

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 list 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 PM_{2.5}, 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, NO_x, VOCs, PM_{2.5} 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

45 on Ding et al. is included in Table S1 in the revised manuscript.

46

47 Evaluations of predicted O₃, NO₂ and PM_{2.5} concentrations are now described in the
48 revised manuscript on page 34, lines 325-328: “Predicted O₃, NO₂ and PM_{2.5}
49 concentrations from the BASE case simulation are evaluated against monitoring data
50 at 12 monitoring sites in Beijing (Table S2) for 11 to 15 June 2017. The average
51 NMB/NME values for O₃, NO₂ and PM_{2.5} across the 12 sites are -8%/29%, -7%/59%
52 and -8%/53%, respectively.”. Table S2 is attached below as Table R1 for the
53 convenience of the reviewer.

54

55 Table R1 Comparison of simulated episode average hourly NO₂ and PM_{2.5} and O₃
56 concentrations with observations averaged from 11 to 15 June 2017 (Obs.: observation,
57 Sim.: simulation). Units: $\mu\text{g m}^{-3}$

Sites	NO ₂				O ₃				PM _{2.5}			
	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%

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

62

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

68

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

71

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

73

74 **Response #5:** Thank you for pointing out the redundant descriptions. The sentences

75 “The results show that these heterogeneous reactions significant increase the
76 atmospheric Cl₂ and ClNO₂ level, leading to an increase of the nitrate concentration by
77 ~10% in the daytime. However, these reactions also lead to a decrease the nocturnal
78 nitrate by ~20%.” in line 25-26 are revised as “The results show that these
79 heterogeneous reactions increase the atmospheric Cl₂ and ClNO₂ level (~100%), which
80 further affect the nitrate formation”

81
82 **Comment #6:** Line 37-39. The ClNO₂ production decreases nitrate during nighttime
83 and increases nitrate during the daytime. Does it mean that the chlorine chemistry
84 changes the temporal pattern of the nitrate formation and therefore the spatial pattern?
85 Does it have any implication to the air quality control? I would love to see a discussion
86 on this implication.

87
88 **Response #6:** While it is true that temporal pattern of nitrate formation was slightly
89 altered, the spatial patterns of nitrate didn’t change significantly during the study period.
90 However, as the ClNO₂ production from the heterogeneous reaction leads to less N₂O₅
91 conversion to non-relative nitrate, it may change the overall lifetime of NO_x and their
92 transport distances. The magnitude of this change and its implications on ozone and
93 PM_{2.5} locally and in the downwind areas should be further studied. We included this
94 in the revised manuscript on page 38, lines 473-477.

95
96 **Comment #7:** Line 50-57. The authors only introduced two production pathways of
97 the secondary nitrate. However, the other pathways, e.g., those in Table 2, also play
98 non-negligible roles. Should add those pathways in the introduction.

99
100 **Response #7:** The other gaseous reactions such as NO₃ + HO₂, VOC + NO₃, and N₂O₅
101 with water vapor are generally negligible in terms of secondary nitrate formation in
102 polluted urban and rural areas, due to low concentrations of NO₃ and HO₂, and low
103 yield of HNO₃ in the VOC + NO₃ reactions. We included them in Table 2 for
104 completeness but we don’t think they should be specifically mentioned in the
105 introduction section. The heterogeneous reaction of NO₂ could be important so we
106 included a sentence in the revised manuscript to mention that:

107
108 “The heterogeneous reaction of NO₂ on particle surface has been shown to be an
109 important source of secondary nitrate” (Abbatt et al., 1998).

110
111 **Comment #8:** A reference is needed for the enhancement effect of NH₃-NH₄⁺ gas-
112 particle equilibrium on the nitrate formation.

113
114 **Response #8:** The reference below are added.

115
116 Kleeman, M.J., Ying, Q., Kaduwela, A., 2005. Control strategies for the reduction of
117 airborne particulate nitrate in California's San Joaquin Valley. Atmospheric
118 Environment 39, 5325-5341.

119

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

122

123 **Comment #9:** Line 57. These papers are not the proper reference for the nitrate
124 formation mechanism, e.g., Brown and Stutz (2012) is a better one for the N_2O_5 (NO_3)
125 chemistry.

126

127 **Response #9:** Revised.

128

129 **Comment #10:** Line 63-72. The authors only introduced three previous works here,
130 and all of them were conducted in China, in the Northern China Plain to be exact. What
131 about similar modeling studies in other regions, e.g., the southern part of China,
132 Northern America, and Europe? For example, Sarwar et al. (2012, 2014) developed the
133 same model, CMAQ, to evaluate the effect of ClNO_2 production on air quality,
134 including the total nitrate, in the US and the Northern Hemisphere. However, these two
135 critical papers are not discussed anywhere in the current manuscript.

136

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

140

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

143

144 **Response #11:** This sentence is removed.

145

146 **Comment #12:** Line 77-80. This statement is not correct. For example, Wang et al.
147 (2016) and Brown et al. (2016) reported extremely high N_2O_5 mixing ratios at a site in
148 Hong Kong (a coastal city) of up to 8ppbv (1min average) or 12ppbv (1min average).
149 This brings up another issue. Should include the average time when report observational
150 results, e.g., 1 s average, 1 min average, or 1h average.

151

152 **Response #12:** High concentrations of N_2O_5 in Hong Kong is likely affected by non-
153 local emissions from city clusters in the Pearl River Delta (PRD) region during some
154 high pollution episodes. We remove the relative clause, “which were significantly
155 higher than those in unpolluted coastal cities and the lower atmosphere in the remote
156 Arctic region.” in the revised manuscript. We agree with the reviewer that it is necessary
157 to point out the averaging time when describing the concentrations and they are
158 included in the revised manuscript.

159

160 The sentences in Line 77-80 are revised as “According to the field measurements in
161 June 2017 in Beijing (Zhou et al., 2018), the 2-min averaged concentrations of reactive
162 Cl_2 and ClNO_2 reached up to 1000 pptv and 1200 pptv, respectively, during some severe

163 air pollution period in summer. The corresponding concentrations of N₂O₅ and nitrate
164 reached as high as 700 pptv (2 min average) and 5 μg m⁻³ (5 min average) from about
165 40 pptv and 1 μg m⁻³”
166

167 **Comment #13:** Line 79-80. There is no Li et al. (2017) in the reference list. Are you
168 referring to Li et al. (2016)? That is not a proper reference here, because that paper is a
169 modeling study that used the measurement results from Wang et al. (2016).
170

171 **Response #13:** Sorry for my carelessness. As the reviewer described, Li et al. (2017)
172 should be Li et al.(2016). We revise it throughout the whole manuscript and here we
173 remove it.
174

175 **Comment #14:** Line 82. These references are not the right ones here. The first
176 measurements of ClNO₂ in the real atmosphere, Osthoff et al. (2008) and Thornton et
177 al. (2010), are better ones.
178

179 **Response #14:** Revised.
180

181 **Comment #15:** Line 102. This is not entirely true. For instance, Hossaini et al. (2016)
182 developed a global chemical transport model (TOMCAT) and included several
183 heterogeneous reactions of chlorine species on chloride-containing aerosol.
184

185 **Response #15:** The reviewer might misread the sentence. We did include the fact that
186 some models have some heterogeneous reactions by saying that “generally missing”
187 and “in most” CTMs. No changes were made regarding this comment.
188

189 **Comment #16:** Line 107-111. I assume the replacement is only in Beijing city but not
190 in the surrounding areas. Is that correct?
191

192 **Response #16:** Yes, replacing coal with natural gas only occurred in Beijing. Reduction
193 of coal consumption in surrounding regions was less than 15% for most other provinces
194 and cities and there were no strict control measures for biomass burning (except Hebei),
195 cooking and municipal solid waste incineration yet. Thus, the Cl emissions estimated
196 for 2014 by Fu et al. (2018) were used for other areas. This is explained in the revised
197 manuscript on page 30, lines 223-228.
198

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

201 ‘Thus, it is important to compile an updated emission inventory for Beijing (and its
202 surrounding areas) to include the emissions from cooking and other sources (coal
203 burning, solid waste burning, biomass burning, etc.).’
204

205 **Response #17:** Thanks for your constructive comment. This sentence is revised to read
206 “Thus, it is necessary to compile an updated emission inventory for Beijing to include

207 the emissions from cooking and other sources (coal burning, solid waste burning,
208 biomass burning, etc.) in order to explore the chlorine species emission on atmospheric
209 nitrate formation.”

210

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

213

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

217

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

220

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

222

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

225

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

229

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

233

234 **Response #21:** Sorry, it’s a typo. It should be 0.5 h following the study by Wu et al
235 (2018). based on a survey data. The emissions were correctly calculated using 0.5 h.
236 Also, ‘restaurant cooking’ has been revised to ‘commercial cooking’.

237

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

239

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

241

242 **Comment #23:** Line 173-174. A brief description is needed for other emissions, which
243 are the precursors of N₂O₅, ClNO₂, and nitrate aerosol.

244

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

249

250 **Comment #24:** Section 2.2. The authors added several reactions to the CMAQ model,

251 and this seems to be one of the major contributions of this study. [**this comment seems**
252 **to be less coherent, so we break it into several sentences and address them**
253 **individually]**

- 254 (1) However, what is the difference between the mechanism in the current study
255 and that in Sarwar et al. (2012, 2014)?
256 (2) I notice that one of the co-authors in the present study is also a co-author of
257 Sarwar et al. (2014).
258 (3) I strongly advise the authors to carefully review the previous works and identify
259 the advantage of the current work, instead of avoiding the comparison between
260 the current study with the previous ones.
261 (4) Besides, did you compare your scheme with Zheng et al. (2015)?
262

263 **Response #24:**

- 264 (1) Sarwar et al. (2012, 2014) only consider the reaction of N_2O_5 with PCl. They
265 did not include those heterogeneous reactions involving Cl_2 production (the
266 reaction of O_3 , OH, HOCl, ClNO₂ and ClONO₂ with PCl).
267 (2) It is correct that one of the authors of Sarwar et al. (2014) happens to be a
268 co-author of this study. We didn't understand why this comment is even
269 relevant, so no changes were made regarding this comment.
270 (3) Previous works were reviewed in the introduction section and discussed
271 throughout the manuscript wherever appropriate.
272 (4) The major difference in Zheng et al.'s treatment of heterogeneous chemistry
273 and our approach is that they chose to use an empirical expression for RH
274 dependent uptake coefficients of NO₂ and SO₂. There is no evidence so far
275 that that RH-dependent expression is any better than simple constant values.
276 Thus, it is out of the scope of this paper to compare Zheng et al.
277

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

280
281 **Response #25:** Zheng et al.(2015) was not the right reference. The current CMAQ
282 model refers to the one used by Hu et al. (2016) and Hu et al. (2017)

283
284 Hu, J., Chen, J., Ying, Q., Zhang, H., 2016. One-Year Simulation of Ozone and
285 Particulate Matter in China Using WRF/CMAQ Modeling System. Atmos. Chem. Phys.
286 16, 10333-10350.

287
288 Hu, J., Wang, P., Ying, Q., Zhang, H., Chen, J., Ge, X., Li, X., Jiang, J., Wang, S., Zhang,
289 J., Zhao, Y., Zhang, Y., 2017. Modeling biogenic and anthropogenic secondary organic
290 aerosol in China. Atmos. Chem. Phys. 17, 77-92.

291
292
293 **Comment #26:** Line 182. Li et al. (2016) is not a proper reference for this equation.
294 Should refer to Bertram and Thornton (2009) or Roberts et al. (2009) with a very similar
295 formula. This brings up another persistent issue that you should use 'Bertram and
296 Thornton (2009)' instead of 'Bertram et al. (2009)'. There are only two authors to that
297 paper. Please check the manuscript for this error.

298

299 **Response #26:** The reference ‘Li et al. (2016)’ is replaced with ‘Bertram and Thornton
300 (2009)’ and we revise the ‘Bertram et al. (2009)’ with ‘Bertram and Thornton (2009)’
301 throughout the manuscript.

302

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

304

305 **Response #27:** Yes.

306

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

311

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

324

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

328

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

331

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

337

338 **Comment #30:** Section 3.1. What about the model performance on the simulation of
339 NO₂, O₃, and PM_{2.5}? These are particularly important to the formation of nitrate
340 aerosol, the sole focus of the current work.

341

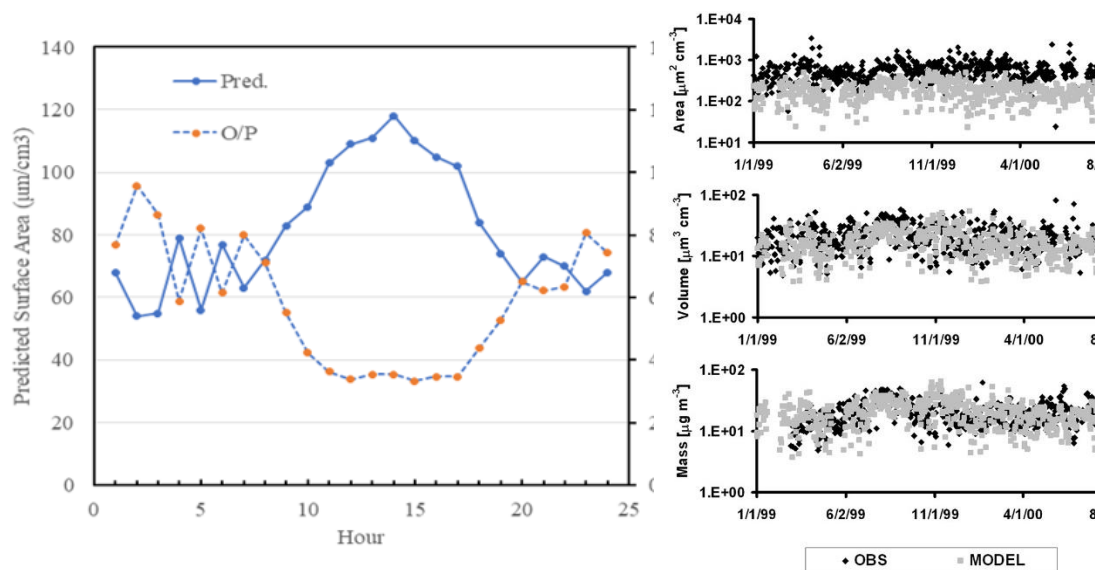
342 **Response #30:** Model performance of these species were included in the revised
343 manuscript. See our response to comment 3 for more details.

344

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

351

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



360 Figure R1a (left panel): Predicted averaged hourly particle wet surface area at IAP (June
361 11-15, 2017) and the ratio of observed to predicted PSA (O/P). R1b (right panel): CMAQ
362 predicted and observed daily particle surface area, volume, and mass concentrations for PM_{2.5}
363 1/1/1999 to 8/31/2000 at the JST station in Atlanta, Georgia. (R1b is adapted from Park et al., 2006).

364

365 **Reference:**

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

368

369

370 **Comment #32:** Line 255. ClNO₂ is underestimated in your cases. Does it mean that

371 nitrate aerosol is over-predicted?

