The Abdus Salam
International Centre for Theoretical Physics

The International Union of Geodesy and Geophysics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

**2339-9**

**Workshop on Atmospheric Deposition: Processesand Environmental Impacts**

***21 - 25 May 2012***

# Links Between Air Quality and Atmospheric Deposition

Christopher Lehmann
*Illinois State Water Survey Prairie Research Institute*
*University of Illinois*
*Urbana Champaign*
*USA*

# Links Between Air Quality and Atmospheric Deposition

Christopher Lehmann
National Atmospheric Deposition Program
Illinois State Water Survey - Prairie Research Institute
University of Illinois, Urbana-Champaign

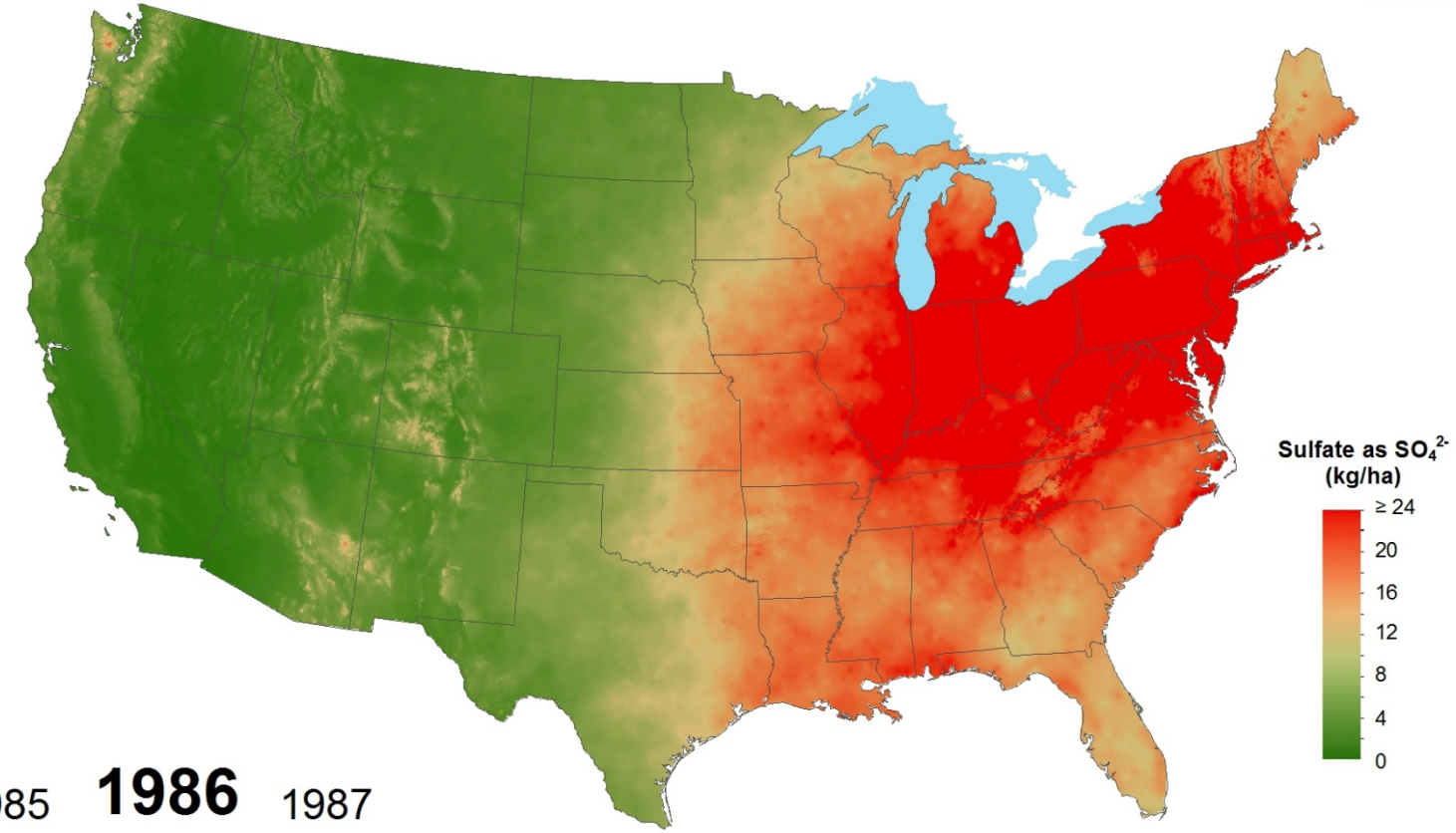
National Atmospheric Deposition Program

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

# Outline

1. Sulfur and nitrogen interactions in the atmosphere
2. Evaluating trends in emissions, air quality, and wet/dry deposition
3. Remarks about passive air samplers

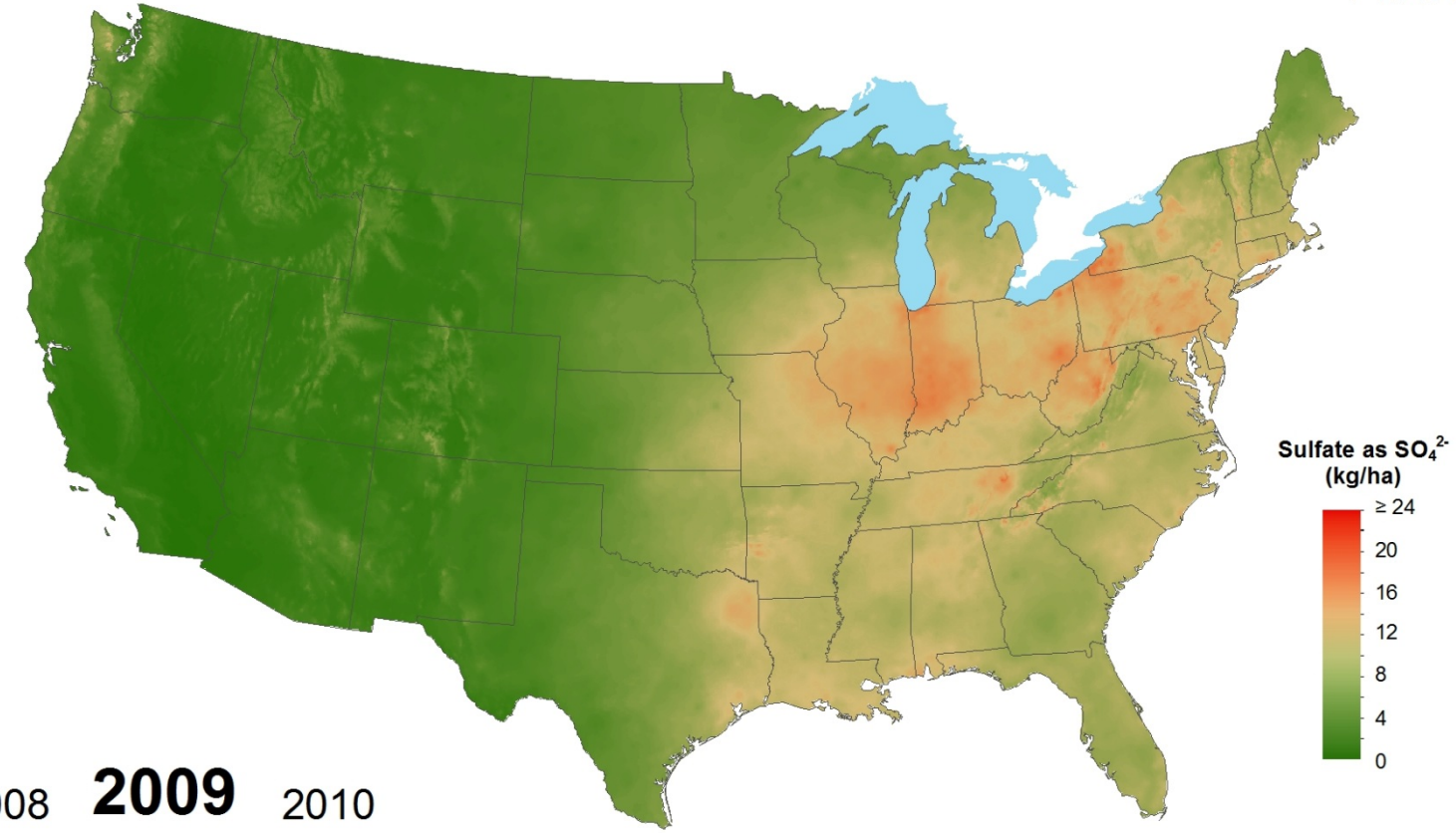
# Sulfate ion wet deposition
# 1986




1985 **1986** 1987

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

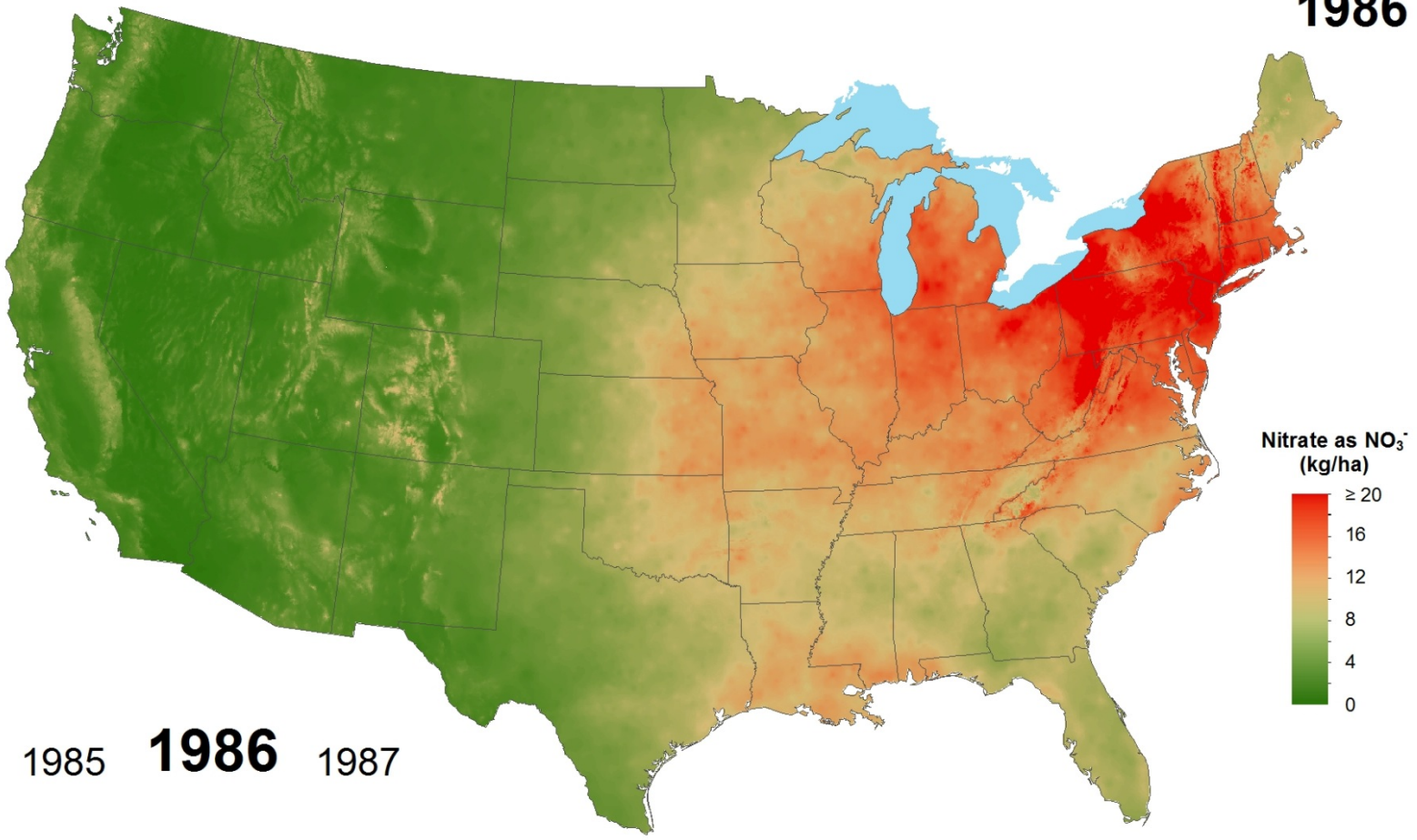
# Sulfate ion wet deposition
# 2009




2008 **2009** 2010

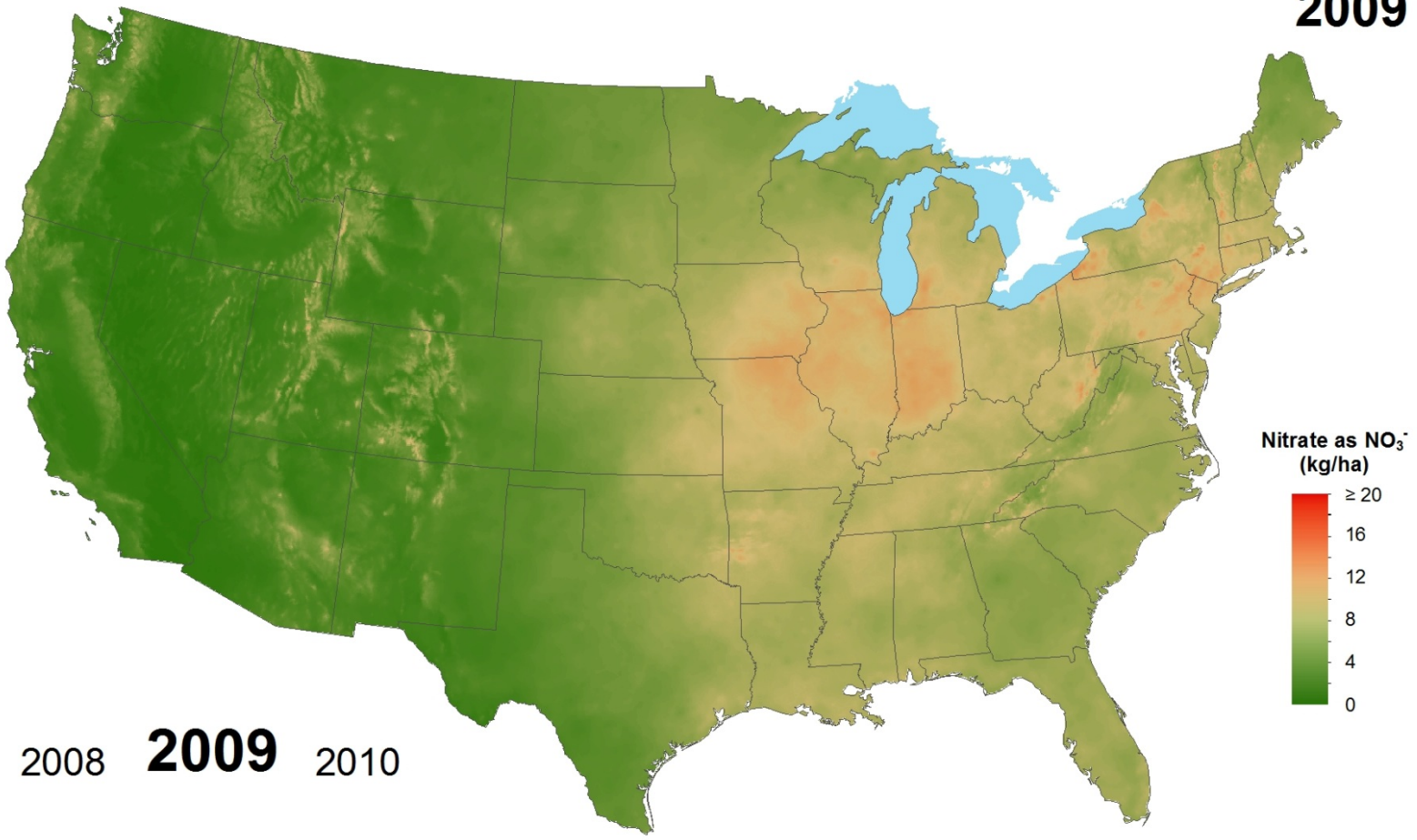
National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

