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

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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 HNO$_3$ and from different heterogeneous pathways. The results show that these heterogeneous reactions increase the atmospheric Cl$_2$ and ClNO$_2$ level, leading to an increase of the nitrate concentration by $\sim$10% in the daytime. However, these reactions also lead to a decrease the nocturnal nitrate by $\sim$20%. Sensitivity analyses of uptake coefficients show that the empirical uptake coefficient for the O$_3$ heterogeneous reaction with chlorinated particles may lead to the large uncertainties in the predicted Cl$_2$ and nitrate concentrations. The N$_2$O$_5$ uptake coefficient with particulate Cl$^-$ concentration dependence performs better to capture the concentration of ClNO$_2$ and nocturnal nitrate concentration. The reaction rate of OH and NO$_2$ in daytime increases by $\sim$15% when the heterogeneous chlorine chemistry is incorporated, resulting more nitrate formation from HNO$_3$ gas-to-particle partitioning. By contrast, the contribution of the heterogeneous reaction of N$_2$O$_5$ to nitrate concentrations decreases by about 27% in the nighttime when its reactions with chlorinated particles are considered. However, the generated gas-phase ClNO$_2$ from the heterogeneous reaction of N$_2$O$_5$ and chlorine-containing particles further decompose to increase the nitrate by 6%. In general, this study highlights the potential of significant underestimation of daytime and overestimation of nighttime nitrate concentrations for chemical transport models without proper chlorine chemistry in the gas and particle phases.