372

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

377

378

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

381

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

389

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

394

395 **Response #34:** We investigated the uncertainty in the predicted nitrate concentrations
396 using the parameterized N₂O₅ uptake coefficients of Bertram and Thornton (2009) by
397 using two sensitivity simulations in the original manuscript. In one simulation, the
398 parameterization of Davis et al. (2008), which is the default N₂O₅ parametrization
399 scheme in CMAQ 5.0.1, was used. It generally yields slightly lower $\gamma_{N_2O_5}$ than the

400 Bertram and Thornton (2009). In the other simulation, the $\gamma_{N_2O_5}$ was fixed at a

401 constant value of 0.09, which is the maximum value derived by Zhou et al. (2018) based
402 on summertime field measurement in urban Beijing. On average, it is 4-6 times higher
403 than those based on Bertram and Thornton (2009). Table 3 in the original manuscript

404 summarized the $\gamma_{N_2O_5}$ averaged for each day and night from these simulations and the

405 corresponding nitrate concentrations. Predicted nitrate concentrations are sensitive to
406 changes in the changes in $\gamma_{N_2O_5}$, with approximately 50% increase in the nitrate when

407 the $\gamma_{N_2O_5}$ is fixed at 0.09. The discussion of these two sensitivity simulations are

408 slightly revised from the original manuscript and can be fond in the revised paper on
409 page 37, lines 431-434.

410

411 **Comment #35:** Line 277-278. The underestimated nitrate concentration could be due
412 to many reasons. For example, is NO₂ underestimated as well? This is another reason
413 to show the evaluation of NO₂ simulation. The uncertainty of the parameterizations of
414 N₂O₅ uptake and ClNO₂ yield (comment 31) could also be applied here. Besides, how
415 did you simulate the most critical OH precursor, i.e., HONO? Did you evaluate your
416 HONO simulation? Did you consider the NO₂ uptake on environmental surfaces? What
417 about other HONO sources? Several recent papers have shown that HONO is very
418 important in simulating nitrate, e.g., Fu et al. (2018).

419

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

425 $2\text{NO}_2(\text{g}) + \text{Cl}^-(\text{aq}) \rightarrow \text{ClNO}(\text{g}) + \text{NO}_3^-(\text{aq})$ (if the NO₂ is redundant, $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightarrow$
426 $\text{HONO}(\text{g}) + \text{NO}_3^-(\text{aq})$).

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

430

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

433

434 **Response #36:** It's redundant. We have deleted it.

435

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

439

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

445

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

448

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

454 emissions ($R=0.31$) and NO_x representing transportation emissions ($R=0.01$) or
455 precursors (HCl ($R=0.08$) and PCl ($R=0.01$))

456

457 Deng, S., Zhang, C., Liu, Y., et al.: A Full-Scale Field Study on Chlorine Emission of Pulverized
458 Coal-Fired Power Plants in China. Research of Environmental Science. In Chinese, 27, 127-133,
459 2014.

460

461 **Comment #39:** Line 316. N_2O_5 uptake process is very complicated. The word,
462 ‘inferior’, is definitely not the one I would use to describe the parameterization based
463 on nitrate and sulfate. concentration. Please revise. The uncertainty of the
464 parameterizations of N_2O_5 uptake and ClNO_2 yield also works here.

465

466 **Response #39:** We completely agree with the reviewer.

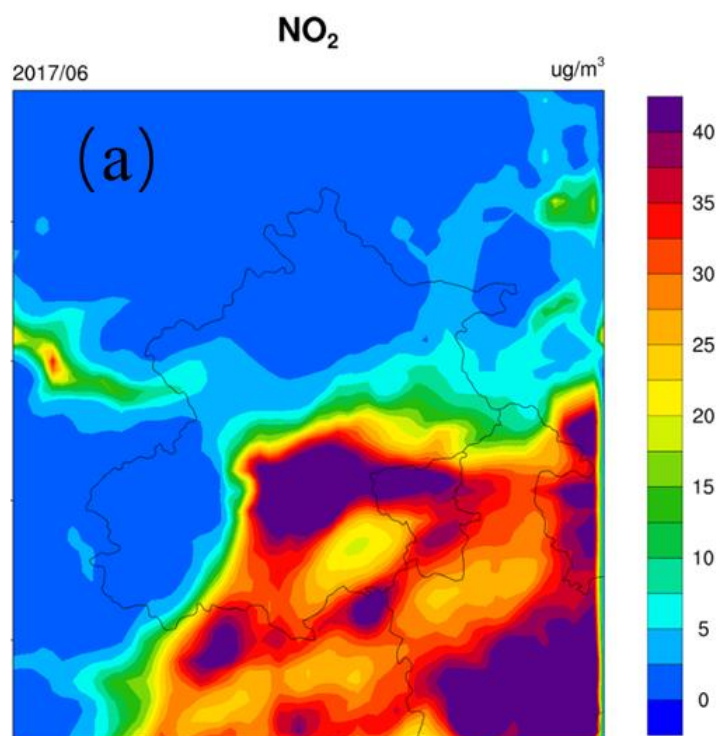
467

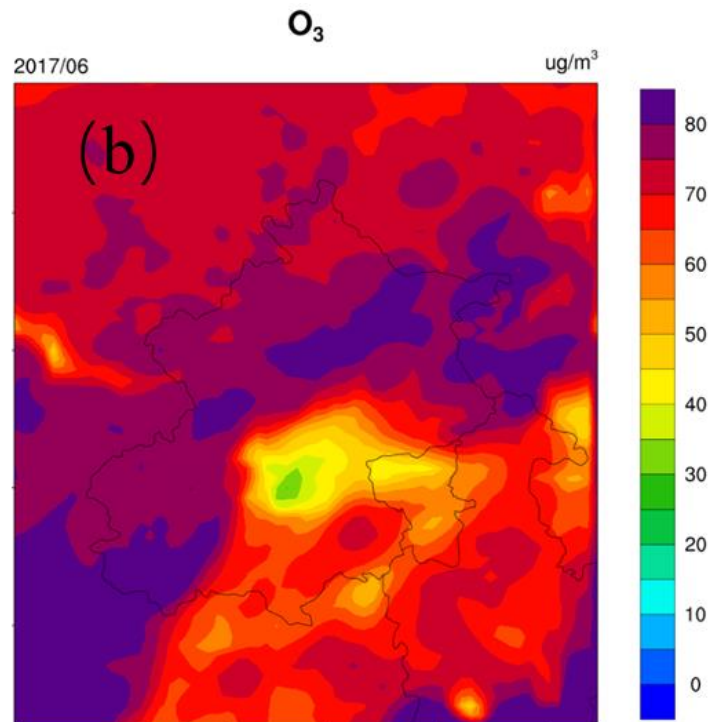
468 **Comment #40:** Section 3.3. I advise to include the simulated results of NO_2 , O_3 , and
469 $\text{PM}_{2.5}$.

470

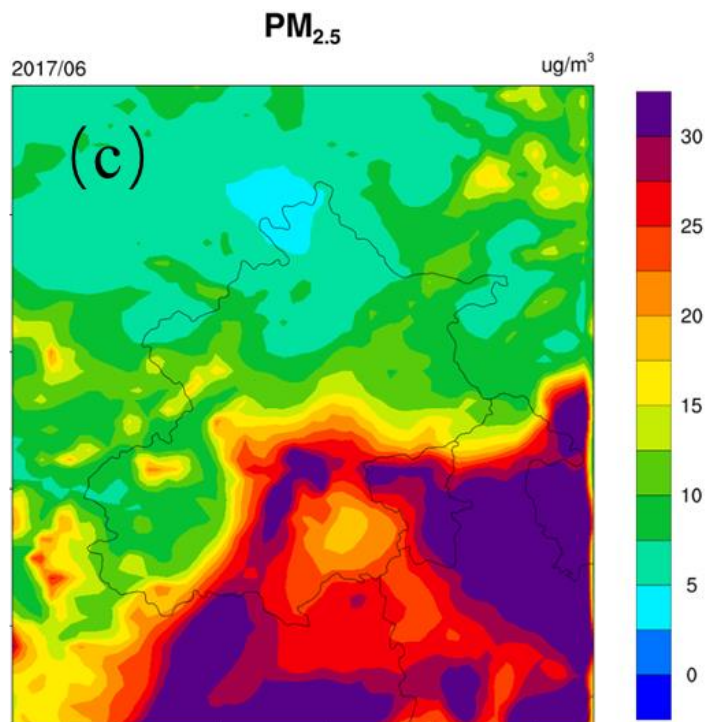
471 **Response #40:** We have included them in SI Figure S3, which also be shown in Figure
472 R2.

473





474



475

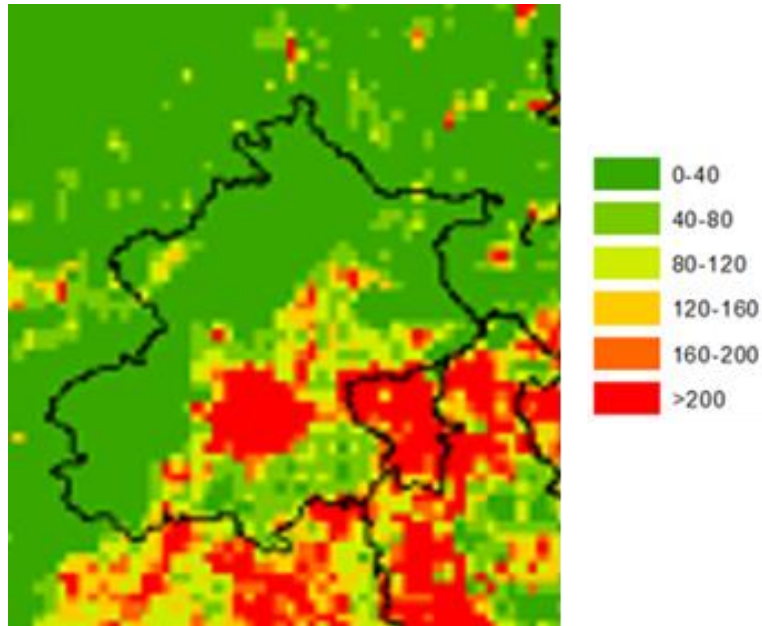
476

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

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

481

482 **Response #41:** We have included it in Figure S2, which is also represented in Figure
 483 R3.



484
 485 **Figure R3 The spatial distribution of PCI emission in Beijing in 2017 (Unit:**
 486 **Kg/year per grid).**

487
 488 **Comment #42:** Line 328-330. The presence of a high concentration of ClNO₂ and Cl₂
 489 away from the fresh emissions does not necessarily mean that ClNO₂ and Cl₂ are easy
 490 to transport.

491 For example, the production of ClNO₂ requires the presence of chloride, NO₂, and O₃.
 492 In the areas close to the fresh emissions, O₃ is commonly low, and the production of
 493 NO₃ (hence N₂O₅ and ClNO₂) is limited. Therefore, the production of ClNO₂ is
 494 generally not found near fresh emissions.

495 As to the Cl₂, perhaps the contribution of direct emission to the level of Cl₂ is not
 496 significant, and Cl₂ is predominantly produced in the atmosphere. So the high levels of
 497 Cl₂ are found away from the fresh emissions.

498
 499 **Response #42:** We agree with the reviewer's opinion and include this comment in page
 500 37, line 444-450 in manuscript.

501
 502 **Comment #43:** Line 336. Why 'more N₂O₅ is converted into nitrate'? Are you
 503 implying that the uptake coefficient calculated with the Bertram and Thornton (2009)
 504 is higher than that with Davis et al. (2008)?

505
 506 **Response #43:** Yes, this is indeed the case. Table 3 compares the uptake coefficient of
 507 N₂O₅ based on the two parameterization and clearly shows that the Bertram and
 508 Thornton equation generally gives higher uptake coefficients. This is also consistent
 509 with the conclusion of McDuffie et al. (2018). We add this explanation in revised
 510 manuscript on page 38, lines 456-460.

511
 512 **Comment #44:** Line 351-352. Was the observation in PKU conducted in the same

513 period?

514

515 **Response #44:** No, the observation in PKU is conducted in November. This is clarified
516 in the revised manuscript.

517

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

520

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

527

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

530

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

534

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

537

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

540

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

542

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

548

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

551

552 **Response #49:** The sentence 'This study aims to improve our understandings on the
553 chlorine chemistry and its impact on nitrate formation, which can provide useful
554 implications on the nitrate pollution control strategies for those regions that suffered
555 serious nitrate pollution.' is revised as 'This study aims to improve our understandings
556 on the chlorine chemistry and its impact on nitrate formation, The chloride chemical

557 mechanism study in this work indicates that not only the NO_x emission is needed to be
558 controlled, but also the emission of reactive chlorine species should be limited as well
559 in order to alleviate the nitrate pollution’

560

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

563

564 **Response #50:** Revised

565

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

568

569 **Response #51:** The reactions R6 and R11 directly affect the nitrate and R13-18
570 indirectly affect it by elevating the OH level due to production of Cl₂. This discussion
571 is included in the revised manuscript on page 27, line 108-111. The references for all
572 reaction have included in Table 3.

573

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

576

577 **Response #52:** The ClNO₂ reacts with particle surface to form nitrate, which is not a
578 photolysis reaction. It is changed to ‘reacts with particle surface’ to make it more
579 specific.

580

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

582

583 **Response #53:** Revised

584

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

586

587 **Response #54:** Revised

588

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

590

591 **Response #55:** Revised

592

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

594

595 **Response #56:** Revised

596

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

598

599 **Response #57:** Revised

600

601 **Comment #58:** Line 145. ‘EF represents the emission factor’ should be ‘ $E_{Fi,j}$
602 represents the emission factor of pollutant j in sector i ’.

603

604 **Response #58:** Revised

605

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

608

609 **Response #59:** Revised

610

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

613

614 **Response #60:** Revised

615

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

617

618 **Response #61:** Revised

619

620 **Comment #62:** Line 166. Delete ‘that’

621

622 **Response #62:** The sentence has been deleted

623

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

625

626 **Response #63:** Revised

627

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

629

630 **Response #64:** Revised

631

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

633

634 **Response #65:** Revised

635

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

637

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

639

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

641

642 **Response #67:** Revised

643

644 **Comment #68:** Line 192. Do you mean ‘equation (5)’, instead of ‘equations (2)’?

645

646 **Response #68:** It should be equation (5).

647

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

649

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

651

652 **Comment #70:** Why did you use different terms for velocity in equation 5 and equation
653 8?

654

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

656

657 **Comment #71:** Line 211. How did you calculate K_h , K_f , K_3/K_2 , and K_4/K_2 ? Are they
658 constants? If so, please add the number.

659

660 **Response #71:** These parameters have been demonstrated. As K_h represents the
661 dimensionless Henry’s law coefficient ($K_h = [N_2O_5]_{aq}/[N_2O_5]_g = 10e(30)$). K_f represents
662 a parameterized function based on water concentration ($K_f = 1.15e^6(1 -$

663 $e^{-1.3e^{-1}[H_2O(l)]})$ and K_3/K_2 and K_4/K_2 are constants obtained by fitting data, which are

664 6×10^{-2} and 29.

665

666 **Comment #72:** Line 216 and line 208. Use the consistent form for units. m^3/m^3 or m^3
667 m^{-3} .

668

669 **Response #72:** Revised

670

671 **Comment #73:** Line 227. Which year?

