

Response to interactive comment on “Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China” by Hui Yun et al. from Anonymous Referee #2

The reviewers’ comments are italicized followed by our responses and changes in manuscript shown in blue and red, respectively. And the corrections are also marked as red color in the revised manuscript.

Yun et al. present a suite of measurements related N_2O_5 formation and subsequent uptake to aerosol that take place in a semi-rural area of China. They show through interpretations of their measurements and some master chemical modeling that nocturnal NO_x chemistry can likely account nearly 50% of aerosol nitrate mass loadings during these heavy pollution events.

This paper is written and presented well for the most part. The measurement methods portion is lacking even considering that an associated reference may describe additional details. Assuming my comments are appropriately addressed and some changes are made that would help to clarify the methods and the paper in general, I would recommend publication.

Response: We appreciate the reviewer for the positive comments and helpful suggestions. The measurement method portion was rewritten and a table was added to present the detection limit and uncertainties for CIMS and other related instruments. More references were cited for details of the instruments.

Table 1. Technique, limit of detection, and uncertainty of measuring instruments for trace gases and aerosols.

Species	Measurement techniques	Uncertainty	Detection limits
CINO ₂ , N ₂ O ₅	CIMS	±25%	6 pptv
HONO	LOPAP	±20%	7 pptv
O ₃	UV photometry	±5%	0.5 ppbv
NO	Chemiluminescence	±20%	0.06 ppbv
NO ₂	Photolytical converter & Chemiluminescence	±20%	0.3 ppbv
NO _y	MoO catalytic converter & Chemiluminescence	±5%	<0.1 ppbv
SO ₂	Pulsed-UV fluorescence	±5%	0.1 ppbv
CO	IR photometry	±5%	4 ppbv
NMHCs	GC-FID/MS	±15-20%	20-300 pptv
OVOCs	DNPH-HPLC	±1-15%	20-450 pptv
PM _{2.5}	MAAP	±10%	<0.1 µg m ⁻³
Aerosol Ions	GAC-IC	±10%	0.01-0.16 µg m ⁻³
OC/EC	RT-4 SUNSET	± 4-6%	0.2 µg cm ⁻²

Comments:

Line 97: recommend changing “highest ever reported value” to something that will age better like “largest reported value to date”.

Response: Adopted.

Line 100: recommend changing “aerosol formation” to “aerosol nitrate formation”

Response: Adopted.

Line 128: the SI would be a great place to see the results of these instrument backgrounds and the extent to which they worked.

Response: We added the relevant information on CIMS.

Line 127-129: Activated carbon packed in a filter was used to determine the instrument background which was 10.2 ± 2.2 and 8.9 ± 2.0 Hz on average for N₂O₅ and CINO₂, respectively.

Line 129: “standard gas of N₂O₅” sounds like you can purchase a standard cylinder of N₂O₅ (which you can't). Even if Wang et al. 2016 outlines these calibrations in more detail, a brief explanation is needed at the minimum. The description of these calibrations needs to be expanded and include ClNO₂ calibrations as well.

Response: The part of “2.2 Chemical ionization mass spectrometer” in the manuscript was rewritten.

Line 129-134: In-situ offline calibration was carried out every day for N₂O₅ and every two days for ClNO₂ by mixing the respective synthetic standard into humidified zero air (with RH controlled at 60% in the present study). The N₂O₅ standard was generated by reacting excess NO₂ with O₃ and determined from the decrease of NO₂, and the ClNO₂ was synthesized by the uptake of a known concentration of N₂O₅ on a NaCl slurry (see Wang T et al., 2016 and Tham et al., 2016 for details).

Line 132-133: How were detection limits calculated? What signal-to-noise was used, etc.? I think the authors only mean the uncertainty is +/- 25% not the precision.

