Atmospheric Nitrogen Measurements with a focus on a possible NOx/SOx secondary standard

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Rich Scheffe, U.S. EPA OAQPS

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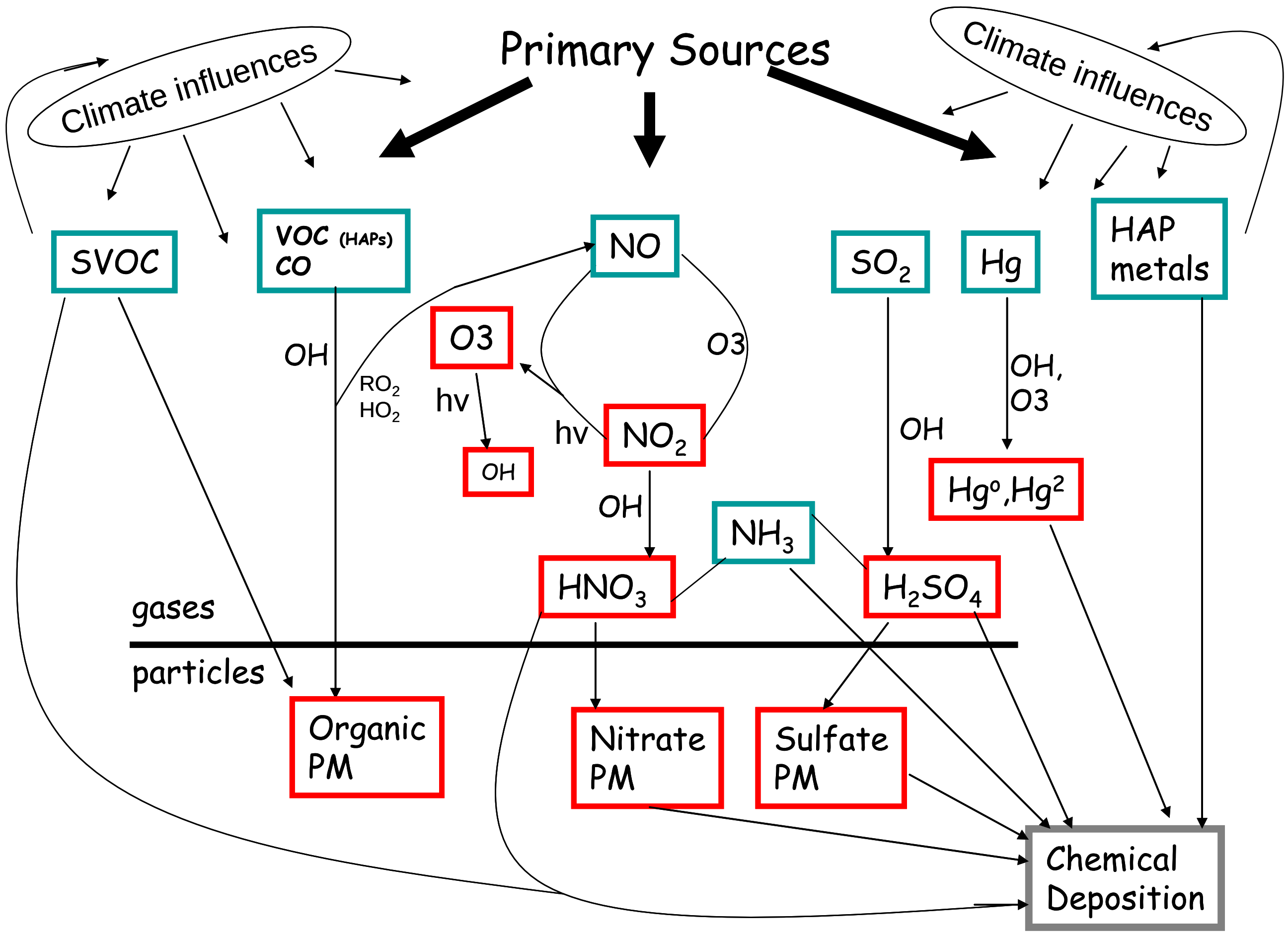
Why Nitrogen?

Emerging (?) Challenges for Air Policy

- Developing Multiple pollutant integrated management strategies
- Assessing and Protecting Ecosystem Health
- Multiple spatial scales of interest
- Intercontinental and Cross-Border Transport
- Maintaining AQM System Efficiency in the face of Changing Climate
- Ongoing Assessments and feedbacks of program progress (accountability)

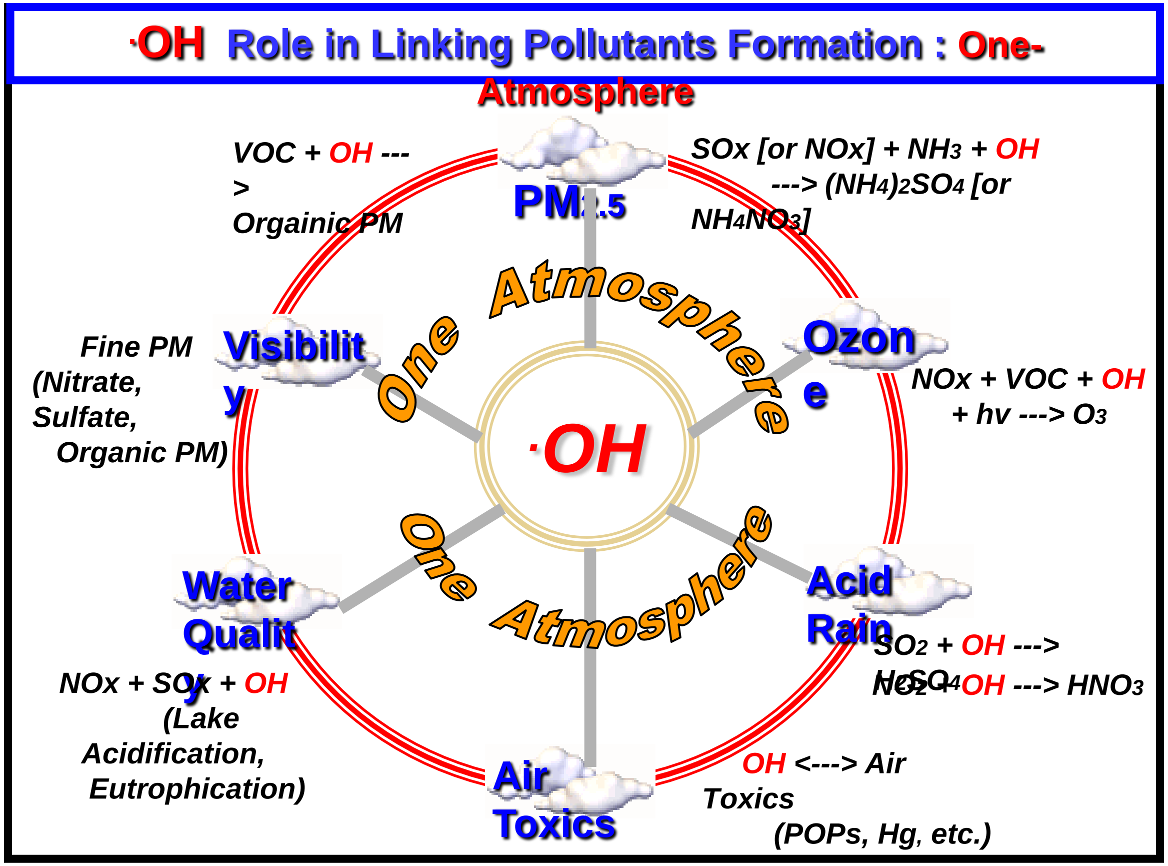
Key atmospheric pollutants and subsequent deposition are interwoven through many of these chemical processes, linking human and ecosystem health



One atmosphere treatment is important for Climate-AQ assessments

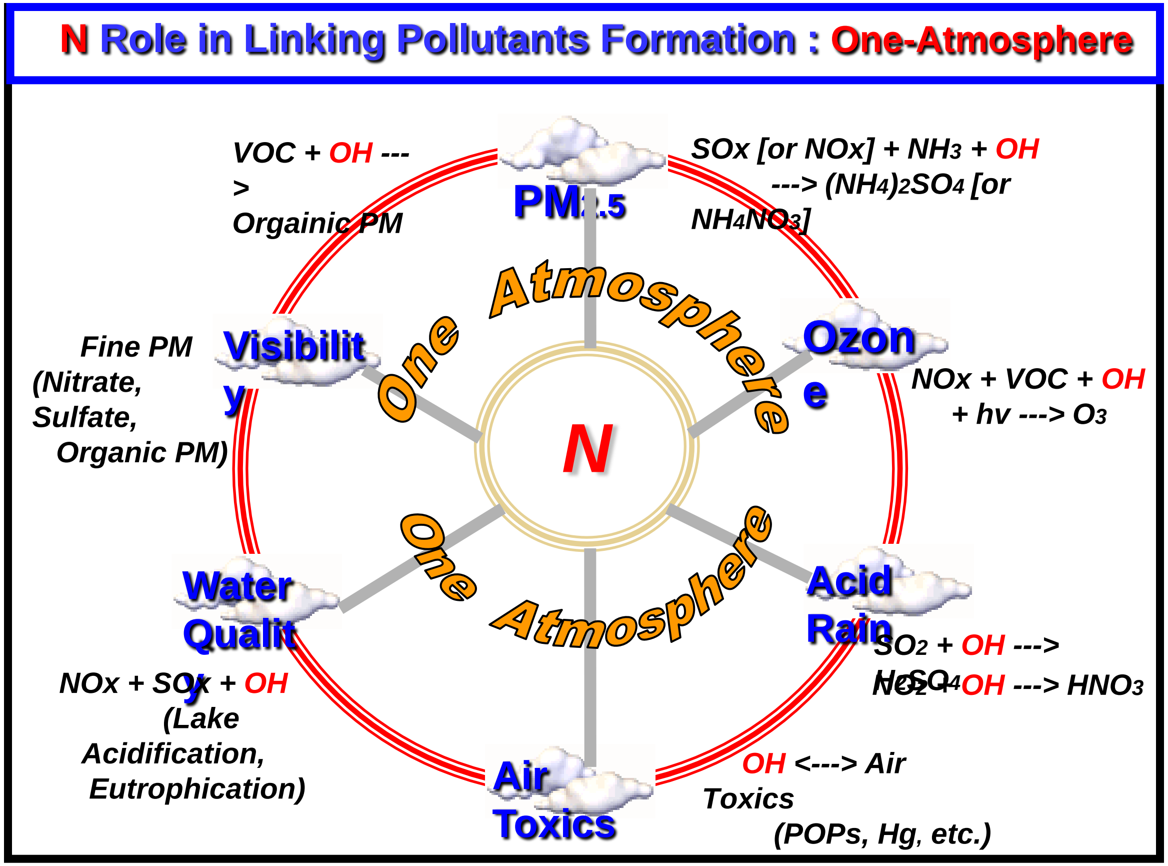
Meteorology and climate affect these reactions which are dependent on temperature, light and moisture.

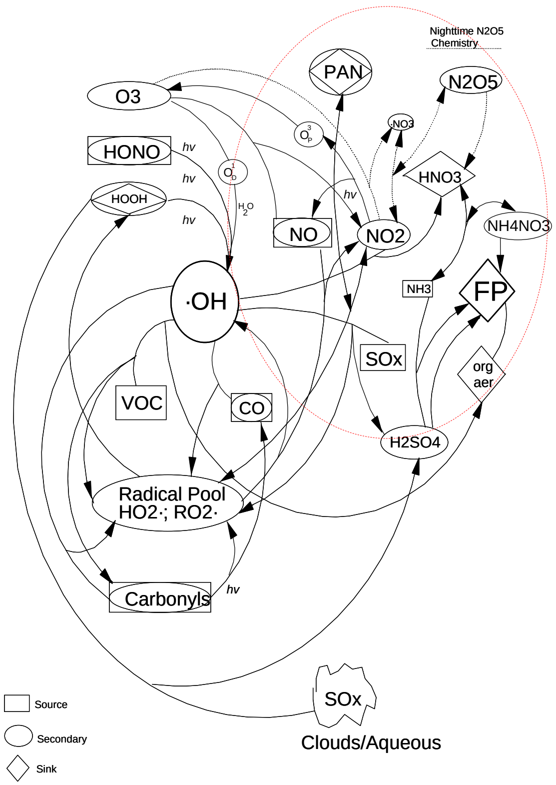
Rekindled appreciation for oxidation processes



