, M., Parrish, D. D., Feshenfeld, F. C., and Ravishankara, A. R.: Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study, J. Geophys. Res. -Atmos., 116, n/a-n/a, 10.1029/2011JD016544, 2011.

Brown, S. S., Dubé, W. P., Tham, Y. J., Zha, Q., Xue, L., Poon, S., Wang, Z., Blake, D. R., Tsui, W., Parrish, D. D., and Wang, T.: Nighttime Chemistry at a High Altitude Site Above Hong Kong, J. Geophys. Res. -Atmos., 10.1002/2015jd024566, 10.1002/2015jd024566, 2016.

Edwards, P. M., Aikin, K. C., Dube, W. P., Fry, J. L., Gilman, J. B., de Gouw, J. A., Graus, M. G., Hanisco, T. F., Holloway, J., Hubler, G., Kaiser, J., Keutsch, F. N., Lerner, B. M., Neuman, J. A., Parrish, D. D., Peischl, J., Pollack, I. B., Ravishankara, A. R., Roberts, J. M., Ryerson, T. B., Trainer, M., Veres, P. R., Wolfe, G. M., Warneke, C., and Brown, S. S.: Transition from high- to low-NOx control of night-time oxidation in the southeastern US, Nature Geosci, 10, 490-495, 10.1038/ngeo2976, 2017.

8. *Page 9, line 14. Similar comment regarding error analysis in Table 2. The authors should provide error bars for the determined gamma and phi values based on measurement uncertainties. Especially important, but not discussed, is the uncertainty in the aerosol size distribution measurement to determine Sa in equation (5). Such measurements often have considerable uncertainty that can be limiting for the gamma determinations.*

Response: We appreciate the reviewer's suggestion. As stated in our previous response #2 and #6, we have included more detailed description of the uncertainty in measurements and analysis in the revised text. The uncertainty in the aerosol surface area determination is also included in the revised text, as follows,

"The particle diameters were corrected for particle hygroscopicity to determine the actual ambient aerosol surface density, and the wet diameters were calculated using growth factors from a size-resolved kappa-Köhler function obtained in a rural site in the NCP (Ma et al., 2016; Tham et al., 2016). The uncertainties associated with the aerosol surface area determination was estimated to be around 30% (Liu et al., 2010; Tham et al., 2016)."

The Figure 8 and 10 are also updated to include the error bars, as shown below.

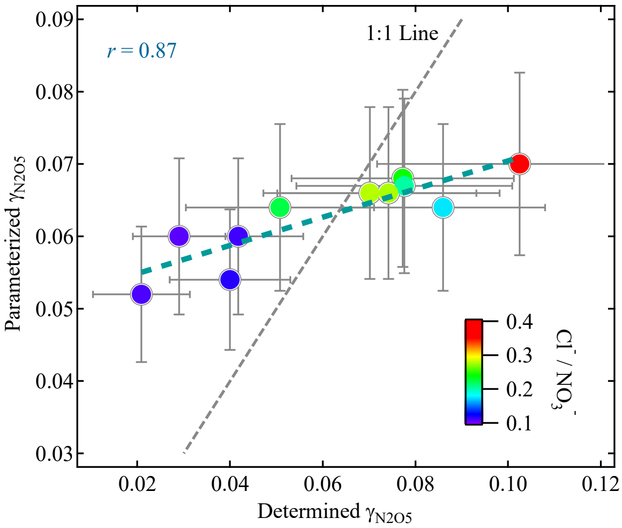


Figure 8: Comparison of field-determined γ with that derived from the parameterization of Bertram and Thornton, (2009). The colors of the markers indicate the corresponding concentrations ratio of particulate chloride to nitrate. The error bars represent the total aggregate uncertainty associated with measurement and derivation.

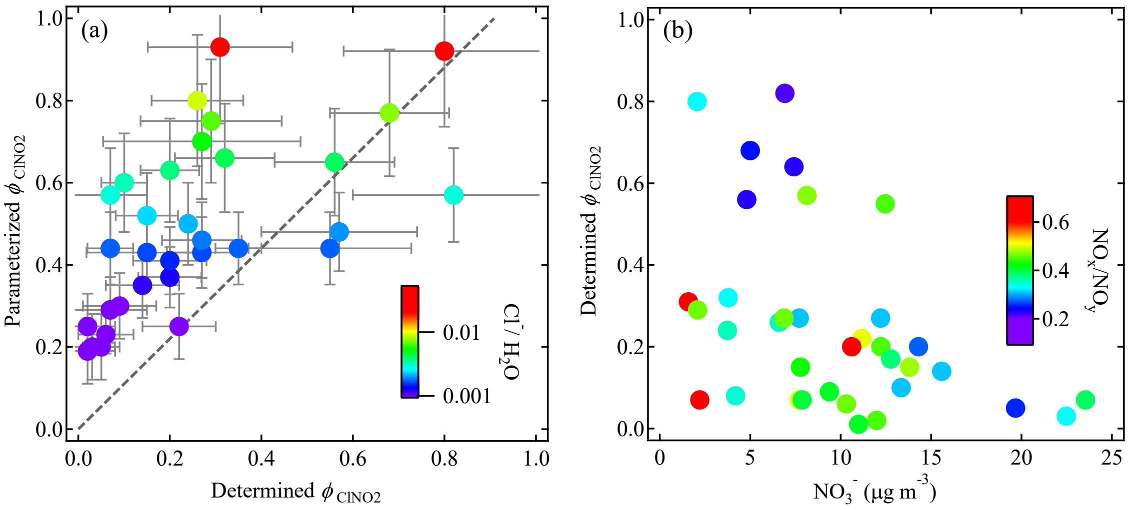


Figure 10: (a) Comparison of field-determined ϕ with that derived from parameterization (Eq. 7), and the colors of the markers represent the corresponding Cl^-/H_2O ratio; (b) relationship between field-determined ϕ and measure nitrate concentrations in aerosols, and colors of markers represent the corresponding NO_x/NO_y ratio. The error bars represent the total aggregate uncertainty as similar as Figure 8.

9. *Page 10, line 17. What does a plot of gamma vs. NO3-/H2O or Cl-/H2O look like? Especially for the nitrate effect, the dependence against the nitrate to liquid water ratio should give the most information.*

Response: We thank the reviewer for the helpful suggestions, and we further examined the relationship between the γ and the aerosol compositions. As the reviewer points out, the γ shows a positive dependence on the ratio of aerosol water to nitrate (H_2O/NO_3^-), which is consistent with the nitrate suppression effect and the observed dependence of uptake on nitrate concentration. However, there is no clear dependence of γ on the ratio of Cl^-/H_2O, which seems reasonable because of the 'cancel out' effect from both positive relationship with H_2O/NO_3^- and Cl^-/NO_3^-, broadly following the parameterization of Bertram and Thornton (2009).
For clarity, we included the relationship of γ with H_2O/NO_3^- in the revised text, and also added the plots of γ vs. H_2O/NO_3^- and Cl^-/NO_3^- in the supplementary, as follows,

"A moderate negative dependence ($r = 0.54$) of determined γ on aerosol nitrate concentration can be inferred, with lower values of γ associated with higher nitrate content (cf. Figure S2a). This pattern is consistent with the nitrate suppress effect on N_2O_5 uptake identified from previous laboratory studies (Mentel et al., 1999), and also similar to the anti-correlation of γ and nitrate from tower measurements in the USA and aircraft measurements over the UK (Wagner et al., 2013; Morgan et al., 2015). The relationship between the γ with the aerosol water to nitrate ratio also exhibits consistent trend with the previous observations and parameterizations (e.g., Bertram and Thornton, 2009; Morgan et al., 2015), with increasing uptake as the ratio increases (Figure S2b)."

References:

Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Physical Chemistry Chemical Physics, 1, 5451-5457, 1999.

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 2009.

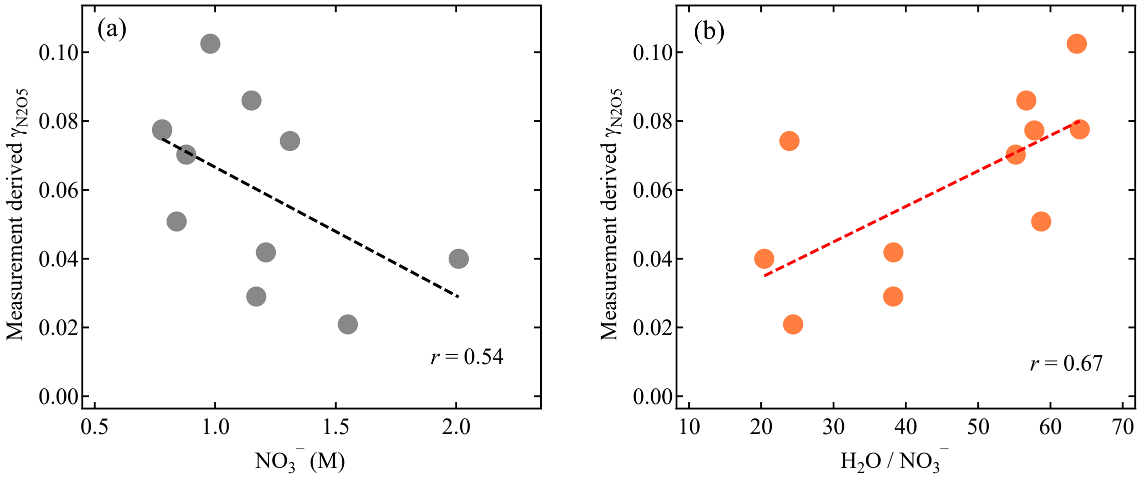


Figure S2: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol nitrate and (b) the molar ratio of aerosol water to nitrate during the study period.

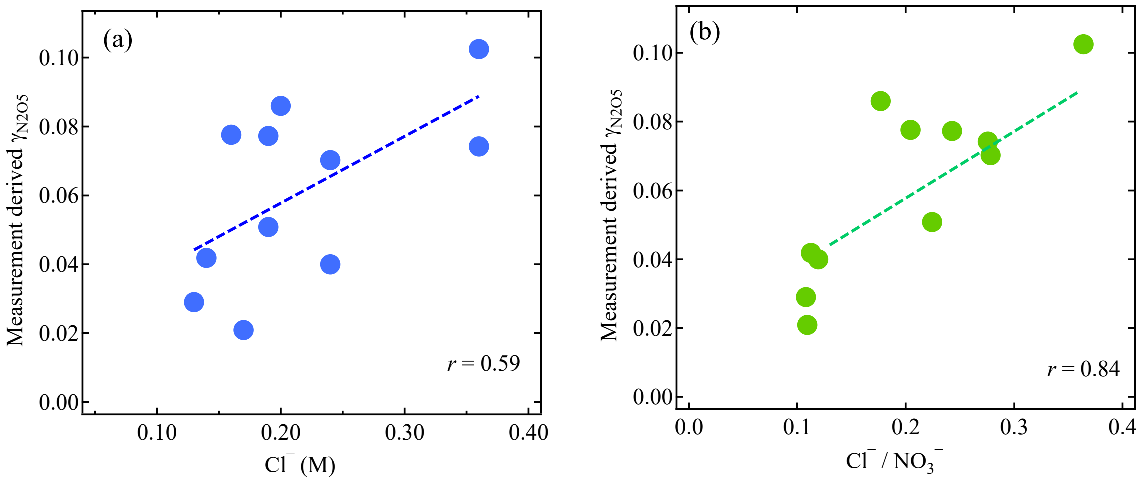


Figure S3: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol chloride and (b) the molar ratio of aerosol chloride to nitrate during the study period.

10. Page 11, equation (6). The analysis measured ClNO2 production relative to N2O5 loss. The denominator is difficult to determine with certainty, and especially if the N2O5 loss rates are too large (see concerns about aerosol surface area and NO3 loss to VOC above), the analysis will produce too small a value for phi(ClNO2). These caveats should be noted. There should be production of aerosol nitrate or nitric acid together with the N2O5 loss. Are any trends in aerosol nitrate or NOz (=NOy-NOx) during the periods of ClNO2 increase available to corroborate the analysis? This approach could be more quantitative than one based on N2O5 loss.

Response: We agree with the reviewer that the potential overestimation of N_2O_5 loss rate could result in smaller yield value for $ClNO_2$. We were aware of the possible uncertainties in the estimation, and have applied an alternative approach to derive the $ClNO_2$ yields from the ratio of observed enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- and HNO_3), according to the method suggested by Riedel et al. (2013). This approach does not need to determine the steady state N_2O_5 loss rate and requires to quantify the branching ratio of observed production of $ClNO_2$ and total nitrate. The derived ϕ values from this approach show comparable results with the original analysis, and the results from two approaches exhibit reasonable agreement with a RMA slope of 0.78 ± 0.08, with r^2 of 0.73. Most of the differences between two groups of data are within 40%. Although either approach requires assumptions and would introduce some uncertainties, the general consistency can serve as a check to corroborate the yield analysis. Given the low-resolution data of aerosol nitrate and gaseous HNO_3 in the present work that could bias the derived total nitrate enhancement, the production ratio approach will only be used as a reference to validate the reliability of the results, and further analysis will still be based on the results from the original method.

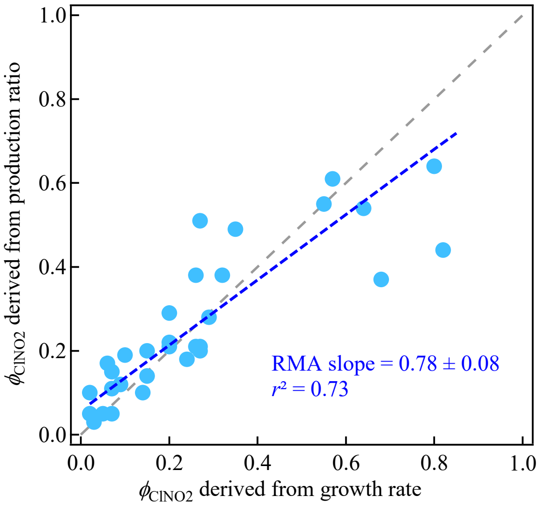


Figure S4: Comparison of estimated $ClNO_2$ yields from two different approaches: approach A using the ratio of the observed $ClNO_2$ growth rate to steady-state N_2O_5 loss rate based on Eq. 6; approach B using the production ratio of observed enhancements of $ClNO_2$ and total nitrate, $\phi = 2/(\Delta NO_3^-/\Delta ClNO_2 + 1)$ according to Riedel et al., 2013.

To make it clearer to the reader, we elaborated the assumptions for the methods and also clarified the caveat in the revised text. The above comparison figure is added in the supplementary, and the related section and discussions are revised to match the changes, as follow:

"To characterize the formation of $ClNO_2$ from rapid heterogeneous N_2O_5 uptake and sufficient particulate chloride, the yields of $ClNO_2$ (ϕ) were examined for different plumes. For regional diffuse pollution cases, the ϕ defined in R3 can be estimated from the ratio between $ClNO_2$ production rate and N_2O_5 loss rate, as the first term in below equation.

$$\phi = \frac{dClNO_2/dt}{k(N_2O_5)_{het}[N_2O_5]} = \frac{[ClNO_2]}{\int k(N_2O_5)_{het}[N_2O_5]\,dt} \qquad (6)$$

$k(N_2O_5)$ values can be determined using the inverse steady-state lifetime analysis described above in Eq. 3, and the production rate of $ClNO_2$ can be derived from the near-linear increase in $ClNO_2$

mixing ratio observed during a period, when the related species (e.g., NO_x, SO_2) and environmental variables (i.e., temperature, RH) were roughly constant. The approach here assumes that the relevant properties of the nocturnal air mass are conserved, and neglects other possible sources and sinks of $ClNO_2$ in the air mass history. For the intercepted coal-fired plumes exhibiting sharp $ClNO_2$ peaks, the observation-based estimation of $ClNO_2$ yield can be derived from the ratio of the observed $ClNO_2$ mixing ratio to the integrated N_2O_5 uptake loss over the plume age (i.e., the second term in Eq. 6). The analysis assumes that no $ClNO_2$ was present at the point of plume emission from the combustion sources and no $ClNO_2$ formation before sunset, and that the γ and ϕ within the power plant plumes did not change during the transport from the source to the measurement site. The potential variability in these quantities likely bias the estimates, but these assumptions are a necessary simplification to represent the averaged values that best describe the observations. It should be noted that the steady-state N_2O_5 loss rate is crucial in the yield estimation, which could be underestimated by potentially overestimating the loss rate in some cases with large uncertainties in N_2O_5 measurement and NO_3 reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the $ClNO_2$ yield from the ratio of enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- + HNO_3) in the cases. Given the low time resolution of nitrate data that could potentially introduce large uncertainties, this approach will only be used as a reference to validate the former analysis based on Eq. 6.