Response: The detection limit was 6 pptv for both N₂O₅ and ClNO₂. It is defined as the signal twice of noise for 1 min averaged data. The noise was the standard error of the 1-min background measurement. The uncertainty of the measurement was estimated to be ± 25 % for both N₂O₅ and ClNO₂ (Wang et al., 2016).

Wang, T., Tham, Y. J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S. C., Dubé, W. P., Blake, D. R., and Louie, P. K.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, *J. Geophys. Res. Atmos.*, 121, 2476–2489, doi: 10.1002/2015JD024556, 2016.

Line 137-138: The detection limits of N₂O₅ and ClNO₂ were both 6 pptv (2 σ , 1 min-averaged data).

Line 150-151: The uncertainty of the measurement was estimated to be ± 25 % for both N₂O₅ and ClNO₂ (Wang T et al., 2016).

Line 169: Here and throughout the paper it's probably best to change “aerosol surface

density” to “aerosol surface area density” for clarity’s sake.

Response: Adopted.

Line 182: consider changing “calculate” to “estimate”

Response: Adopted.

Line 214: change “matters” to “matter”

Response: Adopted.

Line 265/284: k' is often used for a pseudo first order rate constant. Consider using that to help differentiate from other rate constants.

Response: Adopted.

Line 307/309: make pNO_3^- and $p(NO_3^-)$ consistent. Use one or the other. $p(NO_3^-)$ is used in the rest of the paper.

Response: $p(NO_3^-)$ was used in all places of the paper.

Line 313/320 and Figure 6: Do the authors have a firm definition of what is considered “early nighttime” vs “late nighttime”? What times correspond to each period? Are these the same as provided in Table 1?

Response: The periods in the early nighttime in Fig.6 and Fig.7 correspond to the periods in Table 2 in the revised manuscript. And the periods in the later nighttime correspond to the periods in Table 3 in the revised manuscript. The captions of Fig.6 and Fig.7 have been changed to make them better understood.

Line 680-684: Figure 6. Comparison between the measured NO_3^- increase and the NO_3^- formation potential in the early nighttime (periods in Table 2: Jan 3 17:40-19:00, Jan 4 17:00-22:00, Jan 5 17:00-22:00, Jan 6 17:00-22:40, Jan 9 19:00-00:20) and in the later nighttime (periods in Table 3: Jan 3-4 21:00-05:00, Jan 5 01:30-06:50, Jan 5-6 23:40-01:10, Jan 6-7 23:00-06:00, Jan 10 01:50-03:30).

Line 686-694: Figure 7. Comparison between the daytime (7:00 to 17:00 LT, assuming all gas

phase HNO_3 partitioned into particle phase) and nighttime (17:00 to 7:00 LT of the next day) NO_3^- formation potential. The early nighttime in each day represents the periods in Table 2, including Jan 3 17:40-19:00, Jan 4 17:00-22:00, Jan 5 17:00-22:00, Jan 6 17:00-22:40, and Jan 9 19:00-00:20. The later nighttime in each day represents the periods in Table 3, including Jan 3-4 21:00-05:00, Jan 5 01:30-06:50, Jan 5-6 23:40-01:10, Jan 6-7 23:00-06:00, and Jan 10 01:50-03:30.

Line 343-345: please change " cm^{-3} " units to commonly used " molec cm^{-3} ".

Response: Adopted.

Line 359: certainly this approach is relevant to areas outside of China as well? Suggest removing "China".

Response: Adopted.

Table 1: Addition average aerosol nitrate loadings and $\text{PM}_{2.5}$ loadings for these periods would very useful. Consider adding all aerosol data (sulfate, ammonium, OM, etc.).

Response: A table for the average $\text{PM}_{2.5}$ loadings and the average concentrations of the main compositions of $\text{PM}_{2.5}$ were added into SI. We investigated the correlation between N_2O_5 uptake coefficient, ClNO_2 yield and the concentrations of aerosol compositions, and the results did not show any significant dependence of uptake coefficient/yield on any parameters.

