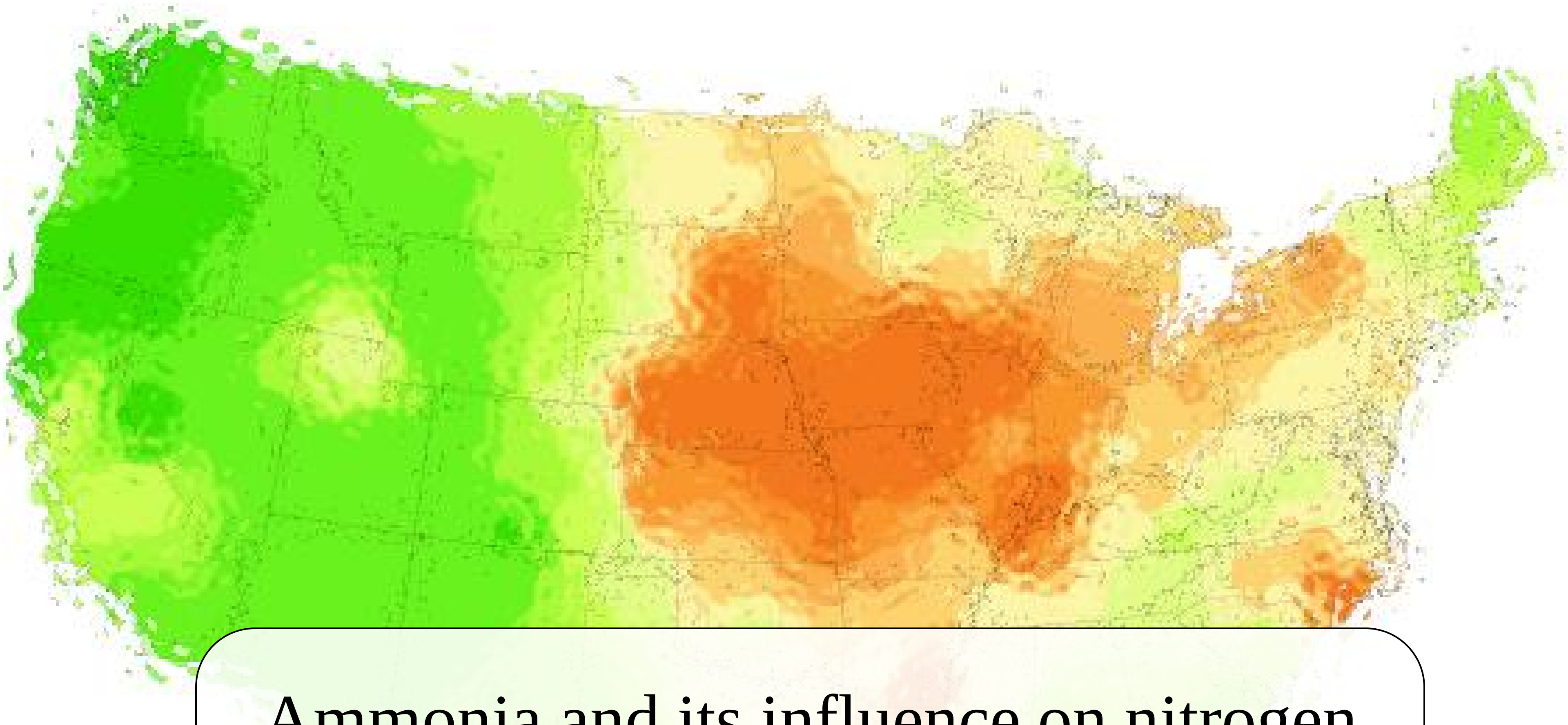

Ammonia and its influence on nitrogen deposition and fine particle formation

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Acknowledgments

- People
  - CSU: Katie Benedict, Yi, Li, Tony Prenni, Ashley Evanoski-Cole, Derek Day, Florian Schwandner, Suresh Raja, Taehyoung Lee, Amy Sullivan, Kip Carrico, Sonia Kreidenweis
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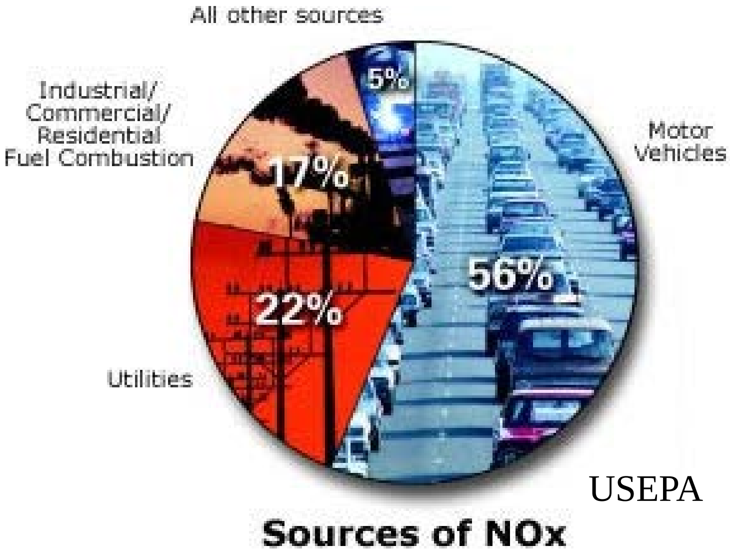
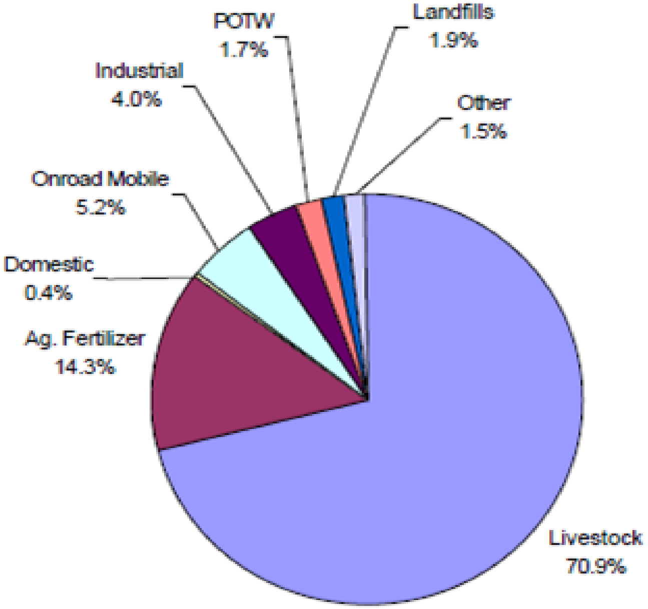
  - ARS: Mark Tigges, John Molenar, Stephen Holcomb, Cassie Archuleta, Lincoln Sherman
  - Shell: Angela Zivkovich
  - UC Davis: Chuck McDade, Jose Mojica, Mark van de Water
  - RTI: Eva Hardison, David Hardison
- Funding
  - U.S. National Park Service
  - U.S. Department of Agriculture
  - Shell Exploration and Production Company

Reactive nitrogen emissions

- Nitrogen oxides
  - **$NO_x = NO + NO_2$**
  - Formed by high temperature reaction of N_2 and O_2
  - NO_x reacts in the atmosphere to form nitric acid (**HNO_3**) and other species
- Ammonia (**NH_3**)
  - Livestock and fertilizer are largest sources



USEPA

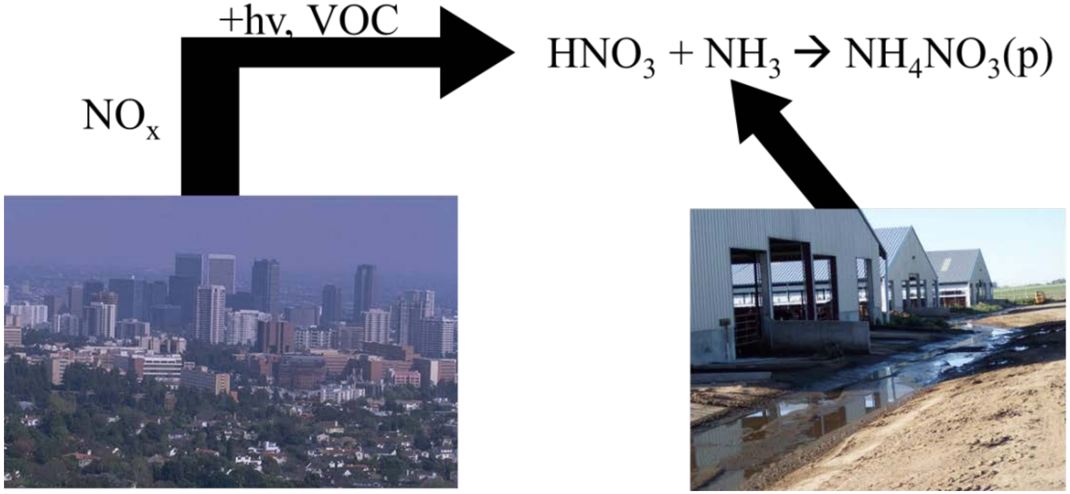


NH_3 emission sources

USEPA (2004)

Particulate atmospheric nitrogen

- Ammonium nitrate
  - $NH_{3(g)} + HNO_{3(g)} <=> NH_4NO_{3(p)}$
  - Sensitive to temperature and relative humidity
- Ammonium sulfate
  - $2\ NH_3 + H_2SO_4 => (NH_4)_2SO_4$
- Particles ~200-600 nm in diameter
  - Long lifetimes in atmosphere (several days)
  - Important cause of haze



NO_x

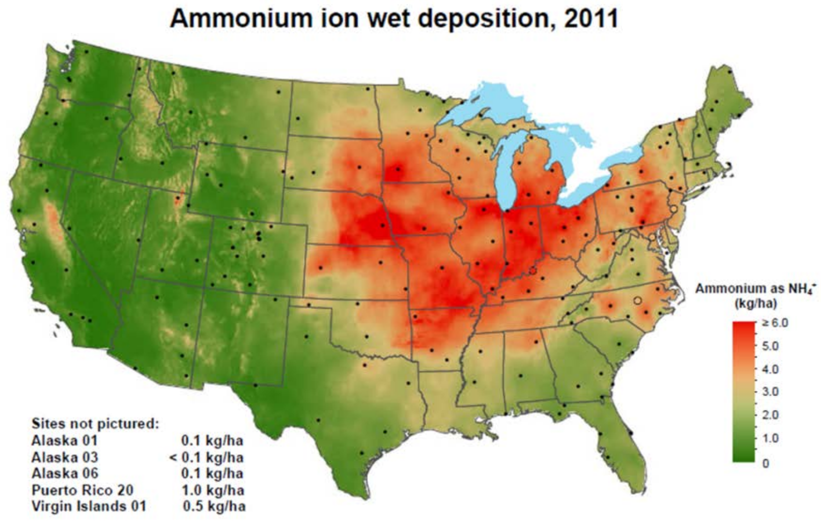
+hv, VOC

$HNO_3 + NH_3 \rightarrow NH_4NO_3(p)$

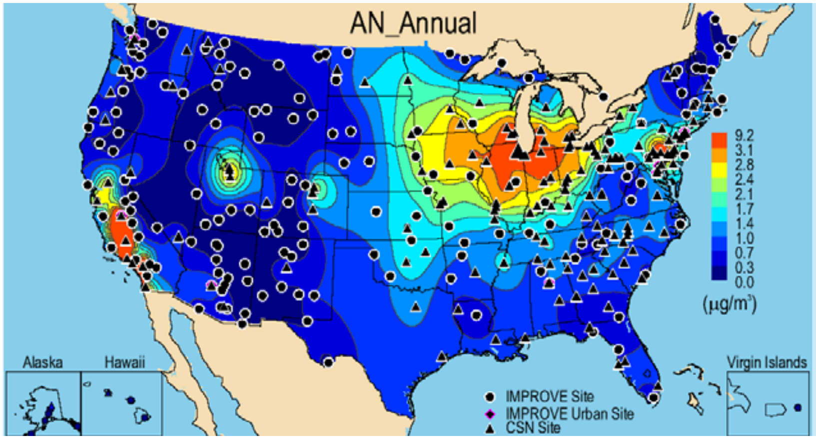
Denver brown cloud (Denver Post)

Reactive nitrogen deposition

- Wet deposition
  - Precipitation scavenges gases and particles and deposits them on surface
  - Easier to measure
- Dry deposition
  - Difficult/expensive to measure
  - Estimate as product of measured concentration and modeled deposition velocity
  - Gas/particle partitioning is key
    - $V_{d,NH3} >> V_{d,NH4+}$
    - $V_{d,HNO3} >> V_{d,NO3-}$



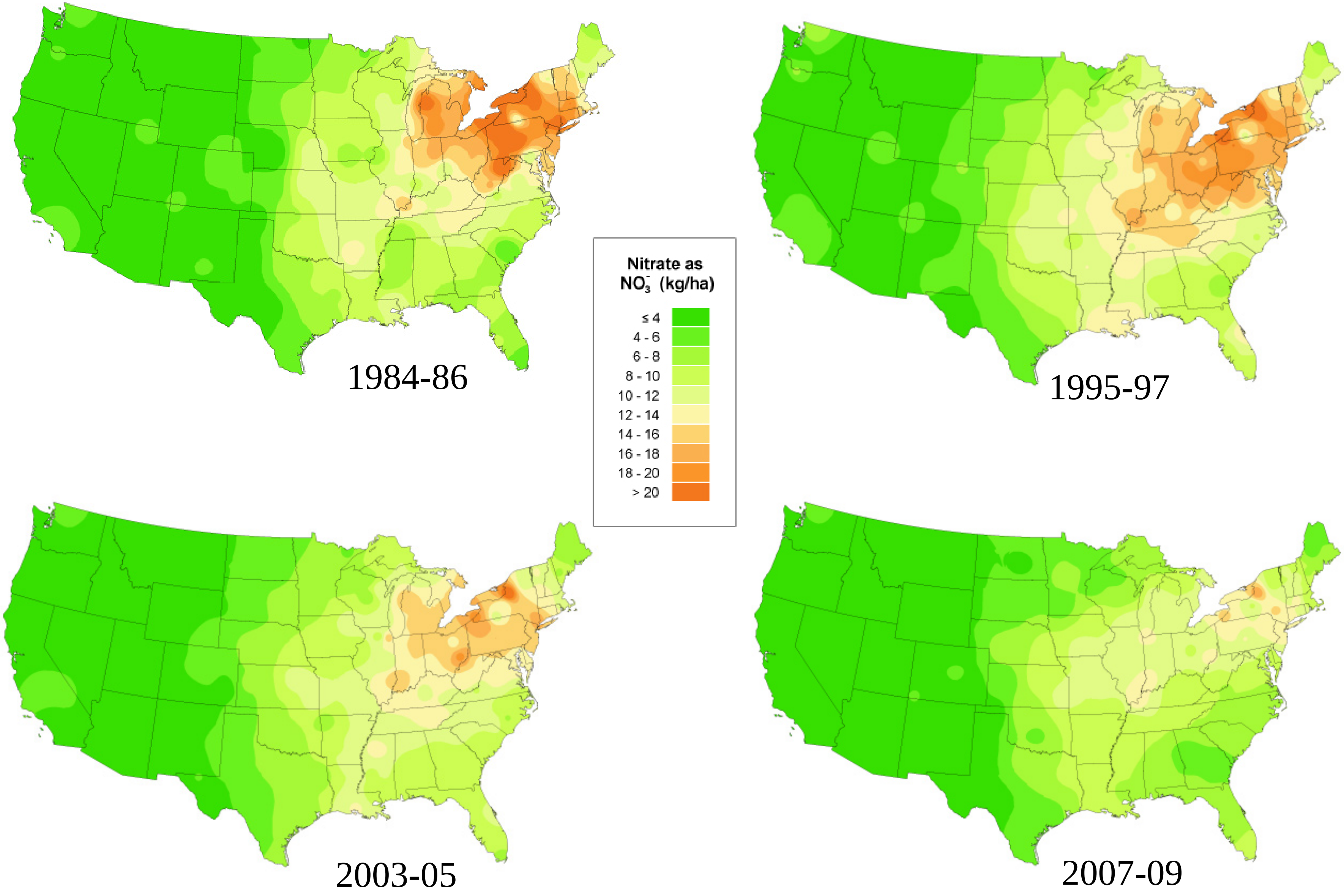
National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu



