Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-1270-RC1, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation in Beijing, China" *by* Xionghui Qiu et al.

Anonymous Referee #1

Received and published: 8 February 2019

General comment:

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.

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.

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

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

Specific comment:

1.Line 26-28. These descriptions are redundant to line 33-36.

2.Line 37-39. The ClNO2 production decreases nitrate during nighttime and increases nitrate during the daytime. Does it mean that the chlorine chemistry changes the temporal pattern of the nitrate formation and therefore the spatial pattern? Does it have any implication to the air quality control? I would love to see a discussion on this implication.

3.Line 50-57. The authors only introduced two production pathways of the secondary nitrate. However, the other pathways, e.g., those in Table 2, also play non-negligible

roles. Should add those pathways in the introduction.

4.Line 54. A reference is needed for the 'enhancement effect of NH3-NH4+ gas-particle equilibrium on the nitrate formation'.

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

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

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

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

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

10.Line 82. These references are not the right ones here. The first measurements of ClNO2 in the real atmosphere, Osthoff et al. (2008) and Thornton et al. (2010), are better ones.

11.Line 102. This is not entirely true. For instance, Hossaini et al. (2016) developed a

global chemical transport model (TOMCAT) and included several heterogeneous reactions of chlorine species on chloride-containing aerosol.

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

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

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

14.Line 128-130. Should add some reference here. Also, 'NH3' should also be considered as a common species.

15.Line 136. Should mention the number (from 2000 Mt in 2014 to 490 Mt in 2017) here.

16.Line 142. Should list the emission factors for different sectors, at least in the supplement. Also, give the reference.

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

18.Line 160. Any reason that you chose '150'?

19.Line 173-174. A brief description is needed for other emissions, which are the precursors of N2O5, ClNO2, and nitrate aerosol.

20.Section 2.2. The authors added several reactions to the CMAQ model, and this seems to be one of the major contributions of this study. However, what is the difference between the mechanism in the current study and that in Sarwar et al. (2012, 2014)? I notice that one of the co-authors in the present study is also a co-author of Sarwar

et al. (2014). I strongly advise the authors to carefully review the previous works and identify the advantage of the current work, instead of avoiding the comparison between the current study with the previous ones.

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

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

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

23.Line 177. H2O means water vapor. Is that right?

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

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

26.Section 3.1. What about the model performance on the simulation of NO2, O3, and PM2.5? These are particularly important to the formation of nitrate aerosol, the sole focus of the current work.

27.Line 251-252. This treatment artificially amplifies the heterogeneous reaction rate by 5 and 10 times. Is it logical to do that based on the comparison with one measurement data set? How does the CMAQ model perform in general in the simulation of surface area? Is it a common issue? Or did it only happen in your simulation? How is the simulation of PM2.5? This highlights the need for the evaluation of the routine air

pollutants, e.g., PM2.5.

28.Line 255. ClNO2 is underestimated in your cases. Does it mean that nitrate aerosol is over-predicted?

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

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

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

32.Line 281-282. What do you mean by 'the nitrate level is higher in the daytime and lower in nighttime'?

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

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

35.Line 316. N2O5 uptake process is very complicated. The word, 'inferior', is definitely not the one I would use to describe the parameterization based on nitrate and sulfate

concentration. Please revise. The uncertainty of the parameterizations of N2O5 uptake and ClNO2 yield also works here.

36.Section 3.3. I advise to include the simulated results of NO2, O3, and PM2.5.

37.Line 328. Should include a figure for the 'intensive emissions of chlorine species'.

38.Line 328-330. The presence of a high concentration of ClNO2 and Cl2 away from the fresh emissions does not necessarily mean that ClNO2 and Cl2 are easy to transport.

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

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

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

40.Line 351-352. Was the observation in PKU conducted in the same period?

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

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

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

44.Line 402-404. Not necessarily correct. See comment above.

