Deposition challenges in a regulatory setting – addressing reduced nitrogen and linking concentration and deposition

Rich Scheffe – U.S. EPA
NADP, San Diego
November 2, 2017

Appreciation: Many EPA, NPS and AmecFoster colleagues

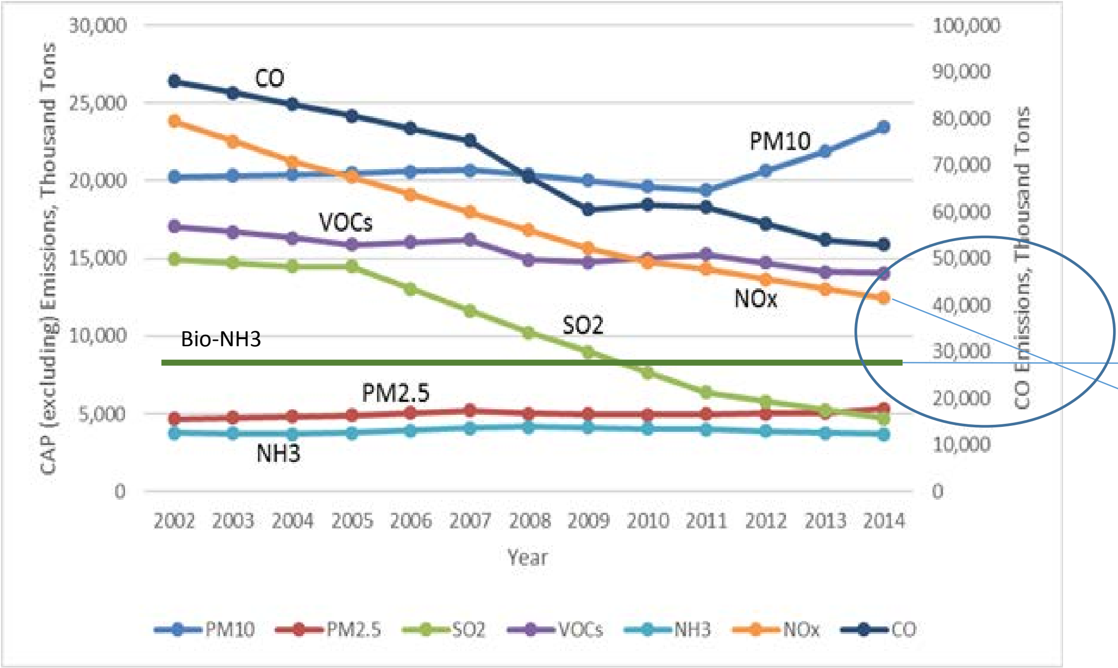
Don Winslow- Mission Bay/Pacific Beach Area fiction

- Dawn Patrol
- Gentleman’s Hour
- The Winter of Frankie’s Machine

Topics

- Why do we care about NH4 and NH3
  - Regulatory driver – secondary standards and more
- Horizontal and vertical characterizations N species
- Linking ambient and deposition states
  - Regulatory perspective
- Monitoring Considerations
  - Routine networks

Biologically relevant N from reduced N emissions should surpass that from oxidized N sources - source : NEI



Conservative; Sun papers; NOx overestimate

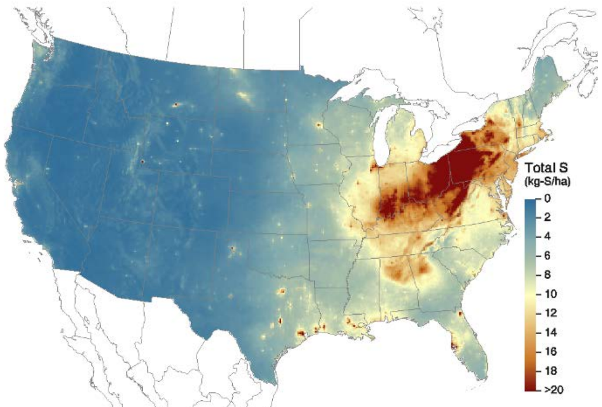
Pollutant	Percent Change in going from 2011 to 2014	Percent Change in going from 2010 to 2014	Percent Change in going from 2002 to 2014
CO	-13	-14	-40
NH_3	-8	-9	-1.9
NO_x	-13	-15	-48
PM_{10}	21	19	16
$PM_{2.5}$	7	8	14
SO_2	-26	-38	-68
VOCs	-8	-6	-18

The bygone days of sulfur transition to N and eventually reduced N impact on N/S/PM review.

