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 #1

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.

The manuscript of Yun et al., reported half month measurement of N2O5, ClNO2 and other relative parameters during heavy haze episodes in Pearl River Delta (PRD) of southern China. The N2O5 uptake coefficient and ClNO2 yield were determined from the observations. The study showed the observation evidence of the enhancement of particulate nitrate in the first several hours can be fully explained by the N2O5 heterogeneous hydrolysis and even comparable with the nitric acid formed by OH+NO2 during daytime. Overall, the paper contributes to the knowledge of N2O5 heterogeneous chemistry and highlight the heterogeneous reactions in the formation of particulate nitrate in southern China. The following comments should be addressed before publishing on ACP.

Response: We appreciate the reviewer for the positive comments which are addressed in detail below.

Major comments:

The steady state assumption to derive the N2O5 uptake coefficient needs to be verified by model simulations under the observed conditions (with input from NO, NO2, O3, VOCs). It is useful to try other method (e.g. Brown et al., 2006) to derive N2O5 uptake coefficient.


Response: The method used to derive the N2O5 uptake coefficient in our manuscript did not require an assumption of NO3 radical being in steady state, but assumed that the change of
NO₃ and N₂O₅ concentrations was mainly caused by NO₃/N₂O₅ chemistry. The value of \( \frac{d([N₂O₅] + [NO₃])}{dt} \) was not required to be nearly zero as the method of Brown et al., 2006, but was calculated with the measured concentration of N₂O₅ and the calculated concentration of NO₃. We believe our method allows more data for use in analysis than the steady-state approach.

Indeed we compare our method with the steady-state approximation (Brown et al., 2006) for calculation of the \( \gamma_{N₂O₅} \) using equation (1) below. The plots of \( \tau_{N₂O₅}^{-1} K_{eq}[NO₂] \) correlated to \( 0.25c_{N₂O₅}S_{a}K_{eq}[NO₂] \) for four selected air masses in short-time periods which were proper to use the steady state assumption are presented in Figure 1 here. The \( \gamma_{N₂O₅-steady-state} \) varied from 0.008 to 0.012 and was comparable to the uptake coefficients derived with the method in the manuscript in the same periods (see Table 1 here).

(1) \( \tau_{N₂O₅}^{-1} K_{eq}[NO₂] \approx k_g + \frac{1}{4} C_{N₂O₅} S_{a} \gamma_{N₂O₅} K_{eq}[NO₂] \)

![Figure 1. Plots of \( \tau_{N₂O₅}^{-1} K_{eq}[NO₂] \) versus \( 0.25c_{N₂O₅}S_{a}K_{eq}[NO₂] \) for selected air masses.](image)
Table 1. Comparison of $\gamma_{\text{N2O5}}$ derived with steady state method and with the method in the manuscript in the same periods.

<table>
<thead>
<tr>
<th>Date</th>
<th>$\gamma_{\text{N2O5}}$-steady-state</th>
<th>$\gamma_{\text{N2O5}}$-in the manuscript</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 4 20:26-21:56</td>
<td>0.009</td>
<td>0.011</td>
</tr>
<tr>
<td>Jan 5 17:48-18:39</td>
<td>0.008</td>
<td>0.007</td>
</tr>
<tr>
<td>Jan 6 19:55-21:00</td>
<td>0.008</td>
<td>0.009</td>
</tr>
<tr>
<td>Jan 9 23:15-00:20</td>
<td>0.012</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Without the need for steady-state assumption, we can make use of more observation data to derive the updated parameters.

The uncertainty of the measured $\text{N}_2\text{O}_5$, NMHC and Sa and the overall uncertainty propagated to $\text{N}_2\text{O}_5$ uptake coefficient and CI$\text{NO}_2$ yield should be carefully evaluated and discussed. As the hygroscopic growth factor is hard to quantify for RH over 90%, the derived $\text{N}_2\text{O}_5$ uptake coefficient for those conditions may subject with larger uncertainties compared with other RH cases. This is an interesting point to be discussed.

Response: The uncertainty of the measured $\text{N}_2\text{O}_5$ and NMHC was $\pm 25\%$ and $\pm 20\%$, respectively, which will influence the item of $\frac{k_{\text{N2O5}+\text{O}_3}[\text{NO}_2][\text{O}_3]}{[\text{N}_2\text{O}_5]}$ and $\frac{\sum k_{\text{VOC}}}{[\text{NO}_2]+K_{\text{eq}}}$ in equation (2) here. According to the calculation in our manuscript, $k'_{\text{N2O5}}$ was two orders of magnitude higher than that of $\frac{\sum k_{\text{VOC}}}{[\text{NO}_2]+K_{\text{eq}}}$ suggesting the value of $\frac{k_{\text{N2O5}+\text{O}_3}[\text{NO}_2][\text{O}_3]}{[\text{N}_2\text{O}_5]}$ was far more than $\frac{\sum k_{\text{VOC}}}{[\text{NO}_2]+K_{\text{eq}}}$. Hence, the uncertainty of $\text{N}_2\text{O}_5$ uptake coefficient was mainly caused by the uncertainty of $\text{N}_2\text{O}_5$, $\text{NO}_2$ ($\pm 20\%$), $\text{O}_3$ ($\pm 5\%$) and Sa. The hygroscopic growth factor is hard to quantify for RH over 90%, thus the calculated Sa would present large uncertainty when RH reached over 90%. The average RH ranged from 59-85% during the selected periods in Table 2 in the revised manuscript. The uncertainty of Sa with RH below 90% was estimated to be around $\pm 30\%$ (Tham et al., 2016; Wang Z et al., 2017). The uncertainty of the calculated $\text{N}_2\text{O}_5$ uptake coefficient was then derived to be $\pm 45\%$. The uncertainty of CI$\text{NO}_2$ yield was mainly caused by the uncertainty of $\text{NO}_2$ ($\pm 20\%$), $\text{O}_3$ ($\pm 5\%$) and CI$\text{NO}_2$ ($\pm 25\%$) and was derived to be $\pm 30\%$. 
The relationship between $N_2O_5$ uptake coefficient, ClNO$_2$ yield and the chemical properties of particles or the meteorological data (such as RH) should be investigated, especially in the part of text around Line 572 (table 1), the reason of the high gamma value in the Jan.3 17:40-20:50 should be addressed as which was much higher than other derived value.

Response: We examined the correlation between $N_2O_5$ uptake coefficient, ClNO$_2$ yield and the concentrations of aerosol compositions or RH, and the results did not show any significant dependence of uptake coefficient/yield on these parameters. The below Table was added in the SI as Table S2.
Table 2. Average values (μg m⁻³) of PM₂.₅ loadings and the composition of PM₂.₅ during the time periods corresponding to Table 2 in the revised manuscript.

<table>
<thead>
<tr>
<th>Date</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>NH₄⁺</th>
<th>OM</th>
<th>EC</th>
<th>PM₂.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 3 17:40-19:00</td>
<td>0.9</td>
<td>19.7</td>
<td>8.8</td>
<td>6.5</td>
<td>37.4</td>
<td>8.0</td>
<td>86.4</td>
</tr>
<tr>
<td>Jan 4 17:00-22:00</td>
<td>1.5</td>
<td>44.3</td>
<td>8.7</td>
<td>12.0</td>
<td>44.6</td>
<td>13.2</td>
<td>150.7</td>
</tr>
<tr>
<td>Jan 5 17:00-22:00</td>
<td>1.6</td>
<td>68.9</td>
<td>15.5</td>
<td>15.3</td>
<td>56.6</td>
<td>14.2</td>
<td>216.6</td>
</tr>
<tr>
<td>Jan 6 17:00-22:40</td>
<td>2.7</td>
<td>40.0</td>
<td>15.7</td>
<td>13.8</td>
<td>54.6</td>
<td>10.5</td>
<td>174.3</td>
</tr>
<tr>
<td>Jan 9 19:00-00:20</td>
<td>0.8</td>
<td>29.9</td>
<td>7.2</td>
<td>8.9</td>
<td>36.7</td>
<td>11.6</td>
<td>117.3</td>
</tr>
</tbody>
</table>

Regarding the Jan 3rd case, the concentration of N₂O₅ and the Sa were both the lowest in the five cases, and the P₉₀₃ was the highest among all cases, leading to high N₂O₅ uptake coefficient. Taking a closer look at the data of that night, it can be divided into two periods with relatively high N₂O₅ of 200 pptv on average from 17:40-19:00 and low N₂O₅ of only 15 pptv on average from 19:10-20:50 (see Table 2 below and Figure 2 data in the red box). The second period was influenced more by fresh emission during the transportation of the air mass as indicated by the more variable NO₂ and O₃, making the calculation of γ₉₀₅ and ϕ₉₂₂ more difficult. In the revised manuscript, we decided to drop the second period, and the γ₉₀₅ was 0.066 (17:40-19:00) in the Jan 3 case.

Table 3. Details for the two parts of the selected period from 17:40-20:50 on the night of Jan 3, 2017.