C. Jang

Rekindled appreciation for Nitrogen





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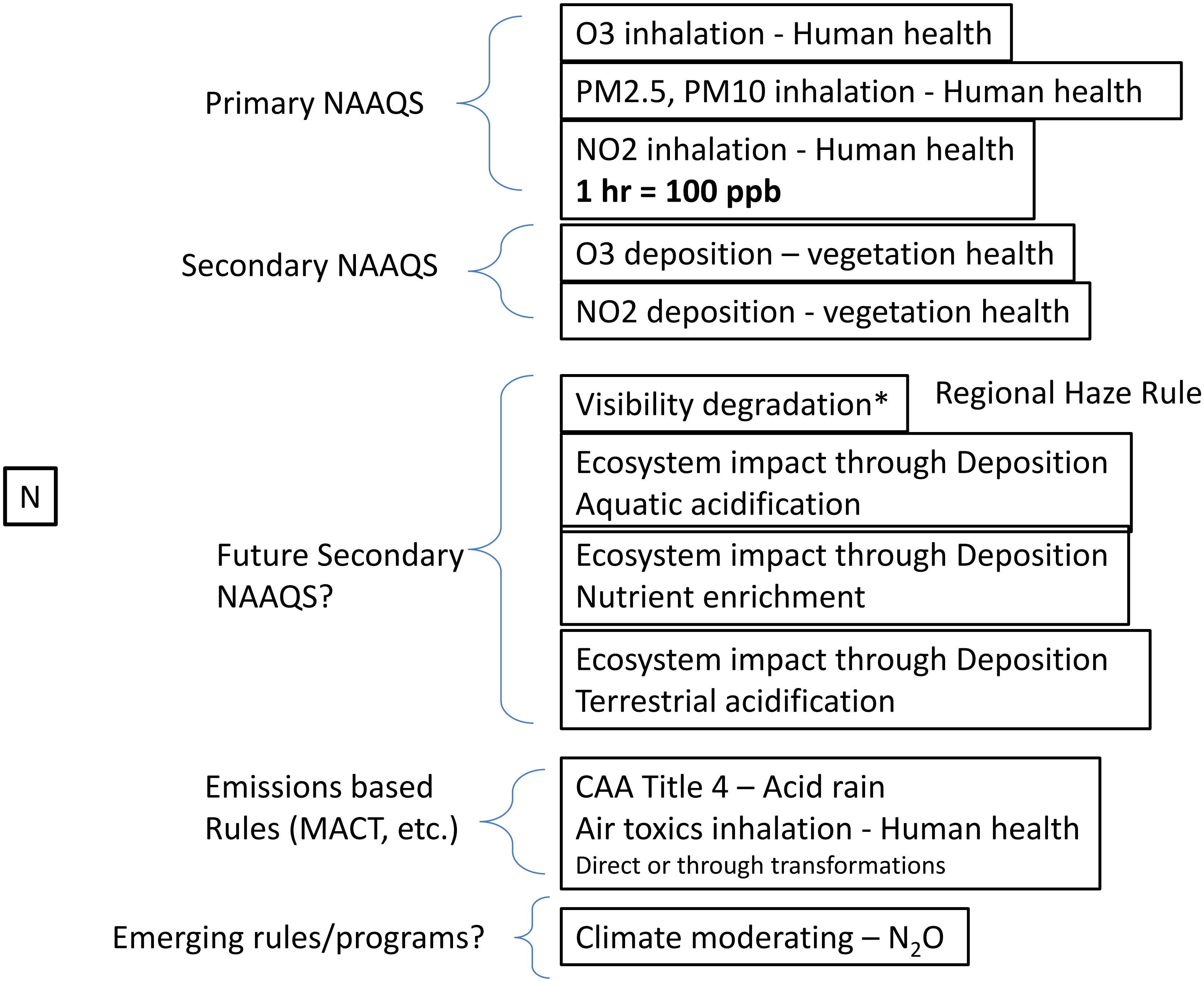
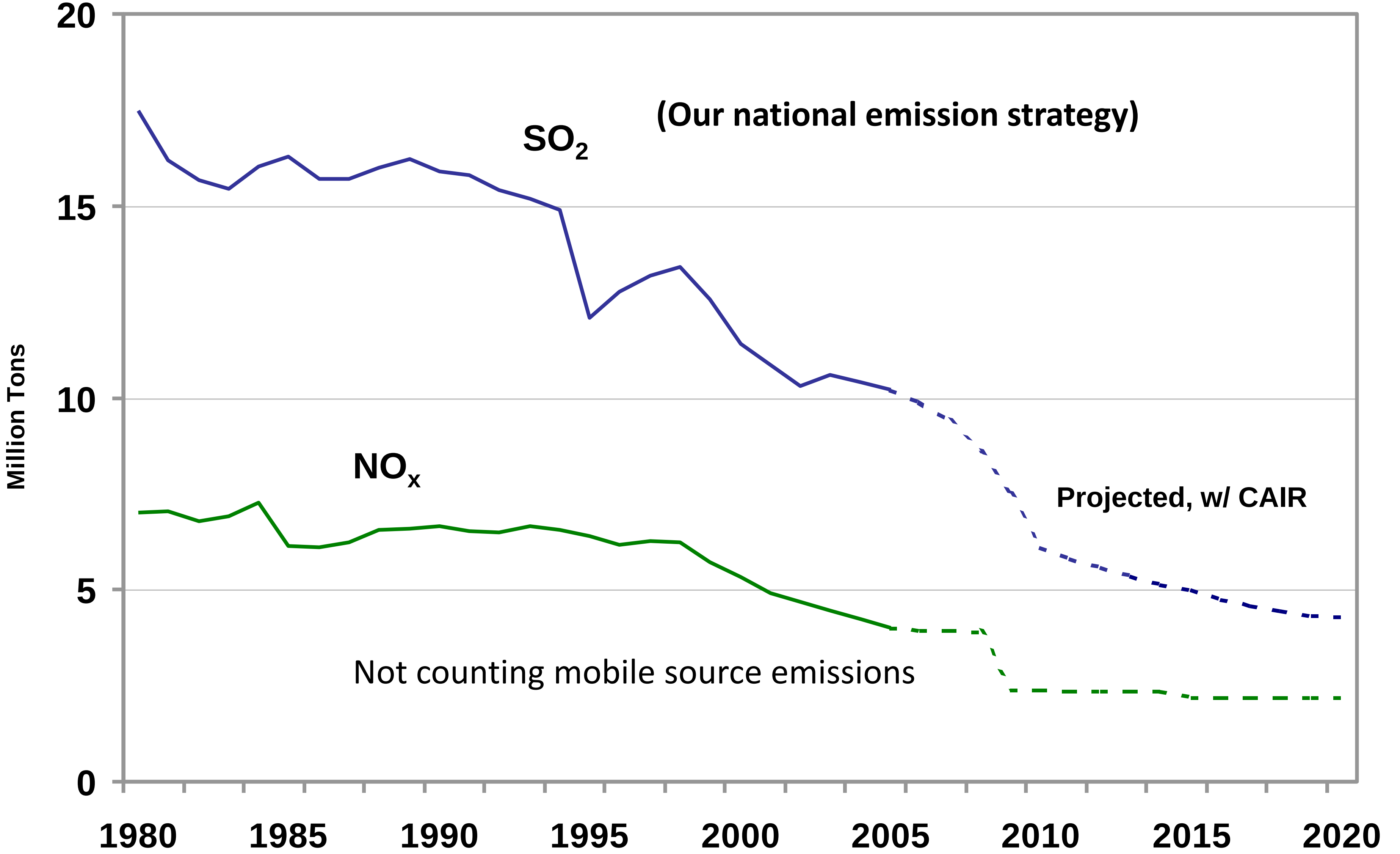

N
Primary NAAQS
O3 inhalation - Human health
PM2.5, PM10 inhalation - Human health
NO2 inhalation - Human health
1 hr = 100 ppb
Secondary NAAQS
O3 deposition – vegetation health
NO2 deposition - vegetation health
Future Secondary NAAQS?
Visibility degradation*
Regional Haze Rule
Ecosystem impact through Deposition
Aquatic acidification
Ecosystem impact through Deposition
Nutrient enrichment
Ecosystem impact through Deposition
Terrestrial acidification
Emissions based Rules (MACT, etc.)
CAA Title 4 – Acid rain
Air toxics inhalation - Human health
Direct or through transformations
Emerging rules/programs?
Climate moderating – N_2O

National NO_x and SO_2 Power Plant Emissions: Historic and Projected with CAIR

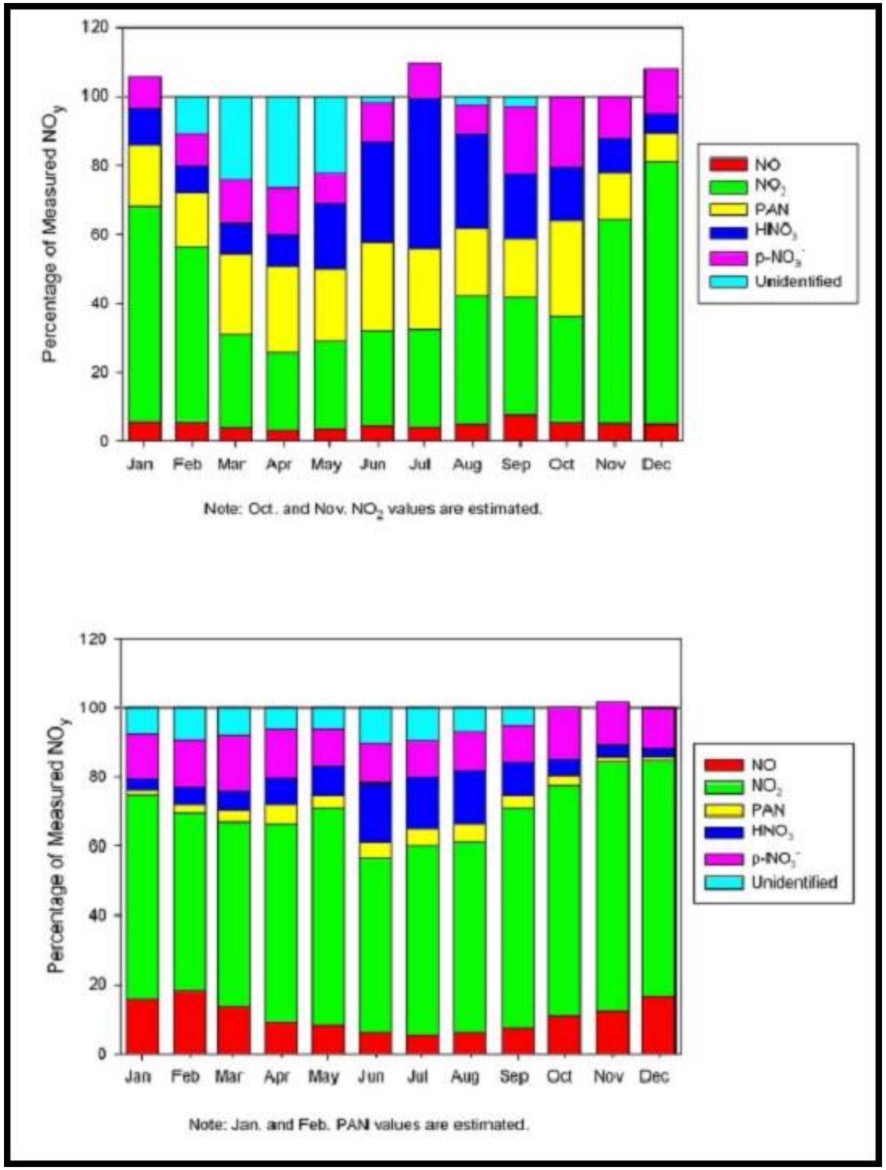


Source: EPA

Atmospheric nitrogen species of interest

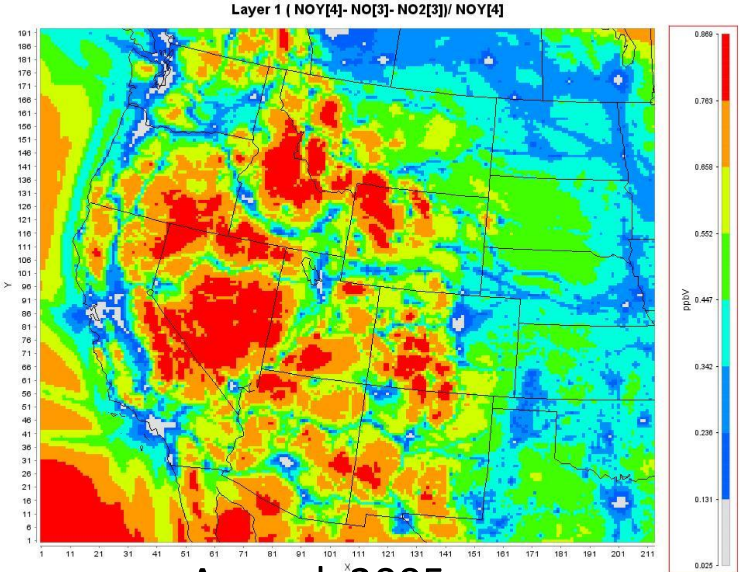
significance for mass budget

- Reactive
  - oxidized species (NOy)
    - NO, NO_2, HNO_3, PAN, p-NO_3, HONO, org-N (non PAN)
    - With N_2O, assumed under the CAA definition of NOx
    - Atmospheric science definitions
      - NOx = NO +NO_2
      - NOz = NOy - NOx
  - Reduced nitrogen
    - NH_3, NH_4
    - NHx = NH_3 + NH_4
- Nonreactive
  - N_2O
- Following are some general patterns regarding the spatial and temporal distribution of NOy species in concentration and deposition

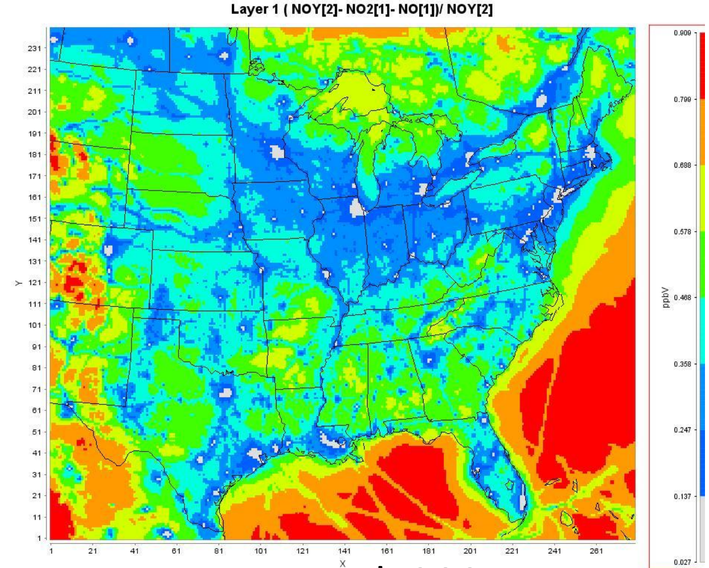


Source; Jason O'Brien, Env. Canada

Examples of the Relative Abundance of Several NO_y Species Measured at Two Rural Southeastern Canadian Sites as a Fraction of the Total Measured NO_y Concentration -- Kejimkujik, NS, (top) and Egbert, ON, (bottom) during 2003. Although both sites are in rural locations, the Kejimkujik, NS site represents more aged air masses as it)ies considerably further downwind from major sources of NOx relative to the Egbert site. (*Source: NARSTO, 2010*)

