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.

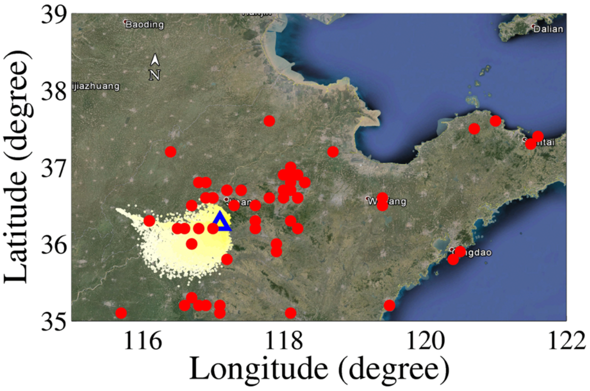
Our responses to the comments, including changes made to the manuscript, are listed point-by-point below.

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

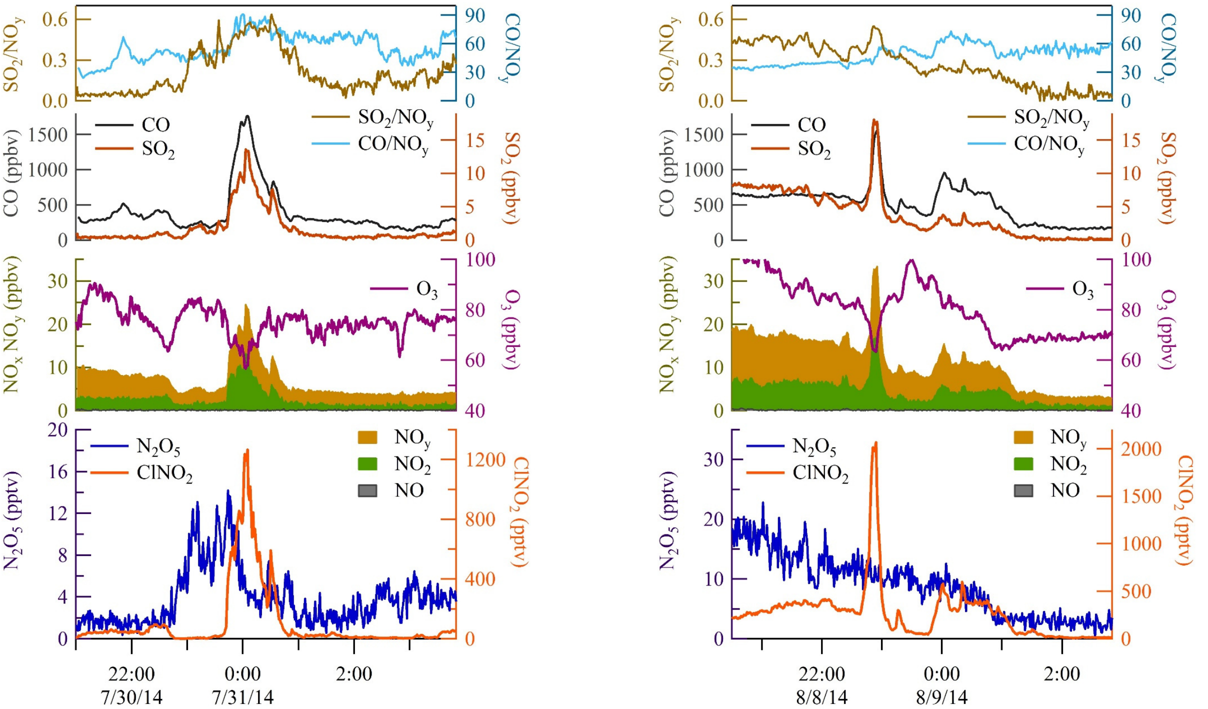
Date	Duration	N_2O_5 (pptv)		$ClNO_2$ (pptv)		O_3	NO_x	NO_x/NO_y	$\Delta SO_2/\Delta NO_y$ [a]	$\Delta CO/\Delta NO_y$ [b]	Cl- (µg cm^{-3})	t_{plume}	ϕ_{ClNO2}
		Mean	Maximum	Mean	Maximum								
30-31 Jul	23:40-0:45	5.9	14.2	528	1265	70	6.5	0.49	0.57	83	2.34	3.2	0.57
3-4 Aug	23:30-0:00	20.1	23.8	506	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.



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.

