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Model Evaluations of Heterogeneous Nitryl Chloride Production

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Nitryl chloride ($ClNO_2$) is an important nighttime precursor to reactive chlorine radicals in the troposphere. Recent ambient observations showed high correlations of $ClNO_2$ and N_2O_5mixing ratios, suggesting that the main production pathway of $ClNO_2$ in the polluted atmosphere is through N_2O_5 heterogeneous hydrolysis on chloride-containing aerosols. Thus in the presence of particulate chloride, N_2O_5 heterogeneous hydrolysis can no longer be considered a removal pathway for NO_x, as $ClNO_2$ is a reservoir species that can release NO_2 during the daytime through photolysis. Consequently, $ClNO_2$ has high potentials for altering the oxidative capacity of the atmosphere. There are many challenges with quantifying the impact of $ClNO_2$ through models, including the parameterization of the N_2O_5 heterogeneous reaction process, which is dependent on meteorological conditions and aerosol compositions, the $ClNO_2$ production yields, and uncertainties with sources of particulate chloride. Using the WRF/Chem model as the host model, we tested several state-of-the-art N_2O_5 heterogeneous hydrolysis parameterizations, taking into account the uptake enhancement by the presence of particulate chloride, and the uptake suppression by nitrate and organic coatings. The model results are evaluated against observations made during the CalNex 2010 measurement campaign. We will present the model performance in simulating $ClNO_2$ by the various parameterization methods, and show the sensitivity of $ClNO_2$ production to spatial and temporal variations in anthropogenic chlorine emission sources, as well as the resulting impact on criteria pollutants in the South Coast Air Basin of California.