Supplement Material for 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

Daun Jeong[1], Roger Seco[1], Dasa Gu[1], Youngro Lee[2], Benjamin A. Nault[3,4], Christoph J. Knote[5], Tom Mcgee[6], John T. Sullivan[6], Jose L. Jimenez[3,4], Pedro Campuzano-Jost[3,4], Donald R. Blake[1], Dianne Sanchez[1], Alex B. Guenther[1], David Tanner[2], L. Gregory Huey[2], Russell Long[7], Bruce E. Anderson[8], Samuel R. Hall[9], Kirk Ullmann[9], Hye-jung Shin[10], Scott C. Herndon[11], YoungJae Lee[10], Danbi Kim[10], Joonyoung Ahn[10], and Saewung Kim[1]

[1]Department of Earth System Science, University of California, Irvine, Irvine, CA, USA
[2]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA
[3]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[4]Department of Chemistry, University of Colorado, Boulder, CO, USA
[5]Meteorologisches Institut, Ludwig-Maximilians-Universität München, München, Germany
[6]Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA
[7]Office of Research and Development, U.S. EPA, Research Triangle Park, NC, USA
[8]NASA Langley Research Center, Hampton, VA, USA
[9]National Center for Atmospheric Research, Boulder, CO, USA
[10]National Institute of Environmental Research, Incheon, South Korea
[11]Aerodyne Research Inc., Billerica, MA, United States

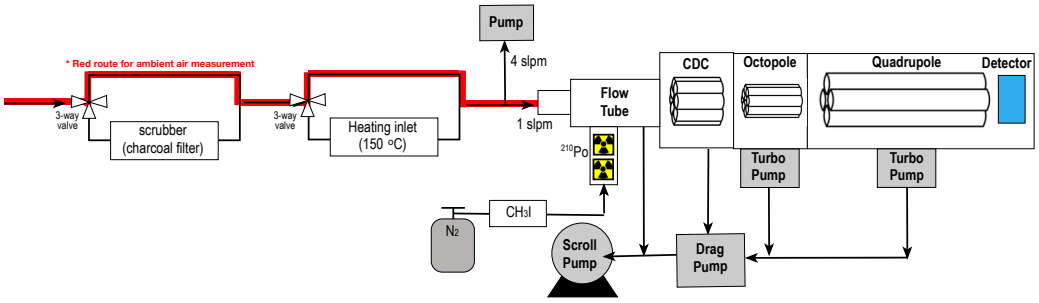

Figure S1. Configuration of the CIMS inlet during the KORUS-AQ 2016.

Description of the Extended Aerosol Inorganics Model

To calculate aerosol liquid water mass concentration and the acidity (pH) of the aerosol, the Extended Aerosol Inorganic Model (E-AIM) was used (Clegg et al., 1998; Friese and Ebel, 2010). Prior studies have shown that either E-AIM and the ISORROPIA-II model can be used to calculate aerosol liquid water concentration and pH, as both thermodynamic models predict similar values (Hennigan et al., 2015; Song et al., 2018). The E-AIM model was ran in the reverse mode. This has been found to be the optimal mode (Hennigan et al., 2015; Song et al., 2018), as it minimizes the errors in the measurements, leading more stable results that better represents the observations. Reverse mode means that total nitrate (aerosol plus gas-phase), sulfate, ammonium, relative humidity, and temperature were the inputs of the model. Gas-phase HNO_3 was measured by California Institute 378 of Technology chemical ionization mass spectrometer (CIT-CIMS) (Crounse et al., 2006), and the aerosol-phase nitrate, sulfate, and ammonium were measured by the University of Colorado AMS (Nault et al., 2018). Total NH_x was not an input, as there was not a gas-phase measurement of NH_3. Guo et al. (2016) showed that ISORROPIA was still able to properly partition total nitrate between the gas- and particle-phase without NH_3 as an input when the model was ran iteratively to estimate NH_3. The E-AIM model was ran similarly, here, and it took approximately 20 iterative runs for convergence on the NH_3 concentration that explained the observed partitioning of nitrate between gas- and particle-phase. To validate E-AIM modeled predictions, the modeled predicted vs observed partitioning of nitrate between gas- and particle-phase were compared (Figure S2). Since the partitioning of nitrate between gas- and particle-phase is a function of the amount of water, temperature, and pH of the aerosol (Guo et al., 2016, 2017), a high correlation and a slope near unity indicates that E-AIM is closely representing the pH and aerosol liquid water. The slopes for HNO_3 and NO_3^- are 1.07 and 0.89, respectively, and the R^2 for HNO_3 and NO_3^- are 0.96 and 0.99, respectively; therefore, E-AIM predicted the observed nitrate partitioning between gas- and particle-phase, providing confidence in the pH and aerosol liquid water concentration.