Hand et al. (2011) IMPROVE report

HISTORICAL CHANGES IN REACTIVE N WET DEPOSITION

Nitrate Ion Wet Deposition



1984-86

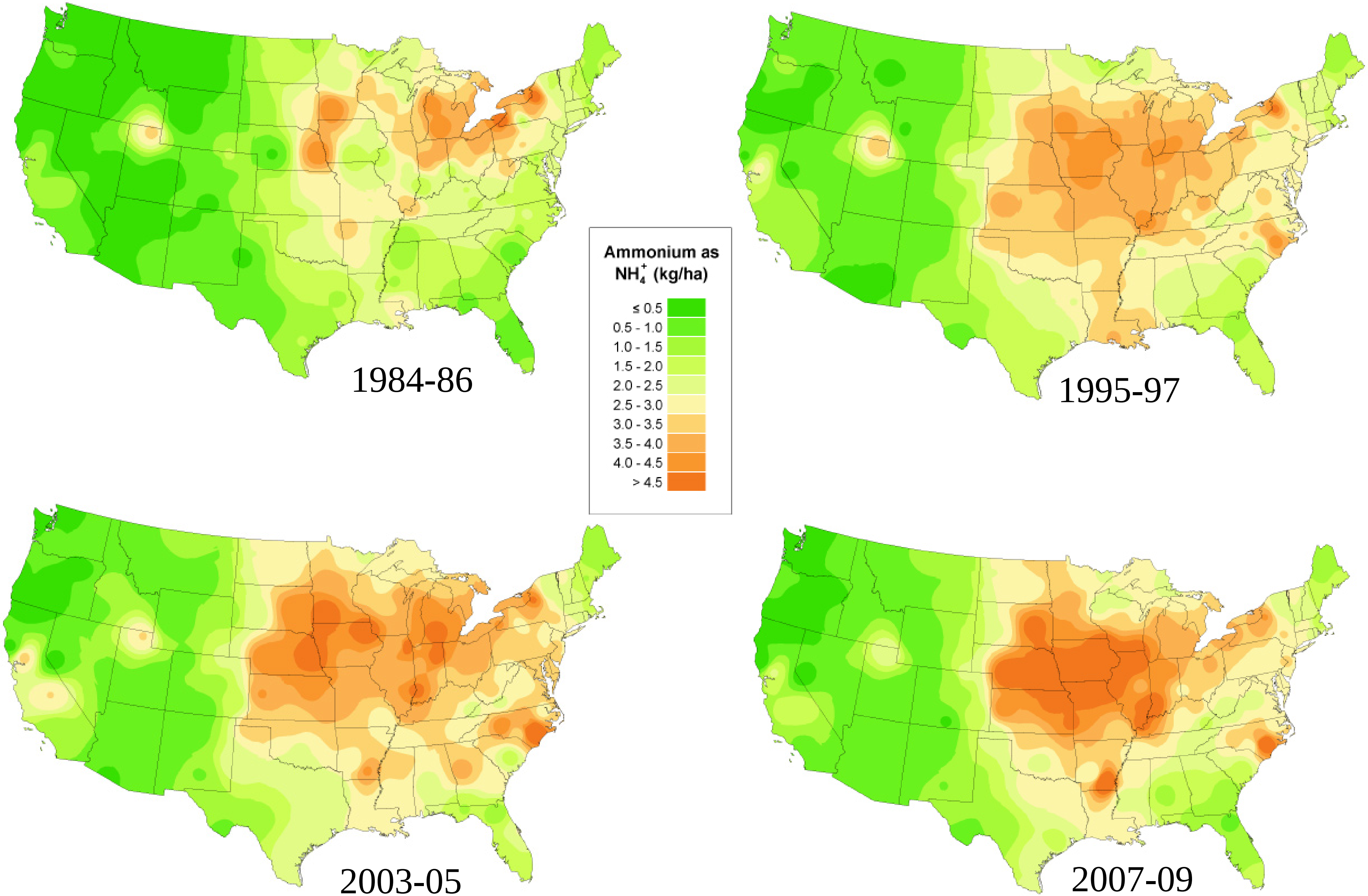
1995-97

2003-05

2007-09

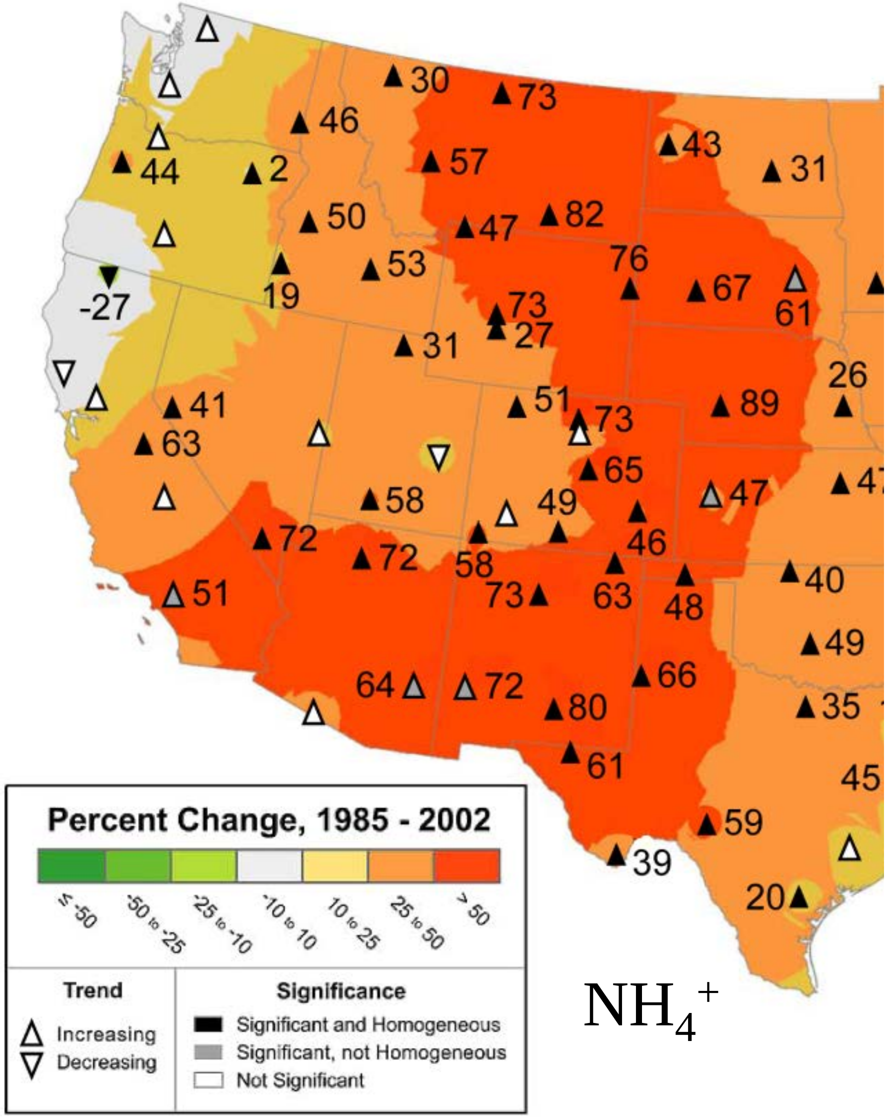
http://nadp.sws.uiuc.edu/data/

Ammonium Ion Wet Deposition



http://nadp.sws.uiuc.edu/data/

Changes in NH_4^+ wet deposition

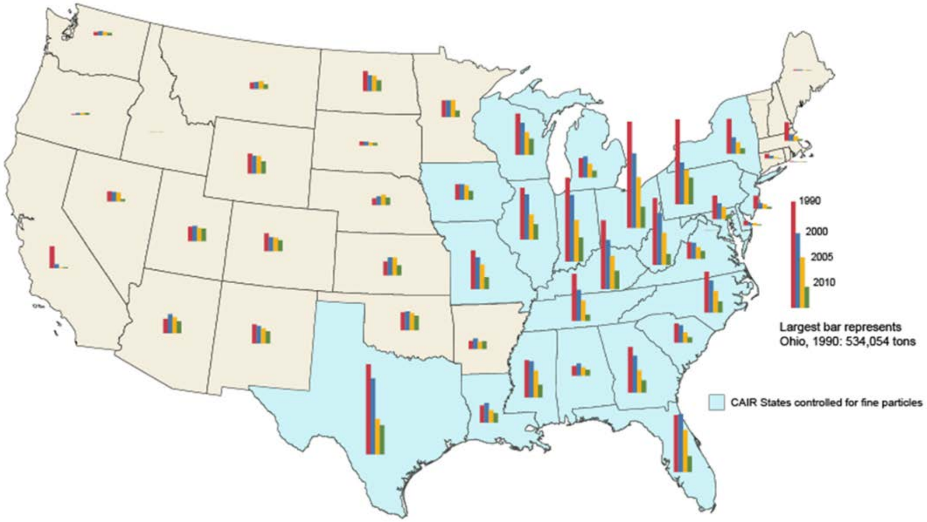


NH_4^+

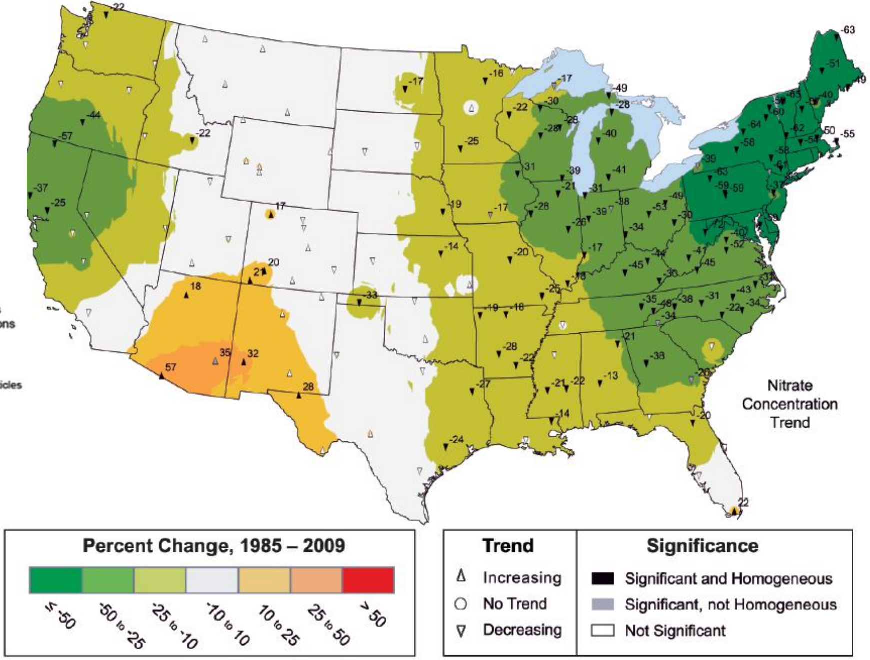
Lehmann et al., 2005

Changes in NO_3^- wet deposition and NO_x emissions

NO_x

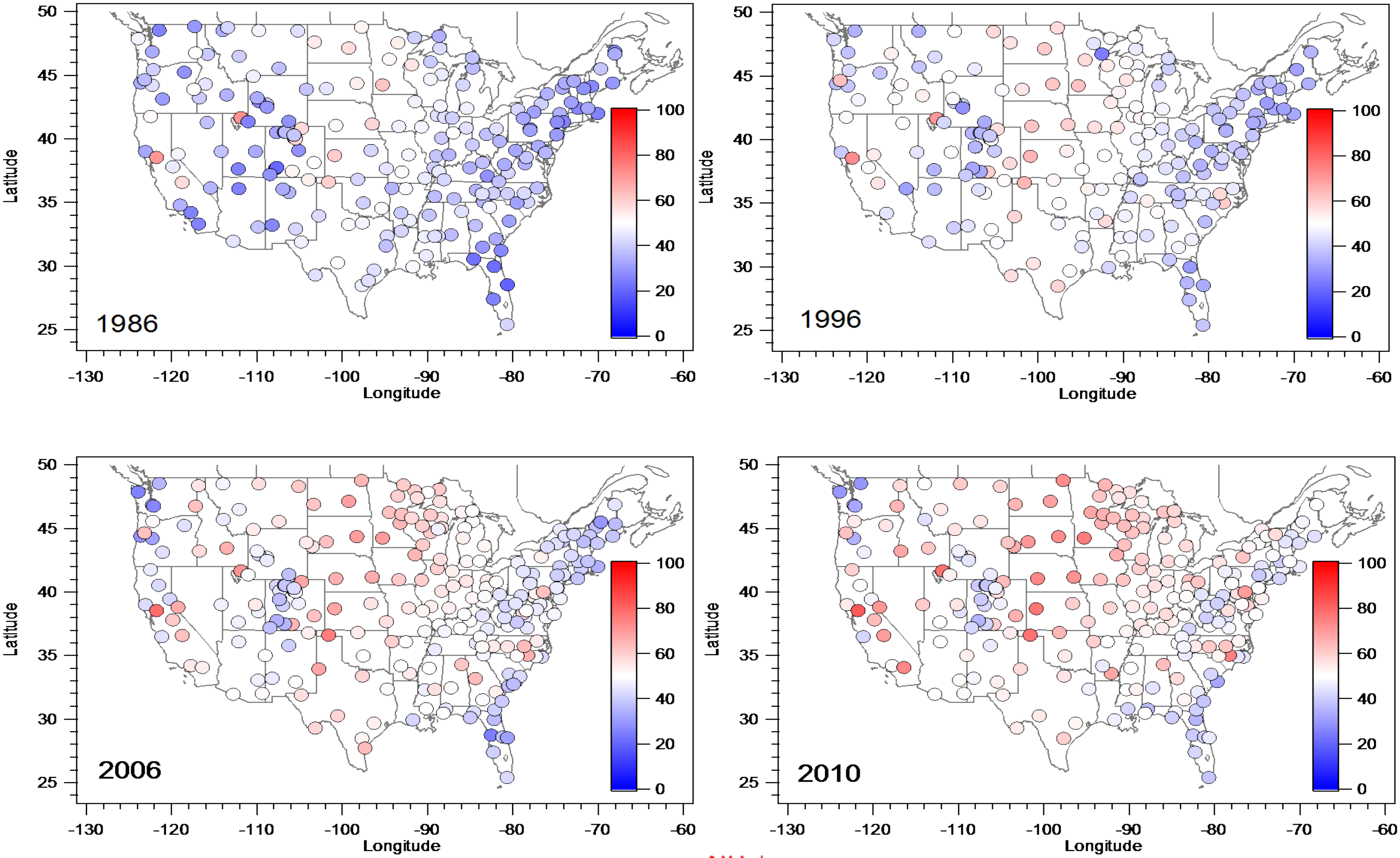


NO_3^-



Lehmann and Gay, 2011

Change in NH_4^+ fraction in U.S. wet inorganic N deposition

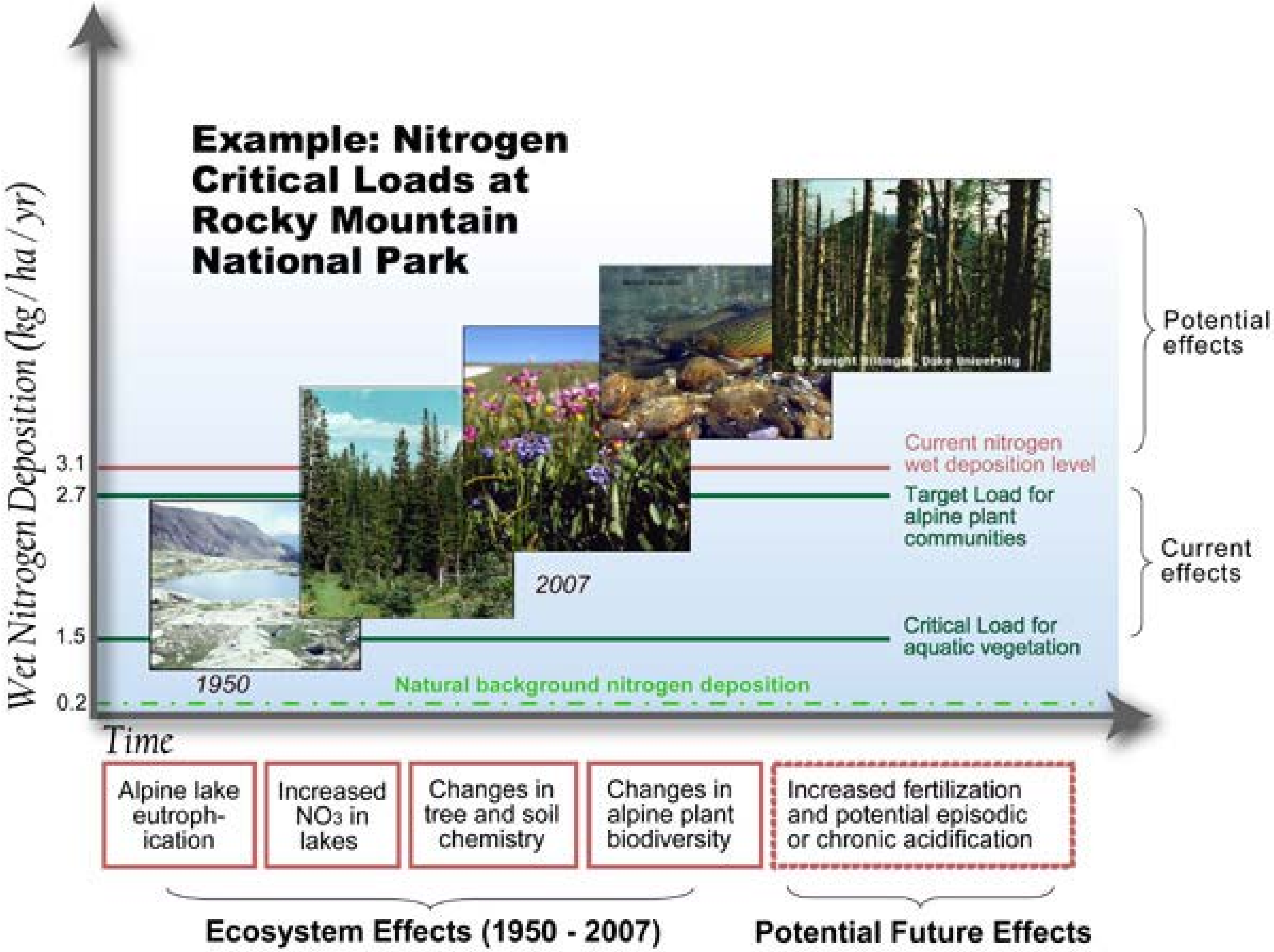


$$NH_4\% = \frac{NH_4^+}{NO_3^- + NH_4^+} \times 100\%$$

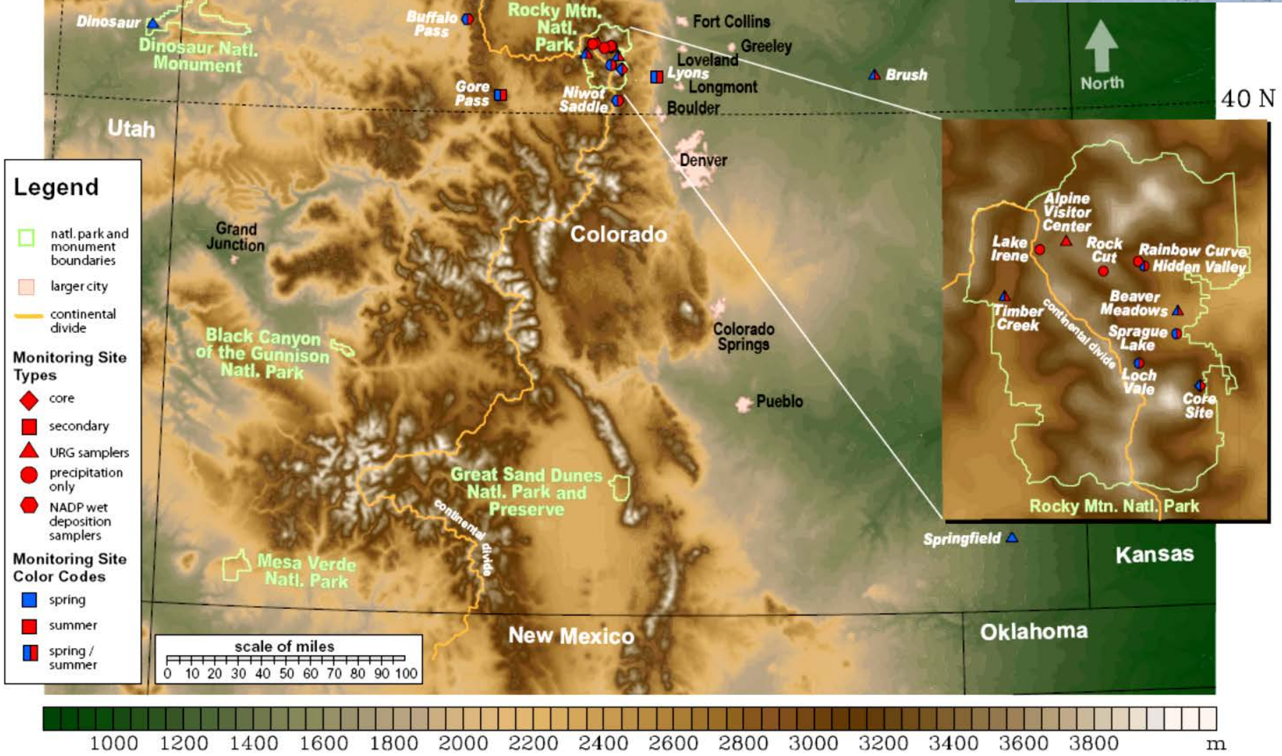
Li et al., in prep

