Chemical Transport Modeling of Nitrogen Deposition in the Western U.S.: A National Park Perspective

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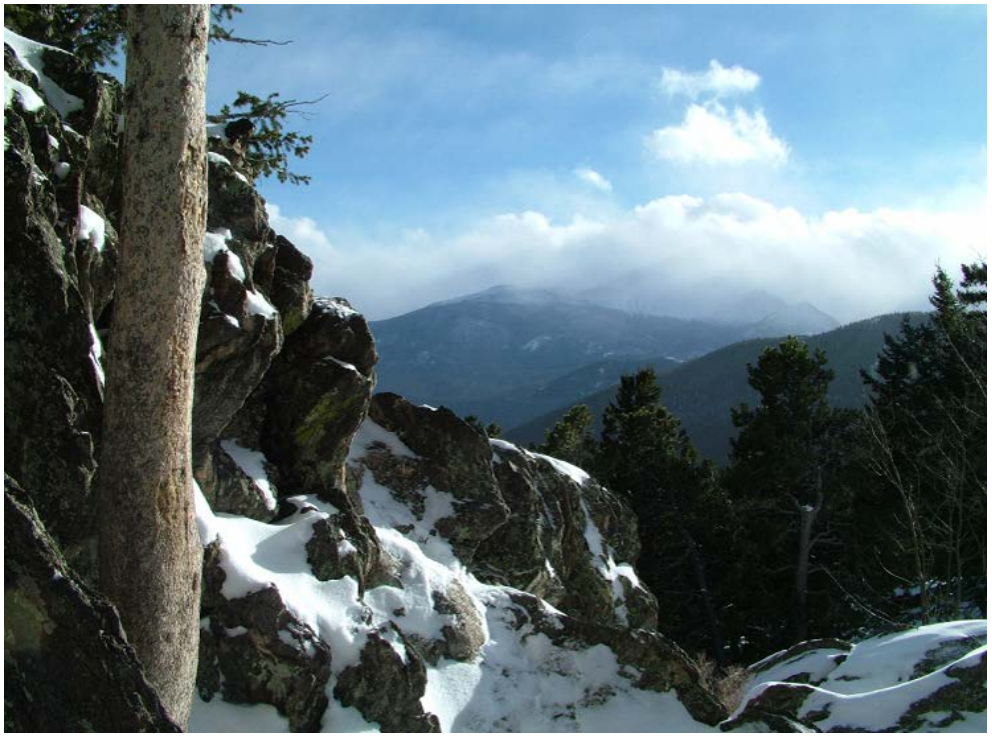

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Characterizing N deposition

- NADP and CASTNet are invaluable resources for investigating trends and patterns in nitrogen deposition

- Unfortunately, it's very hard to measure deposition for
  - All potential nitrogen species of interest,
  - For all places,
  - At all times

- Chemical transport models can help to
  - Estimate deposition in unmonitored areas
  - Round-out the 'total N deposition' budget

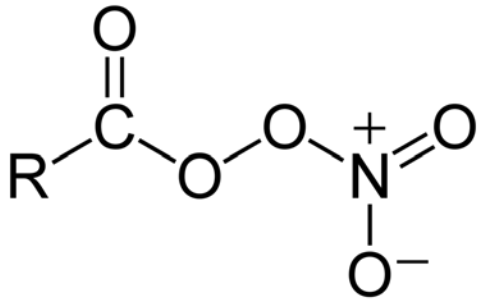
Unknowns: reduced gas-phase N

- Ammonia
  - Sparse observations, but can play a large role

- Reduced organic nitrogen gases
  - e.g., urea, amino acids, methylated amines
  - Emissions, not chemistry, is important
  - Associated with fires?
  - Important?

Unknowns: gas-phase organic nitrates

- Historically, only considered PAN-like compounds, but now chemistry mechanisms treat a wider variety of ON, e.g., isoprene nitrate



- Many of the organic components are ‘lumped’, resulting in average estimates for dry deposition velocity and wet scavenging

- Could be important, especially in more polluted environments, or where lots of isoprene exists