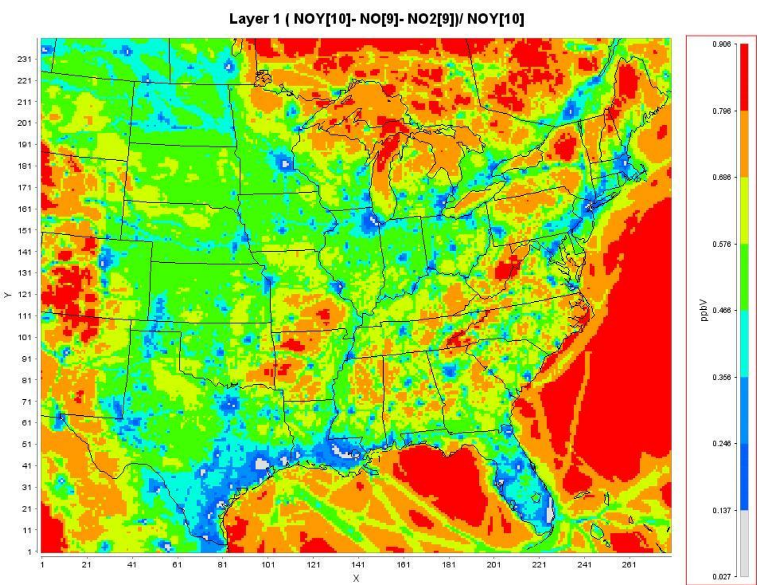


Annual, 2005

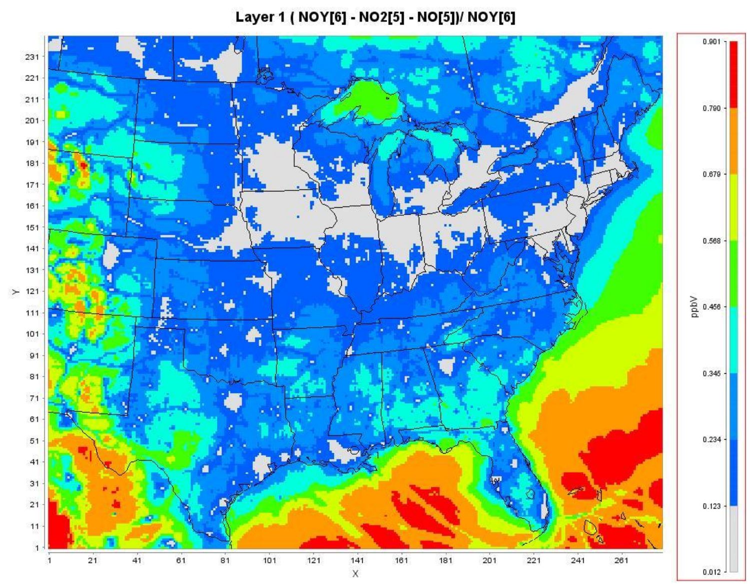


Annual, 2005

NOz/NOy

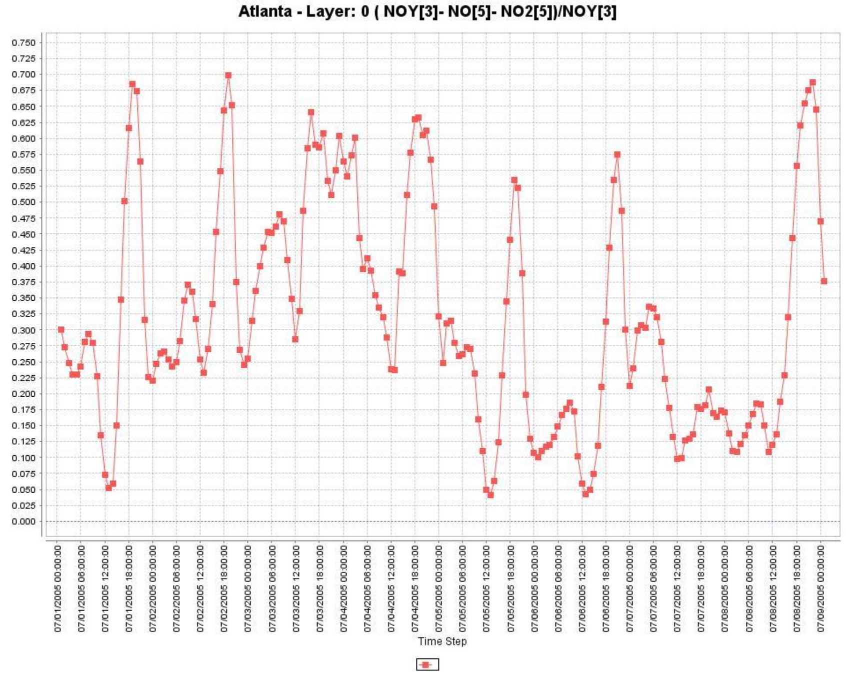


July, 2005

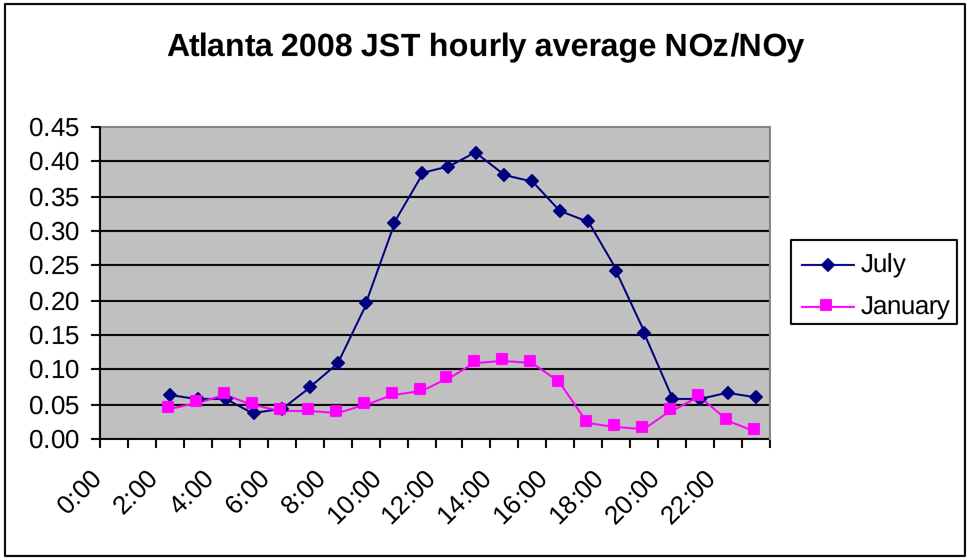


January, 2005

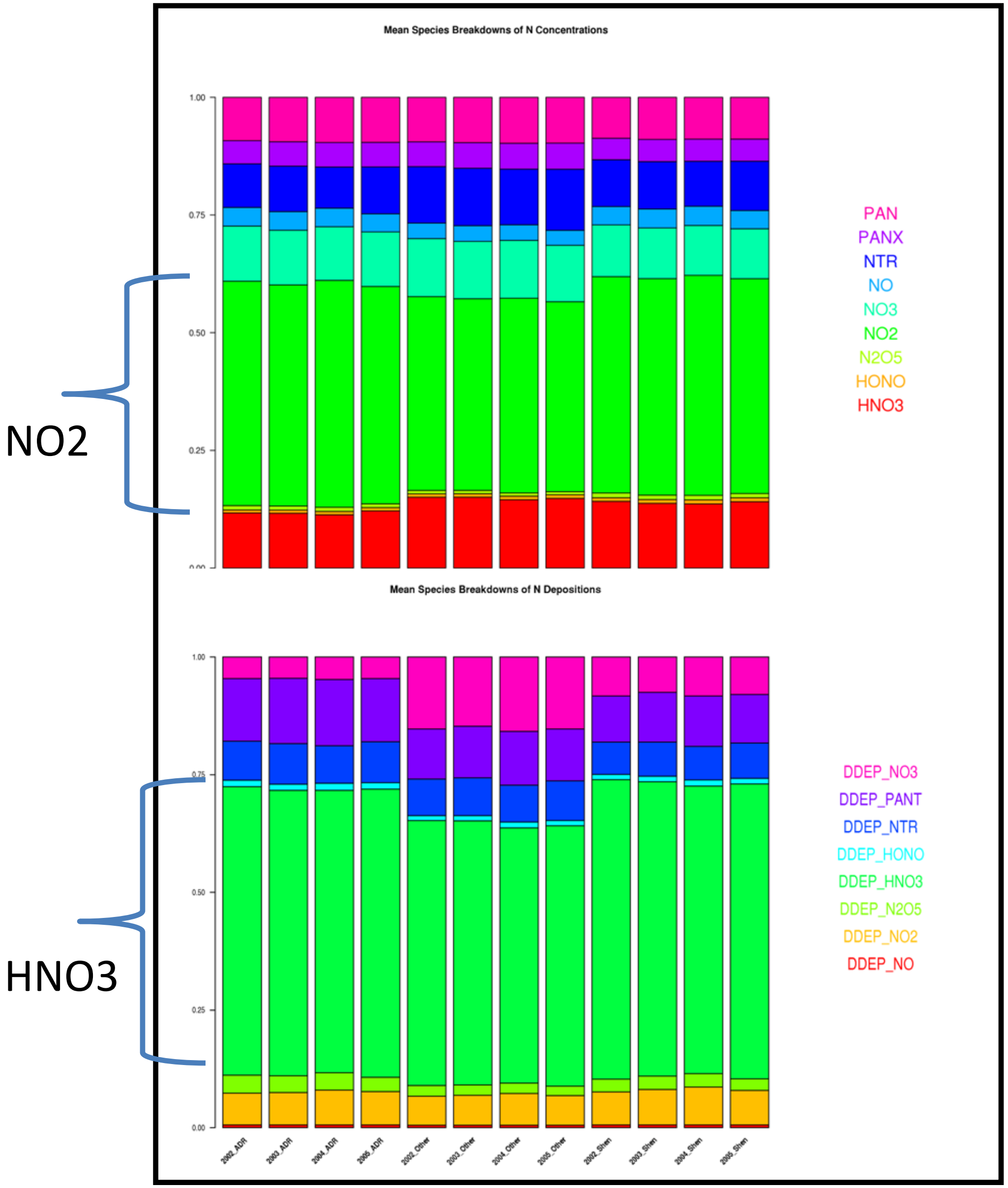
Diurnal profiles of NOz/NOy

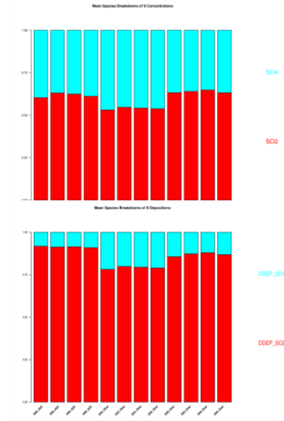


8 day sequence starting July 1, 2005 of NOz/NOy ratios in Atlanta.   The x-axis is GMT.



Observed NOz/NOy ratios at the Jefferson Street site in Atlanta, GA (courtesy of Eric Edgerton).



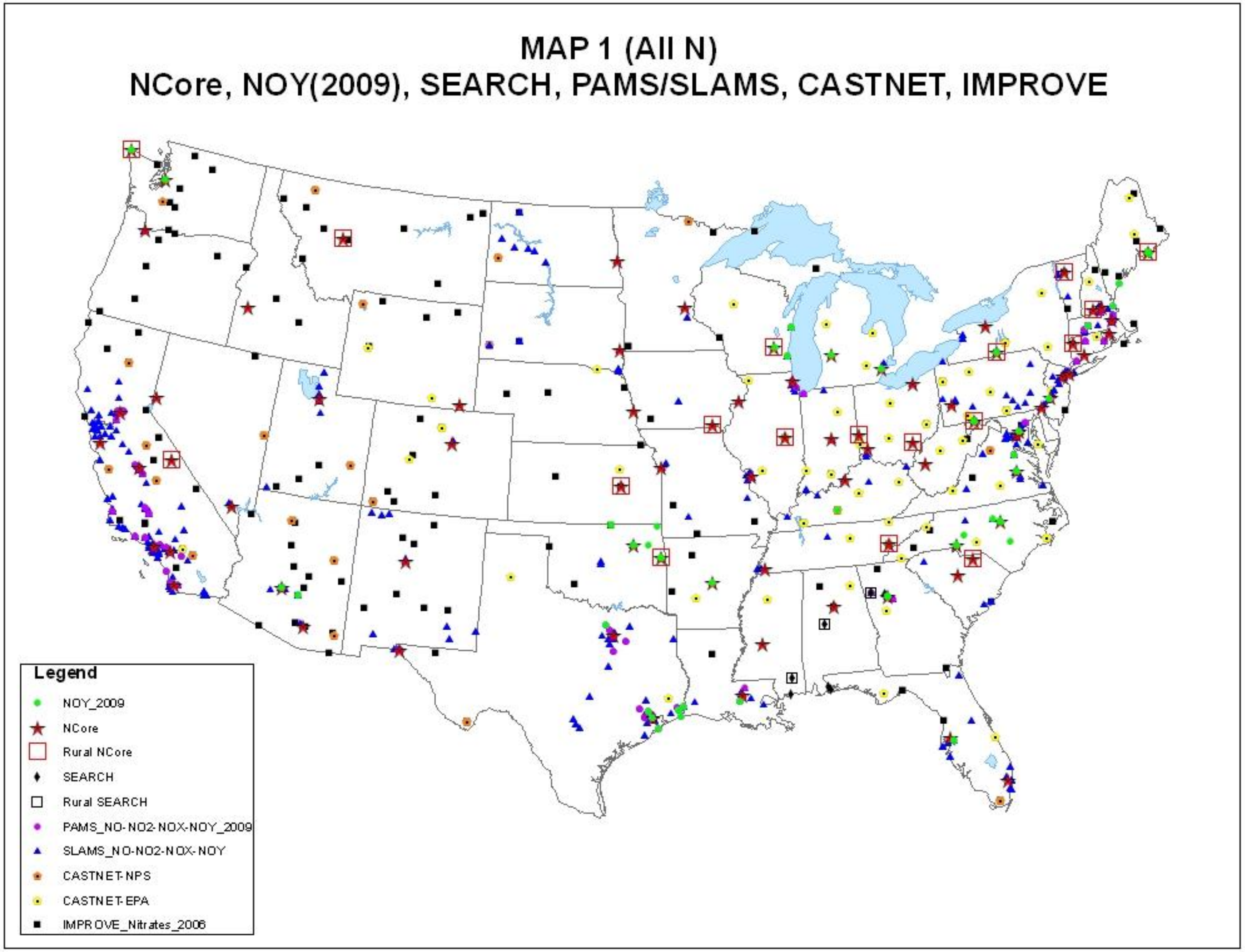


SO2 (blue) and sulfate concentration (top)
And deposition (bottom)