# Nitrate ion wet deposition
# 1986




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

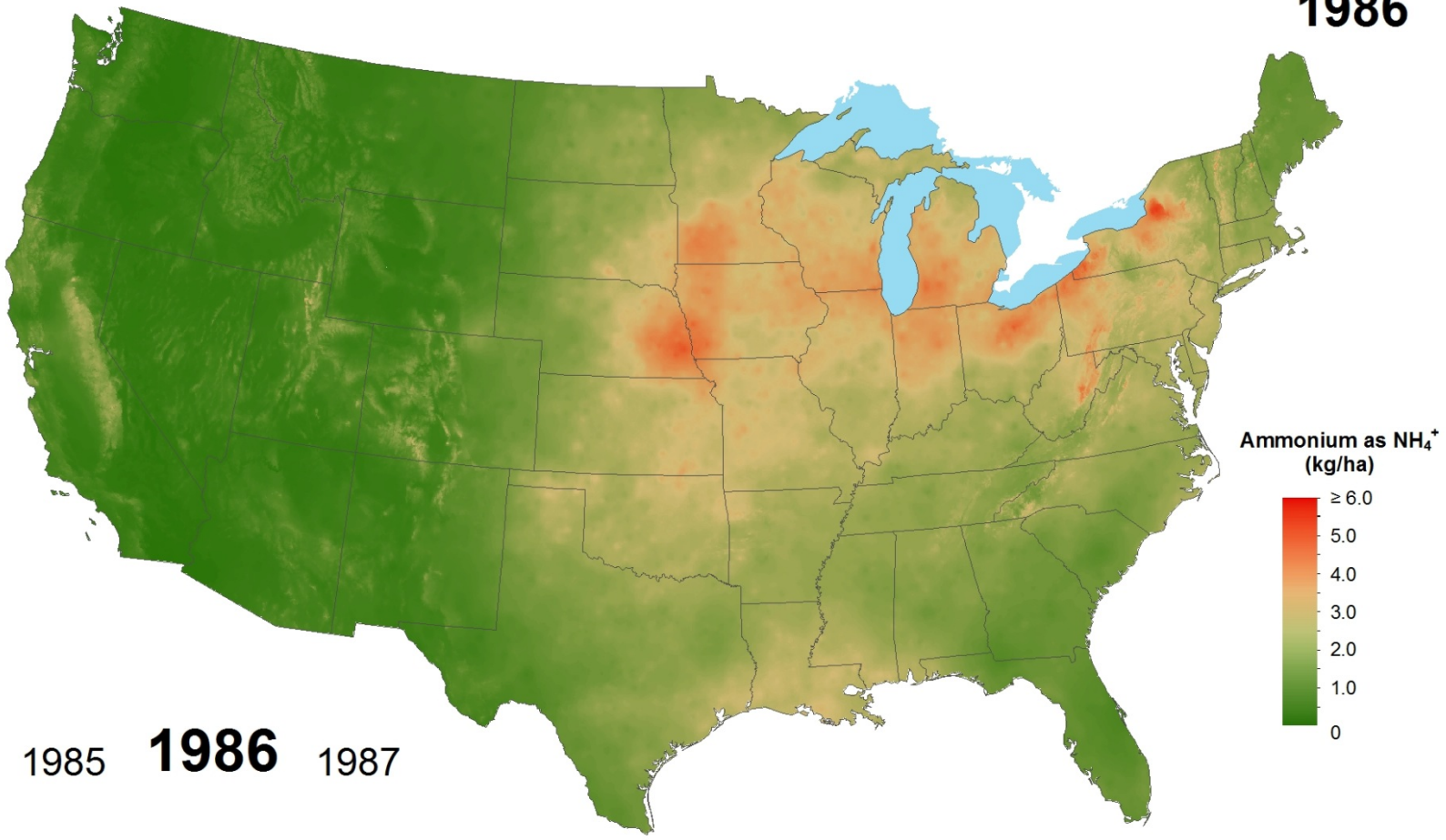
# Nitrate ion wet deposition
# 2009




2008 **2009** 2010

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

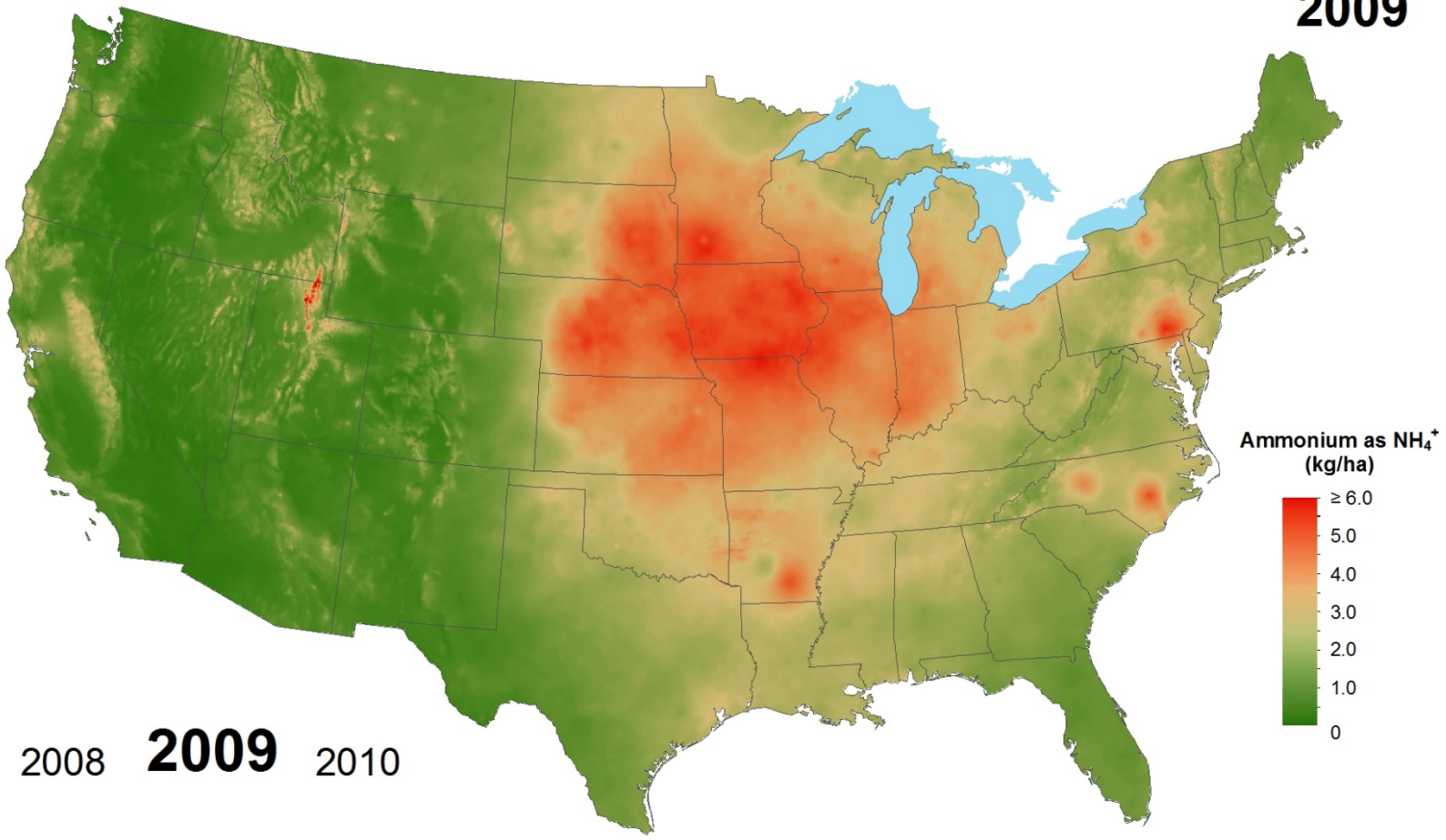
# Ammonium ion wet deposition
# 1986




1985 **1986** 1987

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

# Ammonium ion wet deposition
# 2009




2008 **2009** 2010

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

# Aqueous Phase Chemistry: Sulfate-Ammonia

Considering a system containing only sulfate and ammonia, the following species are formed in transition:

| | |
|---|---|
| 1. Sulfuric Acid: $H_2SO_4$ | $NH_4/SO_4 = 0.00$ |
| 2. Ammonium Bisulfate:$(NH_4)HSO_4$ | $NH_4/SO_4 = 0.50$ |
| 3. Letovicite: $(NH_4)_3H(SO_4)_2$ | $NH_4/SO_4 = 0.75$ |
| 4. Ammonium Sulfate: $(NH_4)_2SO_4$ | $NH_4/SO_4 = 1.00$ |
| 5. “Ammonia Rich” | $NH_4/SO_4 > 1.00$ |

These species have different physical properties that affect long-range transport in the atmosphere