Key resources

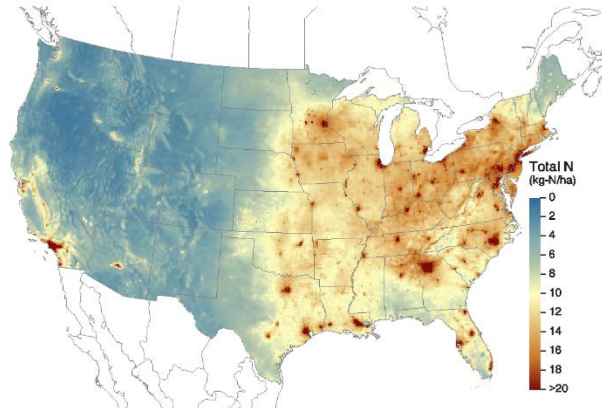
NADP:TDEP deposition

CASTNET and CMAQ



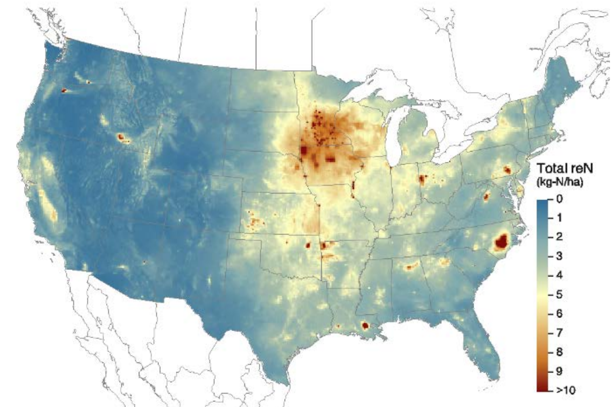
Total deposition of sulfur 2002

Source: CASTNET/CMAQ/NTN/AMON/SEARCH USEPA 06/27/16



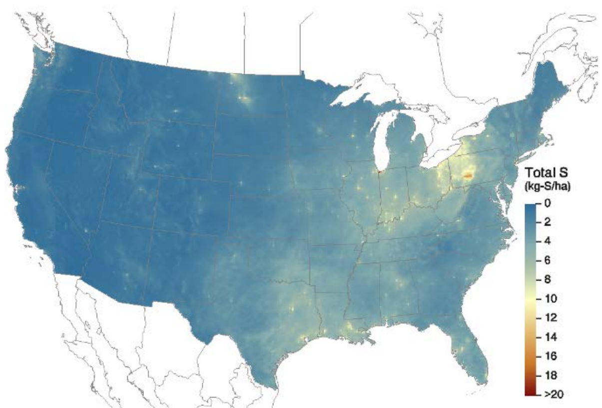
Total deposition of nitrogen 2002

Source: CASTNET/CMAQ/NTN/AMON/SEARCH USEPA 06/27/16



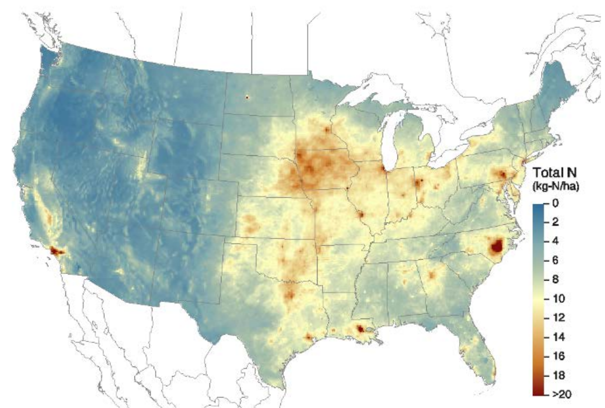
Total deposition of reduced N 2002

Source: CASTNET/CMAQ/NTN/AMON/SEARCH USEPA 06/27/16



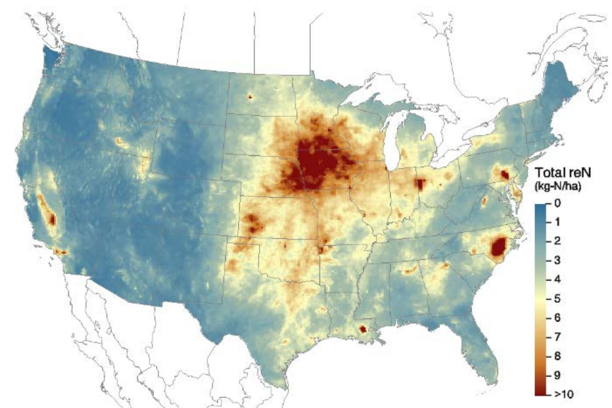
Total deposition of sulfur 2015

Source: CASTNET/CMAQ/NTN/AMON/SEARCH USEPA 09/14/16



Total deposition of nitrogen 2015

Source: CASTNET/CMAQ/NTN/AMON/SEARCH USEPA 09/14/16



Total deposition of reduced N 2015

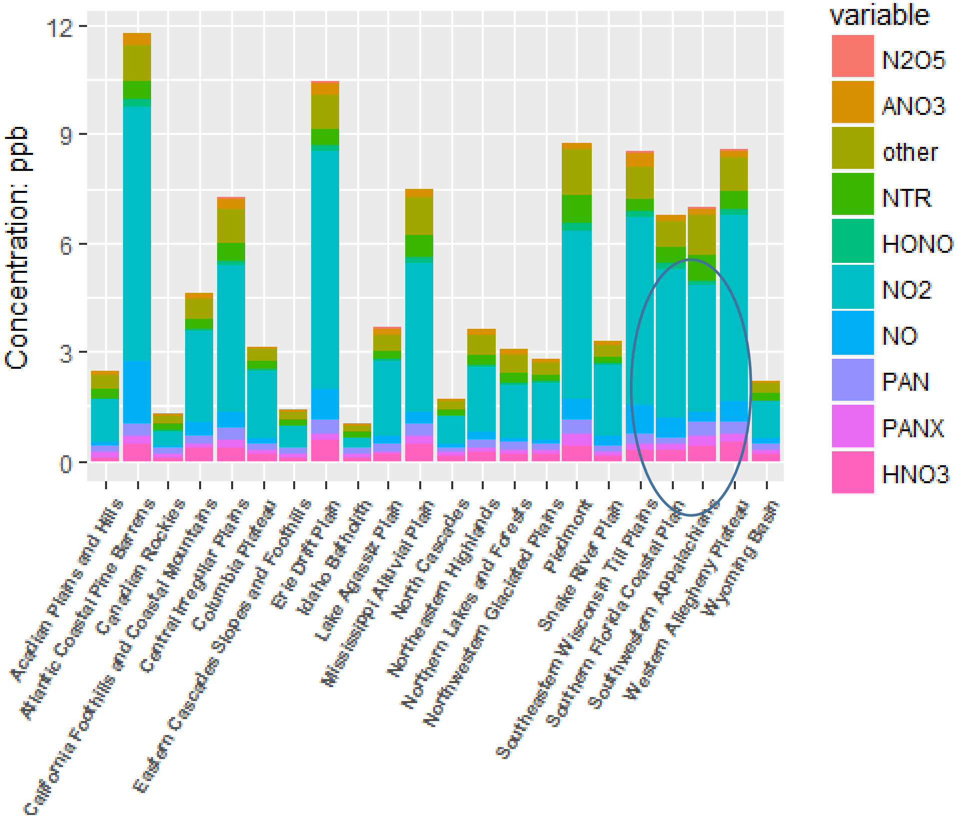
Source: CASTNET/CMAQ/NTN/AMON/SEARCH USEPA 09/14/16

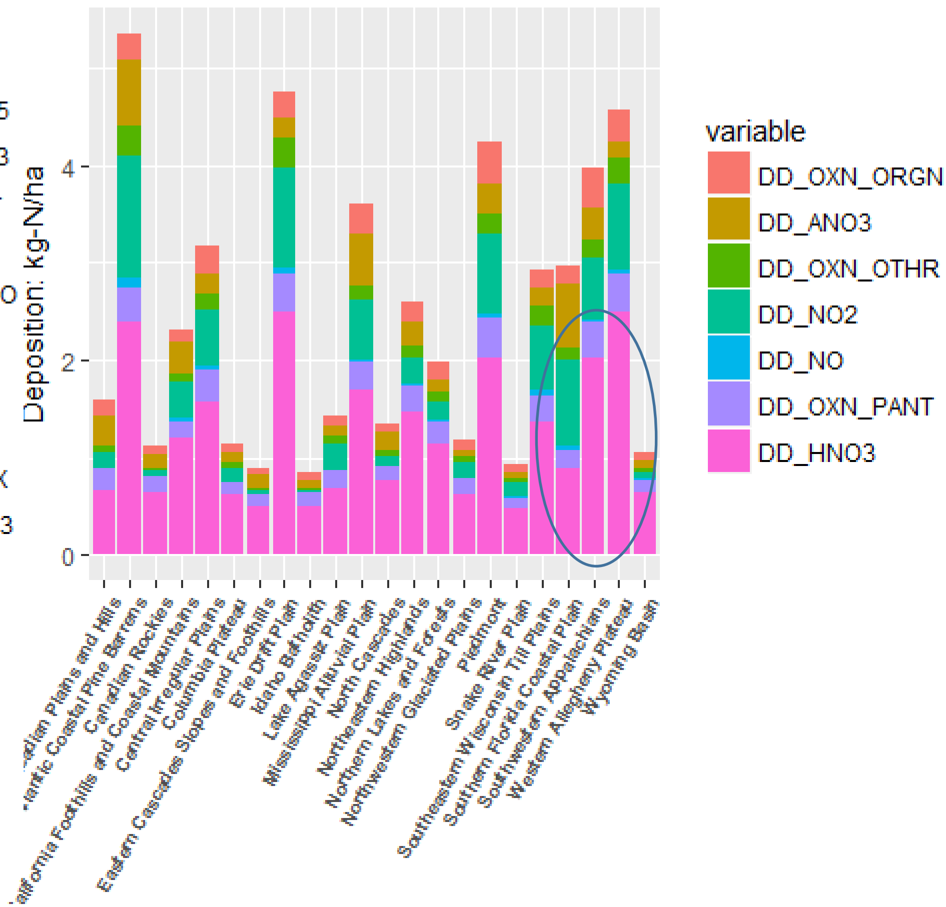
Challenge

Oxidized N: Substantial ambient N mass bound up in NOx and org-nitrates; dry deposition dominated by nitric acid.

- *Limited data on dry dep velocities of NO_2 and nitrates*
- *How do these uncertainties impact our ability to characterize oxidized N environment?*

2011 annual NOy splits for concentration (top) and deposition (bottom) delineated by ecoregion3 (43/86 regions)





Bridging atm. Science communities -Literature consistent regarding reported high bias of mobile source NOx emissions – (courtesy Henderson, Simon; EPA)

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Atmospheres
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Mobile NOx over (2x)

Composition and Ch...

Long-term trends in nitrog... motor vehicles at nationa...

Brian C. McDonald, Timothy R. Dallmann...

First published: 21 September 2012 Full publica...

DOI: 10.1029/2012JD018304 View/save citation

Contents lists available at ScienceDirect

Atmospheric Environment

Mobile NOx over (1.7x)

...DISCOVER-AQ: An evaluation of ...ern US

..., Glenn Diskin [d], Andrew Weinheimer [e], ... Worden [e], Alan Fried [f], ...R. Dickerson [a]

Atmos. Chem. Phys., 16, 13561–13577, 2016
www.atmos-chem-phys.net/16/13561/2016/
doi:10.5194/acp-16-13561-2016
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Atmospheric Chemistry and Physics
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EGU

Non-Power NOx over (1.3-1.6x)

Why do models overestimate surface ozone in the Southeast United States?

Katherine R. Travis[1], Daniel J. Jacob[1,2], Jenny A. Fisher[3,4], Patrick S. Kim[2], Eloise A. Marais[1], Lei Zhu[1], Karen Yu[1], Christopher C. Miller[1], Robert M. Yantosca[1], Melissa P. Sulprizio[1], Anne M. Thompson[5], Paul O. Wennberg[6,7], John D. Crounse[6], Jason M. St. Clair[6], Ronald C. Cohen[8], Joshua L. Laughner[8], Jack E. Dibb[9], Samuel R. Hall[10], Kirk Ullmann[10], Glenn M. Wolfe[11,12], Illana B. Pollack[13], Jeff Peischl[14,15], Jonathan A. Neuman[14,15], and Xianliang Zhou[16,17]

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Atmospheres
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Research Article

Observational constraints o... isoprene oxidation and its contribution to organic aerosol over the Southeast United States

Jingyi Li, Jingqiu Mao, ... Steven S. Brown, Jennifer Kaiser, Fran... Thomas F. Hanisco, ... Jessica B. Gilman, Brian M. Lerner, Carsten Warneke, Joost A. de Gouw, Ann M. Middlebrook, Jin Liao, André Welti, Barron H. Henderson, V. Faye McNeill, Samuel R. Hall, Kirk Ullmann, Leo J. Donner, Fabien Paulot, Larry W. Horowitz

Non-Power NOx over (1.14x)

...nment 131 (2016) 371–381

...ailable at ScienceDirect

...ic Environment

...elsevier.com/locate/atmosenv

Constraining NO_x emissions using satellite NO_2 measurements during 2013 DISCOVER-AQ Texas campaign

Amir Hossein Souri [a], Yunsoo Choi [a,*], Wonbae Jeon [a], Xiangshang Li [a], Shuai Pan [a], Lijun Diao [a], David A. Westenberger [b]

[a] Department of Earth and Atmospheric Sciences, University of Houston, 312 Science & Research Building 1, Houston, TX 77204, USA
[b] Texas Commission on Environmental Quality, 12100 Park 35 Circle, MC 164, Austin, TX 78711, USA

HIGHLIGHTS

- Constraining anthropogenic and biogenic NO_x emissions using OMI.
- A large decrease (30–60%) in anthropogenic emissions in urban areas.
- An increase (52%) in soil-biogenic emissions in rural regions.
- Improvements of simulating NO_2 levels using the constrained emission inventory.

