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 NO_2, O_3, and $PM_{2.5}$, which are the precursors of N_2O_5, $ClNO_2$, 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 SO_2, 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 O_3, NO_2 and $PM_{2.5}$ concentrations are now described in the revised manuscript on page 9, lines 259-262: "Predicted O_3, NO_2 and $PM_{2.5}$ 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 O_3, NO_2 and $PM_{2.5}$ 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 NO_2 and $PM_{2.5}$ and O_3 concentrations with observations averaged from 11 to 15 June 2017 (Obs.: observation, Sim.: simulation). Units: $\mu g\ m^{-3}$

	NO_2				O_3				$PM_{2.5}$			
Sites	Obs.	Sim.	NMB	NME	Obs.	Sim.	NMB	NME	Obs.	Sim.	NMB	NME
WSXG	49	54	11%	55%	99	122	23%	31%	40	38	-6%	53%
DL	21	17	-20%	68%	111	108	-2%	12%	32	29	-10%	52%
DS	47	53	13%	54%	100	114	15%	28%	44	41	-7%	53%
TT	40	48	20%	64%	98	130	33%	45%	37	37	1%	58%
NZG	51	66	28%	62%	111	121	9%	25%	42	39	-7%	52%
GY	55	65	17%	57%	107	116	9%	22%	36	33	-8%	54%
WL	52	41	-21%	54%	92	112	22%	43%	35	33	-7%	54%
XC	43	31	-28%	47%	100	108	8%	12%	33	29	-12%	55%
HR	26	11	-56%	70%	124	105	-15%	27%	27	22	-19%	51%
CP	42	28	-34%	58%	96	91	-5%	27%	33	32	-1%	54%
ATZX	56	62	10%	55%	105	107	1%	18%	33	31	-4%	54%
GC	56	42	-25%	58%	106	107	0%	19%	43	37	-14%	52%

WSXG: Wanshouxigong; DL: Dingling; DS: Dongsi; TT:Tiantan; NZG:Nongzhanguan; GY: Guanyuan; WL: Wanliu; XC:Xincheng; HR:Huairou; CP:Changping; ATZX:Aotizhongxin; GC:Gucheng; NMB: normalized mean bias; NME: normalized mean error.

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_2 and $ClNO_2$ 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%." in line 25-26 are revised as "The results show that these heterogeneous reactions increase the atmospheric Cl_2 and $ClNO_2$ level (~100%), which further affect the nitrate formation"

Comment #6: Line 37-39. The $ClNO_2$ 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 $ClNO_2$ production from the heterogeneous reaction leads to less N_2O_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 14, lines 374-380.

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 $NO_3 + HO_2$, VOC + NO_3, and N_2O_5 with water vapor are generally negligible in terms of secondary nitrate formation in polluted urban and rural areas, due to low concentrations of NO3 and HO2, and low yield of HNO3 in the VOC + NO3 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_2 could be important so we included a sentence in the revised manuscript to mention that:

"The heterogeneous reaction of NO_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_3-NH_4^+ gas-particle equilibrium on the nitrate formation.

Response #8: The reference below are added.

Kleeman, M.J., Ying, Q., Kaduwela, A., 2005. Control strategies for the reduction of airborne particulate nitrate in California's San Joaquin Valley. Atmospheric Environment 39, 5325-5341.

Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley-Interscience, New York.

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 N_2O_5 (NO_3) 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 $ClNO_2$ 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 page15, lines 426-436.

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 N_2O_5 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 report 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 Cl_2 and $ClNO_2$ reached up to 1000 pptv and 1200 pptv, respectively, during some severe air pollution period in summer. The corresponding concentrations of N_2O_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 ClNO2 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 7, lines 179-182.

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. NH_3 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, ClNO2, and nitrate aerosol.