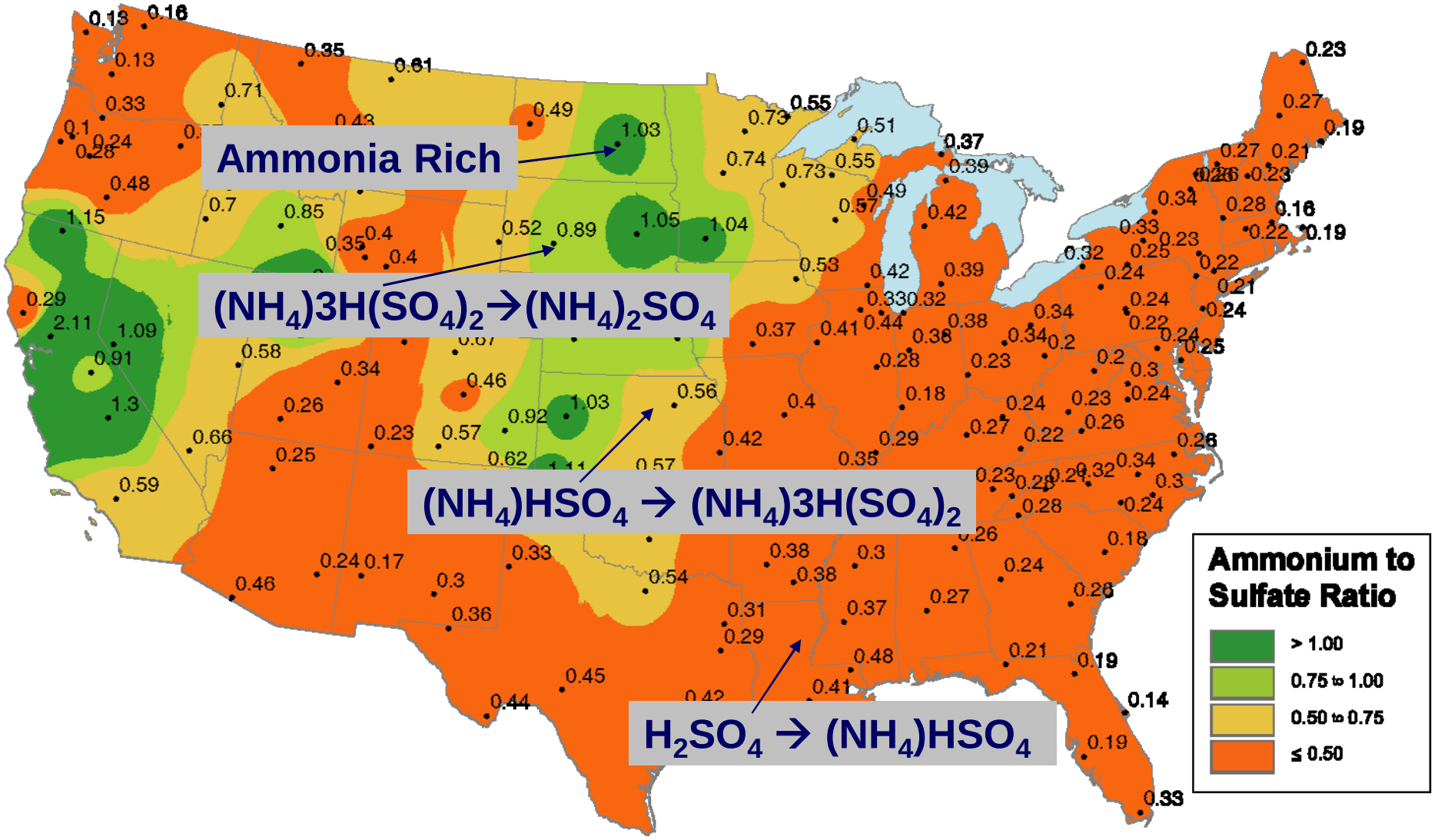
*Seinfeld and Pandis, 1998*

# Impacts of Ammonia-Rich Environment

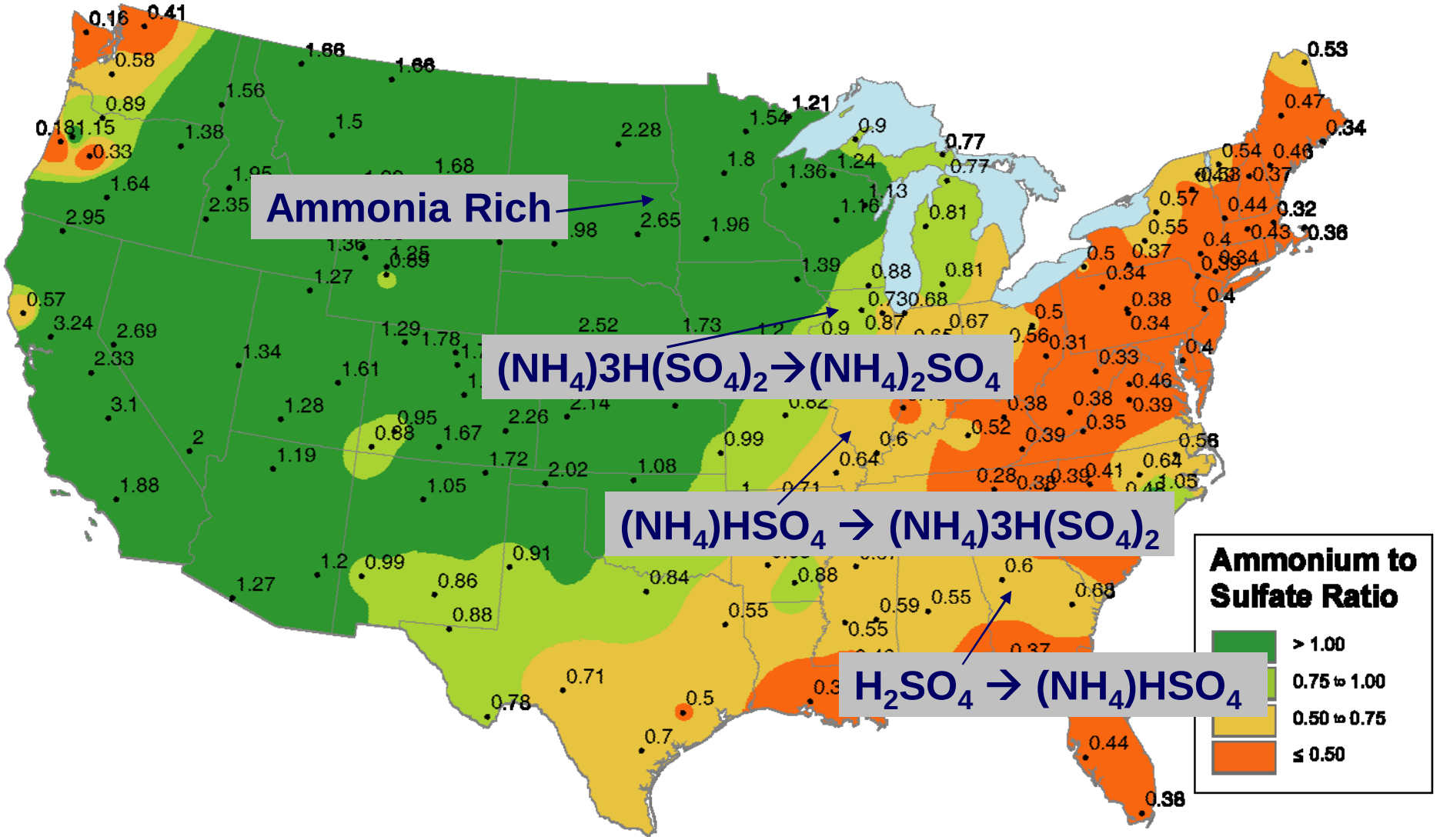
- $(NH_4)_2SO_4$ is most stable form of ammonia and can transport long distances
  - $SO_4^{2-}$ will react with all available $NH_4^+$.
  - $NH_4^+$ in excess of that required to neutralize $SO_4^{2-}$ is available to react with other species, such as $NO_3^-$ to form $NH_4NO_3$.
  - $NH_4NO_3$ is a labile species that will partition between gas and aqueous phases and can deposit locally
  - $NH_3/NH_4^+$ in excess of that required to neutralize acidic species is soluble and can deposit locally

*Seinfeld and Pandis, 1998*

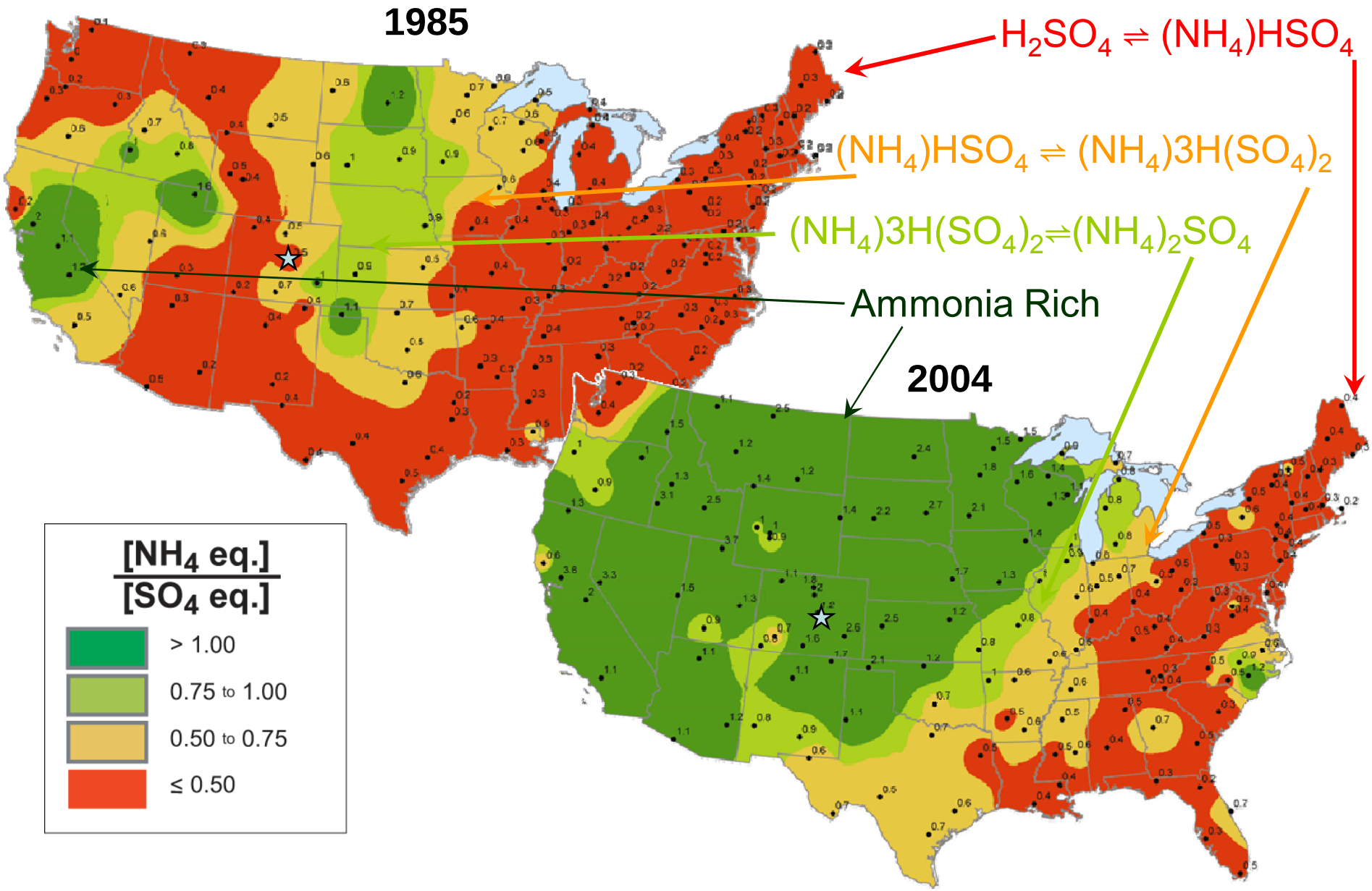
# Ammonium/Sulfate Ratio, 1984-1986



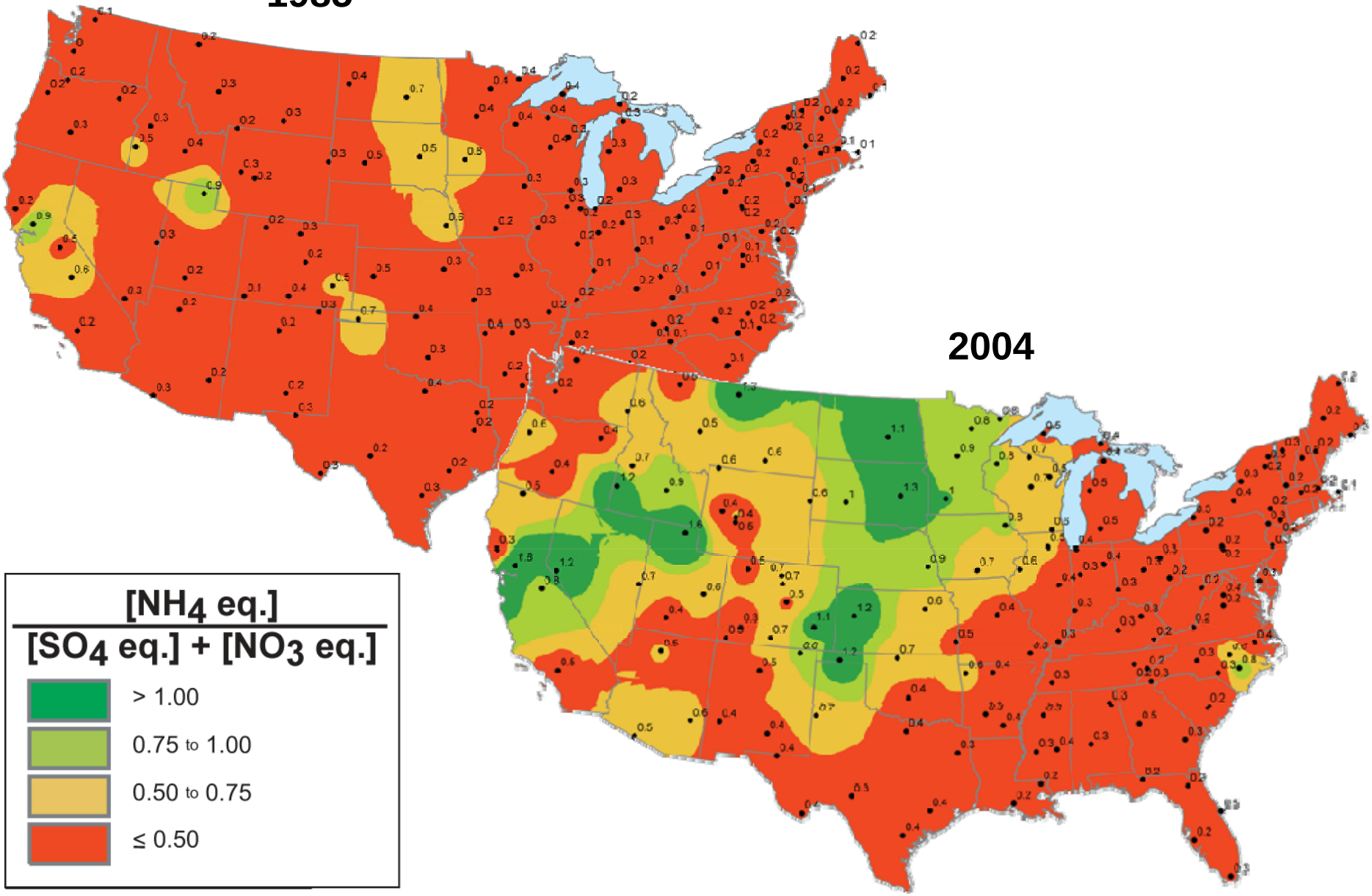
# Ammonium/Sulfate Ratio, 2002-2004



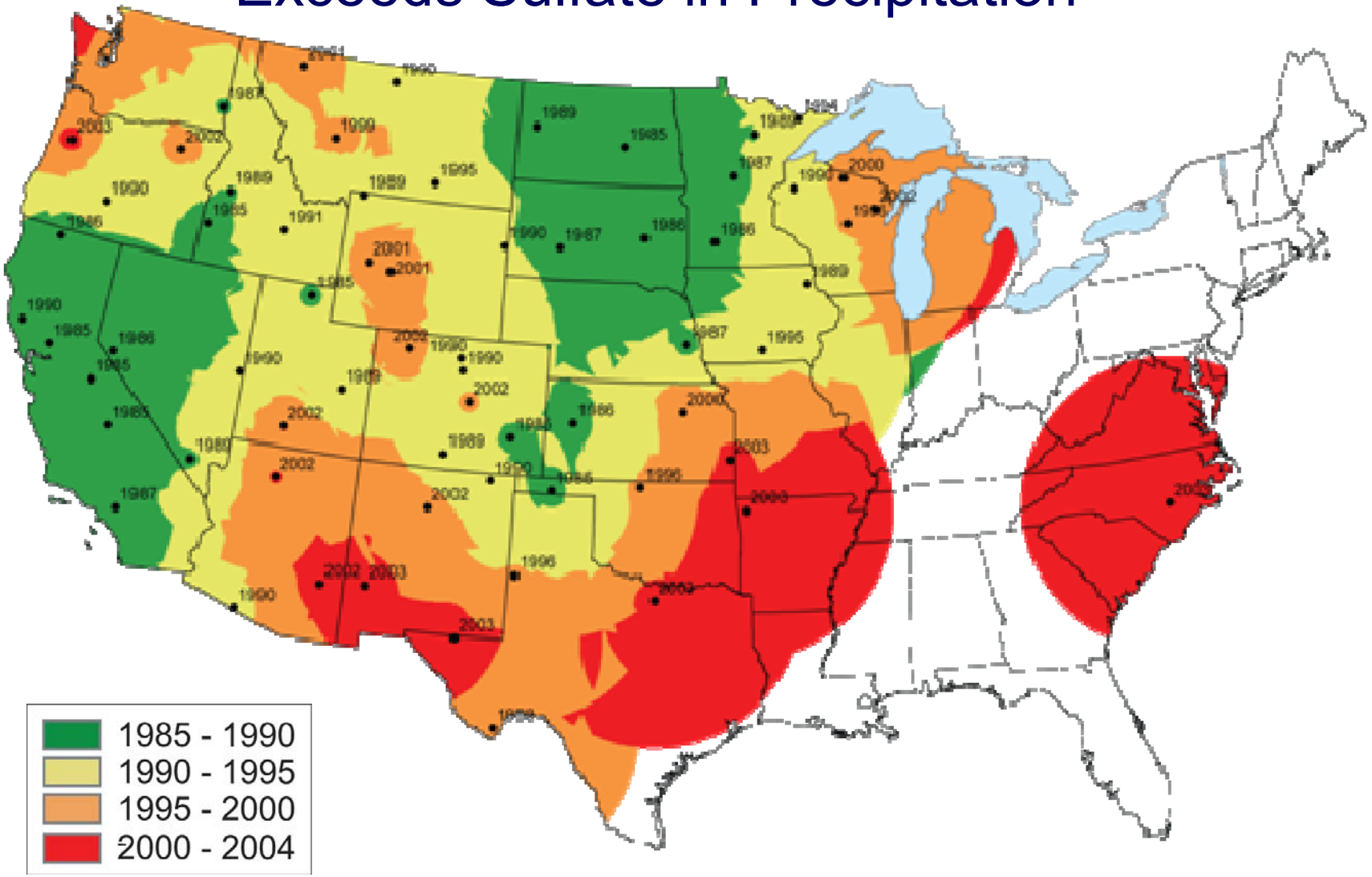
# Ammonium to Sulfate Ratio in Precipitation