Mobile NOx over (1.3x)

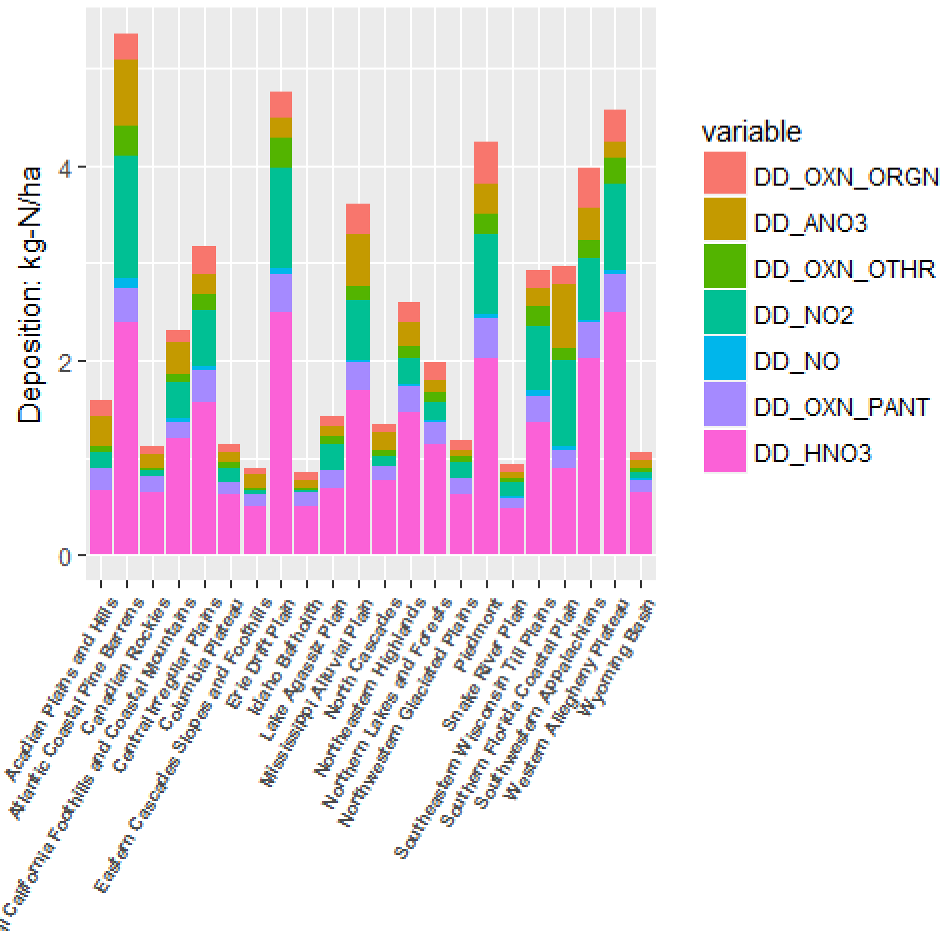
Range of results: 1.14-2
Is it right?

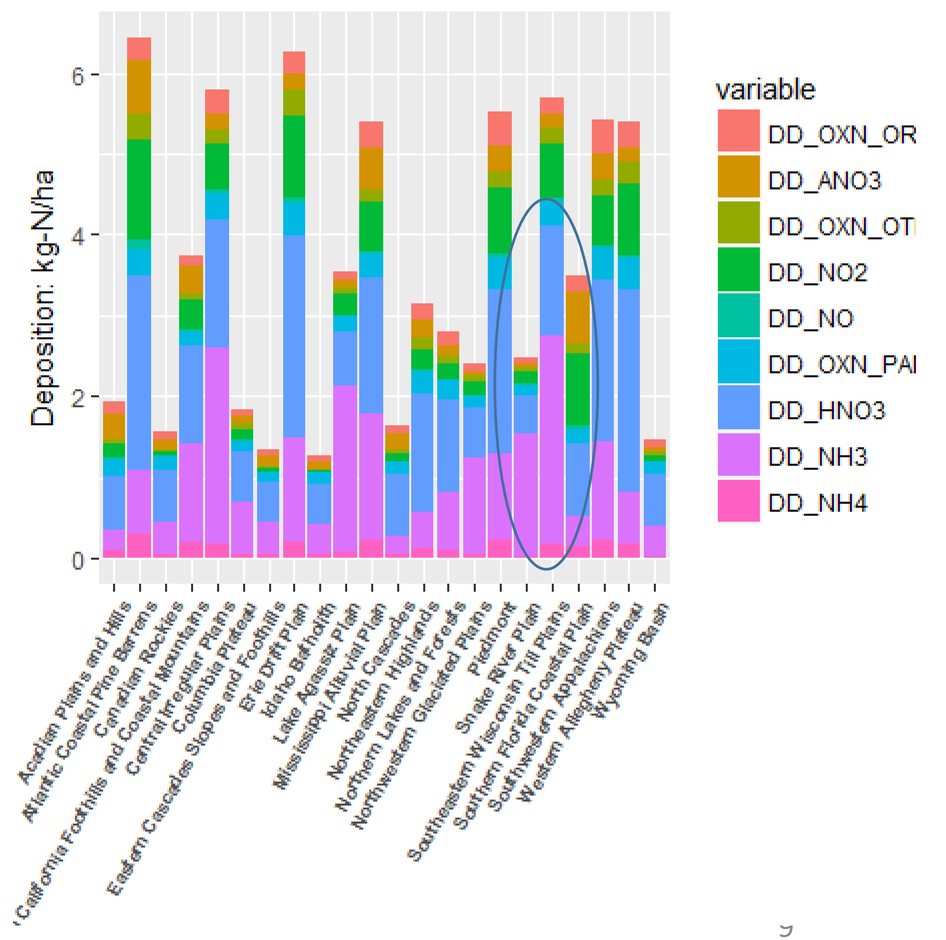
High priority hypotheses - Simon

Spatial allocations (county to grid cell) are incorrect for onroad emissions	
Spatial allocation (county to grid cell) of nonroad equipment is incorrect.	
Spatial allocation onroad activity by MOVES from national to county-level	
Nonroad emissions spatial distribution (national to county) is wrong	
Nonroad emission rates are too high	
Dry deposition velocities for NOy species are too low in models	
Model bias caused by mismatch of modeling grid-cell average compared to measurement location	
Model bias is due to some unique feature of 2011 platform	
Onroad emissions rates are too high	
National nonroad equipment population/activity is overestimated	
Biased temporalization of onroad HD, non-CEMS EGU and nonroad	
Near-road CO/NOx methods for estimating NOx emissions bias are biased	
Model bias caused by issues related to vertical mixing	
MOVES default national inputs inflate emissions / **MOVES inputs used in emissions platform inflate emissions**	
Ambient CO/NOy Methods for estimating NOx Emissions bias are biased	
NOy monitoring network and/or field campaign measurements are uncertain	

Challenge

NHx deposition adds considerable burden – dry deposition of NH3, which dominates NHx dry dep., is beset with several complicated processes with significant uncertainties.





Challenge

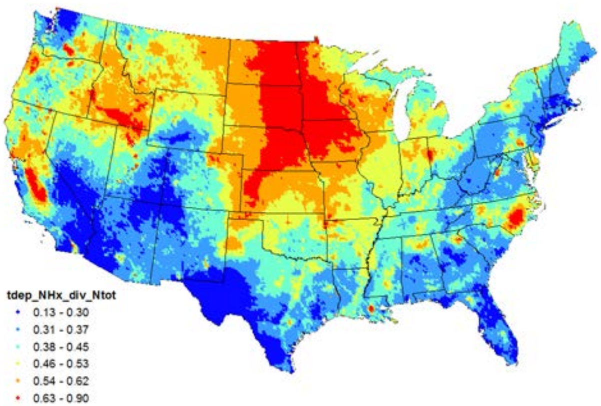
Characterization of pNH_4 deposition and overall impact on reduced and total N deposition – as the NOxSOx secondary NAAQS review has transitioned to the NOxSOxPM secondary review

or, can we use a surface based observation of pNH_4 to estimate contribution to wet and dry deposition deposition

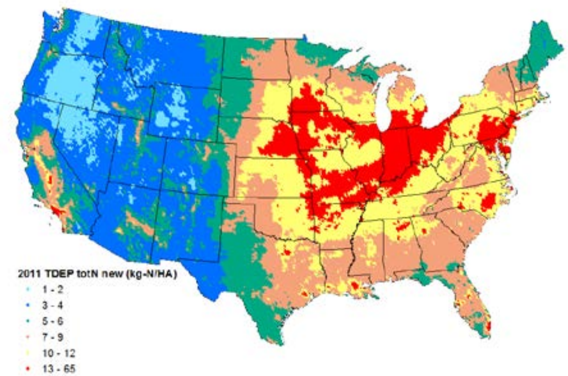
What we know about ammonium (NH_4)

- Basically, all NH_4 is derived from ammonia (NH3)
- NH_4 + NH_3 = NHx, which nationally makes up nearly half of all nitrogen deposition

