Origin of Reactive Nitrogen Deposition in Rocky Mountain NP

Sunrise on Loch Vale
Thomas Mangan: http://www.thomasmangan.net/
Rocky Mountain NP Deposition Studies
RoMANS I: 2006 – March/April (spring) and July/August (summer)
RoMANS II: November 2008-November 2009; April – Sept 2010;
Summer 2014 FRAPPE’; 2015-16 Continuous Monitoring

• Particle composition and gases
  – 24 hr PM$_{2.5}$ and composition
  – 15 minute PM$_{2.5}$ ions (PILS)
  – 24 hr SO$_2$, NH$_3$ and HNO$_3$ (URG)
  – Continuous NO$_x$, NO$_y$, NH$_3$, O$_3$, CO
  – Weekly HiVol – PM$_{2.5}$

• Wet deposition
  – Event and sub-event/hourly
  – Ion chromatography
  – Org N = TN – inorg N

• Other measurements

Co-located with IMPROVE & CASTNet monitors
Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) Study Objectives

- Characterize the atmospheric concentrations of sulfur and reactive nitrogen species in gaseous, particulate and aqueous phases along the east and west sides of the Continental Divide.

- Identify the relative contributions to atmospheric sulfur and nitrogen species in RMNP:
  - from within and outside of the state of Colorado.
  - from emission sources along the Colorado Front Range versus other areas within Colorado.
  - from mobile sources, agricultural activities, large and small point sources within the state of Colorado.
Total Chemically Reactive Nitrogen
(Biologically available N compounds)

- TCRN = NOy’ + NHx’ + Organic
  (Inorganic Oxidized)  (Inorganic Reduced)

Inorganic
- NOy’ ≡ NO + NO₂ + NO₃ + 2xN₂O₅ + HNO₃
  + HONO + HO₂NO₂ + NO₃⁻ (particulate nitrate)
- NHx’ = NH₃ + NH₄

Organic
- Oxidized: R-ONO₂ (organic nitrates such as PAN and alkyl nitrates) + R-ONO (organic nitrites) + …...
- Reduced: + amines (R-NHx) + Nitrile + ….
### Sources of Reduced and Oxidized Gases

<table>
<thead>
<tr>
<th>Compound</th>
<th>Anthropogenic</th>
<th>Naturally Occurring</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO}_3$</td>
<td>Fossil-Fuel Combustion (power plants; mobile; oil and gas) Fertilizer, Prescribed fire</td>
<td>Soil Release; Lightning; Wild fire</td>
</tr>
<tr>
<td>$\text{NH}_3 \rightarrow \text{NH}_4$</td>
<td>Feedlots; Fertilizer; Mobile Waste water treatment</td>
<td>Wild animals – Ecosystem respiration</td>
</tr>
<tr>
<td>Organic N</td>
<td>Feedlots, Fires, Reactions of NOx NH3 with VOC</td>
<td>Vegetation; Fires</td>
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Emission

- NO\textsubscript{X} emissions have been decreasing and are projected to continue to decrease.
- NH\textsubscript{3} emissions have remained stable and are projected to not decrease.
Rocky Mountain NP Nitrogen Deposition Budgets

- Wet N deposition accounts for more than 2/3rds
- Reduced N accounts for more than 1/2 while oxidized less than 1/3 of annual total N deposition

This deposition budget is similar to what we measure today
Oxidized N emissions and deposition have been decreasing, while reduced N deposition has been increasing.

Today there is ~50% more reduced N than oxidized N deposition in RMNP.

To resolve excess nitrogen deposition in RMNP reduced N (i.e. NH$_3$ emissions) will need to be decreased.

To do this, we need to know where the reduced N comes from, i.e. its origin.
ROMANS Apportionment Strategy

(Weight of Evidence)

- Concentration gradients.
- Which way is the wind coming from?
- Simple back trajectories.
- Frequency with which the air mass passes over source areas before it arrives at the receptor - residence time analysis.
- Receptor models.
- Trajectory receptor models.
- Source Oriented Chemical transport models.
- Hybrid Models.
All you have to do is look

Rocky Mtn Alpine Visitor Center

June

Looking West

Looking East
Concentration gradients, 2006

- Concentrations lower in mountains
- Gases dominate at eastern and western sites
  - Highest ammonia at Brush in NE Colorado
- Particles dominate in mountains

