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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of chlorine in tropospheric chemistry" *by* Xuan Wang et al.

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Short Comments on Wang X., et al.: The role of chlorine in tropospheric chemistry

1. The authors state on page 5, line 10 that anthropogenic sources of HCl were not included in their base case GEOS-Chem simulation. Although minor in a global sense, it is worth noting that Lee et al. (2018) reported observations of direct halogen (i.e. HCl, as well as Cl2, ClNO2, Br2, BrNO2, and BrCl) emissions from power plants sampled during the WINTER aircraft campaign. This is also important to note in Section 4.2 where model results are directly compared to WINTER chlorine observations.

2. Page 11, line 3, the authors state that WINTER aircraft observations did not extend to the surface layer. As also noted by one Reviewer, there were a series of missed approaches at airfields that could provide further vertical information.

3. On page 10, Table 5 is referred to as a list of ‘available’ field observations of ClNO2. The GEOS-Chem simulations are then compared to these observations in Table 5 to evaluate the model performance. As noted by both Reviewers, however, there are many additional measurements of ClNO2 that were not included in Table 5. Measurements in addition to those provided by the Reviewers are from: (Edwards et al., 2013; Jeong et al., 2018; Kim et al., 2014; Liu et al., 2017; Osthoff et al., 2008; Phillips et al., 2016; Reyes-Villegas et al., 2018; Tham et al., 2018; Tham et al., 2014; Wang et al., 2018; Wang et al., 2016; Wang et al., 2014; Wild et al., 2016; Yun et al., 2018).

4. The authors include the HOBr + Cl- → BrCl reaction in their mechanism following Abbatt and Waschewsky (1998) and Fickert et al. (1999). They state in the discussion section on page 7 that the Cl source from this reaction is much higher than past simulations. Later in section 5.2, they also include discussion of previous work by Chen at al. (2017) who included a second HOBr + Cl- → Br2 pathway that is dependent on the molar ratio of [Br-]/[Cl-], following Fickert et al. (1999). It is unclear in section 5.2 whether this additional pathway was included in the base case simulation here. If not, the authors should clearly state why it was excluded since the Fickert et al. (1999) laboratory work showed 90% Br2 formation from this reaction at ratios of [Br-]/[Cl-] typically found in ambient sea water. If included, this reaction would help reduce this Cl production pathway relative to previous simulations.

5. The authors have also included the direct reaction of ClNO2 with Cl- to form Cl2 (there is also mention of ClNO2+Br- on page 14, which should be added to Table 2). This reaction is thought to occur via heterogeneous uptake of gas-phase ClNO2 and further reaction with aqueous Cl- (or Br-). As noted by one Reviewer, however, it has been shown by Roberts et al. (2008) that this reaction only occurs at pH < 2 and should be limited here to only highly acidic aerosol. That said, the aerosol during WINTER were highly acidic (pH ∼ -3 to 2) (Guo et al., 2016), which should activate this pathway. Even on these highly acidic aerosol, however, a recent study of WINTER ClNO2 yields by McDuffie et al. (2018a) reported that there was a negative correlation

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between particle acidity and CIMS observations of Cl2, which is opposite the trend expected from this reaction. In addition, there was no clear evidence in that study that gas-phase ClNO2 was being lost to heterogeneous processes (reaction with Cl or Br-). Since there is limited field data to support the presence of direct ClNO2 reactions in ambient aerosol, particularly during WINTER, the authors should consider eliminating direct ClNO2 reactions or provide further evidence to support their inclusion in this work.

6. The heterogeneous yield of ClNO2 is only mentioned in reaction R3 in Table 2, where it is defined using a laboratory-based parameterization from Bertram and Thornton (2009). This parameterization is used to predict both N2O5 uptake coefficient and ClNO2 yield. It is concerning that there is no discussion in this manuscript of the large uncertainties associated with these processes or parameterizations. First, this particular parameterization for N2O5 uptake does not consistently reproduce field-derived observations (e.g., Bertram et al., 2009; McDuffie et al., 2018b; Wagner et al., 2013) and has been adjusted in recent GEOS-Chem simulations (Jaeglé et al., 2018; Shah et al., 2018) to better match nitrate observations during WINTER. While N2O5 is not the topic of this manuscript, this process directly impacts the net production of ClNO2, thus impacting the chlorine chemical mechanism and budget. The authors should therefore consider updating the N2O5 uptake parameterization in their simulations or discuss this as a source of uncertainty in their results. Second, this particular parameterization has over-predicted the ClNO2 production yield in every study that has compared its predictions to field-derived results (McDuffie et al., 2018a; Riedel et al., 2013; Ryder et al., 2015; Tham et al., 2018; Thornton et al., 2010; Wagner et al., 2013; Wang, Z. et al., 2017; Wang, X. et al., 2017). In addition, McDuffie et al. (2018a) recently found that the median WINTER ClNO2 production yield was over-predicted by at least 74% by the Bertram and Thornton (2009) parameterization. Since there are no field studies that support this parameterization as written in R3, the authors should adjust this reaction accordingly and discuss its uncertainties.

