Anonymous Referee #1

Wang et al. report measurements of N2O5 and ClNO2 at a mountain site on the North China Plain. The data contain occasional coal power plant plumes in which ClNO2 mixing ratios were enhanced. N2O5 uptake parameters and ClNO2 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 ClNO2 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 ClNO2 production" cite Riedel, T. P., et al. (2013), 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., 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 SO₂ (>20ppbv), sulfate (>20 μ g cm⁻³) and black carbon (>5 μ g 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 semicontinuous 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 N₂O₅ into the ambient inlet was performed before and after the tubing replacement to monitor the transmission efficiency, and this practice limited the loss of N₂O₅ in the inlet to <10% in the 'clean' tubing and about 30% in the next afternoon. Manual calibrations of N₂O₅ and ClNO₂ were conducted daily to determine the instrument sensitivity, and the average of which during the

observation period was 2.0 ± 0.6 for N₂O₅ and 2.2 ± 0.6 Hz pptv⁻¹ for ClNO₂, respectively. The N₂O₅ standard was synthesized on-line from the reaction between NO₂ and O₃, and the produced N₂O₅ were determined from the decrease in NO₂ (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 ClNO₂ was produced by passing a known concentration of N₂O₅ through a NaCl slurry assuming unity conversion efficiency (Roberts et al., 2009) and negligible ClNO₂ 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 N₂O₅ and ClNO₂, respectively. The reported concentrations were derived by subtracting the background levels. The detection limit was 4 pptv for both N₂O₅ and ClNO₂ (2 σ , 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 $6.0 \pm 4.7 \ \mu g \ m^{-3}$, 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 $0.89 \pm 0.86 \ \mu g \ cm^{-3}$, 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 ClNO₂."

Date	Duration _	N ₂ O ₅ (pptv)		ClNO ₂ (pptv)		0	NO	NO _x	ΔSO_2	ΔCO	Cl⁻ (µg	<i>t</i> ,	¢ chica
		Mean	Maximum	Mean	Maximum	03	INOX	/NO _y	/∆NO _y ^a	/ ΔNO_y^b	cm ⁻³)	lplume	ψ CINO2
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 °	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	0.00-2.00	12.1	40.1	301	534	74	11.8	0.62	2 10	NA	1.88	3.0	0.20

Table 1: Chemical characteristics of coal-fired plumes exhibiting high levels of ClNO₂ observed at Mt. Tai during the summer of 2014

^a It represents the slope of SO₂ 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.

° 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 ClNO₂ yield calculation.



Figure 2 : Time series for N₂O₅, ClNO₂, 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 N₂O₅ 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 N₂O₅ in the early afternoon. Using the photostationary analysis proposed by Brown et al (2005; 2016), we also calculated the daytime steady-state concentration of N₂O₅ for cases with daytime peaks. The predicted N₂O₅ 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 N₂O₅ 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 NO₃ 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 N₂O₅, 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 N₂O₅ 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 N₂O₅ 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 NO₃ production rate (c.f. Figure S1 in the supplement). Daytime N₂O₅ 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 ClNO₂ 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 \pm 9.0 and 6.0 \pm 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 \pm 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 ClNO₂."

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 (SO₄²⁻) were observed in the plumes, with average concentrations ranging from 11.0 to 19.2 μ g m⁻³. The aerosol acidity can be roughly estimated from aerosol neutralization degree, defined as the mole concentration ratio of NH₄⁺ to (2×SO₄²⁻ +NO₃⁻). 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 NH₄⁺, Na⁺, SO₄²⁻, NO₃⁻ 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 N₂O₅ 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 ClNO₂ 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 ClNO₂ production rate and N₂O₅ loss rate, as the first term in below equation:

$$\phi = \frac{d\text{CINO}_2/dt}{k(N_2\text{O}_5)_{\text{het}}[N_2\text{O}_5]} = \frac{[\text{CINO}_2]}{\int k(N_2\text{O}_5)_{\text{het}}[N_2\text{O}_5] \, dt}$$
(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 CINO₂ can be derived from the near-linear increase in CINO₂ mixing ratio observed during a period, when the related species (e.g., NOx, SO₂) 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 CINO₂ in the air mass history. For the intercepted coal-fired plumes exhibiting sharp ClNO₂ peaks, the ClNO₂ yield can be estimated from the ratio of the observed ClNO₂ mixing ratio to the integrated N₂O₅ uptake loss over the plume age (i.e., the second term in Eq. 6). The analysis assumes that no ClNO₂ was present at the point of plume emission from the combustion sources and no ClNO₂ 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 steadystate 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 N₂O₅ measurement and NO₃ reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the ClNO₂ yield from the ratio of enhancements of ClNO₂ and total nitrate (aerosol NO_3^- + HNO₃) 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⁻/H₂O 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⁻/H₂O 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 \sim 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 N₂O₅ 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 [H₂O] 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/H₂O 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 N₂O₅ reactions, $p(NO_3^-)$, can be determined from the ClNO₂ yield and N₂O₅ heterogeneous loss rate as follows:

$$p(NO_3) = (2 - \phi)k_{N_2O_5}[N_2O_5]$$
 (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 NO₃⁻ formation could be predicted

by integrating each derived formation rate over the corresponding analysis period. Similar to N_2O_5 uptake coefficient and ClNO₂ 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 NO₃-VOC reactions. The revised text reads,

"CINO₂ mainly functions as a reservoir of NO_x, rather than as a sink, because the formation of CINO₂ throughout the night with subsequent morning photolysis recycles NO₂ (Behnke et al., 1997). The reactions of NO₃ with VOCs would predominantly produce organic nitrate products (Brown and Stutz, 2012 and references therein), but some fraction of NO₂ can be regenerated in the NO₃ 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 NO₂ from NO₃-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 NO₃ reactivity at the present study, but this assumption does not significantly affect the conclusion because NO₃ loss with VOCs was the minor path comparing to N₂O₅ 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 CINO2 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 NO₂ 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 NO₂ loss via reaction with OH at afternoon condition assuming OH concentration around 2× 10⁶ 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 N₂O₅ 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 μ g m⁻³, with a mean nocturnal formation rate of 2.2 ± 1.4 μ g 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 N₂O₅-ClNO₂ 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_{CINO2} in the y-axis of Figure 10a, and the typo was corrected in the revised figure.