# Ammonium to Sulfate plus Nitrate Ratio in Precipitation

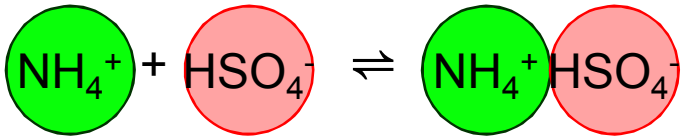


# First Year where Ammonium Exceeds Sulfate in Precipitation

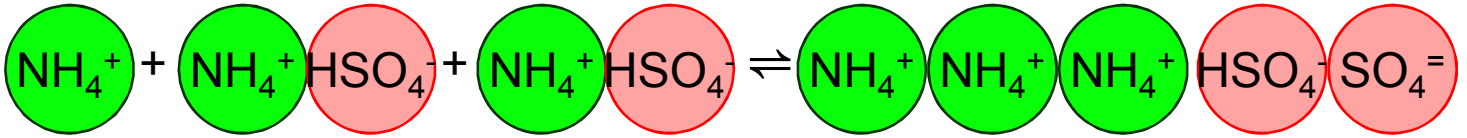


# Sulfate, Ammonium & Nitrate Reactions

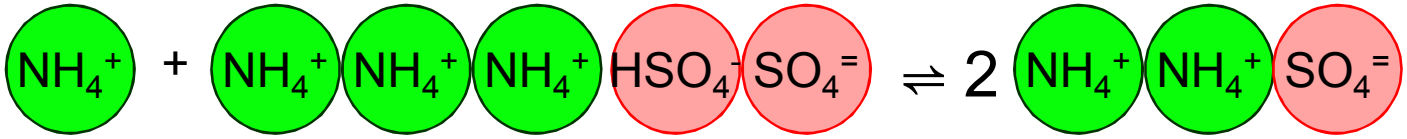
$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} < 1.0$$




$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} = 0.50$$

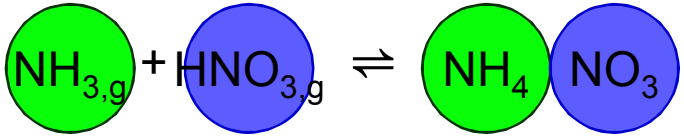



$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} = 0.75$$




$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} = 1.00$$

$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} > 1.0 \qquad \frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}] + [NO_3^- \text{ eq.}]} < 1.0$$



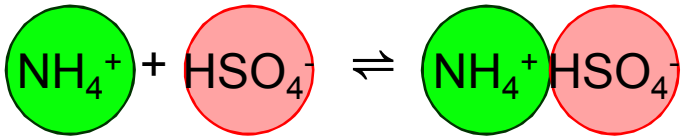

$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}] + [NO_3^- \text{ eq.}]} > 1.0$$


Transport Distance

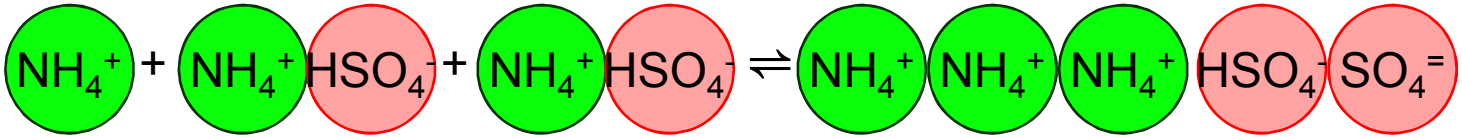
*Seinfeld and Pandis, 1998*

# Sulfate, Ammonium & Nitrate Reactions

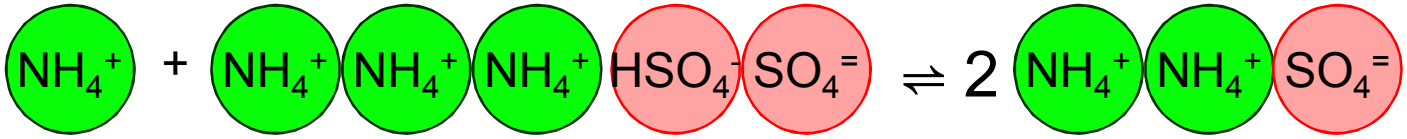
$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} < 1.0$$




$RH_{del.}$ = 39%

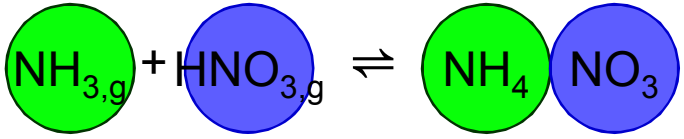



$RH_{del.}$ = 69%




$RH_{del.}$ = 80%

$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}]} > 1.0 \qquad \frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}] + [NO_3^- \text{ eq.}]} < 1.0$$

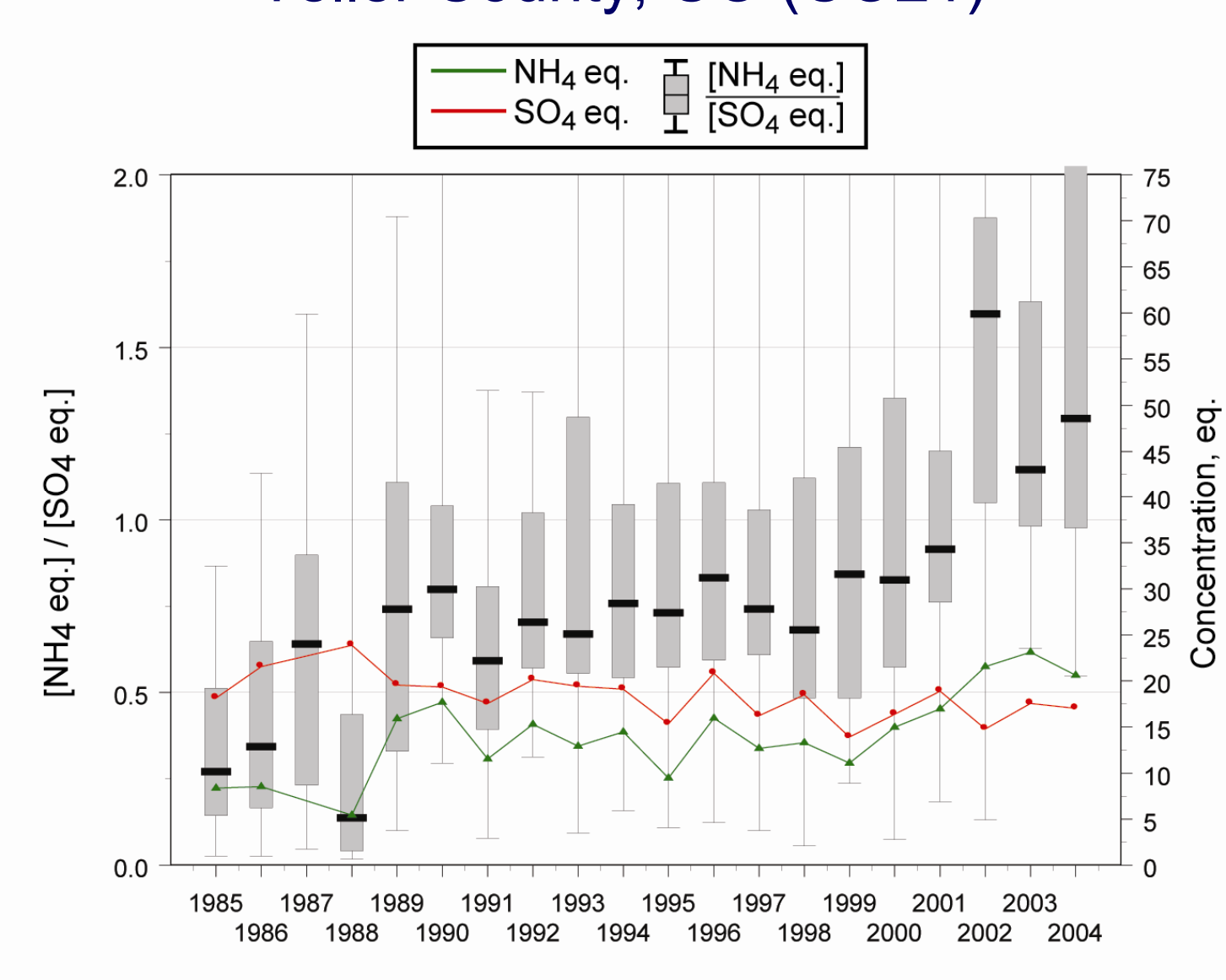



$RH_{del.}$ = 62%

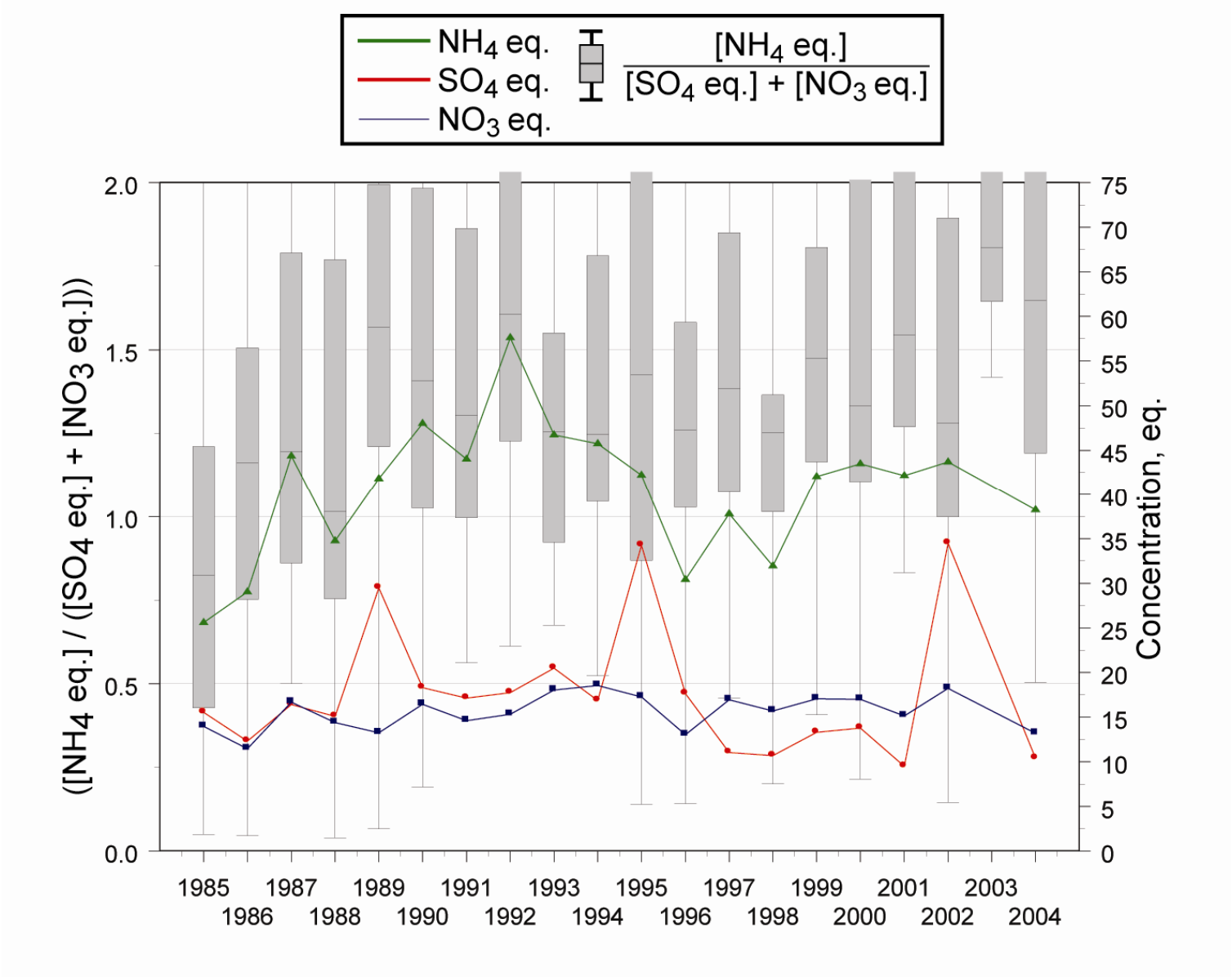
$$\frac{[NH_4^+ \text{ eq.}]}{[SO_4^{2-} \text{ eq.}] + [NO_3^- \text{ eq.}]} > 1.0$$


*Finalayson-Pitts & Pitts, 2000*

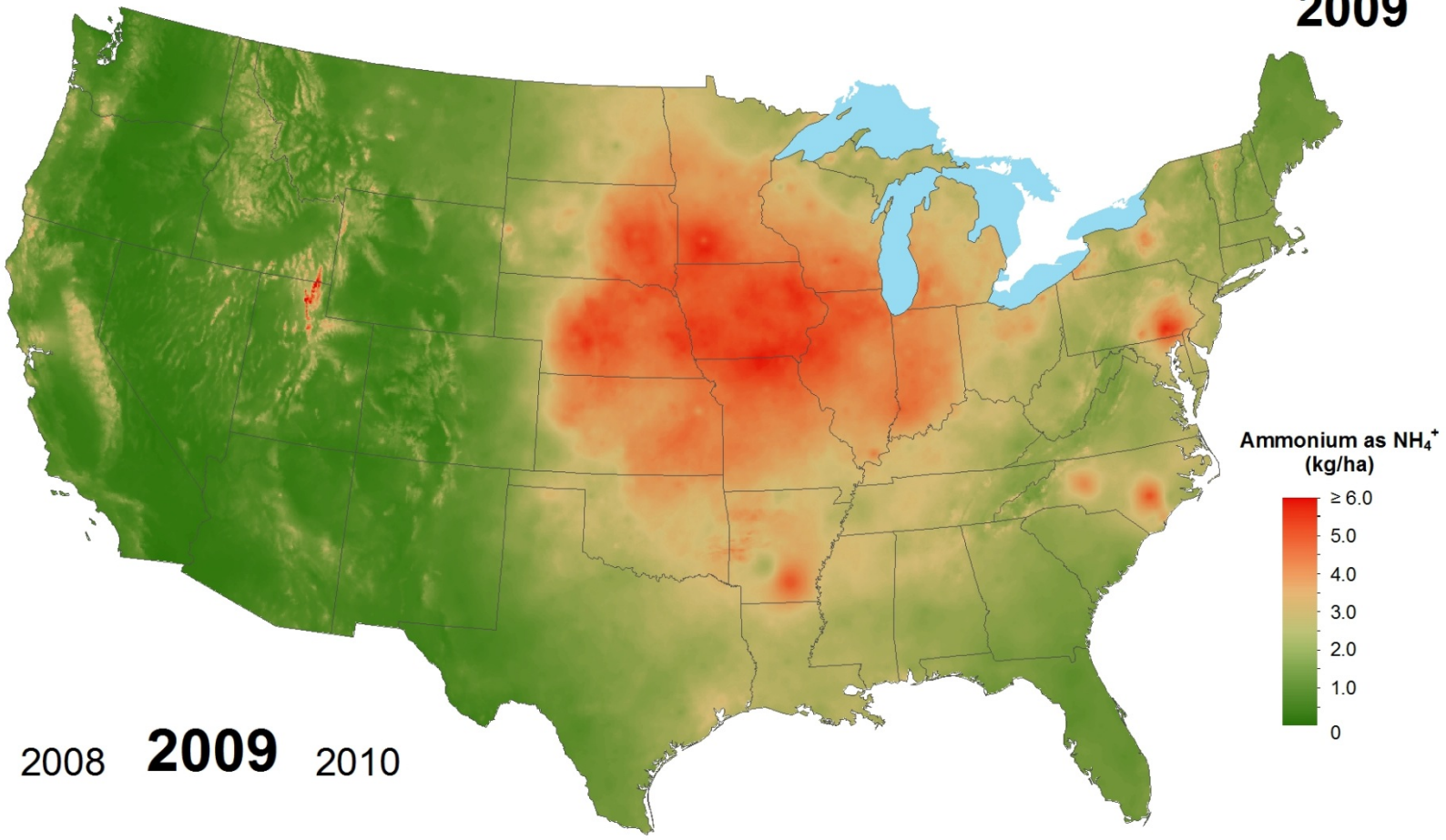
# Ammonium / Sulfate Ratio in Precipitation
# Teller County, CO (CO21)