<table>
<thead>
<tr>
<th>Date</th>
<th>N₂O₅</th>
<th>Max-ClNO₂</th>
<th>NO₂</th>
<th>O₃</th>
<th>RH</th>
<th>Sa</th>
<th>P₉₀₃</th>
<th>k₉₀₃</th>
<th>L₉₂₀₃</th>
<th>k₉₂₀₃/(Kₑq[NO₂])</th>
<th>k₉₂₀₃</th>
<th>10⁻₅ s⁻¹</th>
<th>γ₉₀₅</th>
<th>ϕ₉₂₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 3 17:40-19:00</td>
<td>200</td>
<td>1029</td>
<td>20.0</td>
<td>77.8</td>
<td>59</td>
<td>2170</td>
<td>4.3</td>
<td>0.516</td>
<td>4.3</td>
<td>3.03</td>
<td>8.8</td>
<td>0.066</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Jan 3 19:10-20:50</td>
<td>15</td>
<td>3145</td>
<td>24.7</td>
<td>59.2</td>
<td>78</td>
<td>4970</td>
<td>3.5</td>
<td>0.840</td>
<td>3.5</td>
<td>3.68</td>
<td>41.2</td>
<td>0.162</td>
<td>0.36</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2. Variation of N₂O₅, ClNO₂, NO₃⁻, trace gases and meteorological conditions during the nighttime of Jan 3 to 4, 2017.

The related texts in the original manuscript were also revised carefully. The following sentences were added.

Line 327: The data show that the uptake coefficient ranged from 0.009 to 0.066.

Line 331-335: It is interesting to see much higher $\gamma_{N_2O_5}$ (0.066) on Jan 3 than those in other four nights (0.009-0.015), resulting from higher $P_{NO_3}$ but much lower $S_a$ and relatively low $N_2O_5$ concentrations on Jan 3. We examined known factors affecting the loss of NO₃ and $N_2O_5$ such as the concentrations of NO, NMHCs and aerosol compositions, but found no obvious difference between Jan 3 and other nights.

Line 341-343: The correlation between $\gamma_{N_2O_5}$, $\phi_{ClNO_2}$ and the concentrations of aerosol compositions (see Table S2) or RH was investigated, and the results (not shown here) did not indicate any significant dependence of $\gamma_{N_2O_5}$ or $\phi_{ClNO_2}$ on these parameters.

Minor comments:

The description of the experimental setup of the key relevant parameters needs to be
strengthened, e.g. the limit of detection, the measurement uncertainties and measurement principle should be described.

Response: Table 1 with the limit of detection, the measurement uncertainties and measurement principle was added in the manuscript.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Measurement techniques</th>
<th>Uncertainty</th>
<th>Detection limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>CINO₂, N₂O₅</td>
<td>CIMS</td>
<td>±25%</td>
<td>6 pptv</td>
</tr>
<tr>
<td>HONO</td>
<td>LOPAP</td>
<td>±20%</td>
<td>7 pptv</td>
</tr>
<tr>
<td>O₃</td>
<td>UV photometry</td>
<td>±5%</td>
<td>0.5 ppbv</td>
</tr>
<tr>
<td>NO</td>
<td>Chemiluminescence</td>
<td>±20%</td>
<td>0.06 ppbv</td>
</tr>
<tr>
<td>NO₂</td>
<td>Photolytical converter &amp; Chemiluminescence</td>
<td>±20%</td>
<td>0.3 ppbv</td>
</tr>
<tr>
<td>NO₃</td>
<td>MoO catalytic converter &amp; Chemiluminescence</td>
<td>±5%</td>
<td>&lt;0.1 ppbv</td>
</tr>
<tr>
<td>SO₂</td>
<td>Pulsed-UV fluorescence</td>
<td>±5%</td>
<td>0.1 ppbv</td>
</tr>
<tr>
<td>CO</td>
<td>IR photometry</td>
<td>±5%</td>
<td>4 ppbv</td>
</tr>
<tr>
<td>NMHCs</td>
<td>GC-FID/MS</td>
<td>±15-20%</td>
<td>20-300 pptv</td>
</tr>
<tr>
<td>OVOCs</td>
<td>DNPH-HPLC</td>
<td>±1-15%</td>
<td>20-450 pptv</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>MAAP</td>
<td>±10%</td>
<td>&lt;0.1 μg m⁻³</td>
</tr>
<tr>
<td>Aerosol Ions</td>
<td>GAC-IC</td>
<td>±10%</td>
<td>0.01-0.16 μg m⁻³</td>
</tr>
<tr>
<td>OC/EC</td>
<td>RT-4 SUNSET</td>
<td>±4-6%</td>
<td>0.2 μg cm⁻²</td>
</tr>
</tbody>
</table>


Response: The suggested reference was adopted.

Line 586 (figure 2) please check the data of wind speed, as the WS keep below 3 m s⁻¹ during the whole half month. And the plot style of NO₃ made the concentration of NO₃ hard to follow. The left y-axis of fourth panel should change to PM₂.₅ or other more appropriate name.
Response: We did not find problem with the wind speed data, and the wind speed data shown in the figure was 10 min average. The very low wind speeds in the observation period were consistent with the regional meteorological conditions presented in the pressure contour in the weather chart. We also investigated the regional wind speed in PRD during this period from some websites and found that low wind speed was a regional phenomenon. Our personnel on site in fact felt little wind flow during the period. The figure below shows the wind speed (5 min average) from Dec 23, 2016 to Jan 20, 2017 at Heshan site, and the wind speed reached 7 m s\(^{-1}\) before Jan 2017. Therefore, the low wind speeds were real and conducive to the occurrence of the severe haze.

![Wind Speed Chart](image)

Figure 3. Wind speed from Dec 23, 2016 to Jan 20, 2017 at Heshan site.

The plot style of NO\(_3\), NO\(_2\) and NO was changed in the mentioned Figure. The left y-axis of fourth panel was changed to PM\(_{2.5}\).

*The legend of the early night and later night in figure 6 and 7 should be explained. By the way, how about the NO\(_3\) formation potential intercomparison in the day and night of Jan 9 to 10.*

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. So the captions of Fig.6 and Fig.7 were changed to make them better understood. The comparison of the NO\(_3\) formation potential in the day and night of Jan 9 and 10 was not conducted due to the lack of data of NMHC after Jan 8 which made the model simulation of OH infeasible on the day of Jan 9. In the caption of Fig.7, the explanation was added as follows.
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).

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. The intercomparison of the NO$_3^-$ formation potential in the day and night of Jan 9 and 10 was not conducted due to the lack of data of NMHC after Jan 8 which made the model simulation of OH infeasible on the day of Jan 9.
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.

<table>
<thead>
<tr>
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<th>Measurement techniques</th>
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<th>Detection limits</th>
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<tbody>
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<td>CIMS</td>
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<td>±20%</td>
<td>0.06 ppbv</td>
</tr>
<tr>
<td>NO₂</td>
<td>Photolytical converter &amp;</td>
<td>±20%</td>
<td>0.3 ppbv</td>
</tr>
<tr>
<td></td>
<td>Chemiluminescence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>MoO catalytic converter &amp;</td>
<td>±5%</td>
<td>&lt;0.1 ppbv</td>
</tr>
<tr>
<td></td>
<td>Chemiluminescence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Pulsed-UV fluorescence</td>
<td>±5%</td>
<td>0.1 ppbv</td>
</tr>
<tr>
<td>CO</td>
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<td>±5%</td>
<td>4 ppbv</td>
</tr>
<tr>
<td>NMHCs</td>
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<td>±15-20%</td>
<td>20-300 pptv</td>
</tr>
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<td>20-450 pptv</td>
</tr>
<tr>
<td>PM₂.₅</td>
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<td>&lt;0.1 µg m⁻³</td>
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<tr>
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<td>GAC-IC</td>
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<td>0.01-0.16 µg m⁻³</td>
</tr>
<tr>
<td>OC/EC</td>
<td>RT-4 SUNSET</td>
<td>± 4–6%</td>
<td>0.2 µg cm⁻²</td>
</tr>
</tbody>
</table>

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 ClNO₂,
respectively.

Line 129: “standard gas of N$_2$O$_5$” sounds like you can purchase a standard cylinder of N$_2$O$_5$ (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 ClNO$_2$ 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 N$_2$O$_5$ and every two days for ClNO$_2$ by mixing the respective synthetic standard into humidified zero air (with RH controlled at 60% in the present study). The N$_2$O$_5$ standard was generated by reacting excess NO$_2$ with O$_3$ and determined from the decrease of NO$_2$, and the ClNO$_2$ was synthesized by the uptake of a known concentration of N$_2$O$_5$ 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 N$_2$O$_5$ and ClNO$_2$. 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 N$_2$O$_5$ and ClNO$_2$ (Wang et al., 2016).


Line 137-138: The detection limits of N$_2$O$_5$ and ClNO$_2$ 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 N$_2$O$_5$ and ClNO$_2$ (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 HNO₃ partitioned into particle phase) and nighttime (17:00 to 7:00 LT of the next day) NO₃⁻ 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 PM₂.₅ loadings for these periods would very useful. Consider adding all aerosol data (sulfate, ammonium, OM, etc.).

Response: A table for the average PM₂.₅ loadings and the average concentrations of the main compositions of PM₂.₅ were added into SI. We investigated the correlation between N₂O₅ uptake coefficient, ClNO₂ 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 (µg m⁻³) of PM₂.₅ loadings and the composition of PM₂.₅ during the time periods corresponding to Table 2 in the revised manuscript.

