Response to reviewers’ comments

Thanks to the reviewers for giving us very useful comments to improve our manuscript entitled “Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation in Beijing, China” (acp-2018-1270). Detailed responses to reviewers’ comment are listed below:

Reviewer #1

Comment 1: Qiu et al. further developed a widely-used regional chemical transport model, CMAQ, to include several heterogeneous reactions related to chlorine species and applied the revised model in Beijing to estimate the effect of these heterogeneous reactions on the formation of nitrate aerosol in the summertime. The paper is generally well written and has the potential to contribute to the growing body of the studies on tropospheric halogen chemistry and its impact on air quality. However, there are several major issues and some minor comments that should be addressed before it can be accepted for the publication in Atmospheric Chemistry and Physics.

Response #1: Thanks for the positive comments on this manuscript. The suggestions are addressed in detail in the following.

Comment 2: One of the major concerns is that the authors omitted several important papers related to chlorine and nitrogen chemistry, e.g., Brown and Stutz (2012), Osthoff et al. (2008), Sarwar et al. (2012), and Sarwar et al. (2014). These papers should be included in Section 1 (Introduction and Research background), in Section 2.2 (model development), or Section 3.3 and 3.4 (model results and discussion). See the specific comments below.

Response #2: We have included these important literatures in our revised manuscript, please see the detailed description in Response below.

Comment 3: The second major issue is that the current manuscript does not include any information related to NO₂, O₃, and PM₂.₅, which are the precursors of N₂O₅, ClNO₂, and nitrate. No emission of these pollutants is described. No model evaluation. No simulation results. Without this information, it is difficult to assess the model performance and therefore the outcome of the simulation.

Response #3: Emissions of conventional species, including SO₂, NOₓ, VOCs, PM2.5 and PM10 for anthropogenic sectors for this study period has been developed using tools developed in our group and the method has been described in previous studies (Wang et al., 2014). For this study period, emissions are generated using the same system with updated input data for activities, controls, emission factors and speciation factors for 2017. More details of the emission processing processes are documented by Ding et al. (under review). A summary of the annual emissions in Beijing in 2017 based
on Ding et al. is included in Table S1 in the revised manuscript.

Evaluations of predicted O₃, NO₂ and PM₂.₅ concentrations are now described in the revised manuscript on page 34, lines 325-328: “Predicted O₃, NO₂ and PM₂.₅ concentrations from the BASE case simulation are evaluated against monitoring data at 12 monitoring sites in Beijing (Table S2) for 11 to 15 June 2017. The average NMB/NME values for O₃, NO₂ and PM₂.₅ across the 12 sites are -8%/29%, -7%/59% and -8%/53%, respectively.”. Table S2 is attached below as Table R1 for the convenience of the reviewer.

Table R1 Comparison of simulated episode average hourly NO₂ and PM₂.₅ and O₃ concentrations with observations averaged from 11 to 15 June 2017 (Obs.: observation, Sim.: simulation). Units: µg m⁻³

<table>
<thead>
<tr>
<th>Sites</th>
<th>Obs. Sim. NMB</th>
<th>Obs. Sim. NME</th>
<th>Obs. Sim. NMB</th>
<th>Obs. Sim. NME</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSXG</td>
<td>49 54 11% 55%</td>
<td>99 122 23% 31%</td>
<td>40 38 -6% 53%</td>
<td></td>
</tr>
<tr>
<td>DL</td>
<td>21 17 -20% 68%</td>
<td>111 108 -2% 12%</td>
<td>32 29 -10% 52%</td>
<td></td>
</tr>
<tr>
<td>DS</td>
<td>47 53 13% 54%</td>
<td>100 114 15% 28%</td>
<td>44 41 -7% 53%</td>
<td></td>
</tr>
<tr>
<td>TT</td>
<td>40 48 20% 64%</td>
<td>98 130 33% 45%</td>
<td>37 37 1% 58%</td>
<td></td>
</tr>
<tr>
<td>NZG</td>
<td>51 66 28% 62%</td>
<td>111 121 9% 25%</td>
<td>42 39 -7% 52%</td>
<td></td>
</tr>
<tr>
<td>GY</td>
<td>55 65 17% 57%</td>
<td>107 116 9% 22%</td>
<td>36 33 -8% 54%</td>
<td></td>
</tr>
<tr>
<td>WL</td>
<td>52 41 -21% 54%</td>
<td>92 112 22% 43%</td>
<td>35 33 -7% 54%</td>
<td></td>
</tr>
<tr>
<td>XC</td>
<td>43 31 -28% 47%</td>
<td>100 108 8% 12%</td>
<td>33 29 -12% 55%</td>
<td></td>
</tr>
<tr>
<td>HR</td>
<td>26 11 -56% 70%</td>
<td>124 105 -15% 27%</td>
<td>27 22 -19% 51%</td>
<td></td>
</tr>
<tr>
<td>CP</td>
<td>42 28 -34% 58%</td>
<td>96 91 -5% 27%</td>
<td>33 32 -1% 54%</td>
<td></td>
</tr>
<tr>
<td>ATZX</td>
<td>56 62 10% 55%</td>
<td>105 107 1% 18%</td>
<td>33 31 -4% 54%</td>
<td></td>
</tr>
<tr>
<td>GC</td>
<td>56 42 -25% 58%</td>
<td>106 107 0% 19%</td>
<td>43 37 -14% 52%</td>
<td></td>
</tr>
</tbody>
</table>


Comment #4: The last main problem is that there are too many errors and typos throughout the manuscript, e.g., citing the improper reference, citing the reference that is not in the reference list, the reference list is not organized according to the alphabet, wrong spelling, etc. Please refer to the technical comments. I suggest that the authors carefully read through and thoroughly revise their manuscript.

Response #4: We revise these errors following the reviewer’s comments below and fixed errors and typos throughout the manuscript as much as we can.

Comment #5: Line 26-28. These descriptions are redundant to line 33-36.

Response #5: Thank you for pointing out the redundant descriptions. The sentences
“The results show that these heterogeneous reactions significant increase the atmospheric Cl\textsubscript{2} and ClNO\textsubscript{2} level, leading to an increase of the nitrate concentration by \textasciitilde10\% in the daytime. However, these reactions also lead to a decrease the nocturnal nitrate by \textasciitilde20\%.” in line 25-26 are revised as “The results show that these heterogeneous reactions increase the atmospheric Cl\textsubscript{2} and ClNO\textsubscript{2} level (\textasciitilde100\%), which further affect the nitrate formation”

**Comment #6**: Line 37-39. The CINO\textsubscript{2} production decreases nitrate during nighttime and increases nitrate during the daytime. Does it mean that the chlorine chemistry changes the temporal pattern of the nitrate formation and therefore the spatial pattern? Does it have any implication to the air quality control? I would love to see a discussion on this implication.

**Response #6**: While it is true that temporal pattern of nitrate formation was slightly altered, the spatial patterns of nitrate didn’t change significantly during the study period. However, as the CINO\textsubscript{2} production from the heterogeneous reaction leads to less N\textsubscript{2}O\textsubscript{5} conversion to non-relative nitrate, it may change the overall lifetime of NOx and their transport distances. The magnitude of this change and its implications on ozone and PM2.5 locally and in the downwind areas should be further studied. We included this in the revised manuscript on page 38, lines 473-477.

**Comment #7**: Line 50-57. The authors only introduced two production pathways of the secondary nitrate. However, the other pathways, e.g., those in Table 2, also play non-negligible roles. Should add those pathways in the introduction.

**Response #7**: The other gaseous reactions such as NO\textsubscript{3} + HO\textsubscript{2}, VOC + NO\textsubscript{3}, and N\textsubscript{2}O\textsubscript{5} with water vapor are generally negligible in terms of secondary nitrate formation in polluted urban and rural areas, due to low concentrations of NO\textsubscript{3} and HO\textsubscript{2}, and low yield of HNO\textsubscript{3} in the VOC + NO\textsubscript{3} reactions. We included them in Table 2 for completeness but we don’t think they should be specifically mentioned in the introduction section. The heterogeneous reaction of NO\textsubscript{2} could be important so we included a sentence in the revised manuscript to mention that:

“The heterogeneous reaction of NO\textsubscript{2} on particle surface has been shown to be an important source of secondary nitrate” (Abbatt et al., 1998).

**Comment #8**: A reference is needed for the enhancement effect of NH\textsubscript{3}-NH\textsubscript{4}\textsuperscript{+} gas-particle equilibrium on the nitrate formation.

**Response #8**: The reference below are added.


Comment #9: Line 57. These papers are not the proper reference for the nitrate formation mechanism, e.g., Brown and Stutz (2012) is a better one for the N₂O₅ (NO₃) chemistry.

Response #9: Revised.

Comment #10: Line 63-72. The authors only introduced three previous works here, and all of them were conducted in China, in the Northern China Plain to be exact. What about similar modeling studies in other regions, e.g., the southern part of China, Northern America, and Europe? For example, Sarwar et al. (2012, 2014) developed the same model, CMAQ, to evaluate the effect of ClNO₂ production on air quality, including the total nitrate, in the US and the Northern Hemisphere. However, these two critical papers are not discussed anywhere in the current manuscript.

Response #10: Thanks for your comments. As this is not a review paper, our intention is to include the most relevant studies in this region. We included some discussion of Sarwar et al. (2012, 2014) as requested on page40, lines 537-543.

Comment #11: Line 73, This statement might be true, but the authors did not provide any evidence/reference to support it.

Response #11: This sentence is removed.

Comment #12: Line 77-80. This statement is not correct. For example, Wang et al. (2016) and Brown et al. (2016) reported extremely high N₂O₅ mixing ratios at a site in Hong Kong (a coastal city) of up to 8ppbv (1min average) or 12ppbv (1min average). This brings up another issue. Should include the average time when reporting observational results, e.g., 1 s average, 1 min average, or 1h average.

Response #12: High concentrations of N₂O₅ in Hong Kong is likely affected by non-local emissions from city clusters in the Pearl River Delta (PRD) region during some high pollution episodes. We remove the relative clause, “which were significantly higher than those in unpolluted coastal cities and the lower atmosphere in the remote Arctic region.” in the revised manuscript. We agree with the reviewer that it is necessary to point out the averaging time when describing the concentrations and they are included in the revised manuscript.

The sentences in Line 77-80 are revised as “According to the field measurements in June 2017 in Beijing (Zhou et al., 2018), the 2-min averaged concentrations of reactive Cl₂ and ClNO₂ reached up to 1000 pptv and 1200 pptv, respectively, during some severe
air pollution period in summer. The corresponding concentrations of N$_2$O$_5$ and nitrate reached as high as 700 pptv (2 min average) and 5 μg m$^{-3}$ (5 min average) from about 40 pptv and 1 μg m$^{-3}$.

Comment #13: Line 79-80. There is no Li et al. (2017) in the reference list. Are you referring to Li et al. (2016)? That is not a proper reference here, because that paper is a modeling study that used the measurement results from Wang et al. (2016).

Response #13: Sorry for my carelessness. As the reviewer described, Li et al. (2017) should be Li et al. (2016). We revise it throughout the whole manuscript and here we remove it.

Comment #14: Line 82. These references are not the right ones here. The first measurements of ClNO$_2$ in the real atmosphere, Osthoff et al. (2008) and Thornton et al. (2010), are better ones.

Response #14: Revised.

Comment #15: Line 102. This is not entirely true. For instance, Hossaini et al. (2016) developed a global chemical transport model (TOMCAT) and included several heterogeneous reactions of chlorine species on chloride-containing aerosol.

Response #15: The reviewer might misread the sentence. We did include the fact that some models have some heterogeneous reactions by saying that “generally missing” and “in most” CTMs. No changes were made regarding this comment.

Comment #16: Line 107-111. I assume the replacement is only in Beijing city but not in the surrounding areas. Is that correct?