THE IMPORTANCE OF NH_3 FOR N DEPOSITION AND PARTICLE FORMATION: A FEW EXAMPLES

<u>Concerns about nitrogen deposition</u>

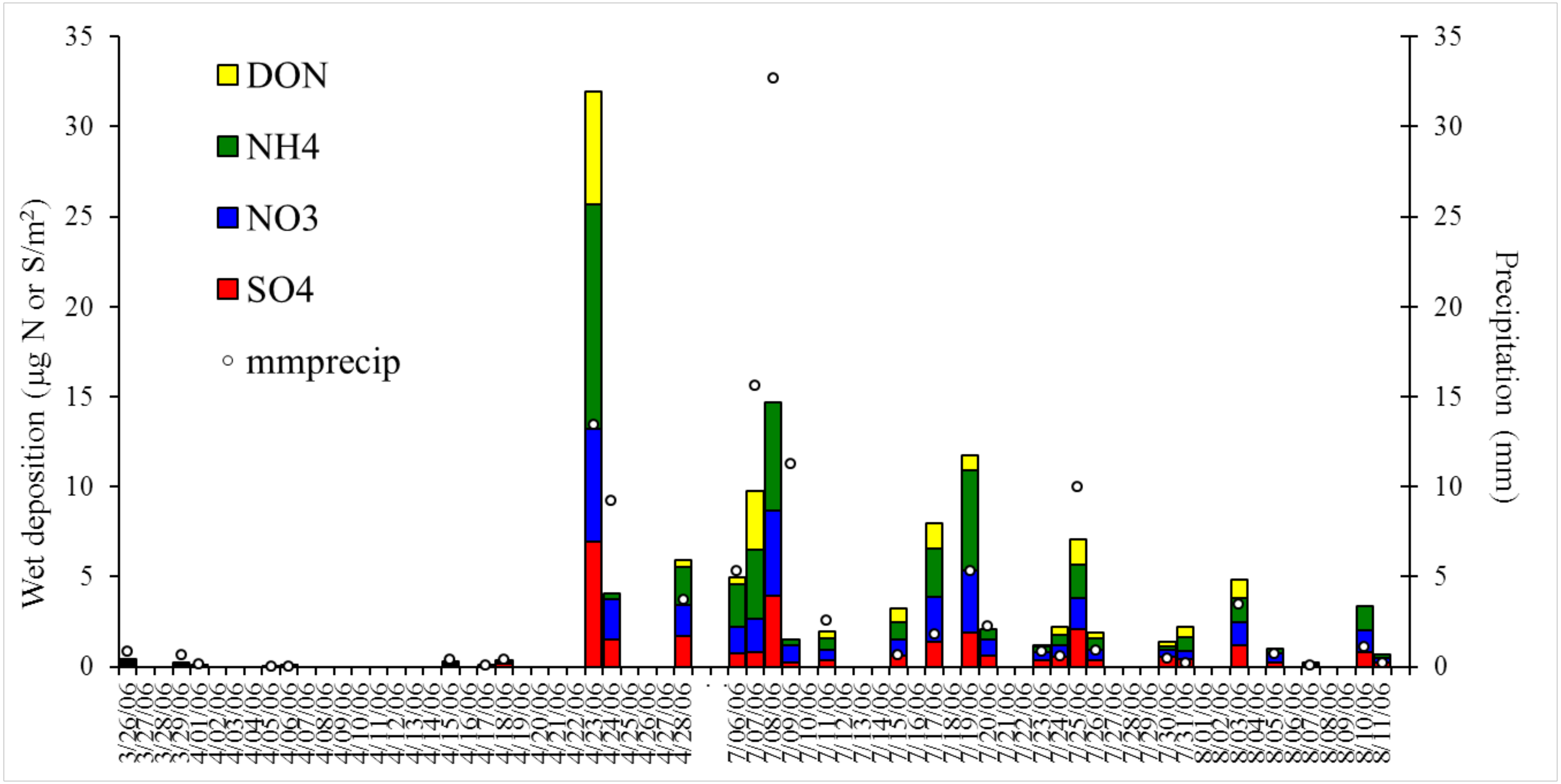


RoMANS (Rocky Mountain Airborne Nitrogen and Sulfur) Study



- Major field studies
  - Spring and Summer 2006
  - 2008-09

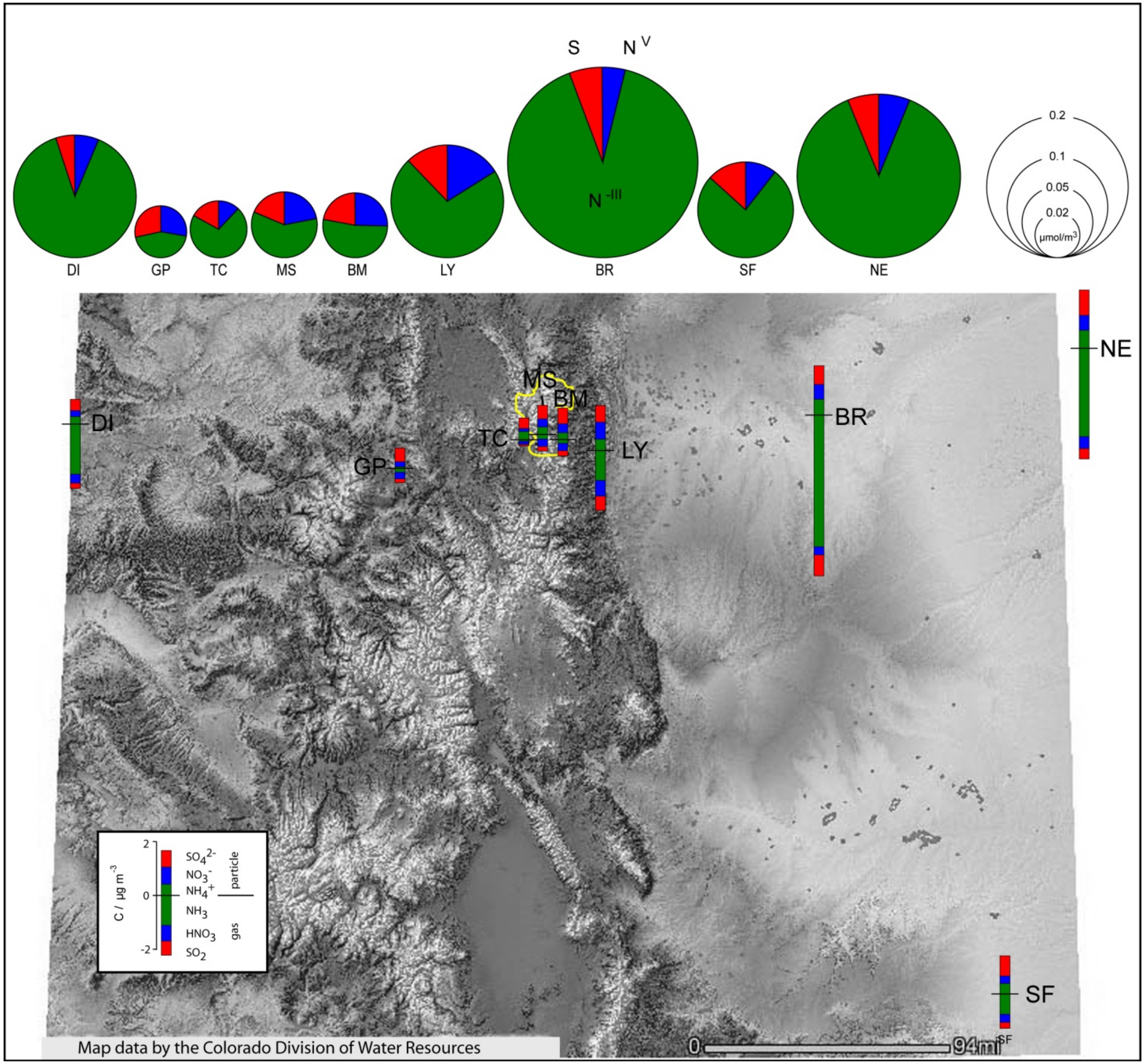
RoMANS 2006 core site wet deposition



- Spring flux dominated by single event -- summer flux contributed by several events
- Substantial oxidized, reduced, and organic N

Spring overview

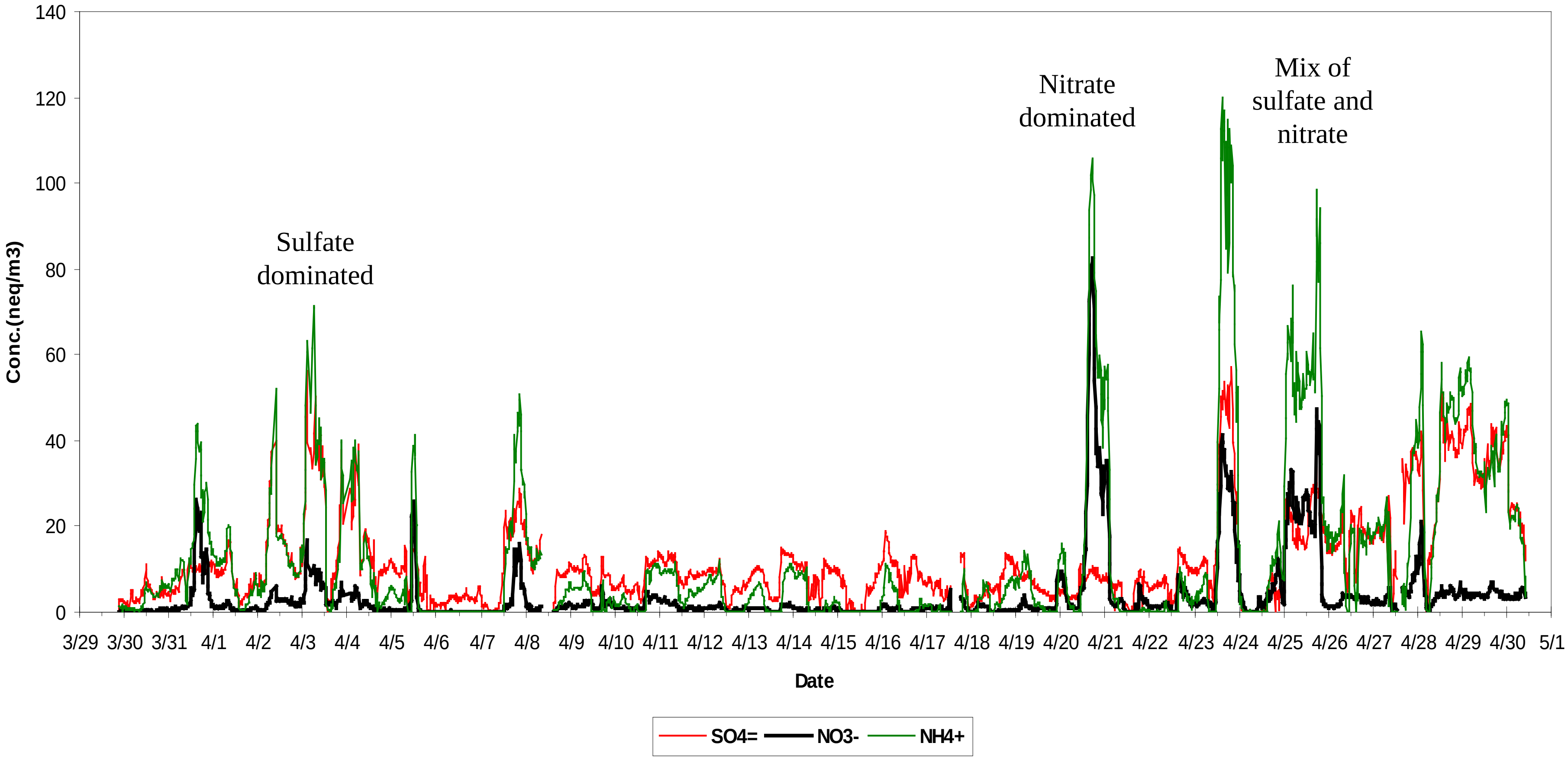
- Strong concentration gradient
- Low concentrations west of RMNP
- High concentrations east of RMNP
- Ammonia peaks in NE Colorado



Map data by the Colorado Division of Water Resources

RMNP particle timelines

- Highly variable concentrations
- Pollutant mix (sulfate, nitrate, and ammonium) varies between episodes