<table>
<thead>
<tr>
<th>Date</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>NH₄⁺</th>
<th>OM</th>
<th>EC</th>
<th>PM₂.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 3 17:40-19:00</td>
<td>0.9</td>
<td>19.7</td>
<td>8.8</td>
<td>6.5</td>
<td>37.4</td>
<td>8.0</td>
<td>86.4</td>
</tr>
<tr>
<td>Jan 4 17:00-22:00</td>
<td>1.5</td>
<td>44.3</td>
<td>8.7</td>
<td>12.0</td>
<td>44.6</td>
<td>13.2</td>
<td>150.7</td>
</tr>
<tr>
<td>Jan 5 17:00-22:00</td>
<td>1.6</td>
<td>68.9</td>
<td>15.5</td>
<td>15.3</td>
<td>56.6</td>
<td>14.2</td>
<td>216.6</td>
</tr>
<tr>
<td>Jan 6 17:00-22:40</td>
<td>2.7</td>
<td>40.0</td>
<td>15.7</td>
<td>13.8</td>
<td>54.6</td>
<td>10.5</td>
<td>174.3</td>
</tr>
<tr>
<td>Jan 9 19:00-00:20</td>
<td>0.8</td>
<td>29.9</td>
<td>7.2</td>
<td>8.9</td>
<td>36.7</td>
<td>11.6</td>
<td>117.3</td>
</tr>
</tbody>
</table>
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$_2$O$_5$ 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\textsubscript{y} levels increased between 18:00-19:00 with enhancement of ClNO\textsubscript{2} 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.
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 #3

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.

The manuscript “Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China” by Yun and Co-authors uses observations of aerosol and gases and model results to study the contribution of heterogeneous chemistry via N$_2$O$_5$ to nitrate formation in PM$_{2.5}$ during severe winter haze episodes.

The measurements were carried out in the rural site of Heshan, located near the Perl River Delta in Southern China. In addition to a comprehensive suite of measurements, Yun and co-authors present the results of a chemical box model to estimate daytime HNO$_3$ mixing ratios. The box model was constrained by observation and its results were used to assess the importance of nighttime N$_2$O$_5$ over daytime HNO$_3$ as source of secondary aerosol nitrate.

The paper is well written, well structured and conveys results of interest for the scientific community. However, the method section (as pointed out by Referees #1 and #2 as well) has to be improved and that some more discussion on 1)uncertainties, 2)sensitivity test of the model and 3)boundary layer dynamic needs to be added before publication.

Response: The description of the measurement method has been rewritten and some related references were added. A table presenting the detection limit and uncertainties for CIMS and other related instruments was added. Sensitivity tests were conducted by reducing 10% of the input concentrations of NMHCs to check the variation of the rate of OH+NO$_2$ during the daytime. We have added discussion on the role of boundary layer dynamics.

1) The description of the measurements should include the detection limits and the uncertainties, in particular for the species that were used to constrain the chemical box model.
Response: Table 1 with detection limits and measurement uncertainties was added in the revised manuscript.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Measurement techniques</th>
<th>Uncertainty</th>
<th>Detection limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClNO&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CIMS</td>
<td>±25%</td>
<td>6 pptv</td>
</tr>
<tr>
<td>HONO</td>
<td>LOPAP</td>
<td>±20%</td>
<td>7 pptv</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>UV photometry</td>
<td>±5%</td>
<td>0.5 ppbv</td>
</tr>
<tr>
<td>NO</td>
<td>Chemiluminescence</td>
<td>±20%</td>
<td>0.06 ppbv</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Photolytical converter &amp; Chemiluminescence</td>
<td>±20%</td>
<td>0.3 ppbv</td>
</tr>
<tr>
<td>NO&lt;sub&gt;y&lt;/sub&gt;</td>
<td>MoO catalytic converter &amp; Chemiluminescence</td>
<td>±5%</td>
<td>&lt;0.1 ppbv</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Pulsed-UV fluorescence</td>
<td>±5%</td>
<td>0.1 ppbv</td>
</tr>
<tr>
<td>CO</td>
<td>IR photometry</td>
<td>±5%</td>
<td>4 ppbv</td>
</tr>
<tr>
<td>NMHCs</td>
<td>GC-FID/MS</td>
<td>±15-20%</td>
<td>20-300 pptv</td>
</tr>
<tr>
<td>OVOCs</td>
<td>DNPH-HPLC</td>
<td>±1-15%</td>
<td>20-450 pptv</td>
</tr>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>MAAP</td>
<td>±10%</td>
<td>&lt;0.1 μg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Aerosol Ions</td>
<td>GAC-IC</td>
<td>±10%</td>
<td>0.01-0.16 μg m&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>OC/EC</td>
<td>RT-4 SUNSET</td>
<td>± 4-6%</td>
<td>0.2 μg cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

2) There should be a discussion in the main text or in the SI about the sensitivity of the box model to the uncertainties of the measurements (this, for example should be communicated with uncertainty bars in figure 7).

Response: Sensitivity tests were carried out by reducing the input concentrations by 10% to check the deviation of the average daytime (7:00-17:00) rate of OH+NO<sub>2</sub> reaction. The method of Relative Increment Reactivity (RIR) was applied here as the index of the sensitivity (see the following equation). R<sub>1</sub> means the original rate of OH+NO<sub>2</sub> reaction, while R<sub>0.9</sub> means the rate of OH+NO<sub>2</sub> reaction after the input concentrations were reduced to 90%.

\[
RIR = \frac{(R_1 - R_{0.9})/R_1}{10\%}
\]

NMHCs were categorized into four groups, including C4HC, LRHC, AROM and OLF, which
represent alkanes with $\geq 4$ carbons, hydrocarbons with low reactivity (including ethane, propane and benzene), reactive aromatics (including all aromatics except for benzene), and reactive olefins (including all alkenes), respectively (Xue et al., 2014). From the following figure, the simulated rate of OH+NO$_2$ reaction was most sensitive to HONO (RIR of 0.6-0.8), followed by NO$_x$ (RIR of 0.2-0.5) and OVOCs (RIR of 0-0.2).

Figure 1. OBM-calculated RIRs to check the sensitivity of the average daytime (7:00-17:00) rate of OH+NO$_2$ reaction to the uncertainties of the measured input data.


Line 211-214: Sensitivity tests were carried out by reducing the input concentrations by 10% to check the deviation of the average daytime (7:00-17:00) rate of OH+NO$_2$ reaction. The simulated rate of OH+NO$_2$ reaction was most sensitive to HONO, followed by NO$_x$ and OVOCs (see Text. S1 and Fig. S2).

3) In paragraph 2.2 a discussion about interference for species with the same nominal mass as I(N$_2$O$_5$)$^-$ and I(ClNO$_2$)$^-$ should be added. How much contribution from other species would Yun and Co-authors expect? If it was not negligible how would change the results from the box model/comparison?

Response: To the best of our knowledge, no interference was reported for I(N$_2$O$_5$)$^-$ at 235 m/z in current publications. Besides, we compared ambient measurements of N$_2$O$_5$ using the...
quadrupole CIMS and NOAA-CRDS in 2016 (Wang et al., 2016), and N$_2$O$_5$ measured by CIMS and CRDS matched well with each other (slope=0.99, R$^2$=0.93). Recent ambient measurement of ClNO$_2$ in Beijing with a ToF-CIMS showed that I(HNO$_3$)(H$_2$O)$^-$ may cause ~10% interference of CINO$_2$ at 208 m/z (Breton et al., 2018), but this kind of interference cannot be resolved by a quadrupole CIMS. For the quadrupole CIMS, we checked the correlation between the measured signal at 208 m/z (t$^{35}$ClNO$_2$) and at 210 m/z (t$^{37}$ClNO$_2$) during the present field campaign. The slope (0.317, R$^2$ = 0.99) was very close to the theoretical value of chlorine isotopic ratio of 0.32. Overall, we do not expect large (>10%) interference to CINO$_2$, and no known interference is known to the N$_2$O$_5$ signal.


4) **Relative humidity (RH) is known to affect measurements carried out with I-CIMS. Was the inlet used in this study humidified? Was the RH controlled/monitored during zero measurements? How could the zero affect the box model results (e.g., over/under estimation of N$_2$O$_5$/ClNO$_2$)? What are the biases that the 6 m sampling line could generate in their results?**

Response: Similar to our previous practice, the effect of RH on the sensitivity of N$_2$O$_5$ and ClNO$_2$ was measured by altering the RH in calibration during the present campaign (see below figure). The sensitivity of N$_2$O$_5$ and ClNO$_2$ in ambient measurement was corrected based on the RH monitored in real-time in the CIMS inlet.
The sensitivity of CIMS as a function of RH for (a) N$_2$O$_5$ at 235 m/z and (b) ClNO$_2$ at 208 m/z at Heshan site.

The inlet in this study was not humidified. Since the sampling period in this study was humid enough (RH>40%) to form the reagent I(H$_2$O)$^-$, a humidified inlet was not necessary.

The RH was not controlled but monitored during zero (and ambient) measurements.

The zero signals were subtracted from the total signals during data processing, thus they do not affect final data and thus modeling results.

The 6 m sampling tubing was replaced every day in late afternoon. The wall loss of N$_2$O$_5$ was measured by injecting synthetic N$_2$O$_5$ each time before and after replacing the sampling tubing. The measured wall loss of N$_2$O$_5$ was ~10% for the clean tubing and increased to ~40% after one day’s sampling. Because our analysis mainly focused on data in the first few hours of evening, the loss was insignificant and thus was not corrected in our final data. However, this bias can be important at later period before tube replacement.

In the revised manuscript, we have added description on dependence of sensitivity on RH and how to correct it and also the above figure as Fig. S1. We also added the following sentences.

Line 134-137: The average sensitivity of N$_2$O$_5$ and ClNO$_2$ was 0.9±0.3 and 0.7±0.2 Hz pptv$^{-1}$, respectively. The dependence of the sensitivity on the relative humidity was measured during the field study (see Fig. S1) which was used to correct for the RH effect based on the measured ambient RH values.

Line 145-150: The loss of N$_2$O$_5$ on the tubing wall was checked on site by injecting N$_2$O$_5$ into
the ambient air before and after the tubing replacement, and the loss was around 10% in the “clean” tubing and increased to nearly 40% in the next afternoon. Because our analysis mainly focused on data in the first few hours of evening, the loss was insignificant and thus was not corrected in our final data. However, this bias can be important at later period before tube replacement.