Response #16: Yes, replacing coal with natural gas only occurred in Beijing. Reduction of coal consumption in surrounding regions was less than 15% for most other provinces and cities and there were no strict control measures for biomass burning (except Hebei), cooking and municipal solid waste incineration yet. Thus, the Cl emissions estimated for 2014 by Fu et al. (2018) were used for other areas. This is explained in the revised manuscript on page 30, lines 223-228.

Comment #17: Line 117-118. This sentence is a bit out-of-blue. The following sentence makes more sense to me.

“Thus, it is important to compile an updated emission inventory for Beijing (and its surrounding areas) to include the emissions from cooking and other sources (coal burning, solid waste burning, biomass burning, etc.).”

Response #17: Thanks for your constructive comment. This sentence is revised to read “Thus, it is necessary to compile an updated emission inventory for Beijing to include
the emissions from cooking and other sources (coal burning, solid waste burning, biomass burning, etc.) in order to explore the chlorine species emission on atmospheric nitrate formation.”

Comment #18: Line 128-130. Should add some reference here. Also, ‘NH3’ should also be considered as a common species.

Response #18: This seems to be a common knowledge among air quality modelers, but we included a citation (Wang et al., 2014) per reviewer’s request. NH3 is added to the sentence and its emission is also summarized in the revised manuscript in Table S1.

Comment #19: Line 136. Should mention the number (from 2000 Mt in 2014 to 490 Mt in 2017) here.

Response #19: This is now included in the revised manuscript.

Comment #20: Line 142. Should list the emission factors for different sectors, at least in the supplement. Also, give the reference.

Response #20: There are quite a number of different emission factors used in the calculation, which have already been summarized in Table 3 of Fu et al. (2018). We added the citation in the revised manuscript.

Comment #21: Line 156-157. Should provide reasons why you chose this number of hours. Three hours of cooking time seem to be a bit long for me. Also, ‘restaurant’ should be ‘social cooking’, is that correct?

Response #21: Sorry, it’s a typo. It should be 0.5 h following the study by Wu et al (2018). based on a survey data. The emissions were correctly calculated using 0.5 h. Also, ‘restaurant cooking’ has been revised to ‘commercial cooking’.

Comment #22: Line 160. Any reason that you chose ‘150’?

Response #22: It’s based on Wu et al. (2018). Citation is now included.

Comment #23: Line 173-174. A brief description is needed for other emissions, which are the precursors of N2O5, CINO2, and nitrate aerosol.

Response #23: We supplement the description of emission in page 30, line 229-231 and this sentence is revised as “Emissions of conventional species for this study period are developed in a separate study that is currently under review and are summarized in Table S1.”

Comment #24: Section 2.2. The authors added several reactions to the CMAQ model,
and this seems to be one of the major contributions of this study. [this comment seems to be less coherent, so we break it into several sentences and address them individually]

(1) However, what is the difference between the mechanism in the current study and that in Sarwar et al. (2012, 2014)?

(2) I notice that one of the co-authors in the present study is also a co-author of Sarwar et al. (2014).

(3) I strongly advise the authors to carefully review the previous works and identify the advantage of the current work, instead of avoiding the comparison between the current study with the previous ones.

(4) Besides, did you compare your scheme with Zheng et al. (2015)?

Response #24:

(1) Sarwar et al. (2012, 2014) only consider the reaction of N$_2$O$_5$ with PCl. They did not include those heterogeneous reactions involving Cl$_2$ production (the reaction of O$_3$, OH, HOCl, ClNO$_2$ and ClONO$_2$ with PCl).

(2) It is correct that one of the authors of Sarwar et al. (2014) happens to be a co-author of this study. We didn’t understand why this comment is even relevant, so no changes were made regarding this comment.

(3) Previous works were reviewed in the introduction section and discussed throughout the manuscript wherever appropriate.

(4) The major difference in Zheng et al.’s treatment of heterogeneous chemistry and our approach is that they chose to use an empirical expression for RH dependent uptake coefficients of NO$_2$ and SO$_2$. There is no evidence so far that that RH-dependent expression is any better than simple constant values. Thus, it is out of the scope of this paper to compare Zheng et al.


Response #25: Zheng et al.(2015) was not the right reference. The current CMAQ model refers to the one used by Hu et al. (2016) and Hu et al. (2017)


Comment #26: Line 182. Li et al. (2016) is not a proper reference for this equation. Should refer to Bertram and Thornton (2009) or Roberts et al. (2009) with a very similar formula. This brings up another persistent issue that you should use ‘Bertram and Thornton (2009)’ instead of ‘Bertram et al. (2009)’. There are only two authors to that paper. Please check the manuscript for this error.
Response #26: The reference ‘Li et al. (2016)’ is replaced with ‘Bertram and Thornton (2009)’ and we revise the ‘Bertram et al. (2009)’ with ‘Bertram and Thornton (2009)’ throughout the manuscript.

Comment #27: Line 177. H2O means water vapor. Is that right?

Response #27: Yes.

Comment #28: Line 220-22. This part is a bit confusing. Why did you call the values ‘preliminary’? Did you get these data from the reference (Keene et al., 1999)? Or did you make a guess on these values? I see that you made some sensitivity cases later. Perhaps you should mention that here.

Response #28: In Keene et al. (1990) [It was incorrectly cited in the original manuscript as Keene et al. (1999). We apologize for this mistake.], the daytime uptake coefficient of O3 was not based on direct experimental measurements but was estimated indirectly based on a steady-state analysis of Cl2 production rate in a hypothesized geochemical cycle of reactive inorganic chlorine in the marine boundary layer. The estimated daytime O3 uptake coefficient was around 10^-4 to 10^-3. Lower nighttime value was further estimated based on the observation of lower Cl2 production in the marine boundary layer at night. In this study, we used the values used by Keene et al. (1990) in their simulations. As both daytime and nighttime values may have significant uncertainties, we choose to call the values used in this study “preliminary”. We add the sentence ‘it’s a simulation-based result, which presents high uncertainty’ behind the above sentence.

Due to the high uncertainty of O3 uptake coefficient, we do some sensitivity case to evaluate how the effect of this uncertainty on the underestimation of atmospheric Cl2 concentration. This is now mentioned right after the sentence in question.

Comment #29: Line 229. Just out of curiosity, is the gas-phase chemistry of chlorine the same as that in Sarwar et al. (2012)?

Response #29: The gas-phase chemistry used by Sarwar (2012) is not as complete. It only has 9 inorganic reactions while the one we used in our study includes 22 inorganic reactions. Most reactions of ClONO and ClONO2 are missing from Sarwar (2012). In addition, Sarwar et al. (2012) used CB05 but we used SAPRC11. The organic reactions are also different but to less a degree.

Comment #30: Section 3.1. What about the model performance on the simulation of NO2, O3, and PM2.5? These are particularly important to the formation of nitrate aerosol, the sole focus of the current work.
Response #30: Model performance of these species were included in the revised manuscript. See our response to comment 3 for more details.

Comment #31: Line 251-252. This treatment artificially amplifies the heterogeneous reaction rate by 5 and 10 times. Is it logical to do that based on the comparison with one measurement data set? How does the CMAQ model perform in general in the simulation of surface area? Is it a common issue? Or did it only happen in your simulation? How is the simulation of PM$_{2.5}$? This highlights the need for the evaluation of the routine air pollutants, e.g., PM$_{2.5}$.

Response #31: Figure R1a below is the detailed comparison of our modeled surface area with observations averaged between June 11-15, 2017. Under-prediction of surface area varies between 6-12 times. CMAQ model performance for surface area has not been extensively studied. In the only study we found in the literature (Park et al., 2006), similar under-prediction of particle surface area was reported. In their study, the mass concentration of PM$_{2.5}$ at Atlanta, United State is generally well reproduced by the CMAQ model but the surface area shows large under-predictions similar to what we have seen in our study (see Figure R1b).

![Graph](image.png)

Figure R1a (left panel): Predicted averaged hourly particle wet surface area at IAP (June 11-15, 2017) and the ratio of observed to predicted PSA (O/P). R1b (right panel): CMAO predicted and observed daily particle surface area, volume, and mass concentrations for PM$_{2.5}$ from 1/1/1999 to 8/31/2000 at the JST station in Atlanta, Georgia. (R1b is adapted from Park et al., 2006).

Reference:

Comment #32: Line 255. ClNO$_2$ is underestimated in your cases. Does it mean that
Nitrate aerosol is over-predicted?

Response #32: Nitrate aerosol is also slightly underpredicted most of the hours. It was over-predicted slightly on the night on June 13. Nitrate concentrations are affected by many other factors so a simple anti-correlation between CINO2 and nitrate cannot be assumed. No changes were made regarding this comment.

Comment #33: Line 258. The O3 will increase or decrease if you change the uptake coefficient of O3. This also calls for the model evaluation on O3.

Response #33: The impacts of heterogeneous chlorine chemistry on O3 formation are complicated. On one hand, O3 is consumed by the heterogeneous reaction with PCl. On the other hand, the generated Cl2 photolyze to produce Cl atom, resulting in the increase of O3. The impact of chlorine chemistry on ozone is a very important by itself and has been explored in a separate manuscript that is currently under review. Model performance of O3 is evaluated by comparing with observations at 12 sites in Beijing. (The average NMB/NME values for O3 across the 12 sites are -8%/29%)

Comment #34: Line 260. Several studies have been reported that the parameterization used in the present study (Bertram and Thornton, 2009) has some uncertainty, including Tham et al. (2018), McDuffie et al. (2018a), McDuffie et al. (2018b) and the references therein. How these uncertainties affect the conclusions should be discussed.

Response #34: We investigated the uncertainty in the predicted nitrate concentrations using the parameterized N2O5 uptake coefficients of Bertram and Thornton (2009) by using two sensitivity simulations in the original manuscript. In one simulation, the parameterization of Davis et al. (2008), which is the default N2O5 parametrization scheme in CMAQ 5.0.1, was used. It generally yields slightly lower $\gamma_{N_2O_5}$ than the Bertram and Thornton (2009). In the other simulation, the $\gamma_{N_2O_5}$ was fixed at a constant value of 0.09, which is the maximum value derived by Zhou et al. (2018) based on summertime field measurement in urban Beijing. On average, it is 4-6 times higher than those based on Bertram and Thornton (2009). Table 3 in the original manuscript summarized the $\gamma_{N_2O_5}$ averaged for each day and night from these simulations and the corresponding nitrate concentrations. Predicted nitrate concentrations are sensitive to changes in the changes in $\gamma_{N_2O_5}$, with approximately 50% increase in the nitrate when the $\gamma_{N_2O_5}$ is fixed at 0.09. The discussion of these two sensitivity simulations are slightly revised from the original manuscript and can be found in the revised paper on page 37, lines 431-434.
Comment #35: Line 277-278. The underestimated nitrate concentration could be due to many reasons. For example, is NO2 underestimated as well? This is another reason to show the evaluation of NO2 simulation. The uncertainty of the parameterizations of N2O5 uptake and CINO2 yield (comment 31) could also be applied here. Besides, how did you simulate the most critical OH precursor, i.e., HONO? Did you evaluate your HONO simulation? Did you consider the NO2 uptake on environmental surfaces? What about other HONO sources? Several recent papers have shown that HONO is very important in simulating nitrate, e.g., Fu et al. (2018).

Response #35: We have evaluated the model performance of NO2, which shows that the NO2 concentration isn’t significantly underestimated (The average NMB/NME values for NO2 across the 12 sites are -7%/59%). In original CMAQ, the NO2 hydrolysis produces HONO and HNO3. However, in the improved CMAQ, this reaction is revised as:

\[ 2\text{NO}_2(g) + \text{Cl}^- (aq) \rightarrow \text{CINO}(g) + \text{NO}_3(aq) \] (if the NO2 is redundant, \[ 2\text{NO}_2(g) + \text{H}_2\text{O} (aq) \rightarrow H\text{ONO}(g) + \text{NO}_3(aq) \].)