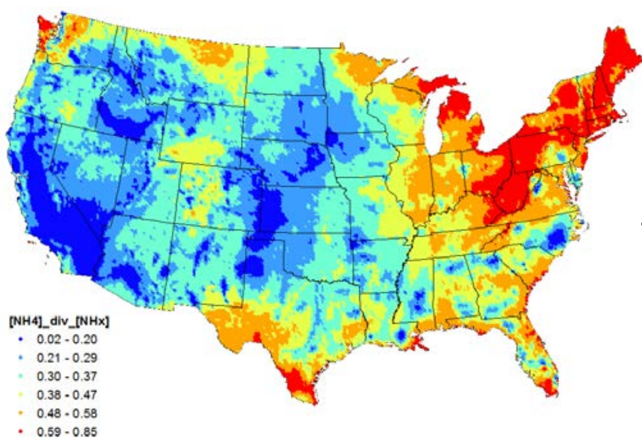
2011 Ratio of NHx to total N deposition



2011 total N deposition



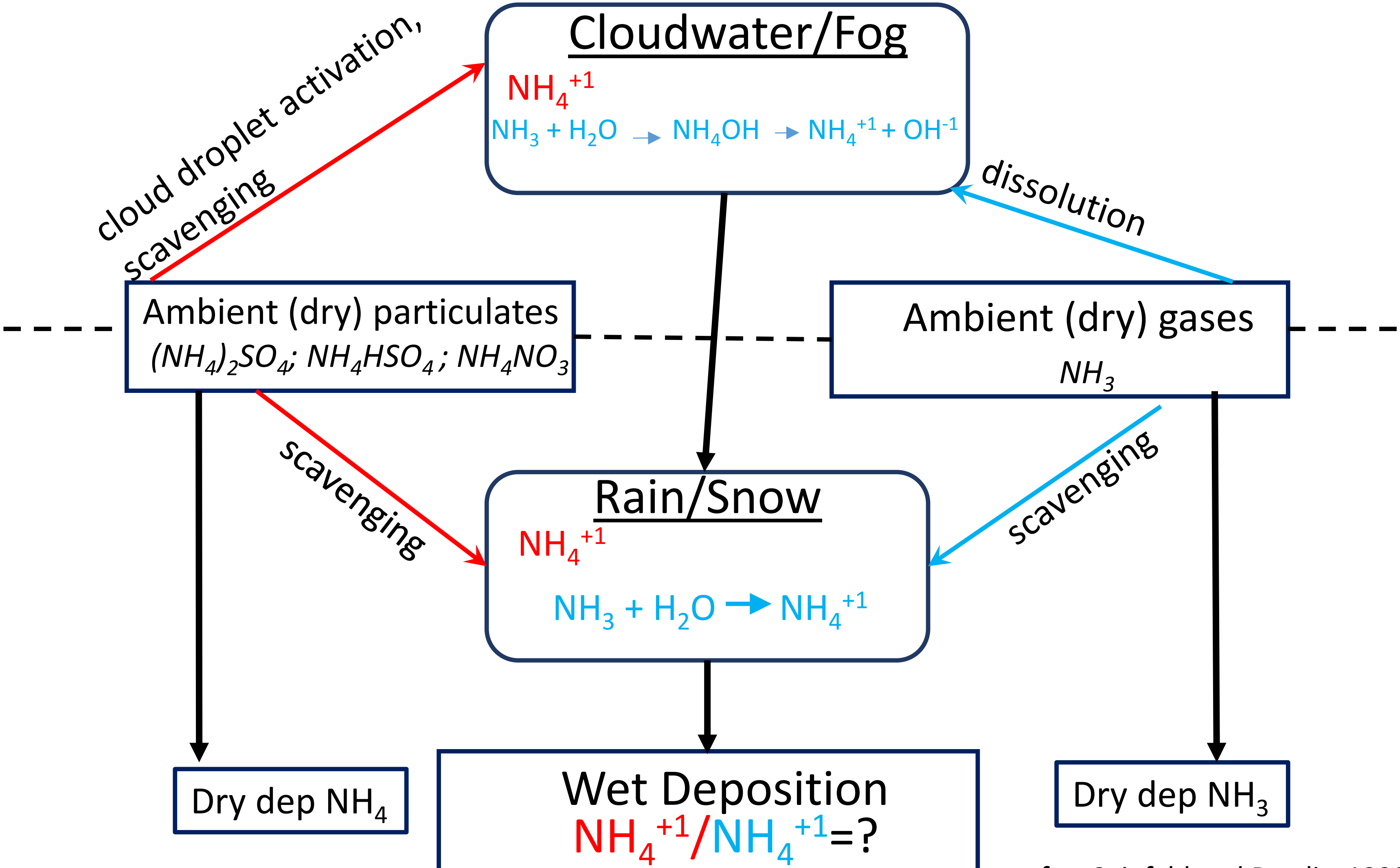
Source: NADP TDEP



2011 pNH_4/NHx concentration

Challenge: how much N deposition is derived from ambient NH_4?

Key Challenge: How can we estimate the contribution of ambient particulate NH_4 (pNH_4)to total nitrogen deposition?



after Seinfeld and Pandis, 1998

Ambient Ratio Method: Estimating pNH_4 contribution to wet deposition

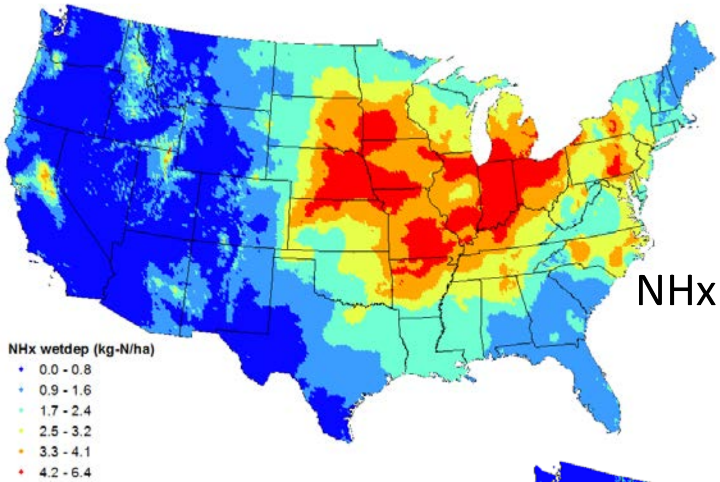
- Assume mass transfer rates, regardless of mechanism, of pNH_4 and NH_3, from ambient to aqueous phase are identical; reasoning:
  - NH_3 is highly soluble and enhanced by dissociation to NH_4^+
  - pNH_4 is efficiently removed through cloud droplet formation and scavenging
- Consequently, the relative rates of loss to the aqueous phase are given by ratios of ambient concentrations, leading to:
  - pNH_4_wet = ([pNH_4]/[NHx]) *wetdepNH_4

  where pNH_4_wet = wet NH4 deposition attributed to pNH_4

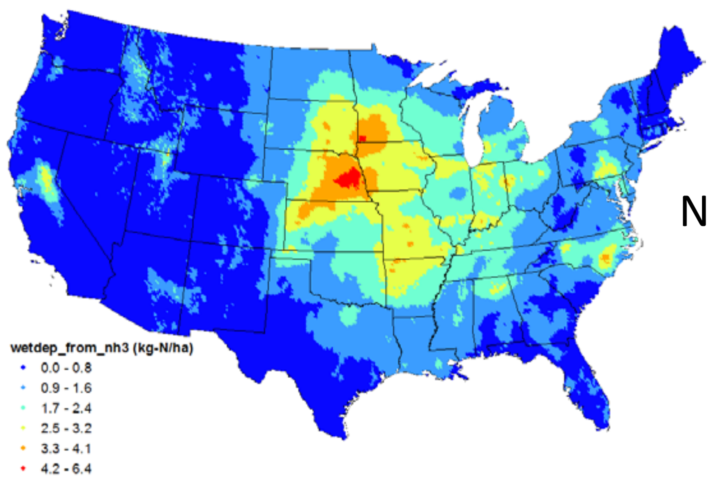
  Note: same approach applied to splitting pNO3 and HNO3

Contribution of pNH_4 to wet NHx deposition

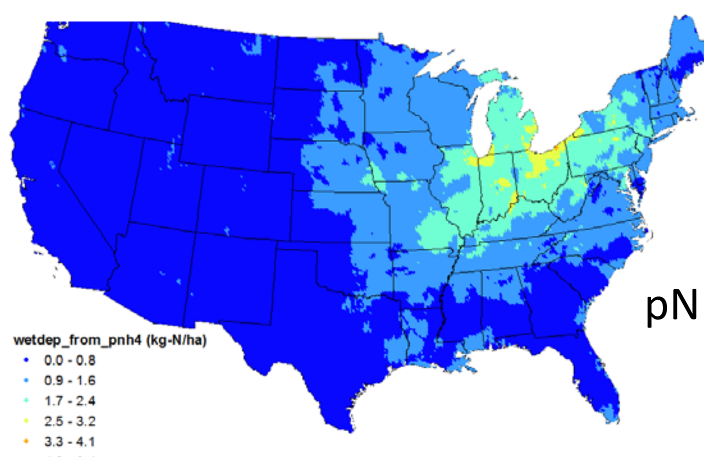
(2011 TDEP deposition with 2011 CMAQ concentrations)



NHx wetdep

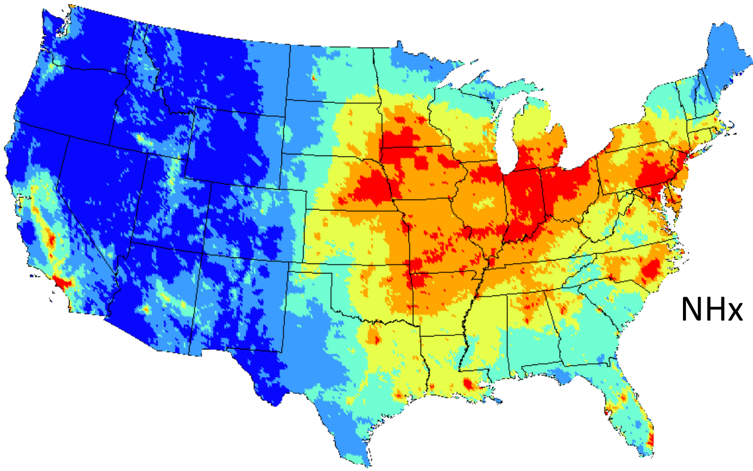


NH_3 wetdep

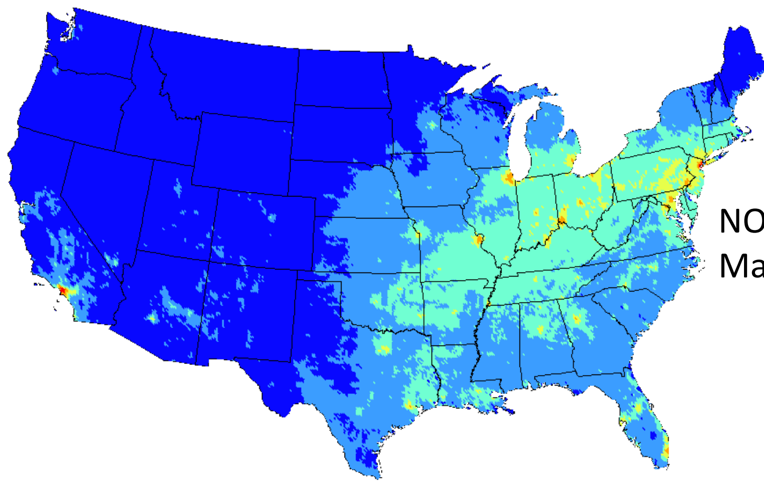


pNH_4 wetdep

Capacity differences between NOy and NOy plus particulate NH_4, referenced to total N deposition.