# Ammonium / (Sulfate + Nitrate) Ratio in Precipitation
# Logan, UT (UT01)



# Ammonium ion wet deposition
# 2009

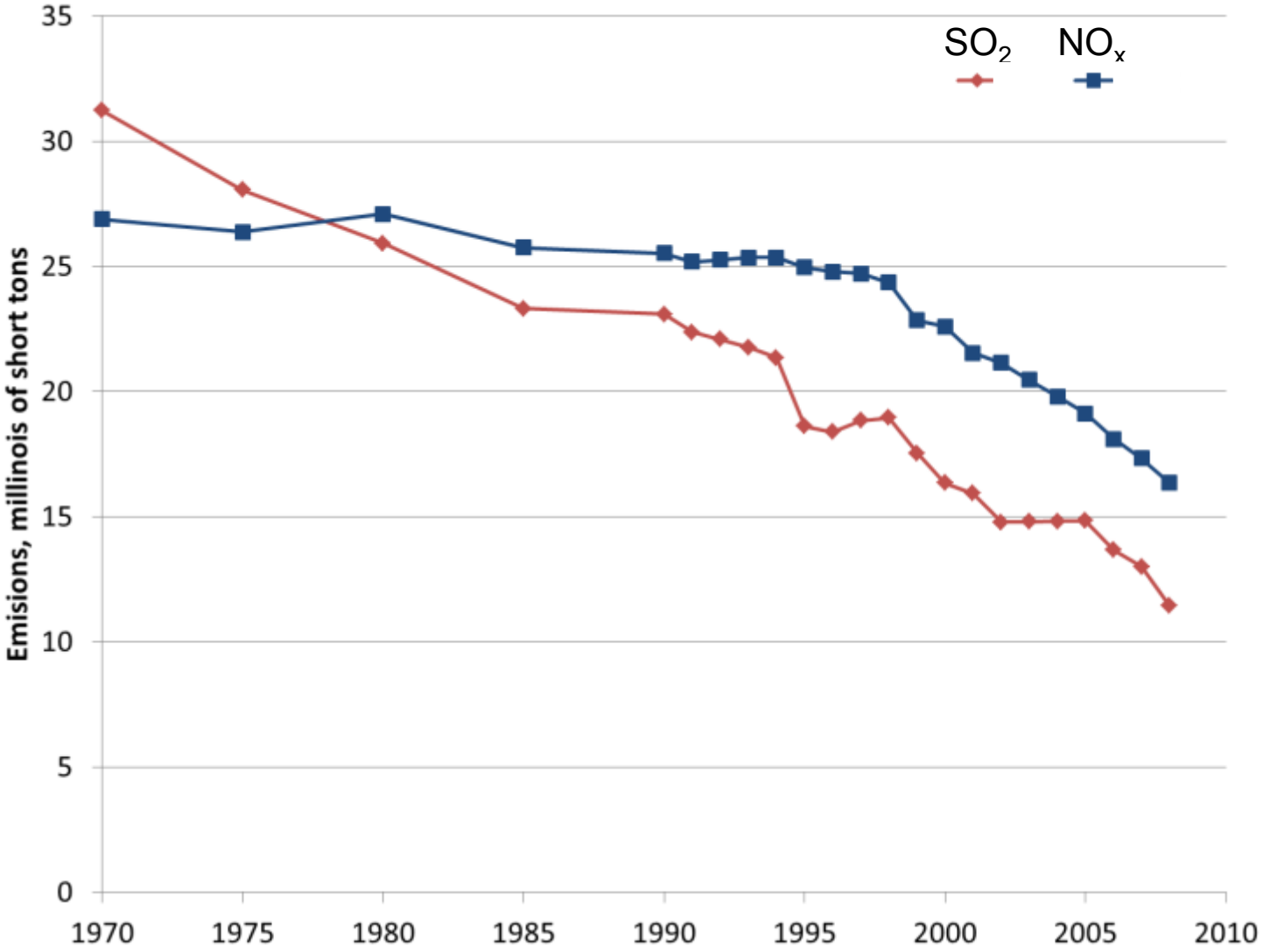



2008 **2009** 2010

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

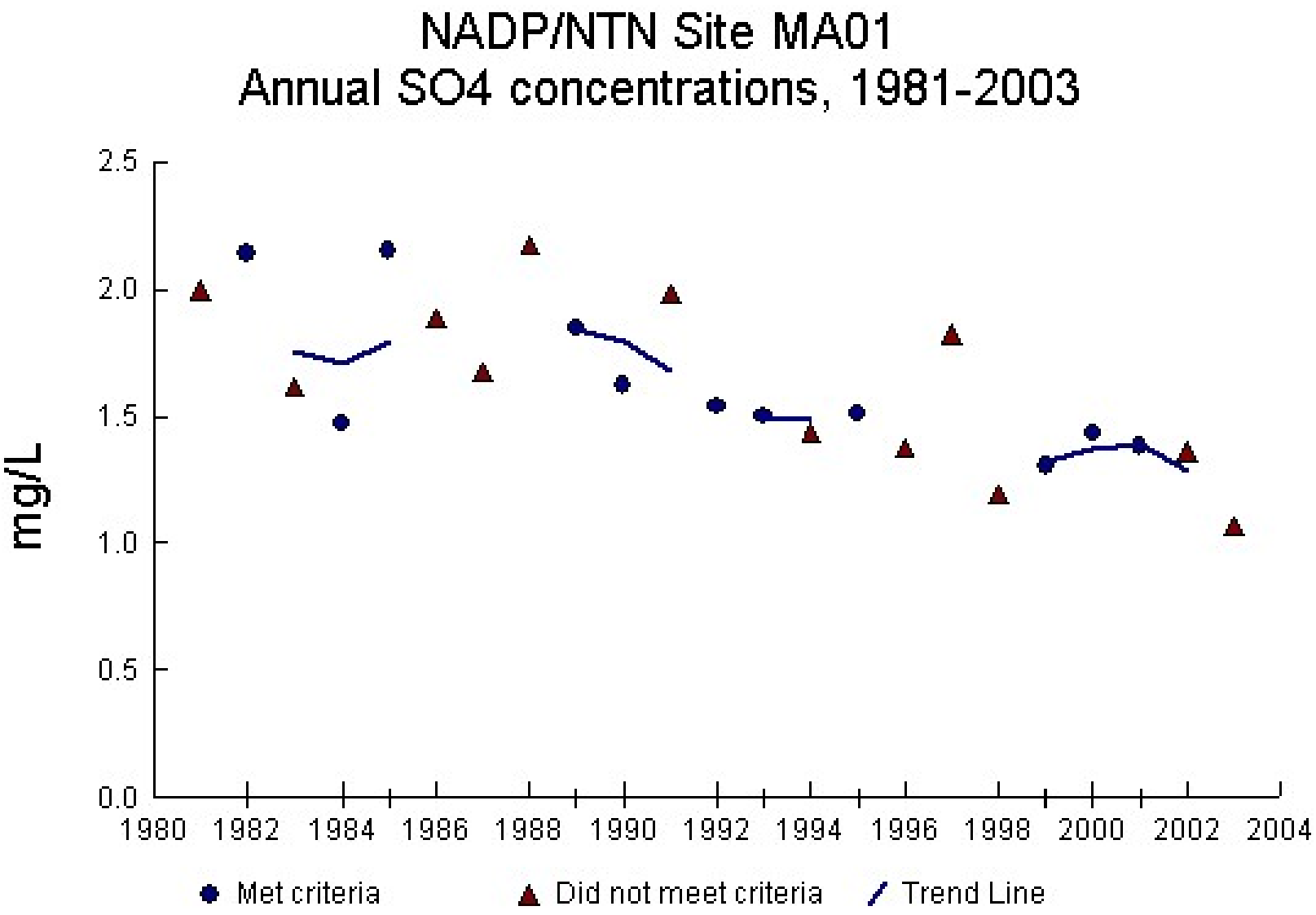
# How do trends in wet deposition compare to trends in emissions?