5) The boundary layer plays a significant role in the time evolution of the concentrations of nitrate in the particle. Yun and Co-authors make little to no mention of its role. For example, one might expect that particulate nitrate would increase also in the early morning hours due to the contribution of the residual layer during the mixing. This doesn’t seem to happen in the observations presented in this work. May the Authors discuss why that would be the case?

Response: This point was also raised by other referees. The description of boundary layer dynamics has been added in the revised version. The absence of nitrate increase in the early morning in our study is consistent with previous observations at the site (Yue et al., 2015). It may be explained by enhanced evaporation of NH$_4$NO$_3$ to HNO$_3$ and NH$_3$ due to increased temperature.


6) An increase in particulate nitrate concentrations (as well as PM$_{2.5}$) could also be due to a dilution effect (same magnitude of aerosol sources but reduced volume in which the aerosols are mixed). I recommend adding a few sentences explaining how the mixing of the residual layer in the morning hours could affect the results presented here.

Response: The following discussion was added in the manuscript.

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.
Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China

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Abstract: Nitrate (NO₃⁻) has become a major component of fine particulate matter (PM₂.5) during hazy days in China. However, the role of the heterogeneous reactions of dinitrogen pentoxide (N₂O₅) in nitrate formation is not well constrained. In January 2017, a severe haze event occurred in the Pearl River Delta (PRD) of southern China during which high levels of PM₂.5 (~400 µg m⁻³) and O₃ (~160 ppbv) were observed at a semi-rural site (Heshan) in the western PRD. Nitrate concentrations were up to 108 µg m⁻³ (1 h time resolution), and the contribution of nitrate to PM₂.5 reached nearly 40%. Concurrent increases in NO₃⁻ and ClNO₂ (with a maximum value of 8.3 ppbv in 1 min time resolution) were observed in the first several hours after sunset, indicating an intense N₂O₅ heterogeneous uptake on aerosols. The formation potential of NO₃⁻ via N₂O₅ heterogeneous reactions was estimated to be 29.0 to 77.3 µg m⁻³ in the early hours (2 to 6 h) after sunset based on the measurement data, which could completely explain the measured increase in the NO₃⁻ concentration during the same time period. Daytime production of nitric acid from the gas-phase reaction of OH + NO₂ was calculated with a chemical box model built using the Master Chemical Mechanism (MCM v3.3.1) and constrained by the measurement data. The integrated nocturnal nitrate formed via N₂O₅ chemistry was comparable to or even higher than the nitric acid formed during the daytime. This study confirms that N₂O₅ heterogeneous chemistry was a significant source of aerosol nitrate during hazy days in southern China.

Keywords: N₂O₅, ClNO₂, nitrate, Pearl River Delta, southern China
1 Introduction

Severe haze in China has been a major concern of the regulatory and scientific communities in recent years. Nitrate was identified as an important component of PM$_{2.5}$ during hazy days in both summer and winter (e.g., Huang et al., 2014; Li et al., 2018; Pathak et al., 2009; Zhang et al., 2015). Moreover, the proportion of nitrate in PM$_{2.5}$ has increased steadily in the last decade due to the lagged control of NO$_x$ emissions compared to SO$_2$ (Fu et al., 2014; Geng et al., 2017; Qu et al., 2017; Reuter et al., 2014; Wang X et al., 2016). As a result, the concentrations of nitrate in PM$_{2.5}$/PM$_{1.0}$ were even higher than those of sulfate during some haze events (Ge et al., 2017; Li et al., 2017; Liu et al., 2015; Yang et al., 2017; Yue et al., 2015).

Nitrate is formed from NO$_x$ in both the daytime and nighttime. During the day, nitric acid (HNO$_3$) is produced through the gas-phase reaction between OH and NO$_2$ (R1), and this pathway is insignificant at night due to very low OH concentrations (e.g., Seinfeld and Pandis, 2016). The nitric acid can react with ammonia (NH$_3$) to form ammonium nitrate (NH$_4$NO$_3$), and an equilibrium can be reached for these three compounds between the gas phase and the particle phase (R2-3). In the nighttime, heterogeneous uptake of N$_2$O$_5$, which is formed from the reactions involving O$_3$, NO$_2$ and NO$_3$, becomes a source of nitrate and also produces gaseous ClNO$_2$ when chloride-containing aerosol is present (R4-7) (Finlayson-Pitts et al., 1989). This nitrate formation pathway is important only at night due to the fast photolysis of NO$_3$ during the day. Compared to the relatively well-understood formation of aerosol nitrate via the OH + NO$_2$ reaction, the contribution from N$_2$O$_5$ heterogeneous reactions has been poorly quantified due to the limited knowledge of key factors controlling the heterogeneous processes, such as the N$_2$O$_5$ uptake coefficient ($\gamma_{N2O5}$) and ClNO$_2$ yield ($\phi_{ClNO2}$) (Brown and Stutz, 2012; Chang et al., 2011).

(R1) OH + NO$_2$ + M $\rightarrow$ HNO$_3$ + M

(R2) HNO$_3$ (g) + NH$_3$ (g) $\leftrightarrow$ NH$_4$NO$_3$ (s)

(R3) HNO$_3$ (g) + NH$_3$ (g) $\leftrightarrow$ NH$_4^+$ (aq) + NO$_3^-$ (aq)

(R4) NO$_2$ + O$_3$ $\rightarrow$ NO$_3$
(R5) $\text{NO}_2 + \text{NO}_3 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M}$

(R6) $\text{NO}_3 + \text{VOCs} \rightarrow \text{products}$

(R7) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \text{ or } \text{Cl}^- (\text{aq}) \rightarrow (2\phi) \text{NO}_3^- (\text{aq}) + \phi \text{ClNO}_2 (\text{g})$

Model studies initially treated $\gamma_{\text{N}_2\text{O}_5}$ as a constant (0.03 to 0.1) (Dentener and Crutzen, 1993; Makar et al., 1998; Munger et al., 1998; Schaap et al., 2004; Wen et al., 2015; Xue et al., 2014), and later utilized several parameterization schemes of $\gamma_{\text{N}_2\text{O}_5}$ and $\phi_{\text{ClNO}_2}$ based on the laboratory investigations of their dependence on aerosol compositions and aerosol water content (Anttila et al., 2006; Bertram and Thornton, 2009; Davis et al., 2008; Evans and Jacob, 2005; Riemer et al., 2009; Riemer et al., 2003; Roberts et al., 2009). However, recent studies found a significant discrepancy between the field-derived and parameterized $\gamma_{\text{N}_2\text{O}_5}$ and $\phi_{\text{ClNO}_2}$ (McDuffie et al., 2018; Phillips et al., 2016; Tham et al., 2018; Wang X et al., 2017; Wang Z et al., 2017; Zhou et al., 2018). These findings suggest that $\text{N}_2\text{O}_5$ uptake is more complicated than previously thought and a better understanding of the uptake process is needed to improve the prediction of nitrate and haze.

In addition to the modeling approach, field measurements of trace gases and aerosol composition have been used to infer the contribution of $\text{N}_2\text{O}_5$ heterogeneous chemistry to nitrate formation. Pathak et al. (2009) postulated the importance of $\text{N}_2\text{O}_5$ heterogeneous reactions to the high aerosol nitrate observed in summertime in Beijing and Shanghai by examining the variation of nitrate with the change in relative humidity (RH) and the equilibrium between anions and cations in PM$_{2.5}$. Pathak et al. (2011) further investigated nitrate formation using a coupled aqueous phase radical mechanism (CAPRAM) and a gas-phase chemistry mechanism (RACM, without ClNO$_2$ chemistry). By constraining the uptake coefficient of $\text{N}_2\text{O}_5$ in the range of 0.001 to 0.1, they reproduced the observed enhancement of nitrate and suggested that $\text{N}_2\text{O}_5$ uptake in aerosols contributed to 50 to 100% of the nighttime increase in nitrate. A similar method was used recently by Wen et al. (2018) to simulate the summertime nitrate formation in the North China Plain (NCP), which demonstrated the dominant contribution of $\text{N}_2\text{O}_5$ heterogeneous reactions to nighttime nitrate formation. Based on the observed covariation of nitrate and RH, Wang et al. (2009)
speculated that N$_2$O$_5$ reactions dominated the nitrate formation on polluted days with high NO$_2$ and O$_3$ in Shanghai. Neither N$_2$O$_5$ nor ClNO$_2$ was measured during these early observation-based studies. A recent study (Wang H et al., 2017) inferred $\gamma_{N_2O_5}$ from the measured N$_2$O$_5$ on four days in urban Beijing and estimated the lower limit of the formation potential of aerosol nitrate assuming a unity $\phi_{ClNO_2}$ because ClNO$_2$ was not measured. Their result showed a comparable contribution to nitrate formation from the N$_2$O$_5$ heterogeneous chemistry as from the daytime pathway of the OH + NO$_2$ reaction.