(Holden et al., 2011)
Wind and NH$_3$ pollution Roses

Winds from the east are less frequent, but they come with high NH$_3$ concentrations

Annual NH$_3$ contribution (Wind * NH$_3$ Roses)

44% of NH$_3$ concentrations are associated with winds from the east
# Quantitative Source Apportionment

<table>
<thead>
<tr>
<th></th>
<th>Advection</th>
<th>Dispersion</th>
<th>Emissions</th>
<th>Chemistry/Removal</th>
<th>Boundary Conditions</th>
<th>Local Sources</th>
<th>Measured Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAMx-PSAT</td>
<td>X (WRF)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Hybrid-PSAT</td>
<td>X (WRF)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
</tr>
<tr>
<td>FMBR</td>
<td>X (WRF)</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<tr>
<td>TrMB</td>
<td>X (multiple winds)</td>
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<td>X</td>
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<tr>
<td>Wind Rose</td>
<td>X (surface winds)</td>
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<td>X</td>
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</tbody>
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![Map of the United States](image)
Comparison of Modeled Source Contributions – Reduced Nitrogen

![Comparison of Modeled Source Contributions](image-url)
Modeled Source Regions

NH3 (Tons/year)
Final Source Apportionment: CAMX-PSAT-Hybrid method

- Over 40% of NHx deposition originates from CO sources, primarily from those in the Front Range and to its east
- About 40% of NHx deposition originates from the rest of the west
  - It’s ultimately a regional issues
- RMNP and local sources are small contributors to N deposition
Source Contribution Efficiency
Not all emissions are equal!

• CO and the rest of the west each have ~40% contribution

• A 10% reduction in CO NH$_3$ emissions has same benefit as a 10% reduction in all other western US emissions
Relative Efficiency of $\text{NH}_x$ Emissions Reductions

To achieve the same benefit as a 0.3 ton reduction in N. Front Range emissions we would need to reduced 1 ton across all of CO or 9.4 tons from CA.
Efficiency of Modeled NH$_x$ Source Contributions to RMNP
Models likely underestimate upslope transport and eastern CO contributions

- CAMx-PSAT underestimated ammonia ($NH_3$) contributions from the east by 30% on average

44% of measured $NH_3$ is associated with eastern winds

31% of modeled $NH_3$ is associated with eastern winds

- CAMx-PSAT underestimated ammonia ($NH_3$) contributions from the east by 30% on average
What about Golf Courses, Wastewater Plants, Lawn Fertilization?

- Loveland golf course - small contribution to background NH$_3$ concentrations
- Wastewater treatment plant has large contributions, but smaller than many CAFO’s

**NH$_3$ Spatial Distribution May–Sep 2010**

**Mobile NH$_3$ meas. May 3$^{rd}$ and 5$^{th}$, 2010**

Day et al.,

- Lamb feedlot, pens cleaned, (~340 µg/m$^3$)
On average the NH$_3$ near the waste water treatment plant was $\sim$25% greater than at CSU,

NH$_3$ at Kersey was $\sim$2280% greater than at CSU
Summary

- Reactive N deposition at RMNP is primarily due to:
  - Oxidized nitrogen (NOy’) - from combustion sources, e.g. cars
    - regulated with generally decreasing emissions and contributions
  - Reduced nitrogen (NHx’) – agriculture the largest source
    - (generally non regulated with flat / increasing emissions)

- About half of the reactive N deposition is due to reduced (NHx’) and a 1/3 from oxidized (NOy’)

- Resolution of the excess reactive N deposition will require reductions of NH₃ emissions from the agriculture sector
Summary

- More than 40% of NHx’ comes from Colorado sources
- Most NHx’ (~70%) of CO reduced N comes from Front Range + Morgan + Weld counties
- NH$_3$ emissions from CO sources east and west of RMNP are the most efficient contributors to the nitrogen deposition
  - A 1 ton NH3 emission reduction in these areas will cause the largest decrease in reduced N deposition in RMNP
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Summary

RMNP 2009 Reactive N Deposition Budget
2/3 – 3/4 wet (rain and snow) and ¼ - 1/3 dry (particles and gases) deposition

~1/2 of N deposition is reduced; 1/4 oxidized; and 1/5 wet dep ON

NH$_3$ is now being measured at some location, but wet ON deposition is not

Dry deposition of reduced and oxidized organic N is still missing