Unknowns: particle organic nitrates

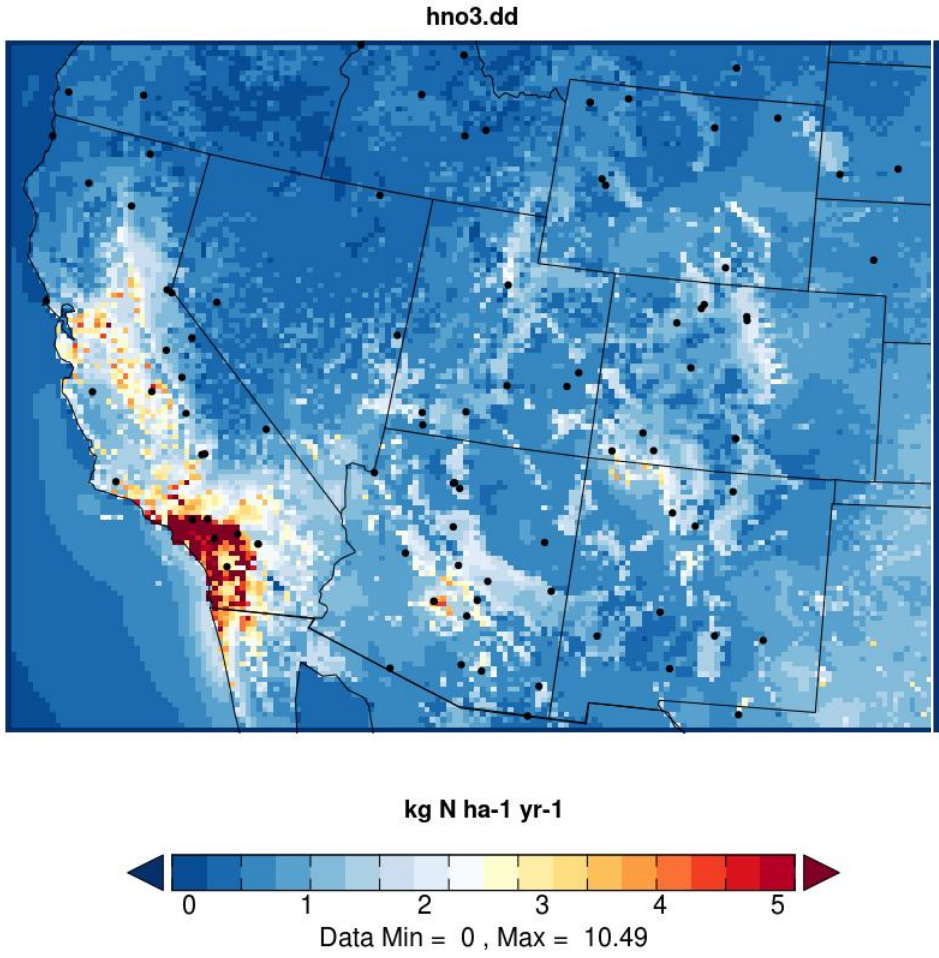
- “There is growing evidence that organo-nitrogen compounds may constitute a significant fraction of the aerosol nitrogen (N) budget. However, very little is known about the abundance and origin of this aerosol fraction.” (Lin et al., 2010)

- Important to overall N dep budget?

