Uncertainties in Ammonia Emissions

Utah Division of Air Quality

Introduction

Ammonia is a key precursor to ammonium nitrate, the predominant PM2.5 component during persistent wintertime inversion periods in northern Utah. During persistent cold air pool periods, ammonium nitrate can consist of over 60% of the PM2.5 filter mass. While NOx emission sources are generally well understood, there are large question marks when it comes to Utah ammonia emission sources. This section will walk through recent studies, current modeling progress, and explore why ammonia remains a large subject of uncertainty in Salt Lake Valley modeling.

2017 Utah Winter Fine Particulate Study Results

Recent 2017 Utah Winter Fine Particulate Study (UWFPS) Twin Otter measurements in the three major air basins (Cache, Utah and eastern Salt Lake Valleys) indicate that across northern Utah the system is most commonly nitrate limited (2017 UWFPS Final Report[1]). Recent analyses of ground based measurements in northern Utah also generally conclude that the system is nitrate limited.

However, the Salt Lake Valley was the least nitrate limited during pollution episodes, with the generally largest ratio of total nitrate to reduced nitrogen. Compared with the Cache and Utah valleys, more ambient NOx (and less ammonia) was observed in the Salt Lake Valley. Whether or not NOx or ammonia is the key factor in controlling ammonium nitrate formation, this could differ regionally within northern Utah.

During the 2017 UWFPS campaign, temporally-integrated ambient ammonia concentrations were obtained for both the Cache Valley and Wasatch Front airshed for three separate, 7-day sampling periods. The sampling network consisted of 36 passive ammonia samplers (25 in Cache Valley, 11 in Wasatch Front). Results are shown below in Figure 1:

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[1] https://documents.deq.utah.gov/air-quality/planning/technical-analysis/research/northern-utah-airpollution/utah-winter-fine-particulate-study/DAQ-2018-004037.pdf
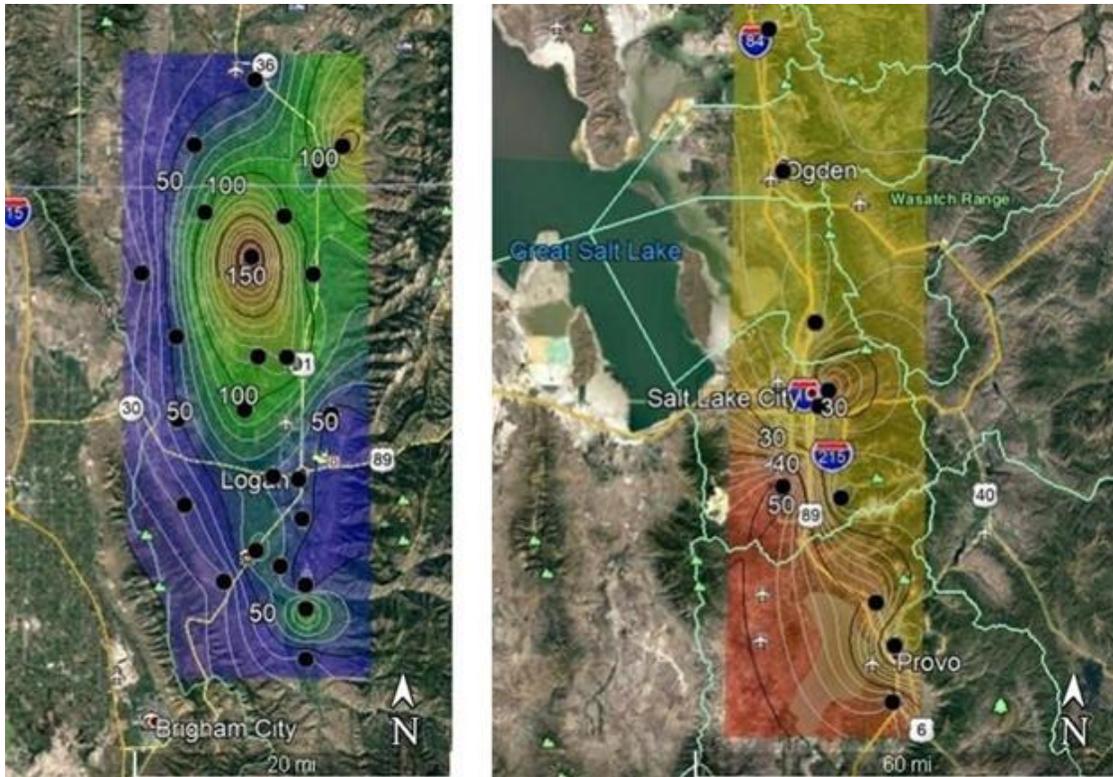
Figure 1: Contour plots of average ambient NH3 concentrations [ppb] for Cache Valley and the Wasatch Front during the 2017 UWFPS. Panel comparison shows concentrations were much higher in the Salt Lake Valley (right) than Cache Valley (left). Sampler locations are depicted by black dots.