In the present study, N$_2$O$_5$, ClNO$_2$, the related chemical and meteorological parameters were measured at a semi-rural site in the Pearl River Delta of southern China from Jan 2 to Jan 15, 2017. A severe haze event was observed during the field study with PM$_{2.5}$ reaching 400 $\mu$g m$^{-3}$ and O$_3$ up to 160 ppbv. ClNO$_2$, which is only known to be produced from N$_2$O$_5$ heterogeneous uptake, reached up to 8.3 ppbv, which is the largest reported value to date and revealed extremely active N$_2$O$_5$ chemistry during the episode. The concurrent measurements of N$_2$O$_5$, ClNO$_2$ and aerosol nitrate provide better constraints for elucidating nighttime NO$_3$/N$_2$O$_5$ chemistry and aerosol nitrate formation. An overview of the measurement data was first presented. The nighttime processes that led to the formation of nitrate (e.g., production of NO$_3$ and N$_2$O$_5$, N$_2$O$_5$ uptake coefficient, ClNO$_2$ yield) were analyzed. The nighttime formation potential of nitrate was estimated based on these data and compared to the measured increase in nitrate. The daytime production of nitric acid via the OH + NO$_2$ reaction was calculated based on a box model using the Master Chemical Mechanism (MCM v3.3.1) and compared to the nighttime formation potential of nitrate.

2 Methods

2.1 Site description

The field observation was conducted at the Guangdong Atmospheric Supersite, a semi-rural site located at Hua Guo Shan (HGS, 22.728°N, 112.929°E) in the southwest of the city of Heshan from Jan 2 to Jan 15, 2017. As shown in Fig. 1, HGS is a hill with a height of 60 m above sea level. All measurement instruments were located on the 4th floor of a four-story building on the top of the hill. The observation site was located in the western PRD where the
economic activity and population density are much less compared to central PRD. There are five main roads near the HGS site, including three national roads (G325, G94 and G15), and two provincial roads (S272 and S270). The hill is covered by subtropical trees and surrounded by similar hills within close range, and a few residents live at the foot of the hill with some farmland in the area.

2.2 Chemical ionization mass spectrometer

\( \text{N}_2\text{O}_5 \) and ClNO\(_2\) were simultaneously observed using a quadrupole chemical ionization mass spectrometer (CIMS, THS Instruments, Atlanta). The same instrument had been used in several previous studies in southern and northern China (Tham et al., 2016; Wang T et al., 2016; Wang Z et al., 2017). The reader can refer to these earlier papers for detailed description of the measurement principle, calibration, and maintenance procedures. Briefly, ambient \( \text{N}_2\text{O}_5 \) and ClNO\(_2\) are converted to ion clusters of \( \text{I} (\text{N}_2\text{O}_5)^- \) and \( \text{I} (\text{ClNO}_2) \) by Iodide ions (I\(^-\)) produced by exposing CH\(_3\)I/N\(_2\) (0.3%v/v) to an alpha radioactive source, 210-Po, and are subsequently detected at 235 and 208 m/z, respectively. 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 \( \text{N}_2\text{O}_5 \) and ClNO\(_2\), respectively. In-situ offline calibration was carried out every day for \( \text{N}_2\text{O}_5 \) and every two days for ClNO\(_2\) by mixing the respective synthetic standard into humidified zero air (with RH controlled at 60% in the present study). The \( \text{N}_2\text{O}_5 \) standard was generated by reacting excess NO\(_2\) with O\(_3\) and determined from the decrease of NO\(_2\), and the ClNO\(_2\) was synthesized by the uptake of a known concentration of \( \text{N}_2\text{O}_5 \) on a NaCl slurry (see Wang T et al., 2016 and Tham et al., 2016 for details). The average sensitivity of \( \text{N}_2\text{O}_5 \) and ClNO\(_2\) was 0.9 ± 0.3 and 0.7 ± 0.2 Hz pptv\(^{-1}\), respectively. The dependence of the sensitivity on the relative humidity was measured during the field study (see Fig. S1) which was used to correct for the RH effect based on the measured ambient RH values. The detection limits of \( \text{N}_2\text{O}_5 \) and ClNO\(_2\) were both 6 pptv (2 σ, 1 min-averaged data).

The inlet of the CIMS instrument was set approximately 1.5 m above the roof with 6 m long PFA-Teflon tubing as the sampling line. The total sampling flow was set as 11 standard liters per minute (SLPM). Four SLPM were diverted into the CIMS, O\(_3\) and NO\(_x\) analyzer, and the remaining part was evacuated directly from the system. The total residence time was less than
1 s in the sampling system. Following our previous practice, the inlet tubing and fittings were replaced every afternoon and washed with an ultrasonic bath to reduce the influence of the tubing wall adhered with deposited particles. The loss of N$_2$O$_5$ on the tubing wall was checked on site by injecting N$_2$O$_5$ into the ambient air before and after the tubing replacement, and the loss was around 10% in the “clean” tubing and increased to nearly 40% in the next afternoon. Because our analysis mainly focused on data in the first few hours of evening, the loss was insignificant and thus was not corrected in our final data. However, this bias can be important at later period before tube replacement. The uncertainty of the measurement was estimated to be ± 25 % for both N$_2$O$_5$ and CINO$_2$ (Wang T et al., 2016). The time resolution for the measurement was approximately 10 s, and the derived data were later averaged to a time resolution of 1 min for further analysis.

2.3 Other measurements

Trace gases of CO, SO$_2$, O$_3$, NO$_x$, total reactive nitrogen (NO$_y$), nitrous acid (HONO), C2 to C10 non-methane hydrocarbons (NMHCs), oxygenated hydrocarbons (OVOCs), and aerosol chemical composition and number concentrations were also measured. Table 1 summarized the principle, detection limit and uncertainty of the measuring instruments.

CO was observed using a gas filter correlation analyzer (Thermo Model 48i). SO$_2$ was measured using a pulsed fluorescence analyzer (Thermo Model 43i). O$_3$ was determined using a UV photometric analyzer (Thermo, Model 49i). NO and NO$_2$ were detected with a chemiluminescence instrument (Thermo, Model 42i) with a photolytic converter to convert NO$_2$ to NO (Xu et al., 2013). NO$_y$ was determined using a chemiluminescence analyzer which was equipped with a molybdenum oxide (MoO) catalytic converter (Thermo, Model 42i-Y). HONO was detected using a long path absorption photometer (QUMA, Model LOPAP-03) (Xu et al., 2015). NMHCs were determined using an online gas chromatograph (GC) coupled with a flame ionization detector (FID) and a mass spectrometer (MS) (Wang et al., 2014). NMHCs were only measured from Jan 2 to Jan 8, 2017 due to the maintenance of the GCMS after Jan 8. OVOCs (e.g., formaldehyde, acetaldehyde, acetone, methyl ethyl ketone) were sampled with 2,4-dinitrophenylhydrazine (DNPH) cartridges every 3 h and were later analyzed with a high-performance liquid chromatography (HPLC) system (Cui et al., 2016).
Concentrations of PM$_{2.5}$ were detected with a multi-angle absorption photometer (MAAP, Thermo Model 5012). The ionic compositions of PM$_{2.5}$ were measured with an ion chromatography (GAC-IC) system equipped with a gas and aerosol collector at a time resolution of 30 min (Dong et al., 2012), and the data were also averaged every 1 h to meet the time resolution of other components of PM$_{2.5}$. Organic carbon (OC) and elemental carbon (EC) were measured with an online OC/EC analyzer (RT-4, SUNSET) with a time resolution of 1 h (Bauer et al., 2009). A scanning mobility particle sizer (SMPS Model 3936L75, TSI) was used to determine the dry-state particle number size distribution, covering the size range from 16.5 to 1000 nm. The ambient (wet) particle number size distributions were estimated based on a size-resolved kappa-Köhler function considering the variation with the relative humidity (Hennig et al., 2005; Liu et al., 2014). In the present study, data with RH greater than 90% were excluded because large uncertainty of the growth factor at very high RH. The aerosol surface area density was then derived using the ambient particle number size distribution (wet) and an assumption of spherical particles with an estimated uncertainty of around 30% (Tham et al., 2016; Wang Z et al., 2017).

Meteorological parameters were measured with a portable weather station (Model WXT520, Vaisala, Finland), including temperature, relative humidity (RH), wind direction, wind speed, and pressure. A pyranometer (CMP22, Kipp & Zonen B.V., Holland) was used to measure the solar radiation and the data were then utilized to derive the photolysis frequency of NO$_2$ based on the method of Trebs et al. (2009).

### 2.4 Chemical box model

To estimate the daytime formation of nitric acid via the reaction of OH + NO$_2$, an observation-based chemical box model developed with the latest version of the Master Chemical Mechanism v3.3.1 (Jenkin et al., 2003; Jenkin et al., 2015; Saunders et al., 2003) and an updated chlorine (Cl) radical chemistry module (Xue et al., 2015) was utilized to estimate the mixing ratio of OH radicals and the reaction rate of OH + NO$_2$. The integrated production of nitric acid during the daytime was then calculated based on the simulation results. The box model was constrained with the observation data every 10 min, including the data of N$_2$O$_5$, CINO$_2$, HONO, O$_3$, NO, NO$_2$, SO$_2$, CO, C2 to C10 NMHCs, OVOCs
(formaldehyde, acetaldehyde, acetone, and MEK), temperature, aerosol surface area density and $J(\text{NO}_2)$, which were first averaged or interpolated. Average concentrations of NMHC species during the daytime (7:00 to 17:00) and nighttime (17:00 to 7:00 of the next day) are shown in Table S1. A function considering the variation of the solar zenith angle (Saunders et al., 2003) was used to calculate the photolysis frequencies of HONO, $\text{O}_3$ and other species in clear sky, which were then corrected with the $J(\text{NO}_2)$ values in the real environment. The $J(\text{ClNO}_2)$ was treated the same as in Tham et al. (2016). The lifetime of unconstrained species respect to the physical loss was set as 8 h in a boundary layer of 1000 m depth (equivalent to $3.47 \times 10^{-5} \text{s}^{-1}$) in order to avoid their accumulation. The model was run from 0:00 of Jan 3 to 11:00 of Jan 8, 2017. To stabilize the intermediate species, the simulation for the first 24 h was repeated six times. Sensitivity tests were carried out by reducing the input concentrations by 10% to check the deviation of the average daytime (7:00-17:00) rate of OH+NO$_2$ reaction. The simulated rate of OH+NO$_2$ reaction was most sensitive to HONO, followed by NO$_x$ and OVOCs (see Text S1 and Fig. S2).