As for HONO (assuming the HONO is produced in nighttime), the CMAQ model have covered the reaction of HONO photolysis to produce OH. However, HONO photolysis affects the OH level just a few hours in the morning and can be neglected.

Comment #36: Line 281-282. What do you mean by ‘the nitrate level is higher in the daytime and lower in nighttime’?

Response #36: It’s redundant. We have deleted it.

Comment #37: Line 290-291. It may be true that the uptake coefficients for these two molecules are the most important parameters. But what about the uptake coefficients for other species/process. Did you run any sensitivity cases to examine that?

Response #37: We haven’t run any sensitivity cases to examine the impact of the uptake coefficient of other species on nitrate. As we demonstrated in manuscript, the gas-to-particle partitioning of HNO3 and the reaction N2O5 with PCl are the major pathways of producing nitrate in daytime and nighttime, so we choose to run sensitivity cases of O3 (O3 uptake is major contributor to Cl2 in R13-R17) and N2O5 uptake coefficients.

Comment #38: Line 293-295. Or maybe just because the direct emission of Cl2 is not well represented in the emission inventory

Response #38: The underprediction is unlikely due to missing primary Cl2 emissions. It is generally accepted that direct Cl2 emissions from power plants or residential coal burning are in a smaller quantity (less than 3% in total Cl, Deng et al., 2014). In addition, Liu et al. (2017) revealed that there is only a weak correlation between Cl2 with other primary emission indicators (K+ for biomass burning (R=0.004), SO2 for power plant
emissions (R=0.31) and NOx representing transportation emissions (R=0.01)) or precursors (HCl (R=0.08) and PCl (R=0.01))


Comment #39: Line 316. N2O5 uptake process is very complicated. The word, ‘inferior’, is definitely not the one I would use to describe the parameterization based on nitrate and sulfate concentration. Please revise. The uncertainty of the parameterizations of N2O5 uptake and ClNO2 yield also works here.

Response #39: We completely agree with the reviewer.

Comment #40: Section 3.3. I advise to include the simulated results of NO2, O3, and PM2.5.

Response #40: We have included them in SI Figure S3, which also be shown in Figure R2.
Figure R2 The spatial distribution of NO$_2$ (a), O$_3$ (b) and PM$_{2.5}$ (c) concentration averaged in 11 to 15, June.

Comment #41: Line 328. Should include a figure for the ‘intensive emissions of chlorine species’

Response #41: We have included it in Figure S2, which is also represented in Figure R3.
Figure R3: The spatial distribution of PCl emission in Beijing in 2017 (Unit: Kg/year per grid).

Comment #42: Line 328-330. The presence of a high concentration of ClNO2 and Cl2 away from the fresh emissions does not necessarily mean that ClNO2 and Cl2 are easy to transport. For example, the production of ClNO2 requires the presence of chloride, NO2, and O3. In the areas close to the fresh emissions, O3 is commonly low, and the production of NO3 (hence N2O5 and ClNO2) is limited. Therefore, the production of ClNO2 is generally not found near fresh emissions. As to the Cl2, perhaps the contribution of direct emission to the level of Cl2 is not significant, and Cl2 is predominantly produced in the atmosphere. So the high levels of Cl2 are found away from the fresh emissions.

Response #42: We agree with the reviewer’s opinion and include this comment in page 37, line 444-450 in manuscript.

Comment #43: Line 336. Why ‘more N2O5 is converted into nitrate’? Are you implying that the uptake coefficient calculated with the Bertram and Thornton (2009) is higher than that with Davis et al. (2008)?

Response #43: Yes, this is indeed the case. Table 3 compares the uptake coefficient of N2O5 based on the two parameterization and clearly shows that the Bertram and Thornton equation generally gives higher uptake coefficients. This is also consistent with the conclusion of McDuffie et al. (2018). We add this explanation in revised manuscript on page 38, lines 456-460.

Comment #44: Line 351-352. Was the observation in PKU conducted in the same
Response #44: No, the observation in PKU is conducted in November. This is clarified in the revised manuscript.

Comment #45: Line 355-357. Are you implying that in cleaner days, the OH level is higher, so the production of HNO3 from OH + NO2 is more important?

Response #45: The sentence in question discusses the relative importance of the homogeneous and heterogeneous pathways in nitrate formation. The difference is likely due to a combination of higher OH concentrations in this study and more surface areas available for heterogeneous reaction in the winter during the PKU study. The difference in OH level between the two studies (this study vs. the PKU study) is mainly driven by the seasonal variation of the solar radiation. This is clarified in the revised manuscript.

Comment #46: Line 371-372. How did you treat the reaction of NO2 + H2O (aq)? Did you revise it to NO2+ Cl- or did you use both?

Response #46: Both reactions are included. The NO2 + Cl reaction is only considered when Cl concentration is greater than zero. No changes were made regarding this comment.

Comment #47: Line 396-397. It is correct that the emission of chlorine species is vital to chlorine chemistry study. But the current study does not demonstrate this point.

Response #47: We agree with the reviewer on this. This sentence is removed in the revised manuscript.


Response #48: The sentence ‘Cl2 and ClNO2 are easy to transport among cities because high concentrations of them are not found in southern region with intensive emissions of chlorine species.’ is revised as ‘High concentration of Cl2 and ClNO2 are not found in southern region with intensive emissions of chlorine species may be related to high O3 concentration generally occurred in suburban’

Comment #49: Line 409-411. What implications? Care to elaborate? See comment 2 for example. But more thoughts are definitely of value to the policymakers.

Response #49: The sentence ‘This study aims to improve our understandings on the chlorine chemistry and its impact on nitrate formation, which can provide useful implications on the nitrate pollution control strategies for those regions that suffered serious nitrate pollution.’ is revised as ‘This study aims to improve our understandings on the chlorine chemistry and its impact on nitrate formation. The chloride chemical
mechanism study in this work indicates that not only the NO$_X$ emission is needed to be controlled, but also the emission of reactive chlorine species should be limited as well in order to alleviate the nitrate pollution.

**Comment #50:** The reference list is not organized according to the alphabet. For example, L is before K, J is after K, Rudich is before Roberts, and Spicer is before Song.

**Response #50:** Revised

**Comment #51:** Table 2. What are the effects of R6, R11, R13-R18 on the production of nitrate aerosol? Also, please provide the reference for all reactions.

**Response #51:** The reactions R6 and R11 directly affect the nitrate and R13-18 indirectly affect it by elevating the OH level due to production of Cl$_2$. This discussion is included in the revised manuscript on page 27, line 108-111. The references for all reaction have included in Table 3.

**Comment #52:** Line 38. ‘photolyze’ is a better word than ‘decompose’ since it is a photolysis reaction.

**Response #52:** The ClNO$_2$ reacts with particle surface to form nitrate, which is not a photolysis reaction. It is changed to ‘reacts with particle surface’ to make it more specific.

**Comment #53:** Line 62. Should add ‘(aq)’ after ‘H2O’

**Response #53:** Revised

**Comment #54:** Line 63. should define CMAQ and WRF-Chem here.

**Response #54:** Revised

**Comment #55:** Line 81. should be ‘chloride-containing’, not ‘chlorine-containing’.

**Response #55:** Revised

**Comment #56:** Line 119. The definition of CMAQ should be moved to line 63.

**Response #56:** Revised

**Comment #57:** Line 130. Add a space between ‘emissions’ and ‘were’.

**Response #57:** Revised
Comment #58: Line 145. ‘EF represents the emission factor’ should be ‘EF_{i,j} represents the emission factor of pollutant j in sector i’.

Response #58: Revised

Comment #59: Line 148-149. ‘had been detailed described’ should be ‘had been described in detail’

Response #59: Revised

Comment #60: Line 158. Add ‘from social cooking’ after ‘Vc is the volume of exhaust gas’.

Response #60: Revised

Comment #61: Line 161. ‘chose’ should be ‘chosen’

Response #61: Revised

Comment #62: Line 166. Delete ‘that’

Response #62: The sentence has been deleted

Comment #63: Line 168. Use the same decimal for all data.

Response #63: Revised

Comment #64: Line 169. ‘Others’ should be ‘Other’.

Response #64: Revised

Comment #65: Line 169. Add the publication year after ‘Fu et al.’

Response #65: Revised

Comment #66: Line 169 and line 171. Two ‘finally’?

Response #66: The redundant ‘finally’ has been deleted.

Comment #67: Line 185. ‘Laboratorial’ should be ‘laboratory’

Response #67: Revised

Comment #68: Line 192. Do you mean ‘equation (5)’, instead of ‘equations (2)’?
Response #68: It should be equation (5).

Comment #69: Line 198. Do you mean ‘equation (6)’, instead of ‘equation (3)’?

Response #69: It should be equation (6).

Comment #70: Why did you use different terms for velocity in equation 5 and equation 8?

Response #70: The equation 5 has been revised as ‘v’.


Response #71: These parameters have been demonstrated. As $K_h$ represents the dimensionless Henry’s law coefficient ($K_h = [N_2O_5]_{aq}/[N_2O_5]_g = 10e(30)$), $K_f$ represents a parameterized function based on water concentration ($K_f = 1.15e^6(1 - e^{-1.3e^{-1}[H_2O(l)()]})$) and $K_3/K_2$ and $K_4/K_2$ are constants obtained by fitting data, which are $6\times10^{-2}$ and 29.

Comment #72: Line 216 and line 208. Use the consistent form for units. m3/m3 or m3 m^-3.

Response #72: Revised

Comment #73: Line 227. Which year?

Response #73: This sentence is revised as ‘These heterogeneous reactions of chlorine are incorporated into revised CMAQ (version 5.0.1) to simulate the distribution of nitrate concentration in Beijing from 11 to 15 June 2017’

Comment #74: Line 232. It is weird to see ‘Figure 3’ before ‘Figure 1 and 2’. Maybe a map with three domains in the supplement as Figure S1 is better.

Response #74: A map with three domains is included as Figure S1(Figure R4 below):
Figure R4 the three nested domain setting in this work.

Comment #75: Line 232. ‘40°E’ should be ‘40°N’.
Response #75: Revised

Comment #76: Line 296. Remove the extra space between ‘empirical’ and ‘and’.
Response #76: Revised

Comment #77: Line 315. Add the year for ‘Davis et al.’. Check through the manuscript for a similar issue.
Response #77: This sentence has been deleted in the revised manuscript.

Comment #78: Line 350. ‘are produced’ should be ‘is produced’.
Response #78: Revised

Comment #79: Line 369. Add ‘of’ between ‘uptake’ and ‘N2O5’.
Response #79: Revised

Comment #80: Line 378. ‘even through’ should be ‘even though’.
Response #80: Revised

Comment #81: Line 396. ‘This’ should be ‘These’.
Response #81: Revised
Comment #82: Line 397. ‘becase’ should be ‘because’.
Response #82: Revised

Comment #83: Line 397. ‘the cornerstones’ should be ‘the cornerstone’ or ‘one of the cornerstones’.
Response #83: Revised

Comment #84: Line 401. ‘chlorine’ should be ‘chloride’.
Response #84: Revised

Comment #85: Line 409. ‘understandings’ should be ‘understandings’.
Response #85: Revised

Comment #86: Figure 3. Should point out the area of BJ and the location of the sampling site. In d, f, and h, should use ΔN2O5, ΔNO3-, and ΔNO3-, instead of N2O5, NO3-, and NO3.
Response #86: The area of BJ and the location of the sampling site is labeled in Figure S1. We have used ΔN2O5, ΔNO3-, and ΔNO3-, instead of N2O5, NO3-, and NO3.

