Ambient Ammonium Contribution to total Nitrogen Deposition

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Evolutional change in National Air Pollution Management

1970

Initial CAA

1990

<u>"Good bye EKMA"</u>
Biogenics
Acid Deposition
Regional science
"1991 NAS Rethinking the ozone …"
NAPAP

2000

<u>"Hello CTMs and PM networks"</u>
8-hr ozone
$PM_{2.5}$ (annual driver)
Regional Rules (Title 4, NOx SIP)

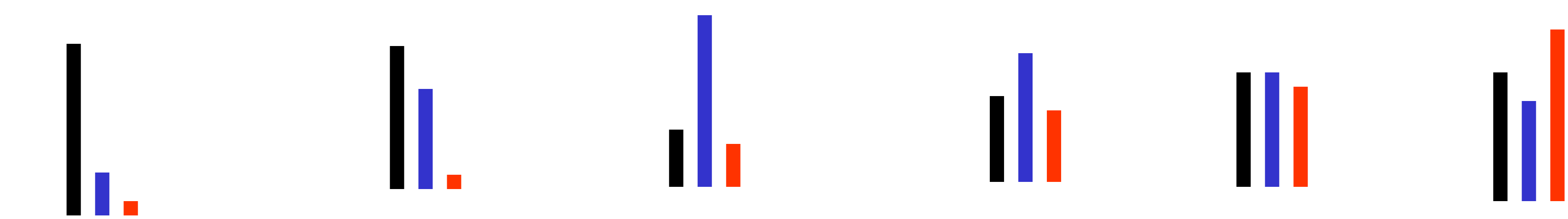
<u>"Great Trades"</u>
Multiple pollutant
Multiple media recognition
"2004 NAS AQM in U.S."

2010

<u>"Western U.S. awakening"</u>
New tighter PM, NO2 and SO2 primary stnds, emphasizing local scales, (O/G, fires, winter O3)

2050

<u>"MDL dilemma"</u>
New lower O3 standard
"background O3"
Climate-AQ
Hemispherical Transport,
HCHO, NH_3



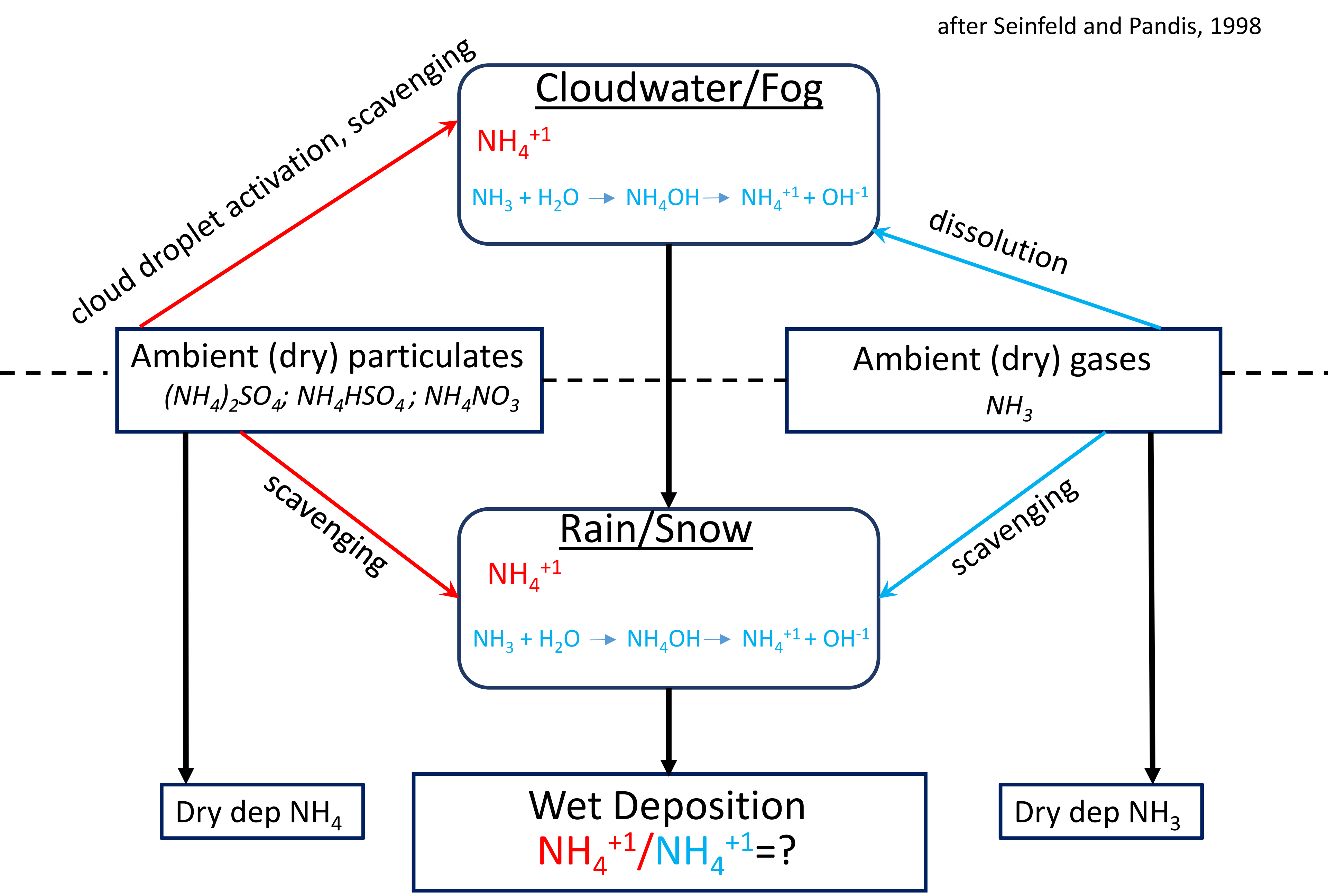
Local/urban
Regional
Hemispheric

Question:

- What is the contribution of ambient particulate NH_4 (pNH_4)to total nitrogen deposition?