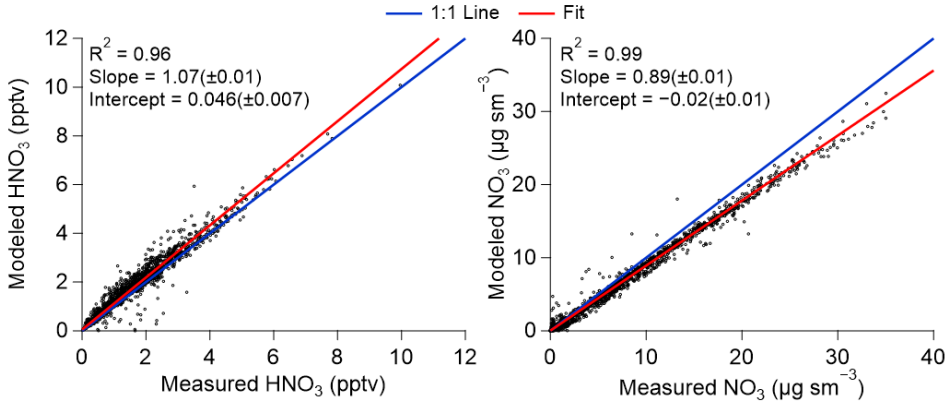

Figure S2. (Left) Comparison of E-AIM modeled and measured (CIT-CIMS) gas-phase HNO_3. (Right) Comparison of E-AIM modeled and measured (CU AMS) particle-phase NO_3^-

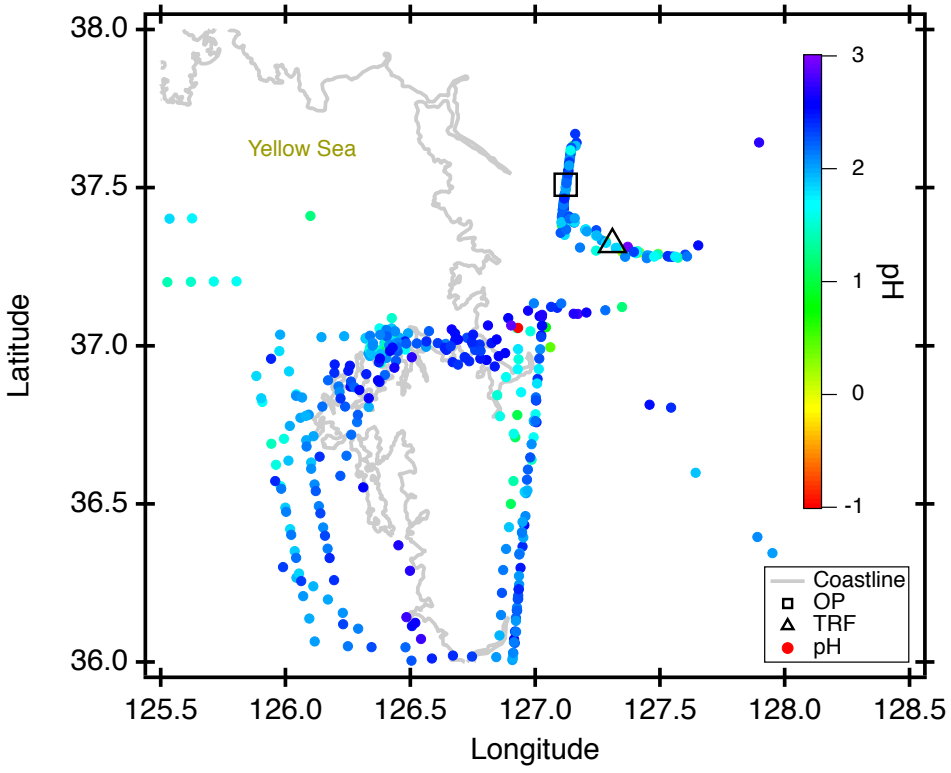

Figure S3. Aerosol pH calculated with E-AIM constrained with airborne measurements.