Response #23: We supplement the description of emission in page 7, line 185-186 and this sentence is revised as "Emissions of conventional species (including SO_2, NO_X, VOCs, $PM_{2.5}$, PM_{10}) for this study period were derived by Ding et al., which are 22.7Gg, 128.6Gg, 24.9Gg, 32.5Gg, 345.9Gg and 29.3Gg for SO_2, NO_X, $PM_{2.5}$, PM_{10}, VOCs and NH_3"

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_2O_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). This is clearly explained in the original text and can be seen also in the revised manuscript on page 16, lines 433-436.

(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 NO2 and SO2. 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.

Comment #25: Line 178. What do you mean by 'current CMAQ model'? Is 'Zheng et al. (2015)' a proper reference for 'current CMAQ model'?

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)

Hu, J., Chen, J., Ying, Q., Zhang, H., 2016. One-Year Simulation of Ozone and Particulate Matter in China Using WRF/CMAQ Modeling System. Atmos. Chem. Phys. 16, 10333-10350.

Hu, J., Wang, P., Ying, Q., Zhang, H., Chen, J., Ge, X., Li, X., Jiang, J., Wang, S., Zhang, J., Zhao, Y., Zhang, Y., 2017. Modeling biogenic and anthropogenic secondary organic aerosol in China. Atmos. Chem. Phys. 17, 77-92.

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 O_3 was not based on direct experimental measurements but was estimated indirectly based on a steady-state analysis of Cl_2 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 Cl_2 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 O_3 uptake coefficient, we do some sensitivity case to evaluate how the effect of this uncertainty on the underestimation of atmospheric Cl_2 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 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).

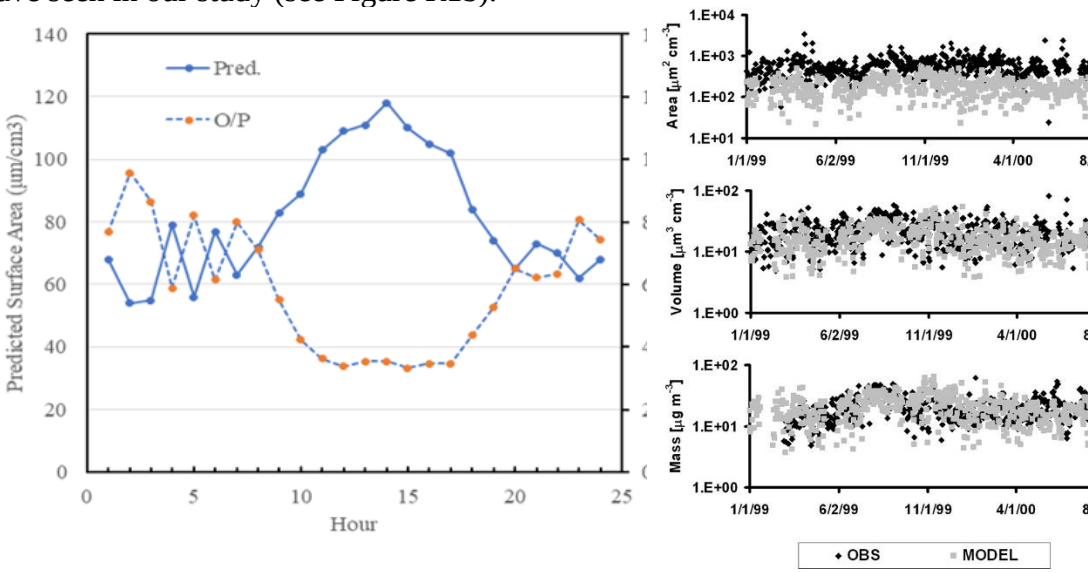


Figure R1a (left panel): Predicted averaged hourly particle wet surface area at IAP (June 11-15, 2017) and the ratio of observed to predicted PSA (O/P). R1b (right panel): CMAO predicted and observed daily particle surface area, volume, and mass concentrations for PM2.5 from 1/1/1999 to 8/31/2000 at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

Reference:

Park, S.K., Marmur, A., Kim, S.B., et al.: Evaluation of fine particle number concentrations in CMAQ. Aerosol Science and Technology, 40, 985-996, 2006.