Challenge:

- Contribution of ambient pNH_4 (or any ambient species) to dry deposition is estimated through models and widely available.
- Also available is wet (or precipitation) concentration of NH_4 (wNH_4) through measurements and models.
- However, wNH_4 is derived from transfer of both ambient NH_3 and pNH_4 to aqueous phase through cloud droplet formation (pNH4), mass transfer of NH_3 to cloud/fog and eventual precipitation scavenging. Noting that virtually all NH_3 transferred to wet phase is hydrated upon dissolution and then dissociates to form wNH_4.
- Consequently, wNH4 reflects the aggregate contribution from ambient NHx without a clear path to delineate separate contributions between pNH4 and NH3.


after Seinfeld and Pandis, 1998
Cloudwater/Fog
NH4+1
NH3 + H2O → NH4OH → NH4+1 + OH-1
cloud droplet activation, scavenging
dissolution
Ambient (dry) particulates
(NH4)2SO4; NH4HSO4; NH4NO3
Ambient (dry) gases
NH3
scavenging
scavenging
Rain/Snow
NH4+1
NH3 + H2O → NH4OH → NH4+1 + OH-1
Dry dep NH4
Wet Deposition
NH4+1/NH4+1=?
Dry dep NH3

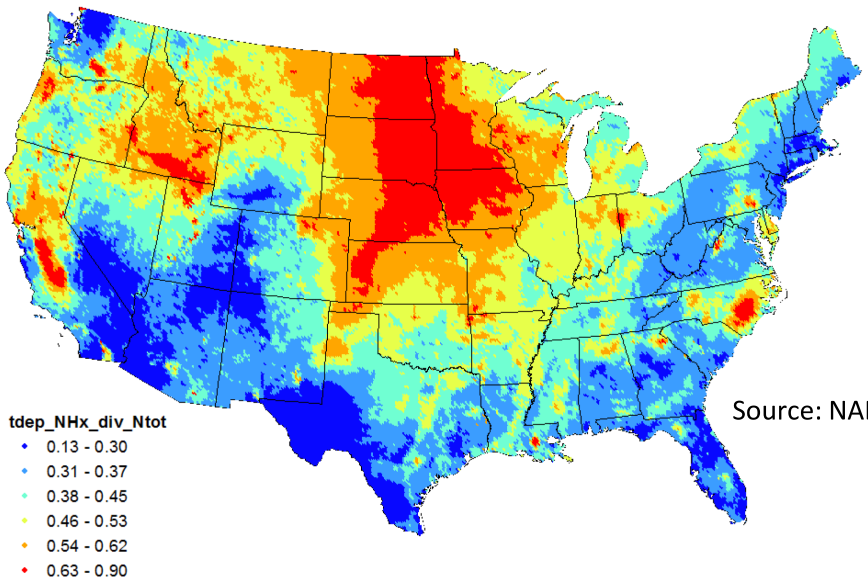
Why do we care?

- Important ecological effects (e.g. eutrophication) are associated with total nitrogen deposition, to which pNH4 (as well as other pollutants) can be a significant contributor
- pNH4, as well as pNO_3 and pSO_4, are components of total PM mass; in addition pNO_3 and pSO_4 are also transformation products of the criteria pollutants of NOx and SOx
- Deposition driven ecosystem effects that have the potential to be adverse to public welfare are important to be considered in the current NAAQS reviews
- Assessing the contribution of the various nitrogen species to the total nitrogen deposition in ecosystems allows us to better understand the emissions sources contributing to adverse ecosystem effects
- Understanding the contribution of the various species to the total ecosystem deposition then helps inform decisions on the best and most appropriate policy option(s) for controlling sources and reducing associated impacts

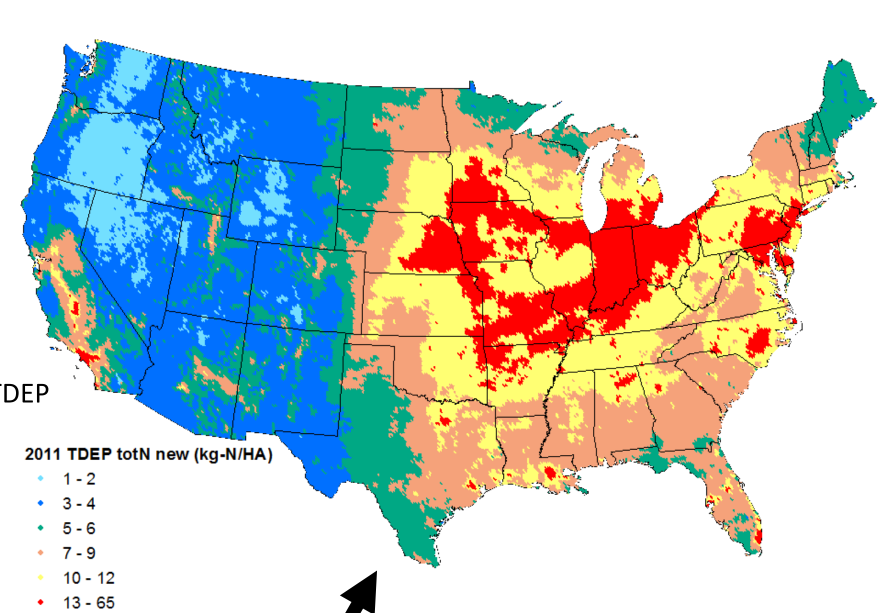
What we know about ammonium (NH_4)