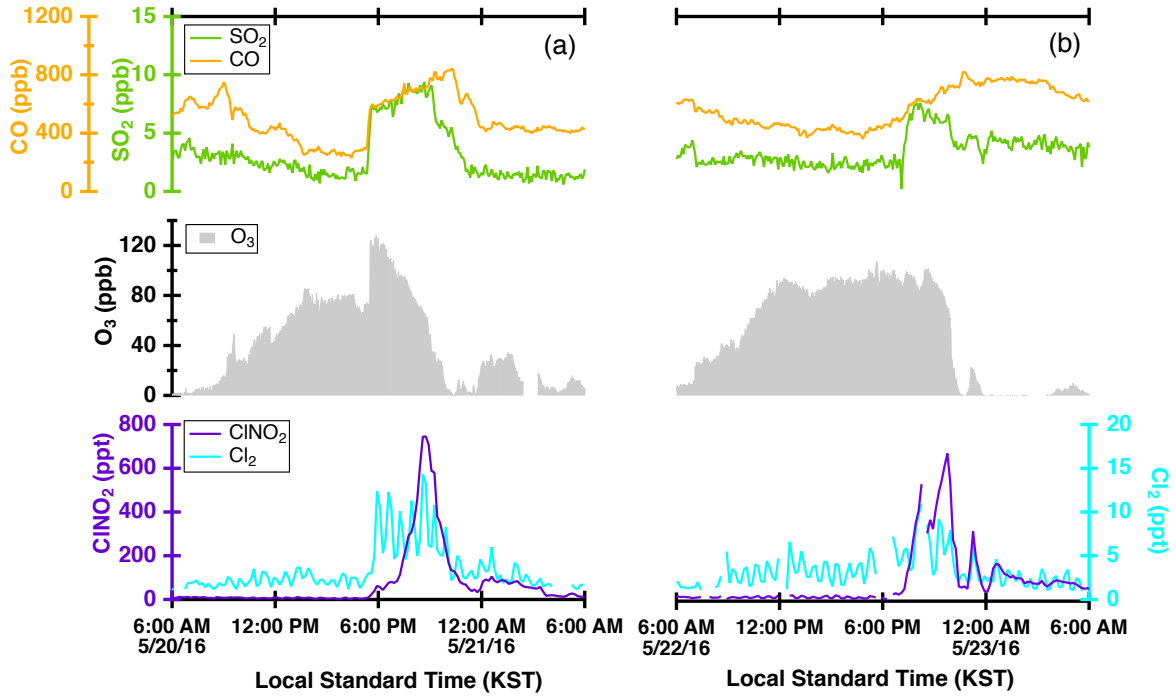

Figure S4. Trace gas measurements at the OP site on May 20th and 22nd.

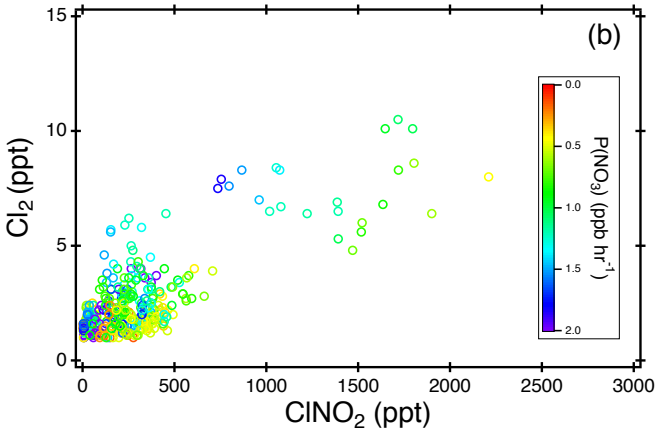

Figure S5. Correlation between Cl_2 and $ClNO_2$ measured at 7:00 - 9:00 am local time. Each data point is a 5 min averaged value and is color coded with the calculated production rate of nitrate.