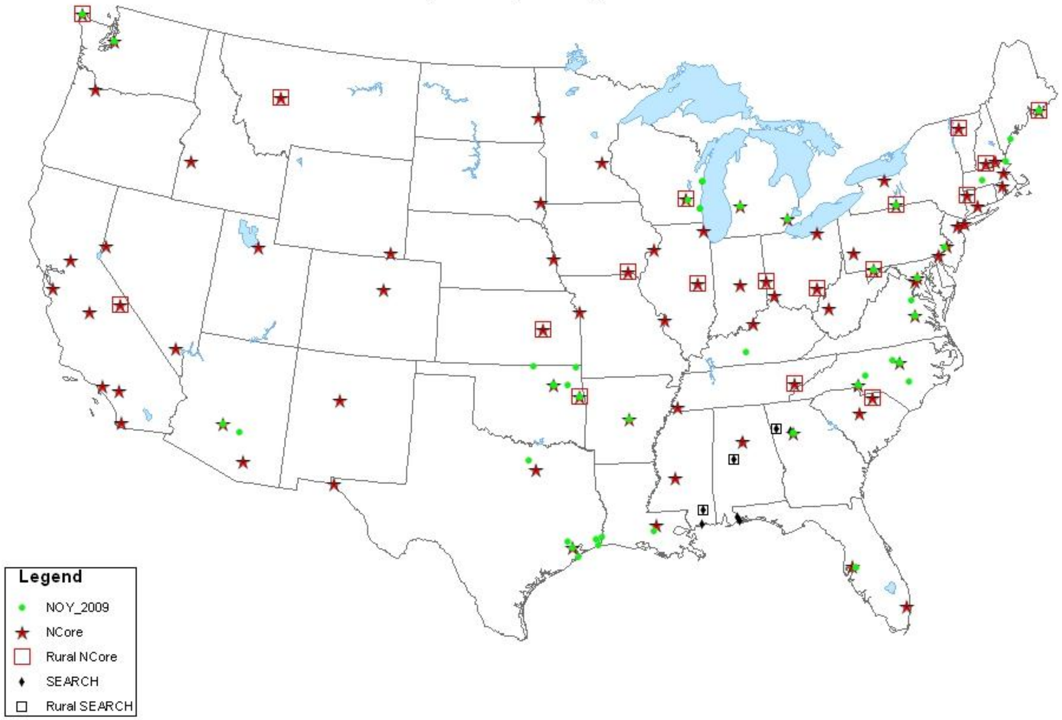
Comparison of NOy species fractions of concentration (top) and deposition (bottom) based on 2002-5 CMAQ for Adirondacks (left), Shenandoah (right) and Eastern U.S domain (center).

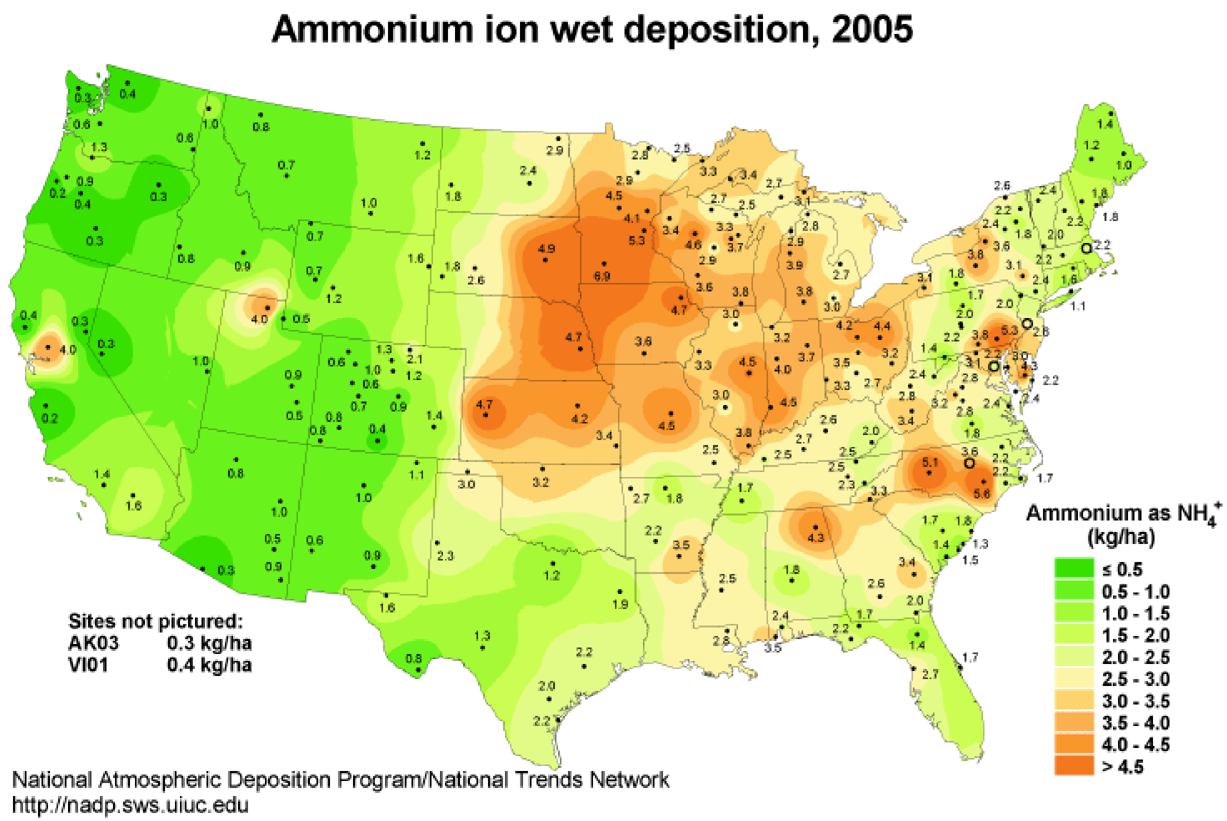
Toolbox of Atmospheric Nitrogen Observations (relatively routine)

- National NAAQS driven networks
- Visibility network (IMPROVE)
- SEARCH
- Dry deposition (CASTNET)
- Wet deposition (NADP)
- Satellites
- IAGOS International Flights
  - Previously MOZAIC and CARIBE

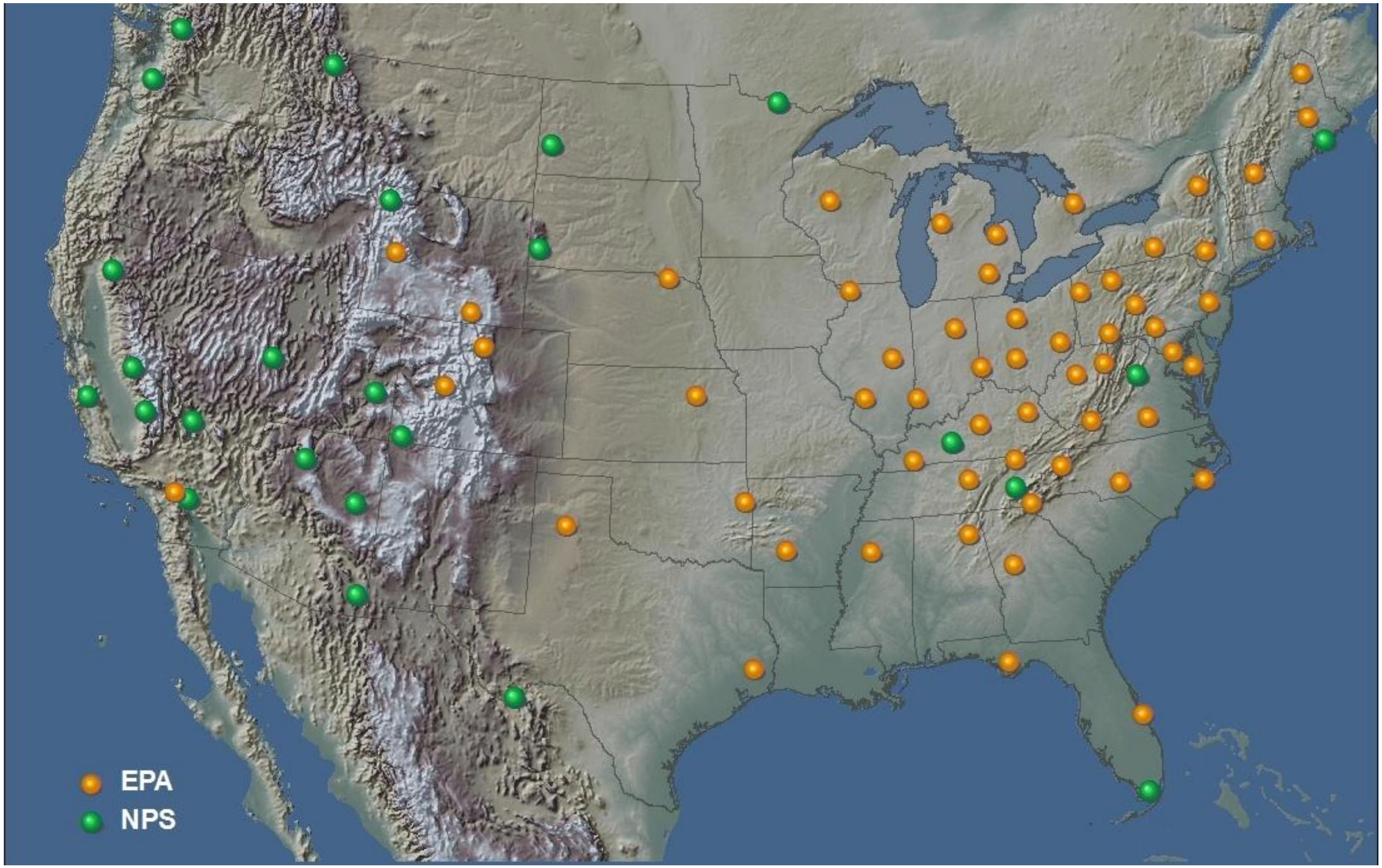

MAP 1 (All N)
NCore, NOY(2009), SEARCH, PAMS/SLAMS, CASTNET, IMPROVE
Legend
NOY_2009
NCore
Rural NCore
SEARCH
Rural SEARCH
PAMS_NO-NO2-NOX-NOY_2009
SLAMS_NO-NO2-NOX-NOY
CASTNET-NPS
CASTNET-EPA
IMPROVE_Nitrates_2006