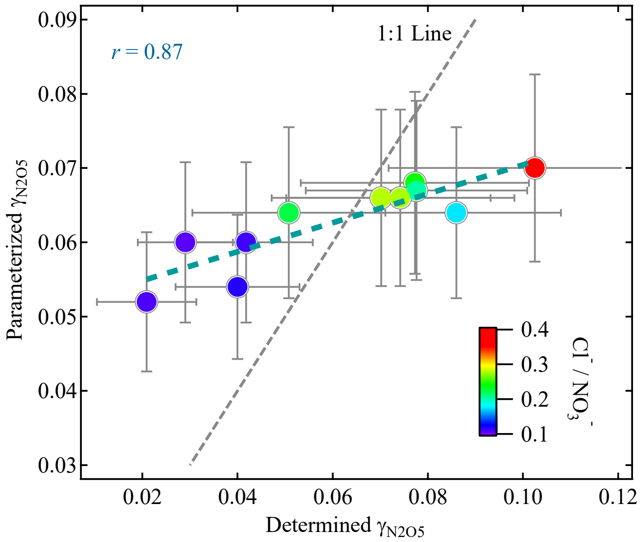


Figure 8: Comparison of field-determined γ with that derived from the parameterization of Bertram and Thornton, (2009). The colors of the markers indicate the corresponding concentrations ratio of particulate chloride to nitrate. The error bars represent the total aggregate uncertainty associated with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

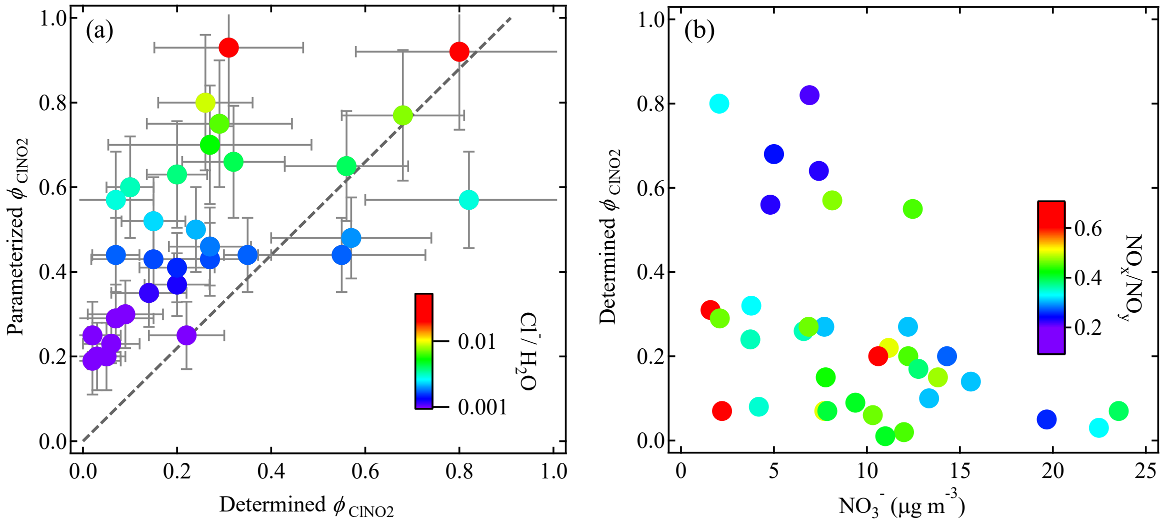


Figure 10: (a) Comparison of field-determined ϕ with that derived from parameterization (Eq. 7), and the colors of the markers represent the corresponding Cl^-/H_2O ratio; (b) relationship between field-determined ϕ and measure nitrate concentrations in aerosols, and colors of markers represent the corresponding 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.