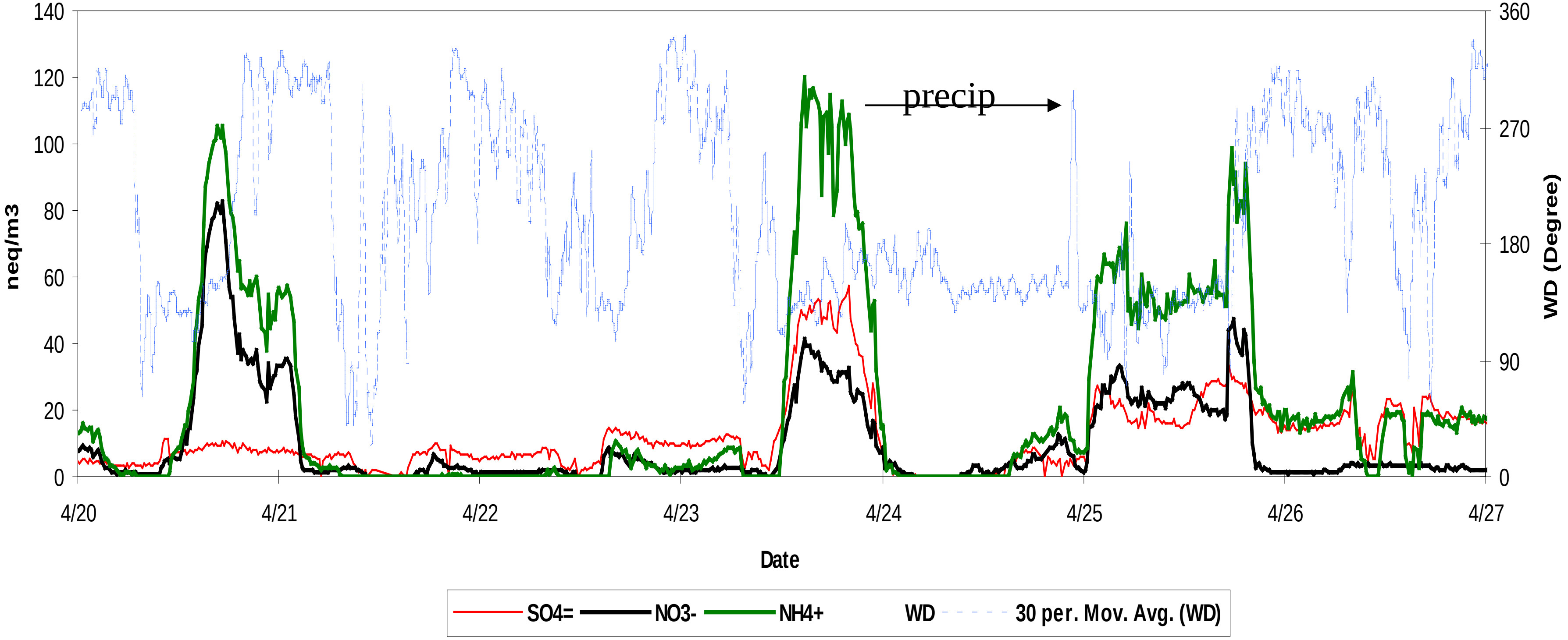
Sulfate dominated

Nitrate dominated

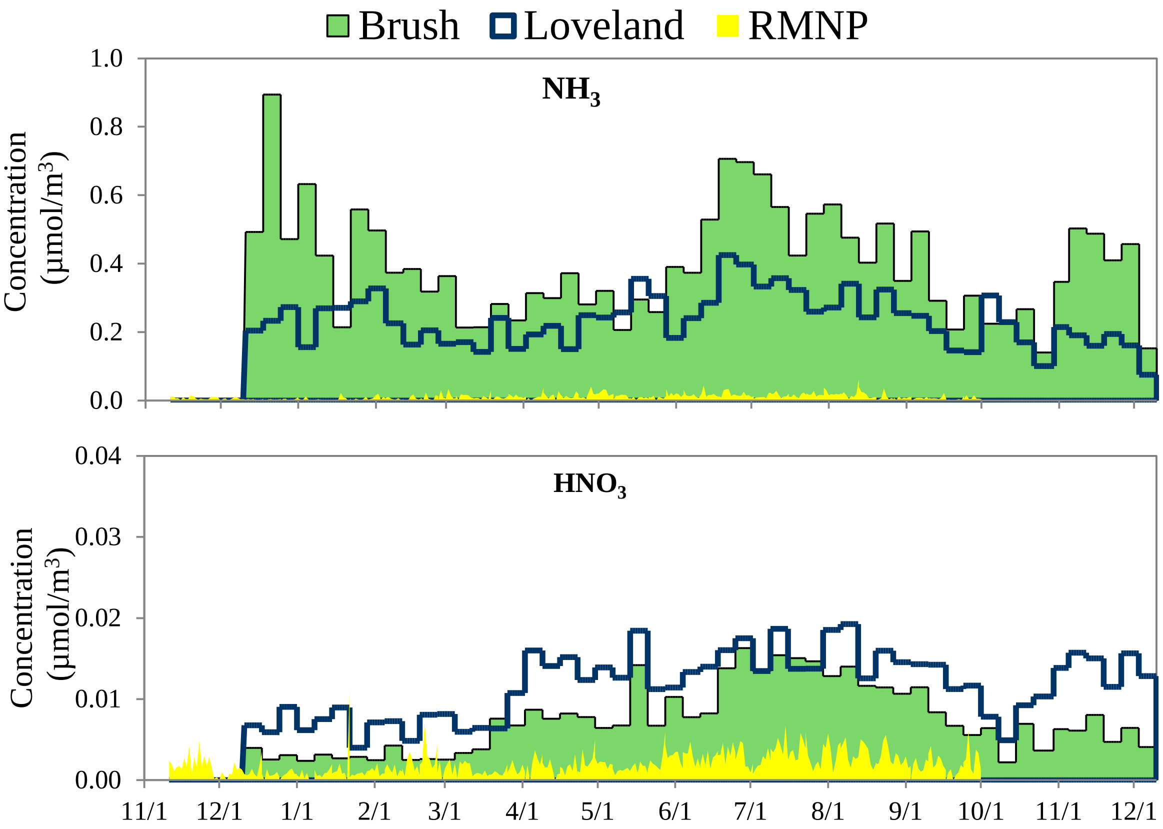
Mix of sulfate and nitrate

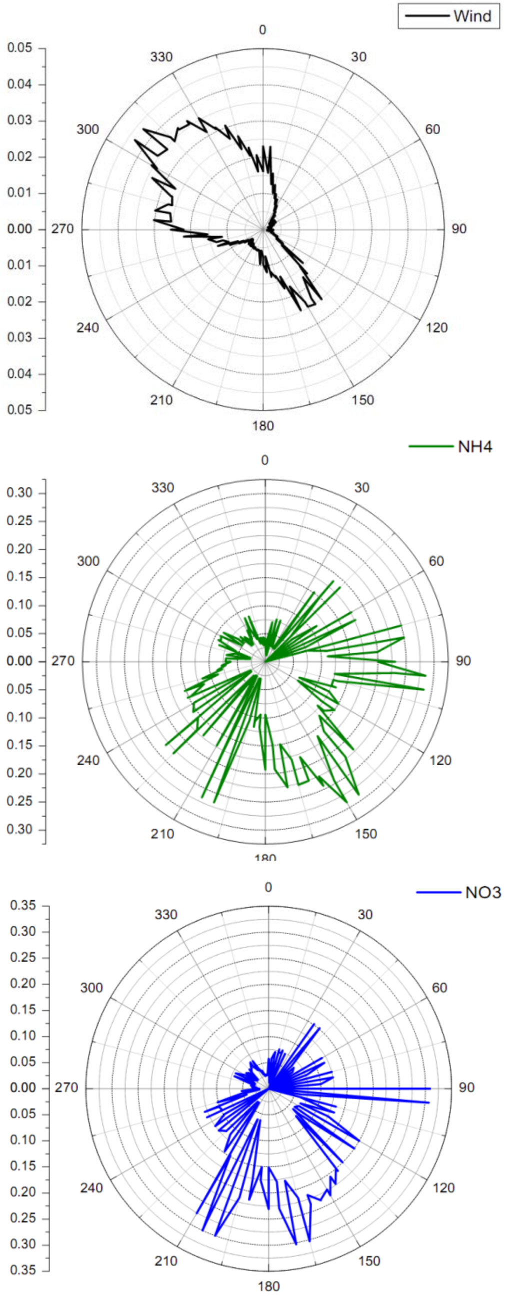
A closer look…

- Ammonium nitrate episodes associated with upslope flow from east of RMNP

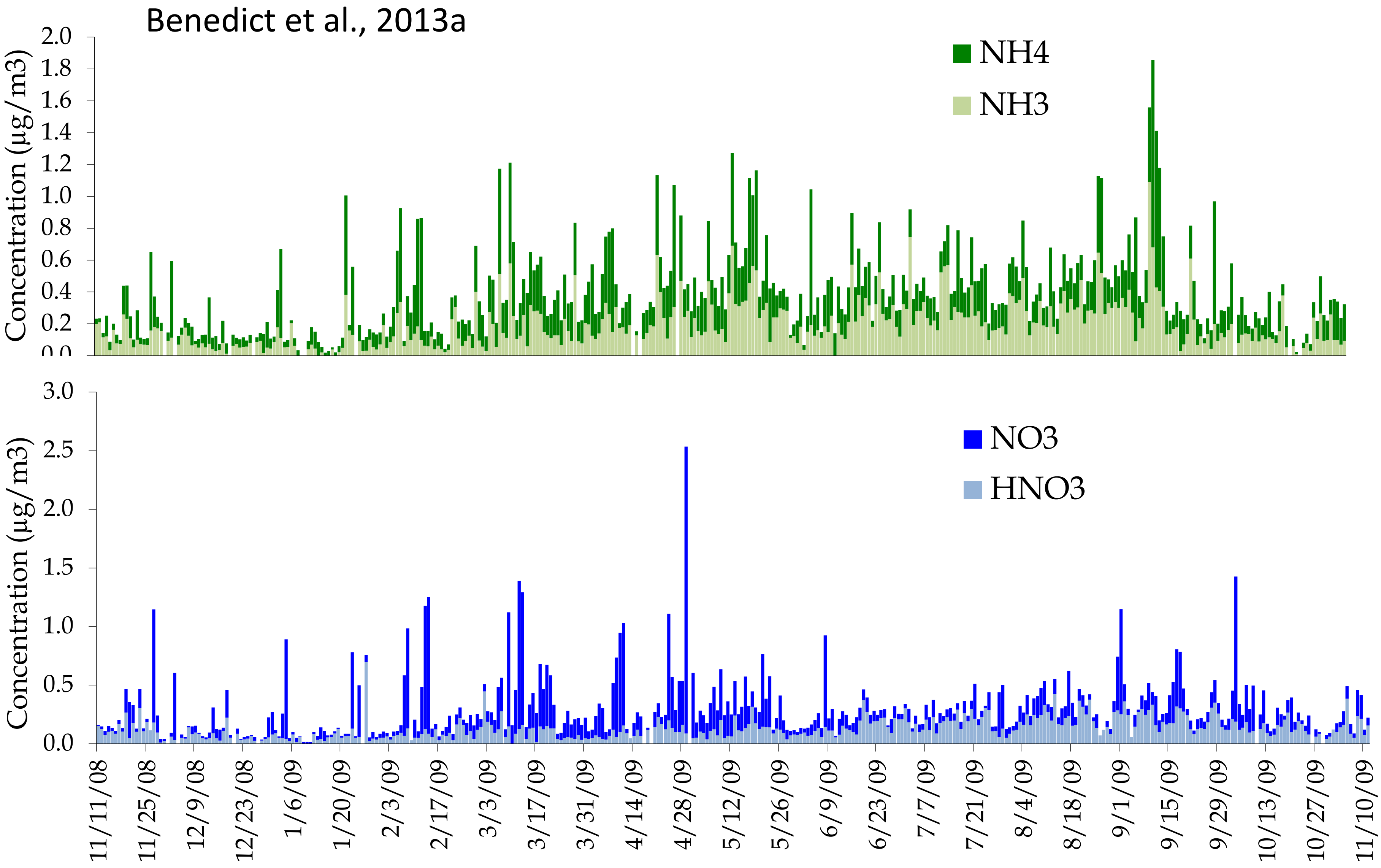


Annual mountain to plains gradient

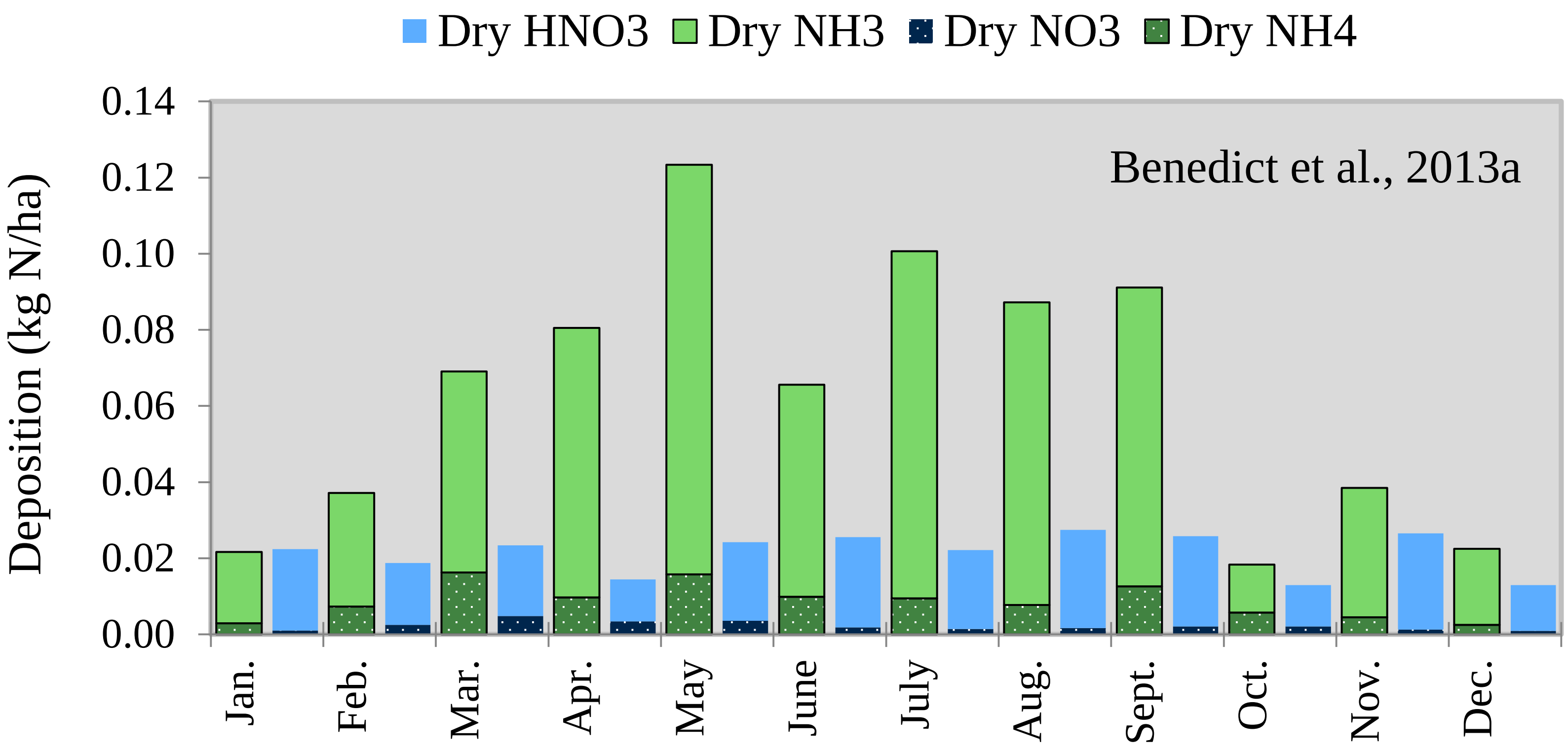




RMNP reactive N concentrations



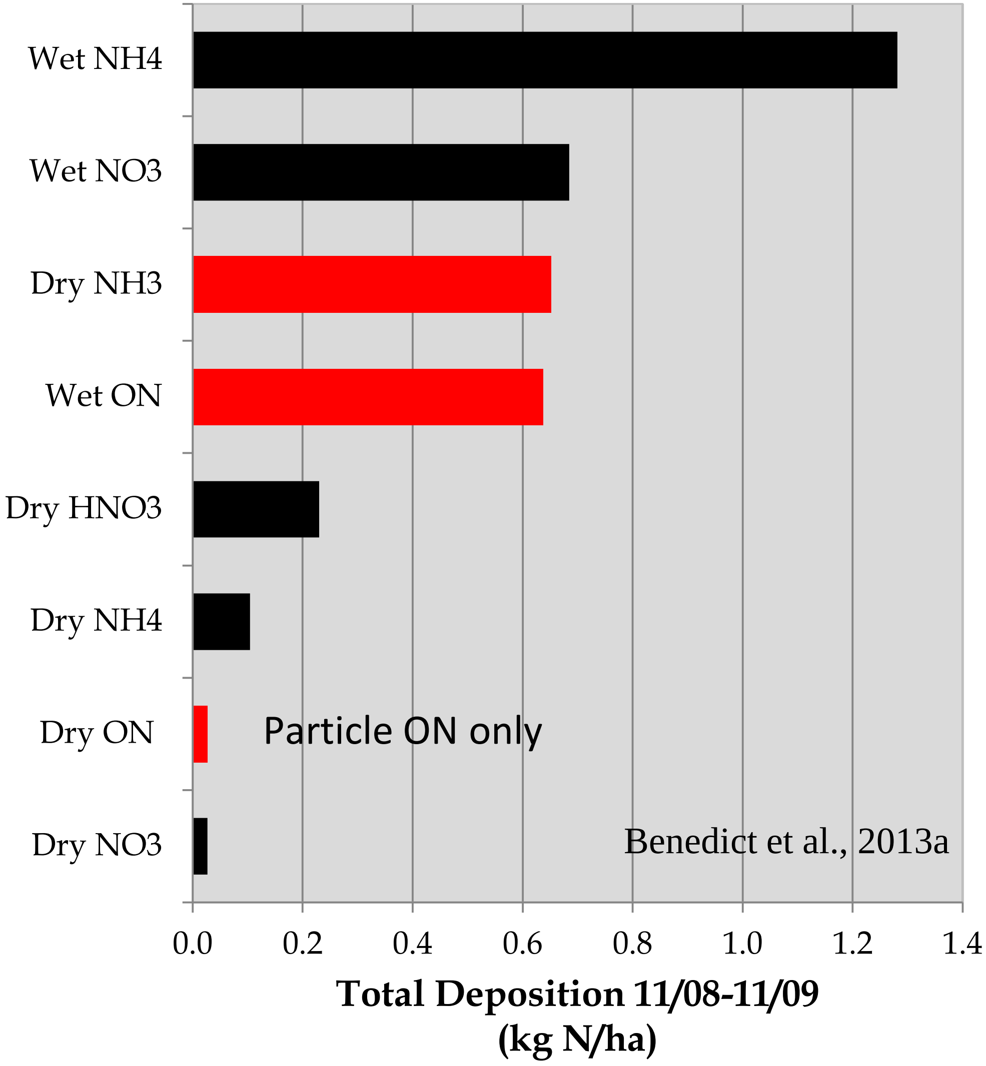
RMNP seasonal dry deposition budget



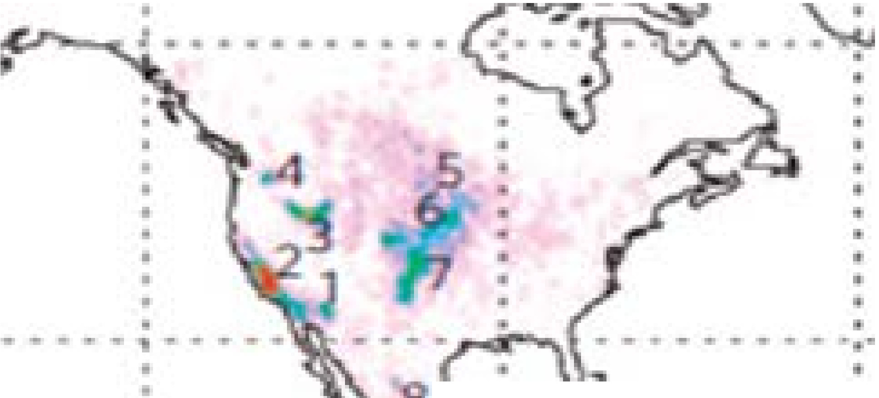
- Ammonia deposition most important; spring and summer peaks