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

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

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

Technical comment:

48.Line 38. 'photolyze' is a better word than 'decompose' since it is a photolysis reaction.

49.Line 62. Should add '(aq)' after 'H2O'.

50. Line 63. should define CMAQ and WRF-Chem here.

51. Line 81. should be 'chloride-containing', not 'chlorine-containing'.

52.Line 119. The definition of CMAQ should be moved to line 63.

53.Line 130. Add a space between 'emissions' and 'were'.

54. Line 145. 'EF represents the emission factor' should be 'EFi,j represents the emission factor of pollutant j in sector i'.

55.Line 148-149. 'had been detailed described' should be 'had been described in detail'.

56.Line 158. Add 'from social cooking' after 'Vc is the volume of exhaust gas'.

57.Line 161. 'chose' should be 'chosen'.

58.Line 166. Delete 'that'.

59.Line 168. Use the same decimal for all data.

60.Line 169. ‘Others’ should be ‘Other’.

61.Line 169. Add the publication year after ‘Fu et al.’

62.Line 169 and line 171. Two ‘finally’?

63.Line 185. ‘Laboratorial’ should be ‘laboratory’.

64.Line 192. Do you mean ‘equation (5)’, instead of ‘equations (2)’?

65.Line 198. Do you mean ‘equation (6)’, instead of ‘equation (3)’?

66. Why did you use different terms for velocity in equation 5 and equation 8?

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

68.Line 216 and line 208. Use the consistent form for units. m3/m3 or m3 m-3.

69.Line 227. Which year?

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

71.Line 232. ‘40oE’ should be ‘40oN’.

72.Line 296. Remove the extra space between ‘empirical’ and ‘and’.

73.Line 315. Add the year for ‘Davis et al.’. Check through the manuscript for a similar issue.

74.Line 350. ‘are produced’ should be ‘is produced’.

75.Line 369. Add ‘of’ between ‘uptake’ and ‘N2O5’.

76.Line 378. ‘even through’ should be ‘even though’.

77.Line 396. ‘This’ should be ‘These’.

78.Line 397. ‘becase’ should be ‘because’.

79.Line 397. ‘the cornerstones’ should be ‘the cornerstone’ or ‘one of the cornerstones’.

80.Line 401. ‘chlorine’ should be ‘chloride’.

81.Line 409. ‘understnadings’ should be ‘understandings’.

82.Figure 3. Should point out the area of BJ and the location of the sampling site. In d, f, and h, should use $\triangle$N2O5, $\triangle$NO3-, and $\triangle$NO3-, instead of N2O5, NO3-, and NO3-

83.Figure 4. In the sub-plot Daytime Gas-phase, the title of Y-axis should be ‘HNO3 production rate (ppt h-1)’. The same revision should be applied to the sub-plot Nighttime Gas-phase. The sub-plot Nighttime Heterogeneous, the title of Y-axis should be ‘Nitrate production rate (μg m-3 h-1)’. No sub-plot daytime Heterogeneous?

Reference:

Brown, S.S. and Stutz, J., 2012. Nighttime radical observations and chemistry. Chemical Society Reviews, 41(19), pp.6405-6447.

Brown, S.S., Dubé, W.P., Tham, Y.J., Zha, Q., Xue, L., Poon, S., Wang, Z., Blake, D.R., Tsui, W., Parrish, D.D. and Wang, T., 2016. Nighttime chemistry at a high altitude site above Hong Kong. Journal of Geophysical Research: Atmospheres, 121(5), pp.2457-2475.

Fu, X., Wang, T., Zhang, L., Li, Q., Wang, Z., Xia, M., Yun, H., Wang, W., Yu, C., Yue, D. and Zhou, Y., 2019. The significant contribution of HONO to secondary pollutants during a severe winter pollution event in southern China. Atmospheric Chemistry and Physics, 19(1), pp.1-14.