672

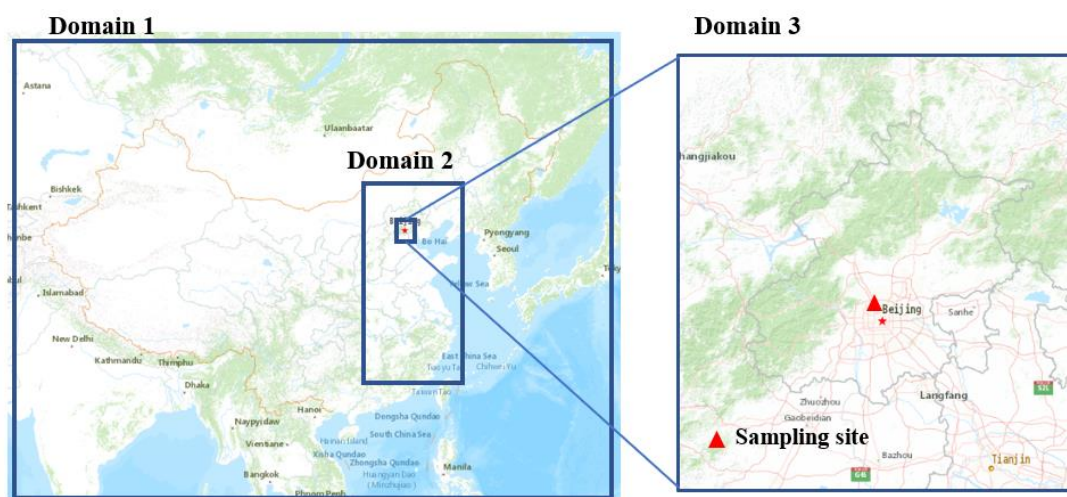
673 **Response #73:** This sentence is revised as ‘These heterogeneous reactions of chlorine
674 are incorporated into revised CMAQ (version 5.0.1) to simulate the distribution of
675 nitrate concentration in Beijing from 11 to 15 June 2017’

676

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

679

680 **Response #74:** A map with three domains is included as Figure S1(Figure R4 below):



681

682 **Figure R4** the three nested domain setting in this work.

683

684 **Comment #75:** Line 232. ‘40°E’ should be ‘40°N’.

685

686 **Response #75:** Revised

687

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

689

690 **Response #76:** Revised

691

692 **Comment #77:** Line 315. Add the year for ‘Davis et al.’. Check through the manuscript
693 for a similar issue.

694

695 **Response #77:** This sentence has been deleted in the revised manuscript.

696

697 **Comment #78:** Line 350. ‘are produced’ should be ‘is produced’.

698

699 **Response #78:** Revised

700

701 **Comment #79:** Line 369. Add ‘of’ between ‘uptake’ and ‘N₂O₅’.

702

703 **Response #79:** Revised

704

705 **Comment #80:** Line 378. ‘even through’ should be ‘even though’.

706

707 **Response #80:** Revised

708

709 **Comment #81:** Line 396. ‘This’ should be ‘These’.

710

711 **Response #81:** Revised

712

713 **Comment #82:** Line 397. ‘becase’ should be ‘because’.

714

715 **Response #82:** Revised

716

717 **Comment #83:** Line 397. ‘the cornerstones’ should be ‘the cornerstone’ or ‘one of the
718 cornerstones’.

719

720 **Response #83:** Revised

721

722 **Comment #84:** Line 401. ‘chlorine’ should be ‘chloride’.

723

724 **Response #84:** Revised

725

726 **Comment #85:** Line 409. ‘understnadings’ should be ‘understandings’.

727

728 **Response #85:** Revised

729

730 **Comment #86:** Figure 3. Should point out the area of BJ and the location of the
731 sampling site. In d, f, and h, should use $\Delta\text{N}_2\text{O}_5$, ΔNO_3^- , and ΔNO_3^- , instead of N_2O_5 ,
732 NO_3^- , and NO_3

733

734 **Response #86:** The area of BJ and the location of the sampling site is labeled in Figure
735 S1. We have used $\Delta\text{N}_2\text{O}_5$, ΔNO_3^- , and ΔNO_3^- , instead of N_2O_5 , NO_3^- , and NO_3 .

736

737 **Comment #87:** Figure 4. In the sub-plot Daytime Gas-phase, the title of Y-axis should
738 be ‘ HNO_3 production rate (ppt h^{-1})’. The same revision should be applied to the sub-
739 plot Nighttime Gas-phase. The sub-plot Nighttime Heterogeneous, the title of Y-axis
740 should be ‘Nitrate production rate ($\mu\text{g m}^{-3} \text{h}^{-1}$)’. No sub-plot daytime Heterogeneous?

741

742 **Response #87:** Revised. Additionally, the heterogeneous reaction of NO_2 with PCL
743 have less contribution to diurnal nitrate (less than 2%) because the extremely lower
744 uptake coefficient. In addition, we supplement the daytime heterogeneous.

745

746

747 **Reviewer #2**

748

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

757

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

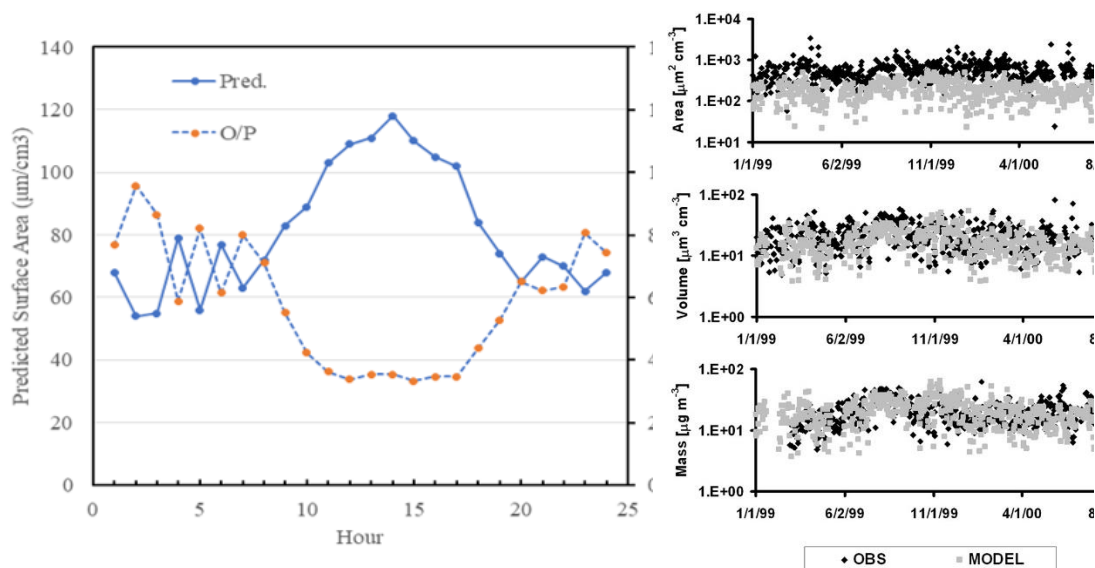
760

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

763

764 **Response #2:** Figure R1a below is the detailed comparison of our modeled surface area
765 with observations averaged between June 11-15, 2017. Under-prediction of surface area
766 varies between 6-12 times. CMAQ model performance for surface area has not been
767 extensively studied. In the only study we found in the literature (Park et al., 2006),
768 similar under-prediction of particle surface area was reported. In their study, the mass
769 concentration of PM_{2.5} at Atlanta, United State is generally well reproduced by the
770 CMAQ model but the surface area shows large under-predictions similar to what we
771 have seen in our study (see Figure R1b).

772



773 Figure R1a (left panel): Predicted averaged hourly particle wet surface area at IAP (June
774 11-15, 2017) and the ratio of observed to predicted PSA (O/P). R1b (right panel): CMAQ
775 predicted and observed daily particle surface area, volume, and mass concentrations for PM_{2.5} from

776 1/1/1999 to 8/31/2000 at the JST station in Atlanta, Georgia. (R1b is adapted from Park et al., 2006).

777

778

779 Reference:

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

782

783

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

787

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

801

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

805

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

807

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

811

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

813

814 **Comment #6:** Line 206, Bertram et al., 2009 correct to Bertram and Thornton, (2009).

815

816 **Response #6:** Revised

817

818 **Comment #7:** Line 335-line 340, this part is confused. Did you mean more N₂O₅
819 convert to nitrate due to the N₂O₅ uptake coefficient calculated by Bertram and

820 Thornton, (2009) is higher than the base case? And the non-significant nitrate increase
821 may be due to the ClNO₂ yield buffered the increasing caused by the application of
822 new N₂O₅ uptake coefficient?

823

824 **Response #7:** This sentence is revised as ‘By incorporating the chlorine heterogeneous
825 reaction, the N₂O₅ concentrations decrease by about 16% because the uptake coefficient
826 calculated with the Bertram and Thornton (2009) is higher than that with Davis et al.
827 (2008).’

828

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

831

832 **Response #8:** The title is revised as ‘Impact of uptake coefficients of O₃ and N₂O₅ on
833 chlorine species and nitrate’

834

835

836

Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation in Beijing, China

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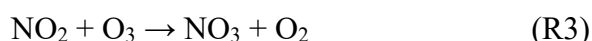
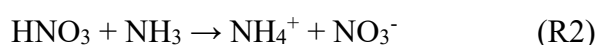
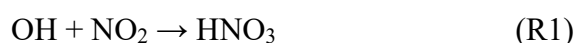
Abstract:

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

35 incorporated, resulting in more nitrate formation from HNO₃ gas-to-particle
 36 partitioning. By contrast, the contribution of the heterogeneous reaction of N₂O₅ to
 37 nitrate concentrations decreases by about 27% in the nighttime when its reactions with
 38 ~~chloriated~~chlorinated particles are considered. However, the generated gas-phase
 39 ClNO₂ from the heterogeneous reaction of N₂O₅ and chlorine-containing particles
 40 further ~~decomposes~~reacts with the particle surface to increase the nitrate by 6%. In
 41 general, this study highlights the potential of significant underestimation of daytime
 42 and overestimation of nighttime nitrate concentrations for chemical transport models
 43 without proper chlorine chemistry in the gas and particle phases.

45 1. Introduction

46 In recent years, nitrate has become the primary component of PM_{2.5} (particulate matter
 47 with aerodynamic diameter less than 2.5μm) in Beijing with sustained and rapid
 48 reduction of SO₂ and primary particulate matter emissions (Ma et al., 2018; Li et al.,
 49 2018; Wen et al., 2018). Observations showed that the relative contributions of
 50 secondary nitrate in PM_{2.5} could reach up to approximately 50% during some severe
 51 haze pollution days (Li et al., 2018). The mechanism of secondary nitrate formation can
 52 be summarized as two major pathways: (1) Gas-to-particle partitioning of HNO₃, which
 53 happens mostly in the daytime. The reaction of OH with NO₂ produces gaseous HNO₃,
 54 which subsequently partition into the particle phase. The existence of NH₃ or basic
 55 particles enhances this process by NH₃-NH₄⁺ gas-particle equilibrium; (Kleeman et al.,
 56 2005; Seinfeld and Pandis, 2006); (2) Hydrolysis of N₂O₅, which is more important at
 57 nighttime. N₂O₅ forms from the reactions of NO₂, O₃ and NO₃ and hydrolyzes to
 58 produce particulate nitrate. They can be summarized as reactions R1-R5 (Ying et al.,
 59 2011; Wang et al., 2018; Li et al., 2018; Brown and Stutz 2012):



65 In addition to reactions R1 and R5, gas phase reactions of NO₃ with HO₂ and VOCs,
 66 N₂O₅ with water vapor (Tuazon et al., 1983) and the heterogeneous reaction of NO₂
 67 with water-containing particle (Goodman et al., 1999) produce HNO₃ or nitrate as well.

68 These reactions are listed in Table 2 as reactions R8, R9 and R10.

69 However, ~~current~~ chemistry transport models (~~CTM, such as CMAQ, WRF-Chem~~
70 ~~etc.)CTMs) incorporated with these mechanisms~~ still can't accurately capture the
71 spatiotemporal distributions of nitrate ~~despite of involving above chemical~~
72 ~~mechanism in some studies in polluted northern China.~~ For example, Chang et al. (2018)
73 showed that the simulated nitrate concentrations derived from the default CMAQ
74 (version 5.0.2) were ~~1.79 to 1.95 times of significantly higher than~~ the observations in
75 summer at two sites adjacent to Beijing. ~~Chen et al. (2017) found the high uncertainty~~
76 ~~(about 20%~50%) of simulated nitrate concentration using CMAQ in Dezhou city~~
77 ~~(Shandong province, adjacent to Beijing), which attributed to the unclear mechanism~~
78 ~~of nitrate formation.~~ Fu et al. (~~2017~~2016) also found that default CMAQ (version 5.0.1)
79 overestimated the simulated nitrate concentrations in the Beijing-Tianjin-Hebei region.

80 ~~Some studies attributed the overestimation of nitrate to the missing of~~ In recent
81 fields studies, it was found that high particulate chlorine chemical
82 mechanism emissions might have a significant impact on the oxidation capacity of the
83 urban atmosphere and thus could affect nitrate concentrations. According to the field
84 measurements in June 2017 in Beijing (Zhou et al., 2018), the 2-min averaged
85 concentrations of reactive molecular chlorine (Cl₂) and nitryl chloride (ClNO₂) reached
86 up to 1000 pptv and 1200 pptv, respectively, during some severe air pollution
87 periods in summer. ~~The corresponding concentrations of N₂O₅ and nitrate rise~~
88 ~~up to 700 pptv and 5 μg m⁻³ from about 40 pptv and 1 μg m⁻³, which Cl₂ concentrations~~
89 were significantly higher than those ~~in~~ observed in North American coastal cities
90 affected by onshore flow and the lower atmosphere in the remote Arctic region (Spicer
91 et al., 1998; ~~Li et al., 2017;~~ Glasow et al., 2010; Liu et al., ~~2017;~~ Some2017). During
92 these pollution events, the corresponding concentrations of N₂O₅ (2-min average) and
93 nitrate (5-min average) rose from 40 pptv and 1 μg m⁻³ to 700 pptv and 5 μg m⁻³. To
94 explain the high levels of ClNO₂, some studies suggested that ~~the~~ reaction R5 should
95 be revised ~~as R6 due to~~ account for ClNO₂ production from the heterogeneous
96 reaction of N₂O₅ on ~~chlorine~~ chloride-containing particle surface particles (CPS) (Wang)
97 (Osthoff et al., 2017; Simon2008; Thornton et al., 2010; Glasow et al., 2010;), as
98 shown in reaction R6:



100 where ϕ represents the molar yield of ClNO₂. ~~By incorporating~~ When Cl⁻ is enough,
101 this reaction leads to lower nitrate concentrations than reaction R5. By incorporating

1102 this reaction into WRF-Chem, Li et al. (~~2017~~2016) found that the improved model
1103 performed better to match the observed nitrate concentrations in Hongkong during 15
1104 November and 5 December 2013. ~~The generated gaseous nitryl chloride~~
1105 ~~(ClNO₂)~~ However, ClNO₂ could affect the formation of nitrate indirectly by increasing
1106 the atmospheric OH after a series of chemical reactions, which are briefly summarized
1107 into three steps: (1) the photolysis of ClNO₂ produces ~~atom~~-chlorine radicals (Cl[•]); (2)
1108 the reaction of Cl[•] with VOCs produces peroxy radical (HO₂ and RO₂); and (3) the
1109 increased HO₂ and RO₂ prompt the formation of OH ~~by participating into free~~
1110 ~~radical~~ through HO_x cycle and NO_x cycle lead to increased HNO₃ production (Young et
1111 al., 2014; Jobson et al., 1994). The overall impact of R6 on nitrate remains to be
1112 investigated.