In contrast, the Utah emission inventory (without ammonia injection) as spatially allocated is shown below:
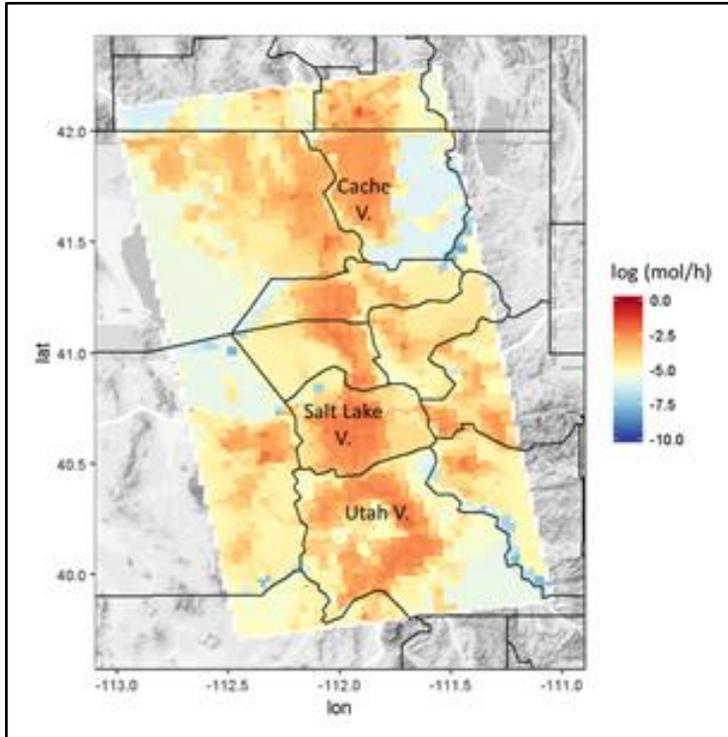
Figure 2: 24-hour average of 2014 NEI NH3 emission rates (moles/hr) allocated across a 1.33 km Northern Utah modeling domain. Emission rates reflect a typical winter weekday in February. Ammonia injection is not included as to highlight the current state of the Utah ammonia emissions inventory.

The comparison between the Figure 1 and Figure 2 makes it quite clear there is a large spatial discrepancy between Utah's ammonia inventory and ambient measurements. The parity in ammonia emissions inventory totals between Salt Lake and Cache County is not realistic, as measured ammonia concentrations are consistently observed to be much higher in Cache County than Salt Lake County.

Ammonia injection

To achieve better agreement between measured and modeled ammonium nitrate, UDAQ conducts ammonia injection. For the purposes of this document, ammonia injection is defined as artificially adding non-inventoried ammonia emissions to the inventoried emissions that are input into the air quality model. The goal of ammonia injection is to try and match observed ammonia with modeled ammonia at controlling nonattainment monitors. UDAQ used 2016 ammonia measurements (via personal communication with Randy Martin, Utah State University) to inform how much modeled ammonia we should achieve with CAMx.

Substantial amounts of artificial ammonia were injected into nonattainment counties for the Salt Lake SIP modeling. In an attempt to account for the spatial differences discussed in the preceding section, UDAQ varies the amount of injected ammonia from county to county. Ammonia is only injected in relatively low elevation areas (< 6,000 ft ASL) in order to better associate the missing ammonia being estimated with anthropogenic sources.