MAP 4
Current & Planned Routine NOY Monitoring Sites
NCore, NOY(2009), SEARCH

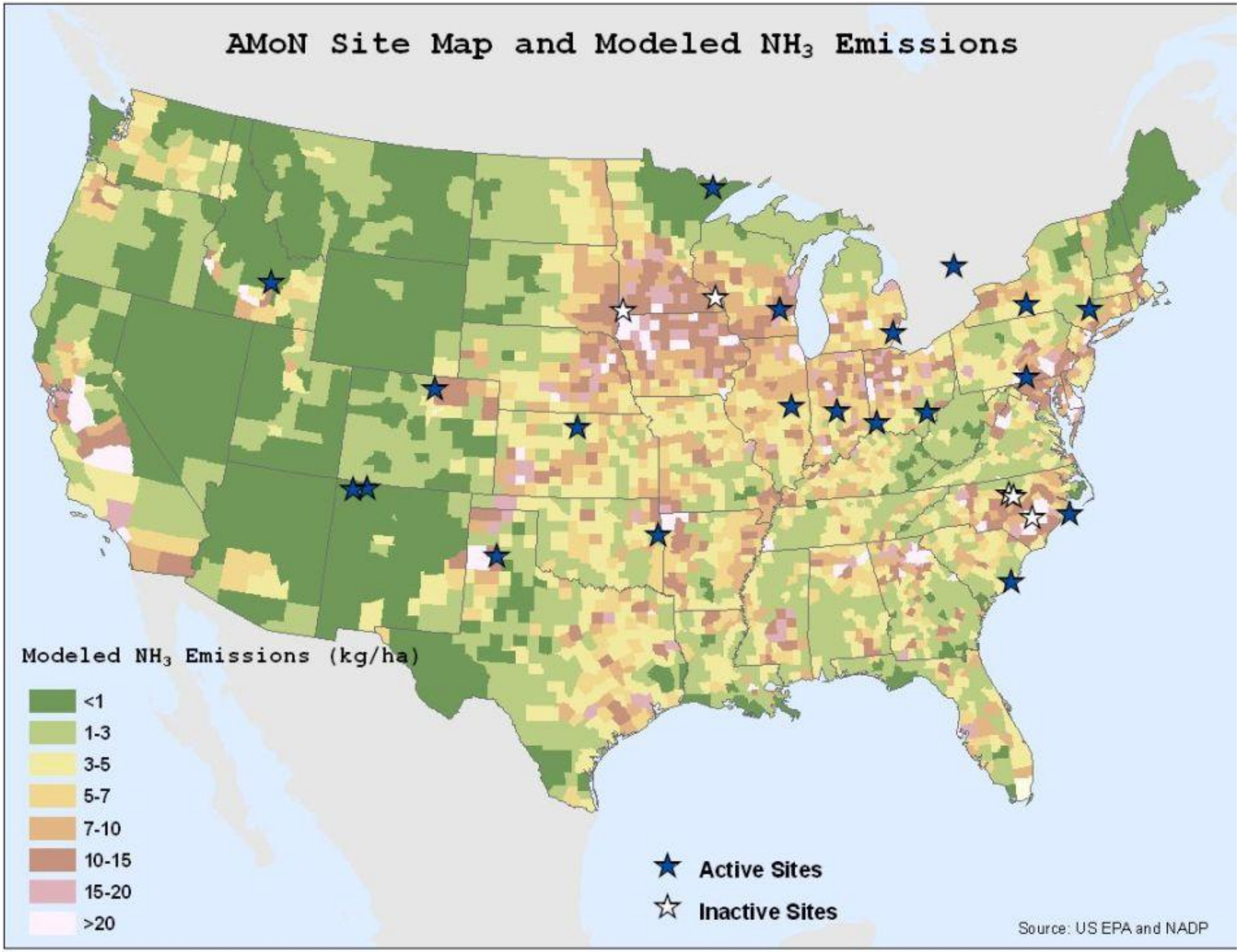




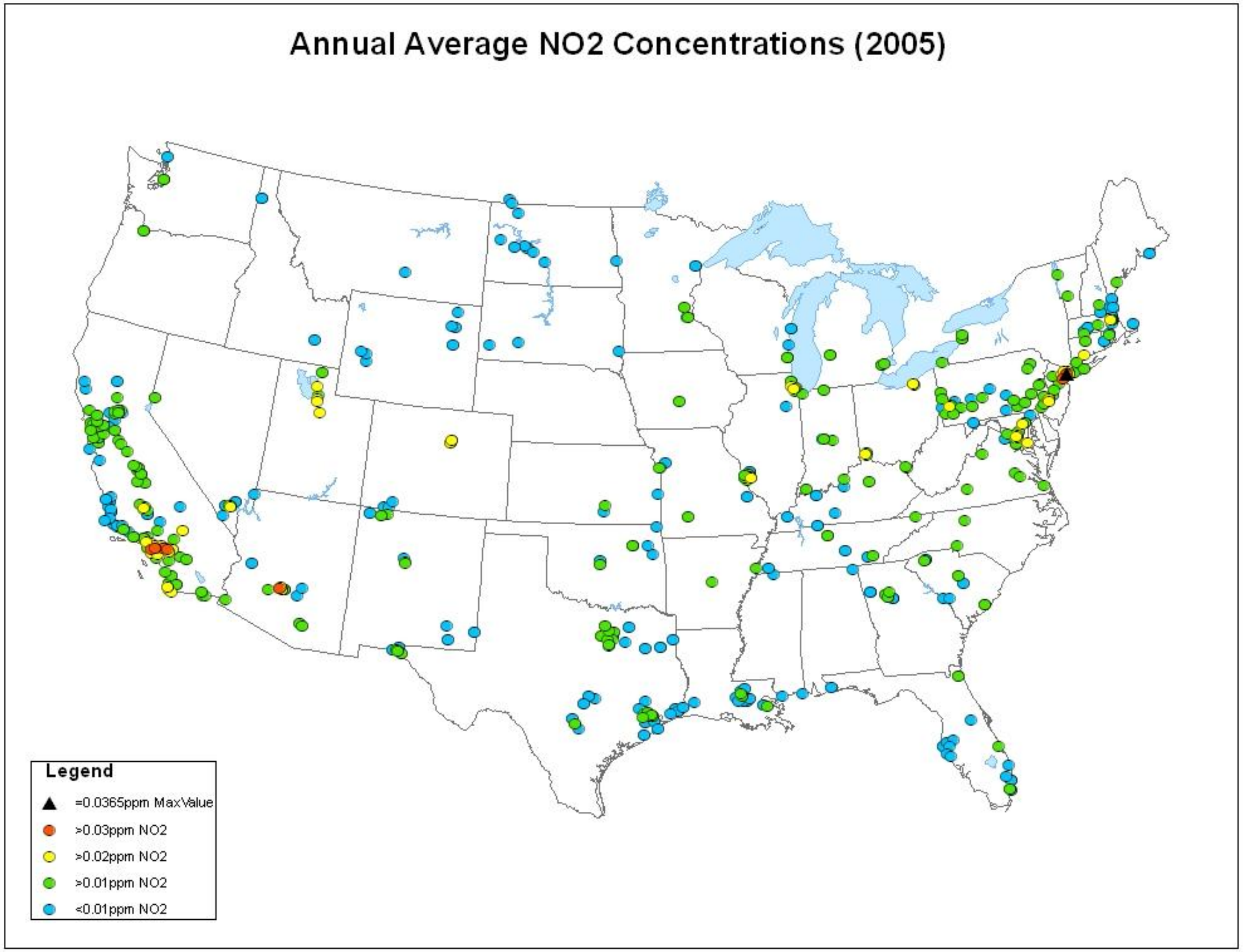
NADP: wet NO3, NH4, org-N?



CASTNET: t-NO3; NH4

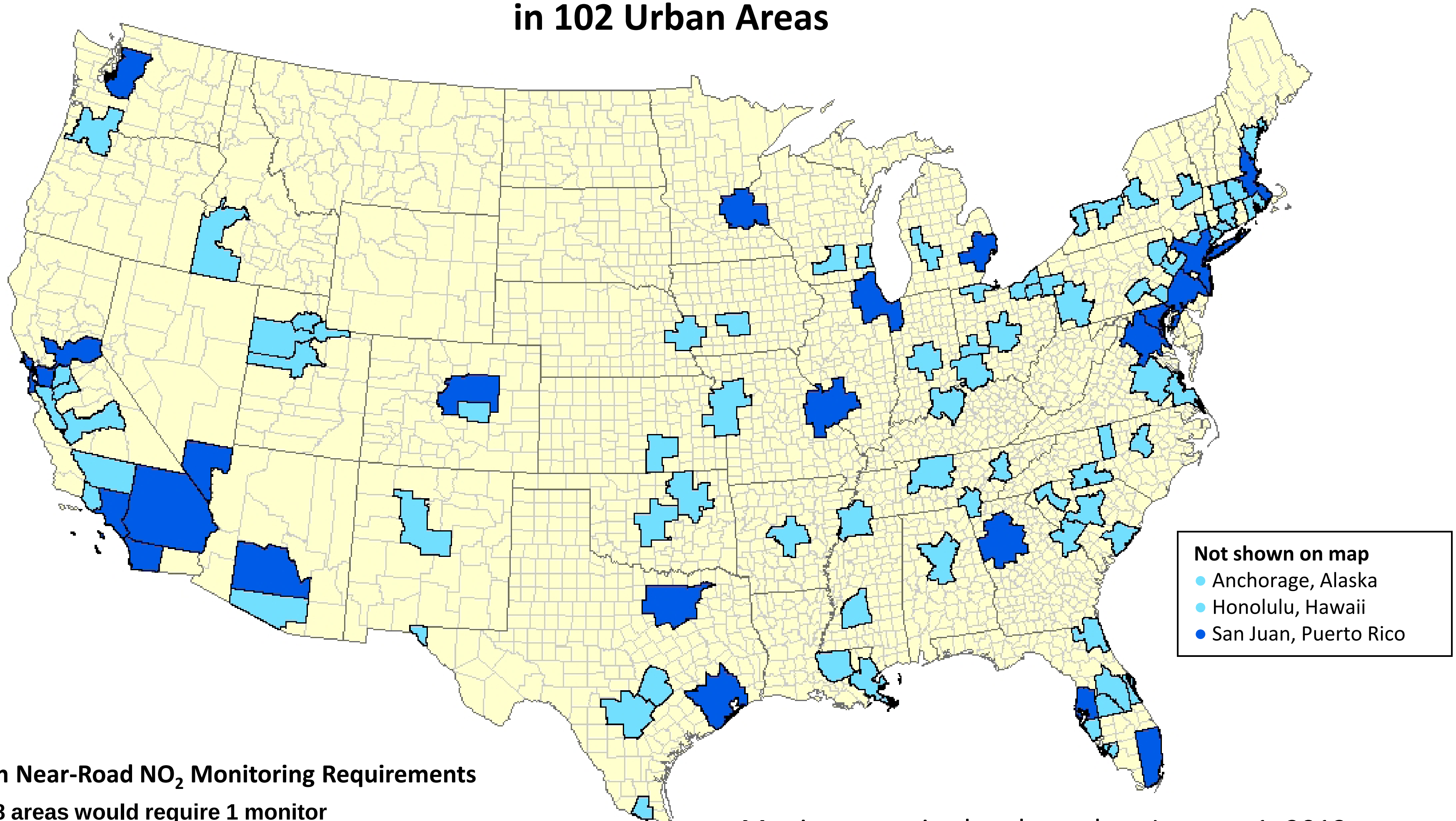


NH3 – NADP AMoN


Annual Average NO2 Concentrations (2005)
Legend
=0.0365ppm MaxValue
>0.03ppm NO2
>0.02ppm NO2
>0.01ppm NO2
<0.01ppm NO2

United States Environmental Protection Agency

Near Road NO_2 Monitors Are Required (1 hr NO_2 NAAQS = 150ppb) in 102 Urban Areas



Minimum Near-Road NO_2 Monitoring Requirements

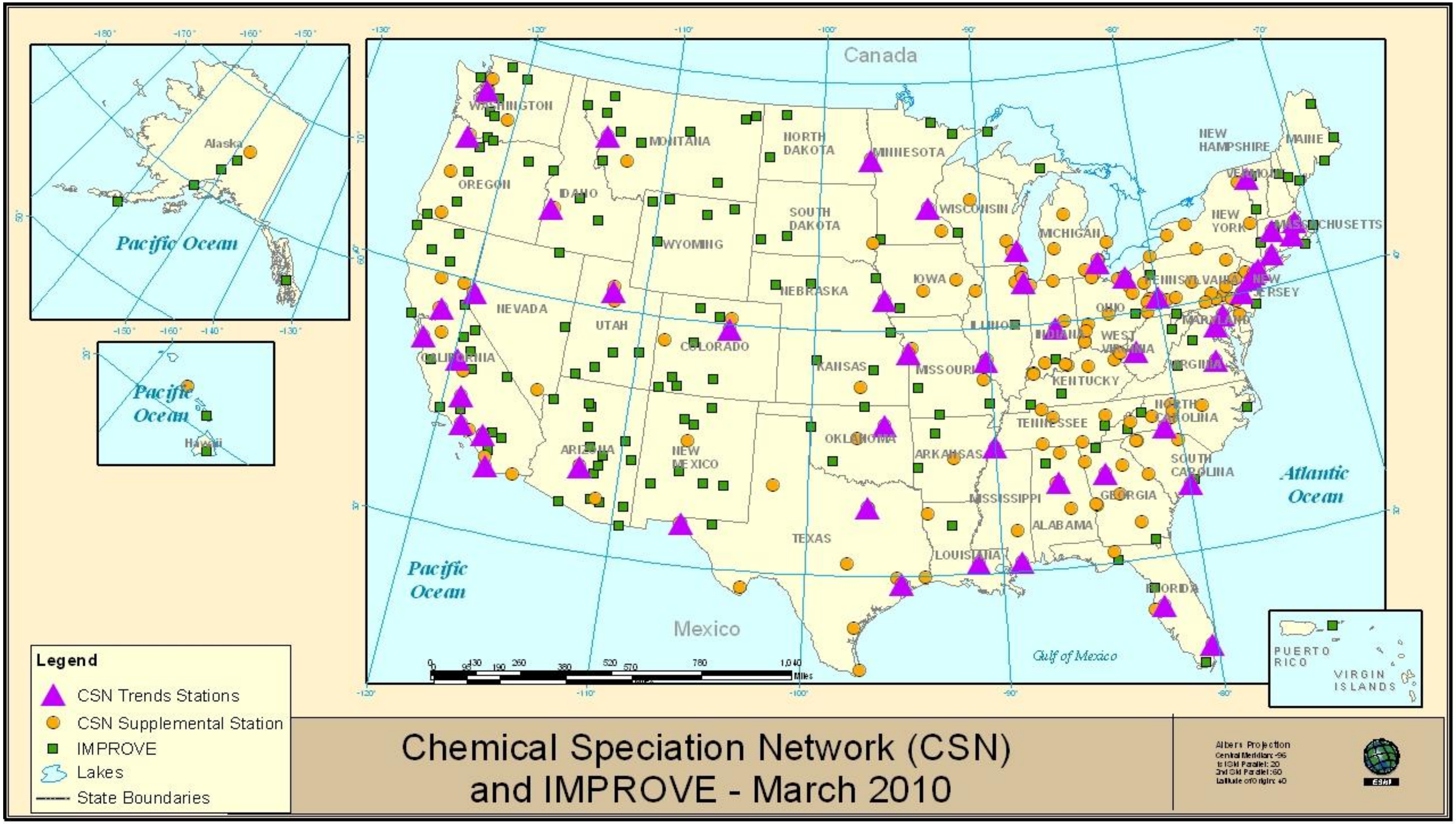
- **78 areas would require 1 monitor** (≥ 500,000 population)
- **24 areas would require 2 monitors** (≥ 2.5 million population or road segments with annual average daily traffic counts ≥ 250,000 vehicles)

Monitors required no later then January 1, 2013

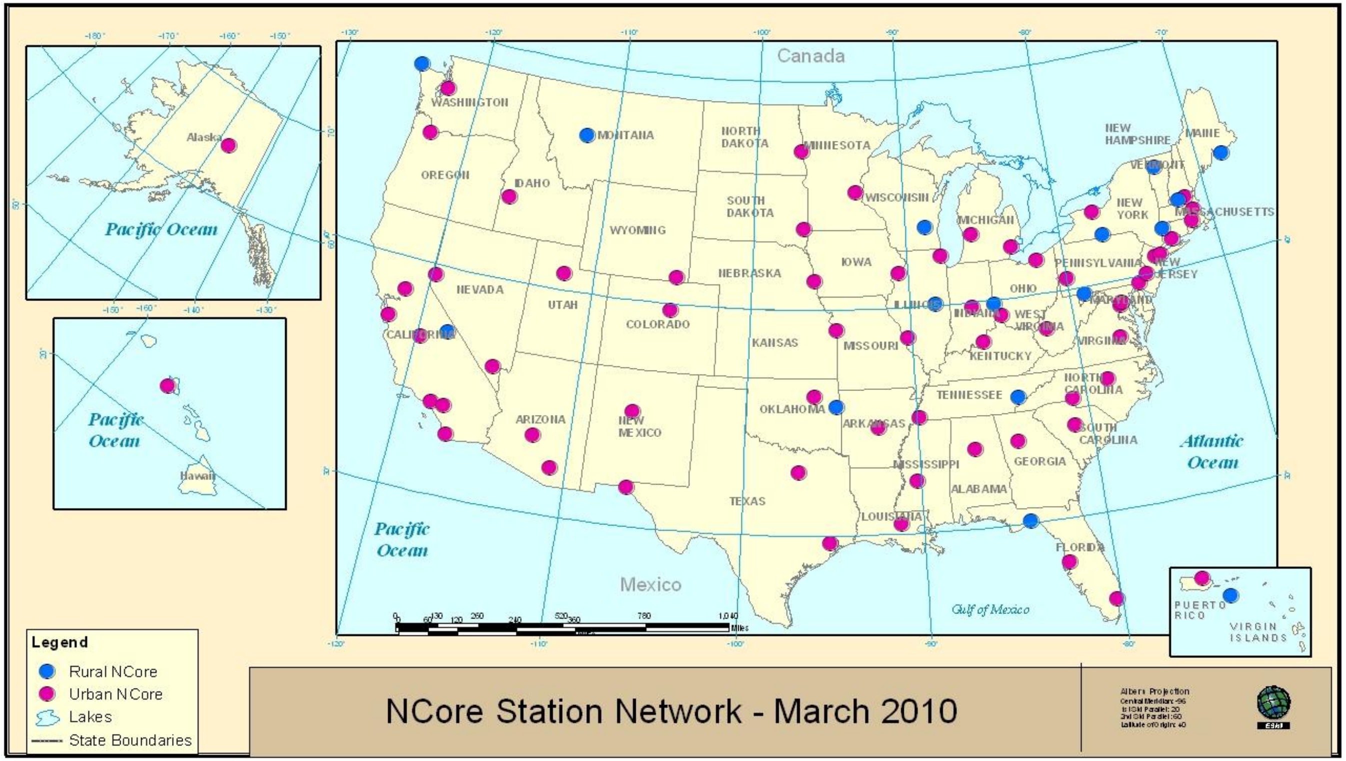
126 total monitors

Approximately 40 additional monitors will be placed in locations to help protect communities that are susceptible and vulnerable to NO2-related health effects

