Missing HCl and Cl sources from UDAQ's emissions inventory

HCl and aerosol chloride play an important role in PM2.5 formation. In the presence of excess ammonia, HCl will partition to aerosol particles forming ammonium chloride, with ammonium chloride accounting for 10-15% of PM2.5 mass during high wintertime PM2.5 pollution episodes[1]. Aerosol chloride can also contribute to the formation of ClNO2, which is a source of radicals for daytime photochemical production of ozone and nitrate, both of which are important contributors to PM2.5 formation. This formation of ClNO2 occurs through the heterogeneous uptake of N2O5 on chloride-containing particles, which is particularly active in the Salt Lake Valley, as shown by recent aircraft measurements (2017 Utah Winter Fine Particulate Study (UWFPS)[2]). However, while chloride is an important contributor to wintertime PM2.5 formation, the sources of HCl and the aerosol chloride are unclear. Measured chloride is significantly underestimated in the model (by about 5 times on peak PM2.5 exceedance day at Hawthorne controlling monitor in Salt Lake Valley, as shown in the model performance evaluation section), suggesting that major sources of chloride and HCl are not included or underestimated in UDAQ's emissions inventory. Potential sources include the Great Salt Lake, road salt, playa dusts from dry salt beds and US Magnesium plant. Aircraft measurements from the 2017 UWFPS showed that chloride mass fraction in PM2.5 is higher in the Great Salt Lake and Salt Lake region compared to other areas in the Salt Lake Valley. Moreover, an analysis of chemical speciation data collected at Hawthorne site over previous years showed that the monthly average sodium ion and chloride concentrations overall increase with snowfall, suggesting that road salt may be a contributor to particulate chloride in winter (Figures 1a-c). The application of salt to roadways for deicing is a common practice in the Salt Lake Valley in winter. These emissions from road salt and the Great Salt Lake are not accounted for in UDAQ's emissions inventory.
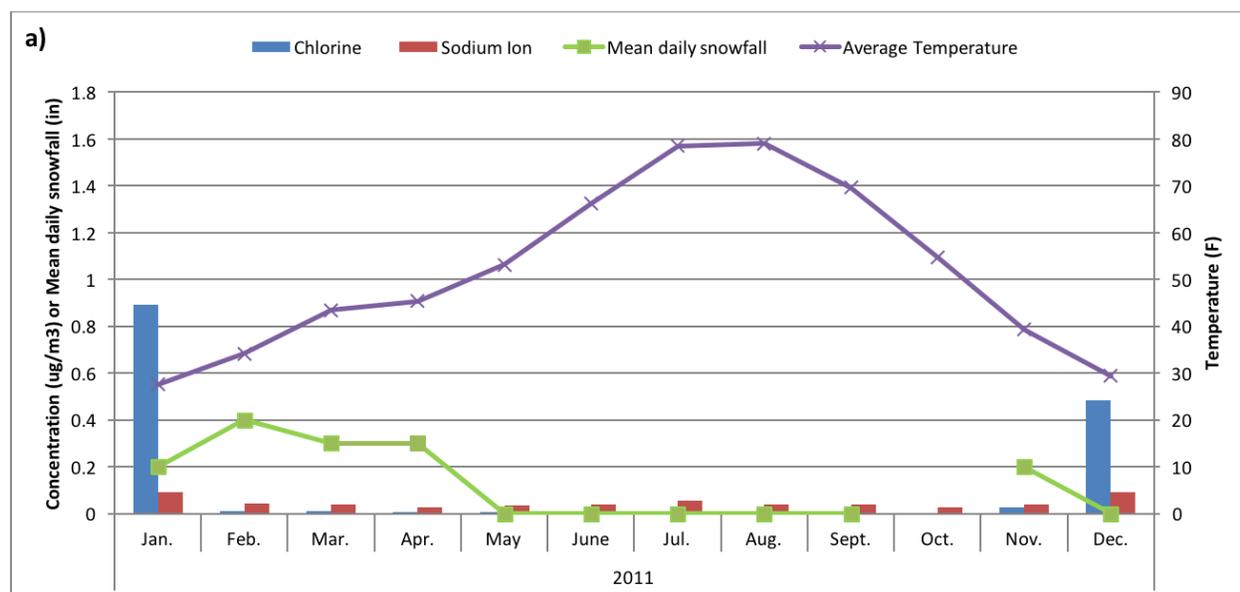
[1] Kelly, K.E., R. Kotchenruther, R. Kuprov, and G.D. Silcox, Receptor model source attributions for Utah's Salt Lake City airshed and the impacts of wintertime secondary ammonium nitrate and ammonium chloride aerosol. Journal of the Air & Waste Management Association, 2013. 63(5): p. 575-590.