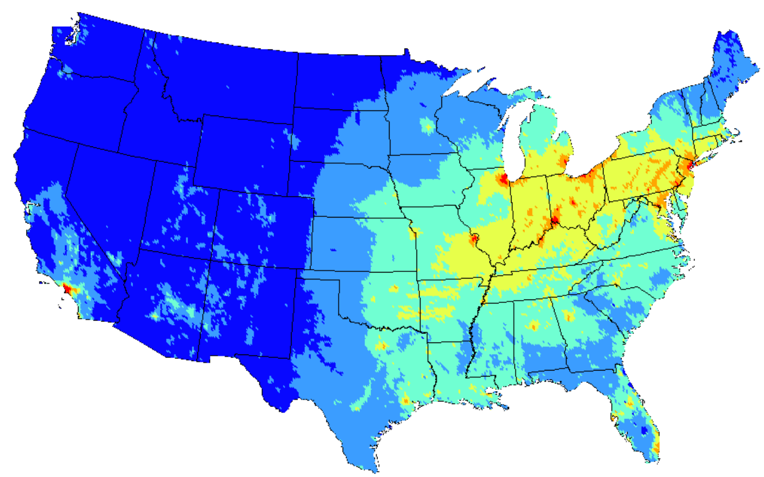


NHx + NOy deposition



NOy deposition
Max = 15

13.0 - 65.4

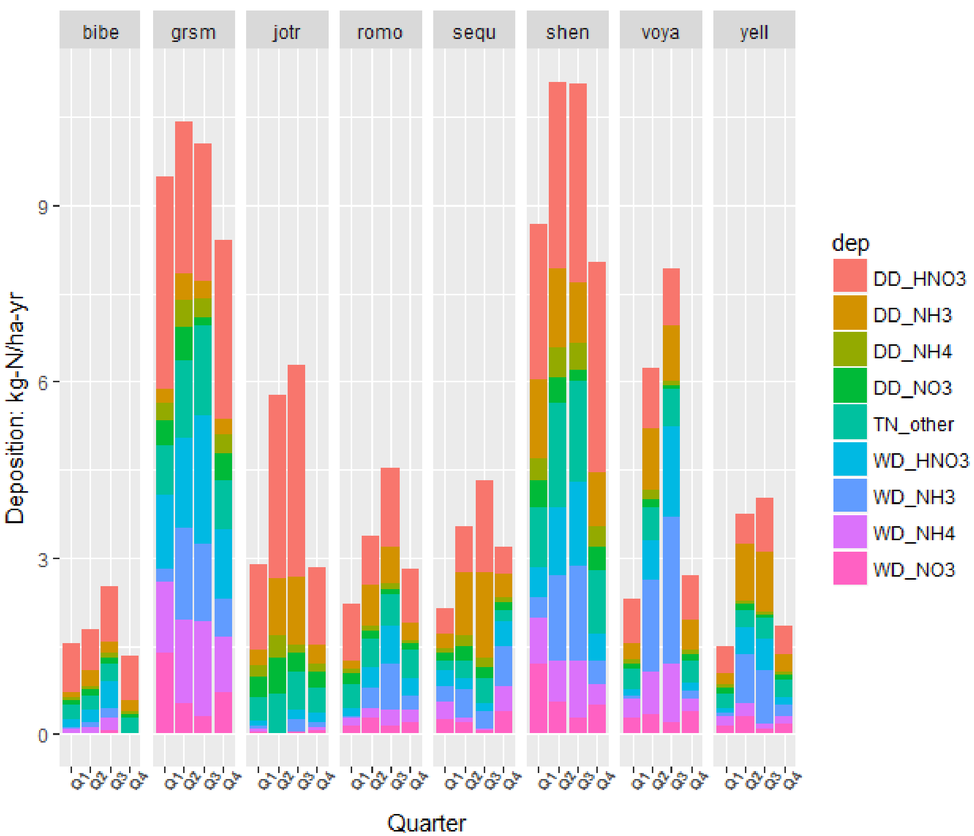


NHx + NOy deposition – NH_3 contributions (including pNH_4) Max =17

pNH_4 Evaluation Approach

- Vetting through community
  - ORD, OAR and NPS deposition experts
  - NADP
  - Manuscript under preparation
- Rationalize through scavenging theory and model parameterizations
- Determine relative bias of using surface values for total column processes
- Role of GEOSchem
  - Outputs separate scavenging estimates of NH3 and pNH4
    - Reproduce results comparable to published GEOSchem adjoint study
    - Analyze inhouse GEOSchem output using both techniques

Components of N deposition delineated by Class 1 area and seasons 2010 comparison of ambient ratio technique to GEOSchem



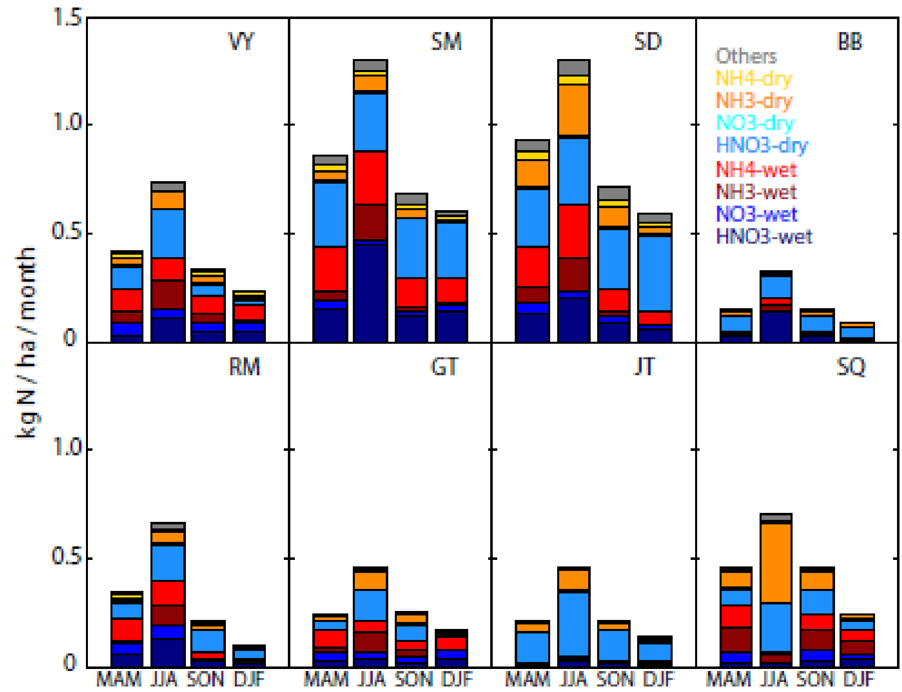
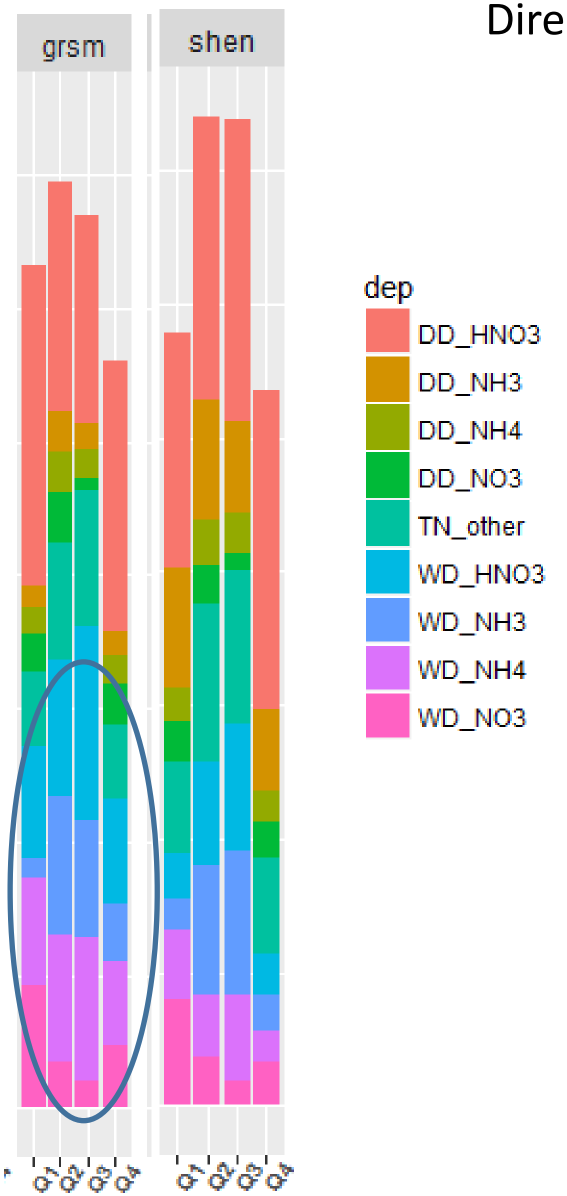
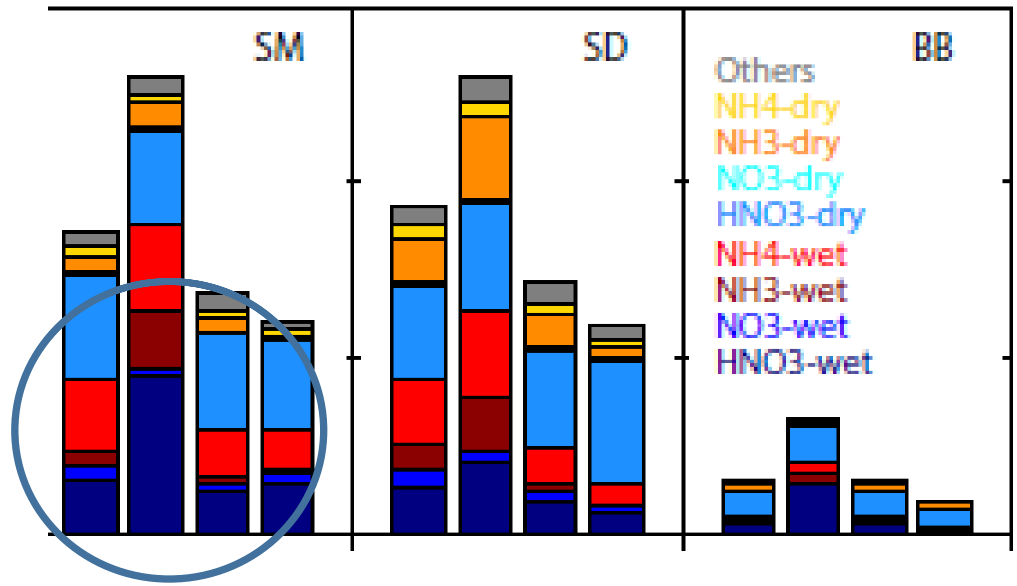