- 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

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

Estimating pNH_4 contribution to wet deposition

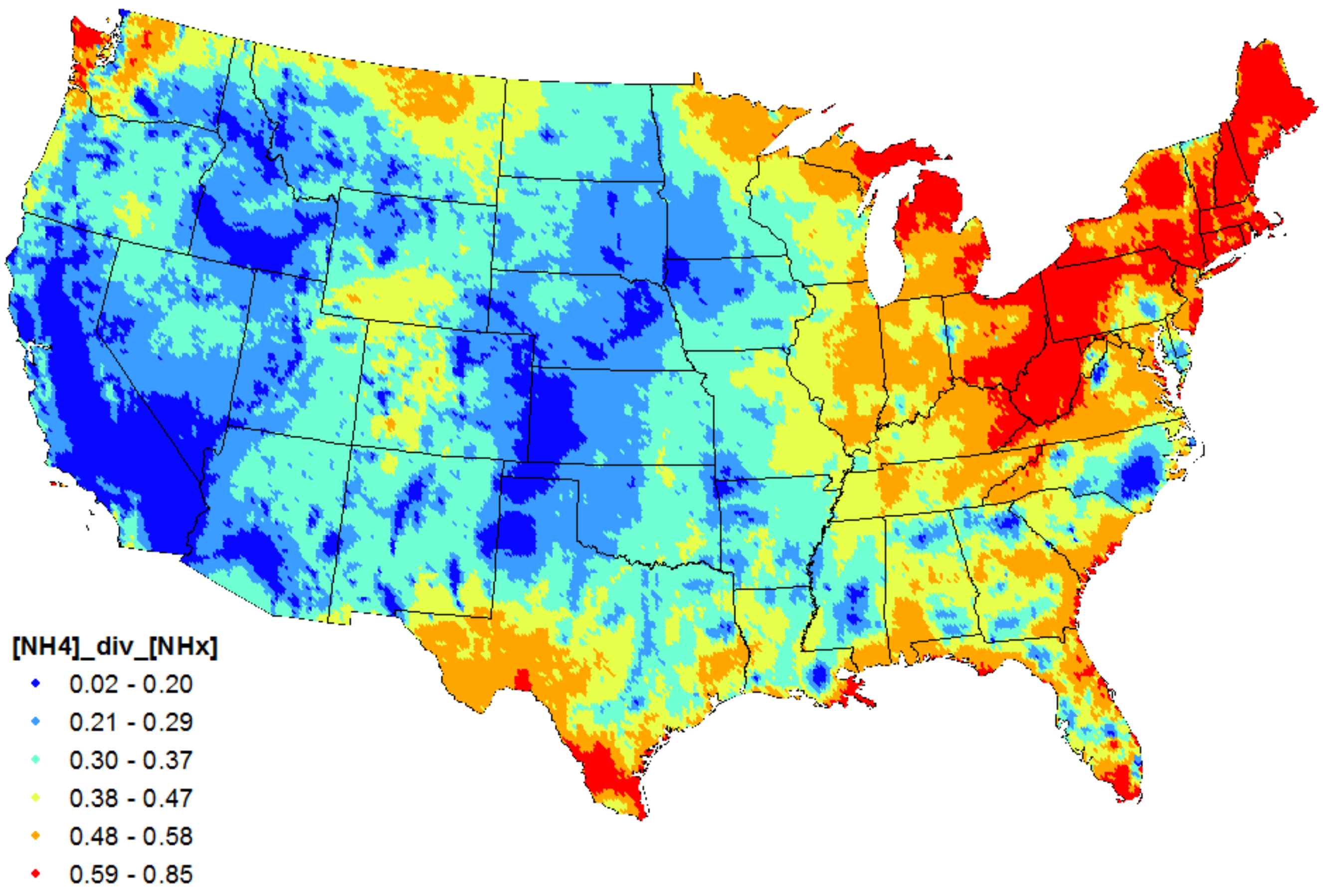
- Assume mass transfer rates, regardless of mechanism, of pNH_4 and NH_3, from ambient to aqueous phase are identical; reasoning:
  - NH_3 is highly soluble and enhanced by dissociation to NH_4^+
  - pNH_4 is efficiently removed through cloud droplet formation and scavenging
- Consequently, the relative 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

  and, [ ] extracted from CMAQ; deposition from TDEP hybrid

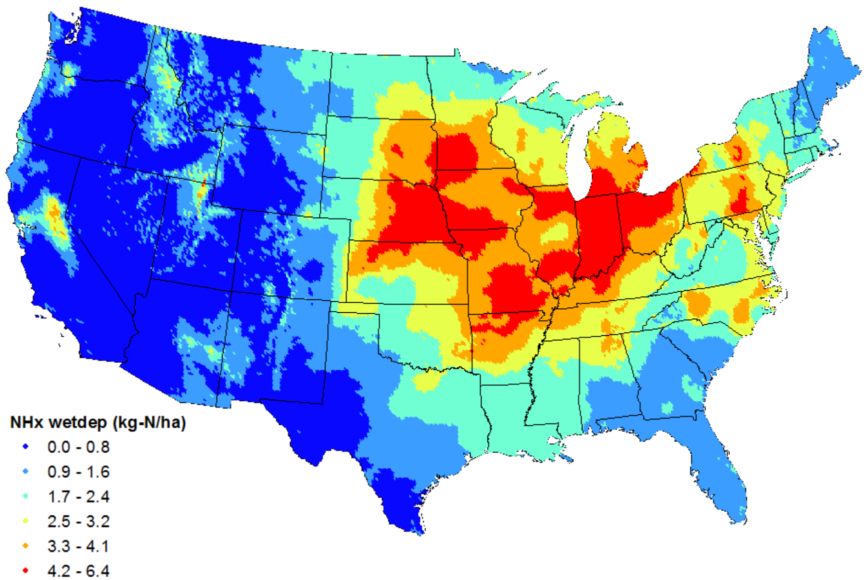
Relative concentration ratios of pNH_4 and NHx