Comment #87: Figure 4. In the sub-plot Daytime Gas-phase, the title of Y-axis should be ‘HNO3 production rate (ppt h-1)’. The same revision should be applied to the sub-plot Nighttime Gas-phase. The sub-plot Nighttime Heterogeneous, the title of Y-axis should be ‘Nitrate production rate (µg m-3 h-1)’. No sub-plot daytime Heterogeneous?
Response #87: Revised. Additionally, the heterogeneous reaction of NO2 with PCl have less contribution to diurnal nitrate (less than 2%) because the extremely lower uptake coefficient. In addition, we supplement the daytime heterogeneous.
Reviewer #2

Comment #1: The manuscript of Qiu et al., reported the influence of chloride chemistry to particulate nitrate formation in the framework of CMAQ. The authors included several chloride reactions into the CMAQ chemical mechanism. This topic is in the scope of ACP, and would benefit the knowledge of the heterogeneous reactions in the formation of particulate nitrate in Beijing, China. While in this paper, the detail of the parameters lacking the foundation and the analysis of model result seems common. Some of the conclusions seems can’t obtain from the model result analysis (see major comments). The following comments should be addressed before publishing in ACP.

Response #1: Thanks for the positive comments on this manuscript. The suggestions are addressed in detail in the following.

Comment #2: Line 250-252, the treatment of aerosol surface area by time 5 or 10 in this model is unconvinced. Should provide more evidence to support the rationality.

Response #2: Figure R1a below is the detailed comparison of our modeled surface area with observations averaged between June 11-15, 2017. Under-prediction of surface area varies between 6-12 times. CMAQ model performance for surface area has not been extensively studied. In the only study we found in the literature (Park et al., 2006), similar under-prediction of particle surface area was reported. In their study, the mass concentration of PM2.5 at Atlanta, United State is generally well reproduced by the CMAQ model but the surface area shows large under-predictions similar to what we have seen in our study (see Figure R1b).

Figure R1a (left panel): Predicted averaged hourly particle wet surface area at IAP (June 11-15, 2017) and the ratio of observed to predicted PSA (O/P). R1b (right panel): CMAO predicted and observed daily particle surface area, volume, and mass concentrations for PM2.5 from
1/1/1999 to 8/31/2000 at the JST station in Atlanta, Georgia. (R1b is adapted from Park et al., 2006).

Reference:

Comment #3: The sensitivity tests used an O3 uptake coefficient enlarged by a factor of 10 without any reference, while the Cl2 simulations do not significantly improved in general. Other possible Cl2 formation channel shall be tested or at least discussed.

Response #3: In Keene et al. (1990) [It was incorrectly cited in the original manuscript as Keene et al. (1999). We apologize for this mistake.], the daytime uptake coefficient of O3 was not based on direct experimental measurements but was estimated indirectly based on a steady-state analysis of Cl2 production rate in a hypothesized geochemical cycle of reactive inorganic chlorine in the marine boundary layer using a 0-D box model. Such an analysis tends to have large uncertainties and Keene et al. (1990) proposed 10^{-4} to 10^{-3}. Nighttime value of 10^{-5} was proposed without much supporting evidence. We chose to increase these uptake coefficients to explore the upper limit of the impact of O3 uptake on Cl2 formation. As there are additional Cl2 formation pathways, our results show that the higher uptake coefficients alone do not lead to significantly higher Cl2 concentrations. The other Cl2 channels are summarized in Table 2 and contributions of these channels to Cl2 concentrations are explored in a separate study as this paper is focused on nitrate.

Comment #4: Line 398-402, I cannot agree with that the parameterization method including chloride of the uptake coefficient of N2O5 has a better performance, at least this kind of conclusion cannot be deduced from the authors analysis (cf. figure 1).

Response #4: Agree. This is removed from the conclusion section.

Comment #5: I suggest that the authors may present a table to summarize all the revisions of the parameters related to the uptake coefficient as well as the related heterogeneous reactions.

Response #5: We summary the revision of parameters in Table S3.


Response #6: Revised

Comment #7: Line 335-line 340, this part is confused. Did you mean more N2O5 convert to nitrate due to the N2O5 uptake coefficient calculated by Bertram and
Thornton, (2009) is higher than the base case? And the non-significant nitrate increase may be due to the ClNO2 yield buffered the increasing caused by the application of new N2O5 uptake coefficient?

**Response #7:** This sentence is revised as ‘By incorporating the chlorine heterogeneous reaction, the N2O5 concentrations decrease by about 16% because the uptake coefficient calculated with the Bertram and Thornton (2009) is higher than that with Davis et al. (2008).’

**Comment #8:** Line 289 the section title should not be the estimation of uptake coefficients of O3 and N2O5, but the influence of the change of these parameters.

**Response #8:** The title is revised as ‘Impact of uptake coefficients of O3 and N2O5 on chlorine species and nitrate’
Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation in Beijing, China

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Abstract:
A comprehensive chlorine heterogeneous chemistry is incorporated into the Community Multiscale Air Quality (CMAQ) model to evaluate the impact of chlorine-related heterogeneous reaction on diurnal and nocturnal nitrate formation and quantify the nitrate formation from gas-to-particle partitioning of HNO₃ and from different heterogeneous pathways. The results show that these heterogeneous reactions increase the atmospheric Cl₂ and ClNO₂ level, leading to an increase of the nitrate concentration by ~10% in the daytime. However, these reactions also lead to a decrease the nocturnal nitrate by ~20% (~100%), which further affect the nitrate formation. Sensitivity analyses of uptake coefficients show that the empirical uptake coefficient for the O₃ heterogeneous reaction with chlorinated particles may lead to the large uncertainties in the predicted Cl₂ and nitrate concentrations. The N₂O₅ uptake coefficient with particulate Cl⁻ concentration dependence performs better to capture the concentration of ClNO₂ and nocturnal nitrate concentration. The reaction rate of OH and NO₂ in daytime increases the nitrate by ~15% when the heterogeneous chlorine chemistry is
incorporated, resulting in more nitrate formation from HNO$_3$ gas-to-particle partitioning. By contrast, the contribution of the heterogeneous reaction of N$_2$O$_5$ to nitrate concentrations decreases by about 27% in the nighttime when its reactions with chlorinated particles are considered. However, the generated gas-phase ClNO$_2$ from the heterogeneous reaction of N$_2$O$_5$ and chlorine-containing particles further decomposes and reacts with the particle surface to increase the nitrate by 6%. In general, this study highlights the potential of significant underestimation of daytime and overestimation of nighttime nitrate concentrations for chemical transport models without proper chlorine chemistry in the gas and particle phases.

1. Introduction

In recent years, nitrate has become the primary component of PM$_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5μm) in Beijing with sustained and rapid reduction of SO$_2$ and primary particulate matter emissions (Ma et al., 2018; Li et al., 2018; Wen et al., 2018). Observations showed that the relative contributions of secondary nitrate in PM$_{2.5}$ could reach up to approximately 50% during some severe haze pollution days (Li et al., 2018). The mechanism of secondary nitrate formation can be summarized as two major pathways: (1) Gas-to-particle partitioning of HNO$_3$, which happens mostly in the daytime. The reaction of OH with NO$_2$ produces gaseous HNO$_3$, which subsequently partition into the particle phase. The existence of NH$_3$ or basic particles enhances this process by NH$_3$–NH$_4^+$ gas-particle equilibrium (Kleeman et al., 2005; Seinfeld and Pandis, 2006); (2) Hydrolysis of N$_2$O$_5$, which is more important at nighttime. N$_2$O$_5$ forms from the reactions of NO$_2$, O$_3$ and NO$_3$ and hydrolyzes to produce particulate nitrate. They can be summarized as reactions R1-R5 (Ying et al., 2011; Wang et al., 2018; Li et al., 2018; Brown and Stutz, 2012):

$$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad \text{(R1)}$$
$$\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- \quad \text{(R2)}$$
$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R3)}$$
$$\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5 \quad \text{(R4)}$$
$$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{NO}_2^--(aq) \rightarrow 2\text{H}^+ + 2\text{NO}_3^- \quad \text{(R5)}$$

In addition to reactions R1 and R5, gas phase reactions of NO$_3$ with HO$_2$ and VOCs, N$_2$O$_5$ with water vapor (Tuazon et al., 1983) and the heterogeneous reaction of NO$_2$ with water-containing particle (Goodman et al., 1999) produce HNO$_3$ or nitrate as well.
Theses reactions are listed in Table 2 as reactions R8, R9 and R10. However, current-chemistry transport models (CTM, such as CMAQ, WRF-Chem etc.) incorporated with these mechanisms still can’t accurately capture the spatiotemporal distributions of nitrate despite involving above chemical mechanism in some studies in polluted northern China. For example, Chang et al. (2018) showed that the simulated nitrate concentrations derived from the default CMAQ (version 5.0.2) were 1.79 to 1.95 times of significantly higher than the observations in summer at two sites adjacent to Beijing. Chen et al. (2017) found the high uncertainty (about 20%~50%) of simulated nitrate concentration using CMAQ in Dezhou city (Shandong province, adjacent to Beijing), which attributed to the unclear mechanism of nitrate formation. Fu et al. (2017) also found that default CMAQ (version 5.0.1) overestimated the simulated nitrate concentrations in the Beijing-Tianjin-Hebei region. Some studies attributed the overestimation of nitrate to the missing of high particulate chlorine chemical mechanism. In recent fields studies, it was found that high particulate chlorine chemical mechanism emissions might have a significant impact on the oxidation capacity of the urban atmosphere and thus could affect nitrate concentrations. According to the field measurements in June 2017 in Beijing (Zhou et al., 2018), the 2-min averaged concentrations of reactive molecular chlorine (Cl2) and nitryl chloride (ClNO2) reached up to 1000 pptv and 1200 pptv, respectively, during some severe air pollution periods in summer. The corresponding concentrations of N2O5 and nitrate rise up to 700pptv and 5μg m⁻³ from about 40 pptv and 1μg m⁻³, which Cl2 concentrations were significantly higher than those observed in North American coastal cities affected by onshore flow and the lower atmosphere in the remote Arctic region (Spicer et al., 1998; Li et al., 2017; Glasow et al., 2010; Liu et al., 2017; Some2017). During these pollution events, the corresponding concentrations of N2O5 (2-min average) and nitrate (5-min average) rose from 40 pptv and 1 μg m⁻³ to 700 pptv and 5 μg m⁻³. To explain the high levels of ClNO2, some studies suggested that the reaction R5 should be revised as R6 due to account for ClNO2 production from the heterogeneous reaction of N2O5 on chlorine-containing particle surface particles (CPS) (Wang (Osthoff et al., 2017; Simon 2008; Thornton et al., 2010; Glasow et al., 2010)), as shown in reaction R6: 

\[ \text{N}_2\text{O}_5 + (1-\phi) \text{H}_2\text{O} + \phi \text{Cl}^- \rightarrow \phi \text{ClNO}_2 + (2-\phi)\text{NO}_3^- \]  

(R6)

where \( \phi \) represents the molar yield of ClNO2. By incorporating this reaction leads to lower nitrate concentrations than reaction R5. By incorporating
this reaction into WRF-Chem, Li et al. (20172016) found that the improved model performed better to match the observed nitrate concentrations in Hongkong during 15 November and 5 December 2013. The generated gaseous nitryl chloride (ClNO$_2$) However, ClNO$_2$ could affect the formation of nitrate indirectly by increasing the atmospheric OH after a series of chemical reactions, which are briefly summarized into three steps: (1) the photolysis of ClNO$_2$ produces atom chlorine radicals (Cl$^*$); (2) the reaction of Cl$^*$ with VOCs produces peroxo radical (HO$_2$ and RO$_2$); and (3) the increased HO$_2$ and RO$_2$ prompt the formation of OH by participating into free radical through HO$_x$ cycle and NO$_x$ cycle to lead to increased HNO$_3$ production (Young et al., 2014; Jobson et al., 1994). The overall impact of R6 on nitrate remains to be investigated.