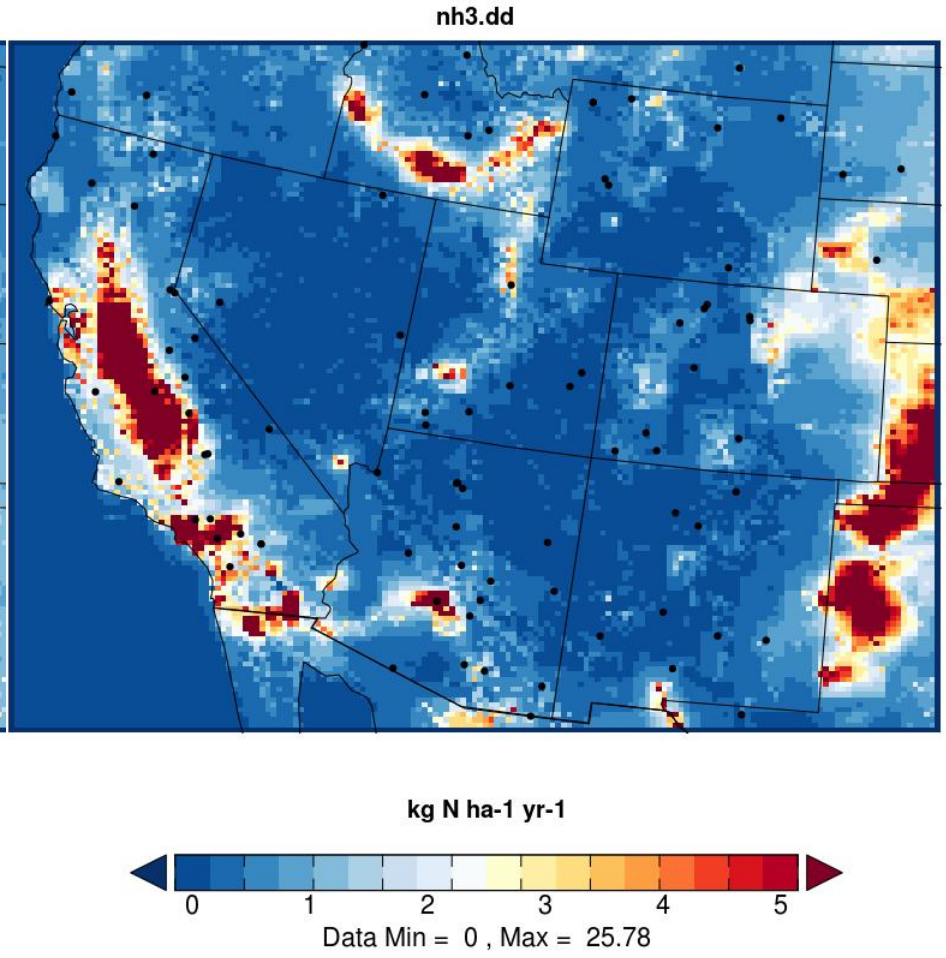
- No attempt to model this yet

Simulated HNO3 and NH3 dry dep

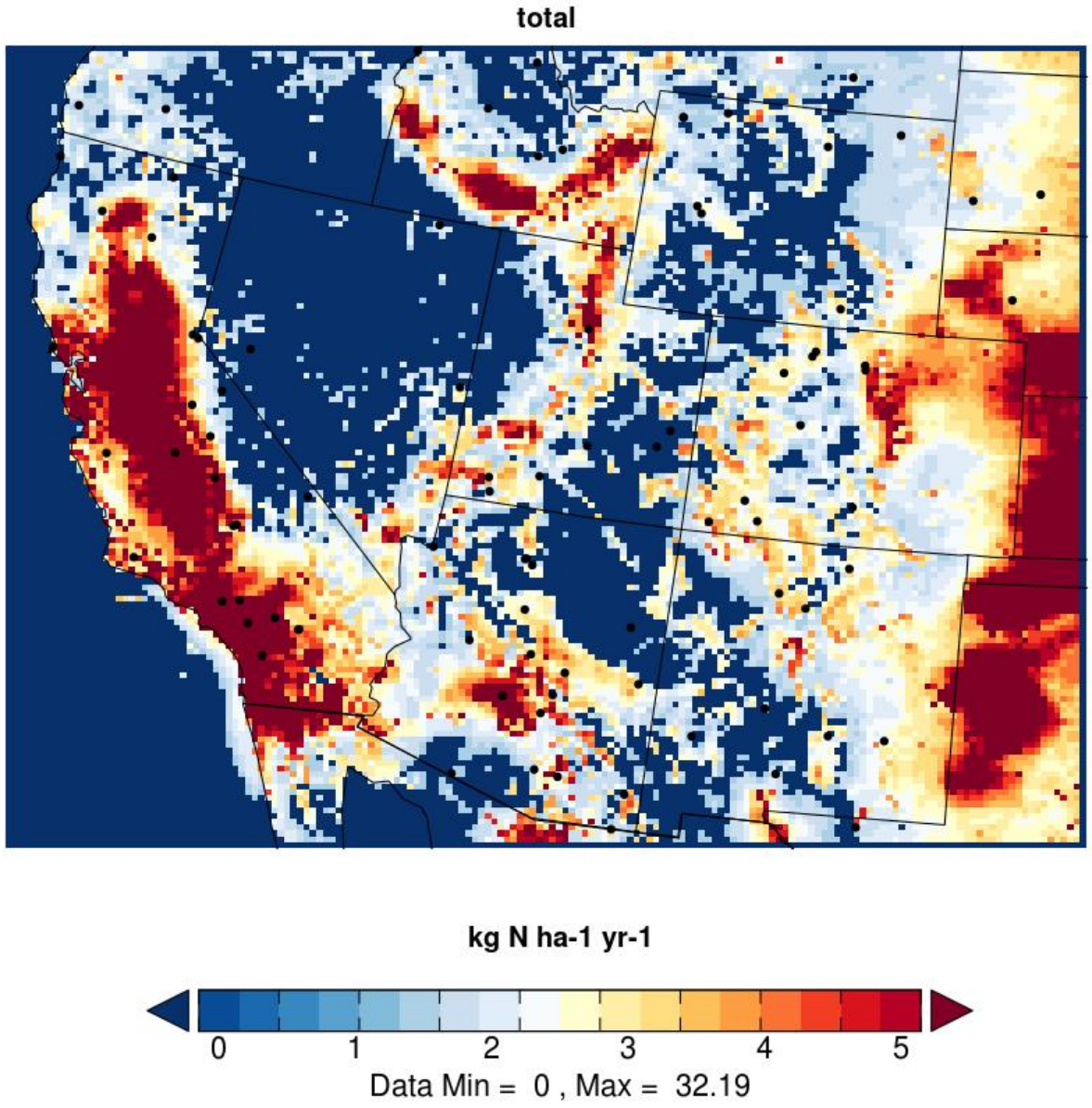
HNO3



NH3



Simulated ‘total’ N deposition