Table S2. Average values ($\mu\text{g m}^{-3}$) of $\text{PM}_{2.5}$ loadings and the composition of $\text{PM}_{2.5}$ during the time periods corresponding to Table 2 in the revised manuscript.

Date	Cl ⁻	NO_3^-	SO_4^{2-}	NH_4^+	OM	EC	$\text{PM}_{2.5}$
Jan 3 17:40-19:00	0.9	19.7	8.8	6.5	37.4	8.0	86.4
Jan 4 17:00-22:00	1.5	44.3	8.7	12.0	44.6	13.2	150.7
Jan 5 17:00-22:00	1.6	68.9	15.5	15.3	56.6	14.2	216.6
Jan 6 17:00-22:40	2.7	40.0	15.7	13.8	54.6	10.5	174.3
Jan 9 19:00-00:20	0.8	29.9	7.2	8.9	36.7	11.6	117.3

Figure 5: Why not include the other aerosol data in this figure? NO_3^- does not track with Sa,

so what is driving up Sa? The other data should explain this.

Response: We examined the measured aerosol composition data. Similar to nitrate, sulfate and ammonium did not show large increase, while $PM_{2.5}$ levels increased, contributing to the increase in Sa_{dry} by about 30% (see figure 1 below). The 5-fold rise in Sa_{wet} was mainly due to the RH increase from ~90% to nearly 100% leading to a sharp increase in the growth factor. For the calculation of N_2O_5 uptake coefficient and $ClNO_2$ yield in the five select cases, the high Sa values under RH more than 90% were not included.

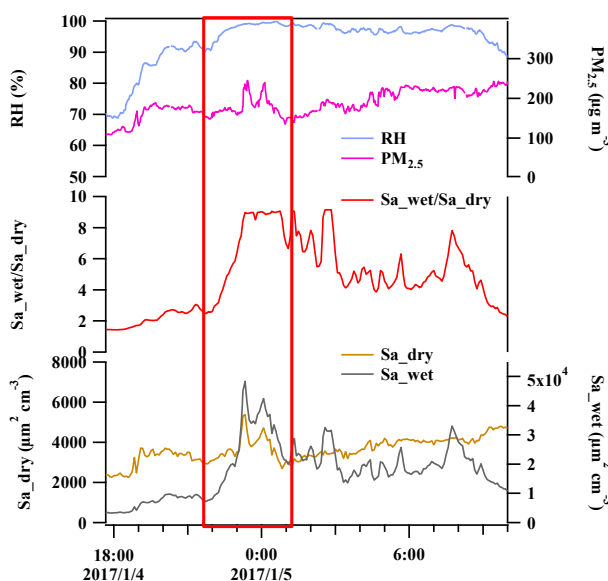


Figure 1. The variation of RH and $PM_{2.5}$ concentrations during the night of Jan 4-5 in the upper panel, the ratio of Sa_{wet}/Sa_{dry} in the middle panel, and Sa under dry conditions and the calculated Sa considering the variation of RH in the lower panel.

Have the authors considered boundary layer effects in any of their analyses? With a shallow nighttime inversion layer and little mixing many of these species could be further concentrated. Are there any measurements taken during the study that would give boundary layer information (sondes, etc.)?

Response: PBL was not measured at the site but should affect the variation of trace gas and aerosol concentration. We have added the following text in the revision.

Line 242-250: Apart from chemical reactions, the evolution of the Planetary Boundary Layer (PBL) also affects the concentrations of trace gas and aerosols. The height of PBL generally

decreases after sunset with the faster drop in temperature of land, which could lead to the accumulation of primary pollutants (and secondary pollutants) at surface if significant local sources are present. For example, on the night Jan 4-5 (see Fig 5), the CO and NO_y levels increased between 18:00-19:00 with enhancement of ClNO₂ and nitrate, indicative of accumulation of primary emissions, but afterward the primary pollutants decreased for three hours while the latter two continued to increase due to the nighttime chemical process.