Two examples of the yield analysis are shown in Figure 9, which indicate the time periods in which $ClNO_2$ concentration increased while other parameters (such as N_2O_5, NO_x, O_3, and SO_2 concentrations) were relatively stable. The ϕ values obtained for these two cases were 0.26 and 0.05 for July 27 and August 6, respectively. Similar analyses were performed for all of other selected cases in which the $ClNO_2$ concentration increased and other relevant parameters were relatively constant for a short period, typically 1-3 h, and the obtained results were summarized in Table 2. The determined ϕ for the seven coal-fired plumes are also listed in Table 1. During the measurement period, ϕ varied from 0.02 to 0.90, with an average of 0.28 ± 0.24 and a median of 0.22. In comparison, the ϕ derived from the production ratio approach showed comparable results with an average of 0.25 ± 0.17, and the ϕ values from two different approaches match reasonably well with a Reduced Major Axis Regression (RMA) slope of 0.78 ± 0.08 and r^2 of 0.73 (cf Figure S4), which corroborates the yield analysis and indicates that the differences are within the overall uncertainty of 40%."

Fast heterogeneous N_2O_5 uptake and $ClNO_2$ production in ~~power plant~~ coal-fired plumes observed in the nocturnal residual layer over the North China Plain

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Abstract. Dinitrogen pentoxide (N_2O_5) and nitryl chloride ($ClNO_2$) are key species in nocturnal tropospheric chemistry, and have significant effects on particulate nitrate formation and the following day's photochemistry through chlorine radical production and NO_x recycling upon photolysis of $ClNO_2$. To better understand the roles of N_2O_5 and $ClNO_2$ in the high aerosol loading environment of northern China, an intensive field study was carried out at a high-altitude site (Mt. Tai, 1465 m a.s.l) in the North China Plain (NCP) during the summer of 2014. Elevated $ClNO_2$ plumes were frequently observed in the nocturnal residual layer with a maximum mixing ratio of 2.1 ppbv (1-min), whilst N_2O_5 was typically present at very low levels (<30 pptv), indicating fast heterogeneous N_2O_5 hydrolysis. Combined analyses of chemical characteristics and backward trajectories indicated that the $ClNO_2$-laden air was caused by the transport of NO_x-rich plumes from the coal-fired industry and power plants in the NCP. The heterogeneous N_2O_5 uptake coefficient (γ) and $ClNO_2$ yield (ϕ) ~~during the campaign~~were estimated from steady-state analysis and observed growth rate of $ClNO_2$. The derived γ and ϕ exhibited high variability, with means of 0.061 ± 0.025 and 0.~~27~~ 28 ± 0.24, respectively. These ~~derived~~ values are higher than those derived from previous laboratory and field studies in other regions, and cannot be well characterized by model parameterizations. Fast heterogeneous N_2O_5 reactions dominated the nocturnal NO_x loss in the residual layer over this region, and contributed to substantial nitrate formation of up to 17 $\mu g\ m^{-3}$. The ~~determined~~ estimated nocturnal nitrate formation rates ranged from 0.2 to 4.8 $\mu g\ m^{-3}\ h$~~r~~$^{-1}$ in various plumes, with a mean of 2.2 ± 1.4 $\mu g\ m^{-3}\ h^{-1}$. The results demonstrate the significance of heterogeneous N_2O_5 reactivity and chlorine activation in the NCP, and their unique and universal roles in fine aerosol formation and NO_x transformation, and thus potential impacts on regional haze pollution in northern China.

1 Introduction

Nitrogen oxides (NO_x=NO+NO_2) plays central roles in the oxidative capacity of the atmosphere and photochemical air pollution. Dinitrogen pentoxide (N_2O_5) is an important reactive intermediate in the oxidation of NO_x, and exists in rapid thermal equilibrium with nitrate radical (NO_3) formed via the reaction between NO_2 and O_3. The heterogeneous hydrolysis of N_2O_5 has been recognized as a key step in nocturnal NO_x removal, and can affect regional air quality by regulating the reactive nitrogen budget and nitrate aerosol formation (e.g., Brown et al., 2006; Abbatt et al., 2012). The heterogeneous reaction of N_2O_5 on and within atmospheric aerosols, fog or cloud droplets, produces soluble nitrate (HNO_3 or NO_3^-) and nitryl chloride ($ClNO_2$) when chloride is available in the aerosols (Finlayson-Pitts et al., 1989).

$$N_2O_5 + H_2O\ (het) \rightarrow 2HNO_3(aq) \qquad (R1)$$

$$N_2O_5 + Cl^-\ (het) \rightarrow NO_3^-(aq) + ClNO_2 \qquad (R2)$$

The rate coefficient of the heterogeneous N_2O_5 reactions is governed by the available reaction surface and N_2O_5 reaction probability (also known as the uptake coefficient γ_{N2O5}), and can be described by the following expression when the gas-phase diffusive effect is negligible.

$$k(N_2O_5)_{het} = \frac{1}{4} c_{N2O5}\, \gamma_{N2O5}\, S_a \qquad (1)$$

Here, c_{N2O5} is the mean molecular speed of N_2O_5, and S_a is the aerosol (or cloud) surface area density. The yield of $ClNO_2$ (ϕ) is defined as the amount of $ClNO_2$ formed per loss of N_2O_5, representing the fraction to $ClNO_2$ formation. Hence, the net reaction of R1 and R2 can be written as follows:

$$N_2O_5 + (H_2O \text{ or } Cl^-)(het) \rightarrow (2 - \phi)\ NO_3^-(aq) + \phi\ ClNO_2 \qquad (R3)$$

The γ_{N2O5} has been experimentally measured on various types of aerosols surfaces (including sulfate, nitrate, black carbon, organic carbon, organic coating sulfate, sea salts, and dust, etc.) in the laboratory, and different parameterizations based on aerosol composition have been proposed in varying degree of complexity (e.g., Evans and Jacob, 2005; Anttila et al., 2006; Davis et al., 2008; Bertram and Thornton, 2009; Griffiths et al., 2009; Riemer et al., 2009; Roberts et al., 2009; Simon et al., 2009; Foley et al., 2010; Chang et al., 2011; Ammann et al., 2013; Tang et al., 2014). Recently, field studies have been carried out to measure ambient N_2O_5 and to derive the γ_{N2O5} from atmospheric observations (e.g., Bertram et al., 2009b; Brown et al., 2009; Morgan et al., 2015; Brown et al., 2016; Chang et al., 2016; Phillips et al., 2016). These field-derived/measured γ_{N2O5} values were found to vary considerably, and the observed range to be significantly larger than that from laboratory studies using synthetic aerosols (Chang et al., 2011; Phillips et al., 2016). Furthermore, inconsistencies between γ_{N2O5} values derived from field measurements and parameterizations were observed in some locations, which implies that γ_{N2O5} has a complex dependence on the aerosol composition, physico-chemical characteristics, and environmental parameters (Chang et al., 2011 and references therein). Similarly, for the $ClNO_2$ yield, the field-determined values exhibited significant variability, ranging from 0.01 to close to unity (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016), which could not be well reproduced (exhibiting a tenfold difference in some cases) by parameterization based on only aerosol chloride and water content (Wagner et al., 2013; Wang et al., 2017b). There are only few studies on the ~~field~~ determination of ϕ ~~is still limited~~from field measurement, and the possible effects of real atmospheric aerosols (including organic composition, mixing state, and chloride partitioning between particle sizes, etc.) have not been well characterized (Mielke et al., 2013; Phillips et al., 2016). This incomplete understanding suggests the necessity of more field measurements of γ and ϕ in various environments, to facilitate the validation and construction of parameterizations suitable for use in air quality models.

$ClNO_2$ formed from nocturnal heterogeneous N_2O_5 uptake can potentially affect the atmospheric oxidative capacity via the production of highly reactive chlorine radicals (Cl) and the recycling of NO_x after photolysis (Simpson et al., 2015) . Elevated $ClNO_2$ mixing ratios were firstly observed in several polluted coast regions (for instance, the coasts of Texas and California, and the Los Angeles Basin), resulting from the strong emission of NO_x and abundant chloride from sea salt aerosols (Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013; Tham et al., 2014). Recently, significant $ClNO_2$ production was also observed in some inland areas (such as Colorado, Hessen, and ~~Canada~~Alberta), with mixing ratio up to several hundreds of pptv or even exceeding 1.0 ppbv (e.g., Thornton et al., 2010; Mielke et al., 2011; Phillips et al., 2012; Riedel et al., 2013; Faxon et al., 2015; Mielke et al., 2016). Anthropogenic sources of chlorine including coal combustion in power plants, industries, and biomass burning may potentially facilitate $ClNO_2$ production (Riedel et al., 2013). The highest $ClNO_2$ mixing ratio yet reported (4.7 ± 0.8 ppbv, 1-min average) was recently observed in the regional plumes at a mountaintop site in southern China, indicating the importance of N_2O_5/$ClNO_2$ chemistry in polluted environments (Wang et al., 2016).

Large anthropogenic emissions of NO_x and increasing O_3 concentrations have been reported in many urban cluster regions in China (Wang et al., 2006; Wang et al., 2017a). Hence, in these regions, nocturnal nitrogen chemistry may be particularly important in the transformation of NO_x and the subsequent effects on daytime photochemistry and secondary aerosol formation. In the areas downwind of Beijing and Shanghai, high concentrations of particulate nitrate (up to 40 $\mu g\ m^{3}$) have been observed and attributed to heterogeneous N_2O_5 uptake on acidic aerosols (Pathak et al., 2009; Pathak et al., 2011). During a more recent field study in a rural site in the North China Plain (NCP), elevated fine nitrate concentrations were observed at night and in the early morning, with hourly maxima of up to 87.2 $\mu g\ m^{3}$ and a 30% contribution to $PM_{2.5}$, which was mainly attributed to the heterogeneous hydrolysis of N_2O_5 (Wen et al., 2015). Active heterogeneous N_2O_5 chemistry has been recently characterized in both rural and urban areas of the NCP via direct measurements of N_2O_5 and $ClNO_2$. Rapid heterogeneous N_2O_5 loss and efficient $ClNO_2$ production were observed, with a maximum $ClNO_2$ mixing ratio of 2.07 ppbv at Wangdu and 0.77 ppbv at Jinan (Tham et al., 2016; Wang et al., 2017b). Moreover, sustained $ClNO_2$ peaks were observed after sunrise in the region, and the downward mixing of $ClNO_2$-rich air in the residual layer was proposed to be the cause of morning peaks (Tham et al., 2016). To confirm these findings and better characterize the chemistry of N_2O_5/$ClNO_2$ and their impacts on regional air quality, it is of great interest to conduct direct field measurements of N_2O_5/$ClNO_2$ in the polluted residual layer.

In the present study, we measured the concentrations of N_2O_5, $ClNO_2$, and related species at a mountaintop site in the NCP during the summer of 2014, and characterized the nighttime nitrogen chemistry within the residual layer over a polluted region of northern China. We examined the frequently intercepted $ClNO_2$-rich plumes at this high elevation site, and investigated nocturnal N_2O_5 reactivity to determine the heterogeneous N_2O_5 uptake coefficients and $ClNO_2$ yields in a variety of air masses, which were also compared to parameterizations utilized in existing models. The effects of heterogeneous N_2O_5 chemistry on particulate nitrate formation and nocturnal NO_x loss were then evaluated based on the observation data.

2. Methodology

2.1 Field Study Site

The measurement site was located on Mount Tai (36.25°N, 117.10°E, 1465 m above sea level) in Shandong Province, China. Mt. Tai is located between the two most developed regions in China (Jing-Jin-Ji and the Yangtze River Delta), and its peak (1545 m a.s.l.) is the highest point within the NCP. Figure 1 shows the location of the measurement site in relation to the surrounding topography. Mt. Tai is 230 km away from the Bohai and Yellow Seas, and~~T~~ the cities of Tai'an and Jinan (the capital of Shandong Province) are located 15 km south and 60 km north of the measurement site, respectively. The altitude of the measurement site is near the top of the boundary layer in the daytime during the summer, and is typically in the residual layer or, occasionally, in the free troposphere at night. This mountaintop site has been previously used in many atmospheric chemistry field studies (e.g., Gao et al., 2005; Wang et al., 2011; Guo et al., 2012; Sun et al., 2016). Previous studies at this site indicated that the site is regionally representative without significant local anthropogenic emissions, and affected by the regional aged air masses and occasional combustion plumes from fossil fuel or biomass in the region (e.g., Zhou et al., 2009; Wang et al., 2011, Guo et al., 2012). ~~Although Mt. Tai is a popular location for tourists, the measurement site is located in an area that is not frequently visited and therefore, should not be significantly affected by local anthropogenic emissions~~ ~~.~~ Intensive measurements were performed from July 24 to August 27, 2014. During this period, the prevailing winds originated from the northeast and northwest. Shandong province is the largest producer of thermal power in China, ~~therefore,~~ and dozens of coal-fired industry and power plants are situated within a radius of 200 km from the mountain site.

2.2 Instrumentation

N_2O_5 and $ClNO_2$ were measured concurrently using iodide ~~quadrupole~~ ion chemical ionization mass spectrometry (CIMS) with a quadrupole mass spectrometer (THS Instruments Inc., USA). The principle and detailed calibration of this CIMS system have been described previously by Wang et al. (2016) and Tham et al. (2016). The same configuration was used in the present study. Briefly, N_2O_5 and $ClNO_2$ were detected as $I(N_2O_5)^-$ and $I(ClNO_2)^-$ clusters via reaction with iodide ions (I^-), which were generated from a mixture of CH_3I (0.3% v/v) and N_2 using an alpha radioactive source, ^{210}Po (NRD, P-2031-2000). The inlet was installed ~ 1.5 m above the roof of a single-story building, and the sampling line was a 5.5 m PFA-Teflon tubing (1/4 in. o.d.) which was replaced daily in the afternoon before sunset and washed in the ultrasonic bath to minimize wall loss caused by deposited particles (Wang et al., 2016). A small proportion (1.7 SLPM) of total sampling flow (~ 11 SLPM) was diverted to the CIMS system, to reduce the residence time of the air samples in the sampling line. A standard addition of N_2O_5 into the ambient inlet was performed before and after the tubing replacement to monitor the transmission efficiency, and this practice limited the loss of N_2O_5 in the inlet to <10% in the ‘clean’ tubing and about 30% in the next afternoon. Manual calibrations of N_2O_5 and $ClNO_2$ were conducted daily to ~~monitor~~ determine the instrument sensitivity, ~~and background.~~the average of which during the observation period was 2.0 ± 0.6 for N_2O_5 and 2.2 ± 0.6 Hz $pptv^{-1}$ for $ClNO_2$, respectively. The N_2O_5 standard was synthesized on-line from the reaction between NO_2 and O_3, and the produced N_2O_5 were determined from the decrease in NO_2 (Wang et al., 2014). This method has been validated with a Cavity Ring Down Spectrometer (CRDS) measurement in previous campaign (Wang et al., 2016). ~~and t~~The $ClNO_2$ was produced by passing a known concentration of N_2O_5 through a NaCl slurry assuming unity conversion efficiency (Roberts et al., 2009) and negligible $ClNO_2$ loss in the system (Wang et al., 2016). The field background was determined by passing the ambient sample through a filter packed with activated carbon, with average levels of 7.8 ± 1.9 and 6.0 ± 1.6 Hz for N_2O_5 and $ClNO_2$, respectively. The reported concentrations were derived by subtracting the background levels. The detection limit was 4 pptv for both N_2O_5 and $ClNO_2$ (2σ, 1 min-averaged data~~).~~), and the uncertainty of the nighttime measurement was estimated to be ± 25% (Tham et al., 2016).