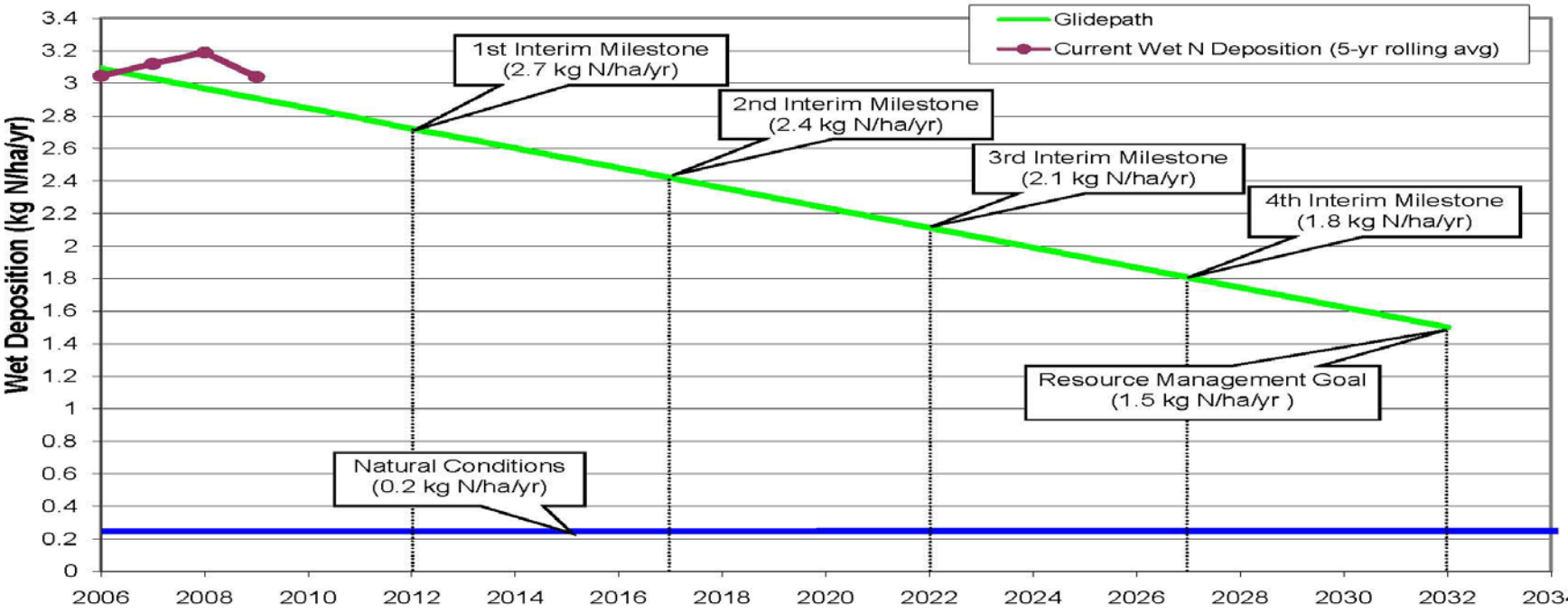


“total N” =
wet N + dry N =

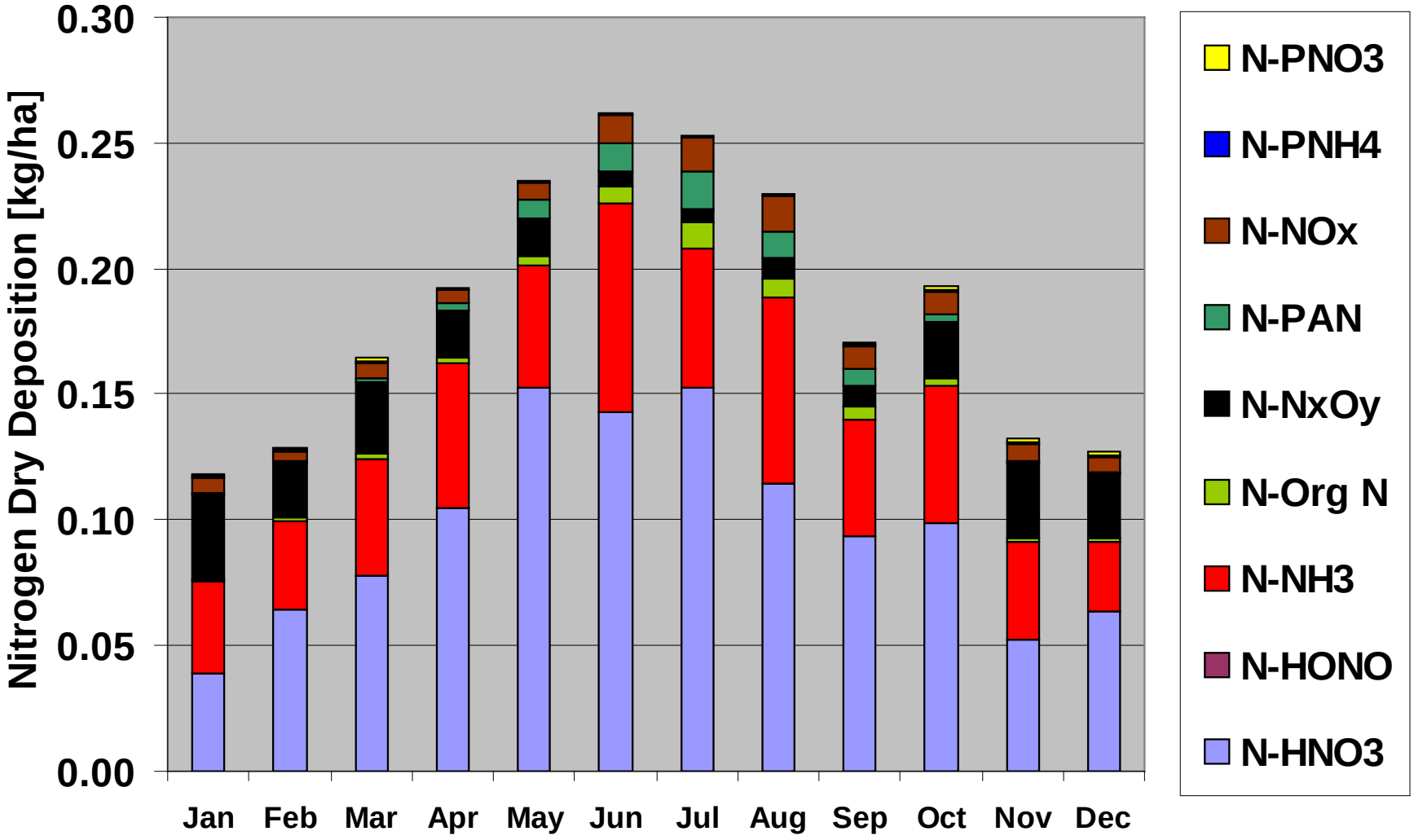
Nitric acid +
Ammonia +
PM nitrate +
PM ammonium +
Organic nitrates +
‘nighttime N’ +
NOx