$PM_{2.5}$ Chemical Speciation Network (CSN) and IMPROVE (p-NO3)



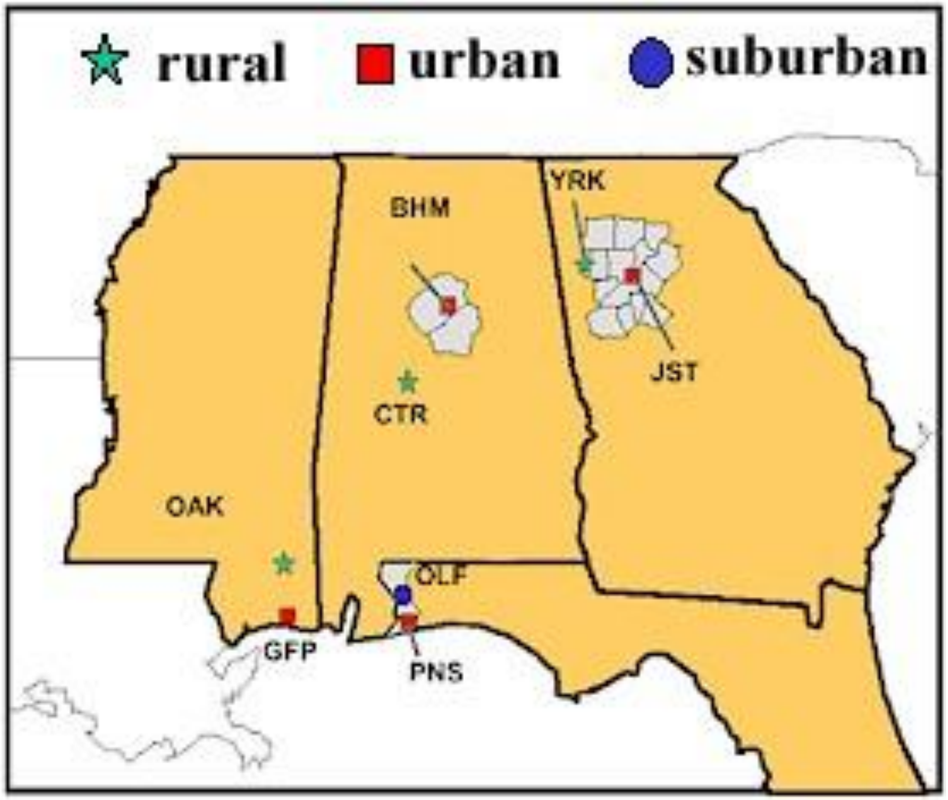
National Core (NCore) Network



- urban (about 63 sites)
- rural (about 17 sites)
- May achieve additional rural coverage with National Parks and CASTNET

- Pollutants Measured - NAAQS multi-pollutant
  - **Particles**
    - $PM_{2.5}$ - continuous mass, filter mass, speciation
    - $PM_{10-2.5}$ - mass
  - **Gases** – O_3 and high sensitivity measurements of CO, SO_2, NO and NO_y.
  - **Meteorology** - basic meteorological parameters
    - Temperature, Wind Speed, Wind Direction, Relative Humidity

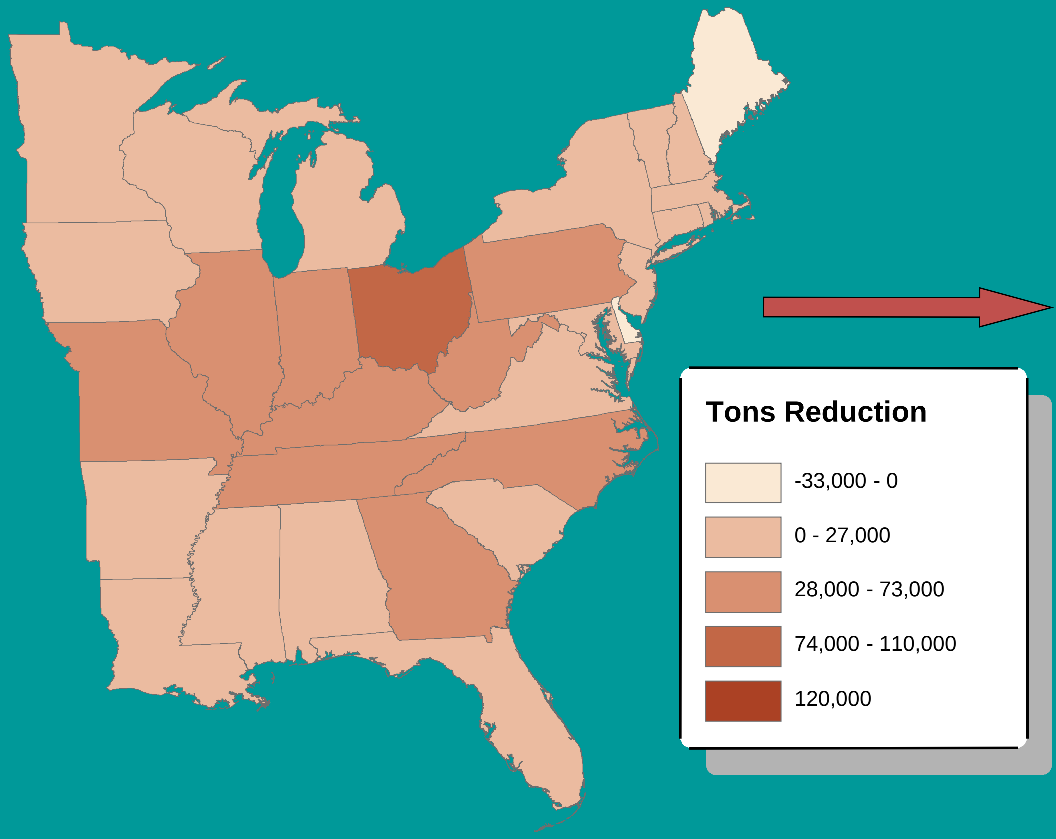
SouthEastern Aerosol Research and Characterization Study (SEARCH)
- only routine U.S. network with continuous NO2, HNO#, NH3
Funded largely by Southern Company – Eric Edgetron, PI



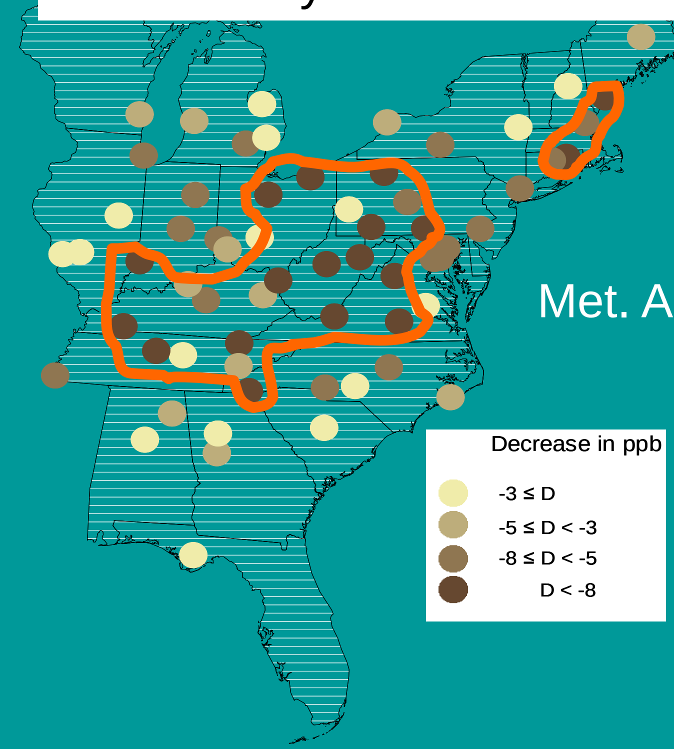
A bit about satellite data, but first,,,

Largest decline in ozone occurs in and downwind of EGU NOx emissions reductions (2002-2004) (analysis constrained by absence ambient NOx data)

EGU NOx Tons Reduced



Decline in "Seasonal Average" 8-Hour Daily Maximum Ozone



Met. Adj.

The major EGU NOx emissions reductions occurs after 2002 (mostly NOx SIP Call)

Average rate of decline in ozone between 1997 and 2002 is 1.1%/year.

Average rate of decline in ozone between 2002 and 2004 is 3.1%/year.

Satellites provide best source of ambient NO_2: Accountability and Trends

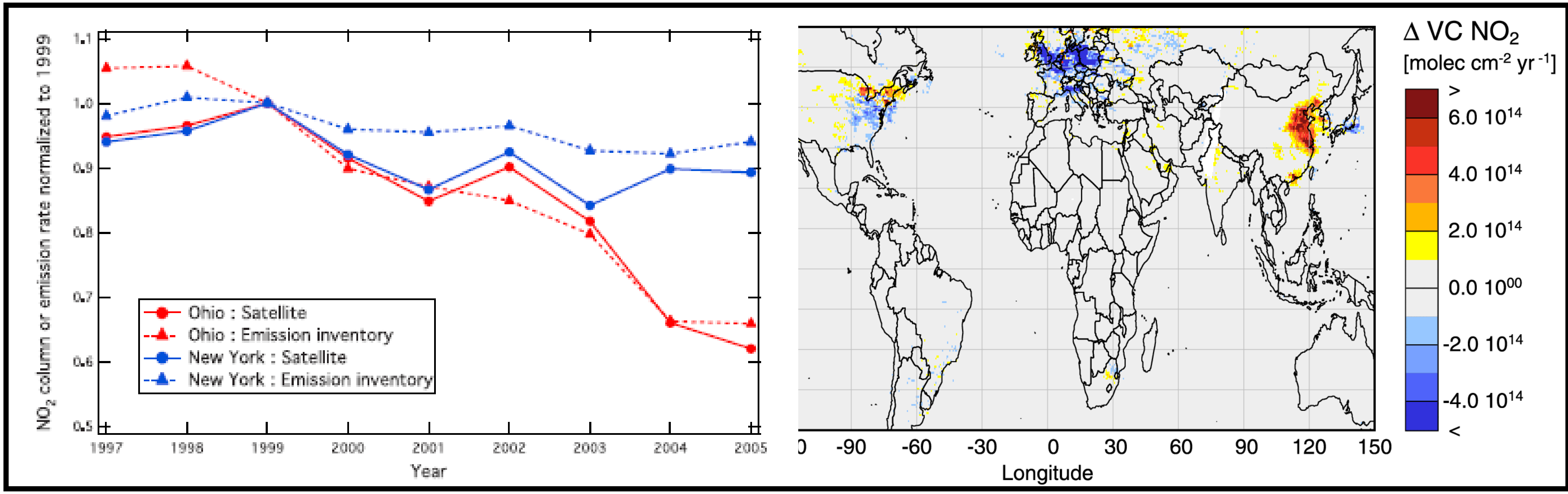


Figure 20. Left - **s**uperimposed Eastern U.S. emission and combined GOME and SCIAMACHY NO2 1997-2002 trends (Kim et al., 2006); right - GOME NO2 trends from 1995 – 2002 (after Richter, 2005). Clear evidence of reductions in midwest U.S. and European NOx emissions, and increased NOx generated in Eastern Asia.