3 Results and discussion

3.1 Overview of the observation

Figure 2 shows the time series of N$_2$O$_5$, ClNO$_2$, components of PM$_{2.5}$, related trace gases and meteorological parameters from 18:40 of Jan 2 to 11:00 of Jan 15, 2017. The average temperature and RH during the measurement period were $17 \pm 4 \degree \text{C}$ and $86 \pm 14\%$, respectively. A severe pollution episode occurred on Jan 3 to 7 due to stagnant meteorological conditions (Fig. 3 (a)), and the concentrations of most pollutants decreased to very low levels on Jan 9 and Jan 12 to 15, which corresponded to the change in weather conditions. The most polluted days were Jan 5 and 6 with the highest PM$_{2.5}$ of 400 $\mu$g m$^{-3}$ and the highest O$_3$ of 160 ppbv. The PM$_{2.5}$ data from the PRD regional air quality monitoring network revealed that the HGS site was within the most polluted area during this haze event (Fig. 3(b)). This pollution event was characterized by concurrent high levels of PM$_{2.5}$ and O$_3$ and was in contrast to the winter haze in north China, which experienced high PM$_{2.5}$ but low O$_3$ (e.g., Sun et al., 2016; Wang H et al., 2018a). The mixing ratios of N$_2$O$_5$ and ClNO$_2$ were up to 3358 pptv and 8324 pptv (1 min time resolution), respectively, indicating active N$_2$O$_5$ heterogeneous chemistry.
Very high concentrations of aerosol nitrate (up to 108 μg m$^{-3}$, 1 h time resolution) were also observed during the multi-day episode. Nitrate contributed to 24% of the total PM$_{2.5}$ mass concentration on average, which was comparable to that of organic matter (OM = 1.7*OC, 28%) and much higher than that of sulfate (16%) and ammonium (11%). The contribution of nitrate to the PM$_{2.5}$ increased with an increase in nitrate concentration, and reached nearly 40% at its highest nitrate level, indicating that nitrate was a dominant component of the PM$_{2.5}$ on the most polluted days. The concentration of NO$_3^-$ exhibited a concurrent increase with that of ClNO$_2$ in the early nighttime on Jan 3 to 4, Jan 4 to 5, Jan 5 to 6 and Jan 9 to 10 (see Fig. 4), suggesting that N$_2$O$_5$ heterogeneous reactions significantly contributed to the formation of nitrate during the nighttime. The measured increases of the NO$_3^-$ concentration during these four nights were 17.1, 50.9, 43.3 and 32.7 μg m$^{-3}$, respectively. A similar increase in ClNO$_2$ was observed on Jan 6 to 7, but the composition of the PM$_{2.5}$ was not available due to instrument maintenance. 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$_x$ levels increased between 18:00-19:00 with enhancement of ClNO$_2$ 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.

In the remainder of this manuscript, we will focus on the detailed analysis of above-mentioned five nights to investigate the role of N$_2$O$_5$ heterogeneous chemistry in nitrate formation.

3.2 N$_2$O$_5$ heterogeneous chemistry on the selected nights

3.2.1 Production of NO$_3^-$ and N$_2$O$_5$

The first step in the nighttime nitrate formation via N$_2$O$_5$ chemistry is the production of NO$_3^-$ and N$_2$O$_5$. To get insight into the key factors affecting the NO$_3$/$N_2O_5$ chemistry, the variation
of N$_2$O$_5$ and production rate of NO$_3$ were examined with some relevant gases and meteorological parameters of the five nights. Fig. 5 shows the data of the night of Jan 4 to 5 as an example. Some common features were identified for all five nights. In general, low wind speed (< 2.0 m s$^{-1}$) at night facilitated the accumulation of air pollutants, and high RH was favorable for N$_2$O$_5$ heterogeneous uptake. In addition, high aerosol surface area density provided interfaces for N$_2$O$_5$ heterogeneous reactions.

In the first couple of hours after sunset (Fig 5, red rectangle), N$_2$O$_5$ exhibited a peak and quickly dropped to hundreds of pptv, while nitrate and ClNO$_2$ concurrently increased, which was indicative of the local production and loss of N$_2$O$_5$. NO was below the detection limit during this period. The production rates of NO$_3$ ($P_{NO_3} = k_{NO_2 + O_3}[NO_2][O_3]$) were the fastest just after sunset and decreased gradually due to reduced O$_3$ levels. There was a period later in the night (22:00 to 01:00) when fresh emissions of NO were observed, and the production of NO$_3$ was suppressed due to the titration of O$_3$ by NO. In the later nighttime, NO was below the detection limit (Fig. 5, blue rectangle). During this period, NO$_3$ and N$_2$O$_5$ were produced at moderate rates, and the very low N$_2$O$_5$ concentrations (below the detection limit) suggested a fast loss of N$_2$O$_5$ probably leading to the local production of ClNO$_2$ and nitrate, which was not revealed in the observed variations of ClNO$_2$ and nitrate. The concentrations of ClNO$_2$ and nitrate during this period fluctuated due to the change in the air masses indicated by the change in SO$_2$ concentrations and wind speeds.

### 3.2.2 N$_2$O$_5$ uptake coefficient and ClNO$_2$ yield

The N$_2$O$_5$ uptake coefficient and ClNO$_2$ yield, together with the reactivity of NO$_3$ with NO and VOCs, determines the loss pathways of NO$_3$ and N$_2$O$_5$. To derive the uptake coefficient of N$_2$O$_5$, a method suggested by McLaren et al. (2010) was applied by treating NO$_3$ and N$_2$O$_5$ as a whole ([NO$_3$] + [N$_2$O$_5$]) without assuming the chemical system in the steady state. This approach considers that the change of NO$_3$ and N$_2$O$_5$ concentrations is mainly due to NO$_3$/N$_2$O$_5$ chemistry, and thus it requires that the air mass have relatively stable chemical conditions and not be subject to fresh NO emissions. It also requires that ClNO$_2$ is produced from the N$_2$O$_5$ chemistry and has an increasing trend to derive the yield of ClNO$_2$. This method is applicable for the early nighttime (red rectangle, section 3.2.1) for these five nights.
The variation rate of $[\text{NO}_3^-] + [\text{N}_2\text{O}_5]$ can be calculated by deducting the production rate of $[\text{NO}_3^-] + [\text{N}_2\text{O}_5]$ with its loss rate as Eq. (1):

$$\frac{d([\text{N}_2\text{O}_5] + [\text{NO}_3^-])}{dt} = P_{\text{NO}_3^-} - L_{\text{N}_2\text{O}_5}$$

The loss of $[\text{NO}_3^-] + [\text{N}_2\text{O}_5]$ is through the NO$_3^-$ reaction with VOCs and N$_2$O$_5$ heterogeneous reactions, which can both be expressed as pseudo first order losses as Eq. (2):

$$L_{\text{N}_2\text{O}_5} + \text{NO}_3^- = L_{\text{NO}_3^-} + L_{\text{N}_2\text{O}_5} = k_{\text{NO}_3^-}[\text{NO}_3^-] + k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5]$$

where $k_{\text{NO}_3^-}$ and $k_{\text{N}_2\text{O}_5}$ represent the total first order rate constants for NO$_3^-$ and N$_2$O$_5$, respectively. The loss rate of N$_2$O$_5$ can then be obtained from Eq. (3):

$$L_{\text{N}_2\text{O}_5} = k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] = k_{\text{NO}_2 + \text{O}_3} [\text{NO}_2][\text{O}_3] - \frac{d[\text{N}_2\text{O}_5]}{dt} - \frac{d[\text{NO}_3^-]}{dt} - k_{\text{NO}_3^-}[\text{NO}_3^-]$$

Because NO$_3^-$ was not measured, it was calculated by assuming an equilibrium of NO$_2$-NO$_3$-N$_2$O$_5$ as shown in Eq. (4). High levels of NO would break this equilibrium. Thus, the periods with detected NO were excluded. $d[\text{NO}_3^-]/dt$ and $d[\text{N}_2\text{O}_5]/dt$ were calculated as the rate of change of NO$_3^-$ and N$_2$O$_5$ in a time resolution of 10 min. $k_{\text{NO}_3^-}$ was derived with the measured concentrations of NMHCs as Eq. (5) by interpolating the data of NMHCs to 10 min time resolution. The NO$_3^-$ reactivity with VOCs ($k_{\text{NO}_3^-}'$) in the early nighttime ranged from 0.516 to 1.54$\times 10^{-3}$ s$^{-1}$ (Table 2), which was higher than those derived at Mt. TMS in winter 2013 (0.17 to 1.1$\times 10^{-3}$ s$^{-1}$) (Brown et al., 2016), but lower than those in the North China Plain during the summertime (2 to 57$\times 10^{-3}$ s$^{-1}$) (Tham et al., 2016; Wang H et al., 2017, 2018b; Wang Z et al., 2017). NMHCs were not measured on Jan 9 to 10, 2017. We used the average $k_{\text{NO}_3^-}'$ in the early nighttime on Jan 3 to 4 as a replacement because these two periods had similar pollution levels for most pollutants. For the later nighttime (Fig. 5, blue rectangle), low levels of N$_2$O$_5$ and moderate levels of $P_{\text{NO}_3^-}$ also made Eq. (3) inapplicable even though NO was not detected.