N deposition at Rocky Mountain NP

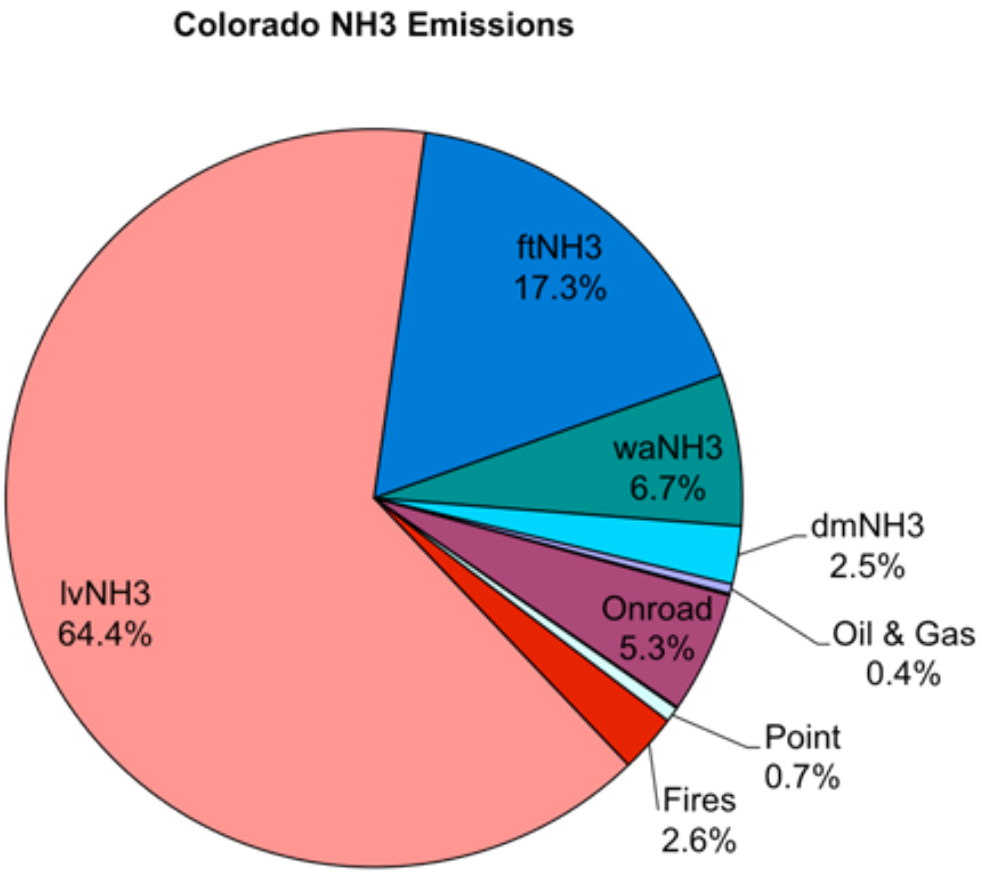
- Nitrogen deposition and ecosystem change has been extensively studied at RMNP
  - NADP and CASTNet sites
  - RoMANS (2006)
  - RoMANS2 (2009)