1113 ~~The reaction of N₂O₅ is not the only heterogeneous reaction that influences the~~
1114 ~~nitrate formation. Some other heterogeneous reactions on CPS can also directly or~~
1115 ~~indirectly affect nitrate formation. For example, the heterogeneous uptake of NO₂ and~~
1116 ~~NO₃ on CPS can produce nitrate (Abbatt et al., 1998, Rudich et al., 1996). The~~ Another
1117 related but unresolved issue is the sources of the high concentrations Cl₂, which could
1118 not be explained by the N₂O₅ heterogeneous reaction with Cl⁻ and the subsequent
1119 reactions of ClNO₂ in the gas phase. It has been reported that the reactions of gaseous
1120 O₃, OH, HO₂, ClNO₂, hypochlorous acid (HOCl), chlorine nitrate (ClONO₂) with CPS
1121 can produce Cl₂ ~~and, which can~~ subsequently photolyze to produce Cl[•] (Knipping et
1122 al., 2000; George et al., 2010; Pratte et al., 2006; Deiber et al., 2004; Faxon et al., 2015);
1123 ~~which can further accelerate the OH formation to affect the reaction R1.~~ However,
1124 these heterogeneous reactions on CPS are generally missing in most of the current
1125 CTMs- and it is unclear whether these reactions will be able to explain the observed Cl₂
1126 concentrations and the overall impact of these reactions on nitrate.

1127 Previously, biomass burning, coal combustion, and waste incineration were
1128 identified as the main sources of gaseous and particulate chlorine compounds in China
1129 from International Global Atmospheric Chemistry Program's Global Emissions
1130 Inventory Activity (GEIA) based on the year 1990 and a localized study by Fu et al.
1131 based on the year 2014 (Keene et al., 1999; Fu et al., 2018). However, recent source
1132 apportionment ~~result~~ results of PM_{2.5} in Beijing showed that the contribution of coal
1133 combustion had extremely decreased from 22.4% in 2014 to 3% in 2017 with the
1134 replacement of ~~natural~~ natural gas (obtained from official website of Beijing Municipal
1135 Bureau of Statistics, available at <http://edu.bjstats.gov.cn/>). ~~But another~~ Another

136 important source — cooking has received attention as its ~~increasingly~~ increasing
137 contribution to PM_{2.5} (accounting for 33% of the residential sector; obtained from the
138 official source apportionment analysis of PM_{2.5} in Beijing in 2017; see
139 <http://www.bjepb.gov.cn/bjhr-b/index/index.html>). Moreover, the high content of
140 particulate sodium chloride was measured from the source characterization studies of
141 PM_{2.5} released from the cooking ~~source~~ activities (Zhang et al., 2016). Thus, it's
142 important is necessary to ascertain compile an updated emission inventory for Beijing
143 to include the relationship between reactive emissions from cooking and other sources
144 (coal burning, solid waste incineration, biomass burning, etc.) in order to explore the
145 emissions of the chlorine species and on atmospheric nitrate formation.

146 In this study, ~~the Community Multiscale Air Quality (a CMAQ)~~ model with an
147 improved chlorine heterogeneous chemistry is applied to simulate summer nitrate
148 concentration in Beijing. ~~We then use the sensitivity analyses~~ Sensitivity simulations
149 are conducted to evaluate the ~~contribution~~ contributions of HNO₃ gas-to-particle
150 partitioning and heterogenous production to aerosol nitrate formation. The results of
151 this work can improve our understandings on nitrate formation and provide useful
152 implications information on ~~the~~ nitrate pollution control strategies in Beijing.

154 2. Emissions, chemical reactions and model description

155 2.1 Emissions

156 Generally, the conventional emission inventories of air pollutants in China only include
157 the common chemical species, such as SO₂, NO_x, VOCs, PM_{2.5}, PM₁₀, NH₃, BC, and
158 OC. ~~No data on chloride~~ (Wang et al., 2014). Chloride compound
159 ~~emissions were~~ emissions were not included. However, the emissions of chlorine species
160 are vital for studying the chlorine chemical mechanism. Recently, the inorganic
161 hydrogen chloride (HCl) and fine particulate chloride (PCl) emission inventories for
162 the sectors of coal combustion, biomass burning, and waste incineration were
163 developed ~~in~~ for the year of 2014 (Qiu et al., ~~2017~~ 2016, Fu et al., 2018, Liu et al., 2018).
164 However, the gaseous chlorine emission was not estimated in these studies. In addition,
165 these studies did not account for the rapid decrease of coal consumption in recent years
166 in Beijing ~~(about 75%, from 2000 Mt in 2014 to 490 Mt in 2017)~~. More importantly,
167 the cooking source, as one of the major contributors to particulate chlorine in Beijing,
168 is not included in current chlorine emission inventories. Thus, ~~we develop~~ a new

emission inventory of reactive chlorine species, which includes HCl, Cl₂ and PCl, 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:~~

$$\text{HCl and Cl}_2: E_{i,j} = \sum_{t,j} A_t \times EF_{t,j} \quad (1)$$

$$\text{PCl: } E_{i,j} = \sum_{t,j} A_t \times EF_{t,j} \times \eta \quad (2)$$

$$E_{i,j} = A_i \times EF_{i,j} \quad (1)$$

where $E_{i,j}$ represents the emission factor of pollutant j in i -sector; A represents the activity data; EF represents the emission factor. ηEF for PCl is estimated by $EF_{i,PCl} = EF_{i,PM2.5} \times f_{Cl,i}$, where $f_{Cl,i}$ represents the content mass fraction of PCl in primary PM_{2.5}.

~~In this study, the Cl₂ production Activity data are obtained from the Beijing Municipal Bureau of Statistics (available at <http://tjj.beijing.gov.cn/>). The Cl₂ 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_{2.5} emission factors and mass fractions of PCl in PM_{2.5} to calculate the methods of emission calculation 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_{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):~~

$$E_j = (V_f \times H_f \times EF_f + V_e \times H_e \times N_e \times n \times EF_e \times (1 - \eta)) \times 365 \quad (3)$$

$$E_{PCl} = [N_f \times V_f \times H_f \times EF_{f,PCl} + V_c \times H_c \times N_c \times n \times EF_{c,PCl} \times (1 - \eta)] \times 365 \quad (2)$$

where N_f is the number of households, V_f is the volume of exhaust gas from a household stove, which equals to (2000 m³/h⁻¹); H_f is the cooking time for a family, which is set as 3h per (0.5 h 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 6h per in a commercial cooking

202 ~~facility (6 h day⁻¹); N_c is the number of restaurant, school~~ restaurants, schools and
203 ~~government department~~ departments. V_c is the volume of exhaust gas, ~~which is set as to~~
204 ~~from a commercial cooking stove (8000 m³ h⁻¹); n is the number of stove~~ stoves for
205 each unit, which equals to 6 for a restaurant and is calculated as ~~the number of students~~
206 ~~divide 150 for school. η is the remove efficient of fume scrubbers, a constant of 30% is~~
207 ~~chosed.~~ one stove per 150 students for each school. η is the removal efficiency of fume
208 scrubbers (30%). $EF_{c,PCl}$ is the emission factor (kg m⁻³) of PCl in commercial cooking.
209 These constants are all based on Wu et al. (2018). The PCl fraction in PM_{2.5} from
210 cooking is take as 10%, based on local measurements. HCl and Cl₂ emissions from
211 cooking are not considered in this study.

212 Activity data, such as coal consumptions, population, crop yields, and production
213 of each industrial sector are obtained from Beijing Municipal Bureau of Statistics
214 (available at <http://tjj.beijing.gov.cn/>). This official data shows that coal combustion has
215 dramatically decrease from more than 2000 Mt from 2014 to 490 Mt in 2017, which
216 indicates that significant reduction of emissions of air pollutants. Part of localized data
217 of PCl, such as the content of PCl in PM_{2.5} discharged from cooking, power plant and
218 biomass burning (10%, 1% and 9.0%, respectively), are obtained based on the localized
219 measurement. Others emission factors are obtained from the study by Fu et al. Finally,
220 ~~the~~ The sectoral emissions of HCl, Cl₂ and PCl, ~~including power plant, industry,~~
221 ~~residential, biomass burning, MSW and cooking, are estimated and listed~~ are
222 summarized in Table 1. ~~Finally,~~ The estimated HCl, Cl₂ and PCl ~~mission~~ emissions in
223 Beijing are 1.89 Gg, ~~0.065Gg~~ 0.07Gg and 0.63Gg respectively. The Cl emissions
224 estimated for 2014 by Fu et al. (2018) were used for other areas. This simplification is
225 a good approximation because replacing coal with natural gas only occurred in Beijing,
226 and reduction of coal consumption in surrounding regions was generally less than 15%.
227 In addition, strict control measures for biomass burning, cooking and municipal solid
228 waste incineration have not been implemented in most regions yet. Emissions of
229 other ~~conventional~~ species for this study period ~~were derived by Ding et al. (are~~
230 developed in a separate study that is currently under- review; emissions and ~~are~~
231 summerized ~~summarized~~ in Table S1).

233 2.2 Chlorine-related heterogeneous reactions

234 ~~In addition to reactions R1 and R5, gas phase reactions of NO₃ with HO₂ or VOCs (R8~~

and R9, see Table 2), N₂O₅ with H₂O and the heterogeneous reaction of NO₂ with water-containing particles are included in current CMAQ model (Zheng et al., 2015). However, these The heterogeneous reactions in original CMAQ (version 5.0.1) are not related to chlorine species. This In this study revises, the original heterogeneous reactions of N₂O₅ and NO₂ (R5 and R10 as in Table 2) are replaced with a revised version which includes production of ClNO₂ from CPS (R6 and R11 by considering the impact of heterogeneous uptake on CPS in Table 2). In reaction R6, the molar yield of ClNO₂ (ϕ_{ClNO_2}) is represented as (Li et al., 2016 equation (3) (Bertram and Thornton, 2009):

$$\phi_{ClNO_2} = \left(1 + \frac{[H_2O]}{483 \times [Cl^-]}\right)^{-1} \quad (43)$$

where ϕ_{ClNO_2} is the yield of ClNO₂, where [H₂O] and [Cl⁻] are the molarities of liquid water and chloride in aerosol volume (mol/m³ m⁻³).

In addition, Laboratory laboratory observations confirmed that the heterogeneous uptakes uptake of some oxidants (such as O₃ and OH) and reactive chlorine species (such as ClNO₂, HOCl, and ClONO₂) could also occur on CPS to produce Cl₂ (R13-R18), which affected the atmospheric OH level after a series of chemical. These reactions are implemented in the model and summarized in Table 2 as R13-R18. Note that the products from the heterogeneous uptake of ClNO₂ on CPS vary with particle acidity. (Riedel et al., 2012; Rossi, 2003). It generates generates Cl₂ 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):

$$\frac{dC}{dt} = -\frac{1}{4}(\bar{c}\gamma A)(v\gamma A)C = -k^{\ddagger} = -k^{\ddagger}C \quad (54)$$

where C represents the concentration of species, \bar{c} ; v represents the thermal velocity of the gas molecules (m s⁻¹); A represents the CMAQ-predicted wet aerosol surface area concentration (m² m⁻³); γ represents the uptake coefficient. Thus, k^{\ddagger} is considered as For all gas phases species (except ClNO₂) 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 $t_0+\Delta t$: $[C]_{t_0+\Delta t}=[C]_{t_0} \exp(-k^{\ddagger}\Delta t)$, where Δt is the operator-splitting time step for heterogeneous reactions.

The parameters of A and \bar{c} are calculated by CMAQ. Considering the consumption and generation rate of ClNO₂, the concentration change of ClNO₂ can be

265 ~~calculated with~~ includes both removal and production terms, as shown in equation (35):

$$\frac{d[\text{ClNO}_2]}{dt} = -k_1^I[\text{ClNO}_2] + k_6^I\phi_{\text{ClNO}_2}[\text{N}_2\text{O}_5] \quad (65)$$

$$= -k_1^I[\text{ClNO}_2] + k_6^I\phi_{\text{ClNO}_2}[\text{N}_2\text{O}_5]_{t0} \exp(-k_1^I t)$$

266 Assuming ϕ_{ClNO_2} is a constant, ~~an analytical solution can be found~~ for equation
267 (7.5) can be obtained, as shown in equation (6):

$$\begin{aligned} [\text{ClNO}_2] &= [\text{ClNO}_2]_{t0} \exp(-k_1^I t) \\ &+ \frac{k_6^I \phi_{\text{ClNO}_2} [\text{N}_2\text{O}_5]_{t0}}{k_1^I - k_6^I} [\exp(-k_6^I t) - \exp(-k_1^I t)] [\text{ClNO}_2]_{t0+\Delta t} \\ &= [\text{ClNO}_2]_{t0} \exp(-k_1^I \Delta t) \\ &+ \frac{k_6^I \phi_{\text{ClNO}_2} [\text{N}_2\text{O}_5]_{t0}}{k_1^I - k_6^I} [\exp(-k_6^I \Delta t) - \exp(-k_1^I \Delta t)] \end{aligned} \quad (76)$$

268 ~~Where~~ k_1^I represents the ~~reaction constant~~ pseudo first-order rate coefficient of
269 ~~either~~ reaction R17 or R18. ~~The variable t represents the time., depending on pH.~~

270 The uptake coefficients γ of gaseous species are obtained from published
271 laboratorial studies. In the original CMAQ, the uptake coefficient of N_2O_5 is determined
272 as a function of the concentrations of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4NO_3 (Davis et al.,
273 2008). In this study, the Cl^- and NO_3^- ~~concentration~~ dependent parameterization (eq. 8)
274 by Bertram et al. for N_2O_5 and Thornton (2009) (equation (7)) is used ~~instead~~ (Bertram
275 et al., 2009). For frozen particles, the uptake coefficient is limited to 0.02, as used in
276 the original CMAQ model.:

$$\begin{aligned} \gamma_{\text{N}_2\text{O}_5} &= \begin{cases} 0.02, & \text{for frozen aerosols} \\ \frac{4V}{vS} K_H K_f \left(1 - \frac{1}{\left(\frac{K_3[\text{H}_2\text{O}]}{K_2[\text{NO}_3^-]} \right) + 1 + \left(\frac{K_4[\text{Cl}^-]}{K_2[\text{NO}_3^-]} \right)} \right) \gamma_{\text{N}_2\text{O}_5} \end{cases} \\ &= \begin{cases} 0.02, & \text{for frozen aerosols} \\ 3.2 \times 10^{-8} K_f \left[1 - \left(1 + \frac{6 \times 10^{-2} [\text{H}_2\text{O}]}{[\text{NO}_3^-]} + \frac{29[\text{Cl}^-]}{[\text{NO}_3^-]} \right)^{-1} \right] \end{cases} \end{aligned} \quad (87)$$

277 In the above equation, V represents the particle volume concentration ($\text{m}^3 \text{m}^{-3}$); S
278 represents the particle surface area concentration ($\text{m}^2 \text{m}^{-3}$); v represents the thermal
279 velocity of N_2O_5 (m s^{-1}); K_H represents the dimensionless Henry's law coefficient. K_f
280 represents a parameterized function based on molarity of water concentration: $K_f =$
281 $1.15 \times 10^6 (1 - e^{-0.13[\text{H}_2\text{O}]})$. NO_3^- and K_3/K_2 and $K_4/K_2 \text{Cl}^-$ concentrations are
282 constants obtained by fitting data also in molarity. The uptake coefficient of OH is

283 expressed ~~within equation (8) as~~ a function of the concentration of PCl following the
284 IUPAC (International Union of Pure and Applied Chemistry) ~~(, available at~~
285 http://iupac.poleether.fr/htdocs/datasheets/pdf/O-H_halide_solutions_VI.A2.1.pdf).

$$\gamma = \min\left(0.04 \times \frac{[Cl^-]}{1000 \times M}, 1\right) \quad (98)$$

286 where M represents the volume of liquid water in aerosol volume (~~m³/m³~~; m⁻³). For
287 frozen particles, the uptake coefficient is limited to 0.02, as used in the original CMAQ
288 model.