- Expect higher ratios in East given available NO_3 and SO_4 relative to West
- Also expect higher ratios in North given temperature dependence on NH_4 - NH_3 thermodynamics
- Spatial patterns mostly dominated by excess NH_3, influenced by NH_3, NOx and SOx emissions, sea salts, and thermodynamics

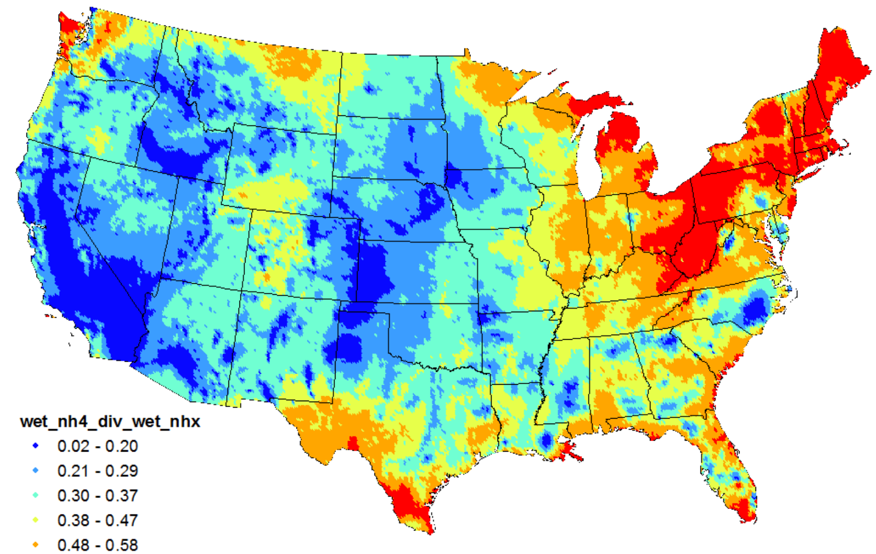


Contribution of pNH_4 to wet NHx deposition

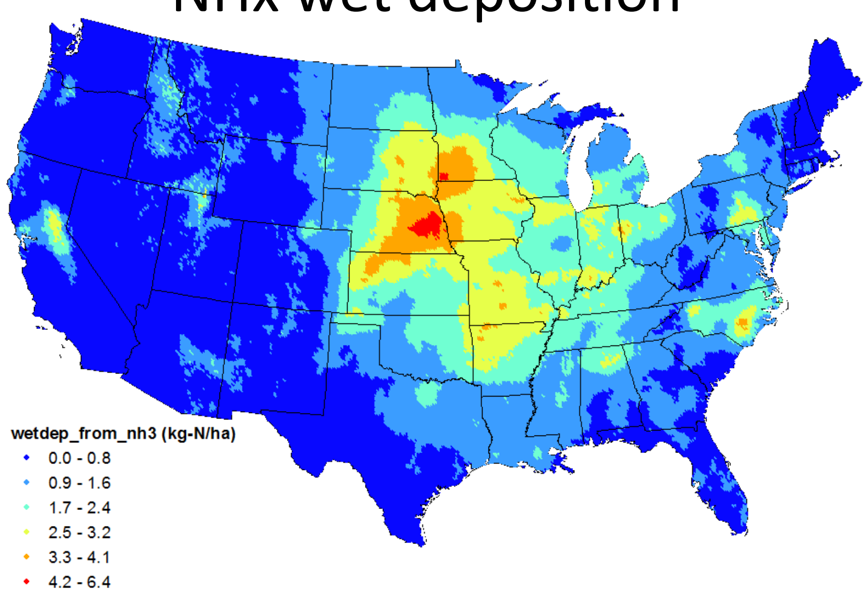