RMNP N deposition – annual budget

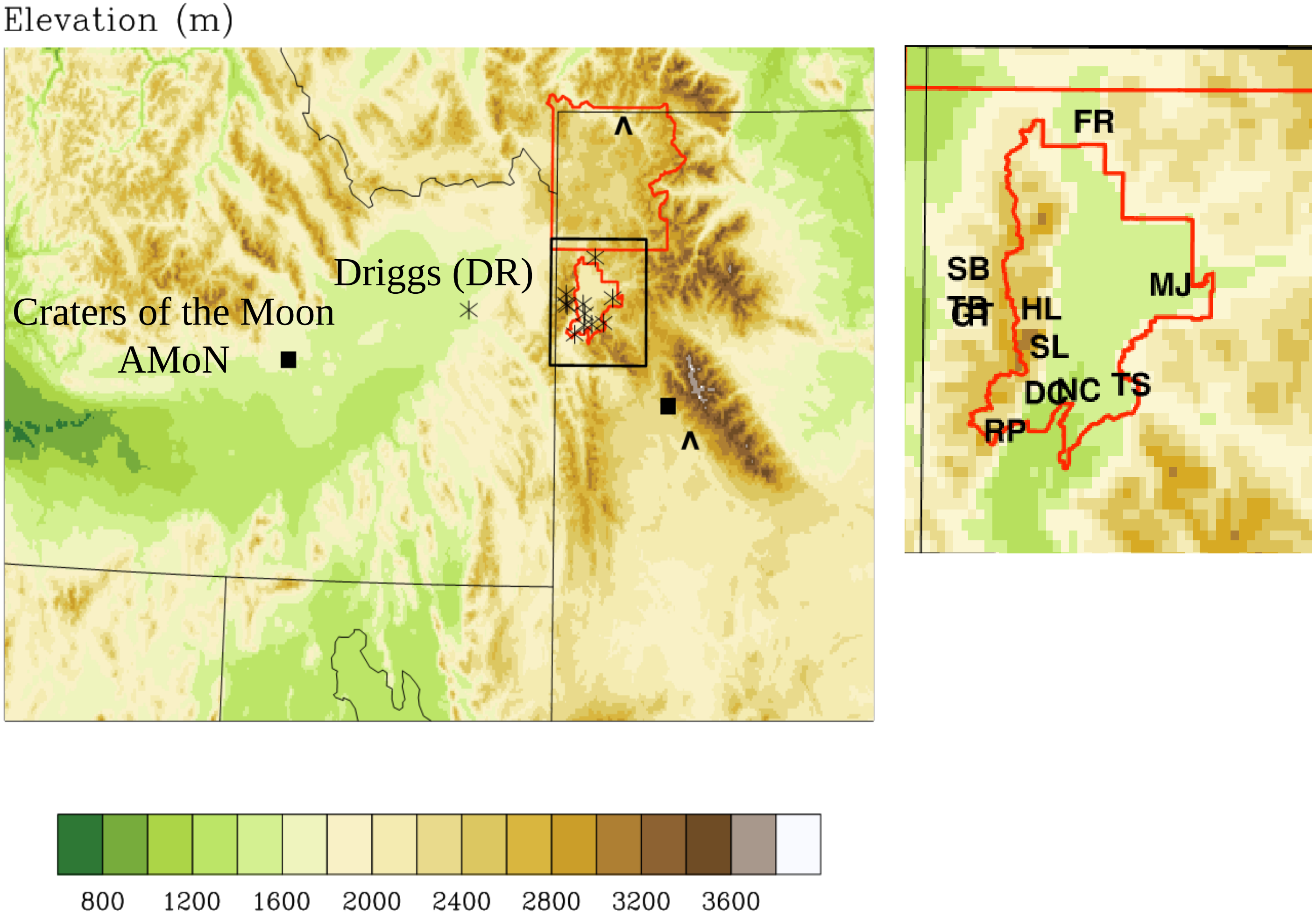
- Wet deposition biggest contributor to N deposition
- Dry deposition strongly dominated by NH_3



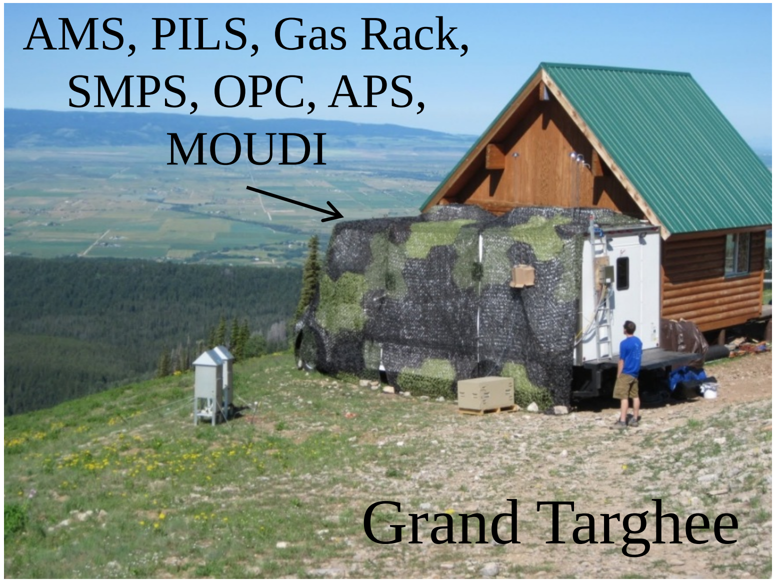
The 2011 Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS)

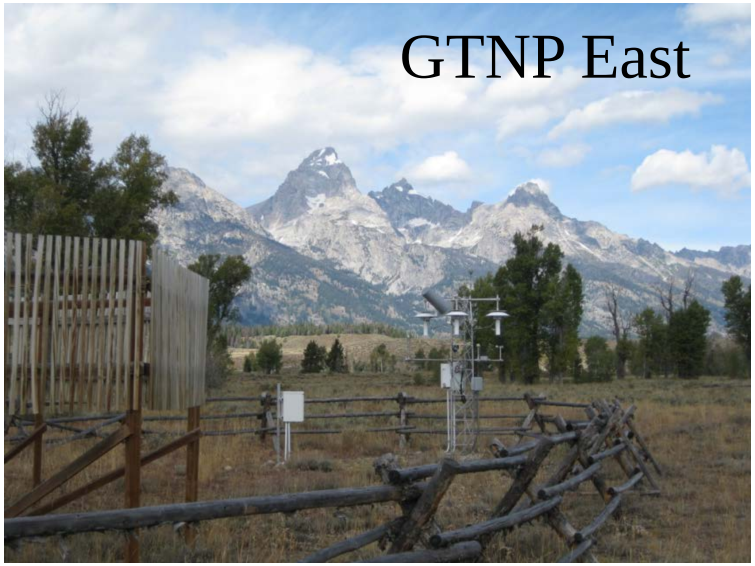


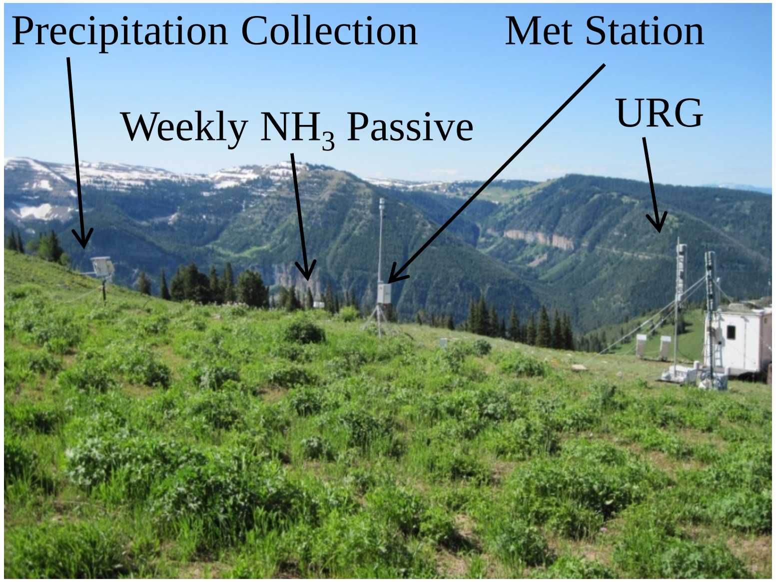
Clarisse et al. (2009)
IASI satellite NH_3

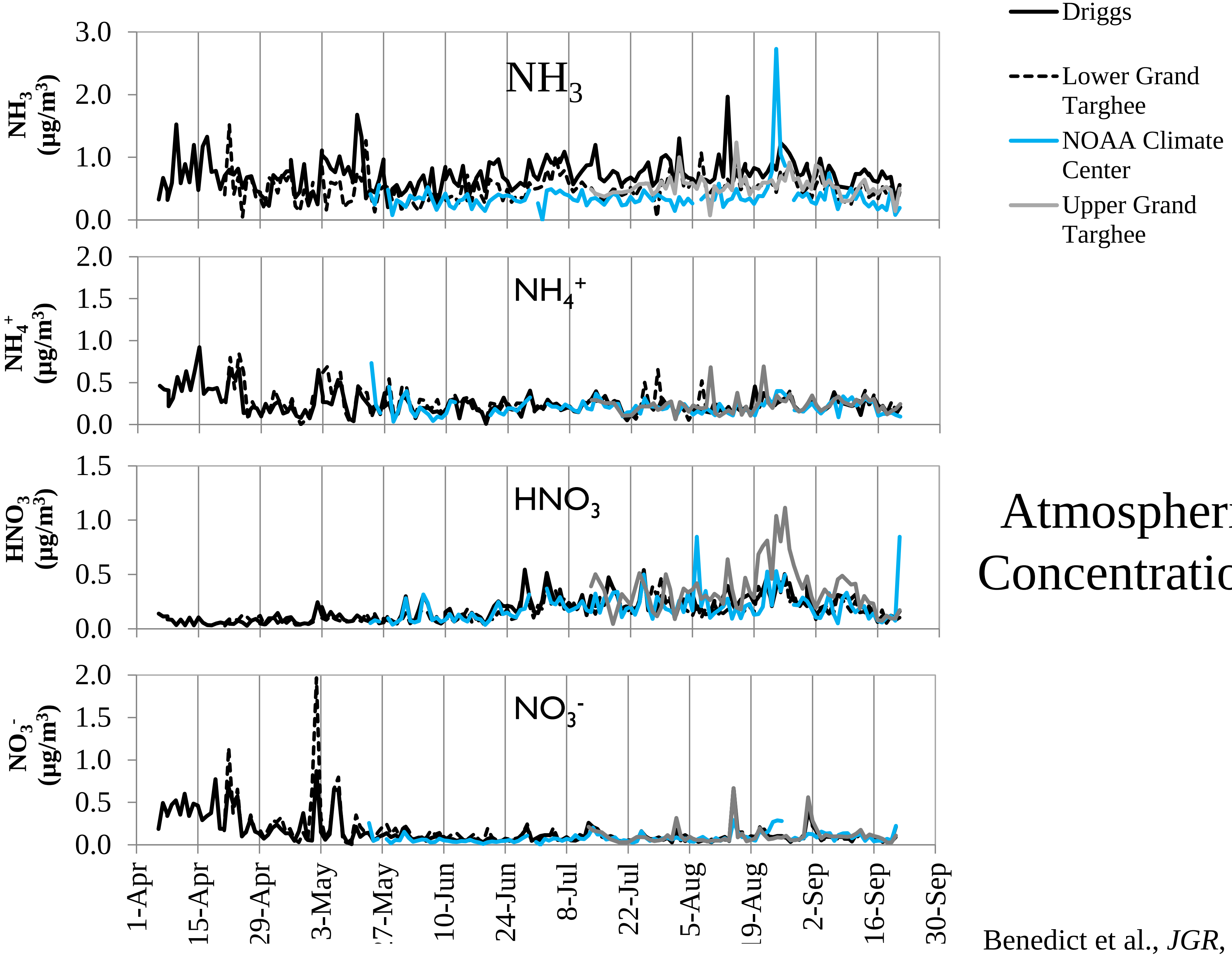


Selected GrandTReNDS sites







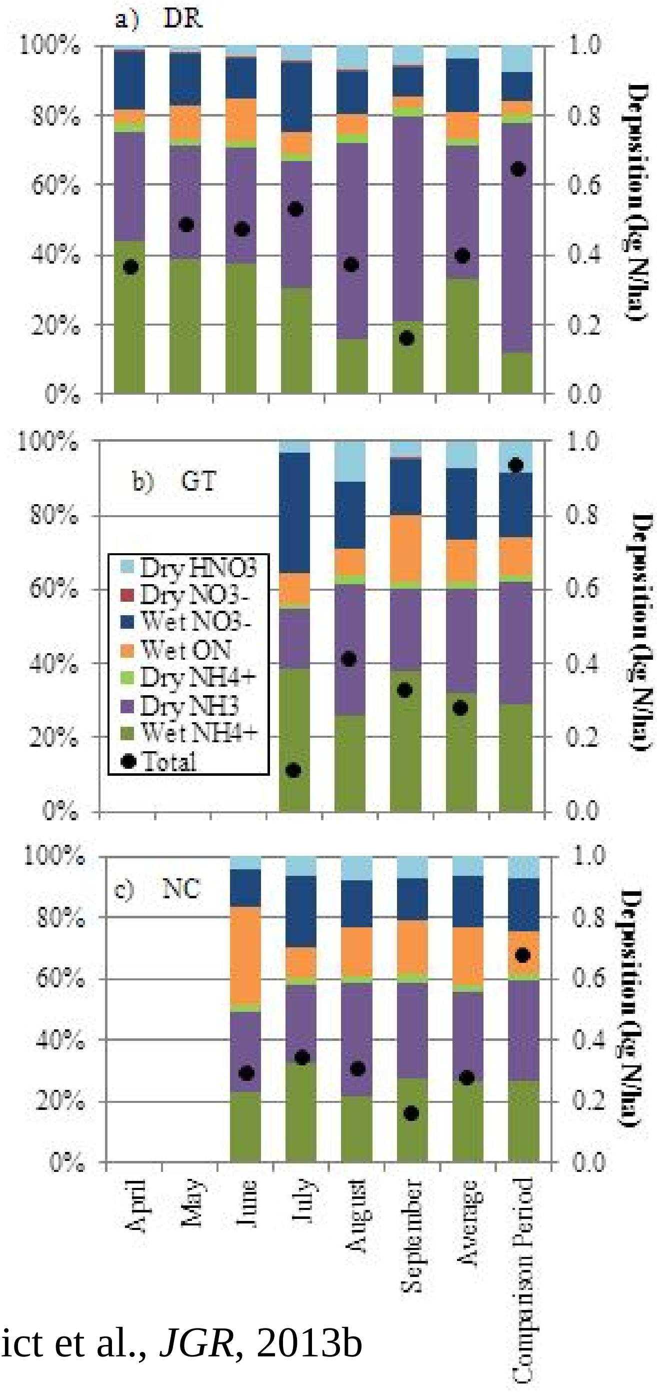


Atmospheric Concentrations

Benedict et al., *JGR*, 2013b

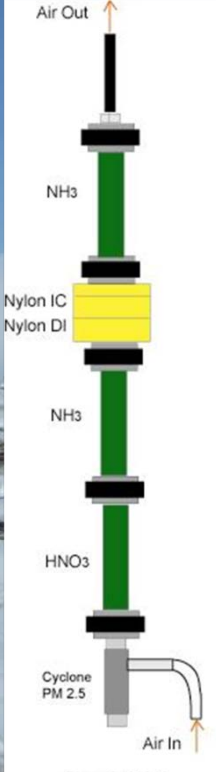
GrandTReNDS deposition budgets

- Reduced nitrogen comprises 50-80% of the N deposition budget
  - even more important here than in Rocky Mountain National Park



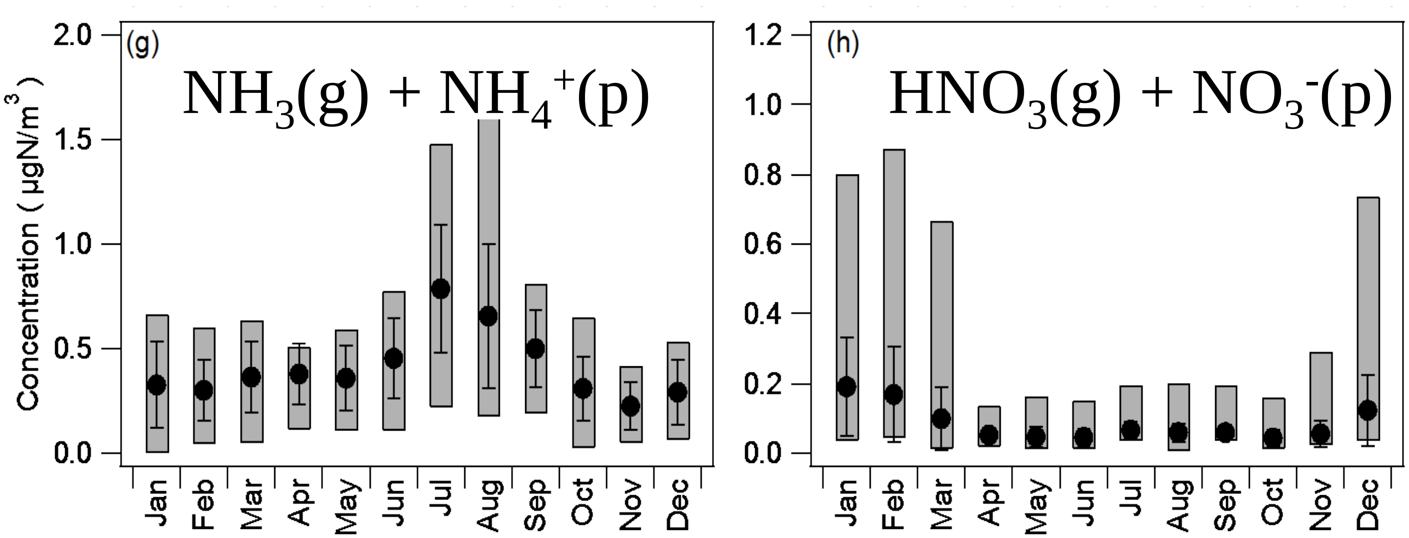
Benedict et al., *JGR*, 2013b

Long-term measurements of the NH_x-NO_x-SO_x system in Boulder, WY – one of the largest U.S. natural gas producing regions



CSU, Air Resource Specialists, Shell

How much NH_3 is available to react with NO_x oxidation products to generate fine particles and lead to haze formation?