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 ClNO2 and nitrate cannot be assumed. No changes were made regarding this comment.

Comment #33: Line 258. The O_3 will increase or decrease if you change the uptake coefficient of O_3. This also calls for the model evaluation on O_3.

Response #33: The impacts of heterogeneous chlorine chemistry on O3 formation are complicated. On one hand, O_3 is consumed by the heterogeneous reaction with PCl. On the other hand, the generated Cl_2 photolyze to produce Cl atom, resulting in the increase of O_3. The impact of chlorine chemistry on ozone is a very important by itself and has been explored in a sperate manuscript that is currently under review. Model performance of O_3 is evaluated by comparing with observations at 12 sites in Beijing (The average NMB/NME values for O_3 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 N_2O_5 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 N_2O_5 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 fond in the revised paper on page 12, lines 340-346.

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 ClNO2 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 NO_2, which shows that the NO_2 concentration isn't significantly underestimated (The average NMB/NME values for NO_2 across the 12 sites are -7%/59%). In original CMAQ, the NO_2 hydrolysis produces HONO and HNO3. However, in the improved CMAQ, this reaction is revised as:

$2NO_2(g) + Cl^-(aq) \rightarrow ClNO(g) + NO_3^-(aq)$ (if the NO2 is redundant, $2NO_2(g) + H_2O(aq) \rightarrow HONO(g) + NO_3^-(aq)$).

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 HNO_3 and the reaction N_2O_5 with PCl are the major pathways of producing nitrate in daytime and nighttime, so we choose to run sensitivity cases of O_3 (O_3 uptake is major contributor to Cl_2 in R13-R17) and N_2O_5 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 Cl_2 emissions. It is generally accepted that direct Cl_2 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 Cl_2 with other primary emission indicators (K^+ for biomass burning (R=0.004), SO_2 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))

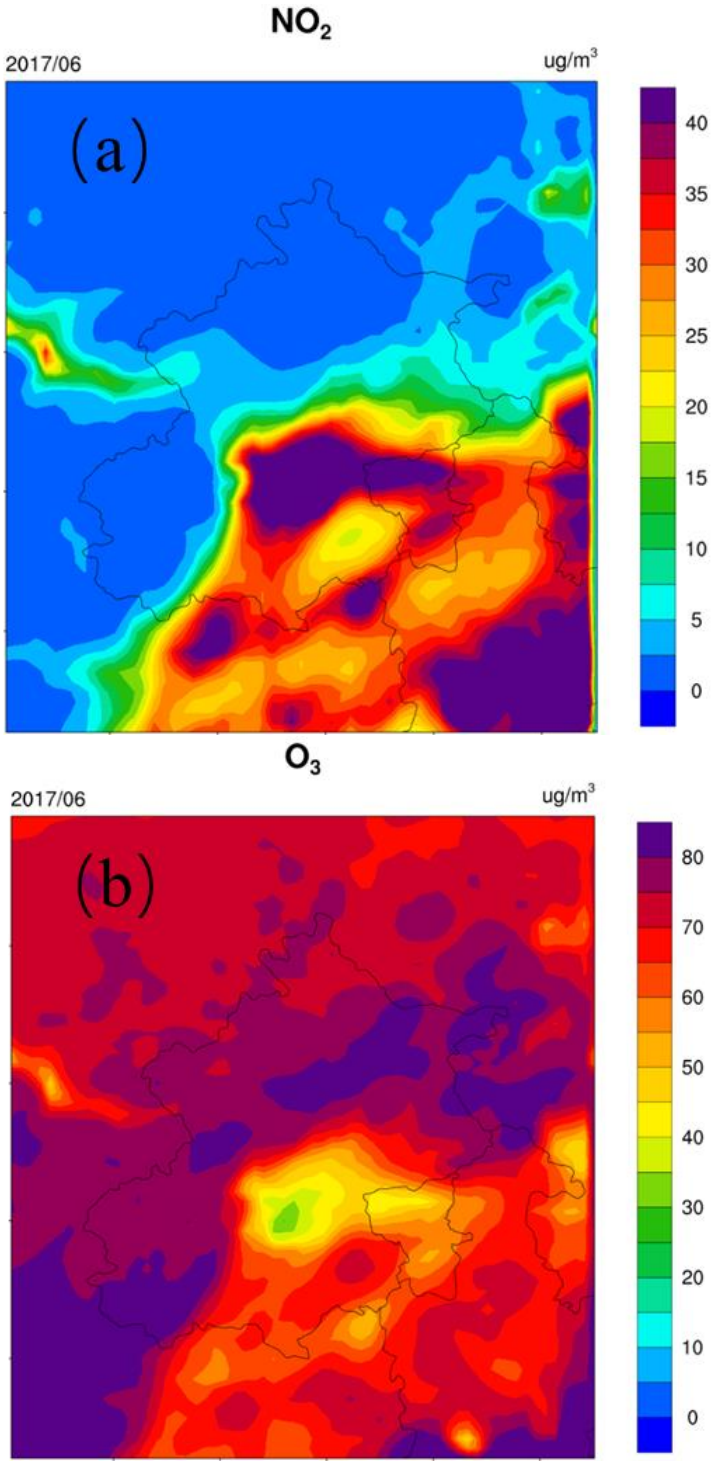
Deng, S., Zhang, C., Liu, Y., et al.: A Full-Scale Field Study on Chlorine Emission of Pulverized Coal-Fired Power Plants in China. Research of Environmental Science. In Chinese, 27, 127-133, 2014.