Note dry dep △



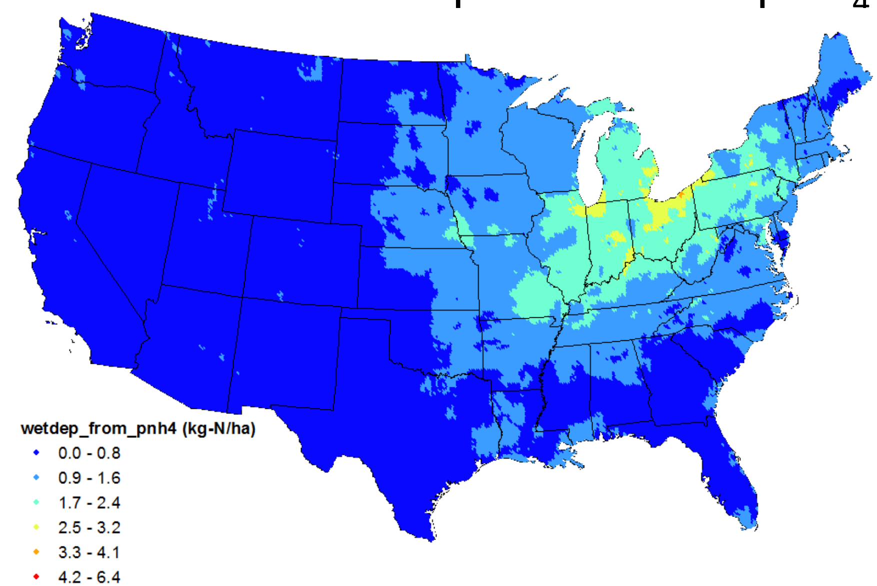
NHx wet deposition



Fraction of NHx wet deposition from pNH_4

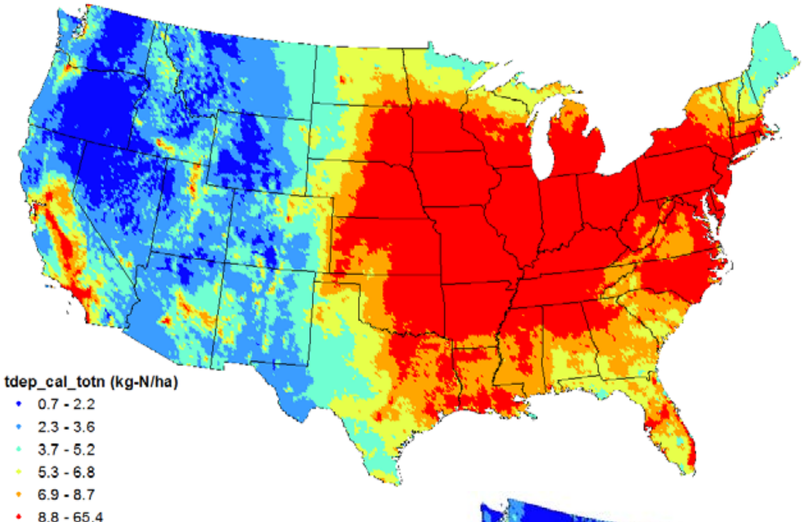


NH_3 cont to NHx wet deposition

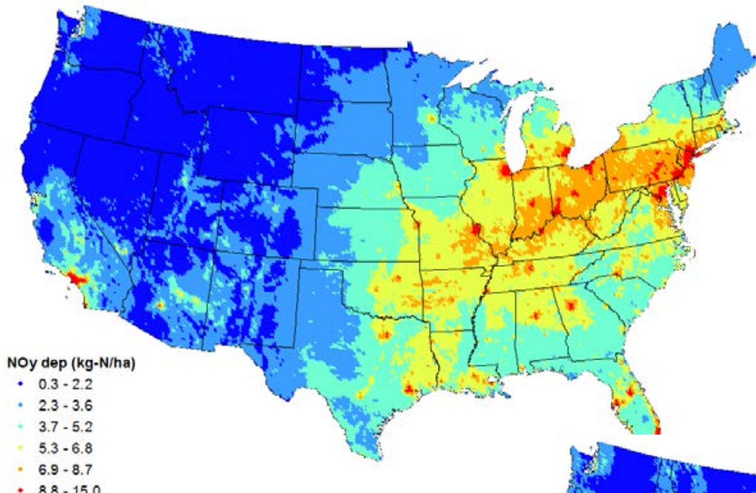


pNH_4 cont to NHx wet deposition

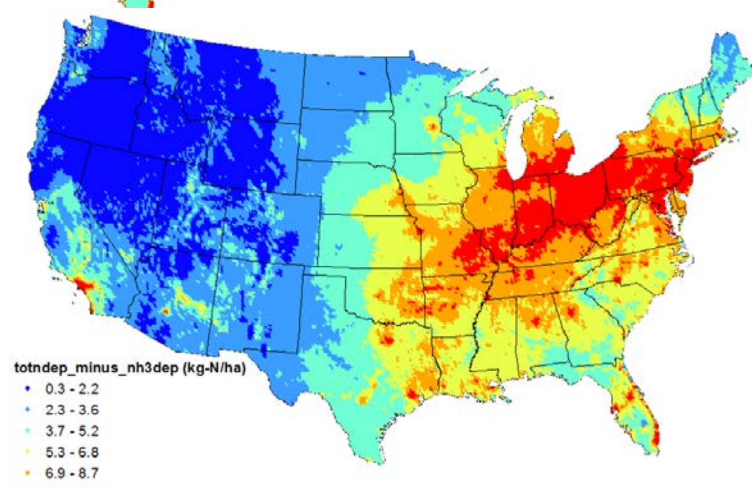
Capacity differences between NOy and NOy plus particulate NH_4, referenced to total N deposition.