References

Bertram, T. H., & Thornton, J. A. (2009). Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride. Atmospheric Chemistry and Physics, 9(21), 8351-8363. https://doi.org/10.5194/acp-9-8351-2009

Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., et al. (2009). Direct observations of N2O5 reactivity on ambient aerosol particles. Geophysical Research Letters, 36(19), L19803 https://doi.org/10.1029/2009GL040248

Edwards, P. M., Young, C. J., Aikin, K., deGouw, J., Dubé, W. P., Geiger, F., et al. (2013). Ozone photochemistry in an oil and natural gas extraction region during winter: simulations of a snow-free season in the Uintah Basin, Utah. Atmospheric Chemistry and Physics, 13(17), 8955-8971. https://doi.org/10.5194/acp-13-8955-2013

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., et al. (2016). Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States. Journal of Geophysical Research: Atmospheres, 121(17), 10,355-10,376. https://doi.org/10.1002/2016JD025311

Jaeglé, L., Shah, V., Thornton, J. A., Lopez-Hilfiker, F. D., Lee, B. H., McDuffie, E. E., et al. (2018). Nitrogen Oxides Emissions, Chemistry, Deposition, and Export Over the Northeast United States During the WINTER Aircraft Campaign. Journal of Geophysical Research: Atmospheres, 0(0). https://doi.org/10.1029/2018JD029133

Jeong, D., Seco, R., Gu, D., Lee, Y., Nault, B. A., Knote, C. J., et al. (2018). Integration of Airborne and Ground Observations of Nitryl Chloride in the Seoul Metropolitan Area and the Implications on Regional Oxidation Capacity During KORUS-AQ 2016. Atmos. Chem. Phys. Discuss., 2018, 1-25. https://doi.org/10.5194/acp-2018-1216

Kim, M. J., Farmer, D. K., & Bertram, T. H. (2014). A controlling role for the air−sea interface in the chemical processing of reactive nitrogen in the coastal marine boundary layer. Proceedings of the National Academy of Sciences of the United States of America, 111(11), 3943-3948. https://doi.org/10.1073/pnas.1318694111

Lee, B. H., Lopez-Hilfiker, F. D., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., McDuffie, E. E., et al. (2018). Airborne observations of reactive inorganic chlorine and bromine species in the exhaust of coal-fired power plants. Journal of Geophysical Research: Atmospheres, 123. https://doi.org/10.1029/2018JD029284

Liu, X., Qu, H., Huey, L. G., Wang, Y., Sjostedt, S., Zeng, L., et al. (2017). High levels of daytime molecular chlorine and nitryl chloride at a rural site on the North China Plain. Environmental Science & Technology, 51(17), 9588-9595. https://doi.org/10.1021/acs.est.7b03039

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez Hilfiker, F., Lee, B. H., Jaeglé, L., et al. (2018a). ClNO2 yields from aircraft measurements during the 2015 WINTER campaign and critical evaluation of the current parameterization. Journal of Geophysical Research: Atmospheres, 0(0). https://doi.org/10.1029/2018JD029358

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., et al. (2018b). Heterogeneous N2O5 uptake duirng winter: Aircraft measurements during the 2015 WINTER campaign and critical evaluation of current parameterizations. Journal of Geophysical Research: Atmospheres, 123(8), 4345-4372. https://doi.org/10.1002/2018JD028336

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., et al. (2008). High levels of nitryl chloride in the polluted subtropical marine boundary layer. Nature Geoscience, 1(5), 324-328. https://doi.org/10.1038/ngeo177

Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., et al. (2016). Estimating N2O5 uptake coefficients using ambient measurements of NO3, N2O5, ClNO2 and particle-phase nitrate. Atmospheric Chemistry and Physics, 16(20), 13231-13249. https://doi.org/10.5194/acp-16-13231-2016

Reyes-Villegas, E., Priestley, M., Ting, Y. C., Haslett, S., Bannan, T., Le Breton, M., et al. (2018). Simultaneous aerosol mass spectrometry and chemical ionisation mass spectrometry measurements during a biomass burning event in the UK: insights into nitrate chemistry. Atmospheric Chemistry and Physics, 18(6), 4093-4111. https://doi.org/10.5194/acp-18-4093-2018

Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., et al. (2013). Chlorine activation within urban or power plant plumes: Vertically resolved ClNO2 and Cl2 measurements from a tall tower in a polluted continental setting. Journal of Geophysical Research: Atmospheres, 118(15), 8702-8715. https://doi.org/10.1002/jgrd.50637

Roberts, J. M., Osthoff, H. D., Brown, S. S., & Ravishankara, A. R. (2008). N2O5 oxidizes chloride to Cl2 in acidic atmospheric aerosol. Science, 321(5892), 1059. https://doi.org/10.1126/science.1158777

Ryder, O. S., Campbell, N. R., Shaloski, M., Al-Mashat, H., Nathanson, G. M., & Bertram, T. H. (2015). Role of organics in regulating ClNO2 production at the air–sea interface. The Journal of Physical Chemistry A, 119(31), 8519-8526. https://doi.org/10.1021/jp5129673

Shah, V., Jaeglé, L., Thornton, J. A., Lopez-Hilfiker, F. D., Lee, B. H., Schroder, J. C., et al. (2018). Chemical feedbacks weaken the wintertime response of particulate sulfate and nitrate to emissions reductions over the eastern United States. Proceedings of the National Academy of Sciences. https://doi.org/10.1073/pnas.1803295115

Tham, Y. J., Yan, C., Xue, L., Zha, Q., Wang, X., & Wang, T. (2014). Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry. Chinese Science Bulletin, 59(4), 356-359. https://doi.org/10.1007/s11434-013-0063-y

Tham, Y. J., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., et al. (2018). Heterogeneous

N2O5 uptake coefficient and production yield of ClNO2 in polluted northern China: Roles of aerosol water content and chemical composition. Atmospheric Chemistry and Physics Discussions, 2018, 1-27. https://doi.org/10.5194/acp-2018-313

Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., et al. (2010). A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. Nature, 464(7286), 271-4. https://doi.org/10.1038/nature08905

Wagner, N. L., Riedel, T. P., Young, C. J., Bahreini, R., Brock, C. A., Dubé, W. P., et al. (2013). N2O5 uptake coefficients and nocturnal NO2 removal rates determined from ambient wintertime measurements. Journal of Geophysical Research: Atmospheres, 118(16), 9331-9350. https://doi.org/10.1002/jgrd.50653

Wang, H., Lu, K., Guo, S., Wu, Z., Shang, D., Tan, Z., et al. (2018). Efficient N2O5 Uptake and NO3 Oxidation in the Outflow of Urban Beijing. Atmospheric Chemistry and Physics Discussions, 2018, 1-27. https://doi.org/10.5194/acp-2018-88

Wang, T., Tham, Y. J., Xue, L., Li, Q., Zha, Q., Wang, Z., et al. (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), 2476-2489. https://doi.org/10.1002/2015JD024556

Wang, X., Wang, T., Yan, C., Tham, Y. J., Xue, L., Xu, Z., & Zha, Q. (2014). Large daytime signals of N2O5 and NO3 inferred at 62 amu in a TD-CIMS: chemical interference or a real atmospheric phenomenon? Atmospheric Measurement Techniques, 7(1), 1. https://doi.org/10.5194/amt-7-1-2014

Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., et al. (2017). Observations of N2O5 and ClNO2 at a polluted urban surface site in North China: High N2O5 uptake coefficients and low ClNO2 product yields. Atmospheric Environment, 156, 125-134. https://doi.org/10.1016/j.atmosenv.2017.02.035

Wang, Z., Wang, W., Tham, Y. J., Li, Q., Wang, H., Wen, L., et al. (2017). Fast heterogeneous N2O5 uptake and ClNO2 production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain. Atmospheric Chemistry and Physics, 17(20), 12361-12378. https://doi.org/10.5194/acp-17-12361-2017

Wild, R. J., Edwards, P. M., Bates, T. S., Cohen, R. C., de Gouw, J. A., Dubé, W. P., et al. (2016). Reactive nitrogen partitioning and its relationship to winter ozone events in Utah. Atmospheric Chemistry and Physics, 16(2), 573-583. https://doi.org/10.5194/acp-16-573-2016

Yun, H., Wang, T., Wang, W., Tham, Y. J., Li, Q., Wang, Z., & Poon, S. C. N. (2018). Nighttime NOx loss and ClNO2 formation in the residual layer of a polluted region: Insights from field measurements and an iterative box model. Science of The Total Environment, 622-623, 727-734. https://doi.org/https://doi.org/10.1016/j.scitotenv.2017.11.352

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