The reaction of N$_2$O$_5$ is not the only heterogeneous reaction that influences the nitrate formation. Some other heterogeneous reactions on CPS can also directly or indirectly affect nitrate formation. For example, the heterogeneous uptake of NO$_2$ and NO$_3$ on CPS can produce nitrate (Abbatt et al., 1998; Rudich et al., 1996). The another related but unresolved issue is the sources of the high concentrations Cl$_2$, which could not be explained by the N$_2$O$_5$ heterogeneous reaction with Cl$^*$ and the subsequent reactions of ClNO$_2$ in the gas phase. It has been reported that the reactions of gaseous O$_3$, OH, HO$_2$, ClNO$_2$, hypochlorous acid (HOCl), chlorine nitrate (ClONO$_2$) with CPS can produce Cl$_2$ and which can subsequently photolyze to produce Cl$^*$ (Knipping et al., 2000; George et al., 2010; Pratte et al., 2006; Deiber et al., 2004; Faxon et al., 2015), which can further accelerate the OH formation to affect the reaction R1). However, these heterogeneous reactions on CPS are generally missing in most of the current CTMs, and it is unclear whether these reactions will be able to explain the observed Cl$_2$ concentrations and the overall impact of these reactions on nitrate.

Previously, biomass burning, coal combustion, and waste incineration were identified as the main sources of gaseous and particulate chlorine compounds in China from International Global Atmospheric Chemistry Program's Global Emissions Inventory Activity (GEIA) based on the year 1990 and a localized study by Fu et al. based on the year 2014 (Keene et al., 1999; Fu et al., 2018). However, recent source apportionment results of PM$_{2.5}$ in Beijing showed that the contribution of coal combustion had extremely decreased from 22.4% in 2014 to 3% in 2017 with the replacement of natural gas (obtained from official website of Beijing Municipal Bureau of Statistics, available at http://edu bjstats gov cn/). But another Another
important source — cooking has received attention as its increasingly contribution to PM$_{2.5}$ (accounting for 33% of the residential sector; obtained from the official source apportionment analysis of PM$_{2.5}$ in Beijing in 2017; see http://www.bjeeb.gov.cn/bjhr-b/index/index.html). Moreover, the high content of particulate sodium chloride was measured from the source characterization studies of PM$_{2.5}$ released from the cooking source activities (Zhang et al., 2016). Thus, it’s important is necessary to ascertain compile an updated emission inventory for Beijing to include the relationship between reactive emissions from cooking and other sources (coal burning, solid waste incineration, biomass burning, etc.) in order to explore the emissions of the chloride species and on atmospheric nitrate formation.

In this study, the Community Multiscale Air Quality (a CMAQ) model with an improved chlorine heterogeneous chemistry is applied to simulate summer nitrate concentration in Beijing. We then use the sensitivity analyses Sensitivity simulations are conducted to evaluate the contribution of HNO$_3$ gas-to-particle partitioning and heterogonous production to aerosol nitrate formation. The results of this work can improve our understandings on nitrate formation and provide useful implications on the nitrate pollution control strategies in Beijing.

2. Emissions, chemical reactions and model description

2.1 Emissions

Generally, the conventional emission inventories of air pollutants in China only include the common chemical species, such as SO$_2$, NO$_X$, VOCs, PM$_{2.5}$, PM$_{10}$, NH$_3$, BC, and OC. No data on chloride (Wang et al., 2014). Chloride compound emissions were not included. However, the emissions of chlorine species are vital for studying the chlorine chemical mechanism. Recently, the inorganic hydrogen chloride (HCl) and fine particulate chloride (PCI) emission inventories for the sectors of coal combustion, biomass burning, and waste incineration were developed in for the year of 2014 (Qiu et al., 2017, 2016, Fu et al., 2018, Liu et al., 2018). However, the gaseous chlorine emission was not estimated in these studies. In addition, these studies did not account for the rapid decrease of coal consumption in recent years in Beijing (about 75% from 2000 Mt in 2014 to 490 Mt in 2017). More importantly, the cooking source, as one of the major contributors to particulate chlorine in Beijing, is not included in current chlorine emission inventories. Thus, we develop a new
emission inventory of reactive chlorine species, which includes HCl, Cl\textsubscript{2} and PCl\textsubscript{2} were developed in this study for the year of 2017.

The emission factor method (equation (1)) is applied to calculate the emissions of these reactive chlorine species, which can be expressed as following equations, from coal combustion, biomass burning, municipal solid waste incineration and industrial processes:

\[
\begin{align*}
\text{HCl and Cl}_2: & \quad E_{i,j} = \sum_{i,j} A_i \times EF_{i,j} \quad (1) \\
\text{PCl:} & \quad E_{i,j} = \sum_{i,j} A_i \times EF_{i,j} \times \eta \quad (2) \\
E_{i,j} &= A_i \times EF_{i,j} \quad (1)
\end{align*}
\]

where \(E_{i,j}\) represents the emission factor of pollutant \(j\) in \(i\)-sector. \(A\) represents the activity data; \(EF\) represents the emission factor. \(\eta\) is the cooking time for a family. The PM\textsubscript{2.5} emission factor for coal combustion is calculated based on the content of Cl in coal, which had been measured by Deng et al (2017). In addition, The PM\textsubscript{2.5} emission factors and mass fractions of PCl in PM\textsubscript{2.5} to calculate the methods of emission caeculation on biomass burning, municipal solid waste (MSW) emissions of Cl had been detailed described in detail by Fu et al. (2018), so we focus on demonstrating the calculation process of cooking source. PCl in PM\textsubscript{2.5} for coal combustion and biomass burning are taken as 1% and 9.0%, respectively, based on local measurements in Beijing.

In this study, the Cl\textsubscript{2}-production Activity data are obtained from the Beijing Municipal Bureau of Statistics (available at http://tjj.beijing.gov.cn/). The Cl\textsubscript{2} emission factor for coal combustion is calculated based on the content of Cl in coal, which had been measured by Deng et al (2017). In addition, The PM\textsubscript{2.5} emission factors and mass fractions of PCl in PM\textsubscript{2.5} to calculate the methods of emission caeculation on biomass burning, municipal solid waste (MSW) emissions of Cl had been detailed described in detail by Fu et al. (2018), so we focus on demonstrating the calculation process of cooking source. PCl in PM\textsubscript{2.5} for coal combustion and biomass burning are taken as 1% and 9.0%, respectively, based on local measurements in Beijing.

The Emissions of PCl from cooking emissions are separately estimated due to the differences of calculation method between social cooking (including school corporation and restaurant etc.) contributions from commercial and household cooking emissions, which are expressed as estimated using equation 3(2):

\[
\begin{align*}
E_F &= (V_f \times H_f \times EF_{F} + V_c \times H_c \times N_c \times n \times EF_c \times (1 - \eta)) \times 365 \quad (3) \\
E_{PCL} &= [N_f \times V_f \times H_f \times EF_{PCL} + V_c \times H_c \times N_c \times n \times EF_{c,PCL} \times (1 - \eta)] \times 365 \quad (2)
\end{align*}
\]

where \(N_f\) is the number of households, \(V_f\) is the volume of exhaust gas from a household stove, which equals to \(2000 \text{ m}^3 \cdot \text{h}^{-1}\); \(H_f\) is the cooking time for a family, which is set as \(3\text{h per day}\); \(EF_F\) is emission factor\(^{-1}\); \(EF_{F,PCL}\) and \(EF_{c,PCL}\) are the emission factors (kg m\(^{-3}\)) of PCl for household and commercial cooking, respectively; \(H_c\) is the cooking time for restaurant, which is set as \(6\text{h per day}\) in a commercial cooking
facility (6 h day−1); $N_c$ is the number of restaurants, schools and government departments. $V_c$ is the volume of exhaust gas, which is set as to from a commercial cooking stove (8000 m$^3$ h$^{-1}$). $n$ is the number of stoves for each unit, which equals to 6 for a restaurant and is calculated as the number of students divide 150 for school. $\eta$ is the remove efficient of fume scrubbers, a constant of 30% is chose one stove per 150 students for each school. $\eta$ is the removal efficiency of fume scrubbers (30%). $E_{FC,PCI}$ is the emission factor (kg m$^{-3}$) of PCl in commercial cooking. These constants are all based on Wu et al. (2018). The PCl fraction in PM$_{2.5}$ from cooking is take as 10%, based on local measurements. HCl and Cl$_2$ emissions from cooking are not considered in this study.

Activity data, such as coal consumptions, population, crop yields, and production of each industrial sector are obtained from Beijing Municipal Bureau of Statistics (available at http://tjj.beijing.gov.cn/). This official data shows that coal combustion has dramatically decrease from more than 2000 Mt from 2014 to 490 Mt in 2017, which indicates that significant reduction of emissions of air pollutants. Part of localized data of PCl, such as the content of PCl in PM$_{2.5}$ discharged from cooking, power plant and biomass burning (10%, 1% and 9.0%, respectively), are obtained based on the localized measurement. Others emission factors are obtained from the study by Fu et al. Finally, the sectoral emissions of HCl, Cl$_2$ and PCl, including power plant, industry, residential, biomass burning, MSW and cooking, are estimated and listed are summarized in Table 1. Finally, the estimated HCl, Cl$_2$ and PCl emissions in Beijing are 1.89 Gg, 0.065Gg07Gg and 0.63Gg respectively. The Cl emissions estimated for 2014 by Fu et al. (2018) were used for other areas. This simplification is a good approximation because replacing coal with natural gas only occurred in Beijing, and reduction of coal consumption in surrounding regions was generally less than 15%.

In addition, strict control measures for biomass burning, cooking and municipal solid waste incineration have not been implemented in most regions yet. Emissions of otherconventional species for this study period were derived by Ding et al. (are developed in a separate study that is currently under review; emissions and are summarized in Table S1).}

2.2 Chlorine-related heterogeneous reactions

In addition to reactions R1 and R5, gas phase reactions of NO$_2$ with H$_2$O or VOCs (R8
and R9, see Table 2). \( \text{N}_2\text{O}_2 \) with \( \text{H}_2\text{O} \) and the heterogeneous reaction of \( \text{NO}_2 \) with water-containing particle are included in current CMAQ model (Zheng et al., 2015). However, these heterogeneous reactions in original CMAQ (version 5.0.1) are not related to chlorine species. This study revises, the original heterogeneous reactions of \( \text{N}_2\text{O}_2 \) and \( \text{NO}_2 \) (R5 and R10 as in Table 2) are replaced with a revised version which includes the production of \( \text{ClNO}_2 \) from CPS (R6 and R11 by considering the impact of heterogeneous uptake on CPS, in Table 2). In reaction R6, the molar yield of \( \text{ClNO}_2 \) \( (\phi_{\text{ClNO}_2}) \) is represented as (Li et al., 2016 equation (3) (Bertram and Thornton, 2009):

\[
\phi_{\text{ClNO}_2} = \left( 1 + \frac{[\text{H}_2\text{O}]}{483 \times [\text{Cl}^-]} \right)^{-1}
\]

where \( \phi_{\text{ClNO}_2} \) is the yield of \( \text{ClNO}_2 \), [\( \text{H}_2\text{O} \)] and [\( \text{Cl}^- \)] are the molarities of liquid water and chloride in aerosol volume (mol/m\(^3\)).