Figure 4. Stacked bar of modeled seasonal Nr deposition showing speciation. Others includes dry deposition of NO_2, PANs, alkyl ni trate, and N_2O_5. Blueish: oxidized N, reddish: reduced N, dark: we deposition, light: dry deposition.

H.-M. Lee et al.: Sources of nitrogen deposition in Federal Class I areas in the US

Directionally similar splits in wet NH4 and wet NH3 deposition

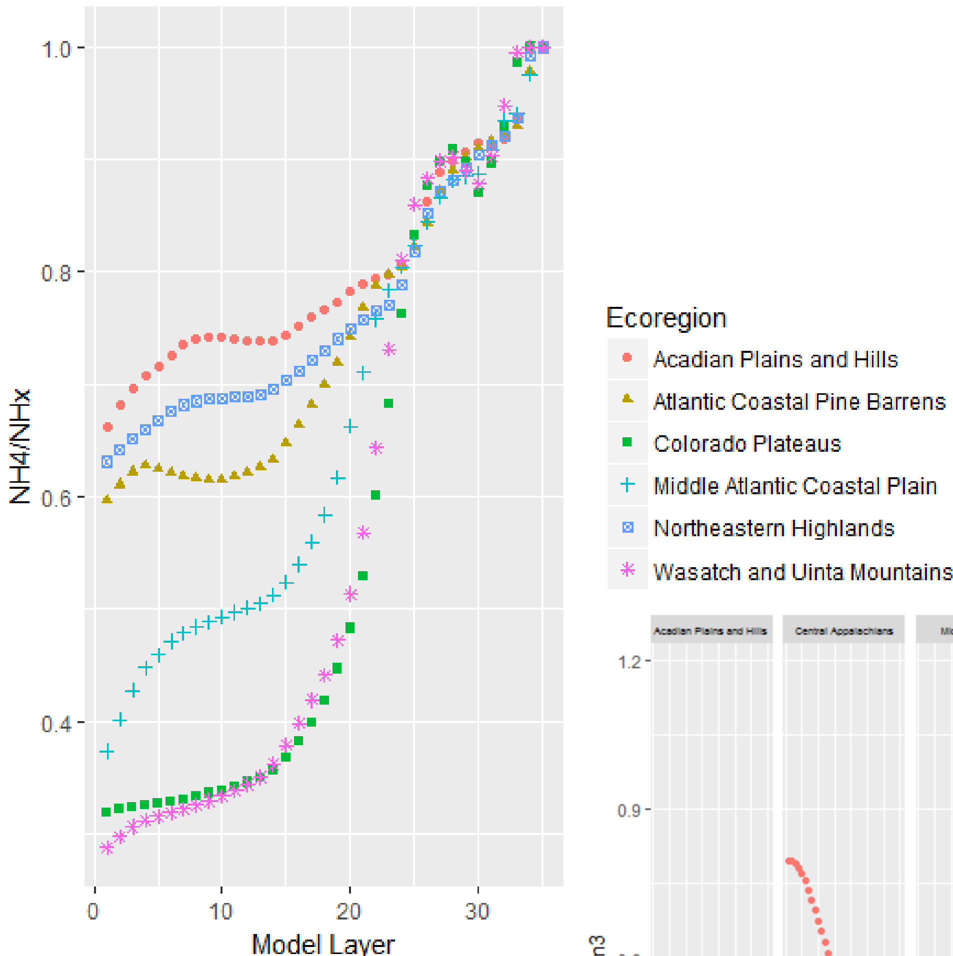


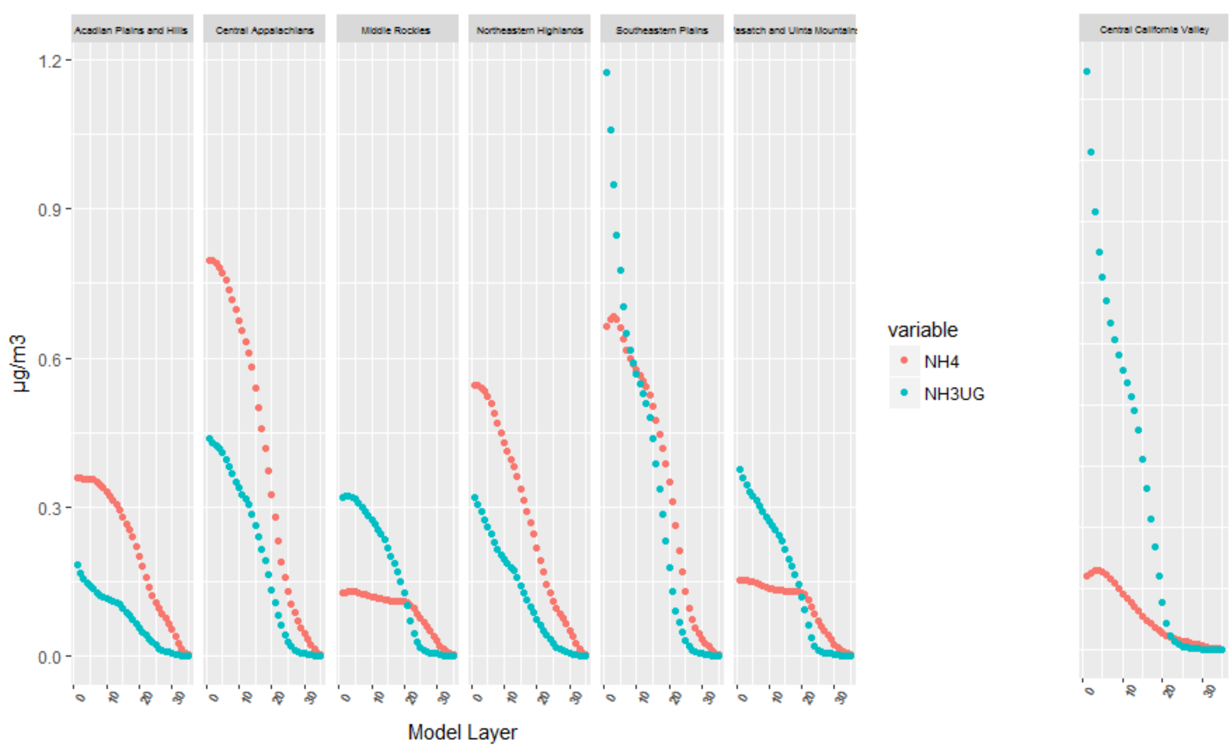


Tracking NHx vertically

- NH4/NHx increases with elevation
  - suggesting ratio technique is conservative

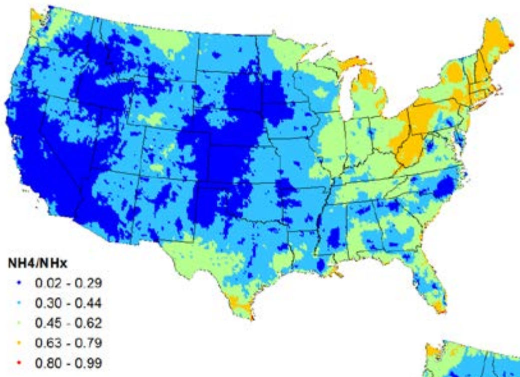
- most of the total column mass subject to scavenging is located in the lower layers
  - suggesting ambient surface layer values are representative
  - further analysis recommended

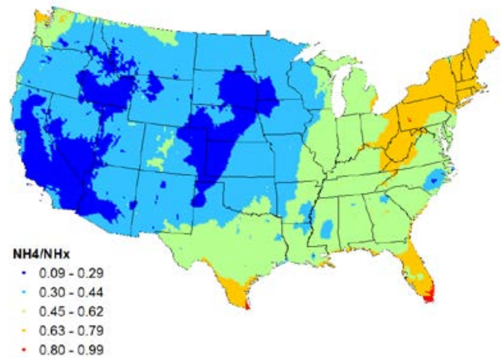


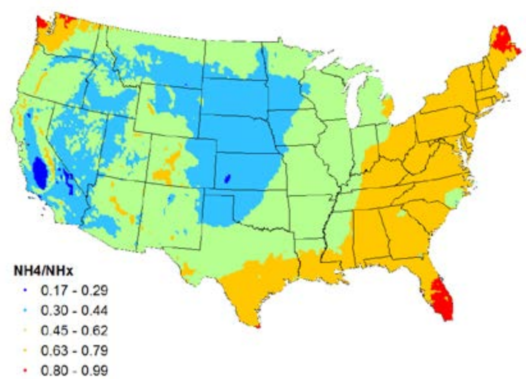


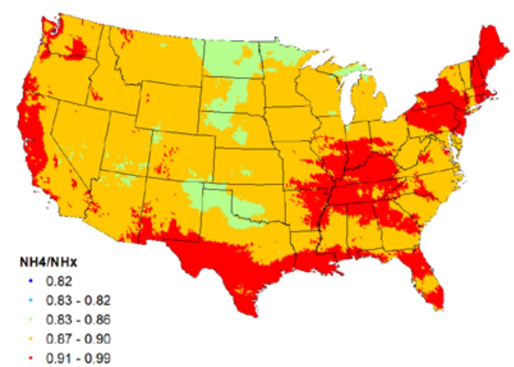
National view of NH4/NHx ratio in ascending model layers
- temperature driven?