289 The uptake coefficients of O₃, NO₃, NO₂, HOCl, ClNO₂, and ClONO₂ are treated
290 as constants. Among of them, the γ ~~value~~values of NO₃, NO₂, HOCl and ClONO₂ are
291 set as 3×10^{-3} , 1×10^{-4} , 1.09×10^{-3} and 0.16 based on ~~the~~ laboratory measurements
292 (Rudich et al., 1996; Abbatt et al., 1998; Pratte et al., 2006; Gebel et al., 2001). A
293 preliminary value of 10^{-3} in the daytime and 10^{-5} at nighttime is chosen for the O₃ uptake
294 coefficient ~~(Keene et al., 1999).~~ The daytime γ_{O_3} is based on the analysis of Cl₂
295 production rate in a hypothesized geochemical cycle of reactive inorganic chlorine in
296 the marine boundary layer by Keene et al. (1990). The lower nighttime value was also
297 recommended by Keene et al. (1990) who noted that Cl₂ production in the marine
298 boundary layer are lower at night. The uptake coefficient of ClNO₂ depends on the
299 particle acidity, with the value of 2.65×10^{-6} for reaction R17 and 6×10^{-3} for reaction
300 R18 (Robert et al., 2008).

302 2.4 CMAQ model configuration

303 These heterogeneous reactions of chlorine are incorporated into a revised CMAQ
304 (based on the CMAQ version 5.0.1) to simulate the distribution of nitrate concentration
305 in Beijing ~~in~~from 11 to 15 June 2017. The revised CMAQ model without heterogeneous
306 reactions of chlorine has been described in detail by Ying et al. (2015) and Hu et al.
307 (2016, 2017). In summary, the gas phase chemical mechanism in the revised CMAQ
308 model is based on the SAPRC-11 (Cater et al., 2012) with a comprehensive gas-
309 phaseinorganic chlorine chemistry of chlorine (Cater et al., 2012; Ying et al., 2015).
310 Reactions of Cl radical with several major VOCs, which lead to production of HCl, are
311 also included. The aerosol module is based on AERO6 with an updated treatment of
312 NO₂ and SO₂ heterogeneous reaction and formation of secondary organic aerosol from
313 isoprene epoxides. Three-level nested domains with the resolutions of 36km, 12km, and

314 4km using Lambert Conformal Conic projection (173×136, 135×228 and 60×66 grid
315 cells) are chosen in this work (~~the domains see Figure 3 for the inner most domain~~).
316 The two true latitudes ~~is are~~ set ~~as~~ 25°N to 25°N and 40°E to 40°E and the origin of the
317 domain is set ~~as~~ at 34°N, 110°E. The left-bottom coordinates of the outmost domain are
318 positioned at x = -3114 km, y = -2448 km. The BASE case (~~simulation using default~~
319 CMAQ heterogeneous reactions of Cl turned off) and HET case (~~with improved~~
320 CMAQ all heterogeneous reactions enabled) are compared to evaluate the impact of
321 heterogeneous chlorine chemistry on nitrate formation.

322

323 3. Results

324 3.1 Model performance evaluation

325 Predicted O₃, NO₂ and PM_{2.5} concentrations from the BASE case simulation are
326 evaluated against monitoring data at 12 sites in Beijing (Table S2) in 11 to 15, June
327 2017. The average NMB/NME values for O₃, NO₂ and PM_{2.5} across the 12 sites are -
328 8%/29%, -7%/59% and -8%/53%, respectively. Predicted hourly Cl₂, ClNO₂ and N₂O₅
329 concentrations were compared with observations measured at the Institute of
330 Atmospheric Physics (IAP), Chinese Academy of Sciences (39.98N°98°N,
331 116.37E°37°E) using a high-resolution time-of-flight chemical ionization mass
332 spectrometer (CIMS) from 11 to 15 June 2017 (for site description, instrument
333 introduction, and analytical method, please refer to the study by Zhou et al. (2018)).
334 Figure 1 shows that the concentrations of Cl₂ and ClNO₂ in BASE case are rather low
335 (close to 0), proving that the gas-phase chemistry is not the major pathway to produce
336 Cl₂ and ClNO₂. By contrast, the simulated Cl₂ and ClNO₂ concentrations in HET case
337 increase significantly, correspondingly the NMB and NME changes from -100% to -
338 54% and 100% to 61% for Cl₂, and from -100% to -58% and 100% to 62% for ClNO₂,
339 respectively (the ~~parameter of total~~ particle surface area (~~TOTSURFA~~) ~~in CMAQ~~
340 concentrations is revised scaled up by ~~multiplying~~ a factor of 5 in daytime and 10 in
341 nighttime because this parameter is underestimated compared ~~with to~~ the ~~study of~~
342 measured concentrations reported by Zhou et al. (2018)). The simulations of Cl₂ and
343 ClNO₂ are improved ~~because as~~ the ~~newly added additional~~ heterogeneous reactions
344 prompt the ~~conversions of production of gas phase molecular~~ chlorine ~~from particle state~~
345 ~~to gaseous state.~~ Overall, however, the Cl₂ and ClNO₂ concentrations are still
346 underestimated. Both BASE and HET simulations generally capture the hourly N₂O₅

347 concentrations as well as the peak values (Figure 1(c)) with similar overall NMB and
348 NME values.

349 ~~The underestimation of Cl_2 may be associated with insufficient chemical~~
350 ~~conversion from ClNO_2 to produce Cl_2 at nighttime. The uncertainty in the uptake~~
351 ~~coefficient of O_3 in daytime could also be an important factor as we believe affecting~~
352 ~~the predicted Cl_2 concentrations as it is found that the uptake heterogeneous reaction of~~
353 ~~O_3 is the major source of Cl_2 during this period of time (see discussion in Section 3.2).~~
354 ~~According to equation (7), the underestimation of ClNO_2 concentration may be due to~~
355 ~~two factors, that is, reaction rate K_6 and N_2O_5 concentration. Because the N_2O_5~~
356 ~~concentration is not substantially underestimated (see Figure 1(c)), we believe that the~~
357 ~~deviation of reaction rate K_6 is the culprit to result in the underestimation of ClNO_2 ,~~
358 ~~thus The influence of different parametrizations of the uptake coefficient of N_2O_5 which~~
359 ~~significantly affects K_6 may be an important factor to affect the accuracy of ClNO_2~~
360 ~~simulation (see further discussion on ClNO_2 and nitrate concentrations are also~~
361 ~~discussed in Section 3.2). The improved CMAQ can accurately capture the diurnal~~
362 ~~variation of N_2O_5 concentration as well as the peak values (Figure 1(c)). In general,~~
363 ~~although the overall NMB and NME of BASE case (-20% and 38%) are slightly better~~
364 ~~than the HET case (-21% and 41%), the improved CMAQ (with the NMB and NME~~
365 ~~of -3% and 14%) perform better than original CMAQ (with the NMB and NME of -33%~~
366 ~~and 52%) in some period of heavy air pollution (such as the nighttime on 12 June and~~
367 ~~13 June).~~

368 Predicted NO_3^- and PCL concentrations are compared with observations measured
369 at an adjacent monitoring site located at the rooftop of School of Environment building
370 in Tsinghua University (THU, 40.00N°00°N, 116.34E°34°E, about 5 km from IAP)
371 using an Online Analyser of Monitoring of Aerosol and Gases (MARGA) from 11 to
372 15 June 2017. According to Figure 1(d), ~~excluding the very high nitrate level in 13 June,~~
373 ~~the simulated nitrate concentration is commonly slightly lower than the observations,~~
374 ~~probably as the result most of the unreasonable NH_3 gas-particle partitioning model in~~
375 ~~our developed CMAQ model (Song et al., 2018). Comparing with the very high nitrate~~
376 ~~concentrations in time. From the evening hours of 12 June to morning hours of 13 June,~~
377 ~~observed and 13 June, we find that the simulated nitrate concentration using improved~~
378 ~~CMAQ is superior to use original CMAQ, while the nitrate level is higher in daytime~~
379 ~~and lower in nighttime, with the both increase significantly. The NMB and NME~~
380 ~~improve from values of hourly nitrate for the HET case (-5% and 39%, respectively) are~~

381 ~~slightly lower than those for the BASE case -10% and 46% to -5% and 39%. Excluding~~
382 ~~the daytime on 15 June, the improved CMAQ%) during this high concentration period.~~
383 The HET case also capture generally captures the hourly day-to-day variation of PCl
384 concentration and perform better than ~~using original CMAQ~~ the BASE case,
385 correspondingly the NMB and NME ~~change are reduced~~ from -48% and 72% to -37%
386 and 67%. The substantial underestimation of PCl in the daytime on 15 June is likely
387 caused by ~~some~~ missing local emissions during this period.

388

389 3.2 Estimation Impact of uptake coefficients of O₃ and N₂O₅ on chlorine species and 390 nitrate

391 The uptake coefficients of O₃ and N₂O₅ may be important factors affecting the accuracy
392 of simulated nitrate concentrations. Some studies have confirmed that the reaction of
393 O₃ on CPS can indirectly affect the nitrate formation by increasing the atmospheric Cl₂
394 and OH level (Li et al., 2016; Liu et al., 2018). According to Figure 1(a), the improved
395 model still substantially underestimates the concentration of Cl₂, which may be
396 associated with the underestimation of the uptake ~~coefficient~~ coefficients of O₃. ~~The~~
397 ~~uptake coefficient of O₃ used in this study is,~~ which are empirical ~~and~~ have not
398 been confirmed by laboratory studies. The uptake coefficients were increased by a
399 factor of 10 (0.01 for daytime and 10⁻⁴ for nighttime) to evaluate the sensitivity of Cl₂
400 production and nitrate formation. to this parameter. Figure 2 shows that the simulated
401 Cl₂ and nitrate concentrations in daytime increase significantly (especially for Cl₂) and
402 sometimes can capture the peak value (such as the daytime peak on 14 June). However,
403 although the NMB and NME of Cl₂ and nitrate improve from -18% and 39% to 1% and
404 28% when the new uptake coefficients are used, the simulated Cl₂ concentrations are
405 still quite different from the observations such as during the daytime in 11 and 12 June,
406 see Figure 2). A non-constant parameterization of the uptake coefficients of O₃ that
407 ~~consider~~ considers the influence of PCl concentrations, meteorology conditions, etc.,
408 similar to those of OH and N₂O₅, might be needed. Further laboratory studies should
409 be conducted to ~~confirm this conclusion, provide a better estimation of this important~~
410 parameter.

411 ~~As described above, Several parameterizations for~~ the uptake coefficient of N₂O₅
412 ~~can be expressed in multiple forms, have been developed for regional and global models~~
413 ~~and have been evaluated in several previous studies (Tham et al., 2019, McDuffie et al.,~~
414 ~~2018a, 2018b).~~ In addition to the parameterization of Bertram ~~et al. and Thornton~~ (2009)

415 used in the HET case, two additional simulations were performed to assess the impact
416 of the uptake coefficient of N_2O_5 on nitrate formation: (1) using . The first simulation
417 uses the original CMAQ parameterization of Davis et al.(2008);) and (2) the
418 maximumsecond simulation uses a constant value of 0.09 from the study, which is the
419 upper limit of the N_2O_5 uptake coefficient derived by Zhou et al. (2018);) based on
420 observations. The results show that the HET case has better agreement with the
421 observations than the two additional from the simulations (Table 3). The Davis et al.
422 with the parameterization is dependent on of Bertram and Thornton (2009) generally
423 agree with the concentration of nitrate and sulfate concentration, which is inferior
424 to results using those based on Davis et al. (2008) and the coefficient used in this study.
425 We conclude that a chlorine related coefficient is more reasonable for the application of
426 simulating reactive chlorine species and nitrate larger constant N_2O_5 leads to slightly
427 better results, which might reflect the fact that the N_2O_5 concentrations in high chlorine
428 emission region are underestimated. Using the uptake coefficient of 0.09 can generally
429 increase the concentration of nitrate in some periods, but it also leads to significant
430 overestimations increase of the nitrate level (such as nighttime on 12-13 June and 13-14
431 June);), which is 4-6 times higher than those based on Bertram and Thornton (2009).
432 Overall, predicted nitrate concentrations are sensitive to changes in the changes in
433 $\gamma_{N_2O_5}$, with approximately 50% increase in the nitrate when a constant of $\gamma_{N_2O_5}$ of
434 0.09 is used.

435

436 3.3 Spatial distributions of nitrate and chlorine species concentrations

437 The regional distributions of averaged Cl_2 , $ClNO_2$, N_2O_5 and NO_3^- concentration from
438 11 to 15 June infor the BASE case and HET case are shown in Figure 3. Compared to
439 original CMAQ, the averaged the BASE case, the episode average concentrations of Cl_2
440 and $ClNO_2$ derived from improved CMAQ the HET case increase significantly in the
441 eastern region of Beijing, reaching up to 23 ppt and 71 ppt from near zero- (Figure 3a
442 and 3b). High concentrations are not found in in southern the southern region with
443 intensive emissions of chlorine species, implying that Cl_2 and - (Figure S2). The
444 production of $ClNO_2$ requires the presence of chloride, NO_2 , and O_3 . In the areas close
445 to the fresh emissions, O_3 is generally low (Figure S3), and the production of NO_3^-
446 (hence N_2O_5 and $ClNO_2$) is limited. Therefore, the production rate of $ClNO_2$ is
447 generally low in areas affected by fresh emissions. Since the contribution of direct

448 emissions to Cl₂ is low and it is predominantly produced secondarily in the atmosphere,
449 high levels of Cl₂ are easy to transport among cities also found away from the fresh
450 emissions.

451 The spatial distribution of N₂O₅ concentration in nighttime concentrations differs
452 from that of other species: (Figure 3c). While the concentrations of most of the species
453 are higher in the southern region, the N₂O₅ concentration is low concentrations are lower
454 in some parts of this region. This is because the O₃ concentration in the core urban areas
455 is low due to high NO_x emissions. By incorporating the chlorine heterogeneous reaction,
456 the The N₂O₅ concentrations decrease by about from the HET case are approximately
457 16% lower on average (Figure 3d) because more N₂O₅ is converted into nitrate. the
458 Bertram and Thornton (2009) parameterization used in the HET case generally gives
459 higher uptake coefficients than the parameterization of Davis et al. (2008) used in the
460 BASE case (Table 3).