The specific reasons for possible missing ammonia sources in the Utah emissions inventory are unclear at this point. Ammonia emissions might be underestimated by the MOVES 2014a model UDAQ uses for calculating mobile emissions. It's also possible that several stationary sources of ammonia are mischaracterized or completely missing from the current Utah emissions inventory.

Ammonia deposition

Currently, there is no bidirectional flux mechanism in CAMx regarding ammonia dry deposition. The omission of such mechanism means that the amount of free ammonia available for secondary aerosol chemistry isn't correctly parameterized. It was discovered that the dry deposition rate for ammonia was initially too high, since there was zero surface resistance to ammonia via a setting in CAMx.

To address the high ammonia dry deposition rate in the air quality model, UDAQ modified CAMx to maximize surface resistance to ammonia and keep as much free ammonia available for chemistry as possible. Recent versions of CAMx released by Ramboll now maximize the surface resistance to ammonia in order to lower the ammonia dry deposition rate. However, bidirectional flux is still not emulated in the model physics at this time.

While we made adjustments to the dry deposition rate of ammonia, the CAMx model does not currently account for the re-volatilization of ammonia. Re-volatilization occurs when some forms of nitrogen (e.g., urea) changes to an ammonia gas. Ammonia is then transported from soil and emitted to the atmosphere.

Why it matters to Utah air quality modeling

Like recent UWFPS observations suggests, UDAQ PM2.5 modeling shows the highest sensitivity to ammonia is in Salt Lake Valley. We speculate this is due to the large relative abundance of NOx emissions in Salt Lake Valley compared to elsewhere in Utah (See Table 1, below). The Salt Lake Valley is more urban and features a relatively small animal agricultural sector compared to Cache Valley. The high abundance of NOx emissions suggests that ammonia potentially plays a more important role in secondary PM2.5 formation.

Nonattainment Area	NOx
Salt Lake	**119.8**
Provo	32.5
Logan	7.1

Table 1: Wintertime 2014 NOx[2] (tons/day) by Daily PM2.5 nonattainment area. The Salt Lake nonattainment area contains much more NOx than the other two regions.

However, a highly significant portion of the ammonia emissions going into CAMx air quality model are due to injection (Table 2, below). Since we don't know the sources of missing Utah ammonia emissions, we don't know of any possible projection factors for the ammonia injection emissions. Therefore, the amount of injected ammonia is kept the same in both base-year and future-year inventories. The effect of holding the amount of injected ammonia constant potentially makes the model stiff and unresponsive to modeled emission controls through the SIP modeled attainment demonstration process.

Salt Lake County	ammonia (tons/day)	Percentage of Total
ammonia injection	1.7	40%
UDAQ inventory	2.5	60%
total ammonia	4.2	100%

Table 2: Total ammonia emissions for Salt Lake County (2016 SIP base-year inventory). The amount of ammonia emissions attributed to injection in the modeling accounts for 40% of total ammonia.

Although a refinement on past methodology, the spatial allocation of injected ammonia emissions is still somewhat crude. Local impacts of ammonia are potentially ignored or washed out by coarse uniform swathes of injected ammonia.

It's also certainly possible that ammonia concentrations vary with respect to several time scales: hourly, weekly, monthly, and yearly. This is not being captured by UDAQ's ammonia injection. Ammonia emissions rates are constant; there is no discernment between weekday and weekend activity. This omission isn't an oversight, but a reflection of the lack of our current understanding in ammonia emissions.

Unfortunately, UDAQ has access to a very limited number of ammonia observations. Although the 2017 UWFPS was helpful, more observational studies are needed to further our understanding of ammonia in Salt Lake Valley. The lack of reliable measurements of ammonia impairs UDAQ's ability to properly characterize ammonia in the atmosphere and thus, provides a weak basis for making improvements in Utah's ammonia emissions inventory.

Steps forward

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[2] https://documents.deq.utah.gov/air-quality/pm25-serious-sip/DAQ-2017-015447.xlsx

An upcoming $210,000 Utah DEQ funded study is planning to take ambient measurements of gaseous ammonia and hydrochloric acid (HCl) during the winter of 2018/2019 and the summer of 2019. Passive sampling will be focused on the Wasatch Front; twenty samplers alone placed within the Salt Lake County airshed. Additional measurements of PM2.5 distribution and composition as well as mobile measurements of temporally-refined ammonia will also be conducted.