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.



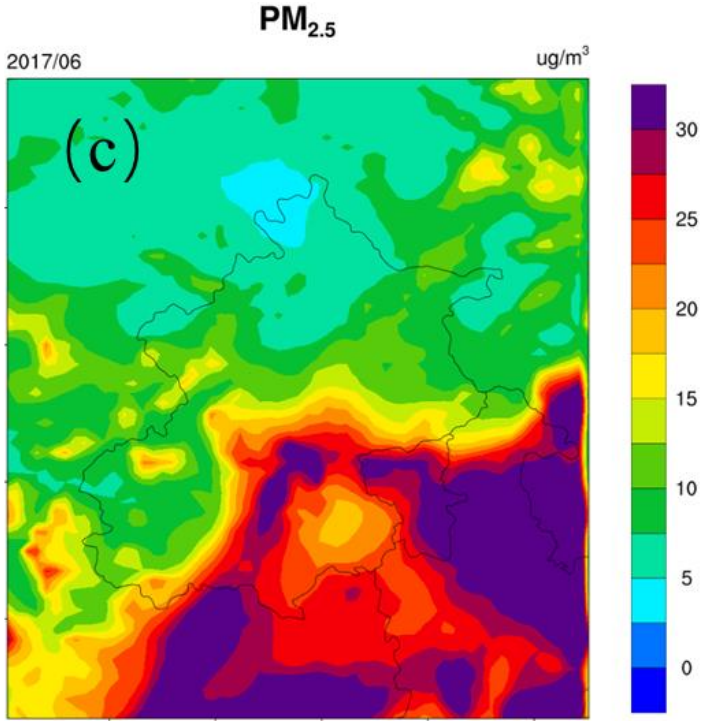


Figure R2 The spatial distribution of NO_2(a), O_3(b) and $PM_{2.5}$(c) concentration averaged in 11 to 15, June.

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.