461 Although the added PCl prompts the higher uptake coefficients of N₂O₅ in the
462 HET case facilitate faster conversion from of N₂O₅ to nitrate, the nitrate concentration
463 in these regions has concentrations do not presented significant always increase.
464 In During daytime hours, nitrate concentrations in the HET case increase due to higher
465 OH (Figure 3e and Figure 3f). At nighttime, in contrast, the nitrate concentration
466 decreases significantly significantly in some regions by about 22%, mainly due to
467 lower molar yield of nitrate from the reduction of 2 mol NO₃⁻ in R5 to 1 mol in R6 for
468 each mole of N₂O₅ reacted. heterogeneous reaction in the HET case (Figure 3g and
469 Figure 3h). Although the generated ClNO₂ produced in the N₂O₅ reaction also further
470 produces nitrate, through a heterogenous reaction when the particle pH in is above 2,
471 which is true for most time is higher than 2 regions (see Figure S1) and S4), the uptake
472 coefficient of ClNO₂ is significantly lower than that of N₂O₅ (0.01~0.09 for N₂O₅ and
473 6 × 10⁻³ for ClNO₂), leading to an overall decrease of nitrate production. As the ClNO₂
474 production from the heterogeneous reaction leads to less N₂O₅ conversion to non-
475 relative nitrate, it may change the overall lifetime of NO_x and their transport distances.
476 The magnitude of this change and its implications on ozone and PM_{2.5} in local and
477 downwind areas should be further studied.

478 479 3.4 Relationship between nitrate formation and chlorine chemistry

480 A CMAQ tagged method (tagging the nitrate concentration produced by the
481 heterogeneous reaction, the rest of nitrate is produced by HNO₃ partitioning) is used to

482 ~~estimate the nitrate production~~ Nitrate productions from the homogeneous and
483 heterogeneous pathways and HNO₃ partitioning pathways. In general, about 58.3% of
484 ~~in Beijing are approximated by the difference in predicted nitrate concentrations~~
485 ~~between the BASE or HET case and a sensitivity case without heterogenous reactions.~~
486 ~~Averaging over the five-day period, approximately 58% of the~~ nitrate originates from
487 HNO₃ ~~gas-to-particle~~ partitioning and ~~41.7% of nitrate are produced~~ 42% is from
488 heterogeneous ~~reaction~~ reactions (Figure 4). This conclusion generally agrees with
489 measurements at ~~a nearby observation site in~~ Peking University (PKU) (Wang et al.,
490 2017), ~~which indicates~~ 52% from the heterogeneous process and 48% from HNO₃
491 partitioning. ~~Two factors may lead to the differences between our simulation and~~ on
492 ~~four polluted days (average in September 2016 reported by Wang et al. (2017). Slightly~~
493 ~~higher contributions of the measurement at PKU. One is the chlorine heterogeneous~~
494 ~~chemistry and the other is the pollution level. More nitrate homogeneous pathway in~~
495 ~~this study is expected to be produced by HNO₃ gas to particle partitioning in cleaner~~
496 ~~days whereas the heterogeneous process is more important in haze days. The averaged~~
497 ~~nitrate level at PKU site because of high OH concentrations during the measurement~~
498 ~~was 14.2 μg m⁻³, about 4 times higher than that in this study day and lower particle~~
499 ~~surface areas at night.~~

500 ~~The production rates of gaseous HNO₃ from different gas phase reactions and~~ The
501 nitrate formation from different ~~homogeneous and~~ heterogeneous ~~reaction~~ pathways in
502 the BASE case and HET case are further studied ~~using process analysis.~~ Contributions
503 ~~of different gas phase pathways are determined using the process analysis tool in~~
504 ~~CMAQ. Contributions of different heterogeneous pathways are determined using a~~
505 ~~zero-out method that turns off one heterogeneous pathway at a time in a series of~~
506 ~~sensitivity simulations.~~ Figure 4 shows that the reaction of OH and NO₂ is always the
507 major pathway ~~to produce gaseous~~ for the formation of nitrate through homogeneous
508 ~~formation of HNO₃ regardless of daytime or nighttime and gas-to-particle partitioning.~~
509 However, its ~~reaction~~ nitrate production rate ~~through this homogeneous pathway~~
510 decreases ~~significantly~~ significantly from daytime to nighttime (from ~~1272 ppt~~ 1.81 μg
511 m⁻³ h⁻¹ to ~~234 ppt~~ 0.33 μg m⁻³ h⁻¹ on average). The ~~nitrate production from~~ other HNO₃
512 ~~production~~ partitioning pathways in ~~the~~ daytime ~~can be ignored because their~~
513 ~~negligible. At nighttime, homogeneous~~ reaction rates are rather low. But at nighttime
514 ~~the reaction rate of N₂O₅ with water vapor presents a rapid increase, reaching up to 12.2~~
515 ~~ppt h⁻¹ from 1.7 ppt h⁻¹, which~~ accounts for approximately 5% of the ~~HNO₃ overall~~

516 homogeneous nitrate formation in the gas phase. For the heterogeneous pathways, ~~all~~
517 ~~of daytime production rate is approximately $0.6 \mu\text{g m}^{-3} \text{h}^{-1}$ with 1/3 of the contributions~~
518 ~~from NO_2 and 2/3 from N_2O_5 . Nighttime production on nitrate from the heterogeneous~~
519 ~~pathways is approximately $3.1 \mu\text{g m}^{-3} \text{h}^{-1}$, of which 85% is due to N_2O_5 and 15% is due~~
520 ~~to NO_2 .~~

521 ~~Comparing the BASE case and the reactions can be neglected in the daytime. At~~
522 ~~nighttime, the heterogeneous uptake N_2O_5 on the particle surface is the major pathway~~
523 ~~to nitrate formation (about $3.07 \mu\text{g m}^{-3} \text{h}^{-1}$, account for 84.8% in heterogeneous~~
524 ~~formation). By contrast, heterogeneous uptake of NO_2 on particulate H_2O has less~~
525 ~~contribution to nitrate (15.2%).~~

526 ~~When HET case shows that, when~~ the chlorine chemistry is included, the gaseous
527 HNO_3 produced by OH reacting with NO_2 increases significantly ~~(in the HET case.~~
528 ~~Correspondingly, the nitrate production rate reaches up to $1487 \text{ ppb} 2.04 \mu\text{g m}^{-3} \text{h}^{-1}$ in~~
529 ~~the daytime and 253 ppt h^{-1} at nighttime)~~ due to increased atmospheric OH
530 concentrations predicted by the chlorine reactions. Similar conclusions are also
531 obtained by Li et al. (2016) and Liu et al. (2017) based on observations and model
532 ~~simulation. Note that the reaction of NO_3 with HO_2 does not increase obviously even~~
533 ~~through the chlorine chemistry also leads to higher atmospheric HO_2 levels (increase~~
534 ~~by more than 20%, Li et al., (2016)) because the atmospheric NO_3 radical level is rather~~
535 ~~low. simulations.~~ The heterogeneous production of nitrate from the reaction of N_2O_5
536 uptake decreases ~~dramatically (about by approximately 27%)~~ in the HET case due to
537 the ~~inclusion of production of gas phase ClNO_2 .~~ According to the study by Sarwar et al.
538 ~~(2012; 2014), including the heterogeneous reactions of chlorine species reaction of~~
539 ~~N_2O_5 with PCl decreased the nocturnal nitrate concentration by 11-21% in the United~~
540 ~~States, which was slightly less than the current study for Beijing. It is likely because~~
541 ~~PCl concentrations in the United States are significantly lower than those in Beijing~~
542 ~~(the monthly PCl concentration is $0.06 \mu\text{g m}^{-3}$ in the United State against $\sim 1 \mu\text{g m}^{-3}$ in~~
543 ~~Beijing) so that PCl is depleted quickly.~~ The contributions of NO_2 uptake to nitrate also
544 decrease by 22% because of the lower rate constant of the reaction of NO_2 with PCl. In
545 contrast, the contribution of ClNO_2 ~~decomposition reacts with particle surface~~ to nitrate
546 production increases by 6% in the HET case. ~~Generally, the~~ The overall nitrate
547 ~~concentrations estimated by original CMAQ concentration in the HET case~~ is about 22%
548 higher than that in the modified CMAQ BASE case during this study period.

549

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 PCl concentrations, meteorology conditions, etc., might be needed, N_2O_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 developed and 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_2O_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)

584

585 **Author contributions.** XQ, QY, SW; and JH ~~conducted~~designed the study; YS, BL, AS,
586 XY provided observation data; XQ, QY, SW, JZ, QX, DD, LD and JX analyzed data.
587 XQ, QY and SW wrote the paper. ~~JZ, DD, YS, BL, AS, XY and QX analyzed data.~~

588

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590

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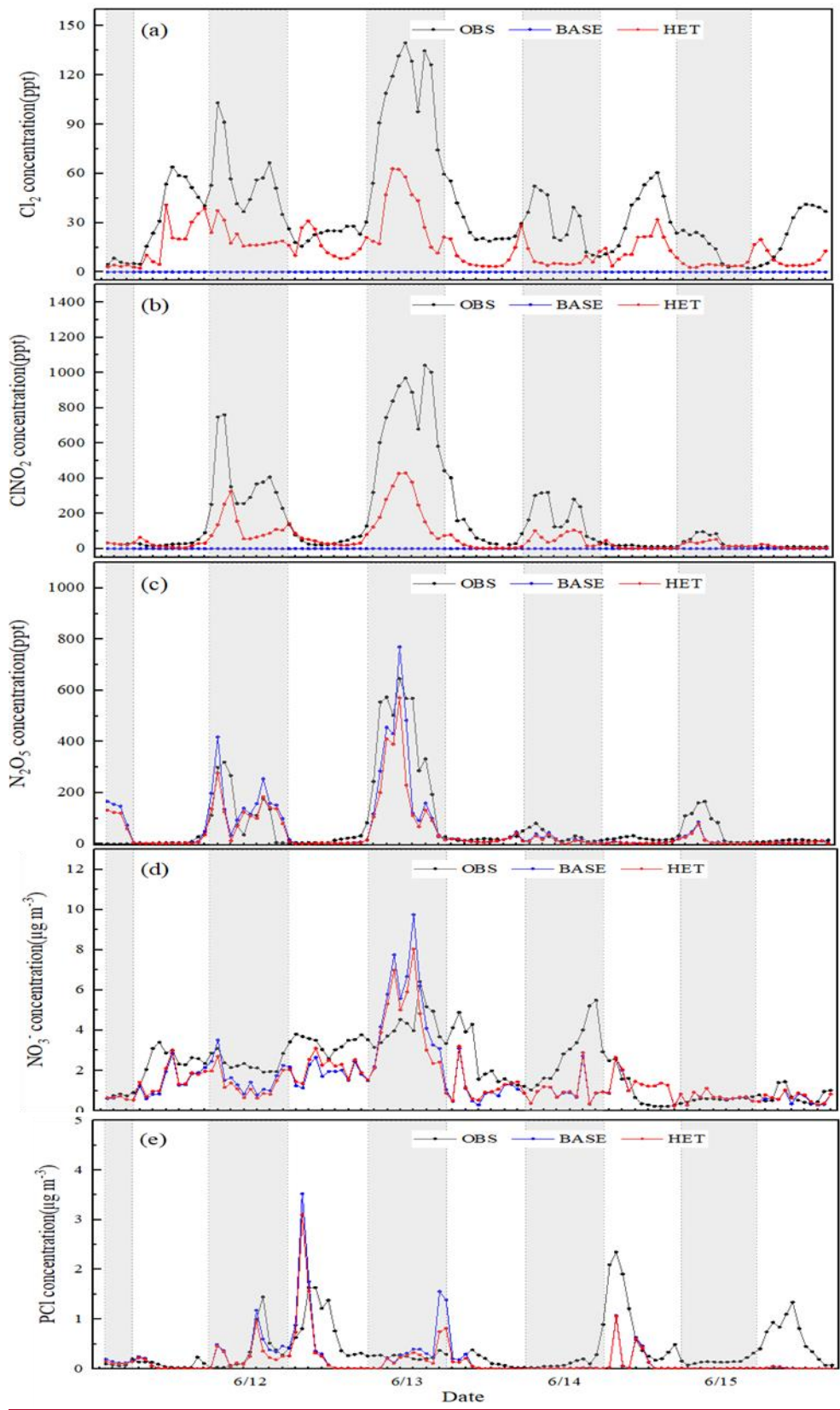
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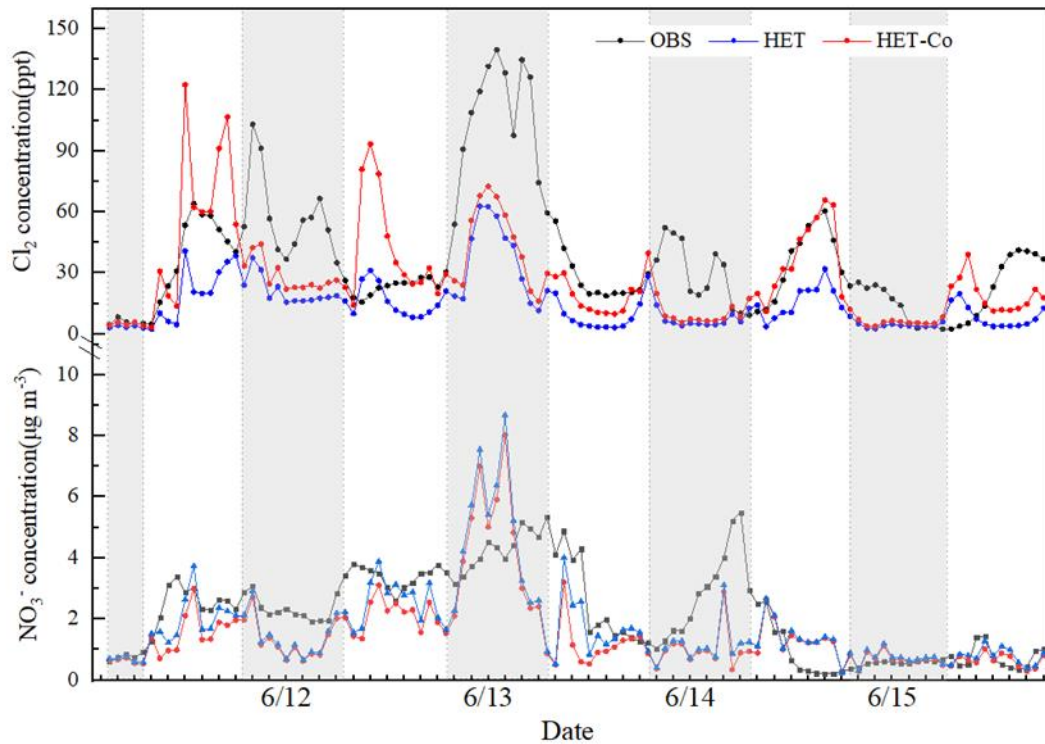
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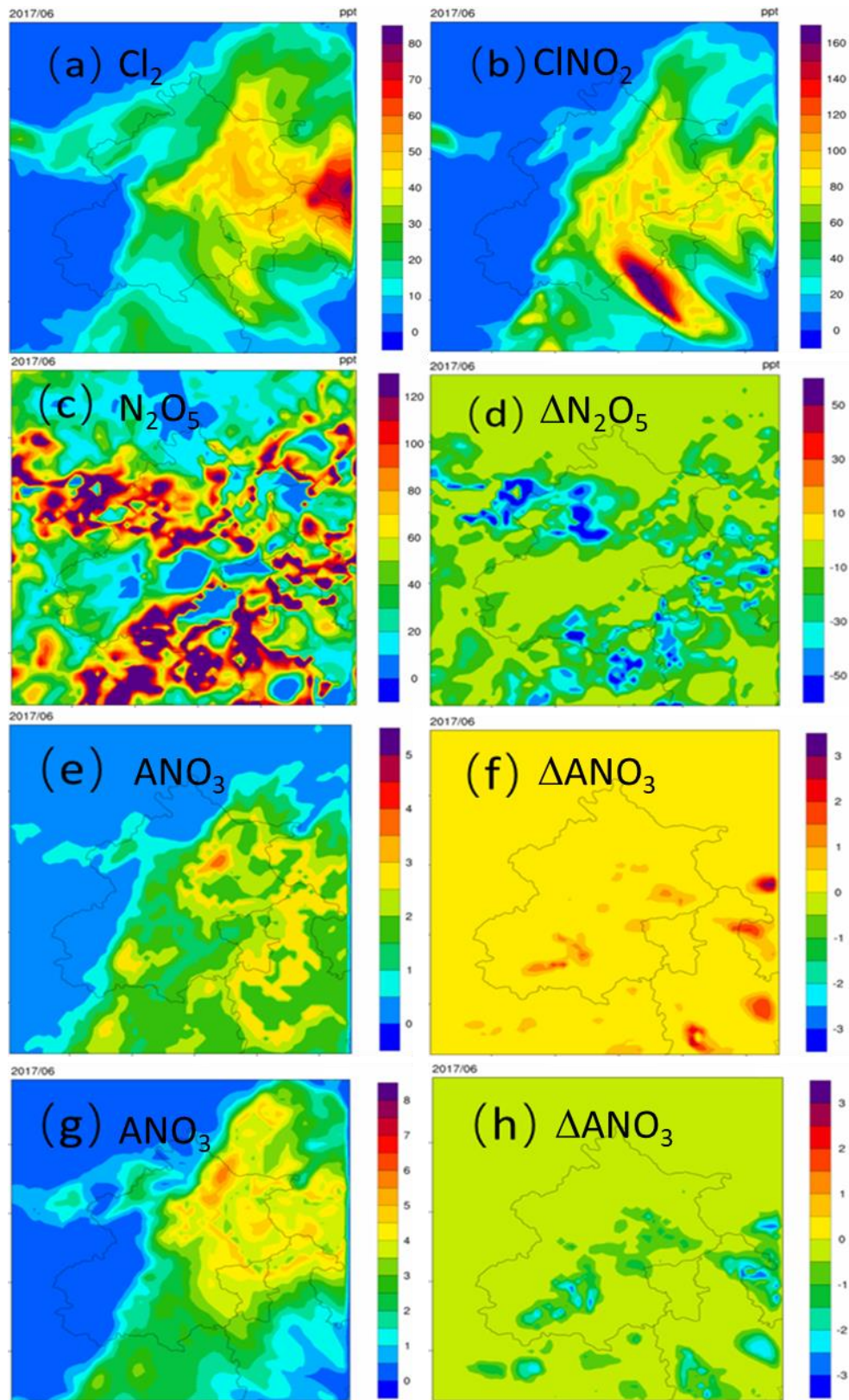
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Figure 1- Comparison of ~~simulated and~~ observed hourly Cl_2 , ClNO_2 , N_2O_5 , NO_3^- and PCl using ~~original and improved CMAQ (the gray presents nighttime)~~ (at Tsinghua University)