In addition, laboratory observations confirmed that the heterogeneous uptake of some oxidants (such as \( \text{O}_3 \) and \( \text{OH} \)) and reactive chlorine species (such as \( \text{ClNO}_2 \), HOCl, and \( \text{ClONO}_2 \)) could also occur on CPS to produce \( \text{Cl}_2 \) (R13−R18), which affected the atmospheric \( \text{OH} \) level after a series of chemical reactions. These reactions are implemented in the model and summarized in Table 2 as R13-R18. Note that the products from the heterogeneous uptake of \( \text{ClNO}_2 \) on CPS vary with particle acidity (Riedel et al., 2012; Rossi, 2003). It generates \( \text{Cl}_2 \) under the condition of pH lower than 2 while but produces nitrate when the pH is and chloride under higher than 2. These pH conditions. The reaction rates of the heterogeneous reaction rates reactions are parameterized as first-order reactions, with the rate of change of gas phase species concentrations determined by equations (24) (Ying et al., 2015):

\[
\frac{dC}{dt} = -\frac{1}{4}(\bar{E}\gamma A)(\nu\gamma A)C - k^1 = -k^1 C
\]

where \( C \) represents the concentration of species, \( \bar{E} \); \( \nu \) represents the thermal velocity of the gas molecules (m s\(^{-1}\)); \( A \) represents the CMAQ-predicted wet aerosol surface area concentration (m\(^2\) m\(^{-3}\)); \( \gamma \) represents the uptake coefficient. Thus, \( k^1 \) is considered as For all gas phases species (except \( \text{ClNO}_2 \)) involved in the heterogeneous reactions (R6 and R11-R18), a constant simple analytical solution can be used to update their concentrations from time \( t_0 \) to \( t_0 + \Delta t \): \[ |C|_{t_0 + \Delta t} = |C|_{t_0} \exp(-k^1\Delta t) \], where \( \Delta t \) is the operator-splitting time step for heterogeneous reactions.

The parameters of \( A \) and \( \bar{E} \) are calculated by CMAQ. Considering the consumption and generation rate of \( \text{ClNO}_2 \), the concentration change of \( \text{ClNO}_2 \) can be
calculated with includes both removal and production terms, as shown in equation (35):
\[
\frac{d[CINO_2]}{dt} = -k_1^1[CINO_2] + k_b^1\phi_{CINO2}[N_2O_5]
\]
(65)

\[
= -k_1^1[CINO_2] + k_b^1\phi_{CINO2}[N_2O_5]t_0 \exp(-k_b^1t)
\]
Assuming \(\phi_{CINO2}\) is a constant, an analytical solution can be found for equation (7), and (7) can be obtained, as shown in equation (6):
\[
[CINO_2] = [CINO_2]_0 \exp(-k_1^1t) + \frac{k_b^1\phi_{CINO2}[N_2O_5]}{k_1^1-k_b^1} \left[\exp(-k_b^1t) - \exp(-k_1^1t)\right][CINO_2]_{t0+\Delta t}
\]
(26)

\[
= [CINO_2]_0 \exp(-k_1^1\Delta t) + \frac{k_b^1\phi_{CINO2}[N_2O_5]}{k_1^1-k_b^1} \left[\exp(-k_b^1\Delta t) - \exp(-k_1^1\Delta t)\right]
\]

Where \(k_1^1\) represents the reaction constant, pseudo first-order rate coefficient of either reaction R17 or R18. The variable \(t\) represents the time, depending on pH.

The uptake coefficients \(\gamma\) of gaseous species are obtained from published laboratorial studies. In the original CMAQ, the uptake coefficient of \(N_2O_5\) is determined as a function of the concentrations of (NH₄)₂SO₄, NH₄HSO₄, and NH₄NO₃ (Davis et al., 2008). In this study, the PCl and NO₃⁻ concentration dependent parameterization (eq. 8) by Bertram et al. for \(N_2O_5\) and Thornton (2009) (equation (7)) is used instead (Bertram et al., 2009). For frozen particles, the uptake coefficient is limited to 0.02, as used in the original CMAQ model:

\[
\gamma_{N_2O_5} = \begin{cases} 
0.02, & \text{for frozen aerosols} \\
\frac{4V}{4V + K_f K_R^1} \left(1 - \frac{1}{\left(K_{SO_4}^2 + [H_2O] \right)}\right) \gamma_{N_2O_5} \\
0.02, & \text{for frozen aerosols}
\end{cases}
\]
(87)

In the above equation, \(V\) represents the particle volume concentration \((m^{-3})\), \(S\) represents the particle surface area concentration \((m^2 \cdot m^{-3})\), \(v\) represents the thermal velocity of \(N_2O_5\) \((m \cdot s^{-1})\), \(K_R\) represents the dimensionless Henry’s law coefficient, \(K_f\) represents a parameterized function based on molarity of water concentration: \(K_f = 1.15 \times 10^6 \left(1 - e^{-0.13[H_2O]} \right)\). \(NO_3^-\) and \(K_2/K_3\) and \(K_1/K_2\) concentrations are constants obtained by fitting data also in molarity. The uptake coefficient of OH is

\[ \gamma = \min(0.04 \times \left[ \frac{[\text{Cl}^-]}{1000 \times M} \right], 1) \]  

(98)

where \( M \) represents the volume of liquid water in aerosol volume (\( \text{m}^3/\text{m}^3 \)). For frozen particles, the uptake coefficient is limited to 0.02, as used in the original CMAQ model.

The uptake coefficients of O\(_3\), NO\(_3\), NO\(_2\), HOCl, ClNO\(_2\), and ClONO\(_2\) are treated as constants. Among of them, the \( \gamma \) values of NO\(_3\), NO\(_2\), HOCl and ClONO\(_2\) are set as 3\( \times \) 10\(^{-3}\), 1\( \times \)10\(^{-4}\), 1.09\( \times \)10\(^{-3}\) and 0.16 based on the laboratory measurements (Rudich et al., 1996; Abbatt et al., 1998; Pratte et al., 2006; Gebel et al., 2001). A preliminary value of 10\(^{-3}\) in the daytime and 10\(^{-5}\) at nighttime is chosen for the O\(_3\) uptake coefficient (Keene et al., 1999). The daytime \( \gamma_{\text{O}_3} \) is based on the analysis of Cl\(_2\) production rate in a hypothesized geochemical cycle of reactive inorganic chlorine in the marine boundary layer by Keene et al. (1990). The lower nighttime value was also recommended by Keene et al. (1990) who noted that Cl\(_2\) production in the marine boundary layer are lower at night. The uptake coefficient of ClNO\(_2\) depends on the particle acidity, with the value of 2.65 \( \times \)10\(^{-6}\) for reaction R17 and 6 \( \times \)10\(^{-3}\) for reaction R18 (Robert et al., 2008).

2.4 CMAQ model configuration

These heterogeneous reactions of chlorine are incorporated into a revised CMAQ (based on the CMAQ version 5.0.1) to simulate the distribution of nitrate concentration in Beijing from 11 to 15 June 2017. The revised CMAQ model without heterogeneous reactions of chlorine has been described in detail by Ying et al. (2015) and Hu et al. (2016, 2017). In summary, the gas phase chemical mechanism in the revised CMAQ model is based on the SAPRC-11 (Cater et al., 2012) with a comprehensive gas-phase inorganic chlorine chemistry of chlorine (Cater et al., 2012; Ying et al., 2015). Reactions of Cl radical with several major VOCs, which lead to production of HCl, are also included. The aerosol module is based on AERO6 with an updated treatment of NO\(_2\) and SO\(_2\) heterogeneous reaction and formation of secondary organic aerosol from isoprene epoxides. Three-level nested domains with the resolutions of 36km, 12km, and
4km using Lambert Conformal Conic projection (173×136, 135×228 and 60×66 grid cells) are chosen in this work (the domains see Figure 3 for the inner most domain). S1). The two true latitudes isare set as 25°N to 25°N and 40°E-40°N and the origin of the domain is set as at 34°N, 110°E. The left-bottom coordinates of the outmost domain are positioned at x = -3114 km, y = -2448 km. The BASE case (simulation using default CMAQ heterogeneous reactions of Cl turned off) and HET case (with improved CMAQ all heterogeneous reactions enabled) are compared to evaluate the impact of heterogeneous chlorine chemistry on nitrate formation.

3. Results

3.1 Model performance evaluation

Predicted O$_3$, NO$_2$ and PM$_{2.5}$ concentrations from the BASE case simulation are evaluated against monitoring data at 12 sites in Beijing (Table S2) in 11 to 15, June 2017. The average NMB/NME values for O$_3$, NO$_2$ and PM$_{2.5}$ across the 12 sites are -8%/29%, -7%/59% and -8%/53%, respectively. Predicted hourly Cl$_2$, ClNO$_2$ and N$_2$O$_5$ concentrations were compared with observations measured at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39.98°N-98°N, 116.37°E-37°E) using a high-resolution time-of-flight chemical ionization mass spectrometer (CIMS) from 11 to 15 June 2017 (for site description, instrument introduction, and analytical method, please refer to the study by Zhou et al. (2018)). Figure 1 shows that the concentrations of Cl$_2$ and ClNO$_2$ in BASE case are rather low (close to 0), proving that the gas-phase chemistry is not the major pathway to produce Cl$_2$ and ClNO$_2$. By contrast, the simulated Cl$_2$ and ClNO$_2$ concentrations in HET case increase significantly, correspondingly the NMB and NME changes from -100% to -54% and 100% to 61% for Cl$_2$, and from -100% to -58% and 100% to 62% for ClNO$_2$, respectively (the parameter of total particle surface area (TOTSURFA) in CMAQ concentrations is revised scaled up by multiplying a factor of 5 in daytime and 10 in nighttime because this parameter is underestimated compared with the study of measured concentrations reported by Zhou et al. (2018)). The simulations of Cl$_2$ and ClNO$_2$ are improved because the newly added additional heterogeneous reactions prompt the conversions of production of gas phase molecular chlorine from particle state to gaseous state. Overall, however, the Cl$_2$ and ClNO$_2$ concentrations are still underestimated. Both BASE and HET simulations generally capture the hourly N$_2$O$_5$
concentrations as well as the peak values (Figure 1(c)) with similar overall NMB and NME values.

The underestimation of Cl\(_2\) may be associated with insufficient chemical conversion from ClNO\(_2\) to produce Cl\(_2\) at nighttime. The uncertainty in the uptake coefficient of O\(_3\) in daytime could also be an important factor as we believe affecting the predicted Cl\(_2\) concentrations as it is found that the uptake heterogeneous reaction of O\(_3\) is the major source of Cl\(_2\) during this period of time (see discussion in Section 3.2). According to equation (7), the underestimation of ClNO\(_2\) concentration may be due to two factors, that is, reaction rate \(K_6\) and N\(_2\)O\(_5\) concentration. Because the N\(_2\)O\(_5\) concentration is not substantially underestimated (see Figure 1(c)), we believe that the deviation of reaction rate \(K_6\) is the culprit to result in the underestimation of ClNO\(_2\), thus. The influence of different parametrizations of the uptake coefficient of N\(_2\)O\(_5\) which significantly affects \(K_6\) may be an important factor to affect the accuracy of ClNO\(_2\) simulation (see further discussion on ClNO\(_2\) and nitrate concentrations are also discussed in Section 3.2). The improved CMAQ can accurately capture the diurnal variation of N\(_2\)O\(_5\) concentration as well as the peak values (Figure 1(c)). In general, although the overall NMB and NME of BASE case (-20% and 38%) are slightly better than the HET case (-21% and 41%), the improved CMAQ—with the NMB and NME of -3% and 14%—perform better than original CMAQ (with the NMB and NME of -33% and 52%) in some period of heavy air pollution (such as the nighttime on 12 June and 13 June).