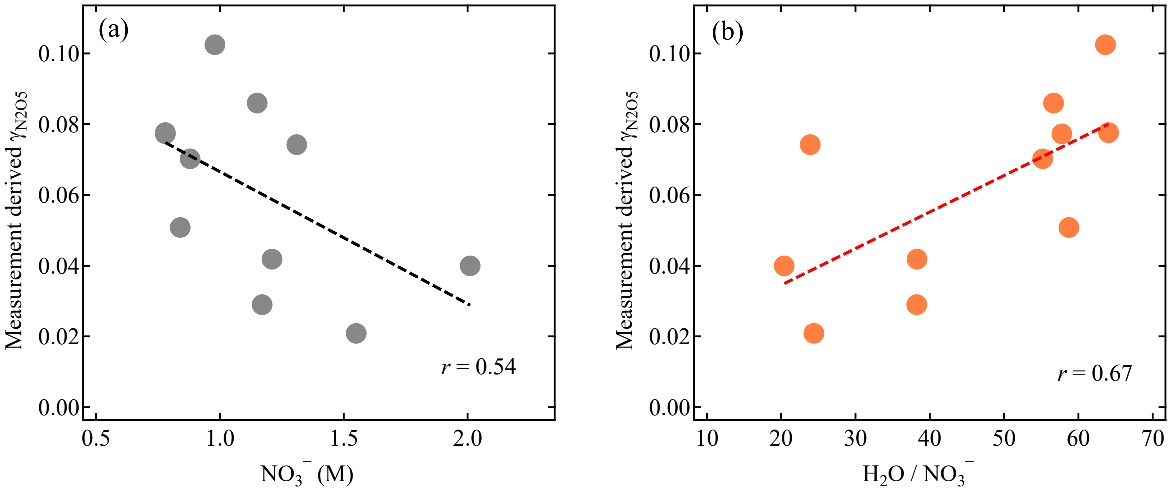


Figure S2: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol nitrate and (b) the molar ratio of aerosol water to nitrate during the study period.

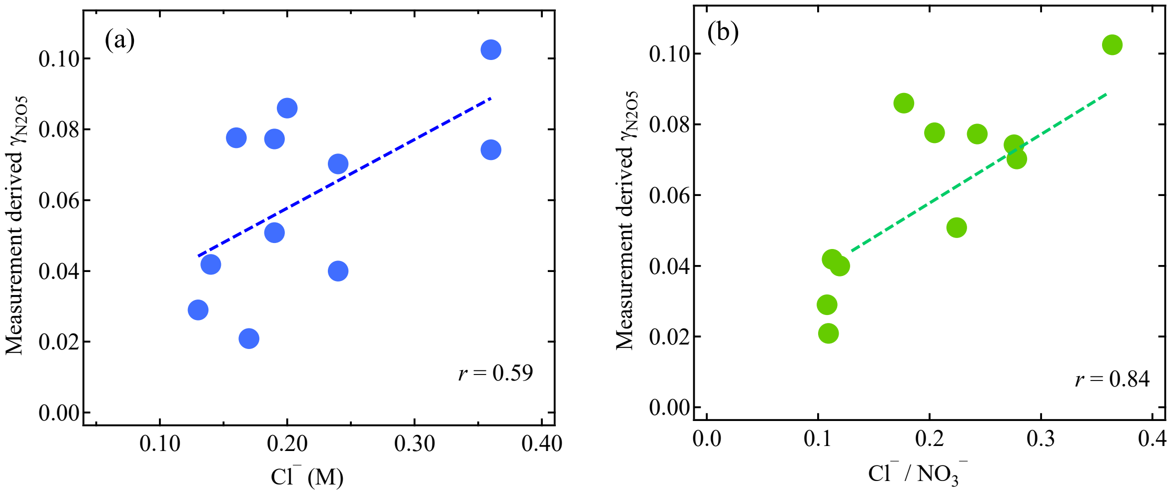


Figure S3: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol chloride and (b) the molar ratio of aerosol chloride to nitrate during the study period.

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.

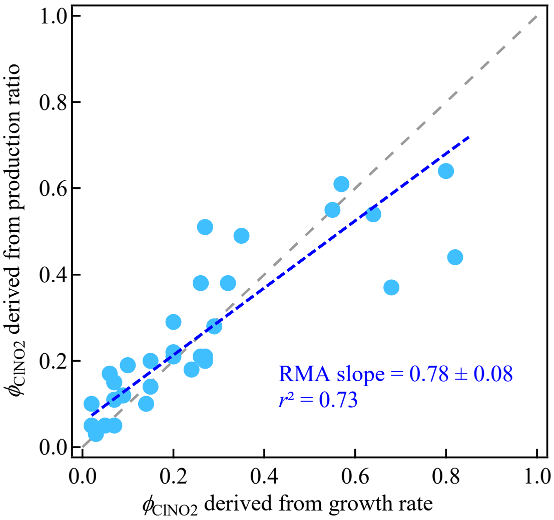


Figure S4: Comparison of estimated $ClNO_2$ yields from two different approaches: approach A using the ratio of the observed $ClNO_2$ growth rate to steady-state N_2O_5 loss rate based on Eq. 6; approach B using the production ratio of observed enhancements of $ClNO_2$ and total nitrate, $\phi = 2/(\Delta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