The related trace gases and aerosol compositions were also measured concurrently during the campaign. All of the instruments were used in our previous field studies, and the setup, precision, and accuracies of these instruments were described previously (Wen et al., 2015; Tham et al., 2016; Wang et al., 2016; Wang et al., 2017b). Briefly, NO and NO_2 were measured using a chemiluminescence analyzer equipped with a blue-light converter (TEI, Model 42I-TL). Total gaseous reactive nitrogen (NO_y) was determined using a chemiluminescence analyzer with an external molybdenum oxide (MoO) catalytic converter (TEI, Model 42CY) with an inlet filter. The NO_y described here is different from that in previous reports (Tham et al., 2016; Wang et al., 2016), because that the particulate nitrate was not included but removed by the filter in the present study. O_3, SO_2, and CO were measured using the ultraviolet photometry, pulsed-UV fluorescence, and IR photometry techniques (TEI, Model 49I, 43C and 48C), respectively. Zero and span calibrations for trace gases were performed weekly during the campaign. Water-soluble ionic compositions of $PM_{2.5}$ (including NH_4^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and NO_3^-) were measured hourly by a Monitor for Aerosols and Gases (MARGA ADI 2080, Applikon-ECN) using on-line ion chromatography.

The particle number and size distribution (5 nm to 10 μm) were measured using a Wide-Range Particle Spectrometer (WPS, Model 1000XP, MSP Corporation, USA). The particle diameters were corrected for particle hygroscopicity to determine the actual ambient aerosol surface density, and the wet diameters were calculated using growth factors from a size-resolved kappa-Köhler function obtained in a rural site in the NCP (Ma et al., 2016; Tham et al., 2016). The uncertainties associated with the aerosol surface area determination was estimated to be around 30% (Liu et al., 2010; Tham et al., 2016). Meteorological data, including temperature, relative humidity (RH), wind vectors and photolysis frequency of NO_2 (J_{NO2}) were measured by an automated meteorological station (JZYG, PC-4) and a filter radiometer (Metcon, Germany). In addition, a Lagrangian particle dispersion model, Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998; Wang et al., 2016), driven by high spatial and temporal meteorological fields from the WRF model, was used to investigate potential source regions of the air masses intercepted at the measurement site. The HYSPLIT model was run 12-h backward with 2500 particles released at the measurement site. Detailed parameterization and setup of the HYSPLIT and WRF models were previously described by Wang et al. (2016) and Tham et al. (2016).

3. Results and Discussion

3.1 Overview of N_2O_5 and $ClNO_2$ measurement

The temporal variations of $ClNO_2$, N_2O_5, related trace gases, aerosol properties, and selected meteorological parameters during the field study at Mt. Tai are depicted in Figure 2. Overall, the observed mixing ratios of $ClNO_2$ were higher than those of N_2O_5, and exhibited significant variations. The average mixing ratios of N_2O_5 and $ClNO_2$ were 6.8 ± 7.7 pptv and 54 ± 106 pptv, respectively. The maximum mixing ratio of N_2O_5 (167 pptv) was observed at 21:00 on August 26, 2014, and most of the other nights during the observation period exhibited peak N_2O_5 mixing ratios below 30 pptv. The average nighttime mixing ratios of O_3 and NO_2 were 77 and 3.0 ppbv, respectively, with an average nitrate radical production rate $p(NO_3)$ of 0.45 ± 0.40 ppb h^{-1}, which is indicative of potentially active NO_3 and N_2O_5 chemistry during the study period. However, the low N_2O_5 mixing ratios observed during most of the nights suggest a rapid loss of N_2O_5, ~~via either heterogeneous uptake or via NO_3 loss.~~ which is consistent with the observed high aerosol surface area (S_a), varied from ~100 to 7800 $\mu m^2\ cm^{-3}$ with a mean value of 1440 $\mu m^2\ cm^{-3}$. The higher RH during nighttime and the frequent occurrence of clouds at the mountaintop site could also account for low N_2O_5 concentrations, because of its rapid heterogeneous loss on cloud droplets.

The highest $ClNO_2$ mixing ratio of 2065 pptv was observed on August 8, 2014, and on 8 of the 35 nights the peak $ClNO_2$ mixing ratios were higher than 500 pptv. The simultaneous increases of SO_2, NO_x and CO with these $ClNO_2$ peaks suggest these air masses originated from coal combustion sources, such as industry and power plants, which will be further discussed in the next section. The elevated $ClNO_2$ levels observed at Mt. Tai are similar to recent measurements at a surface rural site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016), but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world. During the campaign at Mt. Tai, the average concentrations of aerosol sulfate and nitrate were 14.8 ± 9.0 and 6.0 ± 4.7 $\mu g\ m^{-3}$, accounting for 29.5% and 12.0% of $PM_{2.5}$ mass, respectively. The aerosol organic-to-sulfate ratio, a parameter that potentially affects the uptake process (Bertram et al., 2009b), was 0.74 on average and much lower than those from studies mentioned above in Europe and US. Moreover, the nighttime averaged Cl^- concentration was 0.89 ± 0.86 $\mu g\ cm^{-3}$, and was an order of magnitude higher than Na^+, indicating abundant non-oceanic sources of chloride (e.g., from coal combustion and biomass burning in the NCP) (Tham et al., 2016), which could enhance the production of $ClNO_2$.

The mean diurnal variations of N_2O_5, $ClNO_2$, and other relevant chemical species during the study period are shown in Figure 3. Ozone exhibited a typical diurnal pattern for a polluted mountaintop site (Sun et al., 2016), and it began to increase in the late morning and reached an afternoon peak of 88.6 (± 16.6) ppbv with a daily average rise of 24.4 ppbv. The average O_3 kept at elevated levels after sunset and did not begin to decrease until 22:00, and NO_x exhibited a diel maximum of 6.1 ppbv before sunset, resulting in a peak in $p(NO_3)$ just before sunset and relatively high levels in the early night. Gaseous NO_y reached a maximum of 16.4 (± 6.1) ppbv in the morning, and remained stable at a high level during the daytime; the air masses were more aged during the daytime, as indicated by the persistent low NO_x/NO_y ratios (0.2-0.25). Small N_2O_5 peaks were observed immediately after sunset, resulting from the abundant O_3 and NO_2, and was present at low levels near to the detection limit of the CIMS throughout the rest of the night. $ClNO_2$ exhibited clear nighttime elevations resulting from the heterogeneous production after sunset, and reached a diel maximum around midnight. The low N_2O_5 and high $ClNO_2$ concentrations observed at Mt. Tai are similar to the measurement at a rural surface site within the NCP (Tham et al., 2016), suggesting rapid heterogeneous loss of N_2O_5 and production of $ClNO_2$ in this region.

It was also noted that a small N_2O_5 peak (~10 pptv) with larger variability was present in the early afternoon. A simplified photostationary analysis following Brown et al. (2005; 2016) was performed to predict the daytime steady-state N_2O_5 concentrations for the few cases with daytime peaks. The predicted concentrations all showed increasing trends in the afternoon, similar to the observation pattern. However, for individual cases, the absolute values around 15:00 were much lower than observation under clean sky condition, but of the same magnitude as the observation for reduced photolysis and foggy conditions with higher NO_3 production rate (c.f. Figure S1 in the supplement). Daytime N_2O_5 signals with few pptv have also been observed by a CRDS at a mountain site in southern China (Brown et al., 2016), where the concentrations were in accord with steady state estimation in an average sense. Because daily maintenance and calibrations of the CIMS were usually performed during early afternoon periods, the limited daytime data in the present study was not sufficient to make clear whether there were any daytime interferences or sensitivity fluctuations. Thus additional studies are needed to validate the daytime phenomenon and examine the potential reasons, and the following analysis in the present work will mostly focus on nocturnal process.

3.2 High $ClNO_2$ plumes from ~~power plants~~coal-fired point sources

As described above, several plumes with elevated $ClNO_2$ concentrations (> 500 pptv) were observed during the measurement period. Figure 4a illustrates the high $ClNO_2$ case observed during the night of July 30-31, 2014. The $ClNO_2$ concentration peaked sharply at 1265 pptv, which was accompanied by a steep rise in the concentrations of SO_2, NO_x and CO~~ and NO_x, indicating the combustion origin of this plume from power plants~~. The SO_2/NO_y ratio increased from ~0.1 to 0.6 in the plume center, with a $\Delta SO_2/\Delta NO_y$ slope of 0.57, indicating the coal combustion source of the plume. The coincident increase in CO/NO_y ratio from ~30 to 90 suggests that it was likely originated from coal-fired industry facilities, such as cement and steel production plants, which is the largest emitting sector of CO in north China (Streets et al., 2006; Zhang et al., 2009). The 12-h backward particle dispersion trajectories calculated from the HYSPLIT model revealed that the air masses mostly moved slowly from the west, and passed over the region with ~~two large~~cement and steel production industry and power plants before arriving at the measurement site. Figure 5a shows the highest $ClNO_2$ case (2065 ppbv) observed on the night of August 8,

2014. The simultaneous increases in SO_2, ~~CO, and~~ NO_x and CO concentrations, together with the higher SO_2/NO_y ratio (~0.5) comparing to that outside of plume (~0.1) and the campaign average (0.24), again indicate the coal combustion origin of the plume. The relatively lower CO/NO_y ratio of ~50 possibly suggests the plume affected by power plant emission, as shown by the derived backward particle dispersion trajectories~~, again indicate that the air masses originated from the power plants to the west of Mt. Tai~~. Table 1 summarizes the chemical characteristics of the eight cases of high-$ClNO_2$ ~~power plant~~ coal-fired plumes during the study period. In these cases, the average SO_2 mixing ratios ranged from 2.3 to 18.7 ppbv, and the maximum $ClNO_2$ and N_2O_5 mixing ratios ranged from 534 to 2065 ppbv and 7.3 to 40.1 ppbv, respectively, with corresponding $ClNO_2/N_2O_5$ ratios of 25 to 118. The mixing ratios for O_3 and NO_2 ranged from 60 to 106 ppbv and 2.8 to 11.8 ppbv, respectively, resulting in high $p(NO_3)$ values of 0.60 to 1.59 ppbv h^{-1}. The aerosol chloride concentration ranged from 1.01 to 2.34 μg cm^{-3}, which was higher than the nighttime average (0.89 μg cm^{-3}) and conducive to $ClNO_2$ production from R3.

NO_x emissions from the coal combustion sources ~~such as power plants~~ contain abundant NO, which is oxidized rapidly to NO_2 by ambient O_3. Thus, the anti-correlation between O_3 and NO_2 within the observed plumes (cf. Figure 4b and 5b) can be another indicator of the large combustion sources (such as coal-fired power or industry plants). Furthermore, the slope of a plot of O_3 vs. NO_2 for nighttime plumes can be considered as an approximate measure of the plume age, with the assumption of pseudo-first-order kinetics and when the input of NO_x is small comparing to the excess O_3 (Brown et al., 2006). The estimated plume age can be determined as follows:

$$t_{plumes} \approx \ln(1 - S(m+1))/(Sk\overline{O_3}) \qquad (2)$$

where m is the derived slope, k is the rate coefficient for the reaction of NO_2 with O_3, $\bar{O}_3$ is the average O_3 concentration in the plume, and S is a stoichiometric factor that varies between 1 for dominant NO_3 loss and 2 for dominant N_2O_5 loss (Brown et al., 2006). In the present study, heterogeneous N_2O_5 uptake dominated the reactive nitrogen loss, therefore $S = 2$ was used in the calculation. The plume ages for the July 30-31 and August 8 cases were calculated to be 3.2 and 2.1 h, respectively, which are consistent with the moderate NO_x/NO_y ratios of 0.4-0.5, and comparable to those observed in nocturnal power plant plumes in the eastern coast of the USA (Brown et al., 2006; Brown et al., 2007). The slopes of O_3 vs. NO_2 in Figure 4b and 5b steeper than -1.0 also indicate the further reactions of NO_2 with O_3, which favor the formation of NO_3 and N_2O_5. However, the N_2O_5 concentrations only showed a slight increase (Figure 4 case) or no apparent change (Figure 5 case), in contrast to the significant increases in $ClNO_2$ and high $p(NO_3)$ values, which suggests rapid heterogeneous loss of N_2O_5 and significant $ClNO_2$ production during transport of these plumes from their sources.

The elevated $ClNO_2$ concentrations in ~~power plant~~the coal-fired plumes here are comparable to previous observation of power plant plumes via tower measurements in Colorado (Riedel et al., 2013) and at a mountain site in southern China (Wang et al., 2016), but the observed N_2O_5 within the plumes are significantly lower than those in other ~~power plant~~ coal-fired plumes observed via aircraft, tower, and at mountain sites (Brown et al., 2007; Riedel et al., 2013; Brown et al., 2016). The previous measurement at a surface site in the NCP has observed sustained $ClNO_2$ peaks after sunrise, which was proposed to be the cause of the downward mixing of $ClNO_2$-rich air (estimated values of 1.7-4.0 ppbv) in the residual layer (Tham et al., 2016). In the present study, the frequent intercepts of ~~power plant~~ coal-fired plumes with elevated $ClNO_2$ concentrations at Mt. Tai, which ~~were~~ was typically above the nocturnal boundary layer, affirm this hypothesis and provide direct evidence that significant $ClNO_2$ production occurred in the residual layer from the abundant nocturnal NO_x, chloride and background O_3 over the NCP. The similar $ClNO_2$-laden air frequently observed at high-elevation sites in northern and southern China suggest ubiquitous $ClNO_2$ in the polluted residual layer and its importance in the daytime production of ozone in China (Tham et al., 2016; Wang et al., 2016). Moreover, the concurrent nitrate production from heterogeneous N_2O_5 reactions (cf. R3) may also contribute to the formation of haze pollution in these regions.

3.3 N_2O_5 reactivity and heterogeneous uptake coefficient

3.3.1 Reactivity of N_2O_5 and NO_3

The mixing ratios of N_2O_5 depend on the nitrate radical production rate and the reactivity of N_2O_5 and NO_3, including the individual loss rates for N_2O_5 or NO_3 that contribute to the removal of the pair. N_2O_5 reactivity can be assessed using the inverse N_2O_5 steady state lifetime, which is the ratio of $p(NO_3)$ to the observed N_2O_5 mixing ratios (e.g., Brown et al., 2006; Brown et al., 2009; Brown et al., 2016):

$$\tau(N_2O_5)^{-1} = \frac{p(NO_3)}{[N_2O_5]} \approx \frac{k(NO_3)}{K_{eq}[NO_2]} + k(N_2O_5)_{het} \qquad (3)$$

The steady state inverse lifetime of N_2O_5, $\tau(N_2O_5)^{-1}$, is the sum of the N_2O_5 loss rate via heterogeneous loss ($k(N_2O_5)_{het}$) and NO_3 reactions with VOCs ($k(NO_3)$) with a ratio of $K_{eq}[NO_2]$. K_{eq} is the temperature-dependent N_2O_5-NO_3 equilibrium coefficient. High N_2O_5 reactivity was observed in the present study, with average nighttime $\tau(N_2O_5)^{-1}$ of 1.41×10^{-2} s^{-1} before midnight and 1.30×10^{-2} s^{-1} after midnight, corresponding to a nighttime N_2O_5 lifetime of 1.2-1.3 min. This rapid N_2O_5 loss rate is comparable to the results from surface measurements in both urban and rural sites in the NCP (Tham et al., 2016; Wang et al., 2017b). However, this loss rate is significantly higher than those determined from a mountain site in southern China (Brown et al., 2016) and tower and aircraft measurements in the USA (e.g., Brown et al., 2009; Wagner et al., 2013).