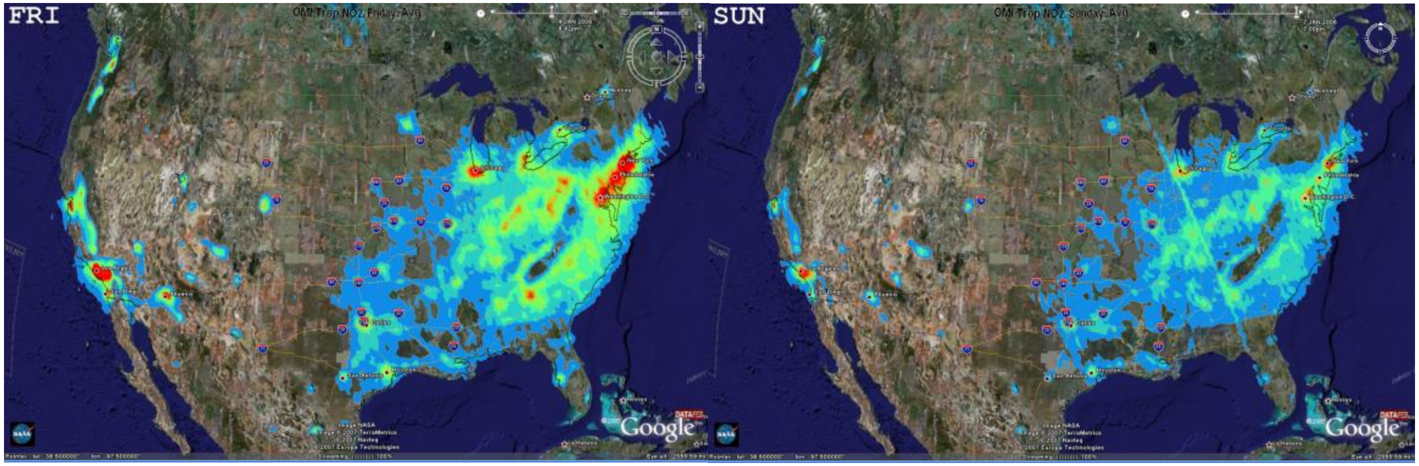
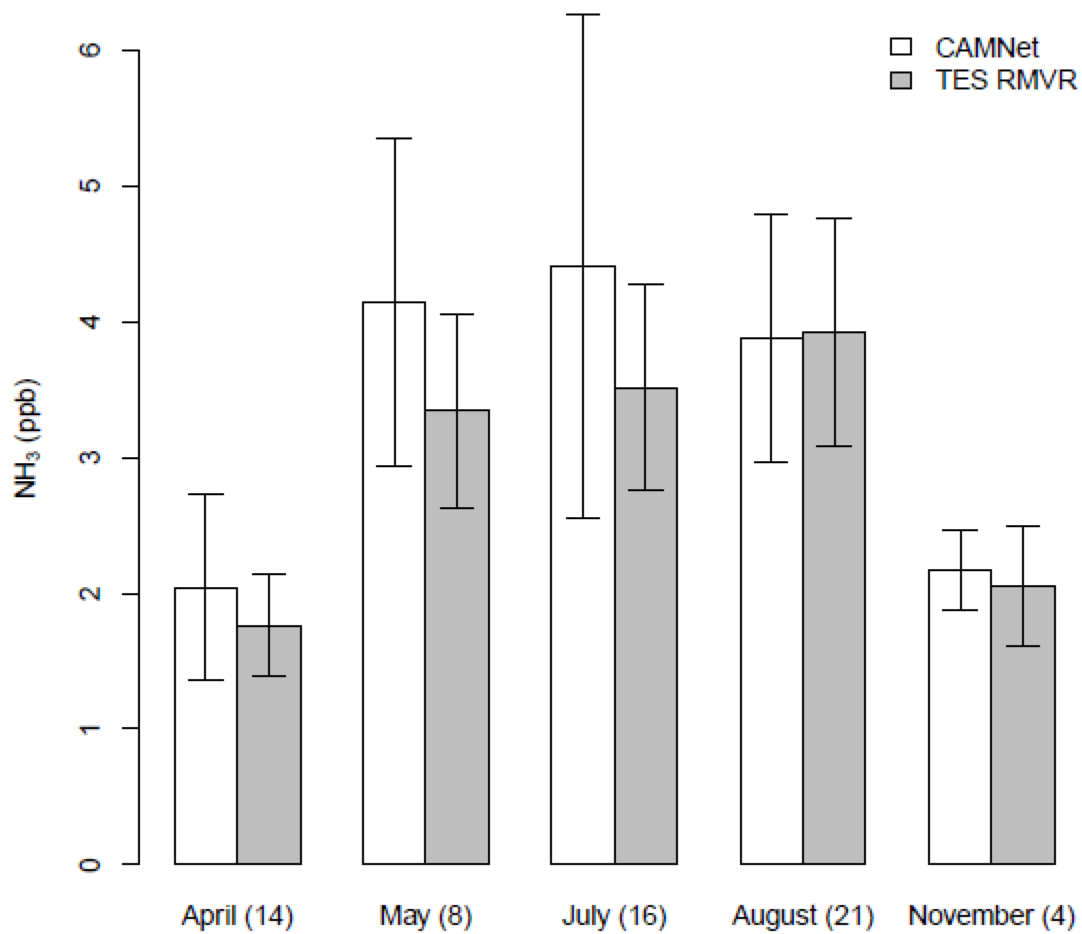


Figure 21. 2004 OMI NO2 column images aggregated for all Fridays (left) and Sundays (right) indicating weekend/weekday patterns associated with reduced Sunday emissions (source, Husar).

Satellite derived NH_3



Average daytime TES RVMR and CAMNet NH3 by month of year for all months with more than three TES observations. Error bars denote the 95th percentile confidence interval for the mean, Pinder et al., 2011 (Pinder et al., in preparation). See poster

Network Strengths and Gaps

- Spatially rich NO3, NH4 precipitation
- Highly leveraged rural network of t-NO3 and NH4
- Many urban based NO and NOx* sites
- Multiple N-species SEARCH
- Fledgling NOy with multiple non-N species
- Emerging NH_3 network through AMoN and possibly NCORE
- Satellite platforms for NO2 and emerging NH3 delineation

- Lack of routine true NO_2, except SEARCH
- Missing N species in rural networks (NO_2, PAN)
- Lack of temporal resolution in CASTNET
- No urban (NH3, NO_2, PAN)
- Limited NH_3
- NH_4 – only CASTNET
- No routine vertical profiling (aircraft)

CMAQ enhancements

(Dennis, Pinder, Schwede, Bash, Walker, Mathur, Foley)

- PRISM adjustment : leveraging observed precip data
  - Basis for current bias adjustments of wet NO3, NH4
  - Related to next 2 points
- Bi-directional NH3 treatment (Dennis et al., 2010)
  - Enhances "transport" characteristics of NH3
  - Adds rationale for ambient NH3 monitoring
- Lightning NOx
  - Evolving
  - Improve wet NO3 performance

PRISM adjusted precipitation (Foley and Dennis)

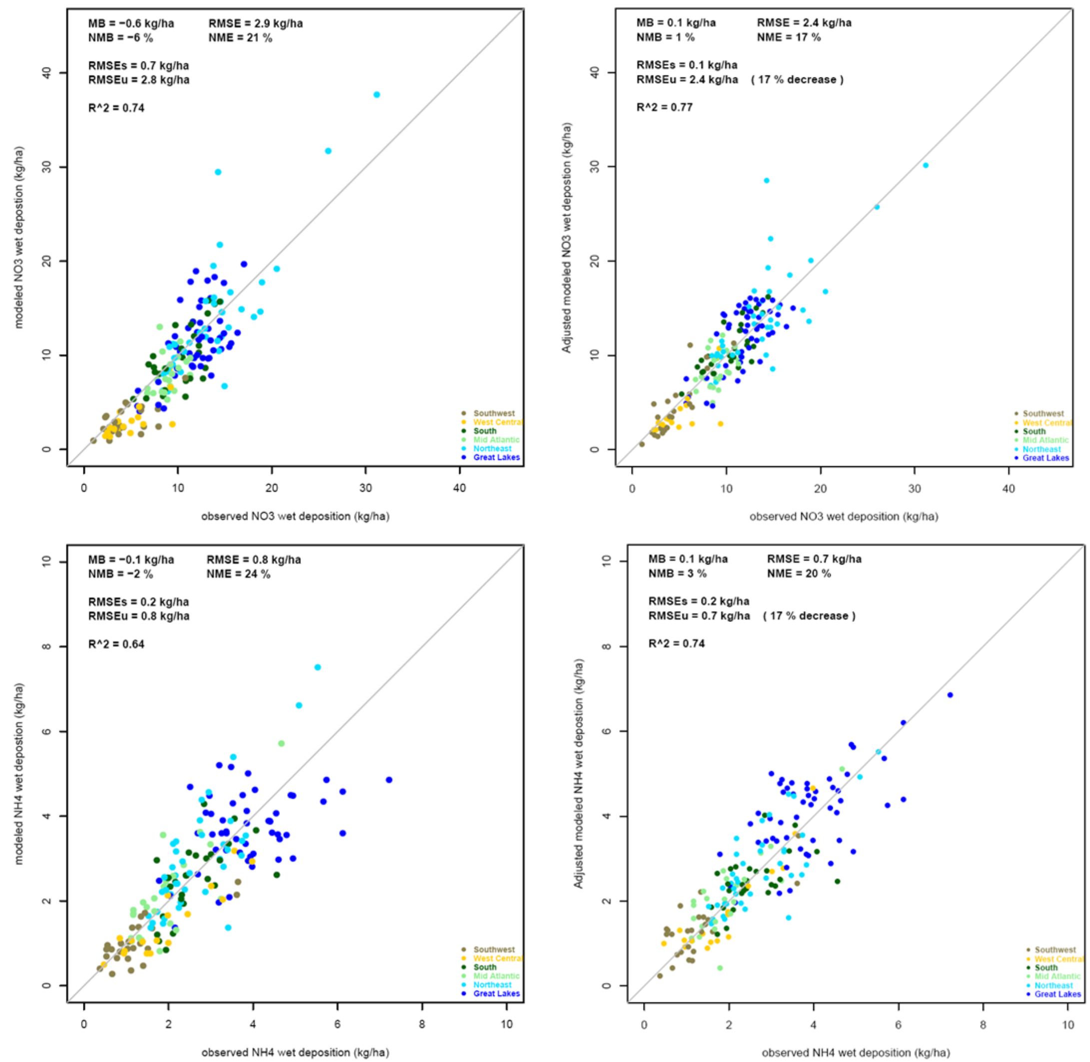


Figure 7-9 Unadjusted (left) and PRISM (right) adjusted CMAQ annual wet deposited nitrate (top) and ammonium (bottom) for 2002 .

Bi-directional flux treatment of ammonia

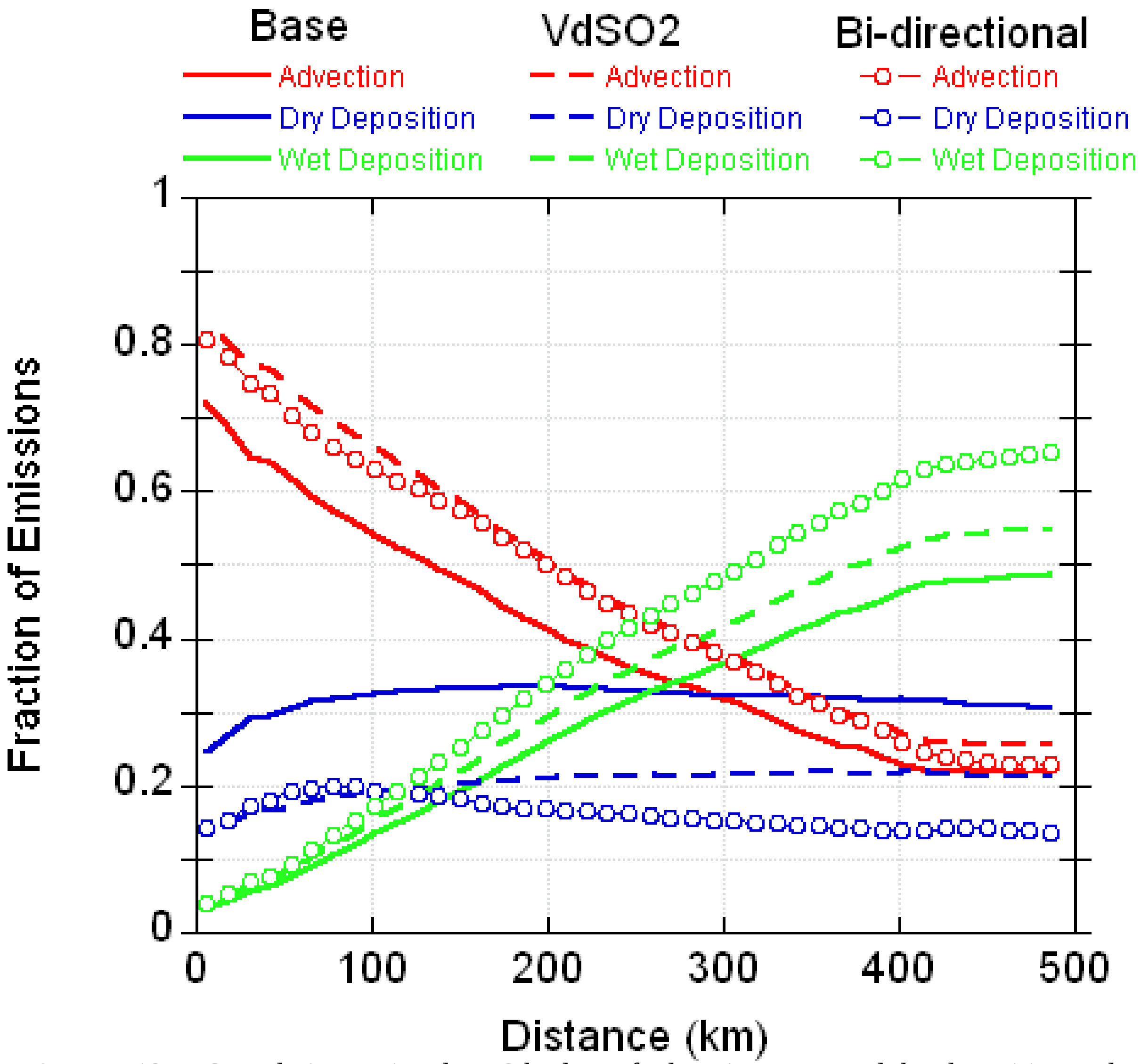
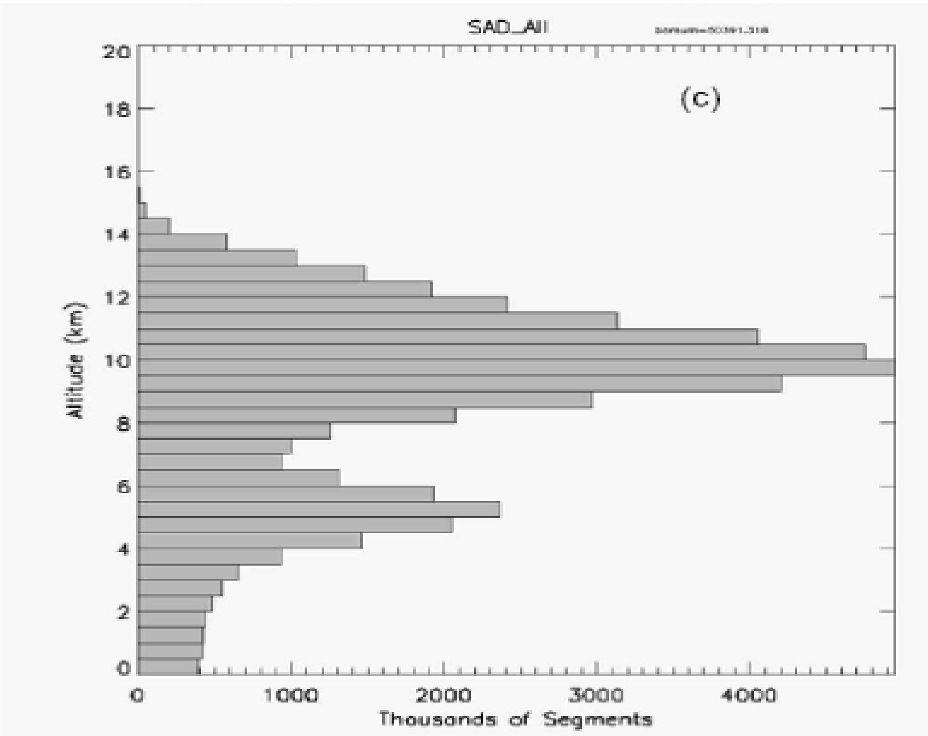
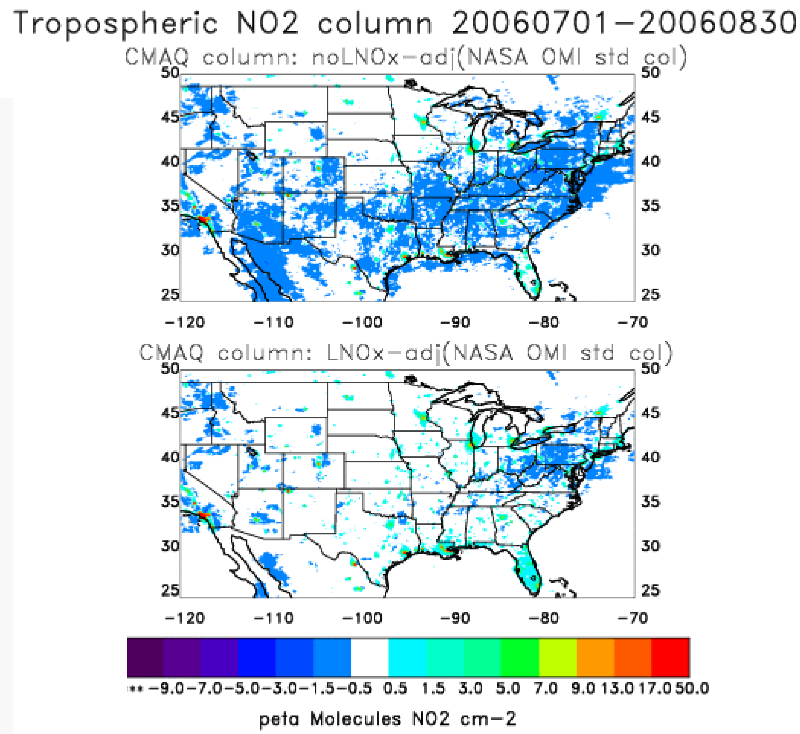