[2] https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfps/finalreport.pdf
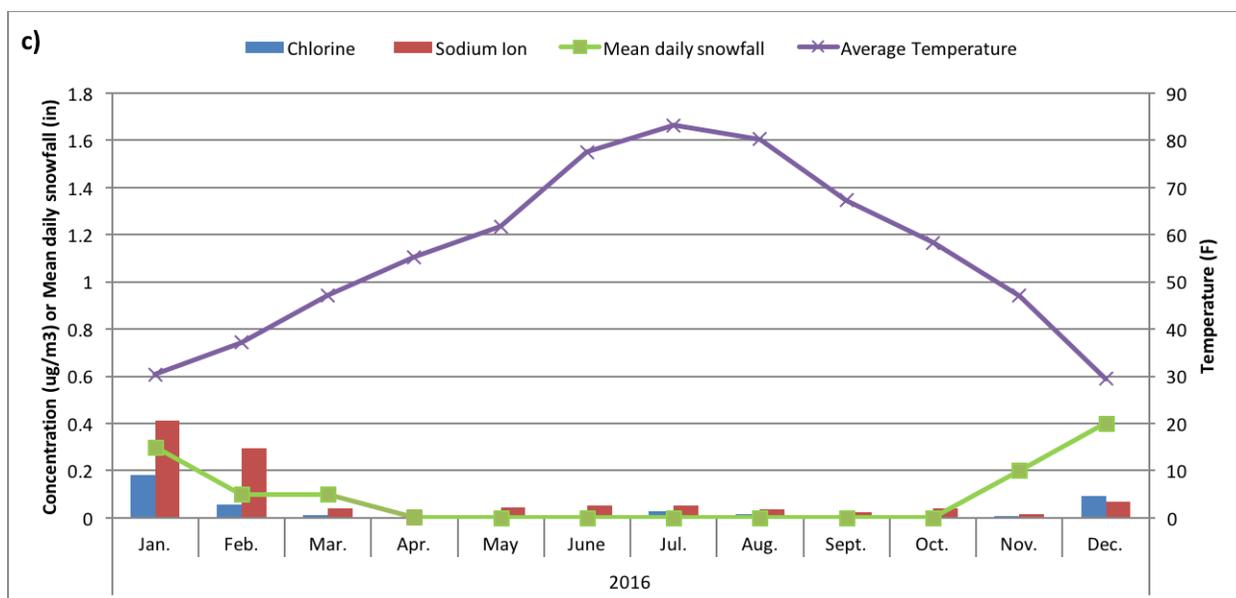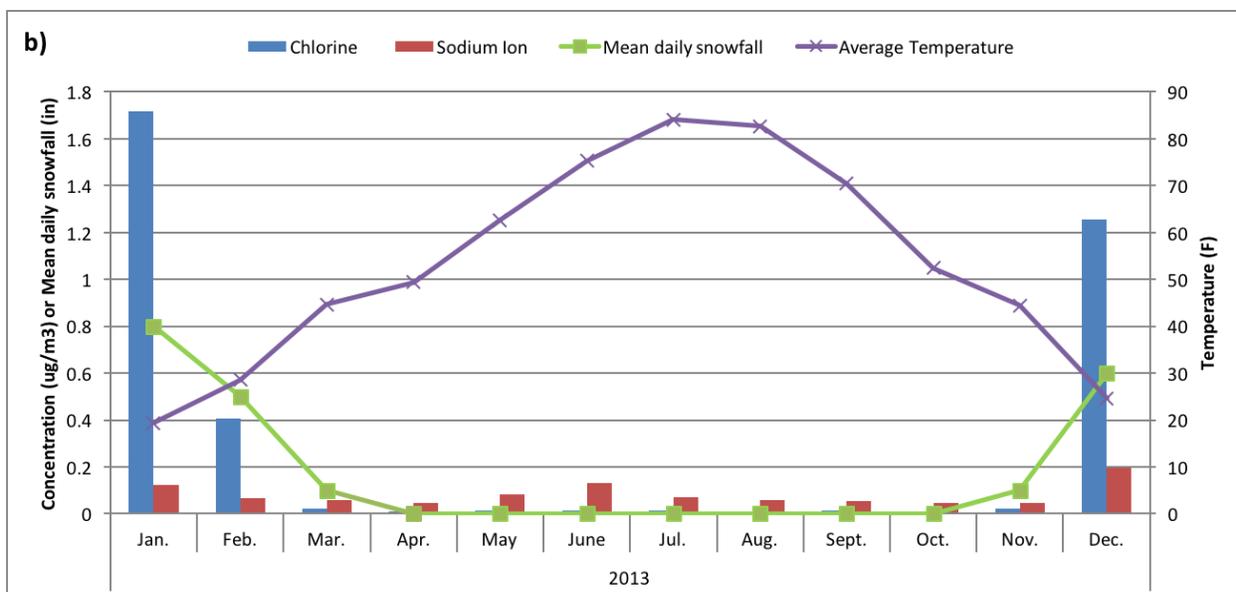
Figures 1a-c. Monthly variation in average chloride and sodium concentration as a function of mean daily snowfall and average temperature at Hawthorne chemical speciation site in the Salt Lake Valley during a) 2011, b) 2013 and c) 2016. Ionic data was retrieved from EPA AQS database. Snowfall data was retrieved from the National Weather Service National Oceanic and Atmospheric Administration (NOAA) Online Weather Data (NOWData, http://w2.weather.gov/climate).

Modeled HCl is also underestimated in the model in the Salt Lake Valley, with maximum hourly modeled values of about 12 and 35 ppb occurring near US Magnesium (Figures 2a-b) on typical exceedance and