The NO_3 reactivity, or loss rate coefficient $k(NO_3)$, can be estimated from the sum of the products of measured VOC concentrations and the bimolecular rate coefficients for the corresponding NO_3-VOC reactions (Atkinson and Arey, 2003):

$$k(NO_3) = k_{NO+NO3}[NO] + \sum_i k_i\,[VOC_i] \qquad (4)$$

Because of the lack of concurrent VOCs measurements in the present study, we used the average VOC speciations measured before sunrise and in the evening at Mt. Tai during our previous study in 2007 (c.f. Table S1) to estimate $k(NO_3)$. The determined nighttime $k(NO_3)$ was 1.33×10^{-2} s^{-1} for the first half of the night and 1.07×10^{-2} s^{-1} for the period after midnight, which is equivalent to an NO_3 lifetime of approximately 1.5 min. The estimated $k(NO_3)$ could be considered as an upper limit for coal-fired plumes because of potential lower biogenic VOC levels within the plumes. The estimation here does not account for the VOC changes between years and the night to night variability, which may result in uncertainties. The $k(NO_3)$ derived by another approach, i.e., from the nighttime steady state fits, provides a consistency check and evaluation of the errors, as described below.

The heterogeneous loss rate, $k(N_2O_5)_{het}$, can be obtained by subtracting the $k(NO_3)/K_{eq}[NO_2]$ from the determined $\tau(N_2O_5)^{-1}$ in Eq.3. Figure 6a shows the averaged total N_2O_5 reactivity and fractions of N_2O_5 loss via NO_3 ($k(NO_3)/K_{eq}[NO_2]$) and heterogeneous N_2O_5 loss during the study period. As shown, the heterogeneous loss was dominant, accounting for 70-80% ~~80% and 71%~~ of total N_2O_5 reactivity with higher fraction before ~~and after~~ midnight~~, respectively~~. Figure 6b shows the contribution of different VOC categories to the average first-order NO_3 loss rate coefficients, $k(NO_3)$. Biogenic monoterpenes accounted for more than half of the NO_3 reactivity, followed by anthropogenic alkenes (such as butene), isoprene and dimethyl sulfide (DMS). Aromatics and alkanes made small contributions (<1%) to the total NO_3 reactivity. Although some unmeasured organic species (e.g, peroxy radicals) could also contribute to a small fraction of NO_3 loss (Brown et al., 2011; Edwards et al., 2017), ~~T~~the dominant ~~contribution to~~ NO_3 reactivity~~-~~ by~~from~~ biogenic VOCs is similar to that observed ~~from~~ at a mountain site in southern China (Brown et al., 2016) and aircraft measurement in residual layer in southeast US (Edwards, et al., 2017), ~~but the absolute value of NO_3 reactivity and~~ whereas the anthropogenic contribution ~~are~~ is much higher in the present study. The estimated NO_3 activity is slightly lower than that obtained from surface site measurements in the NCP (Tham et al., 2016; Wang et al., 2017b), which is in line with the higher abundances of VOCs in the polluted boundary layer.

3.3.2 N_2O_5 uptake coefficient

Because the N_2O_5 uptake coefficient γ is related to the first-order loss rate coefficient of N_2O_5, $k(N_2O_5)_{het}$ (Eq. (1)), then the Eq. (3) can be expressed as follows:

$$\tau(N_2O_5)^{-1} K_{eq}[NO_2] \approx k(NO_3) + \frac{1}{4} c_{N2O5} S_a K_{eq}[NO_2]\gamma(N_2O_5) \qquad (5)$$

The linear relationship between the left-hand side of Eq. (5) and $1/4c_{N2O5}S_aK_{eq}[NO_2]$ will give the N_2O_5 uptake coefficient γ as the slope, and the NO_3 loss rate coefficient $k(NO_3)$ as the intercept (Brown et al., 2009). We selected data for periods in which $d[N_2O_5]/dt$ is close to zero and the lifetime is relatively stable, which best corresponds to steady-state conditions. Figure 7 shows two examples of $\tau(N_2O_5)^{-1}K_{eq}[NO_2]$ versus $1/4c_{N2O5}S_aK_{eq}[NO_2]$ for cases observed on the nights of August 2 and 21, 2014. The γ and $k(NO_3)$ values derived from the linear fits are $\gamma = 0.040$ and $k(NO_3) = 0.025\ s^{-1}$ for August 2 case and $\gamma = 0.078$ and $k(NO_3) = 0.011\ s^{-1}$ for August 21 case. Similar analyses were performed for 11 additional cases during the campaign, and the derived results are summarized in Table 2. The determined γ values range from 0.021 to 0.102, with a mean value of 0.061 ± 0.025. The average $k(NO_3)$ derived from the steady state fits is $0.015 \pm 0.010\ s^{-1}$, which is comparable to that predicted from the VOC ~~measurements~~ concentrations described above, indicating that the estimated results in the present study are reliable and likely representative of averaged conditions in the region. The agreement between these two methods also corroborates the determination of the uptake coefficient from steady state analysis. The estimated uncertainty in each individual determination varied from 35 to 100%, including statistical errors and uncertainty associated with measurements of gaseous and aerosol species (Tham et al., 2016).

Compared with the previous field-determined N_2O_5 uptake coefficients (0.002-0.04) from aircraft, tower, and mountaintop measurements in the USA and southern China (e.g., Brown et al., 2006; Morgan et al., 2015; Brown et al., 2016), the observed γ values in the present study are significantly higher. The large variability of γ at Mt. Tai is similar to that observed at a rural high-elevation site in Germany and a tower measurement in Colorado, with γ ranging from 10^{-3} to 0.11~~obtained from other ambient measurement derivations~~ (Wagner et al., 2013; Phillips et al., 2016). The overall higher averaged γ value at Mt Tai is likely associate with the high RH and aerosol composition with high sulfate but low organic fractions, the condition of which favors more efficient N_2O_5 uptake (Brown et al., 2006; Wagner et al., 2013; Phillips et al., 2016). A recent laboratory study has reported high γ (> 0.05) of isotope-labeled N_2O_5 into aqueous nitrate-containing aerosols and largely enhancement of uptake at higher RH conditions (Gržinić et al., 2016), which help rationalize our field results with larger uptake coefficient than many previous studies. Moreover, a measurement at an urban surface site in Jinan close to Mt. Tai gave similarly high values of γ (0.042-0.092) (Wang et al., 2017b). This may suggest a unique feature of the reactive nitrogen chemistry with rapid heterogeneous N_2O_5 loss over this region, and is consistent with the observed low N_2O_5 levels but relatively high $ClNO_2$ and particulate nitrate produced from the heterogeneous reactions.

Previous laboratory studies have investigated the dependence of γ on aerosol compositions, and have developed mechanistic parameterizations of γ that can be employed in air quality models (Chang et al., 2011 and references therein). A commonly used parameterization was proposed by Bertram and Thornton (2009) and considered the aerosol volume-to-surface ratio (*V*/*S*), concentrations of nitrate, chloride, and water. For comparison, γ values were calculated using this parameterization based on the measured aerosol composition and molarity of water determined from the thermodynamic model with inputs of NH_4^+, Na^+, SO_4^{2-}, NO_3^- and Cl^- (E-AIM model IV, ~~(~~http://www.aim.env.uea.ac.uk~~-~~/aim/model4/model4a.php) (Wexler and Clegg, 2002). An error estimation showed that a 3% change in RH implies an uncertainty in the particle liquid water content of ~5%. In the calculation, mean values of *V*/*S* (64.8 - 77.2 nm) measured in the present study instead of empirical pre-factor *A* were used, and the reaction rate coefficients were employed as the empirical values suggested by Bertram and Thornton (2009).

Figure 8 shows a comparison of the γ values (with total uncertainty) determined from parameterization and measurements. Overall, the parameterized γ shows good correlation ($r = 0.87$) with the observation determined values, and gives an average of 0.063 ± 0.006, which is in good agreement with the average of 0.061 ± 0.025 derived from steady state analysis. However, the γ values from BT-parameterization are in the range of 0.052-0.070, with much lower variability than the measurement determined values. Similar results with compatible averaged γ values between measurements and parameterization predictions but higher variability for measurement derived γ have been reported at a mountain measurement in Germany (Phillips et al., 2016). A distinct difference of γ between the steady-state analysis and the parameterization has also been reported by Chang et al., (2016), who suggested that the uncertainty in determining aerosol water content would introduce errors in the parameterization. Bertram and Thornton (2009) suggested that predicted γ values would plateau and be independent of particulate chemical composition at particle water molarity above 15M. In the present study, the particle water molarity in these cases was consistently above 25 M because of the high RH and frequent cloud cover at the mountain site, which may explain the lower variability of γ values predicted by parameterization.

A moderate negative dependence (r = 0.~~50~~54) of determined γ on aerosol nitrate concentration can be inferred, with lower values of γ associated with higher nitrate content (cf. Figure ~~S1~~S2a). This pattern is consistent with the nitrate suppress effect on N_2O_5 uptake identified from previous laboratory studies (Mentel et al., 1999), and also similar to~~consistent with~~ the anti-correlation of γ and nitrate from tower measurements in the USA and aircraft measurements over the UK (Wagner et al., 2013; Morgan et al., 2015).~~,~~ The relationship between the γ with the aerosol water to nitrate ratio also exhibits consistent trend with the previous observations and parameterizations (e.g., Bertram and Thornton, 2009; Morgan et al., 2015), with increasing uptake as the ratio increases (Figure S2b).

~~and consistent with most of the parameterizations reviewed by Chang et al. (2011). Nevertheless, the moderate correlation observed here may result from the complicated relationship between nitrate and N_2O_5 uptake. Under certain conditions, nitrate can suppress the N_2O_5 uptake (Bertram and Thornton, 2009); but meanwhile, particulate nitrate is a product of N_2O_5 hydrolysis, and thus efficient uptake may be accompanied by higher nitrate concentrations (Phillips et al., 2016). It is very difficult to differentiate nitrate produced in situ from preexisting nitrate; therefore, covariation and suppression effects may disguise the relationship between γ and nitrate.~~

Furthermore, as suggested by Bertram and Thornton (2009), the presence of chloride can offset the suppression of N_2O_5 uptake by nitrate. The determined γ in the present study also show positive dependence on aerosol chloride concentration (r = 0.~~61~~59), indicating the enhancement of N_2O_5 uptake by increased chloride contents in aerosols. This can be better described by the clear positive dependence (r = 0.84) of γ on the molar ratio of particulate chloride to nitrate, as illustrated by the color-coded data in Figure 8 and Figure S3b. The variation in γ values determined in the present study appears to be controlled largely by the particulate chloride-to-nitrate ratio, broadly following the competing effects of nitrate and chloride in the parameterization (Bertram and Thornton, 2009; Ryder et al., 2014). However, the discrepancy between the measurement- and parameterization-derived values may imply that some mechanisms and factors affecting γ under conditions of high humid and pollution (e.g., reacto-diffusive length, salting effects, etc.) (Gaston and Thornton, 2016; Gržinić et al., 2016) should be further explicitly considered in the parameterization. The in situ γ_{N2O5} measurement technique developed by Bertram et al. (2009a) may be useful in directly investigating the complex dependence of γ on different factors in a range of environments.

3.4 $ClNO_2$ production yield

To characterize the formation of $ClNO_2$ from rapid heterogeneous N_2O_5 uptake and sufficient particulate chloride, the yields of $ClNO_2$ (ϕ) were examined for different plumes. For regional diffuse pollution cases, ~~T~~the ϕ defined in R3 can be estimated from the ratio between $ClNO_2$ production rate and N_2O_5 loss rate, as the first term in below equation~~:~~.

$$\phi = \cancel{\frac{\Delta ClNO_2}{\Delta N_2O_5}} \cancel{=} \cancel{\frac{dClNO_2/dt}{dN_2O_5/dt}} \cancel{=} \frac{dClNO_2/dt}{k(N_2O_5)_{het}[N_2O_5]} = \frac{[ClNO_2]}{\int k(N_2O_5)_{het}[N_2O_5]\,dt} \quad (6)$$

$k(N_2O_5)$ values can be determined using the inverse steady-state lifetime analysis described above in Eq. 3, and the production rate of $ClNO_2$ can be derived from the near-linear increase in $ClNO_2$ mixing ratio observed during a period, ~~of~~ when the related species (e.g., NO_x, SO_2) and~~roughly constant composition and~~ environmental variables (e.g, temperature, RH) were roughly constant. The approach here assumes that the relevant properties of the nocturnal air mass are conserved, and neglects other possible sources and sinks of $ClNO_2$ in the air mass history. For the intercepted ~~power plant~~ coal-fired plumes exhibiting sharp $ClNO_2$ peaks, the $ClNO_2$ yield can be estimated from the ratio of the observed $ClNO_2$ mixing ratio to the integrated N_2O_5 uptake loss over the plume age (i.e., the second term in Eq. 6). ~~This~~ The analysis assumes that no $ClNO_2$ was present at the point of plume emission from the combustion sources and no $ClNO_2$ formation before sunset, and that the γ and ϕ within the ~~power plant~~ plumes did not change during the transport from the source to the measurement site. The potential variability in these quantities likely bias the estimates, but these assumptions are a necessary simplification to represent the averaged values that best describe the observations. It should be noted that the steady-state N_2O_5 loss rate is crucial in the yield estimation, which could be underestimated by potentially overestimating the loss rate in some cases with large uncertainties in N_2O_5 measurement and NO_3 reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the $ClNO_2$ yield from the ratio of enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- + HNO_3) in the cases. Given the low time resolution of nitrate data that could potentially introduce large uncertainties, this approach will only be used as a reference to validate the former analysis based on Eq. 6.

Two examples of the yield analysis are shown in Figure 9, which indicate the time periods in which $ClNO_2$ concentration increased while other parameters (such as N_2O_5, NO_x, O_3, and SO_2 concentrations) were relatively stable. The ϕ values obtained for these two cases were 0.26 and 0.05 for July 27 and August 6, respectively. Similar analyses were performed for all of other selected cases in which the $ClNO_2$ concentration increased and other relevant parameters were relatively constant for a short period, typically ~~1~~2-3 h, and the obtained results were summarized in Table 2. The determined ϕ for the seven ~~power plant~~ coal-fired plumes are also listed in Table 1. During the measurement period, ϕ varied from 0.02 to 0.90, with an average of 0.~~27~~ 28 ± 0.24 and a median of 0.~~20~~22. In comparison, the ϕ derived from the production ratio approach showed comparable results with an average of 0.25 ± 0.17, and the ϕ values from two different approaches match reasonably well with a Reduced Major Axis Regression (RMA) slope of 0.78 ± 0.08 and r^2 of 0.73 (cf Figure S4), which corroborates the yield analysis and indicates that the differences are within the overall uncertainty of 40%. The large variability of ϕ is similar to field-derived values in most previous studies, and the mean value is comparable to that in the nocturnal residual layer over continental Colorado (0.18) (Thornton et al., 2010), but lower than that observed at a mountain site in Germany (0.49) (Phillips et al., 2016). The ϕ values for the ~~power plant~~coal-fired plumes (range of 0.20-0.90; average: 0.46 ± 0.24) are generally higher than the campaign average and those from regional diffuse pollution cases. The maximum ϕ (0.90) corresponds to the plume with the highest $ClNO_2$ mixing ratio observed during the campaign. This is consistent with a tower measurement in Colorado, in which higher $ClNO_2$ yields were also observed in inland power plant plumes (Riedel et al., 2013).