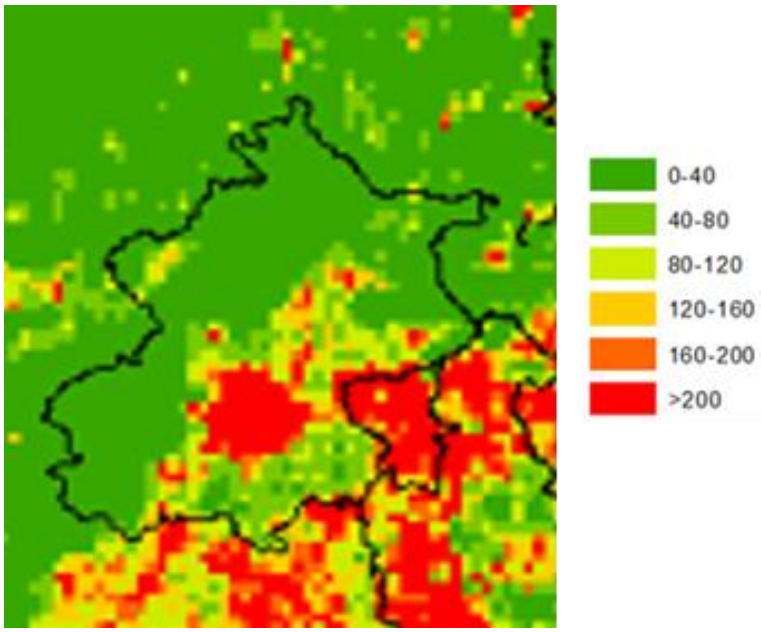


Figure R3 The spatial distribution of PCl emission in Beijing in 2017 (Unit: Kg/year per grid).

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 13, line 354-360 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 13, lines 366-367.

Comment #44: Line 351-352. Was the observation in PKU conducted in the same period?

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.

Comment #48: Line 402-404. Not necessarily correct. See comment above.

Response #48: The sentence 'Cl_2 and $ClNO_2$ 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 Cl_2 and $ClNO_2$ 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 4, line 97-105. 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 ClNO2 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 ‘EFi,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'.

Comment #71: Line 211. How did you calculate Kh, Kf, K3/K2, and K4/K2? Are they constants? If so, please add the number.

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 6×10^{-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):

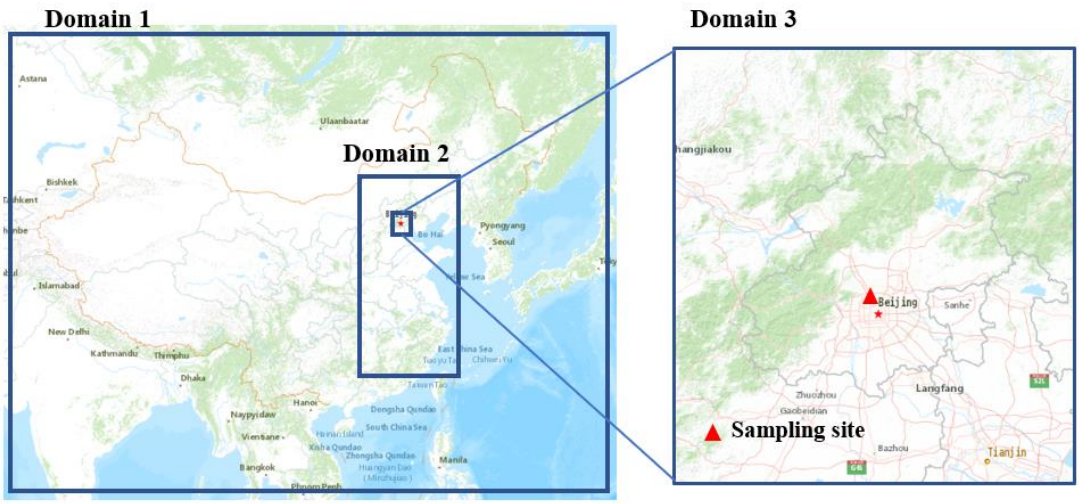


Figure R4 the three nested domain setting in this work.

Comment #75: Line 232. '40ºE' should be '40ºN'.

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. ‘understnadings’ 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.