Missing Nitryl Chloride Chemistry Pathway in CAMx

Halogens play an important role in PM2.5 formation during wintertime inversion episodes. They act as radical sources important for the photochemical production of PM2.5. Nitryl chloride (ClNO2), in particular, is an important source of radicals for daytime photochemical production of ozone and nitrate, as shown by recent aircraft measurements conducted in the Salt Lake Valley (2017 Utah Winter Fine Particulate Study[1]). These measurements showed that ClNO2 is typically elevated over the Salt Lake City and Provo urban regions, reaching mixing ratios greater than 0.8 ppb at night. Similar levels of ClNO2 were also detected in the plume of U.S. Magnesium plant. These measurements also suggested that the chemical pathway where ClNO2 is formed through the heterogeneous uptake of N2O5 on chloride-containing particles is particularly active in the Salt Lake Valley, where ammonium chloride aerosol accounts for 10-15% of PM2.5 mass during high-PM2.5 episodes[2]. This formation of ClNO2 occurs mainly at night since the formation of N2O5, which is produced by a chemical reaction involving NO2 and NO3, is suppressed during the day (R1-R3).

$O_3 + NO_2 \rightarrow NO_3$ (R1)

$NO_2 + NO_3 \rightarrow N_2O_5$ (R2)

$N_2O_5 + Cl^- (het) \rightarrow NO_3^- + ClNO_2$ (R3)

Produced ClNO2 will then photolyze into chlorine radicals and NOx, thereby contributing to the oxidant budget and NOx recycling.

However, while this heterologous pathway for N2O5 uptake on Cl-containing particles is potentially important for PM2.5 formation in the Salt Lake Valley, the carbon bond chemistry mechanisms in CAMx, including cb6r2h that was used in UDAQ's simulations, do not include this pathway. Given ClNO2's role in contributing to the oxidants budget, an exclusion of this pathway in CAMx may increase the model's sensitivity to oxidants and may limit its sensitivity to NOx emissions. Without this pathway, the model may be less responsive to proposed NOx controls.

[1] https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfps/finalreport.pdf.

[2] Kelly, K.E., R. Kotchenruther, R. Kuprov, and G.D. Silcox, Receptor model source attributions for Utah's Salt Lake City airshed and the impacts of wintertime secondary ammonium nitrate and ammonium chloride aerosol. Journal of the Air & Waste Management Association, 2013. 63(5): p. 575-590.