non-exceedance days, respectively. On the other hand, values as high as 100 ppb were observed in the afternoon in the vicinity of US Magnesium during the 2017 UWFPS campaign (Figure 3), suggesting that HCl emissions from US Magnesium may be underestimated in the model.
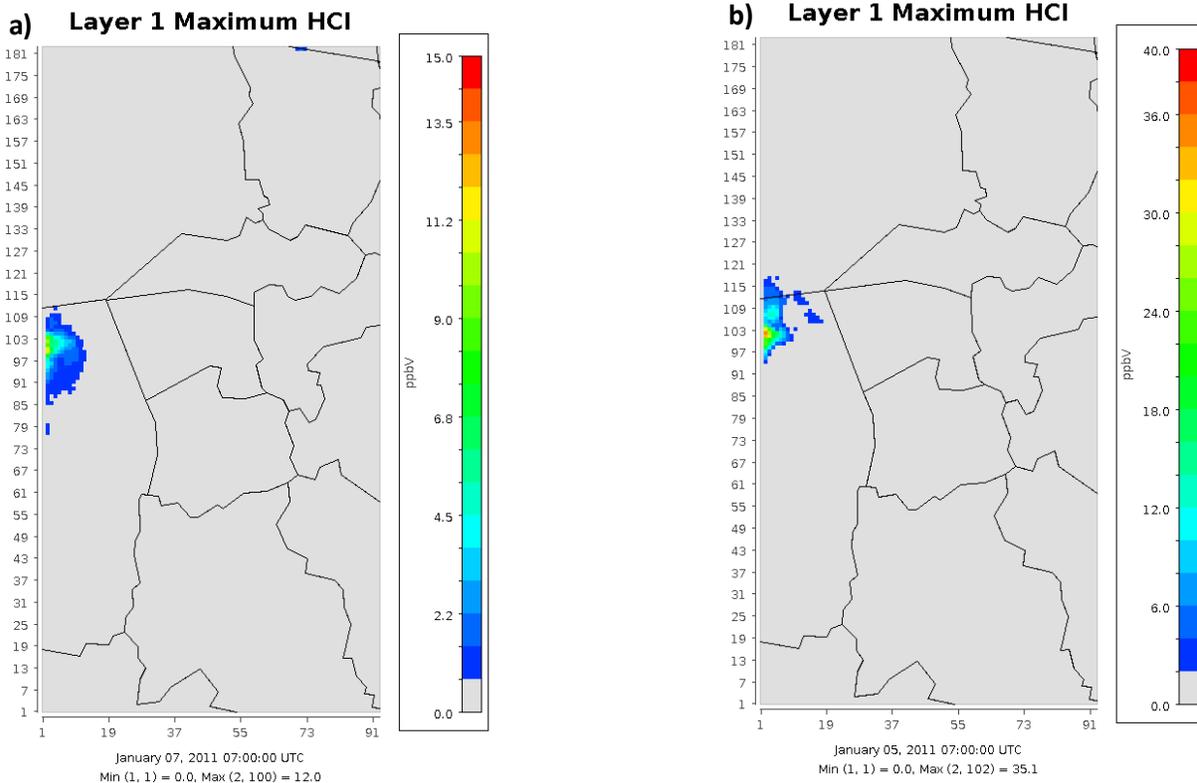
Figures 2a-b. Spatial distribution of maximum hourly HCl concentrations (in ppb) during a typical 24-hr PM2.5 a) exceedance day and b) non-exceedance day.
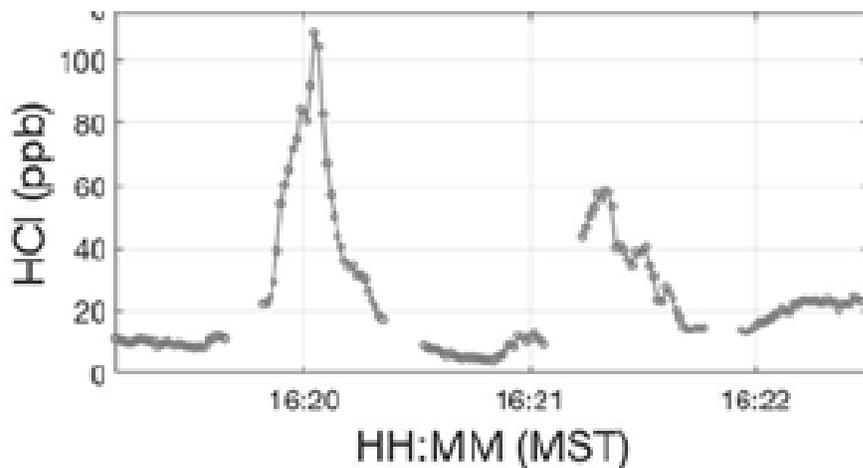

Figure 3. Time series of HCl during an afternoon intercept of the plume from US Magnesium during the 2017 Utah Winter Fine Particulate Study. Figure retrieved from the 2017 Utah Winter Fine Particulate Study, final report, Figure 3.43 (https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2017uwfps/finalreport.pdf).

This underestimation in chloride and HCl emissions adds uncertainty to the modeling results. Furthermore, by not accounting for these emissions and their impact on PM2.5 formation and

the oxidants budget, in particular, the model's sensitivity to NOx controls may be limited. The model may be more sensitive to oxidants and therefore less responsive to proposed NOx controls. Lastly, it is noteworthy that UDAQ is planning a field sampling campaign during winter 2018-2019 and summer 2019 with purpose to improve the emissions inventory for chloride and HCl. During this study, measurements for HCl and particulate chloride will be respectively collected using passive samplers and time-integrated PM2.5 filters at multiple locations across the Wasatch Front and around the Great Salt Lake. Parallel ammonia measurements will also be collected.