Simulated ‘total’ N dry dep at ROMO

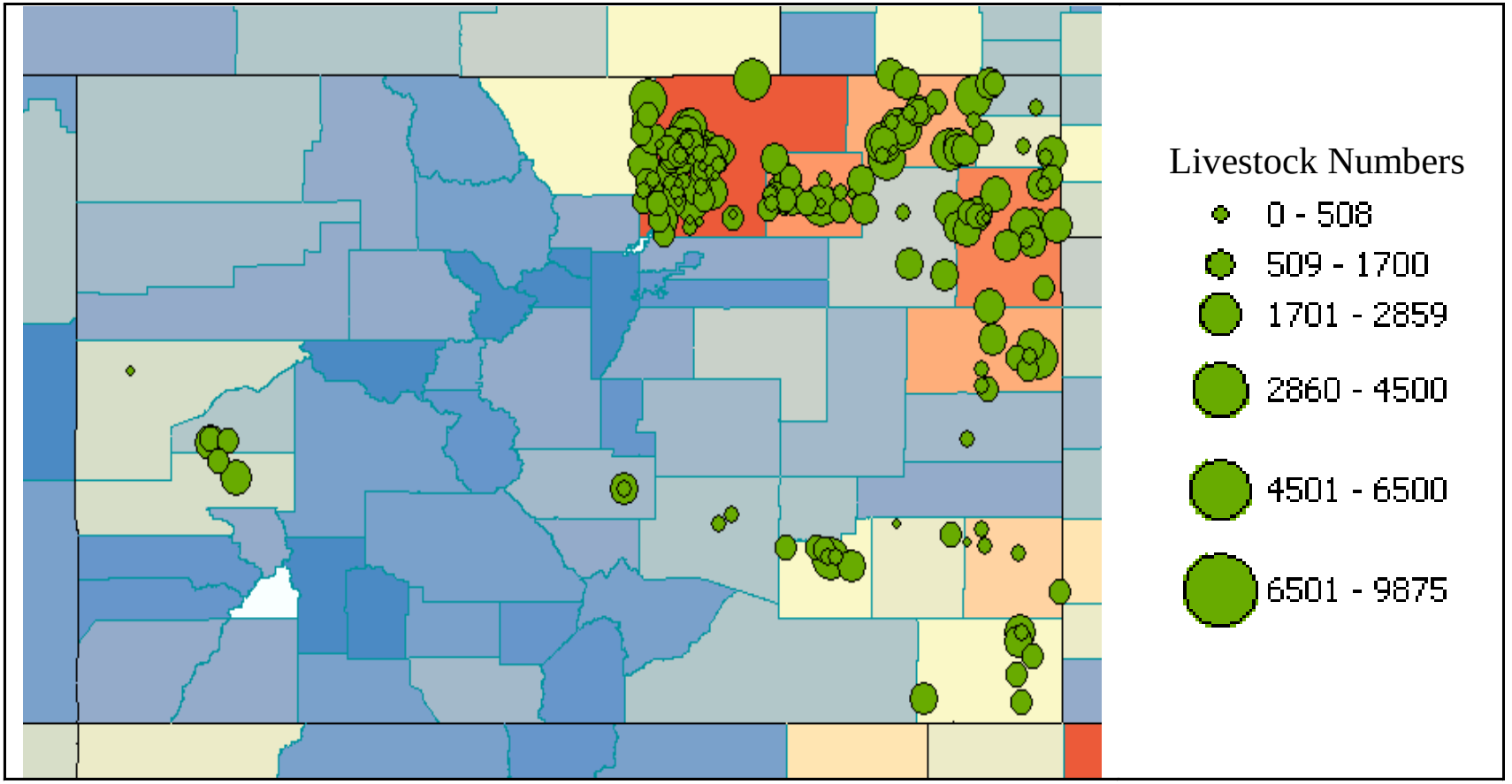


Colorado Romans2 NH3 emissions



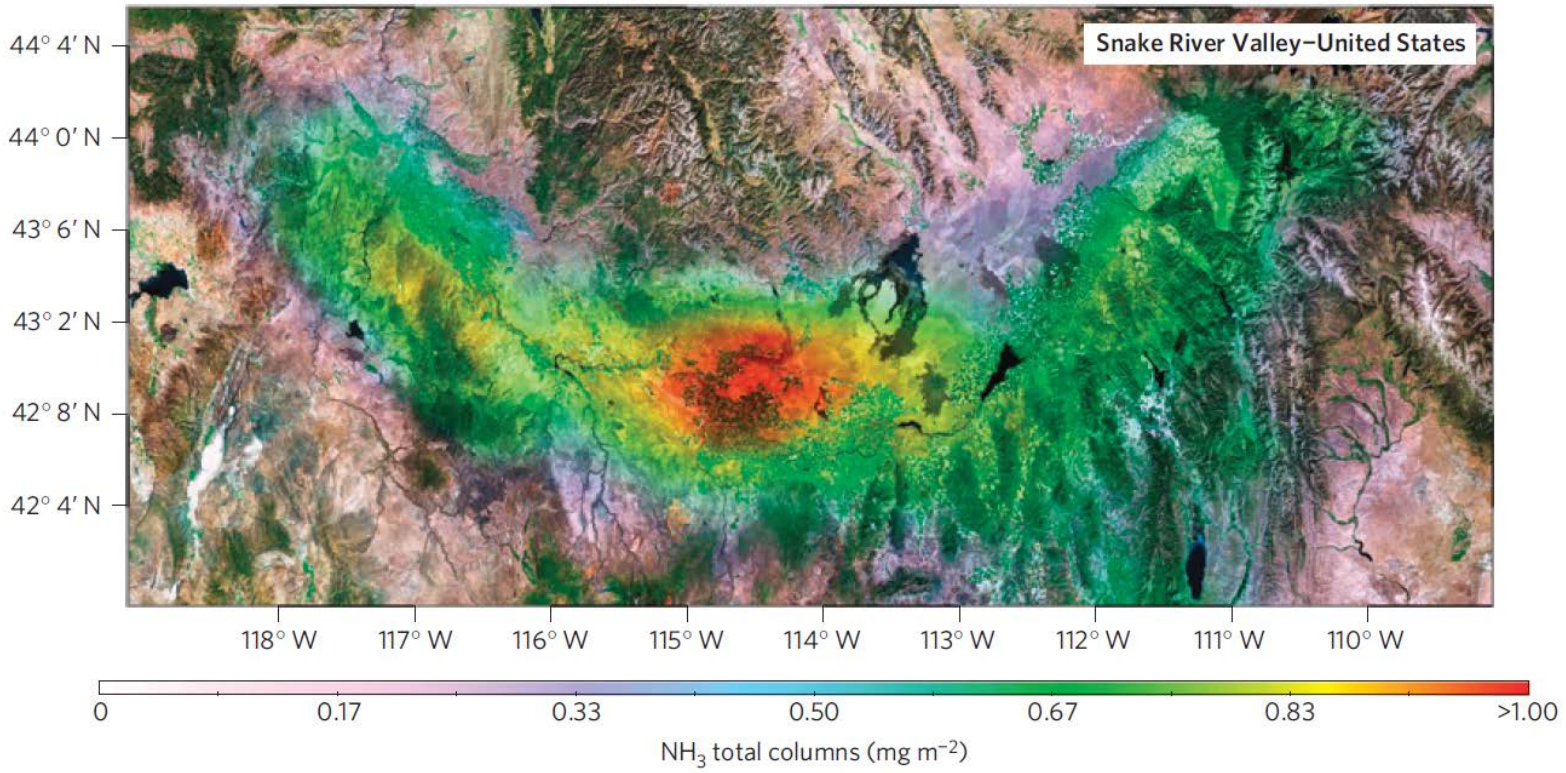
Colorado Totals	NH3 (tons/yr)
Area	76
Onroad	4,484
Nonroad	49
Point	526
Fires	2,152