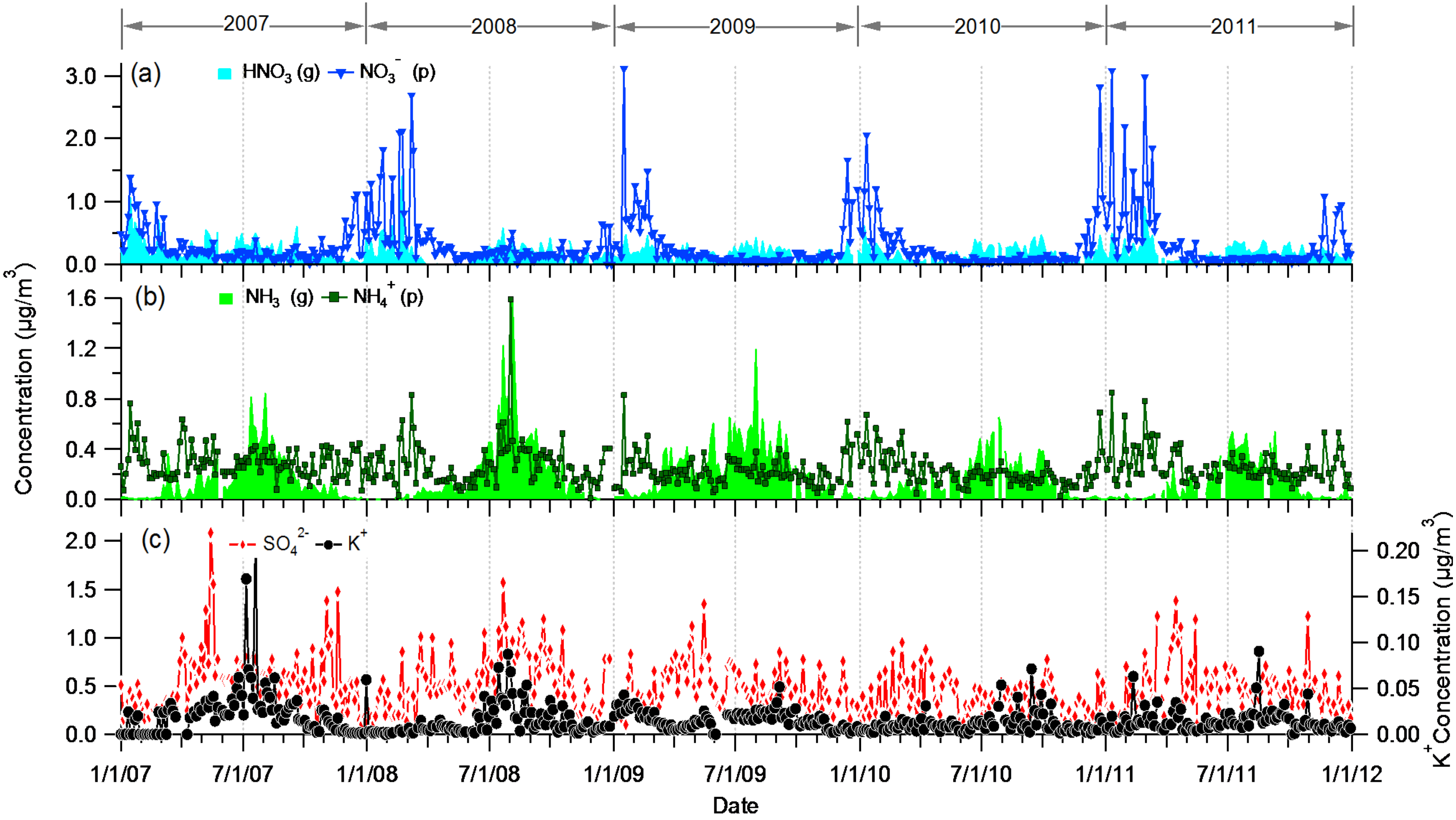


Reduced nitrogen shows typical summer max

Oxidized nitrogen shows unusual winter max tied to winter photochemical smog

Li et al., *Atmos. Env.*, 2013

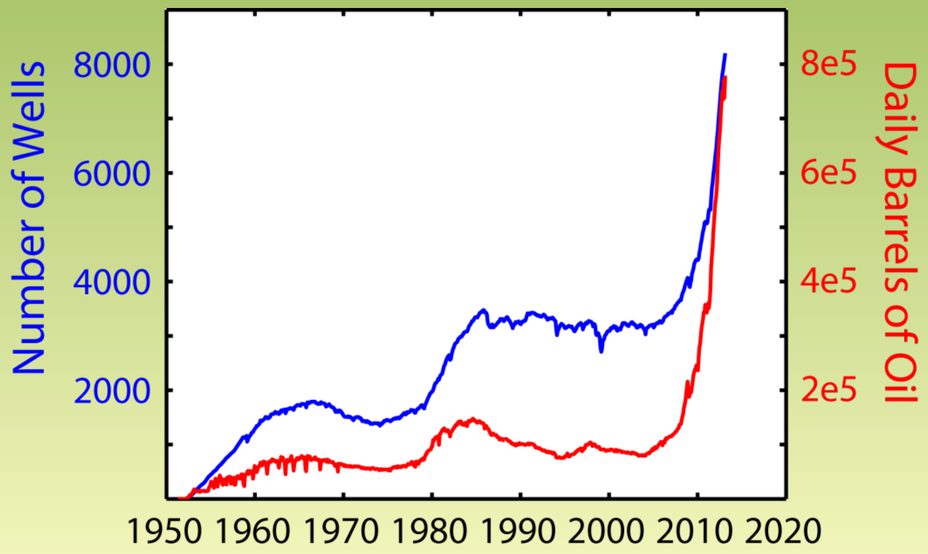
Li et al., Atmos. Env., 2013



- Active winter photochemistry produces high ozone and nitric acid
- Winter fine particle nitrate formation limited by ammonia availability

Bakken Shale Oil and Gas Development

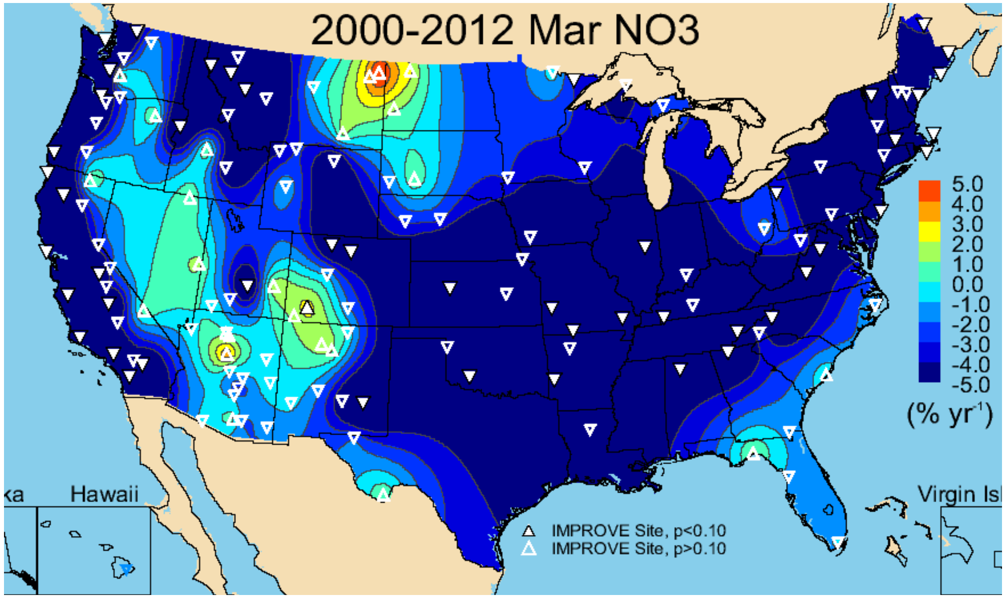
Oil Production in North Dakota



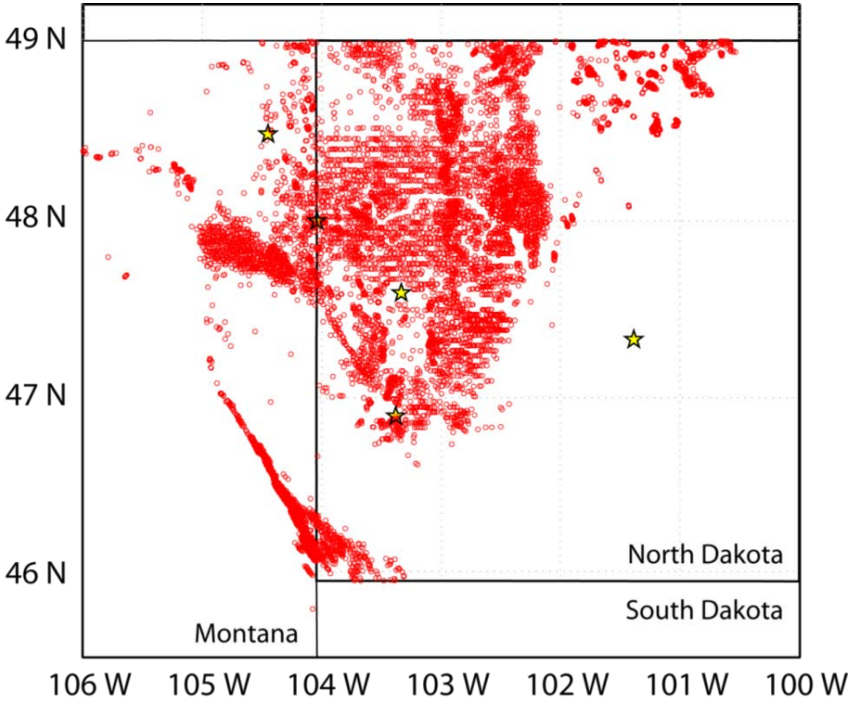
https://www.dmr.nd.gov/oilgas/

Photo: W. Malm

Air quality in the Bakken shale region



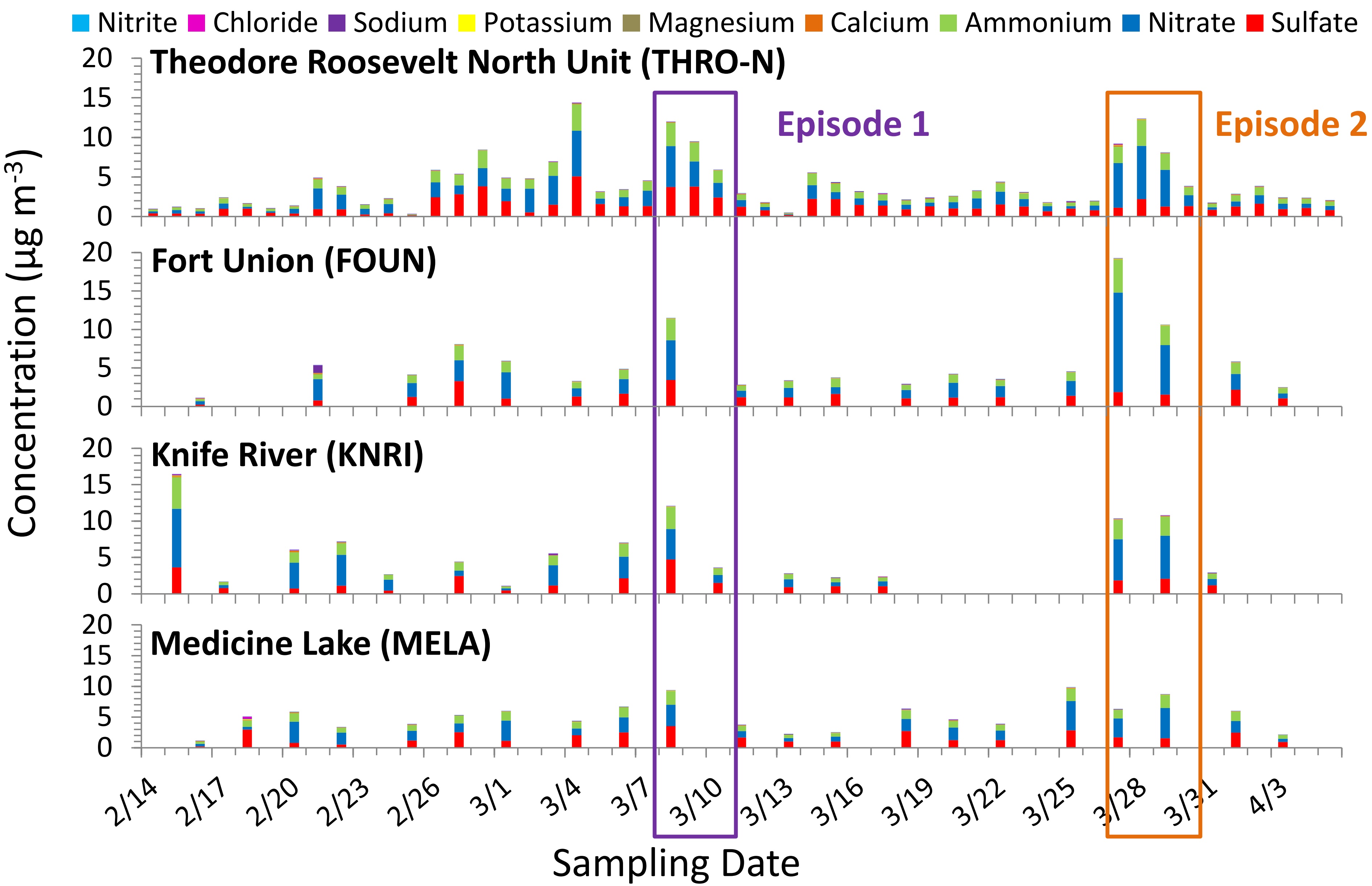
From J. Hand



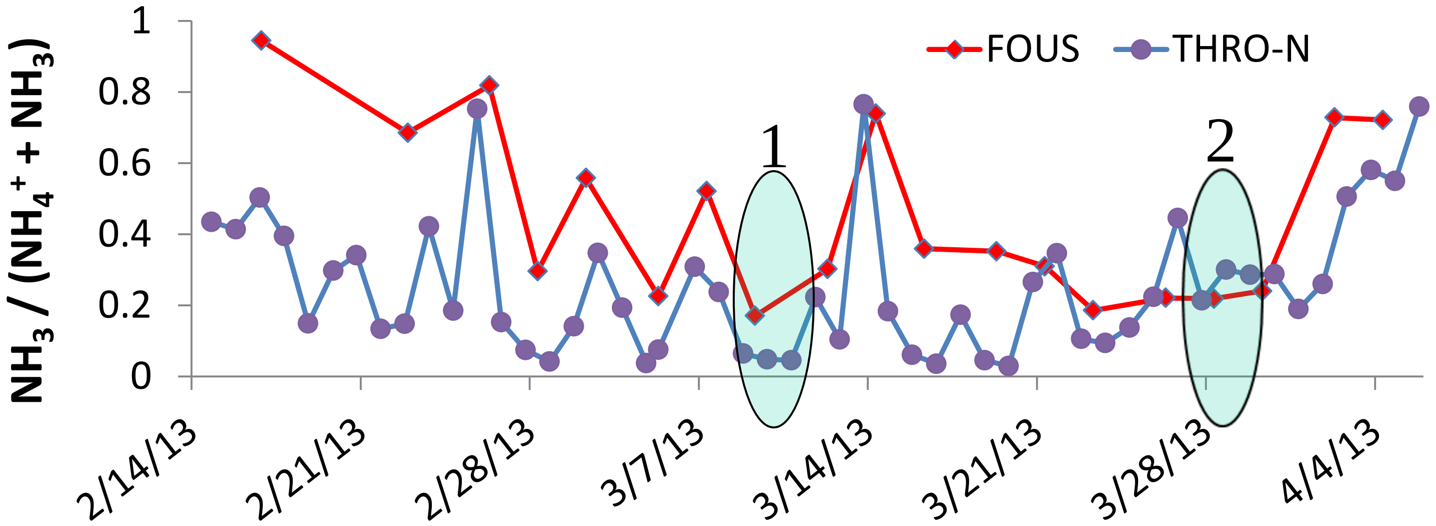
Winter fine particle nitrate increasing in parts of western U.S.

Winter 2013 study conducted across region of extensive oil well drilling to examine air quality impacts

Bakken Particle Composition



Does ammonia limit NH_4NO_3 formation in Bakken?



- Ammonia nearly depleted in Theodore Roosevelt National Park during episode 1, but not episode 2.

- Excess ammonia always available at Fort Union.
  - HNO_3 currently limits NH_4NO_3 formation

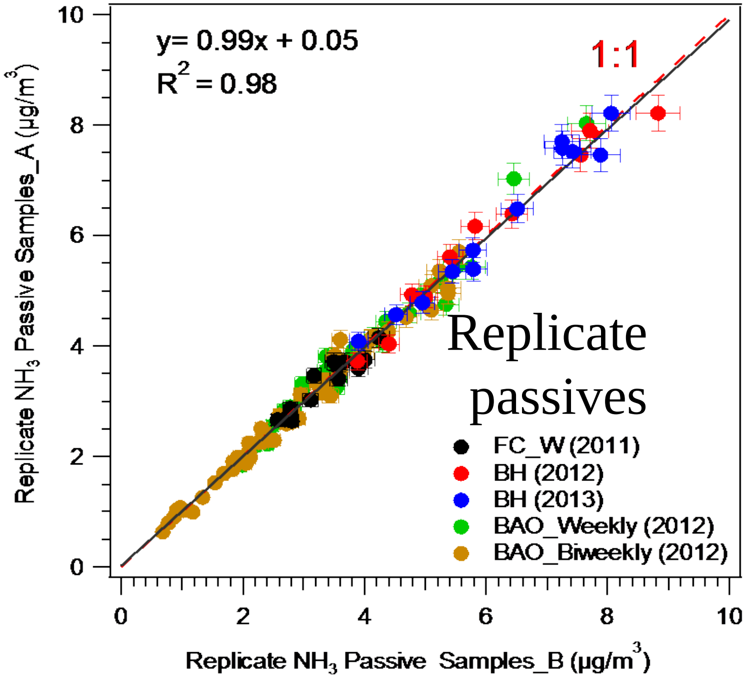
HOW CAN WE ROUTINELY MEASURE NH_3 AND NH_4^+ ?