# Trends in US Emissions

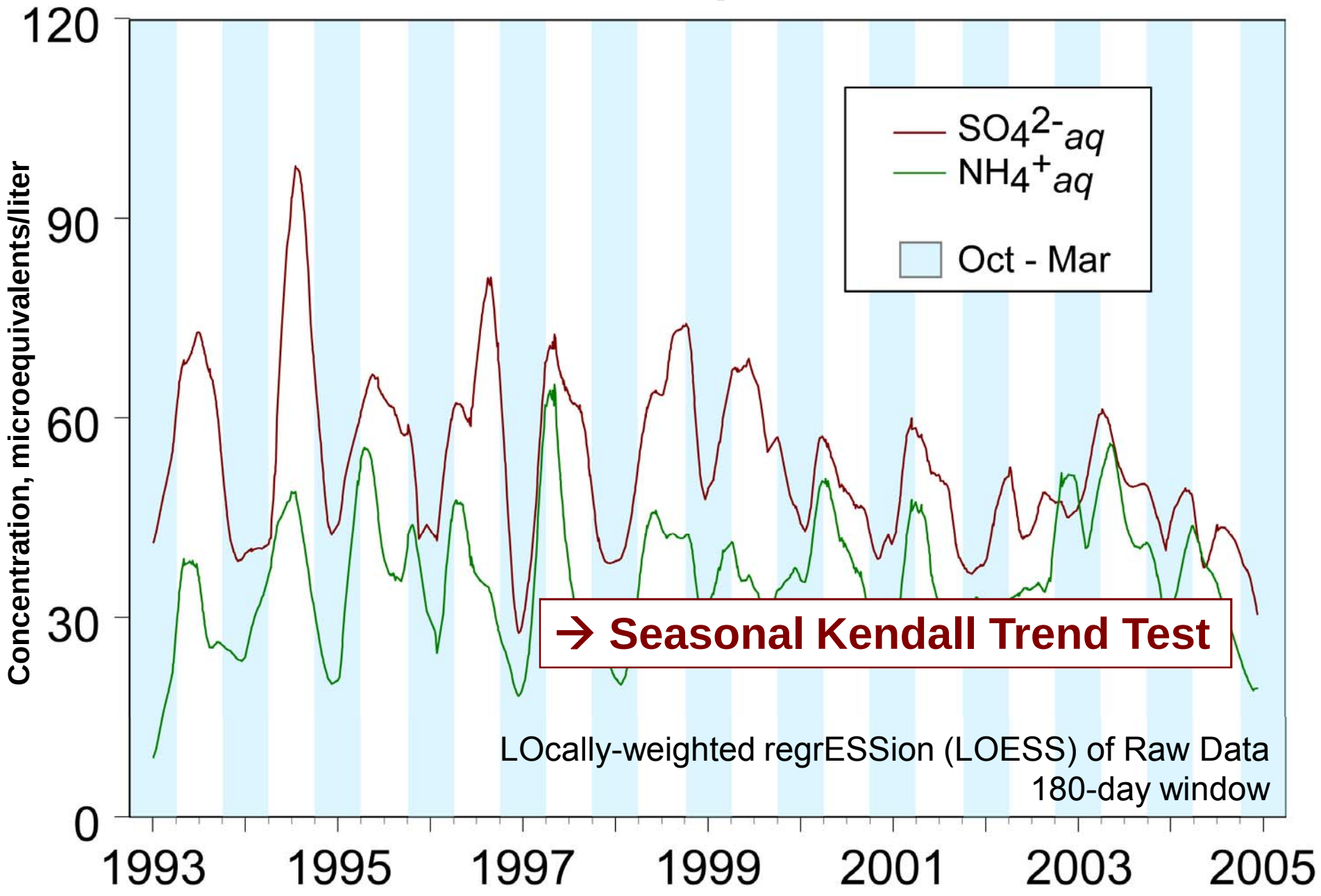



*Source: U.S. EPA*

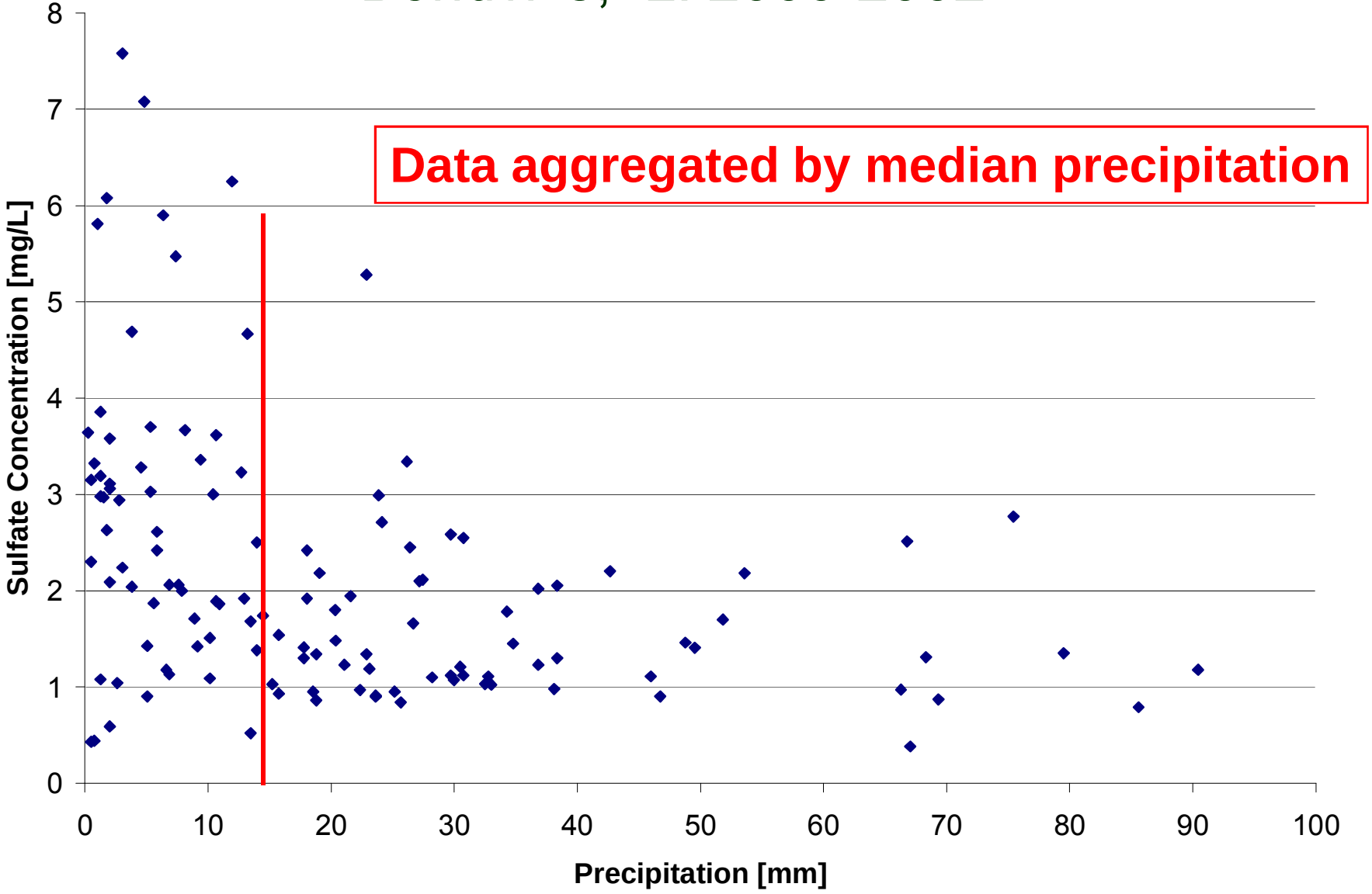
# Evaluating Trends in Real Data



# Concentrations in Precipitation at Bondville, IL

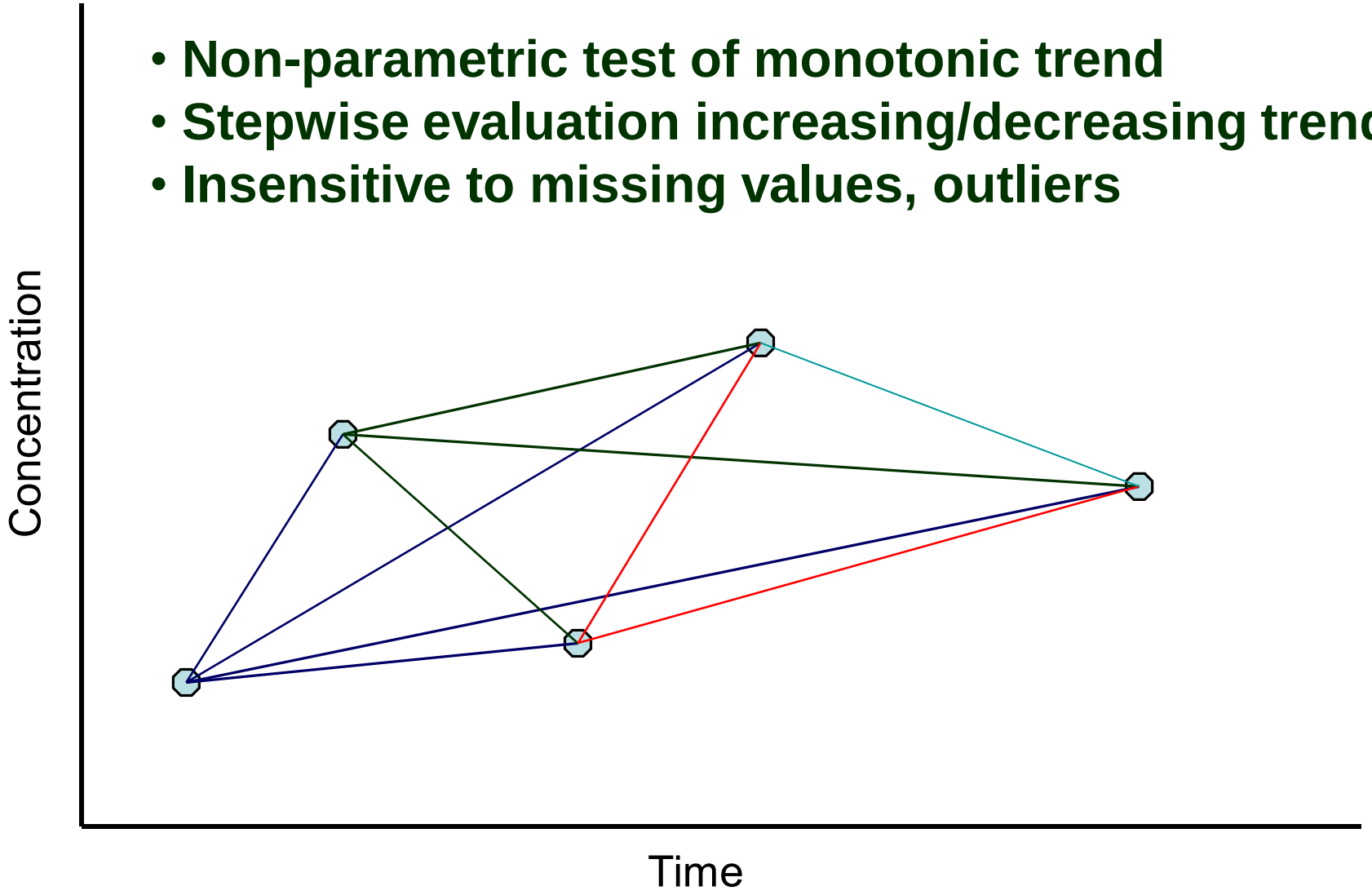


# Sulfate Concentration vs. Precipitation Amount at Bondville, IL: 2000-2002



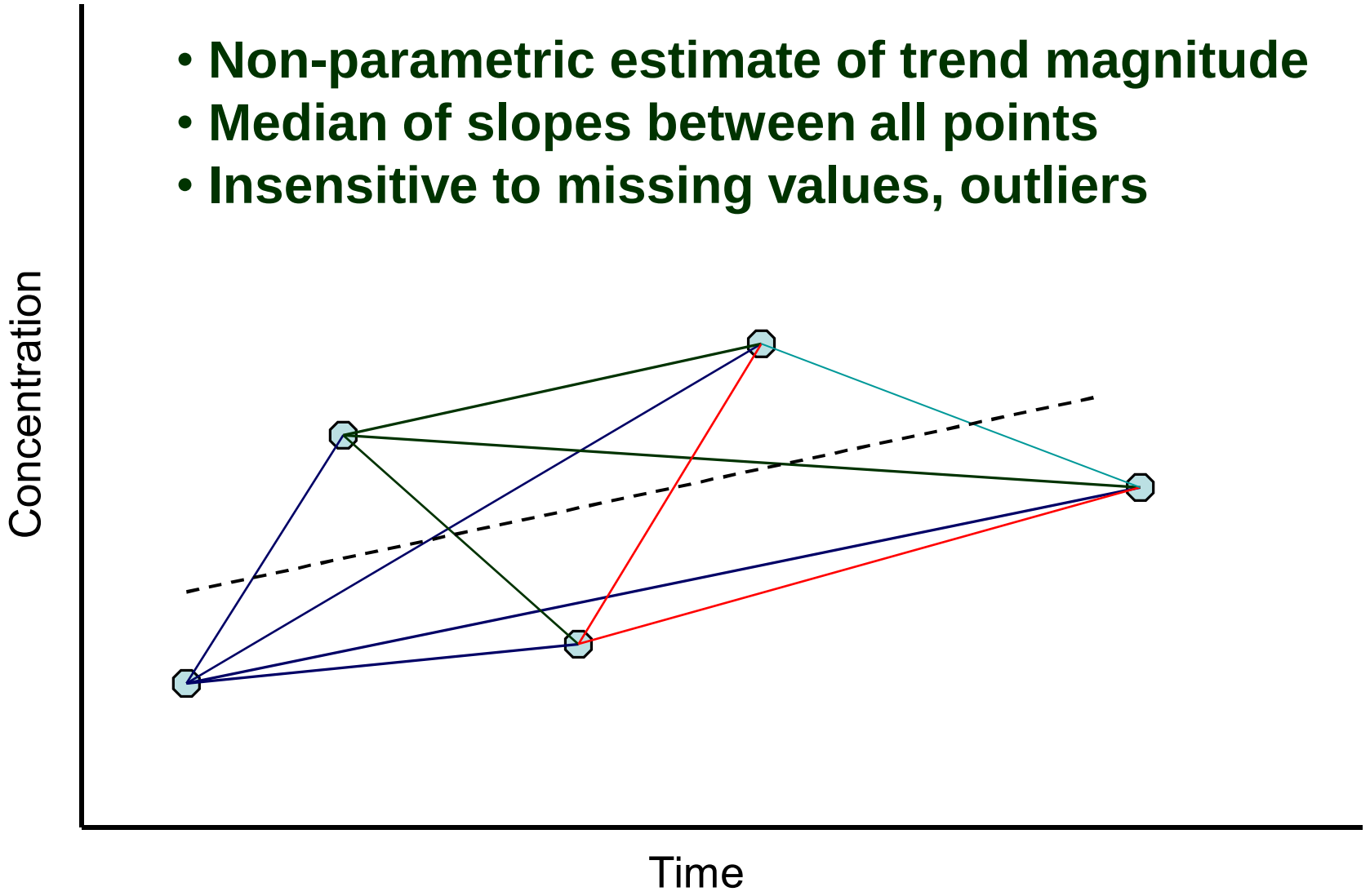
# Kendall Trend Test

- **Non-parametric test of monotonic trend**
- **Stepwise evaluation increasing/decreasing trend**
- **Insensitive to missing values, outliers**



# Sen's Median Estimator

- **Non-parametric estimate of trend magnitude**
- **Median of slopes between all points**
- **Insensitive to missing values, outliers**



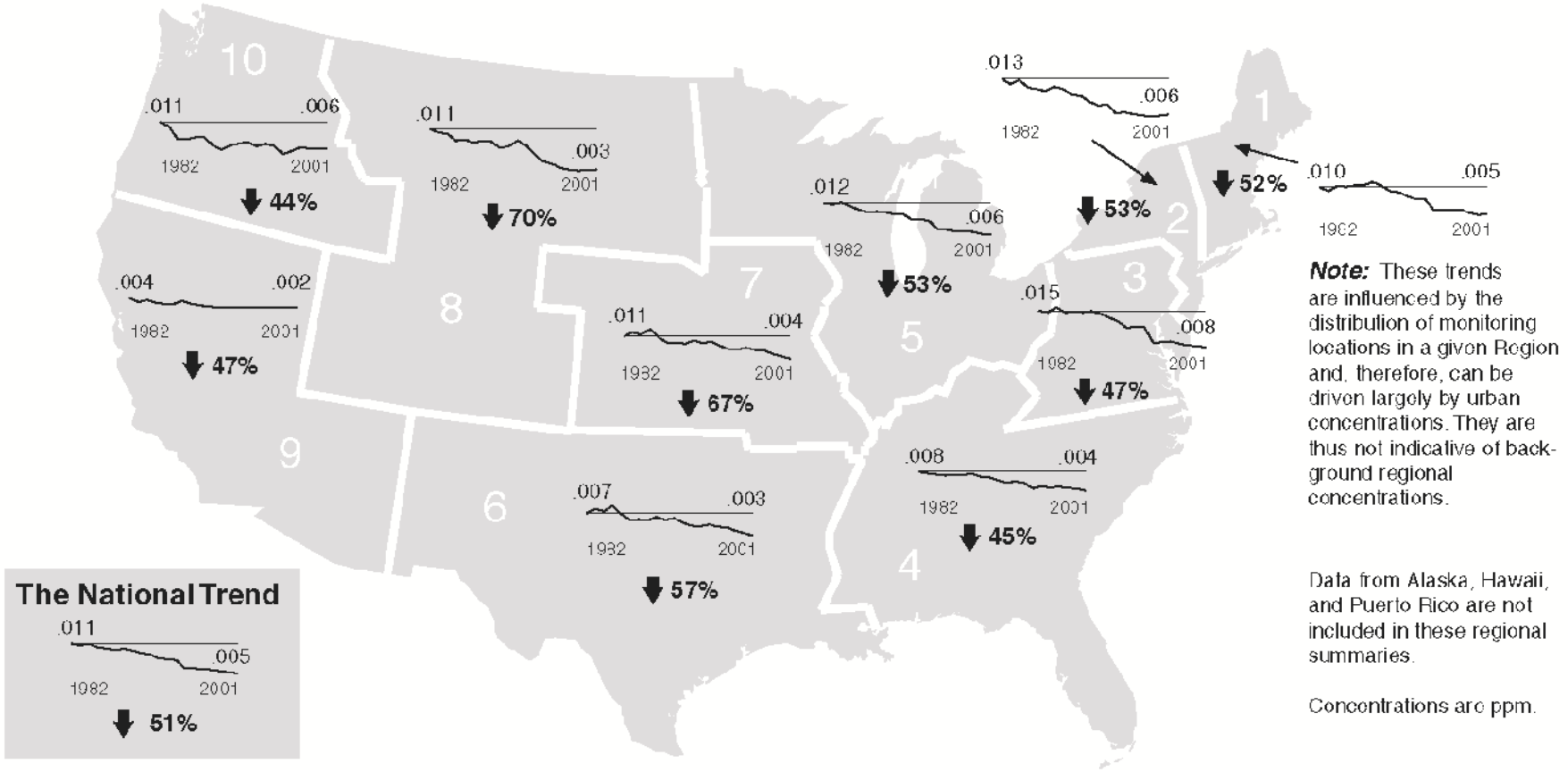
USGS
science for a changing world

# Computer Program for the Kendall Family of Trend Tests

Scientific Investigations Report 2005–5275

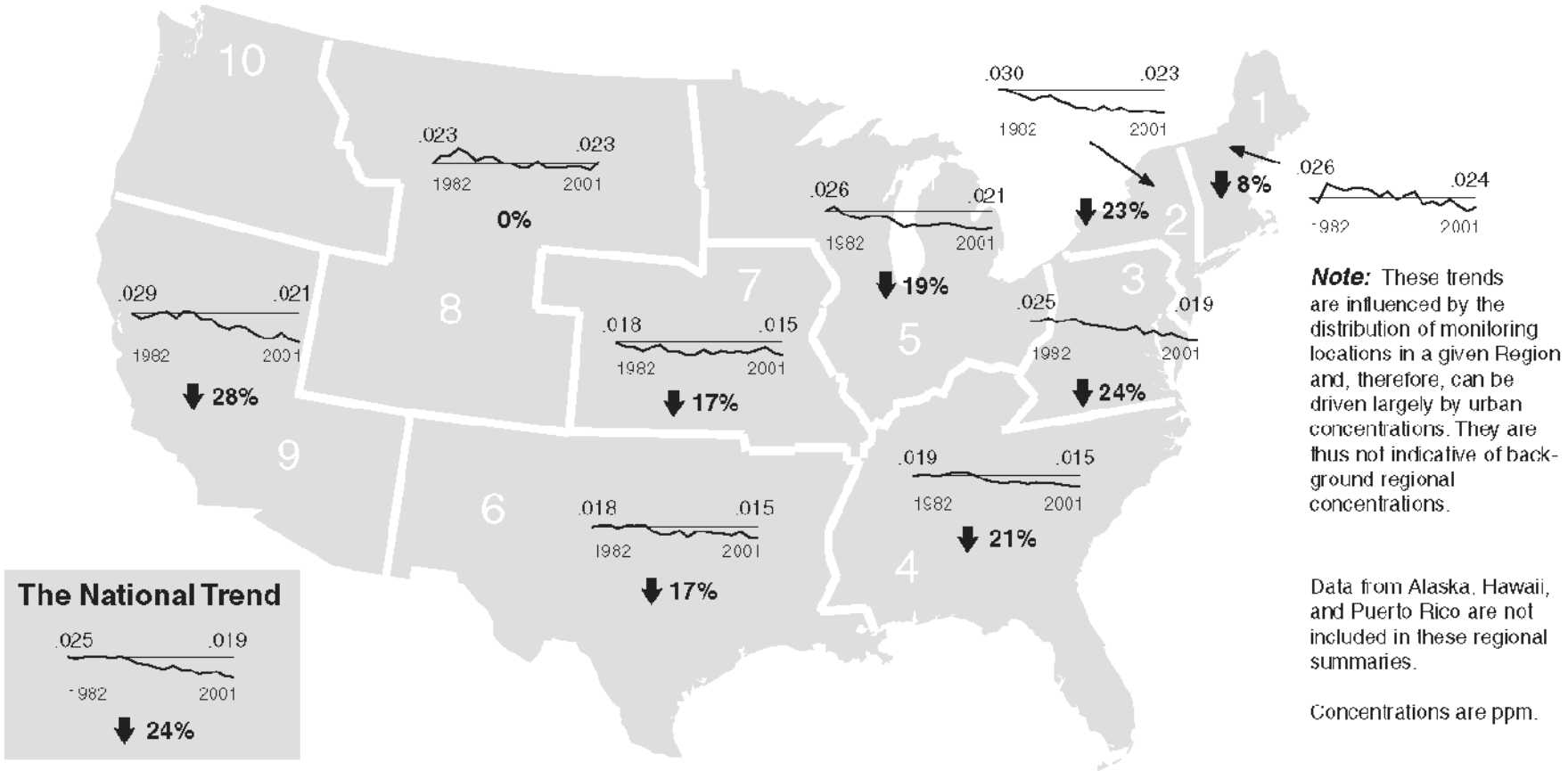
U.S. Department of the Interior
U.S. Geological Survey