Livestock	54,078
Fertilizer	14,527
Wild Animals	5,626
Domestic	2,099
Oil & Gas	350
Biogenic	0
Windblown Dust	0
Total Colorado	*83,967*

Romans2 CAFO location improvements

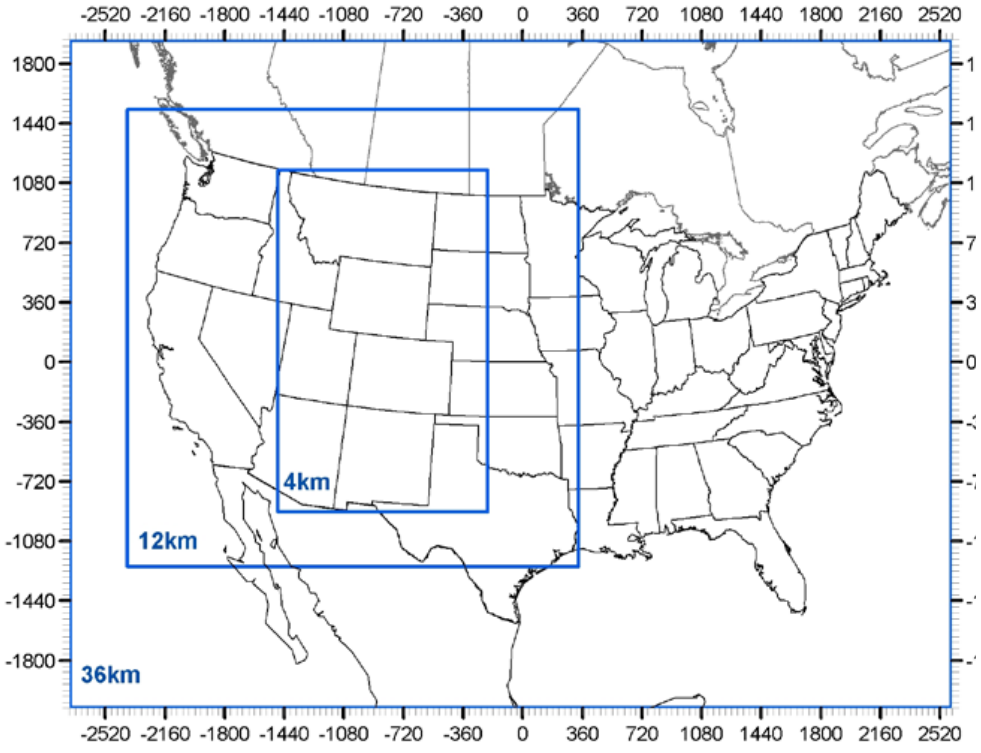


Use a ‘top down’ approach for NH3 EI?