NHx + NOy deposition

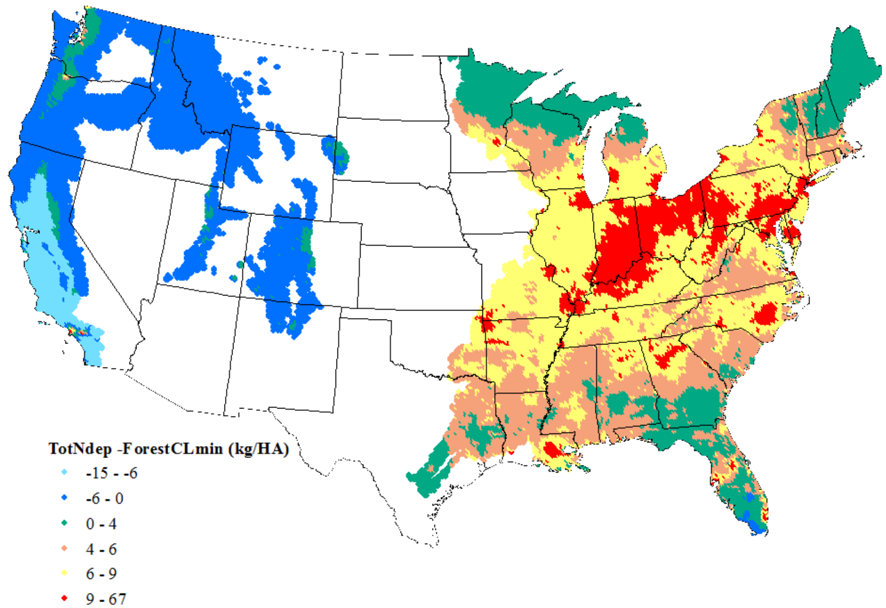


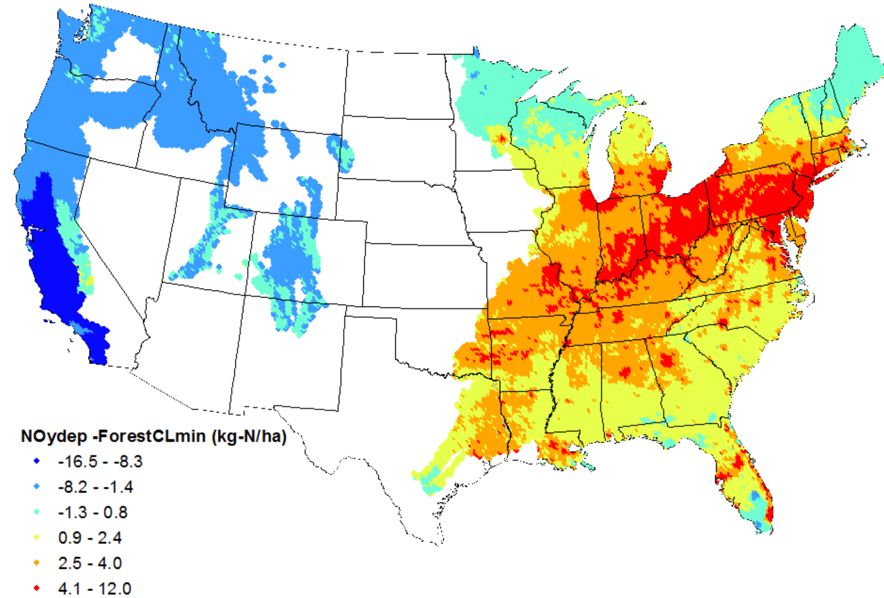
NOy deposition

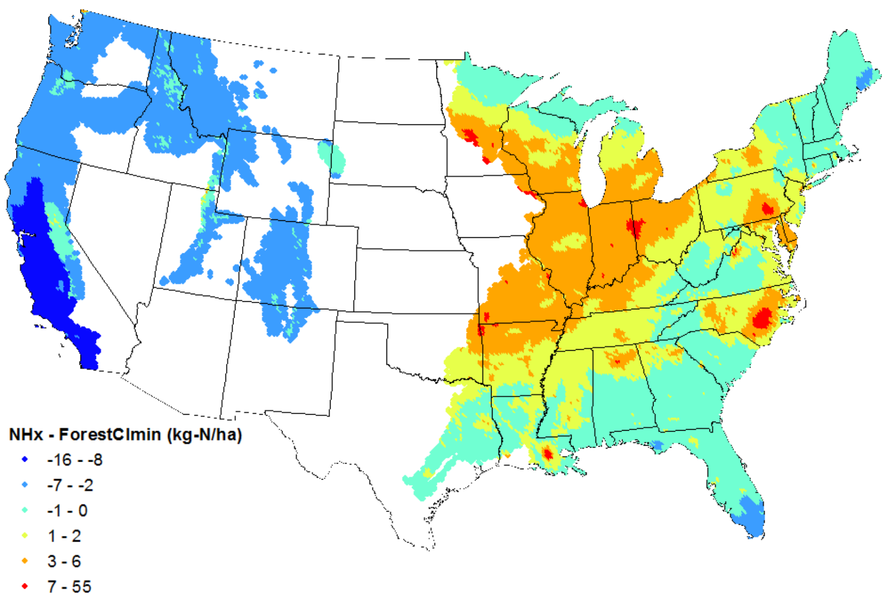


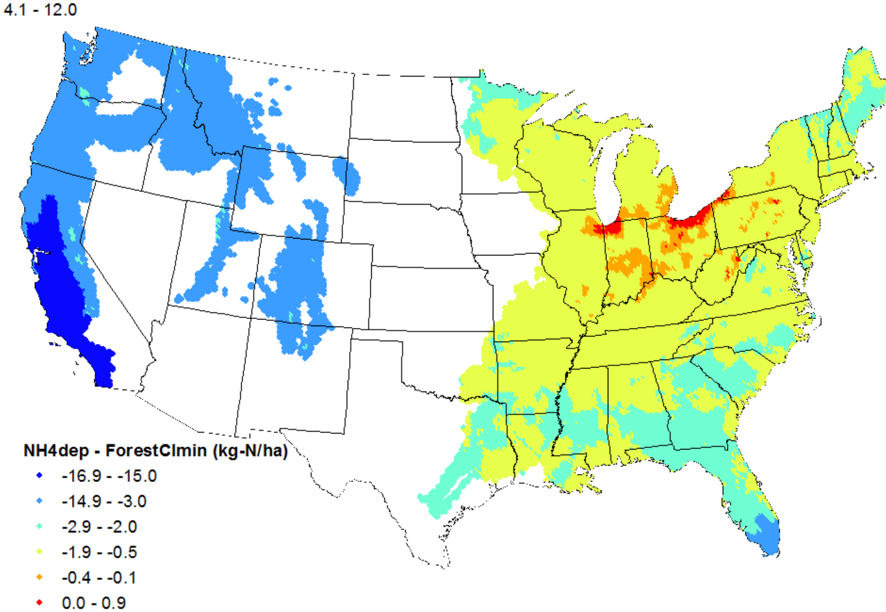
NHx + NOy deposition – NH_3 contributions