U.S. network measurements of inorganic N species concentrations

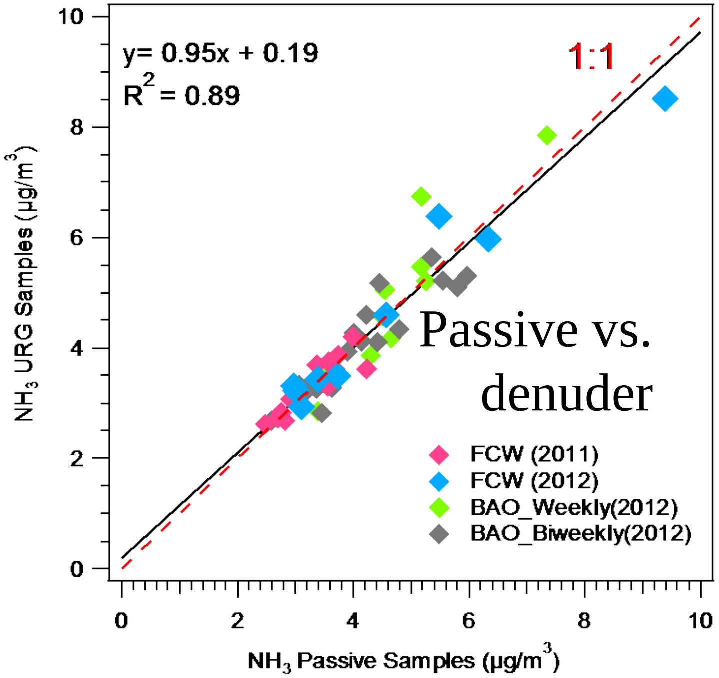
- NO_3^-
  - CASTNet quantifies PM2.5 deposition
  - PM2.5 concentrations also measured by IMPROVE and CSN
- HNO_3
  - CASTNet quantifies weekly concentration/deposition
- NH_4^+
  - CASTNet quantifies weekly concentration/deposition
- NH_3
  - AMoN (bi-weekly)
  - Regional networks (e.g., SEARCH)
  - Short-term/special studies

Radiello passive NH_3 samplers

- Inexpensive
- Greater spatial coverage
- ~1-2 week time resolution
- Excellent precision and good accuracy
- NH_3 only

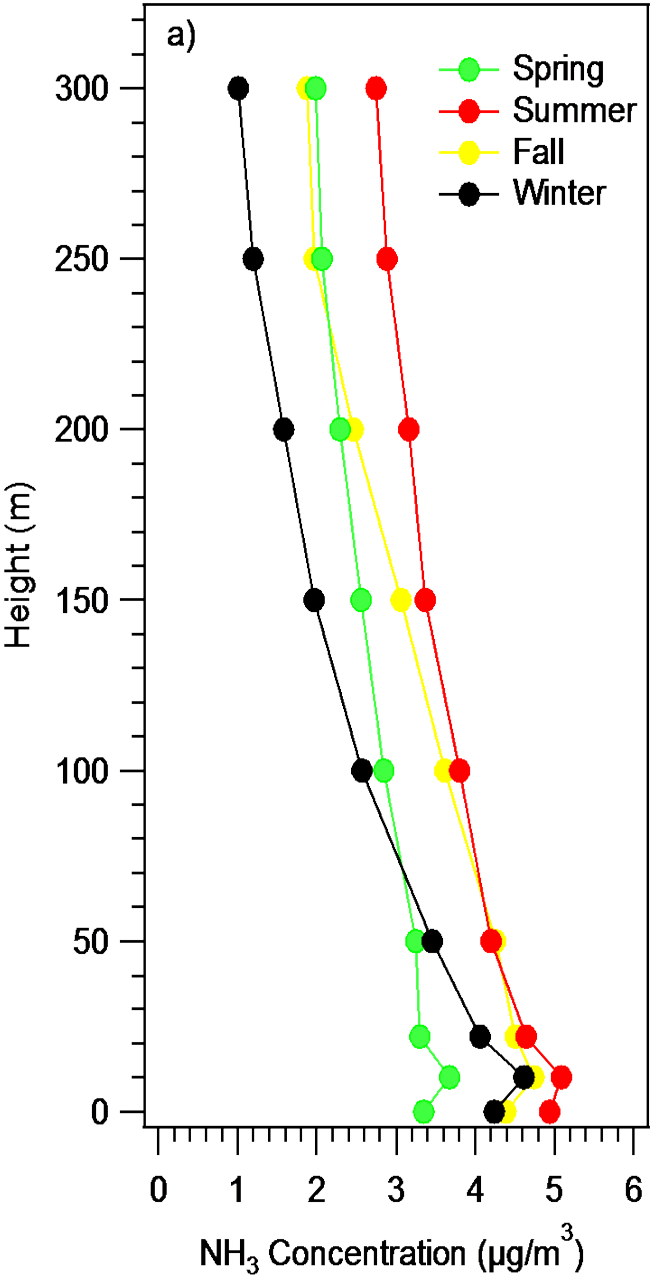


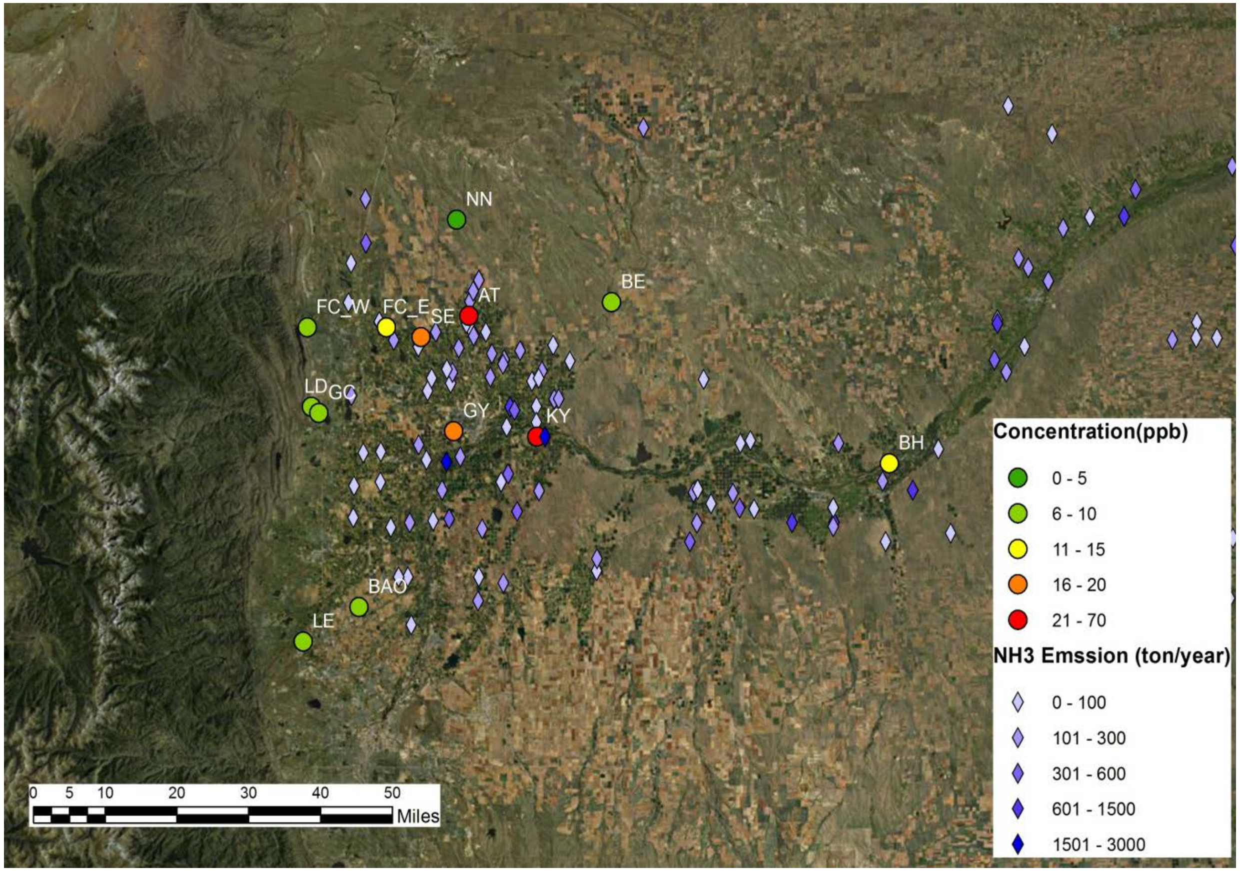
Replicate passives



Passive vs. denuder

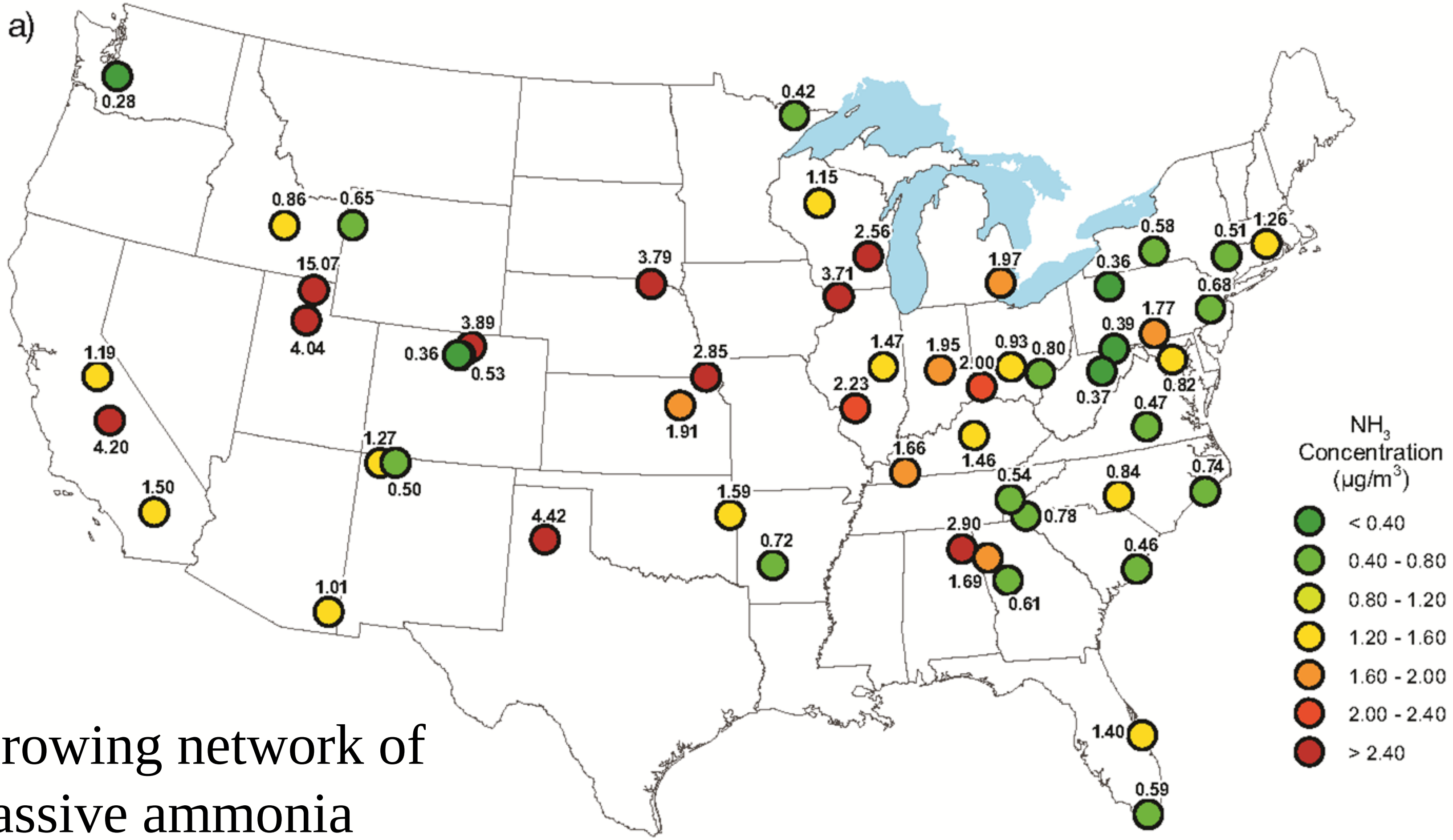
NE Colorado spatial NH_3 gradients





Li et al., in prep

NADP AMoN Network



- Growing network of passive ammonia sampling
- Ideal for NH_3 deposition

Figure courtesy of Chris Lehmann

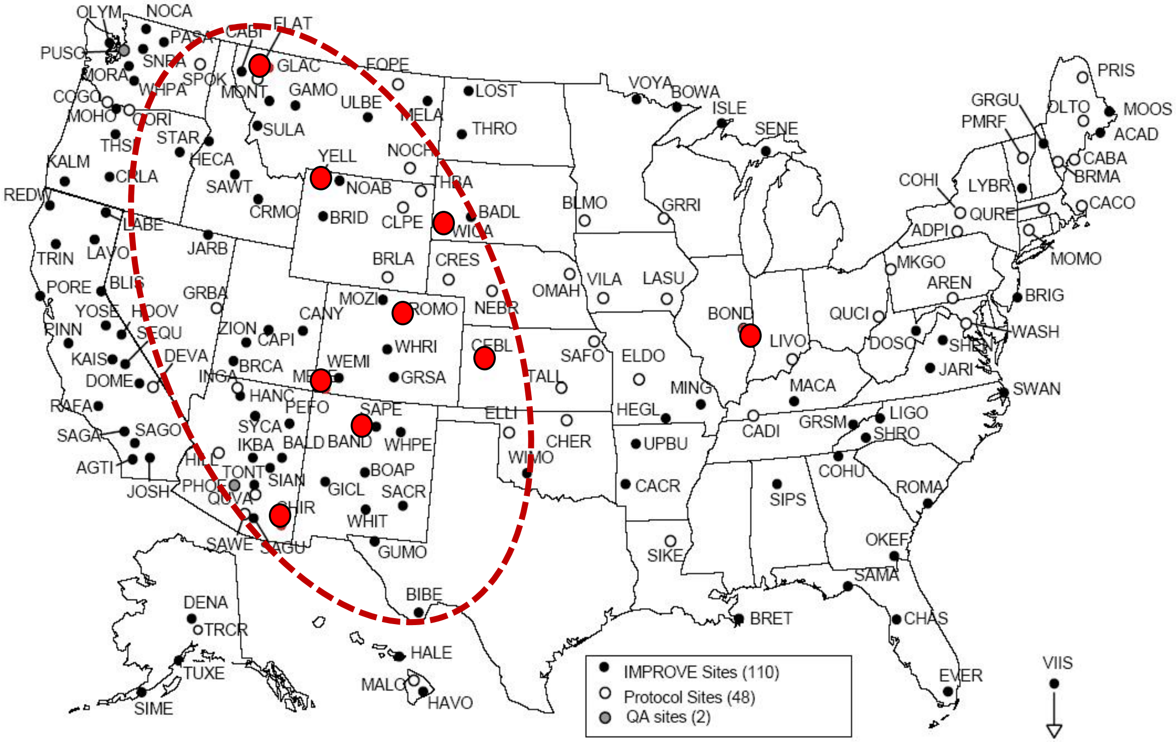
Limitations to AMoN passive sampling approach

- Low time resolution (1-2 weeks is typical) makes source attribution difficult

- Does not measure NH_4^+
  - Leaves total NH_x burden unconstrained
  - Limits ability to understand PM formation
  - Limits ability to validate model simulations

Pilot IMPROVE NH_x network

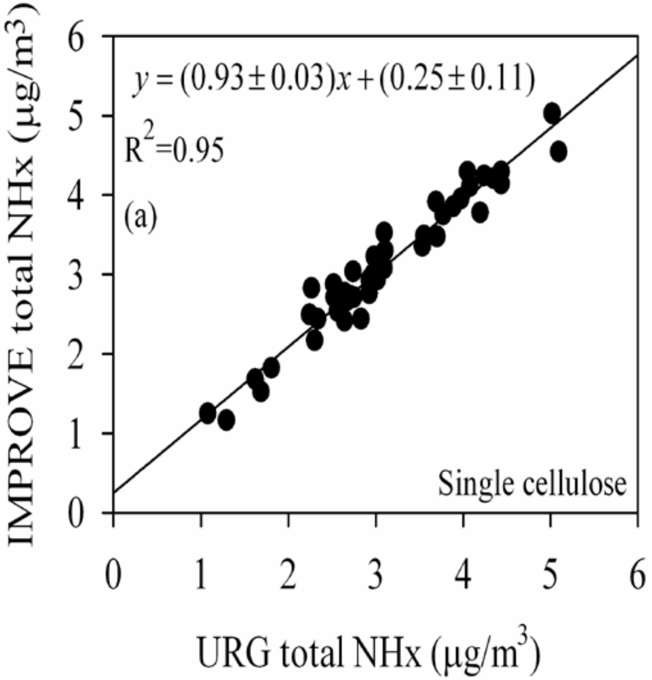
- Rocky Mountain focus
  - 9 sites, 1-in-3 day sampling
  - 4/2011 - 8/2012
- Single phosphorous acid-coated filter to capture $NH_4^+ + NH_3$