Figure 7-13. Cumulative regional NH3 budget of advection, wet- and dry deposition, calculated for an expanding box starting at the high-emitting Sampson County NC cell (from Dennis et al, 2010)

Bias w/o lightning





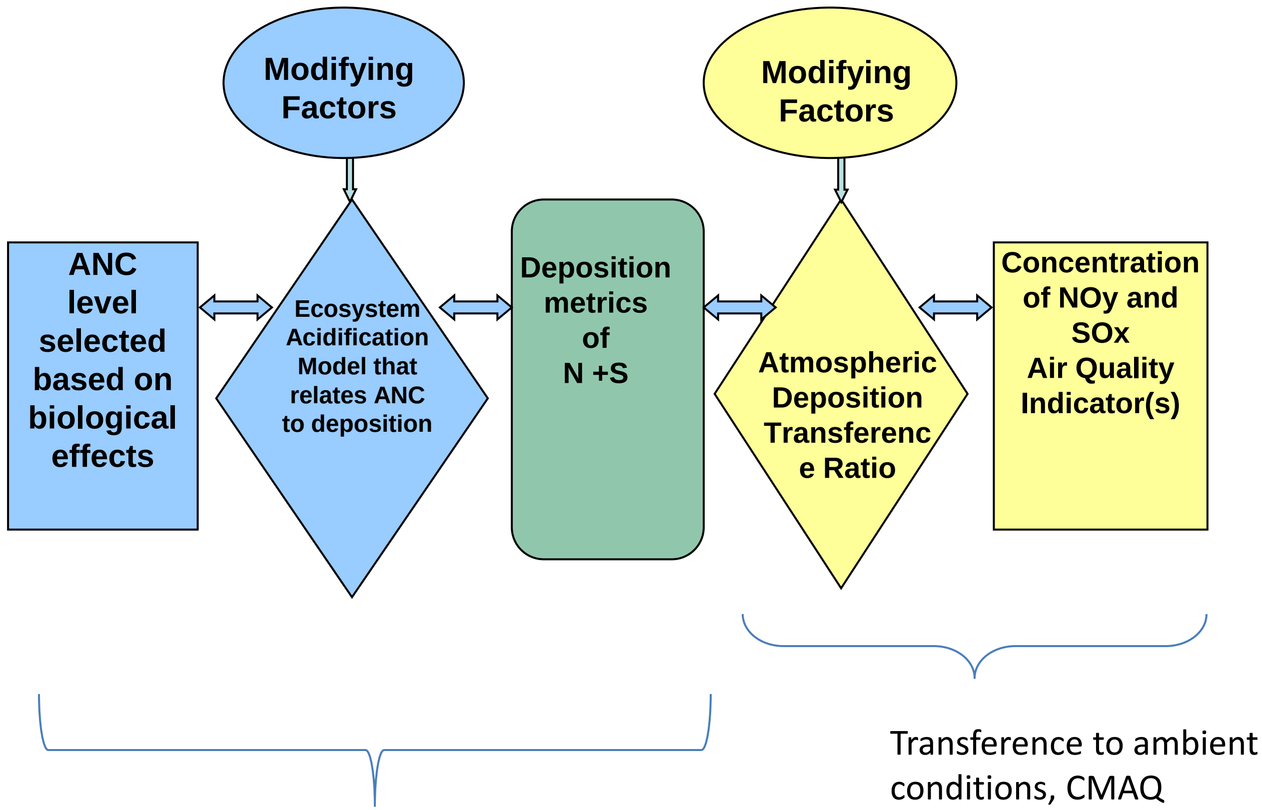
Bias with lightning

Courtesy, Ken Pickering, NASA

How does the TBP NOx/SOx secondary standard deals with N?

- In light of sparse atmospheric observations, while
- Maintaining commensurability with CAA provisions
  - Must have “ambient air indicators”
  - Separate non-listed (not to be regulated) NHx from other N species
  - What observations are recommended

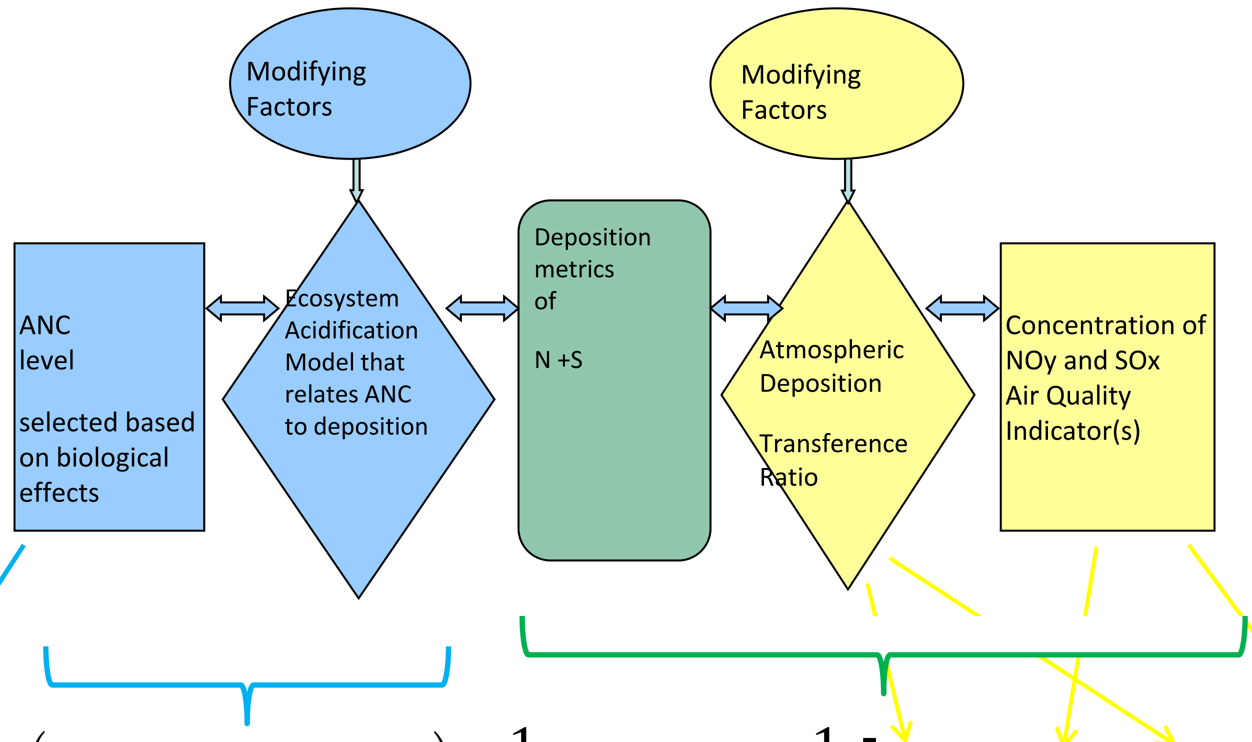
Policy Assessment conceptual framework linking ecological indicator to NAAQS relevant air indictors to ecosystem indicator, ANC



Starts with critical load modeling:

$$CL_{ANC\lim}(N+S)=([BC]_O^* - [ANC_{\lim}])Q + N_{eco}$$

Policy Assessment conceptual framework linking ecological indicator to NAAQS relevant air indictors underlying the form of the standard, AAPI – the SSWC model form with NHx separated and allowable NOy and SOx deposition translated to allowable concentrations of NOy and SOx



$$AAPI = \left(\left[BC\right]_0^* + N_{ECO} / Q\right) - \frac{1}{Q} L(NHx) - \frac{1}{Q}\left[T_{NOy} \cdot NOy + T_{SOx} \cdot SOx\right]$$

Deriving the AAPI from Critical Load Response Function

The suggested acidification model for the catchment scale to express the critical load at a specified ANC is

$$CL_{ANC\lim}(N+S) = ([BC]_O^* - [ANC_{\lim}])Q + N_{eco}$$

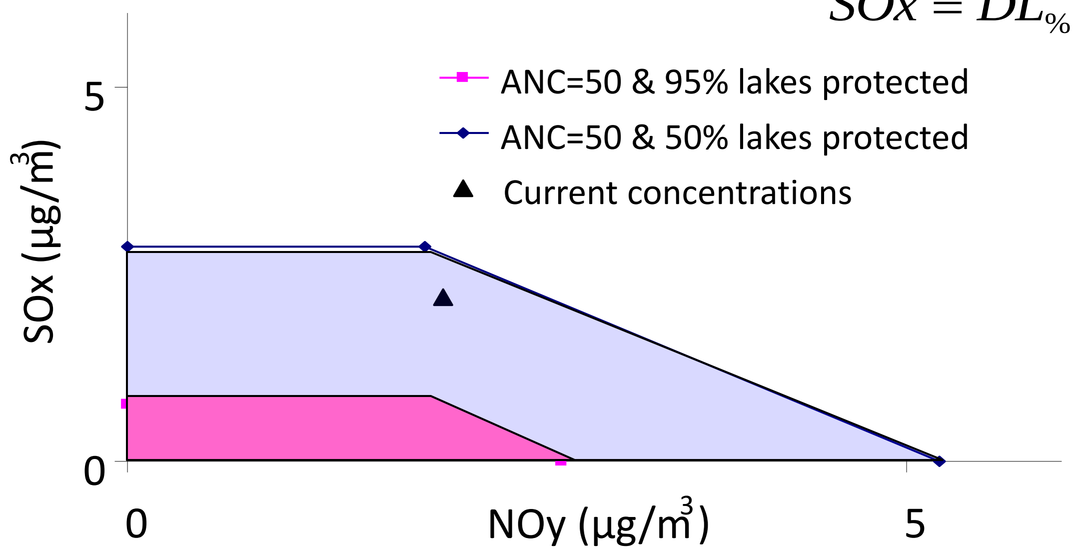
$[BC]_0^*$ = the preindustrial concentration of base cations (equ/L)
ANC_{lim} = a "target" ANC level (equ/L)
Q= surface water runoff (m/yr)
N_{eco}= nitrogen retention and denitrification by the ecosystem

Derivation steps:
- split out N and S CL deposition
- subtract NHx fraction from total N deposition
- transfer oxidized N and S deposition to concentrations
- Rearrange terms to solve for ANC_{lim}
- yields the AAPI (form of the standard)

Tradeoff curve for SOx and NOy atmospheric concentrations

$$NOy = DL_{\%ECO}(N_{ox}) \cdot {}^{1}\!/\!_{T_{NOy}}$$

$$SOx = DL_{\%ECO}(S_{ox}) \cdot {}^{1}\!/\!_{T_{SOx}}$$



Deposition values are multiplied by the ratio of concentrations to depositions for NOx and SOx ($1/V_{NOx}$ and $1/V_{SOx}$) to calculate atmospheric concentrations

$1/T_{SOx}$ = 0.038 (µg/m^3)/(meq/m^2· yr) $1/T_{NOx}$ = 0.043 (µg/m^3)/(meq/m^2 ·yr)

Monitoring Recommendations

- Use existing NOy instruments as the FRM
  - ~ 80 instruments deployed (NCore)
  - Similar QC challenges to PM mass
  - Rely on ORD
- Open inlet for p-SO4 (CASTNET FP)
  - Small fraction of ambient PMcoarse is a significant fraction of deposited sulfate
- Co-locate NH3 and NH4 measurements
- 2-5 sites nationally with speciated NOy
  - True NO2, HNO3, p-NO3 PAN,