Critical Load exceedance example: Forest health in relation to N deposition components



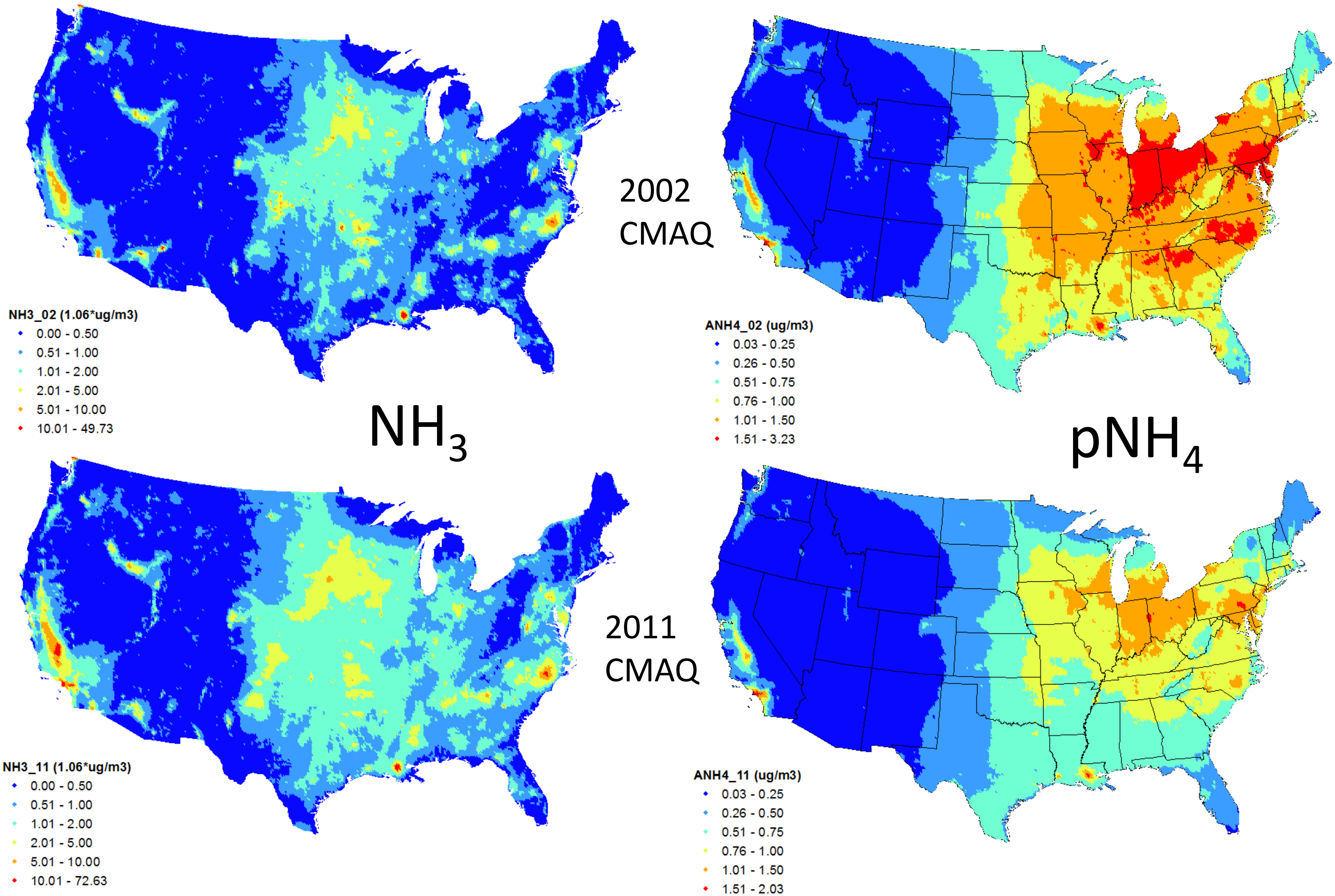






Changes in ambient NH_3 and pNH_4

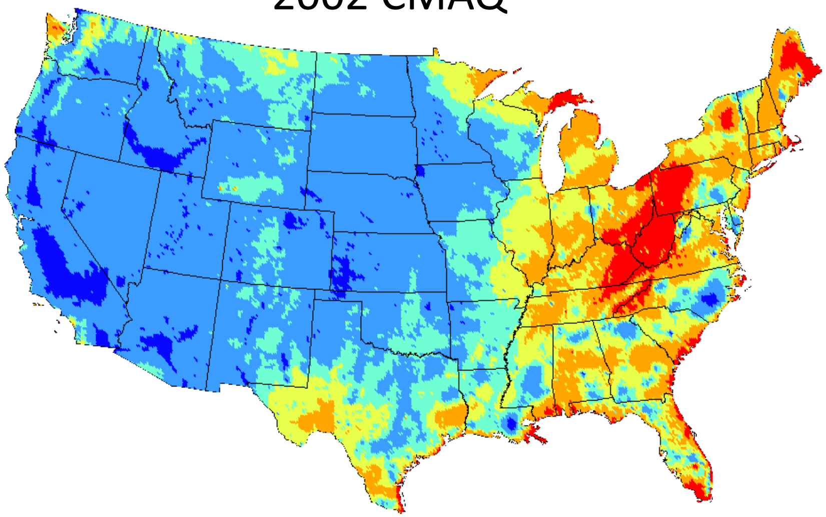
increasing NH_3 trend, decreasing NH_4



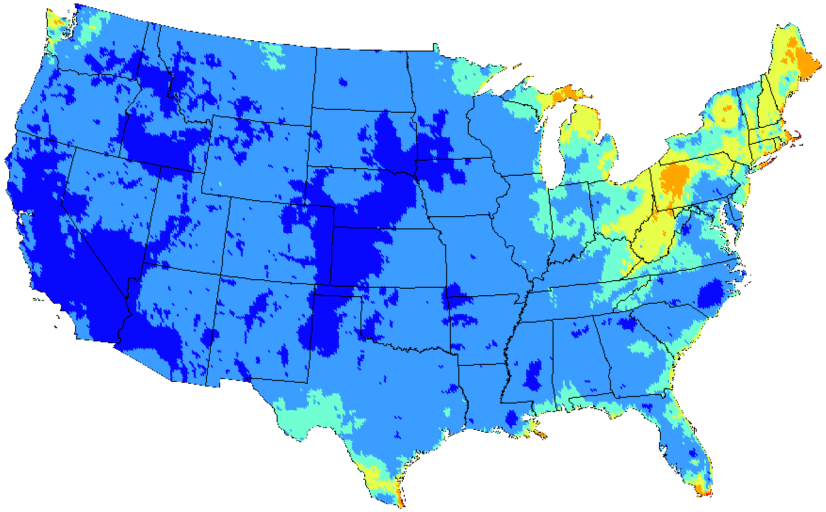
Change in ambient pNH_4/NHx

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

2002 CMAQ

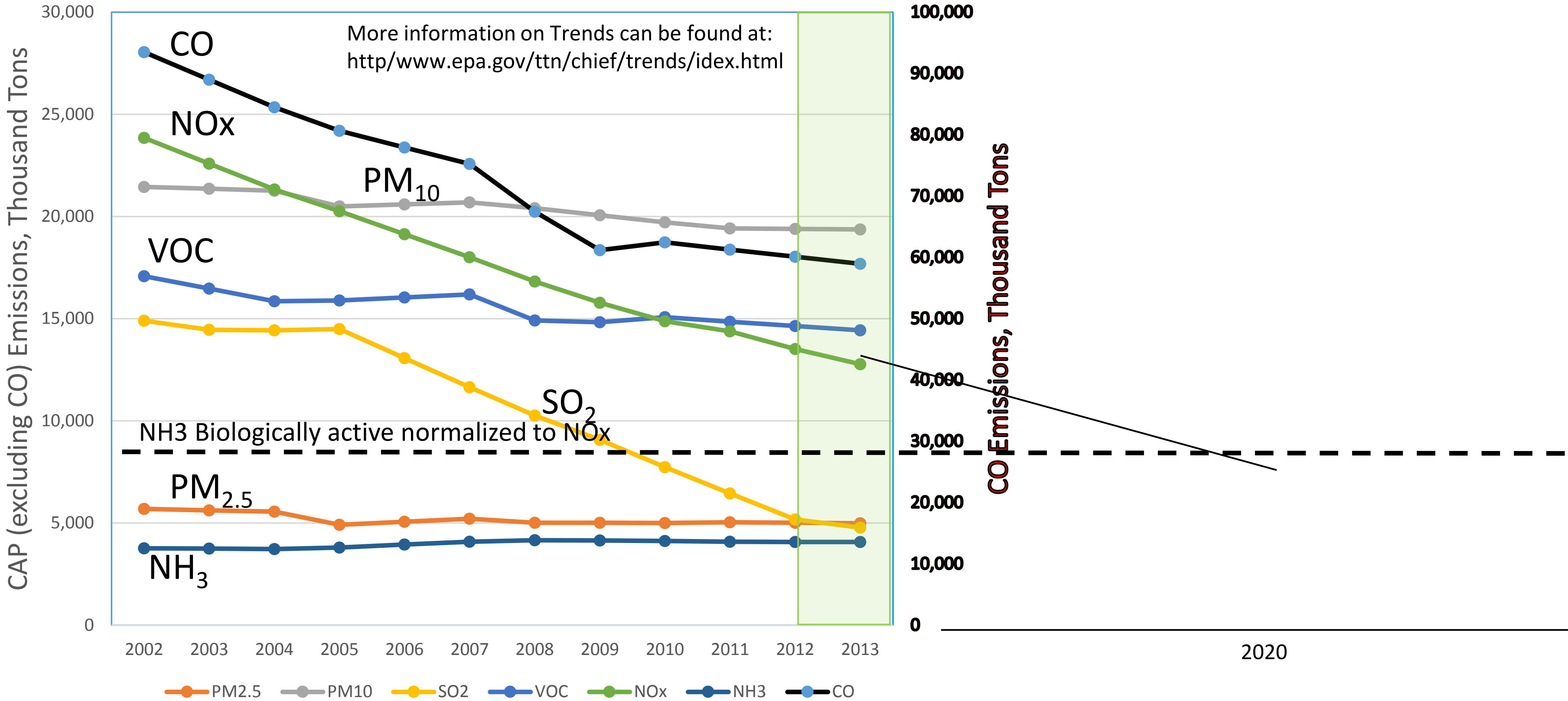


2011 CMAQ



0.81 - 0.97

Emission changes



Next Steps

- Building a weight-of-evidence" argument
  - Examine quantifiable scavenging metrics in CTMs
    - e.g., GEOSchem estimates scavenging of NH_3, but does not include aqueous phase chemistry
  - Develop CMAQ process analysis results specific to NH_3 production and loss, resources permitting
  - Explore other analyses, e.g.
    - Insights from atmospheric column profile data sets
      - Expected enhanced NH_4 above surface level
    - Observation sets before and after precipitation events
    - Temporally resolved analyses of modeled results
      - Are there significant differences in NH_4/NH_3 ratios before precipitation?
- Refine CL exceedance analyses
- Monitoring Implications