# Trends in Sulfur Dioxide




*U.S. EPA, National Air Quality and Emissions Trends Report, 2003*

# Trends in Nitrogen Dioxide

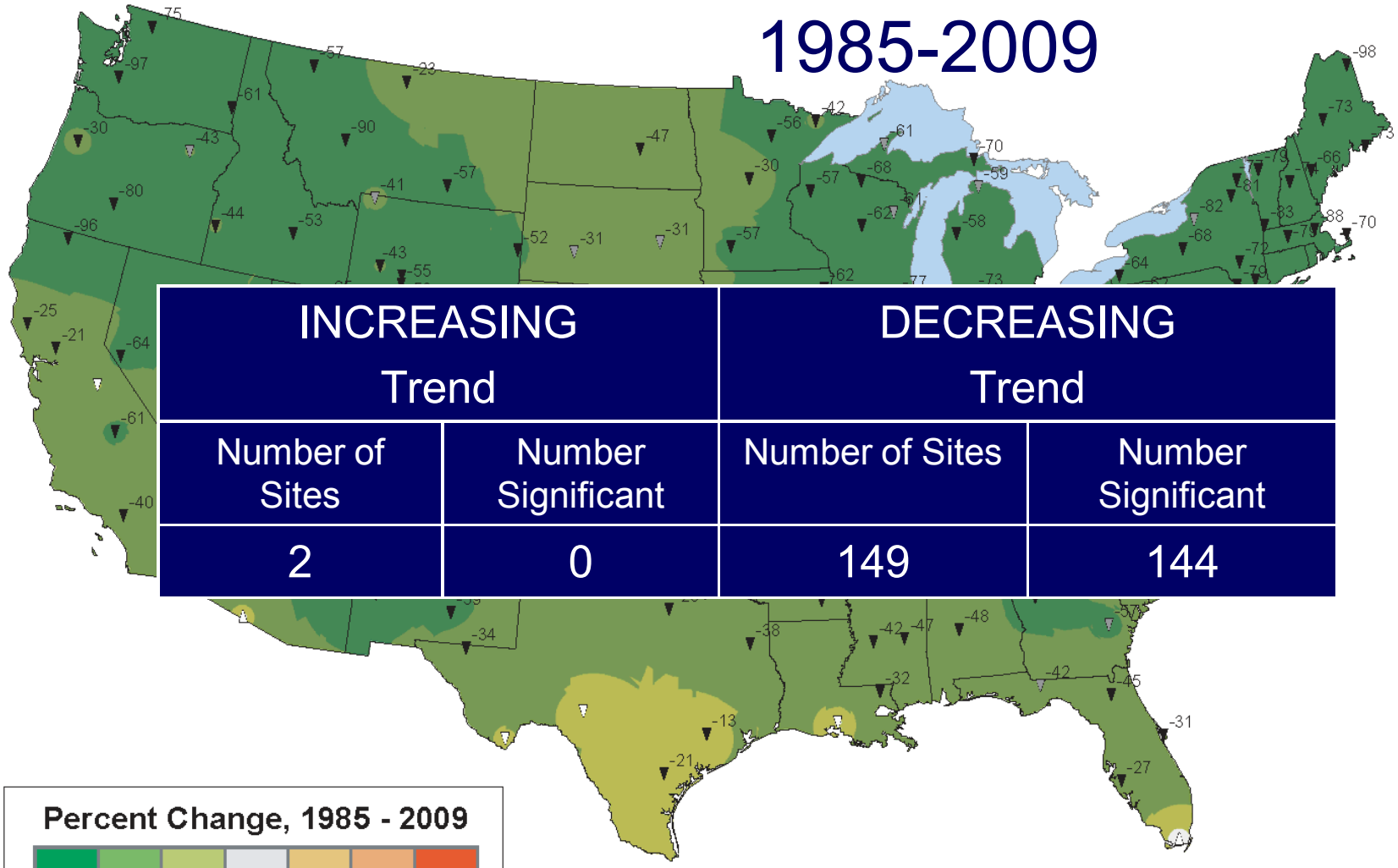



*U.S. EPA, National Air Quality and Emissions Trends Report, 2003*

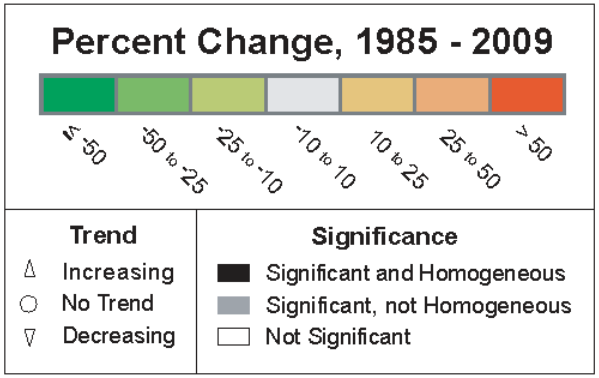
# Evaluating Trends in NADP-NTN Data

- Data from 151 sites, operational between 1985-2009 (~210,000 weekly data sets)
- Precipitation-weighted mean seasonal averages
- Seasonal Kendall Trend Test
  - Null Hypotheses:
    - Trend is zero (no trend)
    - Trends are homogeneous (same in every season)
  - Significance Level
    - $p \leq 0.1$ for trend significance
    - $p > 0.1$ for homogeneity
  - Trend magnitude by Sen's Median Estimator

# Sulfate Trend in Precipitation 1985-2009

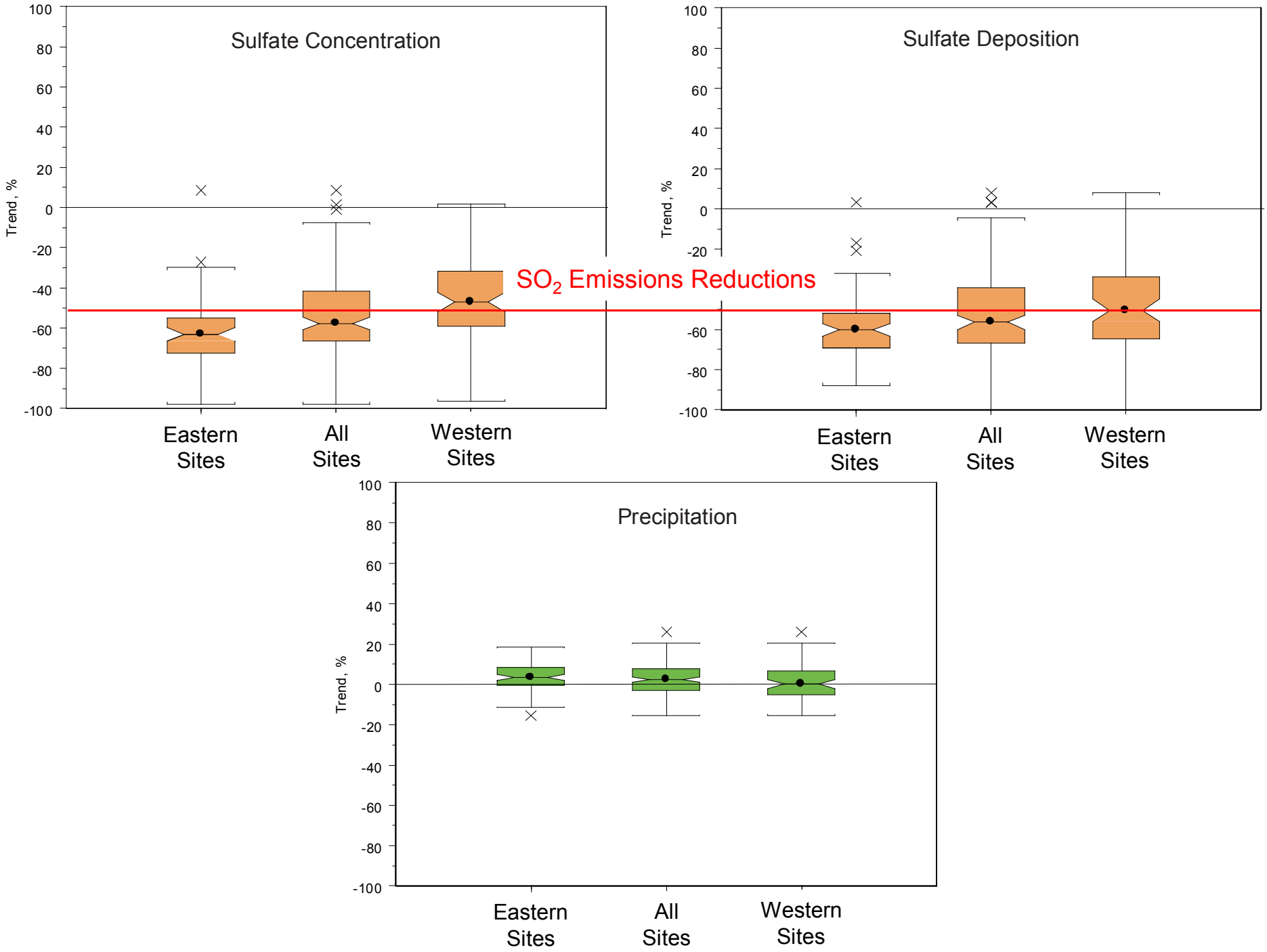


| INCREASING Trend | | DECREASING Trend | |
|---|---|---|---|
| Number of Sites | Number Significant | Number of Sites | Number Significant |
| 2 | 0 | 149 | 144 |

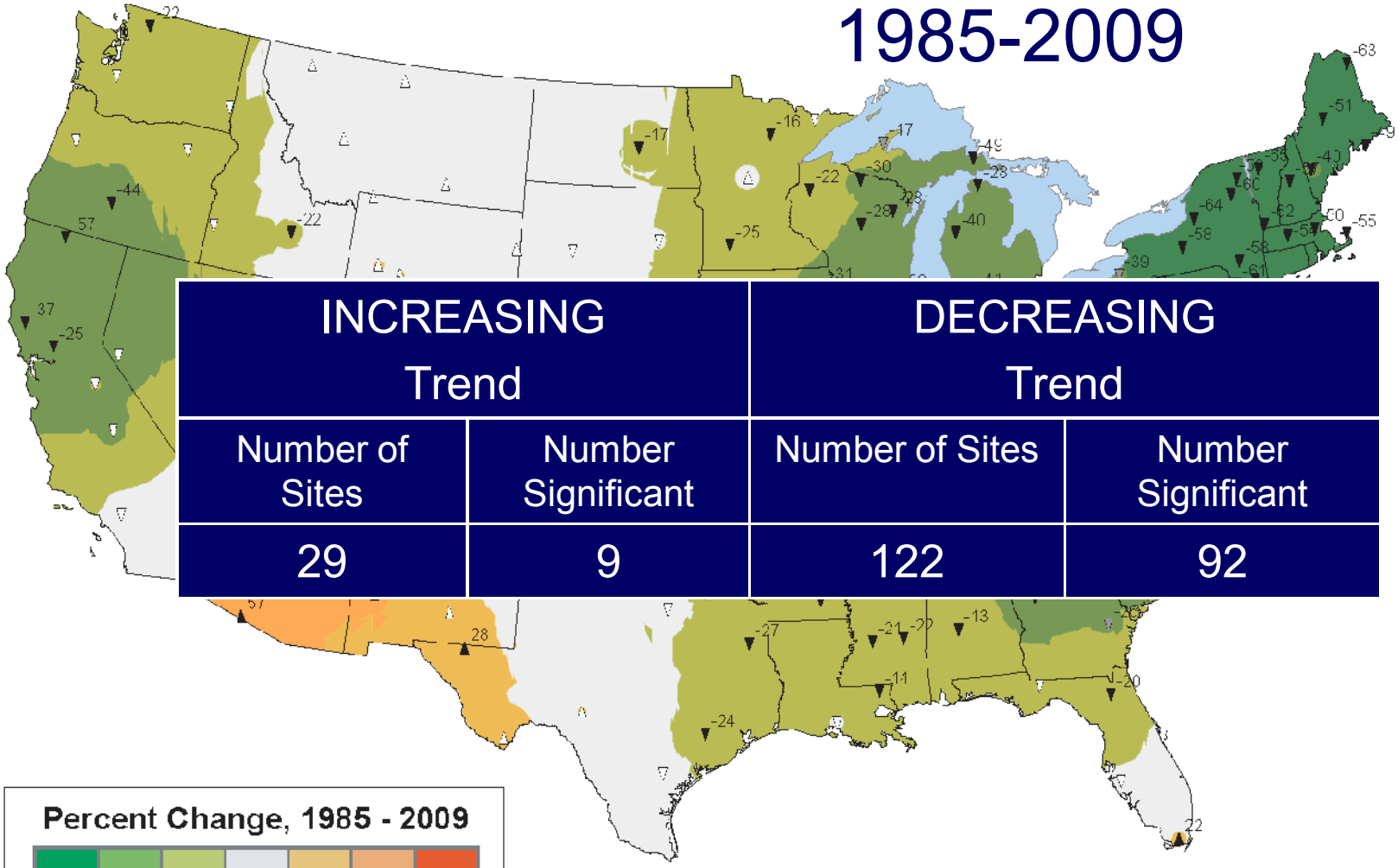



**Trends**

| Emissions | Concentration |
|---|---|
| -51% | -58% |


Sulfate Concentration
Trend, %
100
80
60
40
20
0
-20
-40
-60
-80
-100
Eastern Sites
All Sites
Western Sites
Sulfate Deposition
Trend, %
100
80
60
40
20
0
-20
-60
-80
-100
Eastern Sites
All Sites
Western Sites
SO2 Emissions Reductions
Precipitation
Trend, %
100
80
60
40
20
0
-20
-40
-60
-80
-100
Eastern Sites
All Sites
Western Sites