Hossaini, R., Chipperfield, M.P., SaizâĂŘLopez, A., Fernandez, R., Monks, S., Feng,

W., Brauer, P. and Glasow, R., 2016. A global model of tropospheric chlorine chemistry: Organic versus inorganic sources and impact on methane oxidation. Journal of Geophysical Research: Atmospheres, 121(23).

McDuffie, E.E., Fibiger, D.L., Dubé, W.P., LopezâĂŘHilfiker, F., Lee, B.H., Thornton, J.A., Shah, V., Jaeglé, L., Guo, H., Weber, R.J. and Michael Reeves, J., 2018a. Heterogeneous N2O5 uptake during winter: Aircraft measurements during the 2015 WINTER campaign and critical evaluation of current parameterizations. Journal of Geophysical Research: Atmospheres, 123(8), pp.4345-4372.

McDuffie, E.E., Fibiger, D.L., Dubé, W.P., Lopez Hilfiker, F., Lee, B.H., Jaeglé, L., Guo, H., Weber, R.J., Reeves, J.M., Weinheimer, A.J. and Schroder, J.C., 2018b. ClNO2 yields from aircraft measurements during the 2015 WINTER campaign and critical evaluation of the current parameterization. Journal of Geophysical Research: Atmospheres, 123(22), pp.12-994.

Osthoff, H.D., Roberts, J.M., Ravishankara, A.R., Williams, E.J., Lerner, B.M., Sommariva, R., Bates, T.S., Coffman, D., Quinn, P.K., Dibb, J.E. and Stark, H., 2008. High levels of nitryl chloride in the polluted subtropical marine boundary layer. Nature Geoscience, 1(5), p.324.

Roberts, J.M., Osthoff, H.D., Brown, S.S., Ravishankara, A.R., Coffman, D., Quinn, P. and Bates, T., 2009. Laboratory studies of products of N2O5 uptake on Cl− containing substrates. Geophysical Research Letters, 36(20).

Sarwar, G., Simon, H., Bhave, P. and Yarwood, G., 2012. Examining the impact of heterogeneous nitryl chloride production on air quality across the United States. Atmospheric Chemistry and Physics, 12(14), pp.6455-6473.

Sarwar, G., Simon, H., Xing, J. and Mathur, R., 2014. Importance of tropospheric ClNO2 chemistry across the Northern Hemisphere. Geophysical Research Letters, 41(11), pp.4050-4058.

Simon, H., Kimura, Y., McGaughey, G., Allen, D.T., Brown, S.S., Osthoff, H.D., Roberts, J.M., Byun, D. and Lee, D., 2009. Modeling the impact of ClNO2 on ozone formation in the Houston area. Journal of Geophysical Research: Atmospheres, 114(D7).

Tham, Y.J., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., Ma, N., Yan, C., Kecorius, S., Wiedensohler, A. and Zhang, Y., 2018. Heterogeneous N 2 O 5 uptake coefficient and production yield of ClNO 2 in polluted northern China: roles of aerosol water content and chemical composition. Atmospheric Chemistry and Physics, 18(17), pp.13155-13171.

Thornton, J.A., Kercher, J.P., Riedel, T.P., Wagner, N.L., Cozic, J., Holloway, J.S., Dubé, W.P., Wolfe, G.M., Quinn, P.K., Middlebrook, A.M. and Alexander, B., 2010. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. Nature, 464(7286), p.271.

Wang, T., Tham, Y.J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S.C., Dubé, W.P., Blake, D.R., Louie, P.K. and Luk, C.W., 2016. Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China. Journal of Geophysical Research: Atmospheres, 121(5), pp.2476-2489.

Zheng, B., Zhang, Q., Zhang, Y., He, K.B., Wang, K., Zheng, G.J., Duan, F.K., Ma, Y.L. and Kimoto, T., 2015. Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. Atmospheric Chemistry and Physics (Online), 15(4).

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1270, 2018.