769 in urban Beijing with predictions from the BASE and the HET cases during 11-15
770 June 2017.

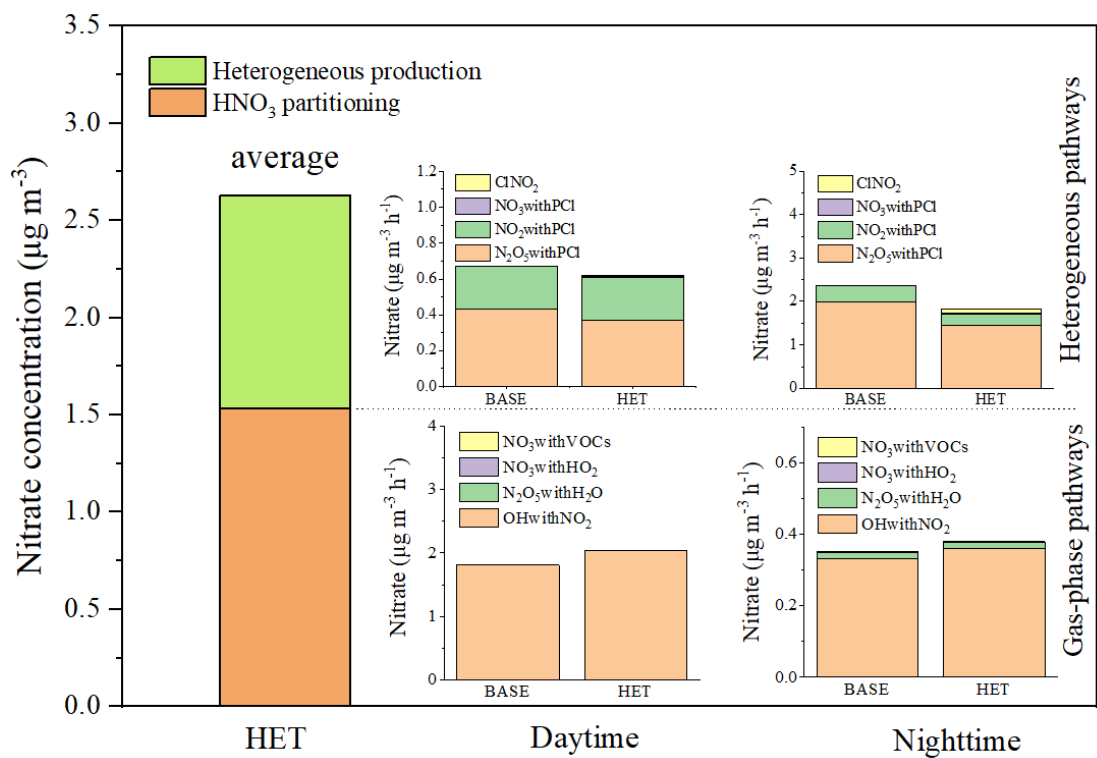


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772 Figure 2: Comparison of ~~simulated~~observed and predicted Cl₂ and NO₃⁻ concentrations
773 under different uptake coefficient of O₃ (HET: daytime $\gamma_{O_3} = 1 \times 10^{-3}$,
774 nighttime $\gamma_{O_3} = 1 \times 10^{-5}$; HET-Co: ~~the scenario of uptake coefficients~~, daytime
775 $\gamma_{O_3} = 1 \times 10^{-2}$, nighttime $\gamma_{O_3} = 1 \times 10^{-4}$).
776



777
 778 Figure 3- Spatial distributions of episode-average (a) Cl_2 , (b) ClNO_2 , (c) N_2O_5 , (e)
 779 daytime nitrate (ANO_3) and (g) NO_3^- -concentration in daytime and nighttime (a-b: nitrate
 780 concentrations of Cl_2 and ClNO_2 from 11-15 June 2017, and the differences in HET case;
 781 e- the episode-average (d- the concentration of) N_2O_5 in HET case and difference
 782 between (HET case and BASE case; e- f: the diurnal concentration of NO_3^- in HET case
 783 and difference between HET case and_ BASE case; g- h: the nocturnal concentration of

784 ~~NO₃⁻ in HET case and difference between HET case and BASE case).~~, (f) daytime
785 nitrate and (g) nighttime nitrate. Units are $\mu\text{g m}^{-3}$.
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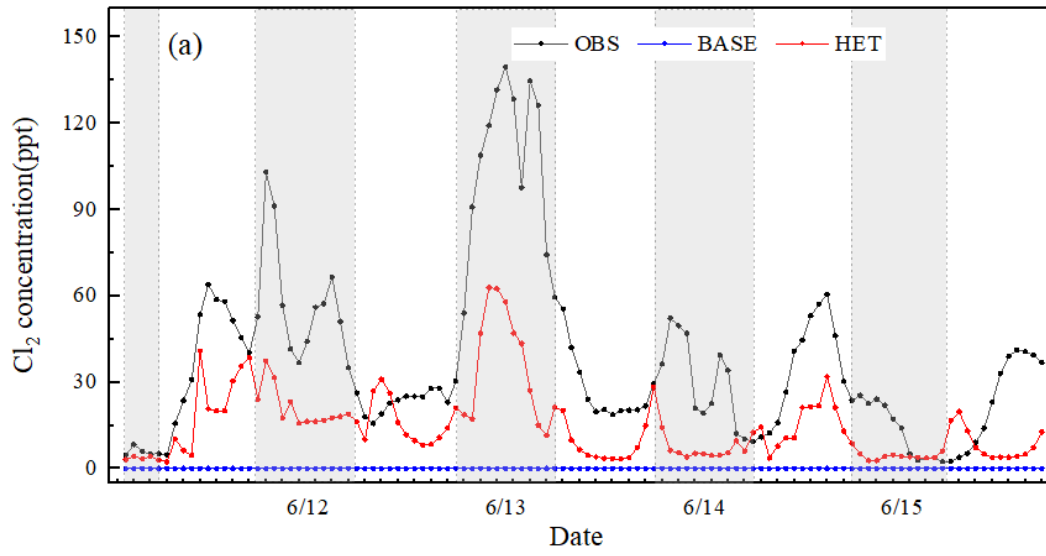
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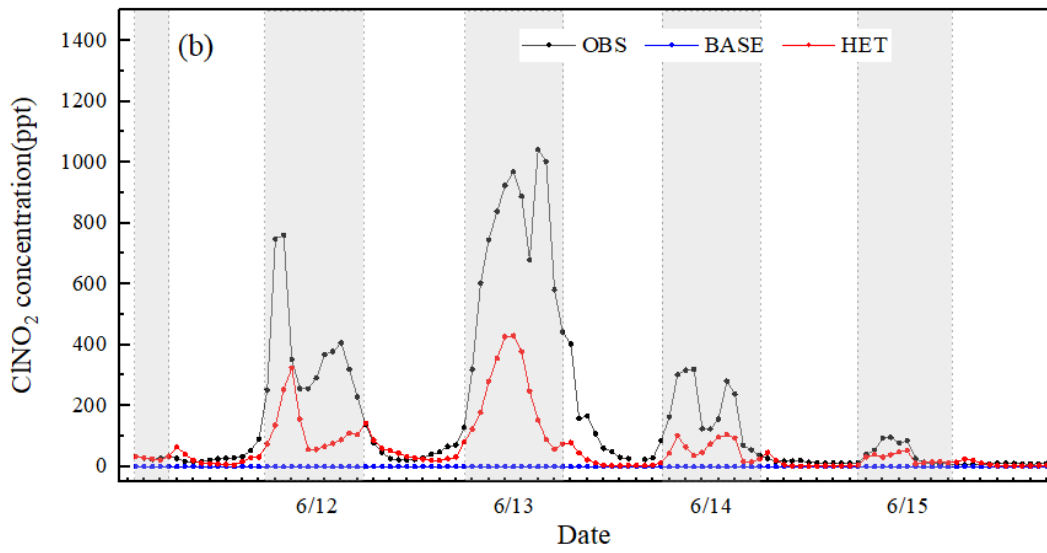
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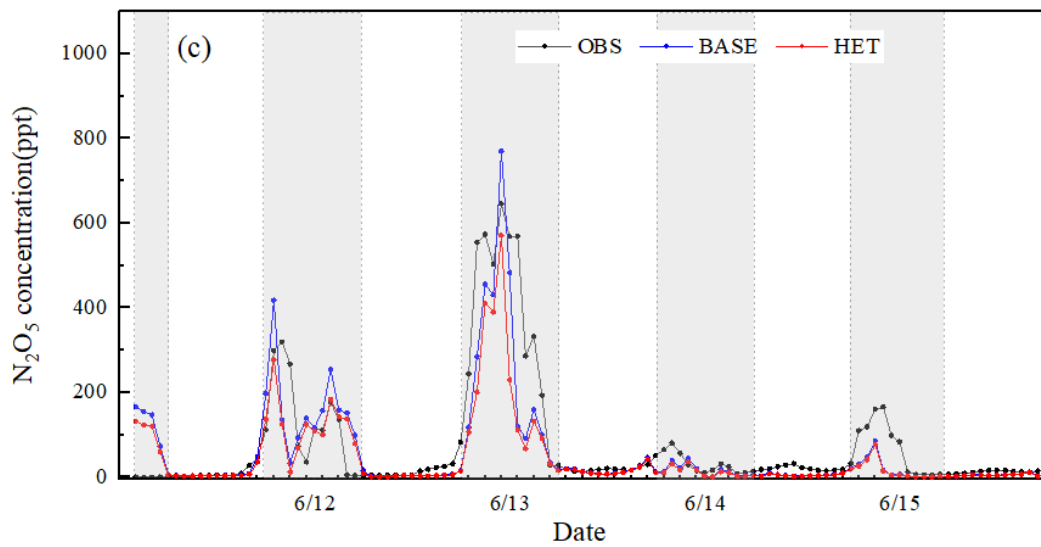
Figure 4. Contributions of different ~~gas phase reaction pathways~~ homogeneous and heterogeneous reaction pathways to nitrate formation.



