Reduced Nitrogen in the Western US in Winter

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Sensitivity of PM$_{2.5}$ to NH$_3$

For dry particles, the presence of excess NH$_3$ allows semi-volatile salts to form, e.g. NH$_4$NO$_3$

For deliquesced particles (and liquid water clouds), NH$_3$ controls the pH of PM$_{2.5}$
- partitioning of semi-volatile gases, e.g. HNO$_3$, HCl, oxalic acid
- rates of some aqueous phase reactions

NH$_3$ can also react with particle phase carbonyls to generate brown (light-absorbing) constituents
Deliquesced $\text{NH}_4\text{NO}_3$ is limited by $\text{NH}_3$ and $\text{NO}_x$.

Franchin et al., *Atmos Chem Phys*, 2018

- Aircraft AMS, CIMS and QCL data from UWFPS 2017 in Utah.
Sources of NH$_3$

Livestock

Fertilizer application

Residential wood combustion

Biomass burning

Mobile sources

Industry

Bidirectional exchange
CalNex implied livestock NH$_3$ sources were significantly underestimated.

GEOS-Chem modelling using NEI 2005

Original NH$_3$ emissions
Livestock emissions x5

Schiferl et al., *JGR*, 2014
Satellite, Aircraft and Ground-based in DISCOVER-AQ

Sun et al., JGR, 2015
Spatial distribution of NH$_3$ in UWFPS

Moravek et al., *ACPD*, 2019
Constraining the NH$_3$ inventory

**STILT footprint** x **NH$_3$ emission inventory** = **NH$_3$ contribution**

Using HRRR met fields at 3x3 km

UDAQ based on NEI 2014

Compare to measurements

Sum

NH$_3$ mixing ratio at receptor (0.87 ppbv)

Moravek et al., *ACPD*, 2019
Underestimate of NH$_3$ emissions in Utah

Wintertime emissions from animal husbandry 4x too low in 2014 UDAQ inventory

Moravek et al., ACPD, 2019
Large seasonality for livestock NH$_3$ emissions in UDAQ inventory

Seasonal cycle imposed on annual emissions
Cycle was inferred through inverse modelling in Gilliland et al., 2006

In contrast, USU inventory from Moore and Martin has equivalent emissions in July and January
CAFO survey in Colorado showed modest seasonality

**Figure 6.** Temperature dependence of the $\Delta C_{\text{NH}_3}/\Delta C_{\text{CH}_4}$ enhancement ratio in each season. The black lines represent the temperature dependence of the ammonia volatilization process and are scaled by a multiplicative factor $A_0$ for each season.
NH\textsubscript{x} deposition at Logan (NADP)

UT01 - Logan (1984-2019)
NH₃ concentration at Logan (AMoN)

UT01 - Logan
(2011-2018)
Biomass Burning Sources of NH$_3$

Poster by Viney Aneja

Bray et al., *Atm Env*, 2018
Biomass Burning Sources of NH$_3$

- **High-temp.**
  - Ethene
  - Formaldehyde
  - MeOH
  - Acetaldehyde
  - Acrolein
  - Acetic acid/glycolaldehyde

- **Low-temp.**
  - $n = 1$
  - $n = 2$
  - $n = 3$
  - $n \geq 4$
  - Ammonia

### Relative Fraction of Factor (ppbv/total VOC ppbv)

<table>
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<tr>
<th></th>
<th>High-T</th>
<th>Low-T</th>
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<tbody>
<tr>
<td>Hydrocarbons</td>
<td>0.223</td>
<td>0.105</td>
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<tr>
<td>Oxygenates ($n$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n = 1$</td>
<td>0.386</td>
<td>0.359</td>
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<tr>
<td>$n = 2$</td>
<td>0.190</td>
<td>0.270</td>
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<tr>
<td>$n = 3$</td>
<td>0.014</td>
<td>0.041</td>
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<tr>
<td>$n \geq 4$</td>
<td>0.001</td>
<td>0.008</td>
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<table>
<thead>
<tr>
<th></th>
<th>High-T</th>
<th>Low-T</th>
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<tbody>
<tr>
<td>N-containing</td>
<td>0.067</td>
<td>0.196</td>
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<tr>
<td>N and O-containing</td>
<td>0.119</td>
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<tr>
<td>S-containing</td>
<td>0.001</td>
<td>0.001</td>
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<tr>
<td>Others</td>
<td>0.000</td>
<td>0.000</td>
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</table>

Sekimoto et al., *ACP*, 2018
Mobile Sources of $\text{NH}_3$

Can be diagnosed through emission ratios with $\text{CO}$, $\text{CO}_2$, $\text{NO}_x$

Gasoline vs diesel?

Differences in emission ratios during winter operating conditions?

Sun et al., *ES&T*, 2016
Key Questions

• How does the sensitivity of PM$_{2.5}$ to NH$_3$ vary
  • spatially across the western U.S. in winter?
  • through time over the course of an extreme episode?

Requires: extensive (ground-based, aircraft, satellite), high-time resolution (hourly or better) measurements of NH$_3$ and p-NH$_4^+$ (plus HNO$_3$ and other PM$_{2.5}$ chemistry)

• What are the emissions of NH$_3$ for each sector and how do they vary seasonally?

Requires: extensive (ground-based, aircraft, satellite), high-time resolution (hourly or better) measurements of NH$_3$ and p-NH$_4^+$ (plus co-emitted species CO, CO$_2$, CH$_4$...
NH$_3$ concentration at SLC (AMoN)

Difficult to interpret without PM$_{2.5}$ NH$_4^+$

UT97 - Salt Lake City (2011-2018)