$$[\text{NO}_3^-] = \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2]^2 \times K_{\text{eq}}}

(5)\quad k_{\text{NO}_3^-}' = \sum k_i[\text{VOC}_i]$$
Finally, the uptake coefficient of \( \text{N}_2\text{O}_5 \) was derived using Eq. (6) for every 10 min and averaged for the whole selected periods. In Eq. (6), \( C_{\text{N}_2\text{O}_5} \) is the mean molecular speed of \( \text{N}_2\text{O}_5 \), and \( S_a \) is the aerosol surface area density. The yield of ClNO\(_2\) was derived from Eq. (7) by dividing the integrated production of ClNO\(_2\) ([ClNO\(_2\)]\text{max}) to the integrated loss of \( \text{N}_2\text{O}_5 \) since sunset.

\[
(6) \quad k'_{\text{N}_2\text{O}_5} = \frac{I_{\text{N}_2\text{O}_5}}{[\text{N}_2\text{O}_5]} = \frac{1}{4} C_{\text{N}_2\text{O}_5} S_a \gamma_{\text{N}_2\text{O}_5}
\]

\[
(7) \quad \phi = \frac{[\text{ClNO}_2]_{\text{max}}}{\int I_{\text{N}_2\text{O}_5} \, dt}
\]

The relative importance of NO\(_3\) reactions with VOCs and \( \text{N}_2\text{O}_5 \) heterogeneous reactions can be examined by comparing the values of the loss coefficient of NO\(_3\) reactions (\( \frac{k_{\text{NO}_3}}{[\text{NO}_2] \times K_{\text{eq}}} \)) and \( \text{N}_2\text{O}_5 \) heterogeneous reactions (\( k'_{\text{N}_2\text{O}_5} \)) (Tham et al., 2016). Based on the calculations, the values of \( \frac{k_{\text{NO}_3}}{[\text{NO}_2] \times K_{\text{eq}}} \) were \( 1.40 \times 10^{-5} \) to \( 6.07 \times 10^{-5} \) s\(^{-1}\) (see Table 2), while that of \( k'_{\text{N}_2\text{O}_5} \) were \( 3.78 \times 10^{-3} \) to \( 9.00 \times 10^{-3} \) s\(^{-1}\), which was two orders of magnitude higher than that of \( \frac{k_{\text{NO}_3}}{[\text{NO}_2] \times K_{\text{eq}}} \), suggesting that \( \text{N}_2\text{O}_5 \) heterogeneous reactions were the dominant loss pathway of NO\(_3\) and \( \text{N}_2\text{O}_5 \).

The average \( \gamma_{\text{N}_2\text{O}_5} \) and \( \phi_{\text{ClNO}_2} \) derived for the early night of the five cases are listed in Table 2. The data show that the uptake coefficient ranged from 0.009 to 0.066, which was comparable to the previous values derived at Mt. Tai Mo Shan (TMS) in Hong Kong (0.004 to 0.022) (Brown et al., 2016) and in the North China Plain (0.006 to 0.102) (Tham et al., 2018; Tham et al., 2016; Wang H et al., 2017, 2018b; Wang X et al., 2017; Wang Z et al., 2017; Zhou et al., 2018). It is interesting to see much higher \( \gamma_{\text{N}_2\text{O}_5} \) (0.066) on Jan 3 than those in other four nights (0.009-0.015), resulting from higher \( P_{\text{NO}_3} \) but much lower \( S_a \) and relatively low \( \text{N}_2\text{O}_5 \) concentrations on Jan 3. We examined known factors affecting the loss of NO\(_3\) and \( \text{N}_2\text{O}_5 \) such as the concentrations of NO, NMHCs and aerosol compositions, but found no obvious difference between Jan 3 and other nights. The yield in this study varied from 0.18 to 0.32, which was similar to most studies in China (Tham et al., 2018; Tham et al., 2016; Wang Z et al., 2017; Yun et al., 2018; Zhou et al., 2018).
The uncertainty of the above $\gamma_{N_2O_5}$ was estimated to be $\pm 45\%$ due to the measurement uncertainty of $N_2O_5$ ($\pm 25\%$), $NO_2$ ($\pm 20\%$), $O_3$ ($\pm 5\%$) and $Sa$ ($\pm 30\%$). The uncertainty of $\phi_{ClNO_2}$ was mainly caused by the uncertainty of $NO_2$ ($\pm 20\%$), $O_3$ ($\pm 5\%$) and $ClNO_2$ ($\pm 25\%$) and was estimated to be $\pm 30\%$. The correlation between $\gamma_{N_2O_5}$, $\phi_{ClNO_2}$ and the concentrations of aerosol compositions (see Table S2) or RH was investigated, and the results (not shown here) did not indicate any significant dependence of $\gamma_{N_2O_5}$ or $\phi_{ClNO_2}$ on these parameters.

3.3 Nitrate formation potential $p(NO_3^-)$ through $N_2O_5$ chemistry

3.3.1 Nighttime $p(NO_3^-)$

The formation potential of $NO_3^-$ through $N_2O_5$ chemistry is the total amount of $NO_3^-$ accumulated from $N_2O_5$ heterogeneous loss. It can be calculated by deducting the integrated loss of $N_2O_5$ with the integrated production of $ClNO_2$ as Eq. (8).

$$p(NO_3^-) = (2-\phi) \int L_{N_2O_5} dt = 2 \int L_{N_2O_5} dt - [ClNO_2]_{max}$$

In the early nighttime, the average loss rate of $N_2O_5$ ($L_{N_2O_5}$) ranged from 1.9 to 4.3 ppbv h$^{-1}$ (Table 2), which was close to the average $P_{NO_3}$ due to the dominance of the $N_2O_5$ heterogeneous reactions in $NO_3$ and $N_2O_5$ loss. Based on the derived $N_2O_5$ loss rate and the maximum $ClNO_2$ concentration, the formation potential of $NO_3^-$ was derived and ranged from 29.0 to 77.3 $\mu g$ m$^{-3}$ as shown in Fig. 6. The measured increase of the $NO_3^-$ concentration in the early nighttime can be completely explained by the integrated production of $NO_3^-$ via the $N_2O_5$ heterogeneous reactions during the same period.

In the later nighttime, the method described in section 3.2.2 was not valid for calculating the $N_2O_5$ heterogeneous loss rate as mentioned above. We attempted to estimate the formation potential of nitrate by assuming that the $N_2O_5$ heterogeneous reactions continued to dominate the loss of $NO_3 + N_2O_5$ in the later nighttime. The $k_{NO_3}$ in the later nighttime were comparable to those in the early nighttime, and the high RH close to 100% in the later nighttime was favorable for the $N_2O_5$ heterogeneous reactions. We assumed that all $NO_3$ was quickly consumed by the $N_2O_5$ heterogeneous reactions, which means that the loss rate of $N_2O_5$ approximated to the production rate of $NO_3$ ($L_{N_2O_5} \approx P_{NO_3}$). As listed in Table 3, the $N_2O_5$ loss
rates ranged from 0.82 to 1.26 ppbv h\(^{-1}\), which were significantly lower than those derived in the early nighttime. The derived N\(_2\)O\(_5\) loss rate here and the yield of ClNO\(_2\) in the early nighttime were used to estimate the formation potential of NO\(_3^-\) in the later nighttime. As shown in Fig. 6, the nitrate produced during these later periods ranged from 7.3 to 40.3 μg m\(^{-3}\), which was lower than those in the early nighttime for four nights, indicating that the nighttime nitrate from N\(_2\)O\(_5\) chemistry was mainly produced in the early nighttime.

3.3.2 Comparison with daytime production of HNO\(_3\)

During the daytime, the formation of NO\(_3^-\) is mainly from the gas-particle partitioning of the gas phase HNO\(_3\) formed through the OH + NO\(_2\) reaction. Hence, the daytime formation potential of HNO\(_3\) (p(HNO\(_3\))) can be treated as the upper limit for the locally-produced daytime aerosol nitrate. To calculate the daytime p(HNO\(_3\)), a box model based on MCM v3.3.1 was used to derive the mixing ratio of OH and the rates of OH + NO\(_2\) as described in section 2.4. This model was previously used in our study at Wangdu in North China (Tham et al., 2016). The calculated mixing ratios of OH at Wangdu with this model compared well with those observed by the laser-induced fluorescence (LIF) technique (Tan et al., 2017). In the present study, the average daytime OH (7:00 to 17:00) mixing ratios were 1.71 to 3.82×10\(^6\) molec cm\(^{-3}\) during Jan 3 to 7 as listed in Table 4 with the maximum values reaching 3.24 to 6.71×10\(^6\) molec cm\(^{-3}\). The detailed results for OH can be found in Fig. S3.

The average production rates of HNO\(_3\) through the OH + NO\(_2\) reaction were 1.40 to 5.21 ppbv h\(^{-1}\) from Jan 3 to Jan 7, and the integrated formation potential of HNO\(_3\) during the daytime was 35.7 to 131.8 μg m\(^{-3}\), which was comparable to the nighttime p(NO\(_3^-\)) ranging from 69.3 to 102.9 μg m\(^{-3}\) (Fig. 7). Nighttime production of nitrate via the heterogeneous uptake of N\(_2\)O\(_5\) accounted for 43.8\% to 57.7\% of the total nitrate (NO\(_3^-\) + HNO\(_3\)) produced in a 24 h period at the site. These results underscored the important role of N\(_2\)O\(_5\) heterogeneous chemistry in nitrate formation in this severe winter haze in southern China.