Similar to that developed for γ, a parameterization of $ClNO_2$ yield as a function of aerosol water and chlorine composition has been proposed based on laboratory studies (Bertram and Thornton, 2009; Roberts et al., 2009):

$$\phi = \frac{[Cl^-]}{k'[H_2O]+[Cl^-]} \qquad (7)$$

We compared the field-derived values to the parameterization for cases with available aerosol compositions, using an empirical k' of 1/450, as recommended by Roberts et al. (2009). The particle liquid water content $[H_2O]$ was calculated from the thermodynamic model (E-AIM model IV) based on measured aerosols composition, as described above. As shown in Figure 10a, the ϕ values predicted by the parameterization are generally higher than those determined from observed $ClNO_2$ production rates, especially at low measurement-determined yields. For measured ϕ values higher than 0.4, smaller differences (<20%) were observed between the two methods, which are within the aggregate uncertainty associated with measurement and derivation. The parameterized ϕ values exhibit positive dependence on the aerosol chloride concentration and the Cl^-/H_2O ratio, as shown by the color code in Fig 10a. The measurement-determined values only exhibit measurable such dependence at low yields, implying the possible biased relationship due to higher aerosol water conditions in the present work. The discrepancy between the parameterization ϕ based upon aerosol composition and those derived from measured $ClNO_2$ concentrations has been found previously (e.g., Wagner et al., 2013), and the underlying causes have not been resolved.

By examining the relationships between the determined yield and other parameters, we found a slightly negative relationship between ϕ and particulate nitrate concentration, as depicted in Figure 10b. Although the data are scattered, the high-yield cases are mostly associated with lower nitrate concentrations, while the ϕ for the high nitrate cases (>15 μg m^{-3}) are smaller. A similar trend was observed for the NO_x/NO_y ratio, which indicates the 'age' of the air masses, suggesting that higher ϕ are usually associated with relatively 'young' air masses exhibiting low nitrate concentrations. More secondary and dissolved organic matters in aged aerosols could be a possible factor contributing to the reduction of $ClNO_2$ production efficiency (Mielke et al., 2013; Ryder et al., 2015; Phillips et al., 2016). Further studies are needed to characterize the combined effects of various parameters on $ClNO_2$ yields, in particular the influences of the aerosol mixing state, chloride availability distribution among particle sizes, organic matter, acidity, other possible loss ways of $ClNO_2$, and potential factors affecting in high humid and polluted conditions (Laskin et al., 2012; Mielke et al., 2013; Wagner et al., 2013; Ryder et al., 2015; Li et al., 2016; Phillips et al., 2016).

3.5 Effects of heterogeneous N_2O_5 reactions on nitrate formation and NO_x processing

In addition to abundant $ClNO_2$ formation, rapid heterogeneous N_2O_5 uptake may also lead to the production of a large amount of nitrate, which is one of the main components of fine particles contributing to haze pollution in northern China (e.g., Huang et al., 2014). Based on the reactions described above, the formation rate of soluble nitrate from N_2O_5 reactions, $p(NO_3^-)$, can be determined from the $ClNO_2$ yield and N_2O_5 heterogeneous loss rate as follows:

$$p(NO_3^-) = \cancel{(2-\phi)\frac{d[N_2O_5]}{dt} =}(2-\phi)k_{N_2O_5}[N_2O_5] \qquad (8)$$

The $p(\mathrm{NO_3^-})$ values obtained for the select cases during the study period ranged from 0.02 to 0.62 ppt s^{-1}, with a mean value of 0.29 ± 0.18 ppt s^{-1}, corresponding to 0.2- 4.8 μg m^{-3} h~~r~~$^{-1}$ and 2.2 ± 1.4 μg m^{-3} h~~r~~$^{-1}$ (Table 2). The derived rates are comparable to the observed increases in nitrate concentrations (2-5 μg m^{-3} h^{-1}) during haze episodes in summer nights at a rural site in the NCP (Wen et al., 2015). By assuming that produced nitrate is conserved and neglecting the deposition and volatilization loss (e.g., via ammonium nitrate), ~~T~~the in-situ NO_3^- formation ~~was~~ could be predicted by integrating each derived formation rate over the corresponding analysis period. Similar to N_2O_5 uptake coefficient and $ClNO_2$ yield determination above, the nitrate formation estimation here assumes a conserved air mass with a constant formation rate over the study period. For ~~power plant~~ coal-fired plumes, we equated the measured nitrate concentrations with the increases by assuming that no aerosol nitrate was directly emitted from the nocturnal point sources. As shown in Figure 11, the predicted nitrate formation shows reasonable agreement with the measured increases in nitrate concentrations (ΔNO_3^-) (RMA slope of 1.14 and r = 0.81). This consistency also can serve as a check to validate ~~for~~ the reliability of ~~the~~ above determined heterogeneous N_2O_5 reactivity and parameters of γ and ϕ. The in-situ nitrate formation from heterogeneous N_2O_5 reactions was predicted to be as high as 17 μg m^{-3}, with a mean value of 4.3 ± 4.5 μg m^{-3}, accounting for 32 (± 27) % of the observed average nitrate concentration during the cases. This is consistent with the maximum nitrate increase of 14.9 μg m^{-3} over south China (Li et al., 2016) and 21% nitrate increase in polluted episodes in Beijing (Su et al., 2017) after considering the heterogeneous N_2O_5 uptake in the regional model simulation. As for a plume undergo continuous chemical processing from dusk to sunrise, the heterogeneous N_2O_5 reactions would lead to substantial nitrate formation (e.g., 22 μg m^{-3} production for a 10-h night), and could contribute significantly to secondary fine aerosols as the main driver of the persistent haze pollution in northern China.

The formation of nitrate (including HNO_3) and its subsequent removal by deposition is the predominant removal mechanism of nitrogen oxides from the atmosphere (Chang et al., 2011). The nocturnal NO_x removal rate depends on the NO_3 radical production rate, heterogeneous N_2O_5 loss rate, NO_3 reaction rate with VOCs, the partitioning between N_2O_5 and NO_3 concentrations, and $ClNO_2$ yield. $ClNO_2$ mainly functions as a reservoir of NO_x, rather than as a sink, because the formation of $ClNO_2$ throughout the night with subsequent morning photolysis recycles NO_2 (Behnke et al., 1997). The reactions of NO_3 with VOCs would predominantly produce organic nitrate products (Brown and Stutz, 2012 and references therein), but some fraction of NO_2 can be regenerated in the NO_3 reactions (i.e., with terpenes) (e.g., Wängberg et al., 1997) or released from the decomposition of organic nitrate during the transport (e.g., Francisco and Krylowski, 2005). For simplicity, we neglect the recycling of NO_2 from NO_3-VOC reactions by assuming the ~~the reactions of NO_3 with VOCs can be assumed to result in the~~ complete removal of reactive nitrogen (Wagner et al., 2013)~~,~~. This would overestimate the NO_x loss since the monoterpenes contribute to around half of NO_3 reactivity in the present study, but~~and~~ this assumption does not significantly affect ~~results~~ the conclusion because the ~~loss of~~ NO_3 loss with VOCs was the minor path comparing to N_2O_5 heterogeneous loss~~accounts for less than 30% of the total N_2O_5 reactivity~~. Thus, the nocturnal NO_x loss rate can be quantified by the following equation:

$$L(\mathrm{NO_x}) = (2-\phi)k_{\mathrm{N_2O_5}}[\mathrm{N_2O_5}] + k_{\mathrm{NO_3}}[\mathrm{NO_3}] = (1-\phi)k_{\mathrm{N_2O_5}}[\mathrm{N_2O_5}] + p[\mathrm{NO_3}] \qquad (9)$$

Using the coefficients described above, we calculated the nocturnal loss rate of NO_x for each case, as summarized in Table 2. The NO_x removal rate varied from 0.19 to 2.34 ppb h^{-1}, with a mean of 1.12 ± 0.63 ppb h^{-1}~~.~~, which corresponds to a pseudo-first order loss rate coefficient of 0.24 ± 0.08 h^{-1} in average for the studied cases. This loss rate is higher than that determined from a mountain site measurement in Taunus, Germany (~0.2 ppb h^{-1} with typical NO_2 level of 1-2 ppb) (Crowley et al., 2010), and the results from aircraft measurements in US over Ohio and Pennsylvania and downwind region of New York (90% and 50% NO_x loss in a 10-hour night, respectively) (Brown et al., 2006). For reference, this nocturnal average loss rate is approximately equivalent to NO_2 loss via reaction with OH at afternoon condition assuming OH concentration around 2×10^6 molecules cm^{-3}, indicating the importance of nocturnal heterogeneous reactions on NO_x processing and budget. ~~tower measurements during wintertime in Colorado, with integrated nocturnal NO_2 loss ranging from 2.2 to 4.4 ppbv (Wagner et al., 2013).~~ Figure 12 shows the relationship between determined NO_x loss rate and observed ambient NO_x concentration at the measurement site. NO_x loss rate appears to be strongly dependent upon NO_x concentrations below 6 pptv (slope = 0.32 h^{-1}; *r* = 0.93); the loss rate became more scattered at higher NO_x conditions, which were typically observed in the ~~power plant~~coal-fired plumes. This result implies that for low NO_x condition (<6 ppbv), 96% of NO_x would be removed after 3-h of nocturnal processing, if no additional NO_x emissions affect the plume during this period.

Comparing NO_x loss to the nitrate formation rates, it can be inferred that the nitrate formation from heterogeneous N_2O_5 uptake is predominant in reactive NO_x loss and account for an average of 87% of the NO_x loss, although this fraction of individual cases varied between 35 to 100%. A box model simulation based on tower measurements at Colorado also reported that the largest proportion of the nitrate radical chemistry is N_2O_5 hydrolysis, which typically accounted for 80% of nitrate radical production, whereas the losses to NO_3-VOC reactions are less than 10% (Wagner et al., 2013). A recent model simulation for southern China also suggested that considering the N_2O_5 uptake and subsequent Cl activation could decrease regional NO_x by more than 16% (Li et al., 2016). The results obtained in the present study demonstrate the significance of fast heterogeneous N_2O_5 chemistry on nocturnal NO_x removal and fine nitrate formation in the polluted residual layer over the NCP.

4. Summary and Conclusions

An intensive field study was conducted at a high-altitude site to characterize the reactive nitrogen chemistry in the polluted nocturnal residual layer over the NCP. The results revealed the frequently elevated $ClNO_2$ mixing ratios (maximum: 2065 pptv) and efficient $ClNO_2$ yields (0.46 ± 0.24) resulting from ~~power plant~~ coal-fired plumes in the residual layer. The presence of $ClNO_2$-laden air in the nocturnal residual layer confirms our previous hypothesis based on a measurement in a rural site in the NCP, that the downward mixing of $ClNO_2$-rich air to the surface in the next morning would have large impacts on early morning photochemistry and ozone production. Rapid heterogeneous N_2O_5 uptake and efficient $ClNO_2$ and nitrate formation were observed during the study period. The γ determined in the present study (average: 0.061 ± 0.025) exhibited a clear dependence on the particulate chloride-to-nitrate ratio, and are higher than those observed in other locations, but consistent with those obtained at a surface site in the same region of the NCP. Laboratory-derived parameterizations predicted comparable mean γ values, but did not represent the high variability of the measured values, and tended to overestimate ϕ in the low yields. These discrepancies suggest that various aerosol physicochemical parameters have complicated effects on N_2O_5 uptake and $ClNO_2$ yield, in particular in high humid and polluted residual layer, which requires further investigation.

Fast heterogeneous N_2O_5 uptake dominated and accounted for a mean of 87% of the regional nocturnal NO_x loss during the study periods in the NCP. The estimated nocturnal loss rate of NO_x is higher than that previously observed in US and Europe, with averaged loss rate and rate coefficient of 1.12 ± 0.63 ppb h^{-1} and 0.24 ± 0.08 h^{-1}, respectively.~~, resulting in a mean loss rate of 1.12 ± 0.63 ppb h^{-1} and accounting for an average of 87% of the nocturnal NO$_x$ loss.~~ Moreover, heterogeneous reactions contributed to substantial nitrate production up to 17 μg m^{-3}, with a mean nocturnal formation rate of 2.2 ± 1.4 μg m^{-3} h~~r~~$^{-1}$, and in-situ production could account for 32 ± 27% of the observed nitrate concentrations in the studied cases. ~~which may help explain the previously observed rapid nighttime growth of fine nitrate aerosols in the NCP.~~ The results may help explain the previously observed rapid nighttime growth of fine nitrate aerosols in the NCP, and demonstrate the ~~significance~~ importance of heterogeneous N_2O_5-$ClNO_2$ chemistry on NO_x and aerosol budgets in the polluted residual layer over the NCP, which underpins the need for further studies regarding their roles in the formation of complex haze pollution in northern China.

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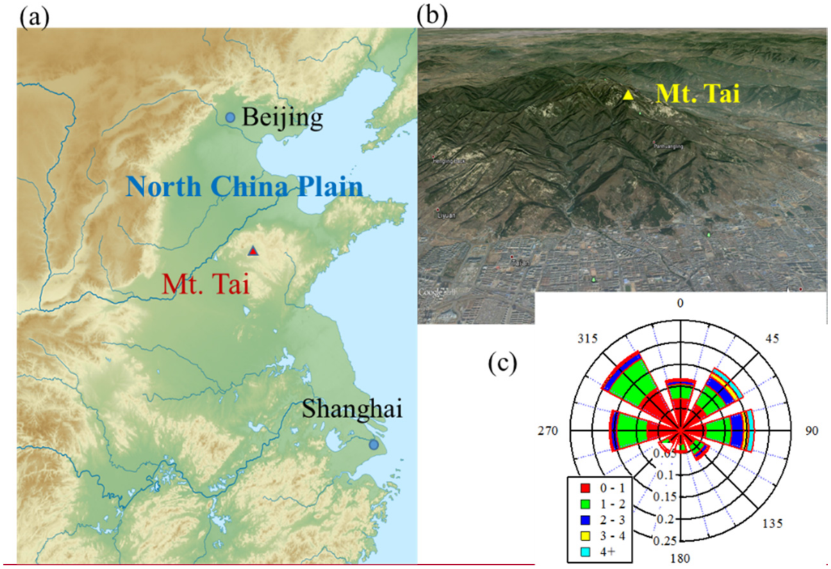
List of Figures