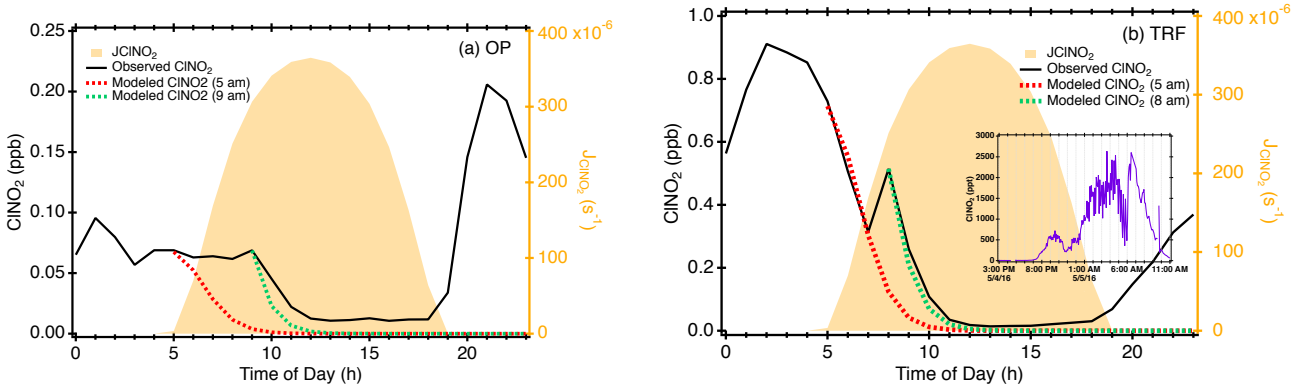

Figure S6. Diurnal variation of measured $ClNO_2$ (black line) and simulated $ClNO_2$ from photolytic loss (dashed line). For the red and green dashed lines, the model was constrained with measured $ClNO_2$ at sunrise and at the time when $ClNO_2$ started decreasing, respectively. J_{ClNO2} used for the photolysis was scaled with airborne measurements. The insert in (b) in the $ClNO_2$ measured on May 5th.

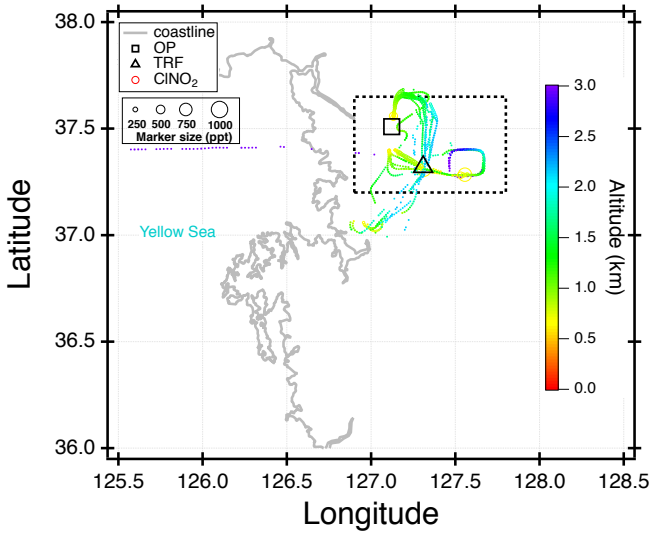

Figure S7. Airborne $ClNO_2$ data collected at 8:00 - 8:30 am local time during the whole campaign above 600 m. The black dashed box is the grid used for plotting vertical distribution of $ClNO_2$ in Figure 5. Markers size is proportional to the concentration of $ClNO_2$ and color coded with altitude.