4 Concluding remarks

With the use of concurrent measurements of nitrate, ClNO\(_2\) and related pollutants, this study demonstrates the important contribution of N\(_2\)O\(_5\) heterogeneous uptake in nitrate formation.
Current chemical transport models have difficulties in simulating this nitrate production pathway. Therefore, more research efforts are needed to improve the representations of $\gamma_{\text{NO}_3}$ and $\phi_{\text{ClNO}_2}$ for better prediction of nitrate in the models. The observation-based approach presented here can be applied to investigate nitrate formation in other areas.

5 Data availability

The data used in this study are available upon request from Tao Wang (cetwang@polyu.edu.hk) and Dingli Yue (dingliyue@163.com).

Author contributions

TW designed the research; WW conducted CIMS measurement; YZ, DY, HY, MX, CY and PS performed the measurements of other parameters used in this study; HY, TW, MX and WW analyzed the data; HY and TW wrote the manuscript. All authors contributed to discussion and commented on the manuscript.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Measurement techniques</th>
<th>Uncertainty</th>
<th>Detection limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClNO₂, N₂O₅</td>
<td>CIMS</td>
<td>±25%</td>
<td>6 pptv</td>
</tr>
<tr>
<td>HONO</td>
<td>LOPAP</td>
<td>±20%</td>
<td>7 pptv</td>
</tr>
<tr>
<td>O₃</td>
<td>UV photometry</td>
<td>±5%</td>
<td>0.5 ppbv</td>
</tr>
<tr>
<td>NO</td>
<td>Chemiluminescence</td>
<td>±20%</td>
<td>0.06 ppbv</td>
</tr>
<tr>
<td>NO₂</td>
<td>Photolytical converter &amp; Chemiluminescence</td>
<td>±20%</td>
<td>0.3 ppbv</td>
</tr>
<tr>
<td>NO₃</td>
<td>MoO catalytic converter &amp; Chemiluminescence</td>
<td>±5%</td>
<td>&lt;0.1 ppbv</td>
</tr>
<tr>
<td>SO₂</td>
<td>Pulsed-UV fluorescence</td>
<td>±5%</td>
<td>0.1 ppbv</td>
</tr>
<tr>
<td>CO</td>
<td>IR photometry</td>
<td>±5%</td>
<td>4 ppbv</td>
</tr>
<tr>
<td>NMHCs</td>
<td>GC-FID/MS</td>
<td>±15-20%</td>
<td>20-300 pptv</td>
</tr>
<tr>
<td>OVOCs</td>
<td>DNPH-HPLC</td>
<td>±1-15%</td>
<td>20-450 pptv</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>MAAP</td>
<td>±10%</td>
<td>&lt;0.1 µg m⁻³</td>
</tr>
<tr>
<td>Aerosol Ions</td>
<td>GAC-IC</td>
<td>±10%</td>
<td>0.01-0.16 µg m⁻³</td>
</tr>
<tr>
<td>OC/EC</td>
<td>RT-4 SUNSET</td>
<td>± 4-6%</td>
<td>0.2 µg cm⁻²</td>
</tr>
</tbody>
</table>

Table 2. Average values of N₂O₅ concentrations, N₂O₅ uptake coefficients, ClNO₂ yields and other related parameters and maximum values of ClNO₂ concentrations in the early nighttime for five selected nights.

<table>
<thead>
<tr>
<th>Date</th>
<th>N₂O₅ Max-ClNO₂</th>
<th>NO₂</th>
<th>O₃</th>
<th>RH</th>
<th>Sa</th>
<th>P₉₅₀</th>
<th>kₙ₉₅₀</th>
<th>L₉₅₀</th>
<th>kₙ₉₅₀/(Keq[N₉₅₀])</th>
<th>kₙ₉₅₀/₅₅₅</th>
<th>T₉₅₀</th>
<th>δClNO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan.3 17:40-19:00</td>
<td>200</td>
<td>1029</td>
<td>20</td>
<td>78</td>
<td>59</td>
<td>2170</td>
<td>4.3</td>
<td>0.516</td>
<td>4.3</td>
<td>3.03</td>
<td>8.81</td>
<td>0.066</td>
</tr>
<tr>
<td>Jan 4 17:00-22:00</td>
<td>700</td>
<td>4608</td>
<td>24</td>
<td>61</td>
<td>82</td>
<td>6452</td>
<td>3.3</td>
<td>1.54</td>
<td>3.2</td>
<td>6.07</td>
<td>4.16</td>
<td>0.009</td>
</tr>
<tr>
<td>Jan 5 17:00-22:00</td>
<td>338</td>
<td>4828</td>
<td>18</td>
<td>73</td>
<td>81</td>
<td>8399</td>
<td>3.4</td>
<td>0.790</td>
<td>3.3</td>
<td>4.06</td>
<td>9.00</td>
<td>0.015</td>
</tr>
<tr>
<td>Jan 6 17:00-22:40</td>
<td>326</td>
<td>2908</td>
<td>13</td>
<td>82</td>
<td>77</td>
<td>5092</td>
<td>2.8</td>
<td>0.677</td>
<td>2.6</td>
<td>4.95</td>
<td>3.78</td>
<td>0.013</td>
</tr>
<tr>
<td>Jan 9 19:00-00:20</td>
<td>121</td>
<td>2553</td>
<td>19</td>
<td>41</td>
<td>85</td>
<td>5173</td>
<td>1.9</td>
<td>0.516</td>
<td>1.9</td>
<td>1.40</td>
<td>4.28</td>
<td>0.015</td>
</tr>
</tbody>
</table>
Table 3. Average values of N$_2$O$_5$ loss rate and related parameters for selected periods in the later nighttime.

<table>
<thead>
<tr>
<th>Date</th>
<th>NO$_2$ ppbv</th>
<th>O$_3$ ppbv</th>
<th>P$_{NO3}$ ppbv h$^{-1}$</th>
<th>k'$_{NO3}$ 10$^{-3}$ s$^{-1}$</th>
<th>L$_{N2O5}$ ppbv h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 3-4 21:00-05:00</td>
<td>20.8</td>
<td>20.7</td>
<td>1.00</td>
<td>0.684</td>
<td>1.00</td>
</tr>
<tr>
<td>Jan 5 01:30-06:50</td>
<td>22.4</td>
<td>19.5</td>
<td>0.96</td>
<td>1.45</td>
<td>0.96</td>
</tr>
<tr>
<td>Jan 5-6 23:40-01:10</td>
<td>21.1</td>
<td>25.5</td>
<td>1.26</td>
<td>1.13</td>
<td>1.26</td>
</tr>
<tr>
<td>Jan 6-7 23:00-06:00</td>
<td>22.1</td>
<td>14.4</td>
<td>0.82</td>
<td>0.709</td>
<td>0.82</td>
</tr>
<tr>
<td>Jan 10 01:50-03:30</td>
<td>24.8</td>
<td>15.6</td>
<td>0.90</td>
<td>/</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 4. Average OH mixing ratio and rate of OH + NO$_2$ during the daytime (7:00 to 17:00 LT) from Jan 3 to Jan 7, 2017.

<table>
<thead>
<tr>
<th>Date</th>
<th>OH (molec cm$^{-3}$)</th>
<th>NO$_2$ (ppbv)</th>
<th>OH + NO$_2$ (ppbv h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 3</td>
<td>2.18×10$^6$</td>
<td>36.2</td>
<td>3.49</td>
</tr>
<tr>
<td>Jan 4</td>
<td>2.47×10$^6$</td>
<td>23.6</td>
<td>2.60</td>
</tr>
<tr>
<td>Jan 5</td>
<td>2.62×10$^6$</td>
<td>30.8</td>
<td>3.09</td>
</tr>
<tr>
<td>Jan 6</td>
<td>3.82×10$^6$</td>
<td>31.5</td>
<td>5.21</td>
</tr>
<tr>
<td>Jan 7</td>
<td>1.71×10$^6$</td>
<td>18.4</td>
<td>1.40</td>
</tr>
</tbody>
</table>
Figure 1. (a) Google map images of the Pearl River Delta in the Guangdong Province and measurement site (Hua Guo Shan). (b) The topography and major roads (shown by number) adjacent to the measurement site.

Figure 2. Time series of $N_2O_5$, ClNO$_2$, components of PM$_{2.5}$, related trace gases and meteorological parameters from 18:40 of Jan 2 to 11:00 of Jan 15, 2017. The inserted figure shows the variation of the ratio of nitrate to PM$_{2.5}$ with increasing nitrate concentration. The green rectangles in the figure indicate the five days used for detailed analysis.
Figure 3. (a) Surface weather chart at 08:00 LT on Jan 6, 2017 downloaded from the website of the Hong Kong Observatory indicating stagnant conditions. (b) The distribution of PM$_{2.5}$ concentrations in the PRD region at 09:00 LT on Jan 6, 2017. This figure was captured from the website. http://113.108.142.147:20031/GDPublish/publish.aspx.

Figure 4. The covariance of aerosol nitrate and ClNO$_2$ in the early nighttime (in 30 min time resolution) for four nights.
Figure 5. Variation of $\text{N}_2\text{O}_5$, ClNO$_2$, NO$_3^-$, trace gases and meteorological conditions during the nighttime of Jan 4 to 5, 2017 as an example for the five selected nights.

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).
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. The intercomparison of the NO$_3^-$ formation potential in the day and night of Jan 9 and 10 was not conducted due to the lack of data of NMHC after Jan 8 which made the model simulation of OH infeasible on the day of Jan 9.