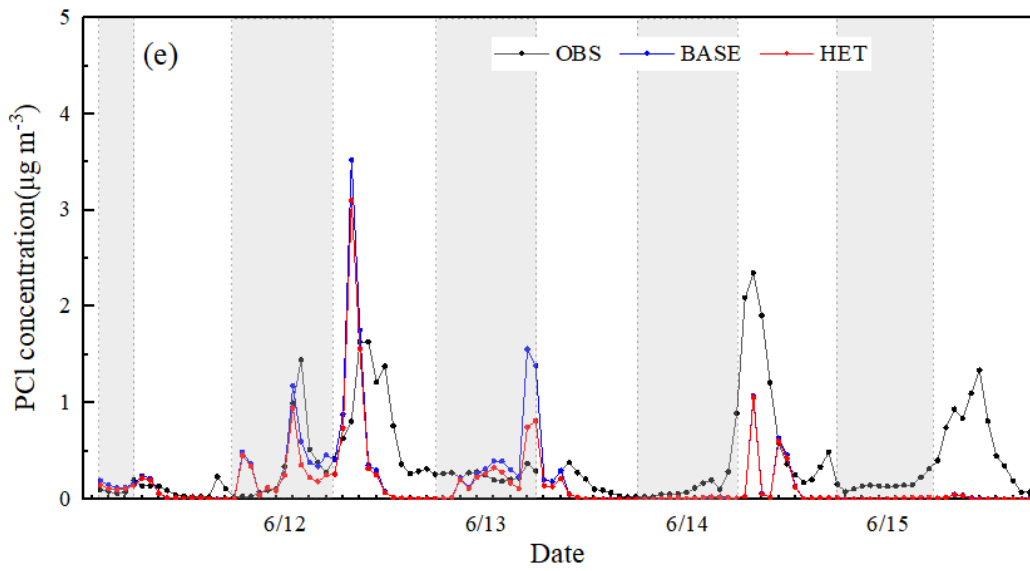
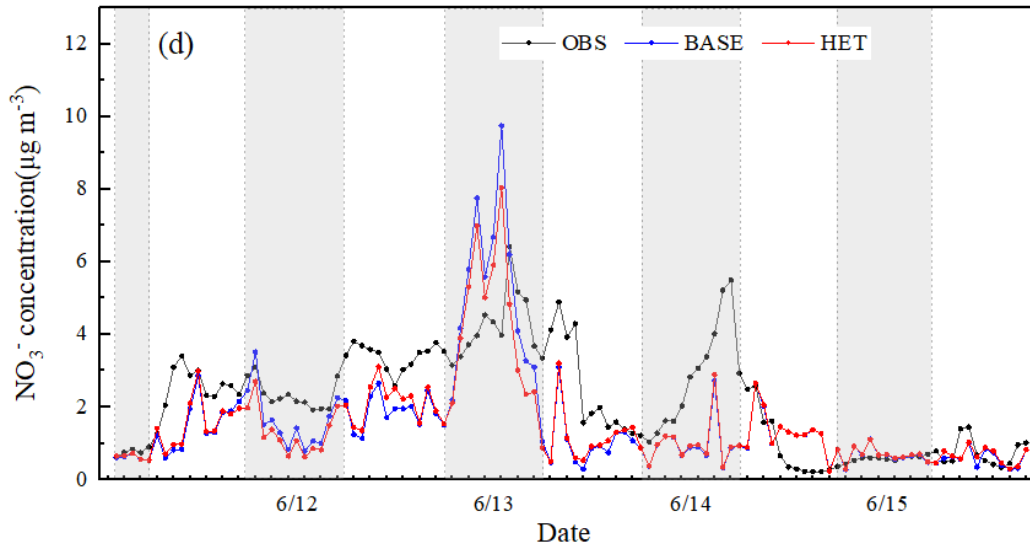
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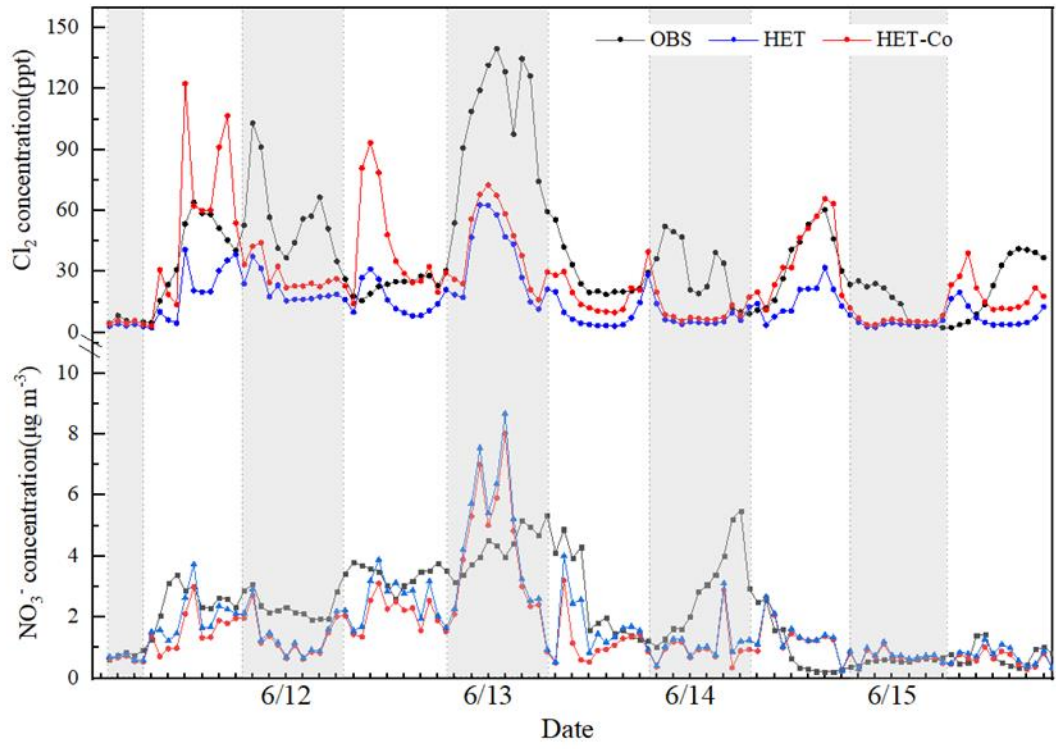
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Figure 1



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Figure 2

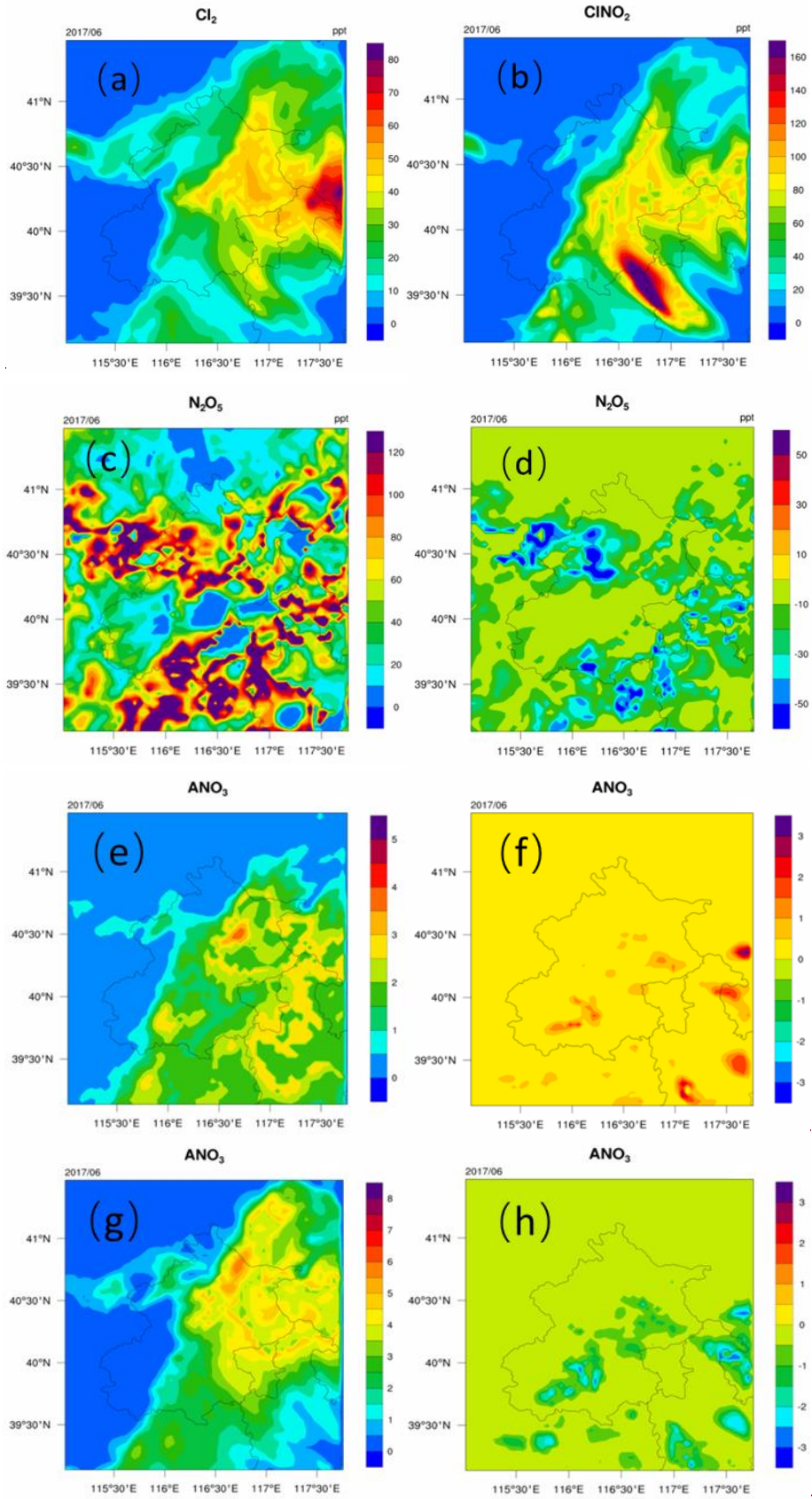
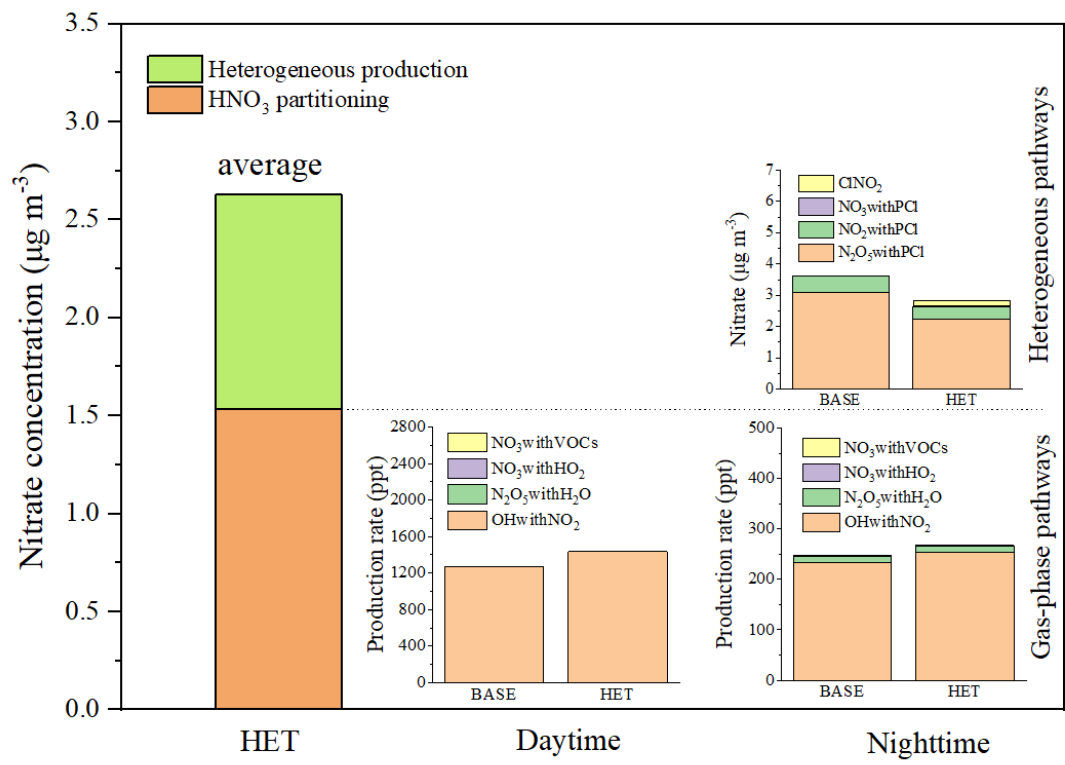


Figure 3—
 Note: the distribution of Cl_2 and $ClNO_2$ in HET minus BASE have not been shown because their concentrations in BASE case are rather low (close to 0)



810
 811 **Figure 4**
 812

813 Table 1 The sectoral emissions of HCl, Cl₂ and PCl₅ in Beijing in 2017. Unit: Mg year⁻¹
 814 ¹

Sector	Emissions		
	HCl	Cl ₂	PCl ₅
Power plant	22.8	1.2	6.75
Industry	587.3	20.1	89.2
Residential	202.4	8.1	34.7
Biomass burning	0.182	0	0.14
Municipal solid waste	1080.2	0	8.47
Cooking	0	0	426.8
Total	1892.9	29.4	566.1

815

816

817 Table 2 Major gas-phase and heterogeneous pathway of producing nitrate in original CMAQ and newly added or revised heterogeneous reactions
 818 in improved CMAQ.

Type	Reactions	No.	Reference	Comment
Original CMAQ				
Gas-phase chemistry	$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$	R1		
	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3$	R7		
	$\text{HO}_2 + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{OH} + \text{NO}_2$	R8		
	$\text{NO}_3 + \text{VOCs}^a \rightarrow \text{HNO}_3$	R9		
Heterogeneous chemistry	$\text{N}_2\text{O}_5(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{HNO}_3(\text{g}) + \text{HNO}_3(\text{g})$	R5		
	$\text{NO}_2 + \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{HONO}(\text{g}) + \text{HNO}_3(\text{g})$	R10		
Improved CMAQ				
Newly added or revised heterogeneous reactions	$\text{N}_2\text{O}_5(\text{g}) + \text{H}_2\text{O}(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{ClONO}_2(\text{g}) + \text{NO}_3^-(\text{aq})$	R6	Bertram and Thornton (2009)	Revise R5
	$2\text{NO}_2(\text{g}) + \text{Cl}^-(\text{aq}) \rightarrow \text{ClNO}(\text{g}) + \text{NO}_3^-(\text{aq})$	R11	Abbatt et al. (1998)	Revise R10
	$\text{NO}_3(\text{g}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{NO}_3^-(\text{aq})$	R12	Rudich et al. (1996)	Increase NO_3^-
	$2\text{Cl}^-(\text{aq}) + \text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	R13	Abbatt et al. (1998)	Affect OH
	$\text{OH} + 2\text{OH}^-(\text{g}) + \text{Cl}^-(\text{aq}) \rightarrow 2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	R14	George et al. (2010)	Affect OH
	$\text{ClONO}_2(\text{g}) + \text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{NO}_3^-(\text{aq})$	R15	Deiber et al. (2004)	Affect OH
	$\text{HOCl}(\text{g}) + \text{Cl}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{aq})$	R16	Pratte et al. (2006)	Affect OH
	$\text{ClONO}_2(\text{g}) + \text{Cl}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{HONO}(\text{aq})$	R17	Riedel et al. (2012)	Affect OH
	$\text{ClONO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{Cl}^- + \text{NO}_3^- + 2\text{H}^+$ (pH ≥ 2.0)	R18	Rossi (2003)	Increase NO_3^-

819 ^a: presents different VOCs species. In the SAPRC-11 mechanism, the VOCs species include CCHO (Acetaldehyde), RCHO (Lumped C3+
 820 Aldehydes), GLY (Glyoxal), MGLY (Methyl Glyoxal), PHEN (phenols), BALD (Aromatic aldehydes), MACR (Methacrolein), IPRD (Lumped

821 isoprene product species).
822

823 Table 3 ~~The Observed day (D) and night (N) NO₃⁻ concentrations (Obs.) and predicted~~
 824 ~~uptake coefficient of N₂O₅ in different Scenarios and its impact on (γ_{N₂O₅) and nitrate (unit:}~~
 825 ~~μg·m⁻³) (uptake coefficient concentrations (Pred.) using the parameterizations of γ_{N₂O₅}~~
 826 ~~derives from by Bertram and Thornton (2009) (Scenario 1), Davis et al. (Scenario 1), Davie~~
 827 ~~et al. (Scenario 2), and ., (2008) (Scenario 2) and the upper-limit value derived by Zhou et~~
 828 ~~al. (2018), respectively) (Scenario 3)~~

	<u>NO₃⁻</u>		Scenario1		Scenario2		Scenario3	
	<u>Obs.</u>	<u>γ_{N₂O₅}</u>	<u>NO₃⁻Pred.</u>	<u>γ_{N₂O₅}</u>	<u>NO₃⁻Pred.</u>	<u>γ_{N₂O₅}</u>	<u>NO₃⁻Pred.</u>	
06/11-D	2.54	0.033	1.59	0.008	1.32	0.09	2.17	
06/11-12-N	2.42	0.043	1.67	0.037	1.37	0.09	2.12	
06/12-D	3.39	0.028	2.16	0.032	2.74	0.09	3.13	
06/12-13-N	4.24	0.021	4.02	0.022	4.05	0.09	6.04	
06/13-D	2.57	0.012	1.18	0.008	1.06	0.09	2.47	
06/13-14-N	4.10	0.022	4.45	0.022	4.45	0.09	7.13	
06/14-D	0.95	0.001	1.34	0.001	1.33	0.09	1.64	
06/14-15-N	2.75	0.013	1.00	0.007	0.96	0.09	2.33	
06/15-D	0.75	0.001	0.66	0.001	0.66	0.09	1.11	

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