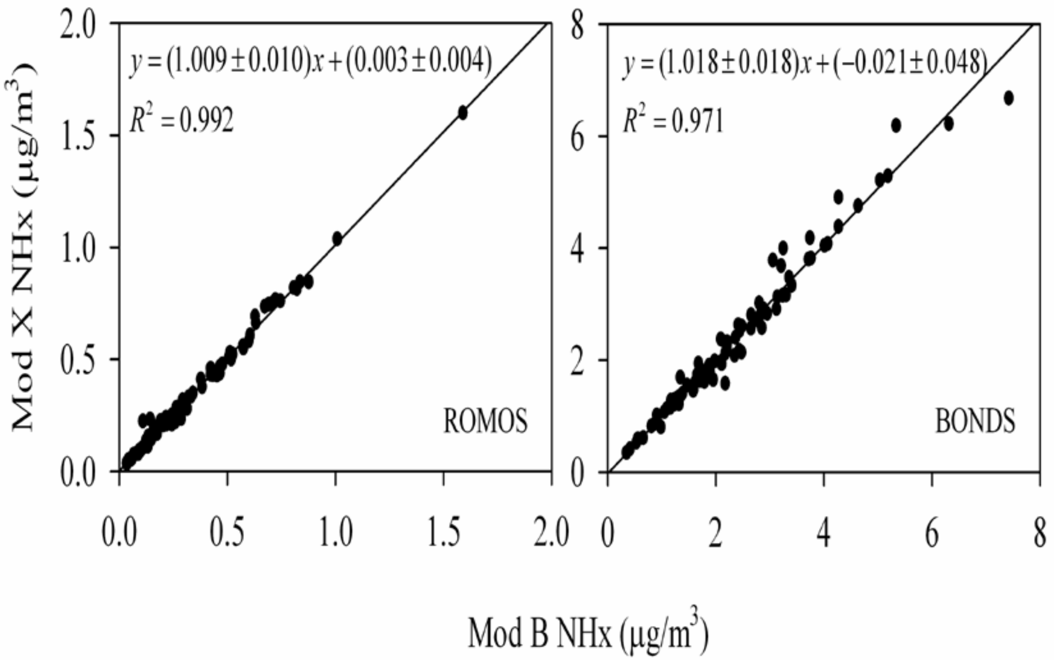


- ● IMPROVE Sites (110)
- ○ Protocol Sites (48)
- ● QA sites (2)

NH_x measurement quality

- Good accuracy vs. reference URG denuder/filter-pack (denuder + filter + backup denuder)

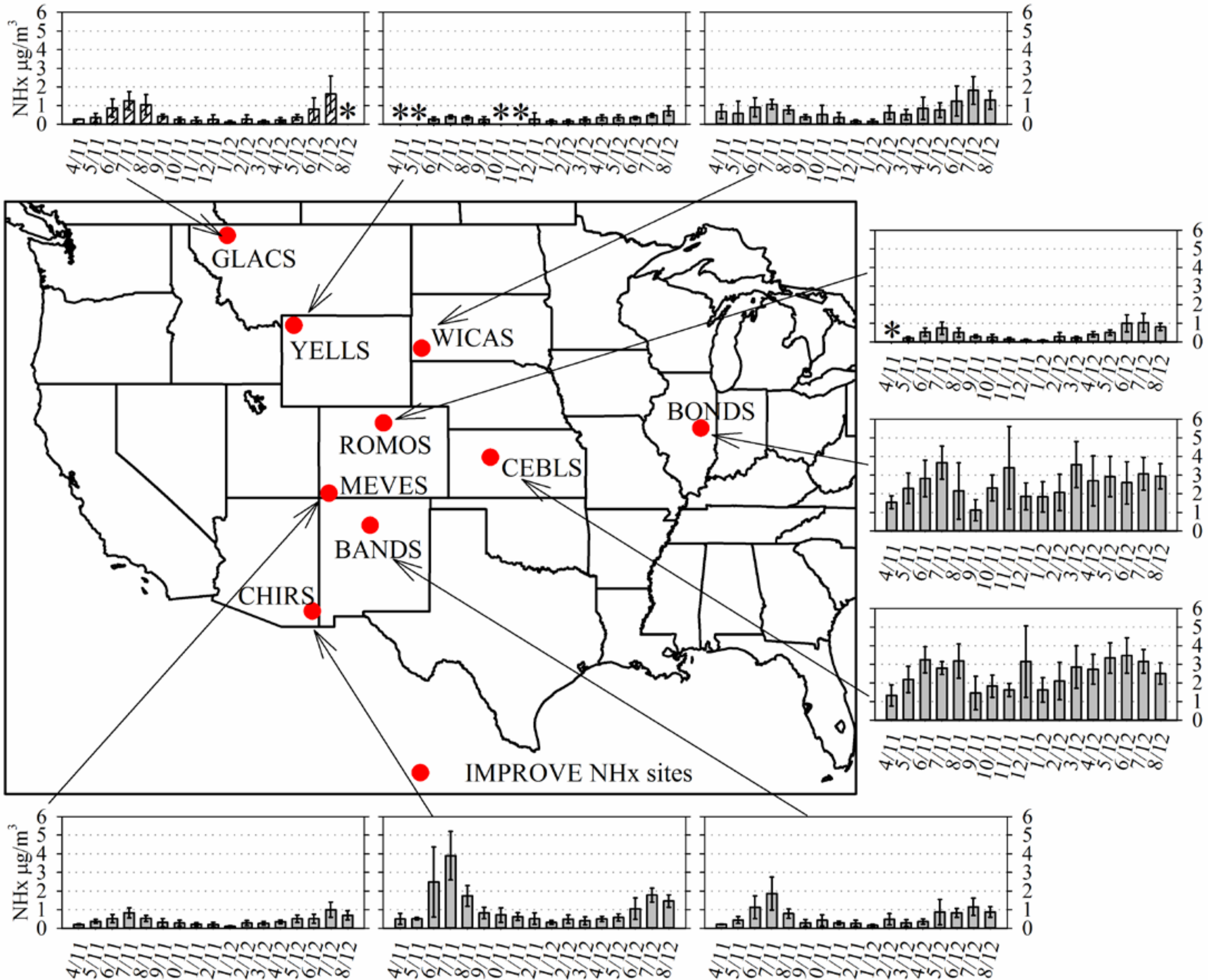




- Excellent field precision demonstrated by co-located samplers

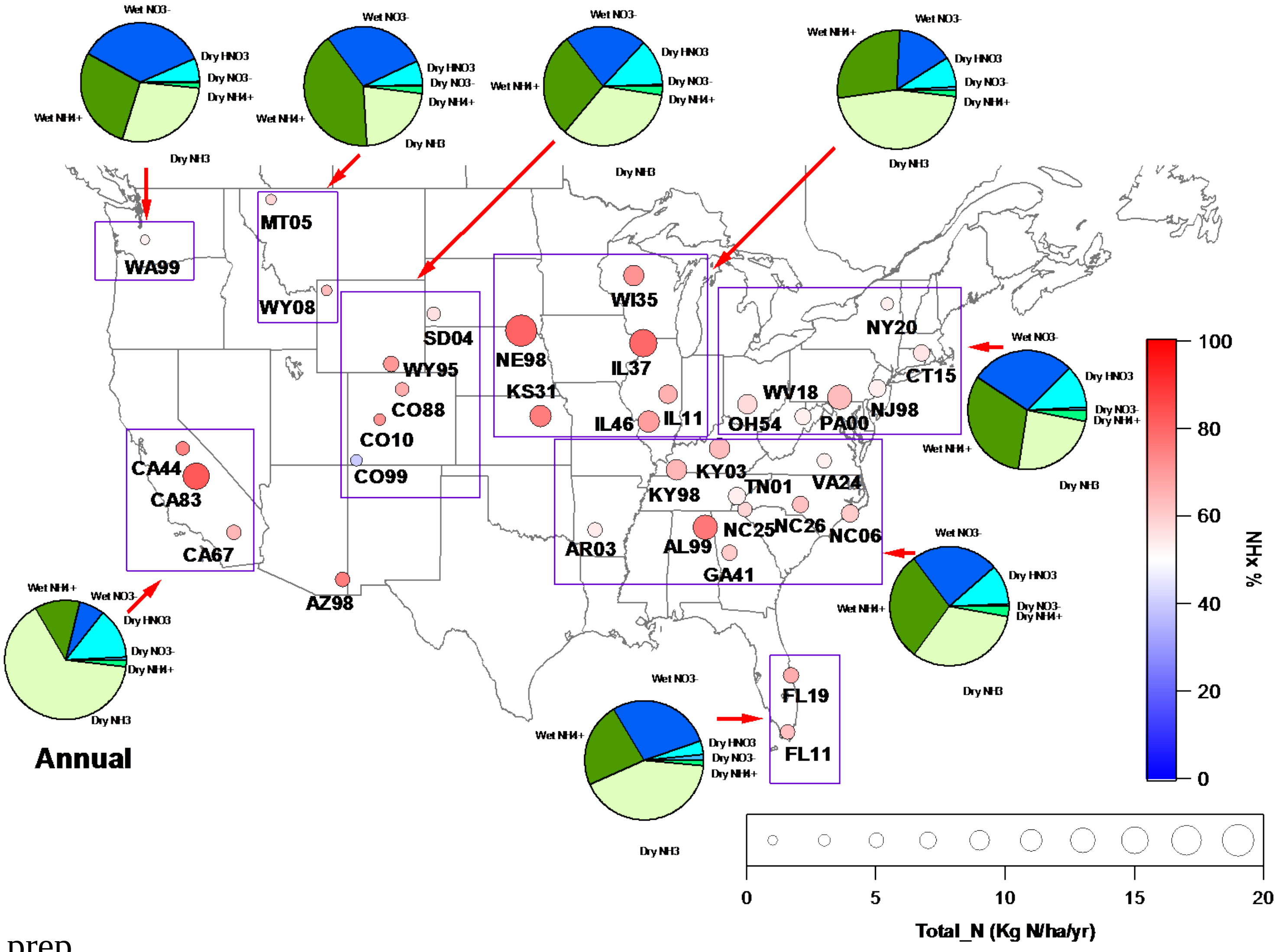
IMPROVE NHx data overview

- Highest concentrations at eastern and southern sites
- Seasonal cycle apparent at all sites
- Fall/winter secondary max in ag regions
- Fire influence at Chiricahua in 2011



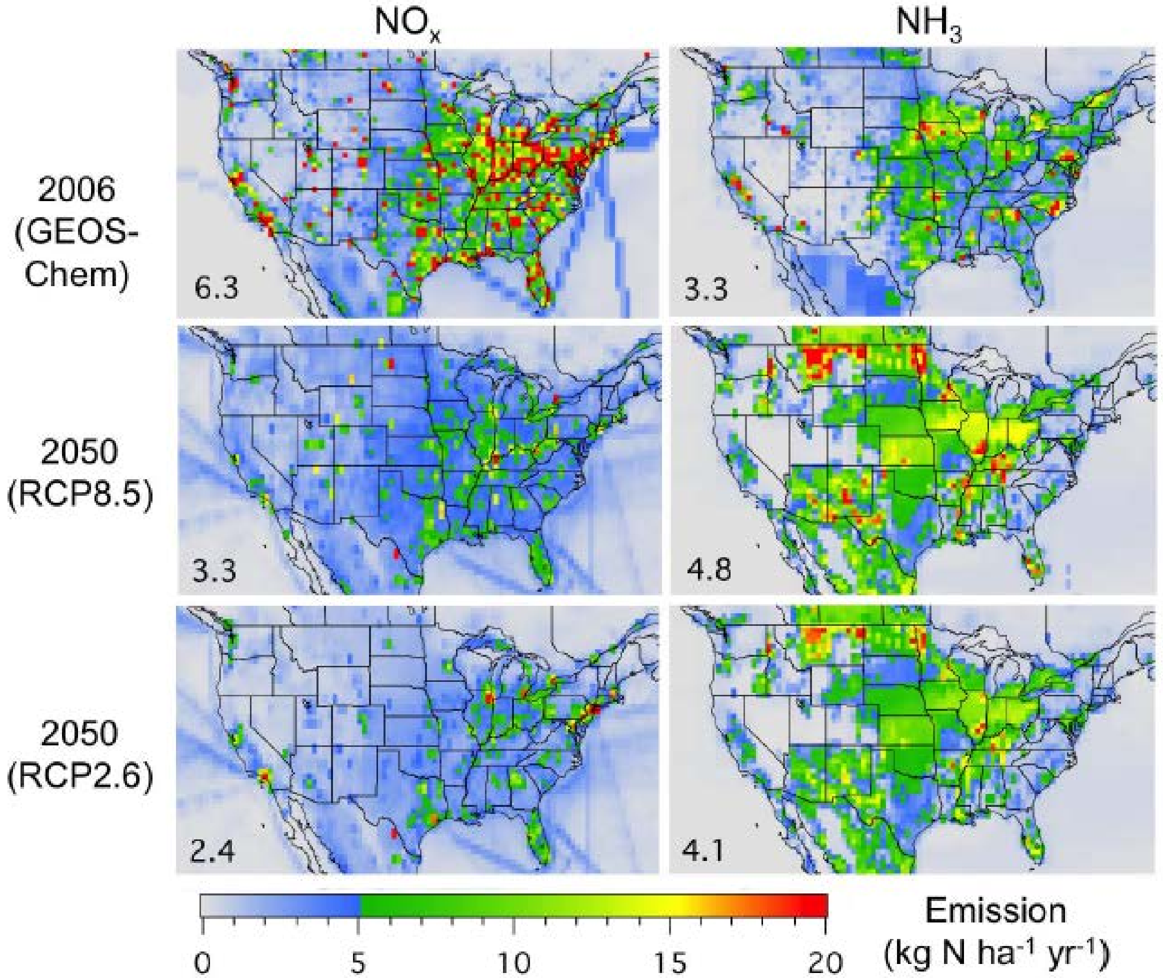
Chen et al., 2014

Total N deposition budgets: wet + dry



Li et al., in prep

Anticipated future emissions changes will make NH_x increasingly even more important



NO_x expected to decrease while NH_3 increases

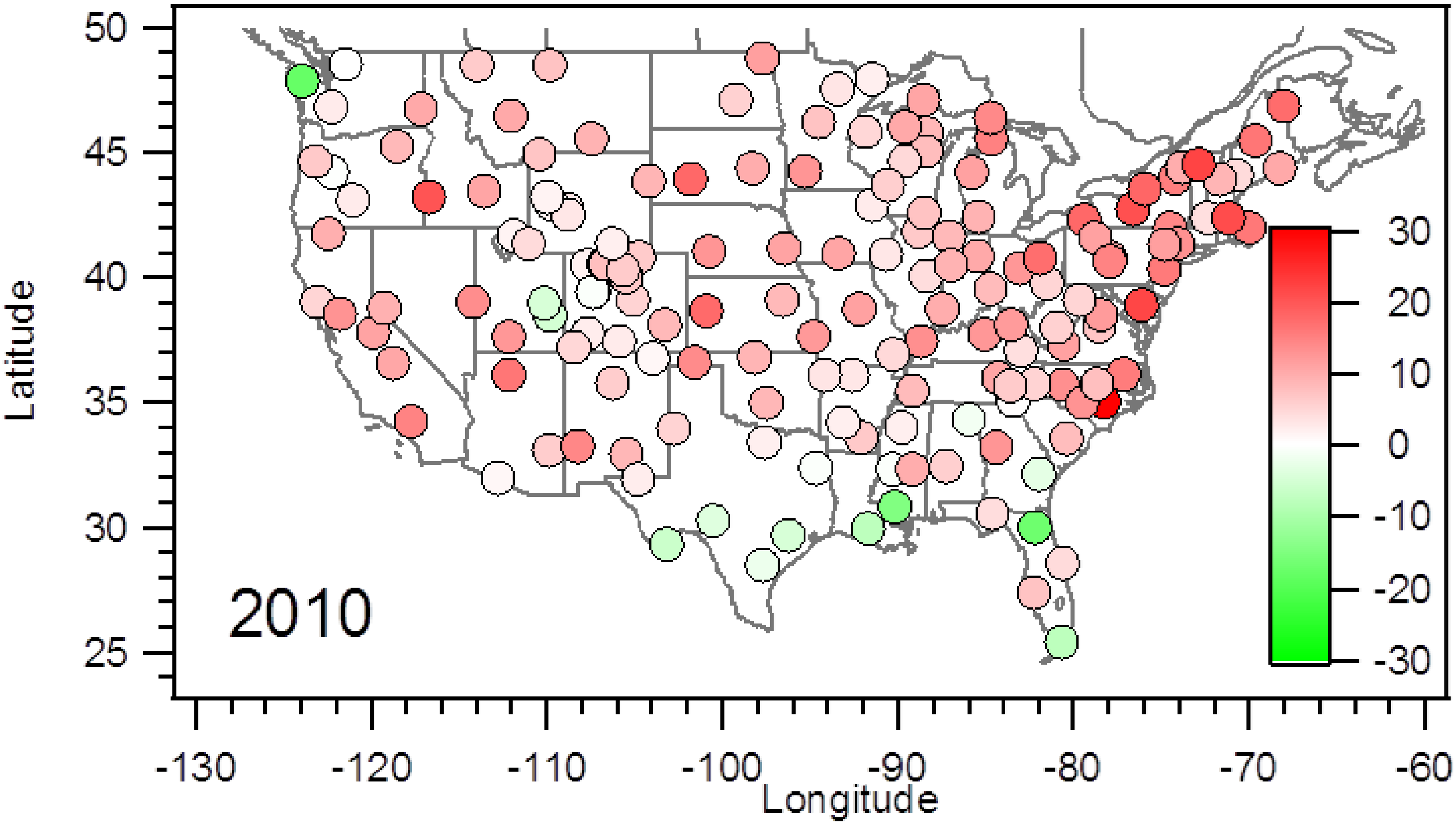
Ellis et al., 2012

Fig. 1. NO_x and NH_3 emissions in North America for 2006 and 2050. Numbers inset give contiguous US totals (Tg N yr^{1}). 2050 emissions are from the RCP8.5 and RCP2.6 scenarios

Summary

- Ammonia is an important contributor to dry & wet deposition of reactive N
- As NO_x emissions decrease, NH_x is an increasingly important component of N deposition
- Ammonia also a key factor affecting PM acidity and NH_4NO_3 formation
  - Abundant ammonia supports greater NH_4NO_3 PM formation and haze
- Network measurements needed to routinely characterize NH_3 and NH_4^+ at higher time resolution to
  - Understand PM formation
  - Validate air quality models
  - Attribute source contributions

Increase in NH_4^+ fraction



- A sizable increase in the NH_4^+ fraction (absolute % change) of wet inorganic nitrogen deposition is seen across most of the country (2010 – 1989)