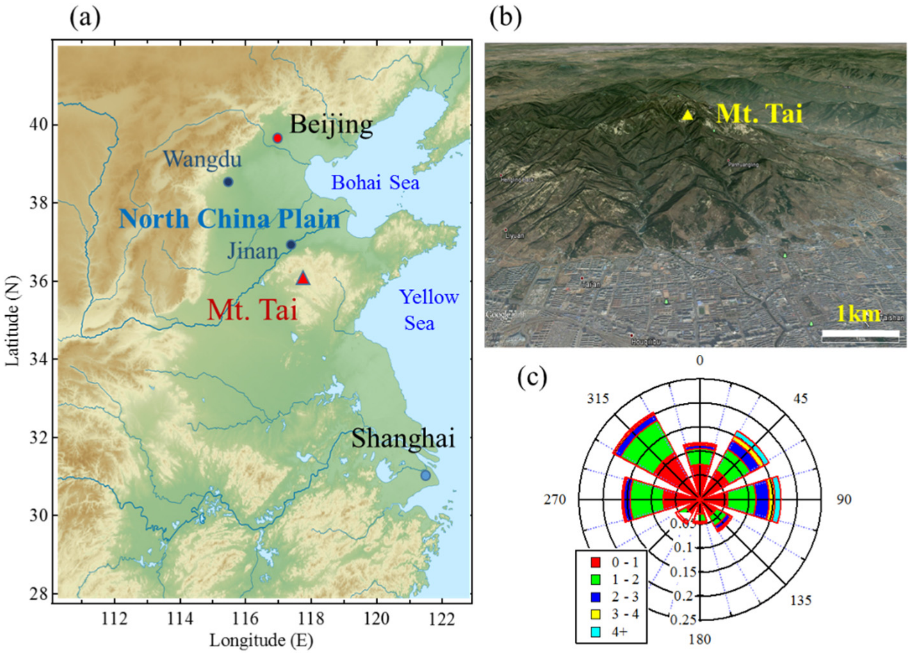
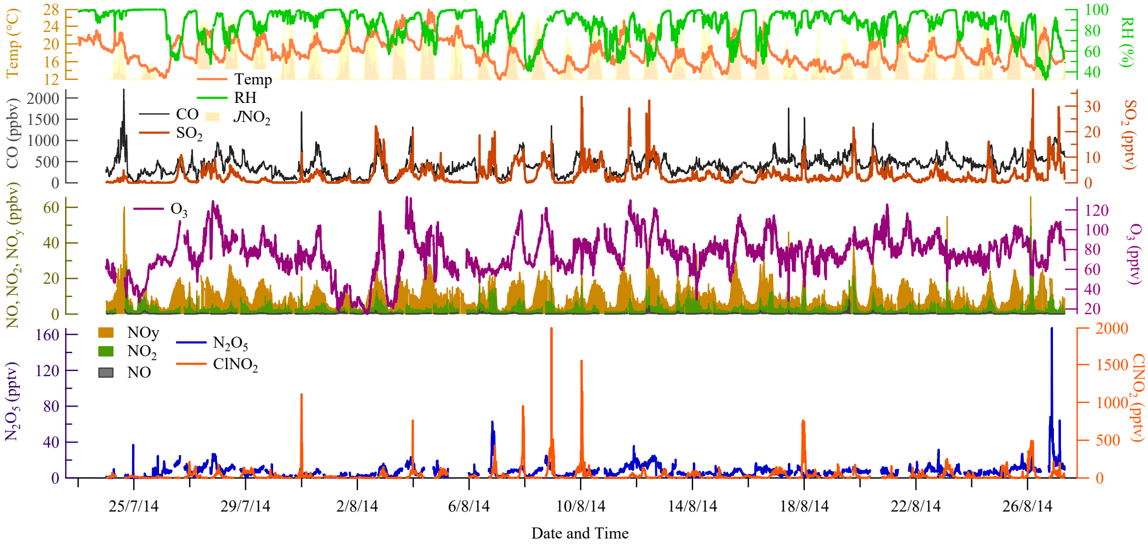


Figure 1: (a) Map of northern China showing the location of the mountaintop measurement site (Mt. Tai) in the North China Plain, ~~and~~(b) expanded topographic view of Mt. Tai and surrounding areas~~.~~ and (c) ~~The inset shows a~~a wind rose for the study period of summer 2014.



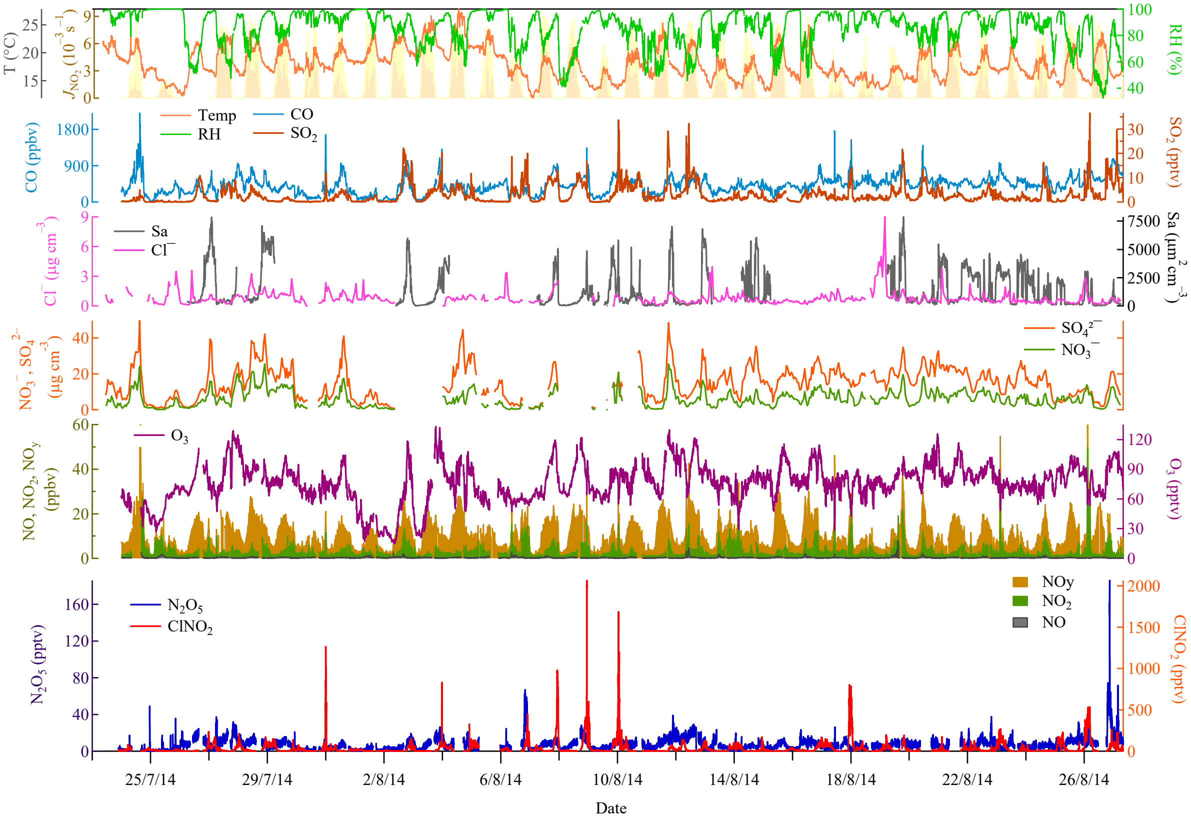
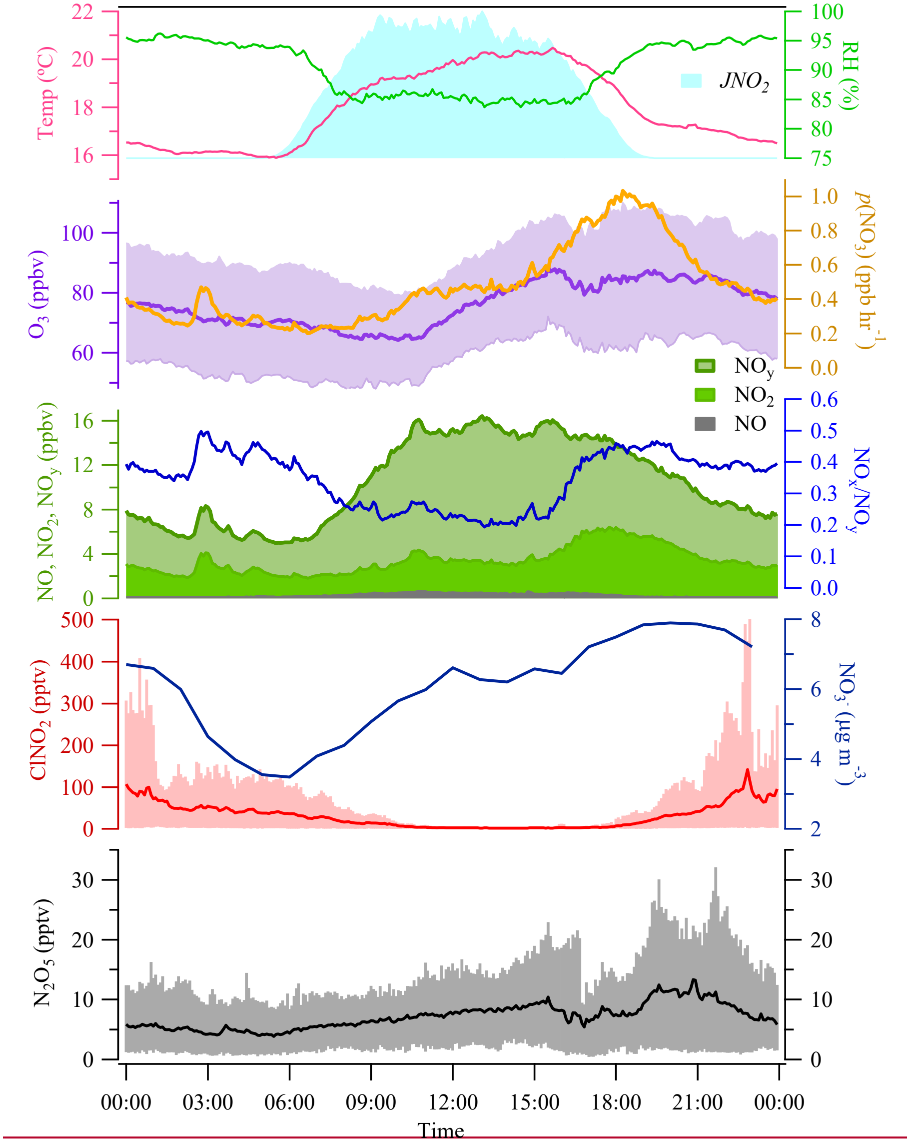


Figure 2: Time series (1-min time resolution) for N$_2$O$_5$, ClNO$_2$, related trace gases, aerosol properties, and meteorological data measured at Mt. Tai from July 24 to August 27, 2014.


Temp (°C)
22
20
18
16
RH (%)
100
95
90
85
80
75
JNO₂
O₃ (ppbv)
100
80
60
p(NO₃) (ppb hr⁻¹)
1.0
0.8
0.6
0.4
0.2
0.0
NOy
NO₂
NO
NO, NO₂, NOy (ppbv)
16
12
8
4
0
NOx/NOy
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ClNO₂ (pptv)
500
400
300
200
100
0
NO₃⁻ (µg m⁻³)
8
6
4
2
N₂O₅ (pptv)
30
20
10
0
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
00:00
Time

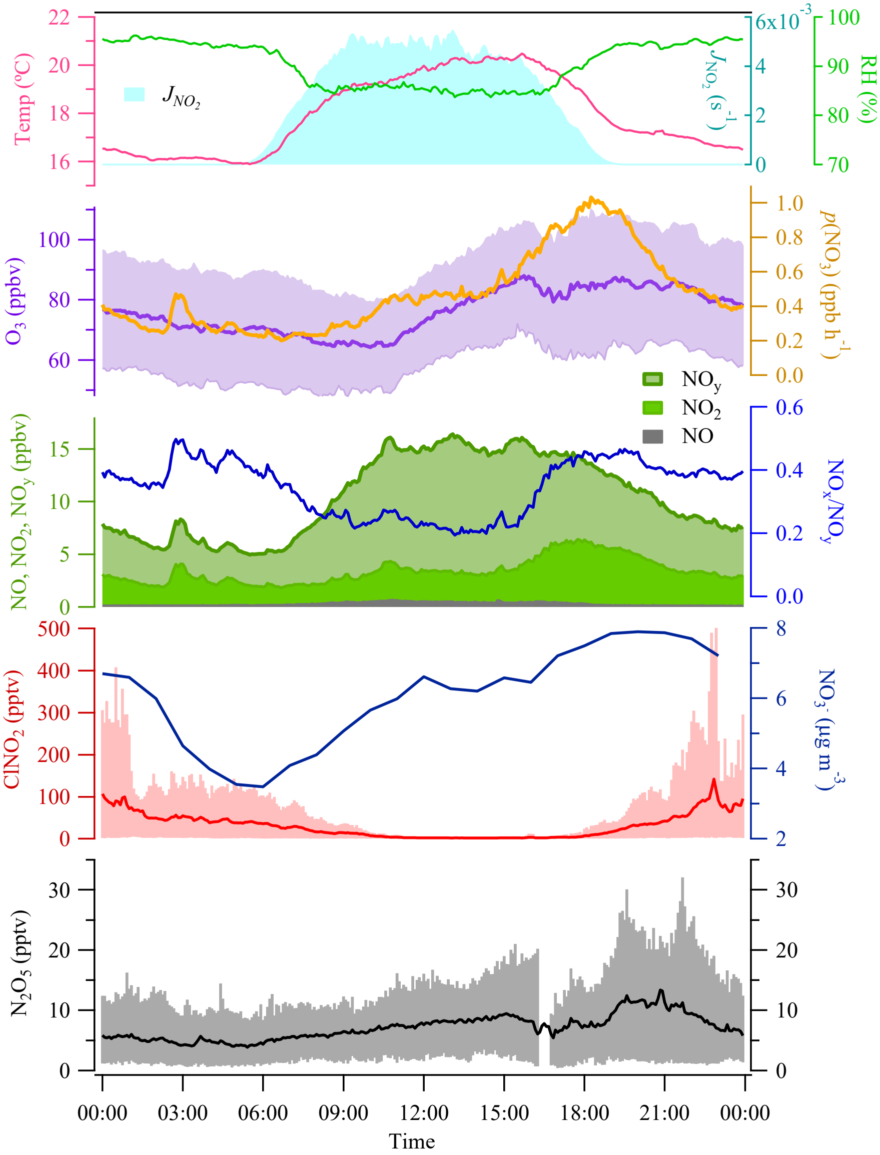
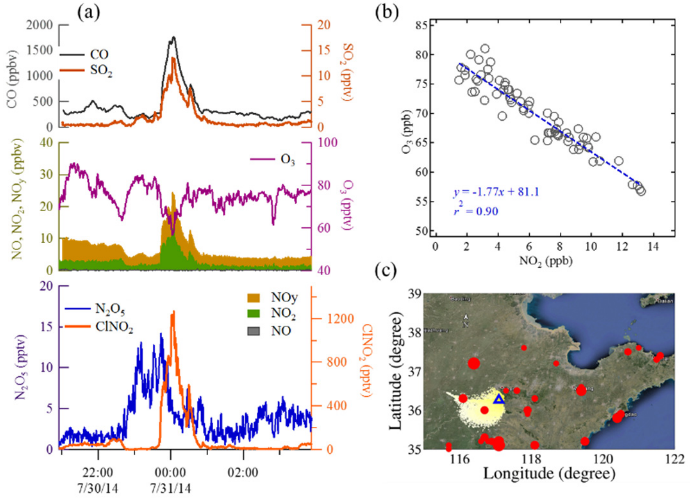


Figure 3: Diurnal variations of N_2O_5, $ClNO_2$, NO_x, NO_y, O_3, particulate nitrate, nitrate radical production rate $p(NO_3)$ and meteorological parameters during the study period at Mt. Tai. Shaded area in O_3 shows 2σ variation, and vertical bars in N_2O_5 and $ClNO_2$ represent 10-90th percentile ranges.