L1, L10, L20, L30







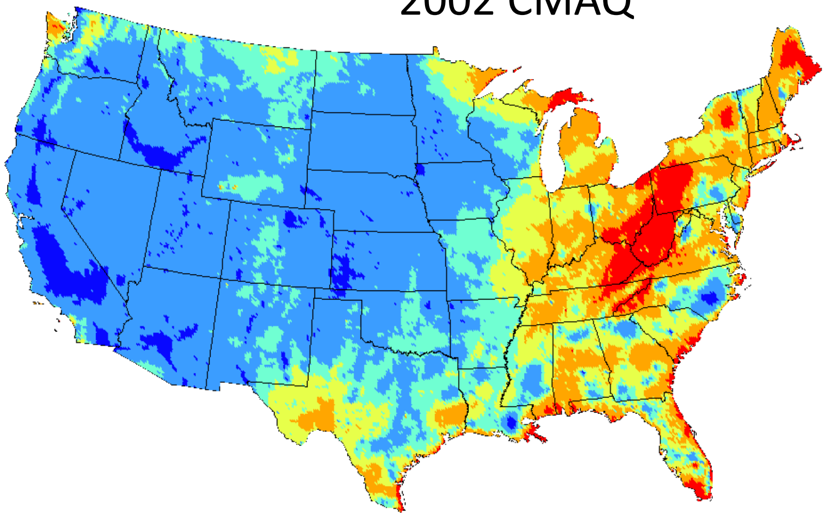


NH3 freedom

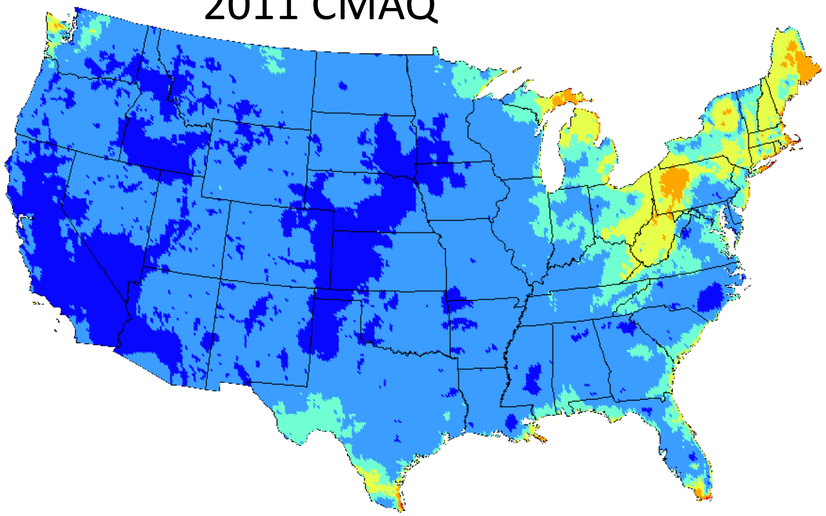
Looking ahead, does it matter? - Change in ambient pNH_4/NHx

Reflecting reductions in NOx and SOx emissions leading to more relative free NH_3

2002 CMAQ



2011 CMAQ



0.81 - 0.97

Monitoring implications

- Limited observational base given that population weighting does not drive areas of focus?
- The inclusion of PM, and specifically pNH4, injects a component not captured adequately in current routine networks
- To improve characterization of reduced inorganic nitrogen, a pilot project has been initiated to provide a potential network option to measure NHx

Development of NHx Monitoring Pilot Study

NHx Pilot Study: Details

- Purpose
  - Demonstrate application of existing method successful in western and Midwest U.S. environments to warm humid southeast U.S. locations
- Approach uses existing IMPROVE and CSN infrastructure
  - Reduces NH3 volatization by using acid impregnated cellulose filters in place of nylon filters
  - Two sites (Duke Forest, NC; Gainesville, FL) running co-located Improve, CSN and AMoN (passive NH3)
    - Produce 1/3 day 24 hr NHx, biweekly NH3, and seasonal/annual pNH4 by difference
  - Follows Chen et al., study (2014 Atmospheric Environment)

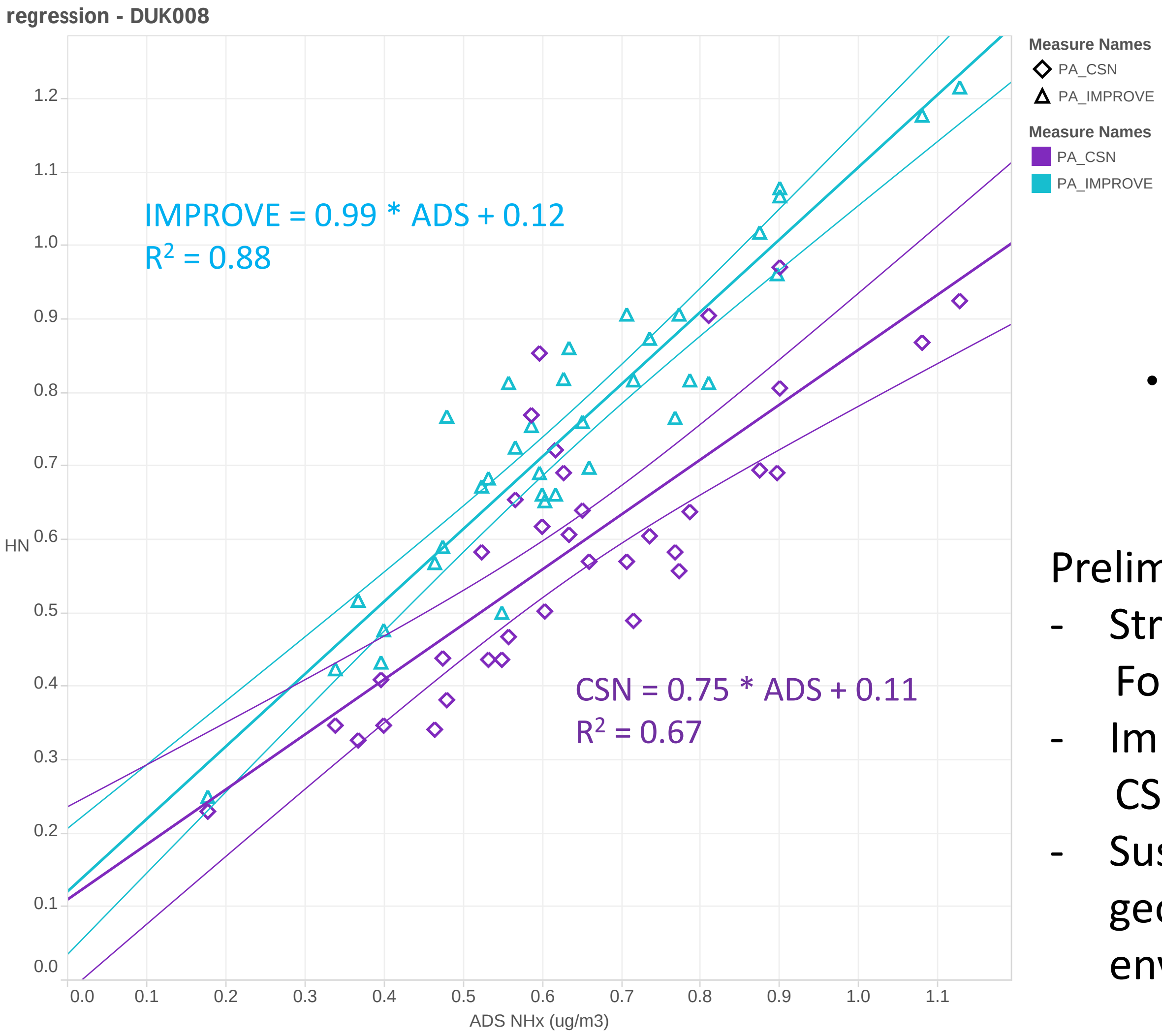
Seasonal ambient ammonia and ammonium concentrations in a pilot IMPROVE NHx monitoring network in the western United States

Xi Chen [a,1], Derek Day [b], Bret Schichtel [b], William Malm [b], Ashleigh K. Matzoll [c], Jose Mojica [c], Charles E. McDade [c], Eva D. Hardison [d], David L. Hardison [d], Steven Walters [d,2], Mark Van De Water [c], Jeffrey L. Collett Jr. [a,*]

- Study started May/2017 and runs for 6 months to capture warm and shoulder seasons
- Assuming satisfactory performance, a practical and leveraged option for SLTs would be available to increase characterization of reduced N.
  - Important metric for model and emissions evaluation
  - Potential indicator in a future secondary standard

CHARACTERIZATION OF REDUCED NITROGEN AT IMPROVE AND CSN MONITORING SITES

Christopher Rogers[1], John Walker[2], Rich Scheffe[3], Kevin Mishoe[4], Doris Chen[2], Katherine Barry[4], Joann Rice[3], Melissa Puchalski[5], Bret Schichtel[6]