Predicted NO\(_3^-\) and PCl concentrations are compared with observations measured at an adjacent monitoring site located at the rooftop of School of Environment building in Tsinghua University (THU, 40.00°N, 116.34°E, about 5 km from IAP) using an Online Analyser of Monitoring of Aerosol and Gases (MARGA) from 11 to 15 June 2017. According to Figure 1(d), excluding the very high nitrate level in 13 June, the simulated nitrate concentration is commonly slightly lower than the observations, probably as the result of the unreasonable NH\(_4^+\)-gas-particle partitioning model in our developed CMAQ model (Song et al., 2018). Comparing with the very high nitrate concentrations in time. From the evening hours of 12 June to morning hours of 13 June, observed and 13 June, we find that the simulated nitrate concentration using improved CMAQ is superior to use original CMAQ, while the nitrate level is higher in daytime and lower in nighttime, with the both increase significantly. The NMB and NME improve from values of hourly nitrate for the HET case (-5% and 39%, respectively) are
slightly lower than those for the BASE case -10% and 46% to -5% and 39%. Excluding the daytime on 15 June, the improved CMAQ% during this high concentration period. The HET case also captures the hourly-day-to-day variation of PCI concentration and perform better than using original CMAQ the BASE case, correspondingly the NMB and NME change are reduced from -48% and 72% to -37% and 67%. The substantial underestimation of PCI in the daytime on 15 June is likely caused by some missing local emissions during this period.

3.2 Estimation Impact of uptake coefficients of O₃ and N₂O₅ on chlorine species and nitrate

The uptake coefficients of O₃ and N₂O₅ may be important factors affecting the accuracy of simulated nitrate concentrations. Some studies have confirmed that the reaction of O₃ on CPS can indirectly affect the nitrate formation by increasing the atmospheric Cl₂ and OH level (Li et al., 2016; Liu et al., 2018). According to Figure 1(a), the improved model still substantially underestimates the concentration of Cl₂, which may be associated with the underestimation of the uptake coefficient of O₃. The uptake coefficient of O₃ used in this study is empirical and has not been confirmed by laboratory studies. The uptake coefficients were increased by a factor of 10 (0.01 for daytime and 10⁻⁴ for nighttime) to evaluate the sensitivity of Cl₂ production and nitrate formation to this parameter. Figure 2 shows that the simulated Cl₂ and nitrate concentrations in daytime increase significantly (especially for Cl₂) and sometimes can capture the peak value (such as the daytime peak on 14 June). However, although the NMB and NME of Cl₂ and nitrate improve from -18% and 39% to 1% and 28% when the new uptake coefficients are used, the simulated Cl₂ concentrations are still quite different from the observations such as during the daytime in 11 and 12 June, see Figure 2). A non-constant parameterization of the uptake coefficients of O₃ that considers the influence of PCI concentrations, meteorology conditions, etc., similar to those of OH and N₂O₅, might be needed. Further laboratory studies should be conducted to provide a better estimation of this important parameter.

As described above, several parameterizations for the uptake coefficient of N₂O₅ can be expressed in multiple forms have been developed for regional and global models and have been evaluated in several previous studies (Tham et al., 2019, McDuffie et al., 2018a, 2018b). In addition to the parameterization of Bertram et al. and Thornton (2009)
used in the HET case, two additional simulations were performed to assess the impact of the uptake coefficient of N$_2$O$_5$ on nitrate formation. The first simulation uses the original CMAQ parameterization of Davis et al. (2008) and (2) the maximum second simulation uses a constant value of 0.09 from the study, which is the upper limit of the N$_2$O$_5$ uptake coefficient derived by Zhou et al. (2018) based on observations. The results show that the HET case has better agreement with the observations than the two additional from the simulations (Table 3). The Davis et al. with the parameterization is dependent on Bertram and Thornton (2009) generally agree with the concentration of nitrate and sulfate concentration, which is inferior to results using those based on Davis et al. (2008) and the coefficient used in this study. We conclude that a chlorine-related coefficient is more reasonable for the application of simulating reactive chlorine species and nitrate; larger constant N$_2$O$_5$ leads to slightly better results, which might reflect the fact that the N$_2$O$_5$ concentrations in high chlorine emission regions are underestimated. Using the uptake coefficient of 0.09 can generally increase the concentration of nitrate in some periods, but it also leads to significant overestimation of the nitrate level (such as nighttime on 12-13 June and 13-14 June), which is 4-6 times higher than those based on Bertram and Thornton (2009).

Overall, predicted nitrate concentrations are sensitive to changes in the changes in $\gamma_{N_2O_5}$, with approximately 50% increase in the nitrate when a constant of $\gamma_{N_2O_5}$ of 0.09 is used.

3.3 Spatial distributions of nitrate and chlorine species concentrations

The regional distributions of averaged Cl$_2$, ClNO$_2$, N$_2$O$_5$ and NO$_3^-$ concentration from 11 to 15 June for the BASE case and HET case are shown in Figure 3. Compared to original CMAQ, the averaged the BASE case, the episode average concentrations of Cl$_2$ and ClNO$_2$ derived from improved CMAQ the HET case increase significantly in the eastern region of Beijing, reaching up to 23 ppt and 71 ppt from near zero. Fig. 3a and 3b). High concentrations are not found in the southern region with intensive emissions of chlorine species, implying that Cl$_2$ and (Figure S2). The production of ClNO$_2$ requires the presence of chloride, NO$_2$, and O$_3$. In the areas close to the fresh emissions, O$_3$ is generally low (Figure S3), and the production of NO$_3^-$ (hence N$_2$O$_5$ and ClNO$_2$) is limited. Therefore, the production rate of ClNO$_2$ is generally low in areas affected by fresh emissions. Since the contribution of direct
emissions to Cl$_2$ is low and it is predominantly produced secondarily in the atmosphere, high levels of Cl$_2$ are easy to transport among cities, also found away from the fresh emissions.

The spatial distribution of N$_2$O$_5$ concentrations differs from that of other species, (Figure 3c). While the concentrations of most of the species are higher in the southern region, the N$_2$O$_5$ concentration is low. Concentrations are lower in some parts of this region. This is because the O$_3$ concentration in the core urban areas is low due to high NO$_x$ emissions. By incorporating the chlorine heterogeneous reaction, the N$_2$O$_5$ concentrations decrease by about 16% lower on average (Figure 3d) because more N$_2$O$_5$ is converted into nitrate, the Bertram and Thornton (2009) parameterization used in the HET case generally gives higher uptake coefficients than the parameterization of Davis et al. (2008) used in the BASE case (Table 3).

Although the added PCI prompts the higher uptake coefficients of N$_2$O$_5$ in the HET case facilitate faster conversion from N$_2$O$_5$ to nitrate, the nitrate concentrations in these regions have not increased significantly in some regions by about 22%, mainly due to lower molar yield of nitrate from the reduction of 2 mol NO$_3^-$ in R5 to 1 mol in R6 for each mole of N$_2$O$_5$ reacted. The heterogeneous reaction in the HET case (Figure 3g and Figure 3h). Although the generated ClNO$_2$ produced in the N$_2$O$_5$ reaction also further produces nitrate, through a heterogenous reaction when the particle pH is above 2, which is true for most time in regions (see Figure S1 and S4), the uptake coefficient of ClNO$_2$ is significantly lower than that of N$_2$O$_5$ (0.01–0.09 for N$_2$O$_5$ and 6 × 10$^{-3}$ for ClNO$_2$), leading to an overall decrease of nitrate production. As the ClNO$_2$ production from the heterogeneous reaction leads to less N$_2$O$_5$ conversion to non-relative nitrate, it may change the overall lifetime of NOx and their transport distances. The magnitude of this change and its implications on ozone and PM$_{2.5}$ in local and downwind areas should be further studied.

3.4 Relationship between nitrate formation and chlorine chemistry

A CMAQ tagged method (tagging the nitrate concentration produced by the heterogeneous reaction, the rest of nitrate is produced by HNO$_3$ partitioning) is used to
estimate the nitrate production from the homogeneous and heterogeneous pathways and HNO$_3$ partitioning pathways. In general, about 58.3% of the nitrate in Beijing are approximated by the difference in predicted nitrate concentrations between the BASE or HET case and a sensitivity case without heterogeneous reactions. Averaging over the five-day period, approximately 58% of the nitrate originates from heterogeneous reaction pathways (Figure 4). This conclusion generally agrees with measurements at a nearby observation site in Peking University (PKU) (Wang et al., 2017), which indicates 52% from the heterogeneous process and 48% from HNO$_3$ partitioning. Two factors may lead to the differences between our simulation and measurements at PKU. One is the chlorine heterogeneous chemistry and the other is the pollution level. More nitrate-homogeneous pathway in this study is expected to be produced by HNO$_3$-gas to-particle partitioning in cleaner days whereas the heterogeneous process is more important in haze days. The averaged nitrate level at PKU site because of high OH concentrations during the measurement was 14.2 µg m$^{-3}$, about 4 times higher than that in this study during day and lower particle surface areas at night.

The production rates of gaseous HNO$_3$ from different gas-phase reactions and The nitrate formation from different homogeneous and heterogeneous reaction pathways in the BASE case and HET case are further studied using process analysis. Contributions of different gas phase pathways are determined using the process analysis tool in CMAQ. Contributions of different heterogeneous pathways are determined using a zero-out method that turns off one heterogeneous pathway at a time in a series of sensitivity simulations. Figure 4 shows that the reaction of OH and NO$_2$ is always the major pathway to produce gaseous for the formation of nitrate through homogeneous formation of HNO$_3$ regardless of daytime or nighttime. Natural gas-to-particle partitioning, however, decreases significantly from daytime to nighttime (from 4272 ppt 1.81 µg m$^{-3}$ h$^{-1}$ to 234 ppt 0.33 µg m$^{-3}$ h$^{-1}$ on average). The nitrate production from other HNO$_3$ production partitioning pathways in the daytime can be ignored because their is negligible. At nighttime, homogeneous reaction rates are rather low. But at nighttime the reaction rate of N$_2$O$_5$ with water vapor presents a rapid increase, reaching up to 12.2 ppt h$^{-1}$ from 1.7 ppt h$^{-1}$, which accounts for approximately 5% of the HNO$_3$ overall...
homogeneous nitrate formation in the gas phase. For the heterogeneous pathways, all of daytime production rate is approximately 0.6 μg m⁻³ h⁻¹ with 1/3 of the contributions from NO₂ and 2/3 from N₂O₅. Nighttime production on nitrate from the heterogeneous pathways is approximately 3.1 μg m⁻³ h⁻¹, of which 85% is due to N₂O₅ and 15% is due to NO₂.

Comparing the BASE case and the reactions can be neglected in the daytime. At nighttime, the heterogeneous uptake N₂O₅ on the particle surface is the major pathway to nitrate formation (about 3.07 μg m⁻³ h⁻¹, account for 84.8% in heterogeneous formation). By contrast, heterogeneous uptake of NO₂ on particulate H₂O has less contribution to nitrate (15.2%).

When HET case shows that, when the chlorine chemistry is included, the gaseous HNO₃ produced by OH reacting with NO₂ increases significantly (in the HET case). Correspondingly, the nitrate production rate reaches up to 1487 ppb 2.04 μg m⁻³ h⁻¹ in the daytime and 253 ppt h⁻¹ at nighttime) due to increased atmospheric OH concentrations predicted by the chlorine reactions. Similar conclusions are also obtained by Li et al. (2016) and Liu et al. (2017) based on observations and model simulation. Note that the reaction of NO₂ with HO₂ does not increase obviously even through the chlorine chemistry also leads to higher atmospheric HO₂ levels (increase by more than 20%, Li et al., (2016)) because the atmospheric NO₂ radical level is rather low simulations. The heterogeneous production of nitrate from the reaction of N₂O₅ uptake decreases dramatically (about by approximately 27%)% in the HET case due to the inclusion of production of gas phase CINO₂. According to the study by Sarwar et al. (2012; 2014), including the heterogeneous reactions of chlorine species reaction of N₂O₅ with PCI decreased the nocturnal nitrate concentration by 11-21% in the United States, which was slightly less than the current study for Beijing. It is likely because PCI concentrations in the United States are significantly lower than those in Beijing (the monthly PCI concentration is 0.06 μg m⁻³ in the United State against ~1 μg m⁻³ in Beijing) so that PCI is depleted quickly. The contributions of NO₂ uptake to nitrate also decrease by 22% because of the lower rate constant of the reaction of NO₂ with PCI. In contrast, the contribution of CINO₂ decomposition reacts with particle surface to nitrate production increases by 6% in the HET case. Generally, the overall nitrate concentrations estimated by original CMAQ concentration in the HET case is about 22% higher than that in the modified CMAQ BASE case during this study period.
4. Conclusions

Current chemistry transport models are evaluated to have high uncertainty in the simulation of nitrate, especially for the period of heavy air pollution. In this work, an improved modified CMAQ model incorporated with chlorine-heterogeneous chemistry is developed to evaluate the impact of chlorine-related heterogeneous reaction on nitrate formation and quantify the contributions from gas-to-particle partitioning of HNO$_3$ and from different heterogeneous reactions.