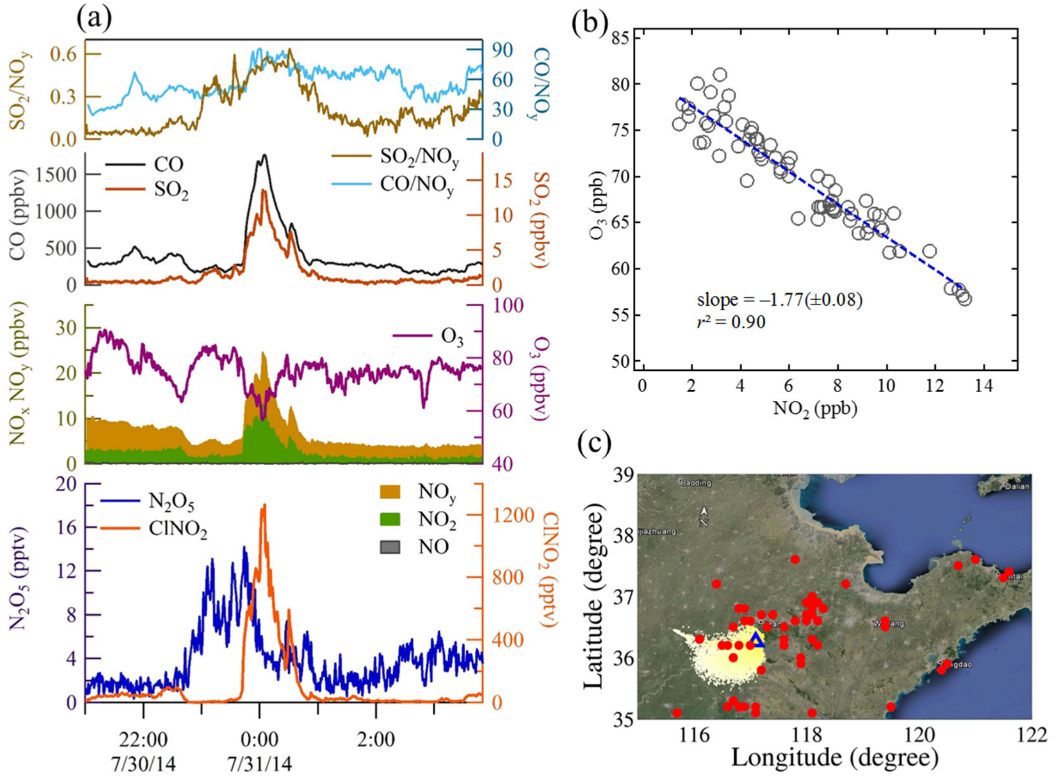
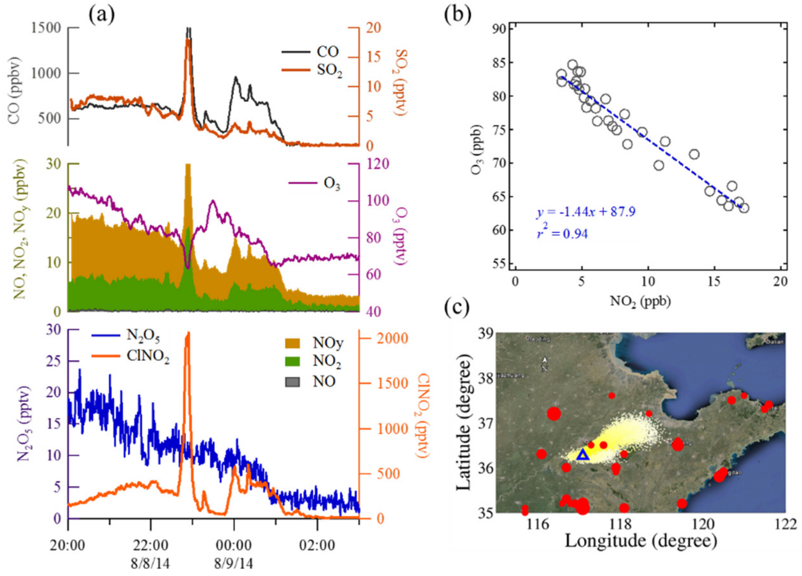


Figure 4: (a) Time series for ClNO$_2$, N$_2$O$_5$, and related trace gases observed within the high-ClNO$_2$ ~~power plant~~coal-fired plume during the night of July 30-31, 2014. (b) Plot of O$_3$ versus NO$_2$ concentrations for the ~~power plant~~ plume; plume age was determined from the plot using Eq. (2). (c) 12-h HYSPLIT backward particle dispersion image depicting air masses arriving at the measurement site (blue triangle) at the time of the plume, and red dots indicating the location of major coal-fired facilities in cement and steel production and power plants in the region~~, with the size of dots showing their generation capacities~~.



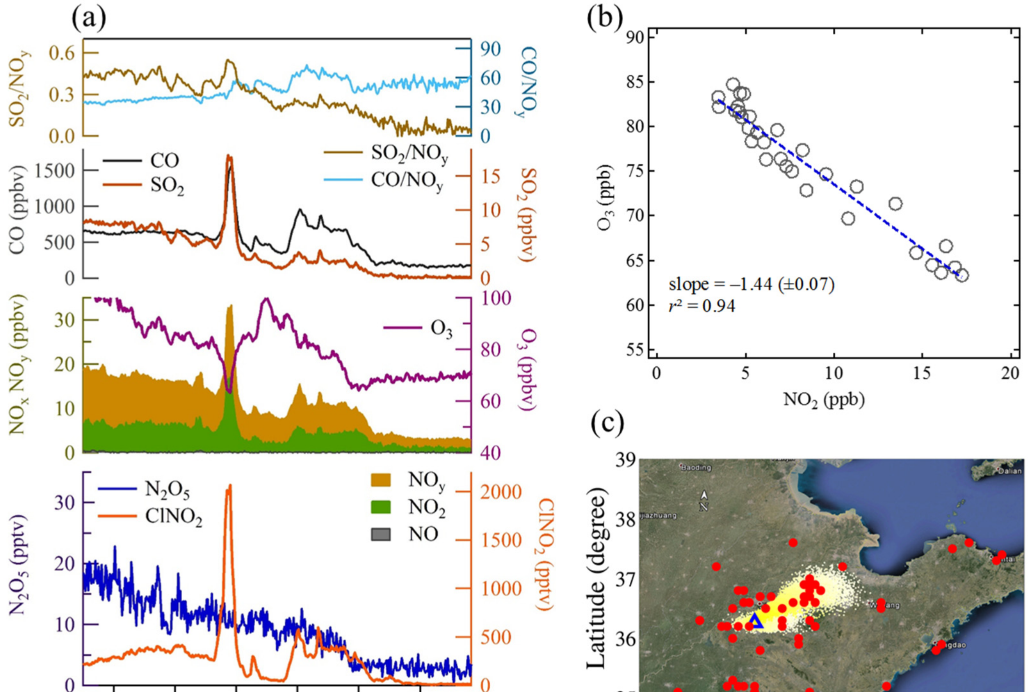


Figure 5: Same as Figure 4 but for a plume observed during the night of August 8-9, 2014.

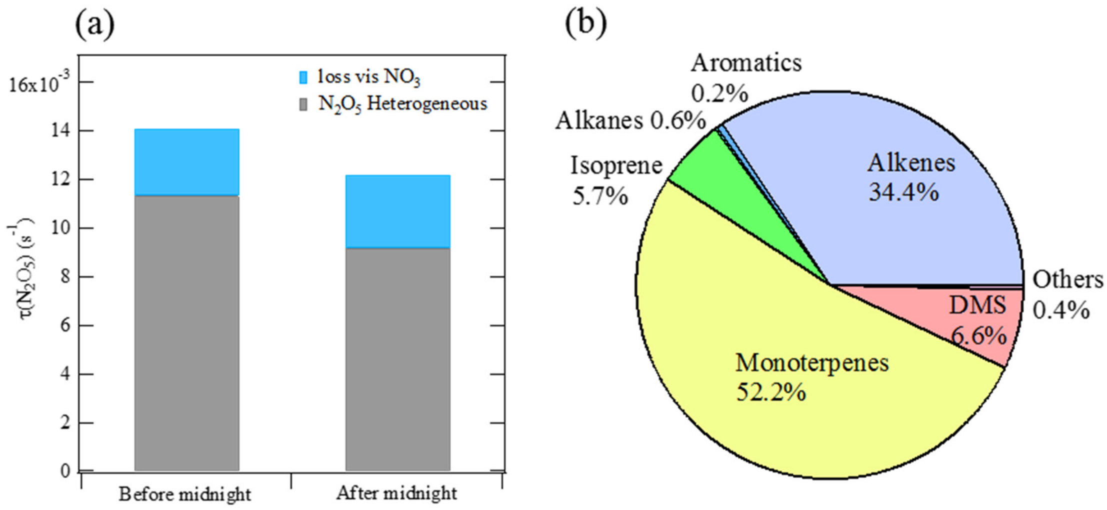
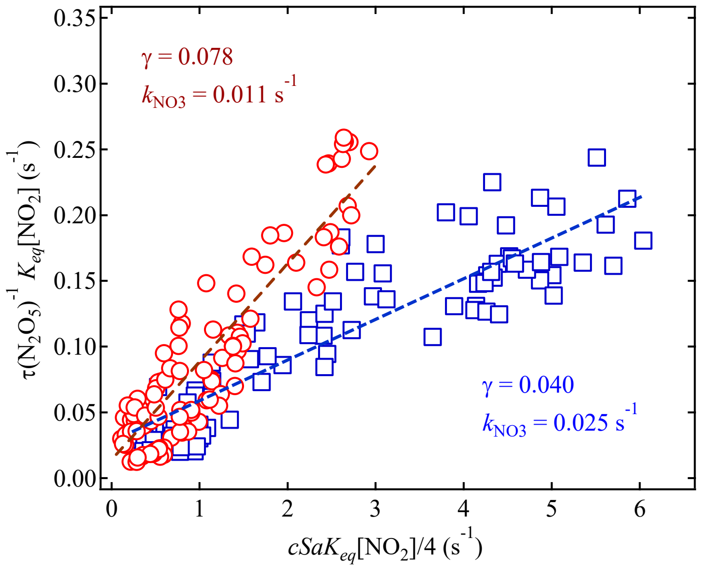


Figure 6: (a) Fractions of N_2O_5 loss rate coefficients through NO_3 loss and the heterogeneous reaction of N_2O_5 before (19:00-24:00) and after midnight (1:00-5:00); (b) pie chart shoing the average nighttime contributions of different categories of VOCs to NO_3 reactivity during the study period.



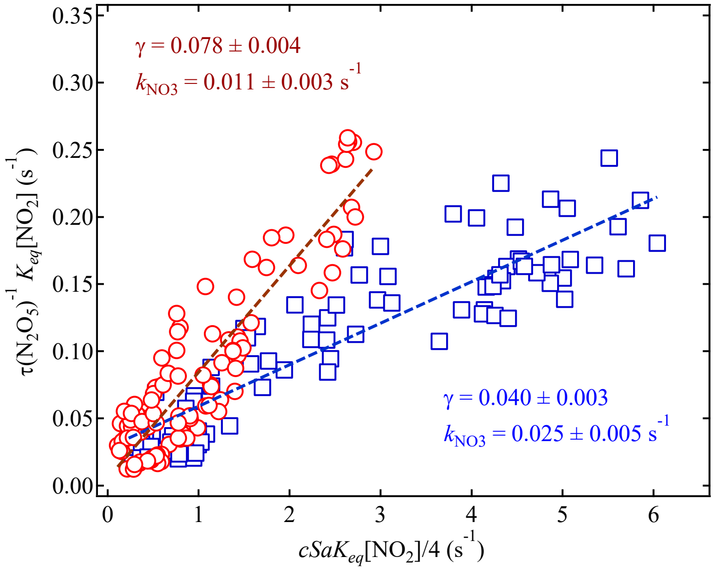
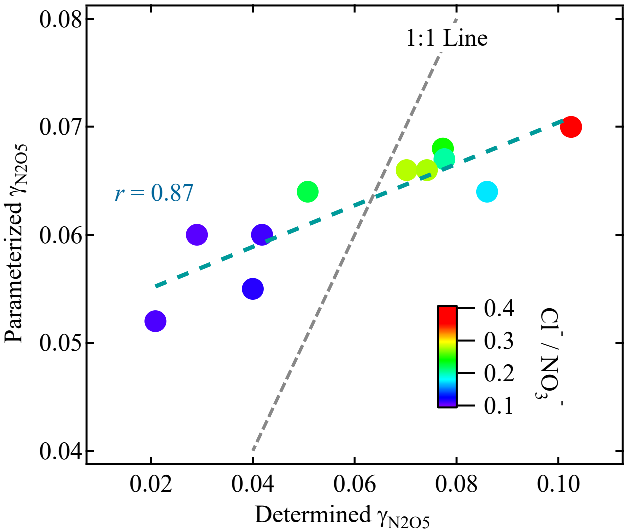


Figure 7: Example fits of inverse N_2O_5 steady-state lifetimes according to Eq. (5) for two cases observed on the nights of August 2 and 21, 2014. The best fit values of γ and k_{NO3} are shown.



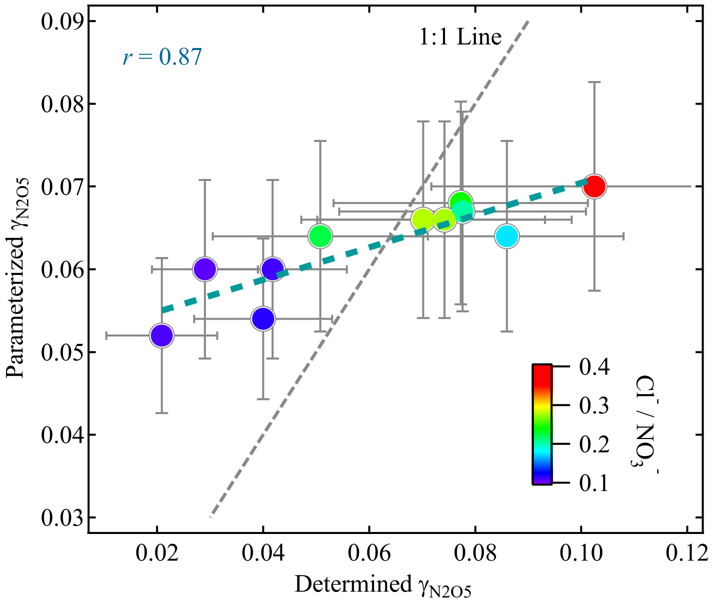


Figure 8: Comparison of field-determined γ with that derived from the parameterization of Bertram and Thornton, (2009). The colors of the markers indicate the corresponding concentrations ratio of particulate chloride to nitrate. The error bars represent the total aggregate uncertainty associated with measurement and derivation.