- Duke Forest, NC

Preliminary Mixed results

- Stronger correlations at Duke Forest (shown)
- Improve captures more NHx than CSN or ADS
- Suspect impacts related to inlet geometry, flow differences and wet environment (including reference)

ADS = reference sampler

Challenge
Linking concentration to deposition - Transference Ratios

Transference Ratios (T-ratios)

- Unique aspect of linking deposition based effects to a NAAQS based structure relying on ambient concentrations
  - Conceived by Adam Reff for previous NAAQS review
- Defined as:
  - Total deposition(x)/concentration(x)
    - Where x is related to a NAAQS indicator; e.g., NOy or SOx (SO_2 plus SO4) as in last review.
    - Essentially an aggregated deposition velocity over species, wet and dry phases, time and space of choice.
- Relevant challenges include:
  - Conceptual construct and not a fundamental system property
  - Relatedly, how much aggregation in species, phases, time and space and how that impacts variability and uncertainty?
    - Basis for estimating uncertainty – highly constrained by lack of observations?
  - Different results from different modeling platforms

Key References and Evaluations

- Reff analyses in Final PA for 2012 NOx/SOX review; demonstrated
- Sickle and Shadwick: “Transference ratios” to predict total oxidized sulfur and nitrogen deposition- Parts 1 (monitoring) and 2 (modeling) – Atmospheric Environment 2013 (77)
- ***Koo, Knipping, Kumar…Russell***: Chemical transport model consistency in simulating regulatory outcomes and the relationship to model performance: Atmospheric Environment 2015 (116)
- Scheffe, R., J. Lynch, A. Reff, J. T. Kelly, B. Hubbell, T. Greaver, and J. T. Smith (2014) The Aquatic Acidification Index: A new regulatory metric linking atmospheric and biogeochemical models to assess potential aquatic ecosystem recovery. Water, Air, & Soil Pollution 25: 1838 [see supplementary material]
- Example and expected forthcoming evaluations as part of the REA

Sickle and Shadwick: *"Transference ratios" to predict total oxidized sulfur and nitrogen deposition- Parts 1 (monitoring) and 2 (modeling)"* – Atmospheric Environment 2013 (77)

- Part 1 (monitoring: 1990-2004 CASTNET)
  - Only effort to use observations to estimate T-ratios
  - high variability associated with wet deposition (not to confuse as dry dep is major uncertainty)
  - Dramatic improvements in variability when aggregating annually (~30%) from weekly (~235%)
- Part 2 (modeling: 2002-2006 CMAQ)
  - RDs between modeled and measured values (aggregated over a year) range from -37 to 63% across 17 sites, with a mean RD of 2% for T_OXN for all sites
  - Conc[OXN] (nitric acid and nitrate) may serve as an equivalent indicator for NOy deposition, relative to conc[NOy]
    - Implies CASTNET FP NO3 may be a practical, cost-effective indicator (originally suggested by Gary Lear)
  - Confirmed minimal CV in temporal variability of T-ratios from year to year
  - Suggested using a representative monitored value of a specific grid cell(point) with a more aggregated deposition value to reduce spatial variability of T-ratios
    - In practice, justification for using a single "representative" monitoring site

Koo, ***Knipping, Kumar…Russell “***Chemical transport model consistency in simulating regulatory outcomes and the relationship to model performance” Atmospheric Environment 2015 (116)

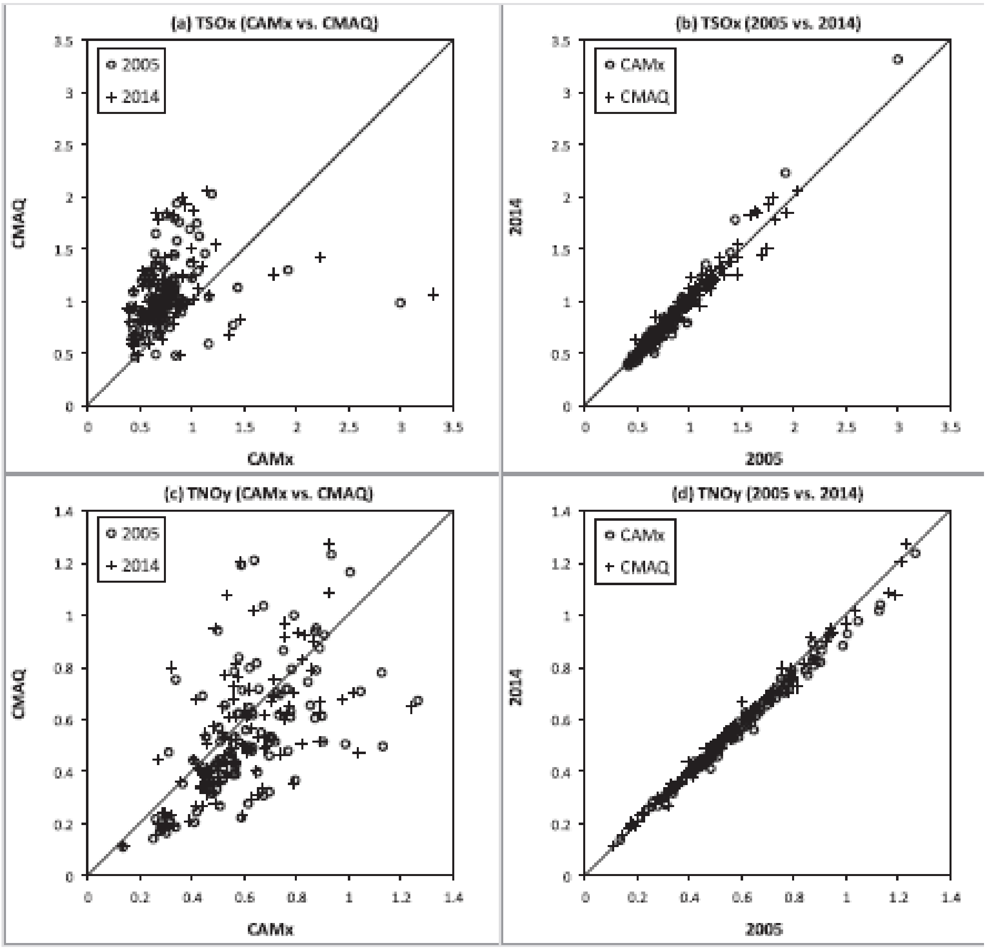


Fig. 10. Scatter plots of (a) TSOx by CAMx vs. CMAQ, (b) TSOx in 2005 vs. 2014, (c) TNOy by CAMx vs. CMAQ, and (d) TNOy in 2005 vs. 2014 at the IMPROVE monitoring

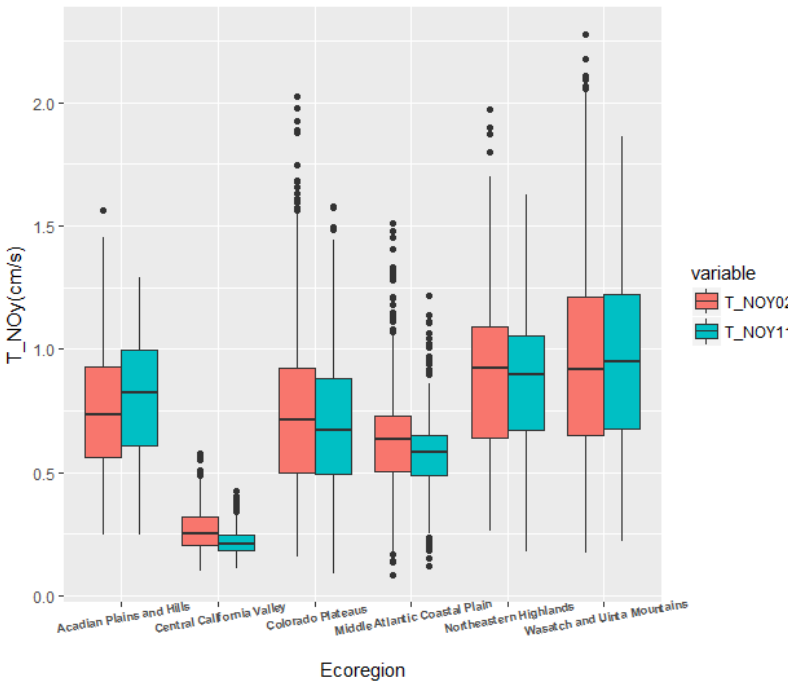
Ku et al. 2015

Illustrates

- Disagreement between CMAQ and CAMx
- Further confirmation of temporal stability of T-ratios

T-ratio analyses for this REA

- Based on 2002-2012(++) CMAQ simulations
  - Data extractions and data base structure completed
- Limitations in using surface values to reflect full atmospheric column processes (e.g., wet deposition)
- Influence of model platforms
  - Exploring difference between CMAQ and CAMx
  - Relative priority?
- Recasting as per indicator options
  - Alternative indicators and structures



Composition: Types of air indicators (t-ratios)

- We view the development of air indicators as:
  - Initiated by overarching technical concerns (NHx as an example)
  - Then encouraged by policy objectives (focus on pNH4)
  - Modified as needed by technical constraints (ongoing)
- Types of indicators by species groupings (explanations follow in subsequent slides)
  - Just NOy
    - Missing major component (pNH4)
    - Can use a surrogate TNO3 (HNO3 and pNO3)
  - NOy+pNH4
    - Seems a reasonable start
    - Could substitute TNO3 for NOy to ease monitoring burden
  - Total Inorganic reactive N (NOy + NHx)
    - Biologically most relevant
    - Measurable
    - Includes NH3 which is not a direct component of PM, NOx or SOx
    - Can argue that all pNH4 is linked to NHx

Thank you!

Original Reff analyses from 1st review (2002-2005 & 2030 CMAQ)

- (left) illustrating limited spatial variability in ADK and SHEN study regions
- (below) temporal stability - key operational requirement