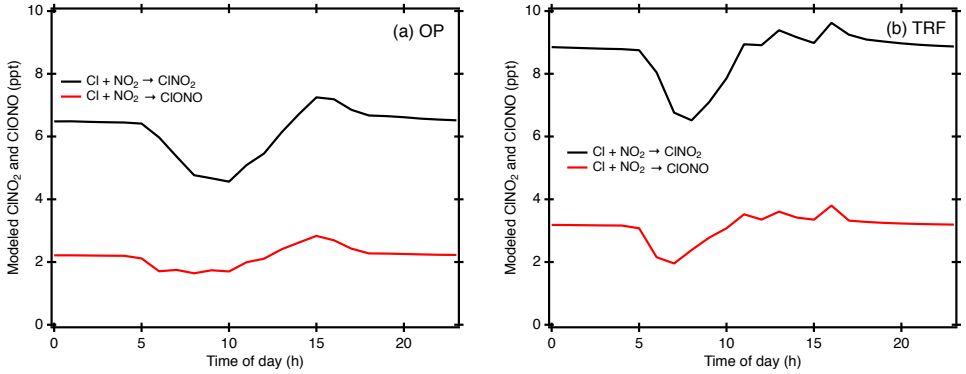

Figure S8. Simulated $ClNO_2$ and ClONO produced from gas phase reaction of Cl· + NO_2 (i.e., $Cl\cdot_{(g)}$ + $NO_{2(g)}$ + M $\rightarrow$ $ClNO_{2(g)}$ + M, k = 3.6×10^{-12}; $Cl\cdot_{(g)}$ + $NO_{2(g)}$ + M $\rightarrow$ $ClONO_{(g)}$ + M, k= 1.63×10^{-12}, (Burkholder et al., 2015)) The model was constrained with Cl_2 and NO_2 observations with J values from the aircraft.

References

Burkholder, J. B., Sander, S. P., Abbatt, J. P. D., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18., Tech. rep., Jet Propulsion Laboratory, Pasadena, CA, 2015.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System $H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O$ at Tropospheric Temperatures, J. Phys. Chem. A, 102, 2137–2154, https://doi.org/10.1021/jp973042r, http://pubs.acs.org/doi/abs/10.1021/jp973042r, 1998.

Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of gas-phase hydroperoxides by chemical ionization mass spectrometry, Anal. Chem., 78, 6726–6732, https://doi.org/10.1021/ac0604235, 2006.

Friese, E. and Ebel, A.: Temperature Dependent Thermodynamic Model of the System $H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O$, J. Phys. Chem. A, 114, 11 595–11 631, https://doi.org/10.1021/jp101041j, 2010.

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, J. Geophys. Res., 121, 10 355–10 376, https://doi.org/10.1002/2016JD025311, 2016.

Guo, H., Liu, J., Froyd, K. D., Roberts, J. M., Veres, P. R., Hayes, P. L., Jimenez, J. L., Nenes, A., and Weber, R. J.: Fine particle pH and gas-particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign, Atmos. Chem. Phy., 17, 5703–5719, https://doi.org/10.5194/acp-17-5703-2017, 2017.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phy., 15, 2775–2790, https://doi.org/10.5194/acp-15-2775-2015, 2015.

Nault, B. A., Campuzano-Jost, P., Day, D. A., Schroder, J. C., Anderson, B., Beyersdorf, A. J., Blake, D. R., Brune, W. H., Choi, Y., Corr, C. A., de Gouw, J. A., Dibb, J., DiGangi, J. P., Diskin, G. S., Fried, A., Huey, L. G., Kim, M. J., Knote, C. J., Lamb, K. D., Lee, T., Park, T., Pusede, S. E., Scheuer, E., Thornhill, K. L., Woo, J.-H., and Jimenez, J. L.: Secondary Organic Aerosol Production from Local Emissions Dominates the Organic Aerosol Budget over Seoul, South Korea, during KORUS-AQ, Atmos. Chem. Phy. Discuss., https://doi.org/10.5194/acp-2018-838, https://www.atmos-chem-phys-discuss.net/acp-2018-838/, 2018.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phy., 18, 7423–7438, https://doi.org/10.5194/acp-18-7423-2018, 2018.