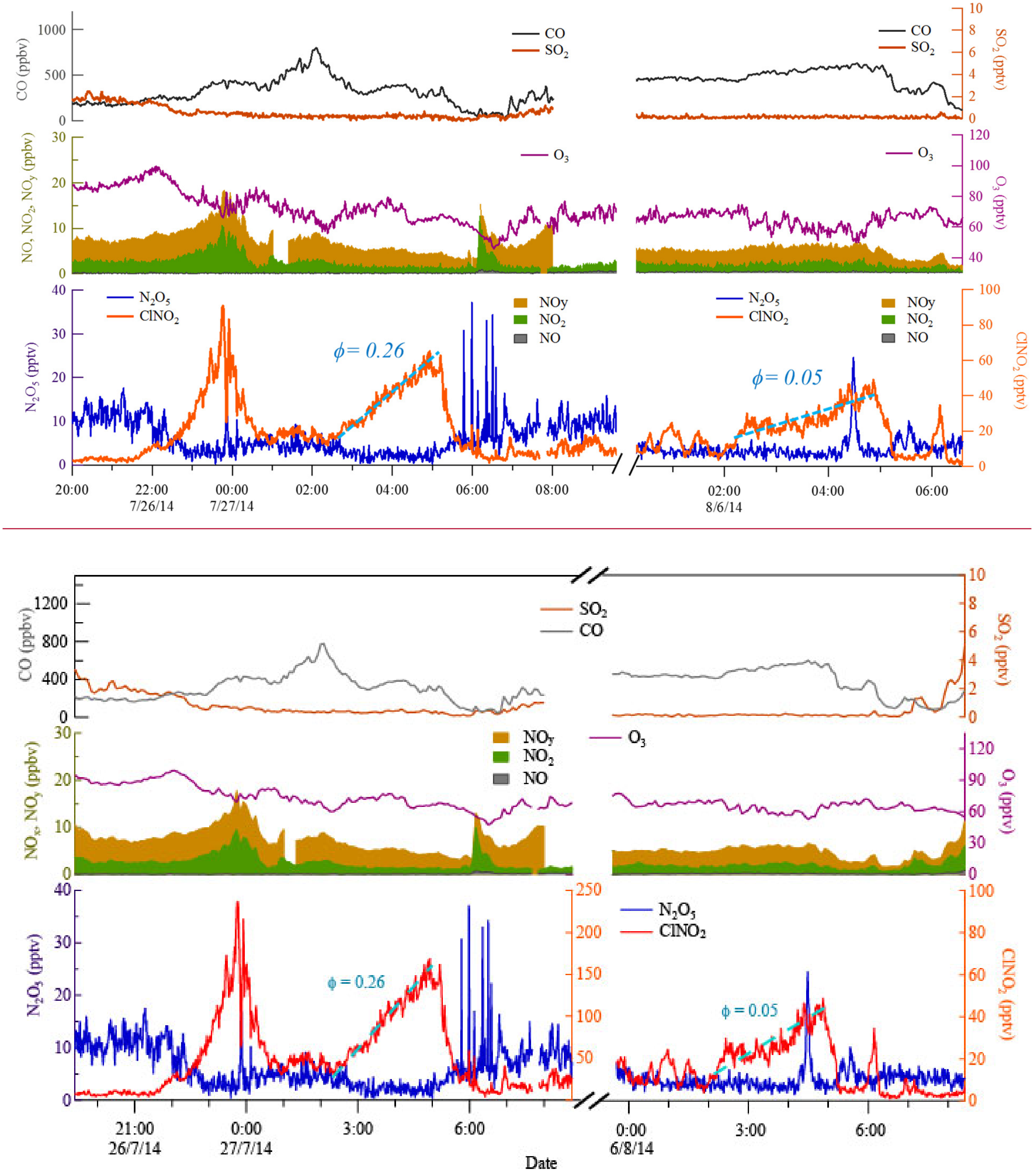
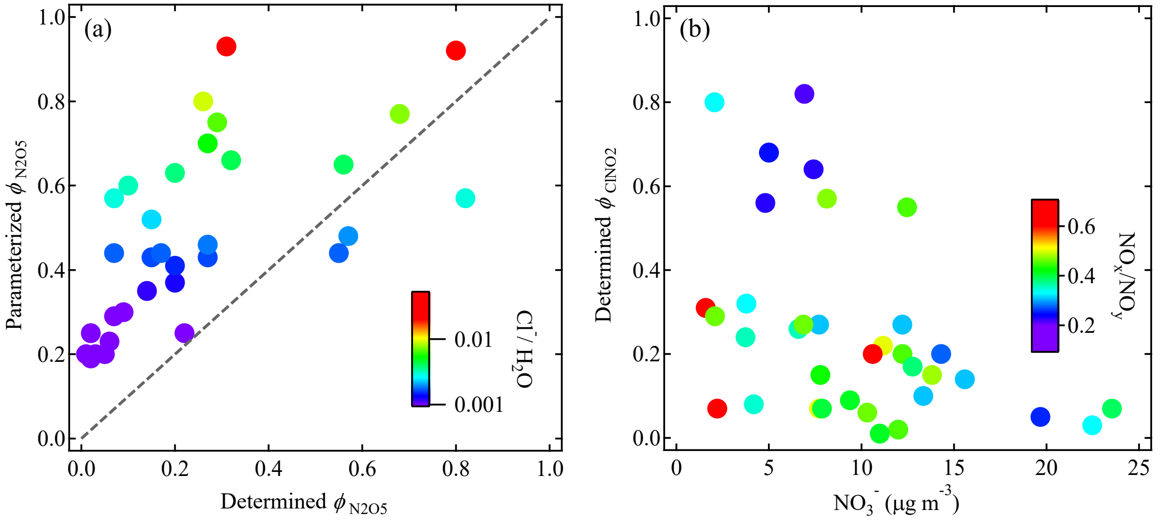


Figure 9: Examples of ClNO$_2$ yields determined for two cases on July 27 and August 6, 2014. The ClNO$_2$ mixing ratios increased steadily, while those of NO$_x$, O$_3$, and SO$_2$ did not change significantly during the studied periods.



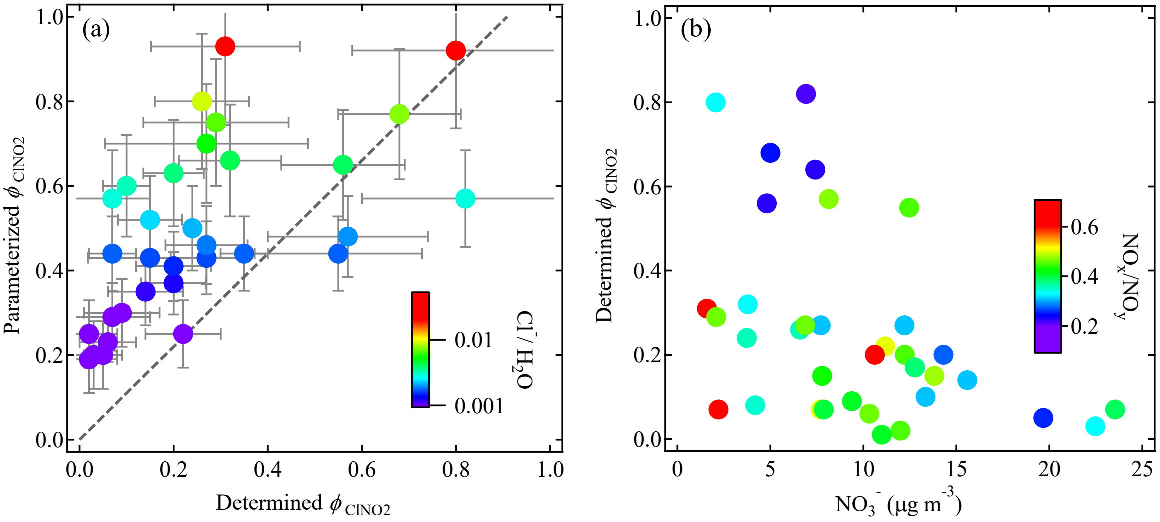
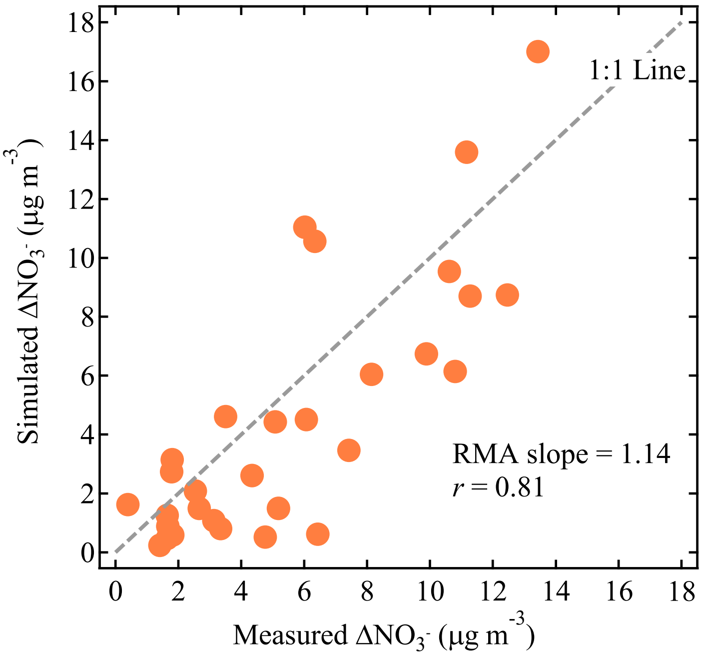


Figure 10: (a) Comparison of field-determined ϕ with that derived from parameterization (Eq. 7), and the colors of the markers represent the corresponding Cl^-/H_2O ratio; (b) relationship between field-determined ϕ and measure nitrate concentrations in aerosols, and colors of markers represent the corresponding NO_x/NO_y ratio. The error bars represent the total aggregate uncertainty as similar as Figure 8.



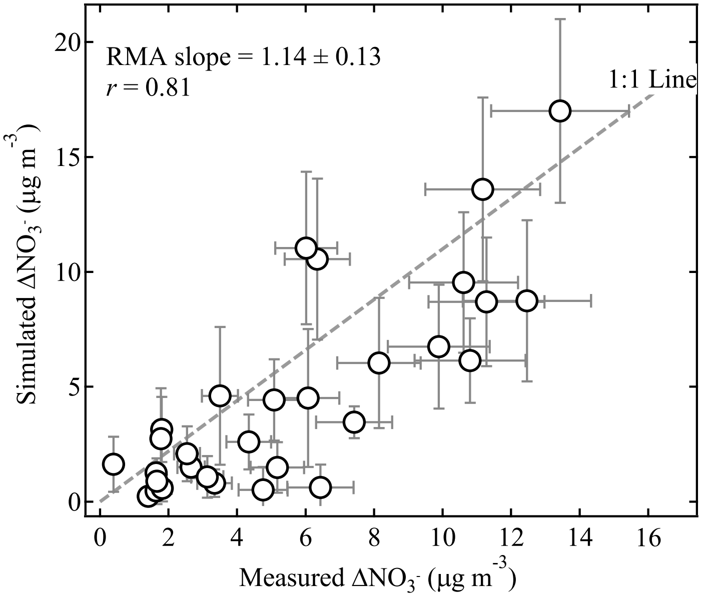
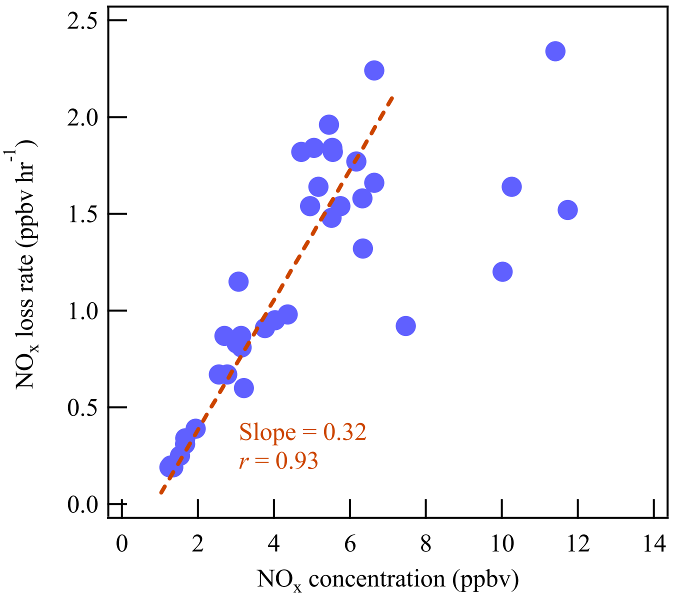


Figure 11: Comparison of predicted nitrate production based on integrating the derived nitrate formation rate with the measured increase in nitrate concentrations (ΔNO_3^-) over the analysis time period.



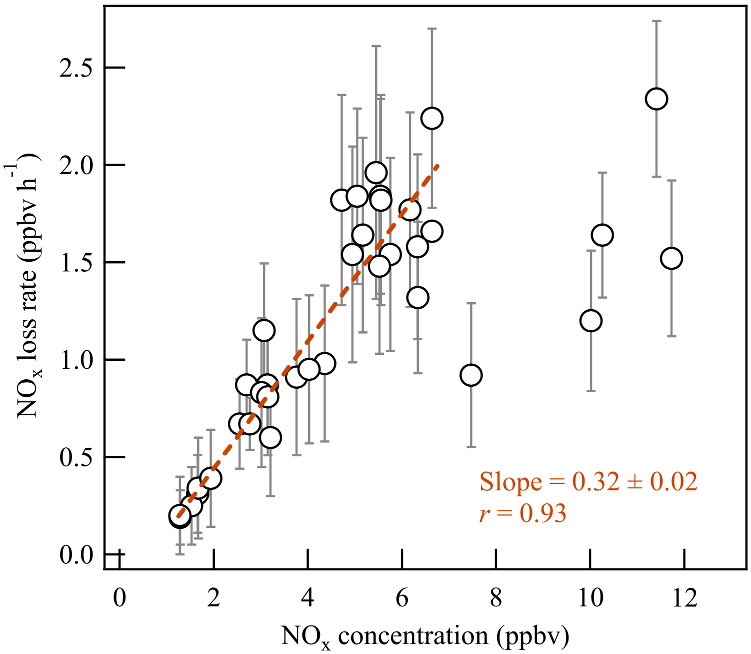


Figure 12: Relationship between determined NO_x loss rate and observed ambient NO_x concentration at the measurement site during the study period.

Table 1: Chemical characteristics of ~~power plant~~coal-fired plumes exhibiting high levels of $ClNO_2$ observed at Mt. Tai during the summer of 2014

Date	Duration	N_2O_5 (pptv)		$ClNO_2$ (pptv)		O_3	NO_x	NO_x /NO_y	ΔSO_2 /ΔNO_y [a]	ΔCO /ΔNO_y [b]	Cl^- (μg cm^{-3})	t_{plume}	ϕ $_{ClNO2}$
		Mean	Maximum	Mean	Maximum								
30-31 Jul	23:40-0:45	5.9	14.2	528	1265	70	6.5	0.49	0.57	83	2.34	3.2	0.57
3-4 Aug	23:30-0:00	20.1	23.8	506	833	106	2.8	0.22	2.43	108	NA [c]	4.9	0.64
7 Aug	21:30-23:30	10.5	14.9	606	976	91	5.8	0.36	1.36	50	2.24	5.5	0.35 [d]
8 Aug	22:00-23:10	11.0	15.1	841	2065	76	8.5	0.45	0.65	45	NA	2.1	0.90
8-9 Aug	23:40-01:15	6.8	12.6	315	599	77	4.3	0.41	0.54	85	NA	4.4	0.23
10 Aug	0:00-2:00	10.5	15.5	692	1684	72	6.2	0.43	1.67	50	1.10	4.6	0.55
17-18 Aug	22:00-01:30	3.5	7.7	409	802	60	9.5	0.55	0.48	33	1.01	4.6	0.26 [d]
25-26 Aug	0:00-5:00	12.1	40.1	301	534	74	11.8	0.62	2.10	NA	1.88	3.0	0.20

[a] It represents the slope of SO_2 vs NO_y in plumes, and the overall slope for entire campaign was 0.31 with r^2 of 0.31.

[b] Same to above note with the campaign overall slope of 15.7 and r^2 of 0.23.

[c] Data not available in the case.

[d] For t_{plumes} longer than the nocturnal processing period since sunset, the time since sunset was used in the $ClNO_2$ yield calculation.

Table 2: Statistical summary of determined N_2O_5 uptake coefficients γ, $ClNO_2$ yields ϕ, nitrate formation rates and nocturnal NO_x removal rates at Mt. Tai during the study period.

	γ_{N2O5}	k_{NO3}	ϕ_{ClNO2}	NO_3^- formation rate (ppt s^{-1})	NO_3^- formation rate (μg m^{-3} h~~r~~$^{-1}$)	~~NO_x removal rate (ppt s^{-1})~~	NO_x removal rate (ppb h~~r~~$^{-1}$)	NO_x loss rate coefficient (h^{-1})
Mean	0.061	0.015	0.27	0.29	2.2	~~0.31~~	1.12	0.24
SD	0.025	0.010	0.24	0.18	1.4	~~0.17~~	0.63	0.08
Median	0.070	0.011	0.20	0.26	2.0	~~0.27~~	0.98	0.24
Min	0.021	0.003	0.02	0.02	0.2	~~0.05~~	0.19	0.05
Max	0.102	0.034	0.90	0.62	4.8	~~0.65~~	2.34	0.38