- Clarisse et al., 2009, Nature Geoscience
- IASI – Infrared Atmospheric Sounding Interferometer
- “good qualitative agreement”
- “emissions significantly underestimated in northern hemisphere”



WestJumpAQS modeling for ‘08, ‘11

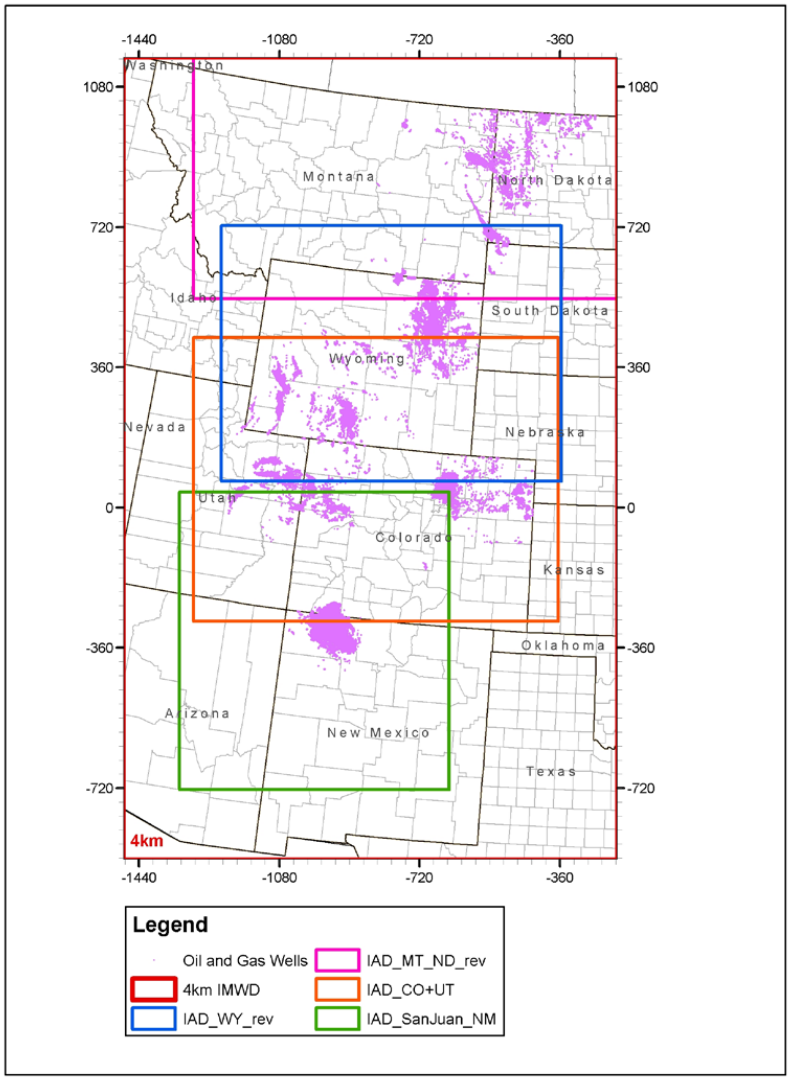


Modeling Domain

36km: 148 x 112 (-2736, -2088) to (2592, 1944)
12km*: 227 x 230 (-2388, -1236) to (336, 1542)
04km*: 317 x 515 (-1480, -904) to (-212, 1156)

* includes buffer cells

4 km Intermountain



Carbon Bond 6 (CB6)

- Latest version of ‘carbon bond’ mechanism
- Used in WRF-Chem, CMAQ, CAMx
- Updates germane to nitrogen
  - More detailed treatment of org-N
  - Surface hydrolysis of N2O5 to make HNO3

CB6 vs. CB05 chemical mechanisms:

Gas-phase reactions: 218 vs. 156
Photolysis reactions: 28 vs. 23
Gas-phase species: 77 vs. 51

Summary

- What is the role of unmonitored N?
  - Ammonia
  - Gas-phase reduced organic N
  - Gas-phase organic nitrates
  - Particle organic nitrates

- Ammonia is important, but do other species make a significant contribution to N deposition budget?

Summary (cont'd)

- Models can be useful to address gaps:
  - NH3 (yes)
  - PAN and homologues (yes)
  - NOx (yes)
  - Nighttime radicals (maybe)
  - Other gas-phase organic nitrates (maybe)
  - Org N on particles (not yet)
  - Reduced org N gases (not yet)

Summary (cont'd)

- Accounting for 'missing' nitrogen can almost double the estimated dry deposition at RMNP (1.2 vs 2.2 kg/ha/yr).

Species	N-flux [kg/ha yr]	contribution
HNO_3	1.16	53%
NH_3	0.60	28%
N_xO_y	0.22	10%
PAN + Org N	0.11	5%
Other N species	0.12	6%