This results show four meaningful conclusions: (1) the emission inventories of for the production of molecular chlorine and other reactive chlorine species are important because it is the cornerstones of studying chlorine chemistry; (2) The sensitivity analysis shows that a non-constant parameterization of the uptake coefficients of O$_3$ that consider the influence of PCI concentrations, meteorology conditions, etc., might be needed. N$_2$O$_5$ uptake coefficient expressed as a function of the concentrations of chlorine can capture the nitrate concentration better than others; (3) Cl$_2$ and ClNO$_2$ are easy to transport among cities because high concentrations of them are not found in southern impacted by its impact on of the nitrate formation predictions are evaluated. The contributions from different homogenous and heterogeneous pathways to nitrate formation are also quantified. High concentration of Cl$_2$ and ClNO$_2$ do not occur in the southern part of the Beijing-Tianjin-Hebei region with intensive emissions of chlorine species. (4) more importantly, current as higher concentrations of O$_3$ and N$_2$O$_5$ associated with the heterogeneous formation of these species generally occurred in the downwind areas. CTMs without a complete treatment of the chlorine chemistry can significantly underestimate the nitrate level daytime nitrate formation from the homogeneous pathways, particularly from HNO$_3$ gas-to-particle partitioning due to underestimation of the reaction rate of OH with NO$_2$ concentrations and overestimate the nighttime nitrate formation from the heterogeneous formation pathways due to missing chlorine heterogeneous chemistry.

This study aims to improve our understandings on the chlorine chemistry and its impact on nitrate formation, which can provide useful implications on the nitrate pollution control strategies for those regions that suffered serious nitrate pollution.

Data availability. The data in this study are available from the authors upon request (shxwang@tsinghua.edu.cn)
Author contributions. XQ, QY, SW, and JH conducted the study; YS, BL, AS, XY provided observation data; XQ, QY, SW, JZ, QX, DD, LD and JX analyzed data. XQ, QY and SW wrote the paper. JZ, DD, YS, BL, AS, XY and QX analyzed data.

Competing interests. The authors declare that they have no conflict of interest.

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Figure 1. Comparison of simulated and observed hourly Cl₂, ClNO₂, N₂O₅, (at the Institute of Atmospheric Physics, Chinese Academy of Sciences), NO₃⁻ and PCl using original and improved CMAQ (the gray presents nighttime) (at Tsinghua University)
in urban Beijing with predictions from the BASE and the HET cases during 11-15 June 2017.

Figure 2. Comparison of simulated observed and predicted Cl₂ and NO₃⁻ concentrations under different uptake coefficient of O₃ (HET: daytime \( \gamma_{O_3} = 1 \times 10^{-3} \), nighttime \( \gamma_{O_3} = 1 \times 10^{-5} \); HET-Co: the scenario of uptake coefficients daytime \( \gamma_{O_3} = 1 \times 10^{-2} \), nighttime \( \gamma_{O_3} = 1 \times 10^{-4} \)).
Figure 3. Spatial distributions of episode-average (a) Cl$_2$, (b) ClNO$_2$, (c) N$_2$O$_5$, (e) daytime nitrate (ANO$_3$) and (g) NO$_3^-$ concentration in daytime and nighttime (a-b: nitrate concentrations of Cl$_2$ and ClNO$_2$ from 11-15 June 2017, and the differences in HET case; e-the episode-average (d: the concentration of) N$_2$O$_5$ in HET case and difference between HET case and BASE case; e-f: the diurnal concentration of NO$_3^-$ in HET case and difference between HET case and BASE case; g-h: the nocturnal concentration of...
NO$_2^-$ in HET case and difference between HET case and BASE case). (f) daytime nitrate and (g) nighttime nitrate. Units are $\mu$g m$^{-3}$. 
Figure 4. Contributions of different gas-phase reaction pathways—homogeneous and heterogeneous reaction pathways—to nitrate formation.
Figure 1
Figure 2
Figure 3
Note: the distribution of Cl₂ and CINO₂ in HET minus BASE have not been shown because their concentrations in BASE case are rather low (close to 0)
Figure 4

Average Nitrate Concentration (µg m⁻²)

HET Daytime Nighttime

Heterogeneous production HNO₃ partitioning

Production rate (ppt)

BASE HET BASE HET BASE HET

Gas-phase pathways

Heterogeneous pathways

Nitrate (µg m⁻²)

BASE HET BASE HET

NOₓ+ VOCs NOₓ+ H₂SO₄ NOₒ(NO₂ + H₂O) OH+ HNO₂
<table>
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<th>PCl</th>
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<td>Municipal solid waste</td>
<td>1080.2</td>
<td>0</td>
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<td>Cooking</td>
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<td>0</td>
<td>426.8</td>
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<tr>
<td>Total</td>
<td>1892.9</td>
<td>29.4</td>
<td>566.1</td>
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</tbody>
</table>

Table 1 The sectoral emissions of HCl, Cl₂ and PCl in Beijing in 2017. Unit: Mg year⁻¹.
Table 2 Major gas-phase and heterogeneous pathway of producing nitrate in original CMAQ and newly added or revised heterogeneous reactions in improved CMAQ.

<table>
<thead>
<tr>
<th>Type</th>
<th>Reactions</th>
<th>No.</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Original CMAQ</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-phase chemistry</td>
<td>OH + NO₂ → HNO₃</td>
<td>R1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N₂O₅ + H₂O → HNO₃</td>
<td>R7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HO₂⁺ + NO₃ → HNO₃ + OH + NO₂.0.2HNO₃ + 0.8OH + 0.8NO₂</td>
<td>R8</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>NO₃ + VOCs⁹ → HNO₃</td>
<td>R9</td>
<td></td>
<td></td>
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<tr>
<td>Heterogeneous chemistry</td>
<td>N₂O₅(g) → H₂O(aq) → 2HNO₃(g)2H⁺ + 2NO₃⁻</td>
<td>R5</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>NO₂NO₂(g) + H₂O(aq) → HONO(g) + HNO₃(g)H⁺ + NO₃⁻</td>
<td>R10</td>
<td></td>
<td></td>
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<tr>
<td><strong>Improved CMAQ</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newly added or revised heterogeneous reactions</td>
<td>N₂O₅(g) + H₂O(aq) + Cl⁻(aq) → ClNO₂(g) + NO₃⁻ Cl⁻</td>
<td>R6</td>
<td>Bertram and Thornton (2009)</td>
<td>Revise R5</td>
</tr>
<tr>
<td></td>
<td>2NO₂(g) + Cl⁻(aq) → ClNO₂(g) + NO₃⁻</td>
<td>R11</td>
<td>Abbott et al. (1998)</td>
<td>Revise R10</td>
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<tr>
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<td>N₂O₅(g) + 2Cl⁻(aq) → Cl₂(g) + NO₃⁻</td>
<td>R12</td>
<td>Rudich et al. (1996)</td>
<td>Increase NO₃⁻</td>
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<tr>
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<td>2Cl⁻(aq) + O₃(g) + 2Cl⁻ + H₂O(aq) → Cl₂(g) + 2OH⁻(aq)</td>
<td>R13</td>
<td>Abbott et al. (1998)</td>
<td>Affect OH</td>
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<tr>
<td></td>
<td>OH⁻2OH(g) + Cl⁻(aq) → 2Cl⁻ → Cl₂(g) + 2OH⁻(aq)</td>
<td>R14</td>
<td>George et al. (2010)</td>
<td>Affect OH</td>
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<tr>
<td></td>
<td>ClINO₂(g) + Cl⁻(aq) + H⁺(aq)⁻ → Cl₂(g) + HNO₃(g)NO₂⁻</td>
<td>R15</td>
<td>Deiber et al. (2004)</td>
<td>Affect OH</td>
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<td>HOCI(g) + Cl⁻(aq) + H⁺(aq)⁻ → Cl₂(g) + H₂O(aq)</td>
<td>R16</td>
<td>Pratte et al. (2006)</td>
<td>Affect OH</td>
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<tr>
<td></td>
<td>ClINO₂(g) + Cl⁻(aq) + H⁺(aq)⁻ → Cl₂(g) + HONO(aq)</td>
<td>R17</td>
<td>Riedel et al. (2012)</td>
<td>Affect OH</td>
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<tr>
<td></td>
<td>(PH₅) (pH &lt; 2.0)</td>
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<tr>
<td></td>
<td>CINO₂(g) + H₂O(aq) → Cl⁻ + NO₃⁻ + 2H⁺ (pH ≥ 2.0)</td>
<td>R18</td>
<td>Rossi (2003)</td>
<td>Increase NO₃⁻</td>
</tr>
</tbody>
</table>

⁹: presents different VOCs species. In the SAPRC-11 mechanism, the VOCs species include CCHO (Acetaldehyde), RCHO (Lumped C3+ Aldehydes), GLY (Glyoxal), MGLY (Methyl Glyoxal), PHEN (phenols), BALD (Aromatic aldehydes), MACR (Methacrolein), IPRD (Lumped
isoprene product species).
The observed day (D) and night (N) NO$_3^-$ concentrations (Obs.) and predicted uptake coefficient of N$_2$O$_5$ in different scenarios and its impact on ($\gamma_{N_2O_5}$) and nitrate (unit: µg m$^{-3}$) (uptake coefficient concentrations (Pred.)) using the parameterizations of $\gamma_{N_2O_5}$ derivates from by Bertram and Thornton (2009) (Scenario 1), Davis et al. (Scenario 1), Davie et al. (Scenario 2), and . (2008) (Scenario 2) and the upper-limit value derived by Zhou et al. (2018), respectively (Scenario 3).

<table>
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<tr>
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<th>Scenario1</th>
<th>Scenario2</th>
<th>Scenario3</th>
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<td>$\gamma_{N_2O_5}$</td>
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<tr>
<td>NO$_3^-$ Obs.</td>
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<td>$\gamma_{N_2O_5}$</td>
<td>$\gamma_{N_2O_5}$</td>
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<td>06/11-D</td>
<td>2.54</td>
<td>0.033</td>
<td>1.59</td>
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<tr>
<td>06/11-12-N</td>
<td>2.42</td>
<td>0.043</td>
<td>1.67</td>
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<tr>
<td>06/12-D</td>
<td>3.39</td>
<td>0.028</td>
<td>2.16</td>
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<tr>
<td>06/12-13-N</td>
<td>4.24</td>
<td>0.021</td>
<td>4.02</td>
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<tr>
<td>06/13-D</td>
<td>2.57</td>
<td>0.012</td>
<td>1.18</td>
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<td>06/13-14-N</td>
<td>4.10</td>
<td>0.022</td>
<td>4.45</td>
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<td>06/14-D</td>
<td>0.95</td>
<td>0.001</td>
<td>1.34</td>
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<tr>
<td>06/14-15-N</td>
<td>2.75</td>
<td>0.013</td>
<td>1.00</td>
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<tr>
<td>06/15-D</td>
<td>0.75</td>
<td>0.001</td>
<td>0.66</td>
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