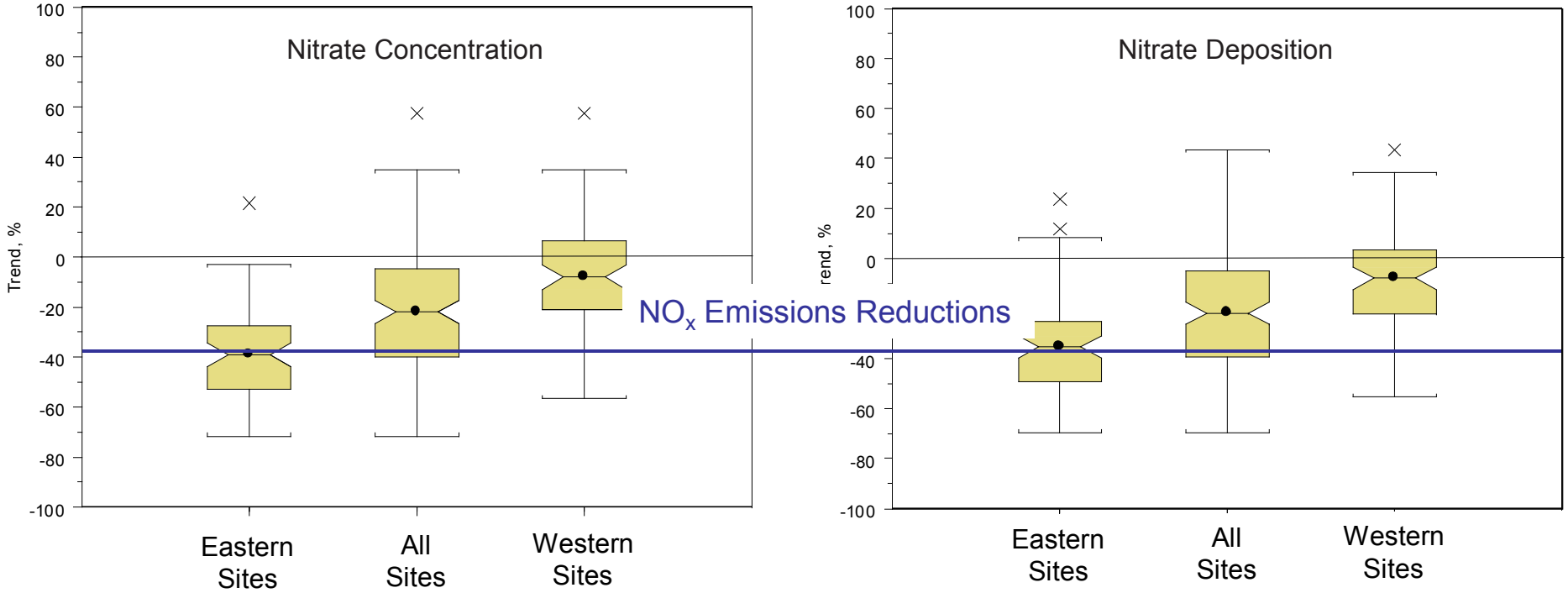
# Nitrate Trend in Precipitation 1985-2009




| INCREASING Trend | | DECREASING Trend | |
|---|---|---|---|
| Number of Sites | Number Significant | Number of Sites | Number Significant |
| 29 | 9 | 122 | 92 |

**Trends**

| Emissions | Concentration |
|---|---|
| -37% | -22% |

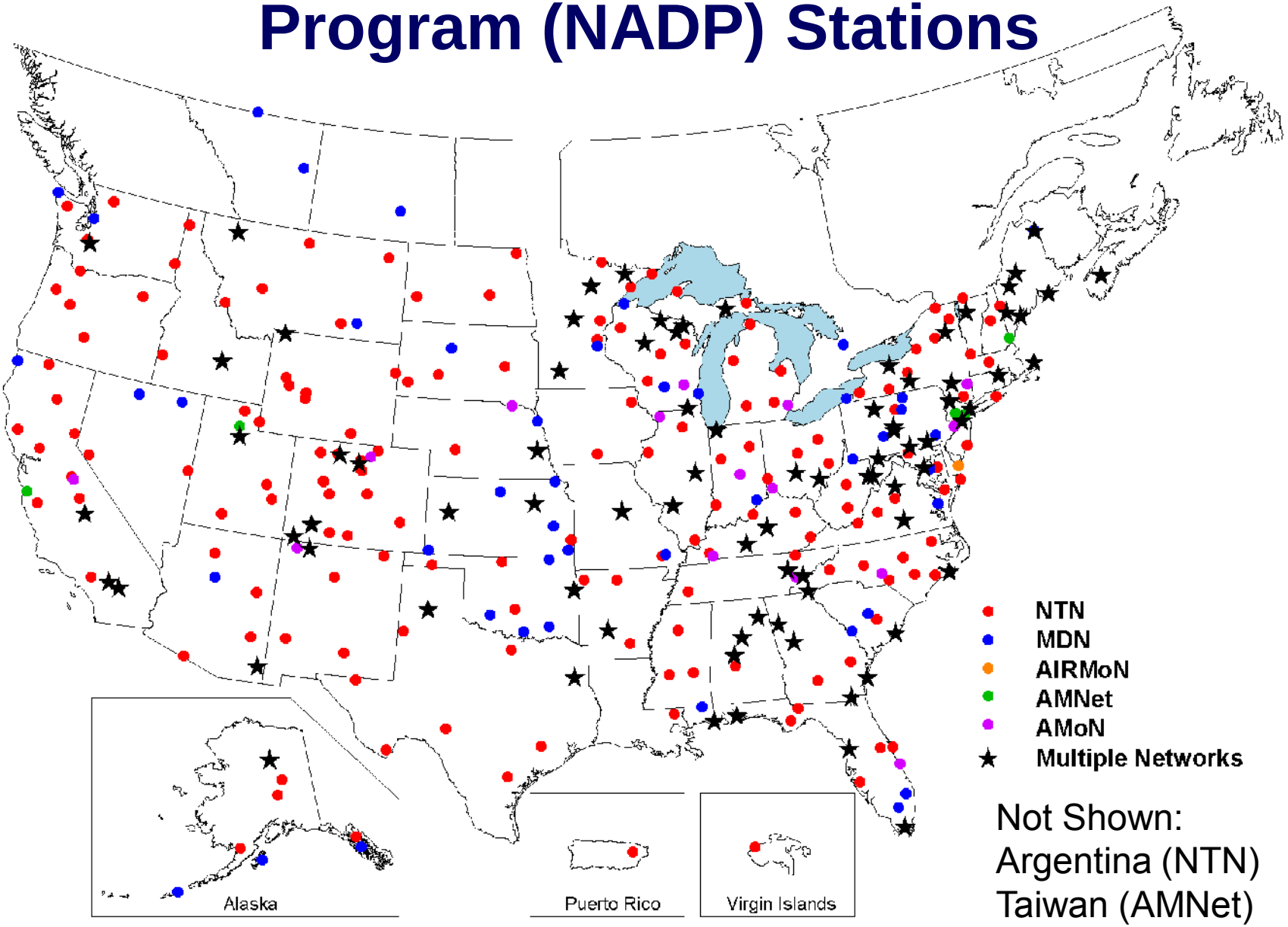

Nitrate Concentration
Trend, %
100
80
60
40
20
0
-20
-40
-60
-80
-100
Eastern Sites
All Sites
Western Sites
NOx Emissions Reductions
Nitrate Deposition
rend, %
100
80
60
40
20
0
-40
-60
-80
-100
Eastern Sites
All Sites
Western Sites

For trend analysis method, details see:

http://nadp.isws.illinois.edu/dl/clehmann/trends/

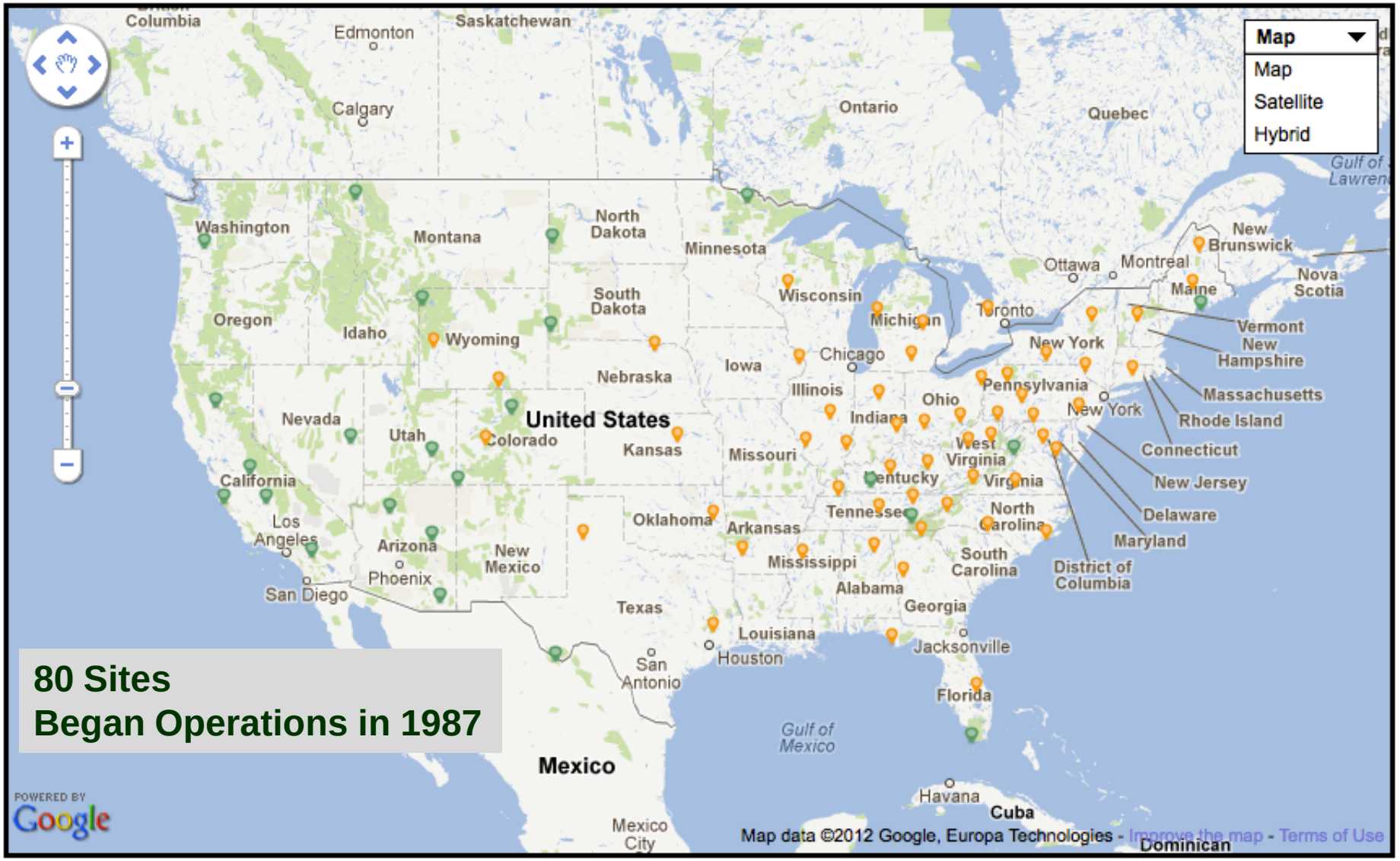
# How do trends in emissions compare to trends in air quality and wet/dry deposition?

# National Atmospheric Deposition Program (NADP) Stations

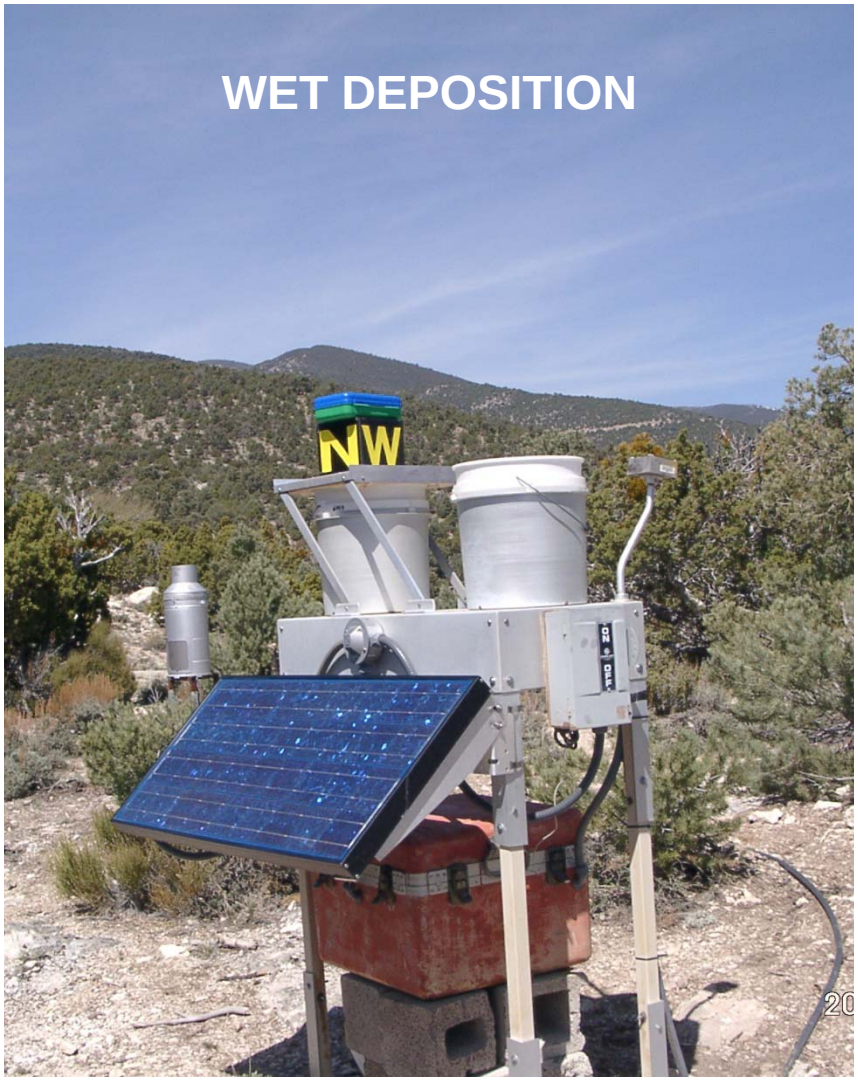



Not Shown:
Argentina (NTN)
Taiwan (AMNet)

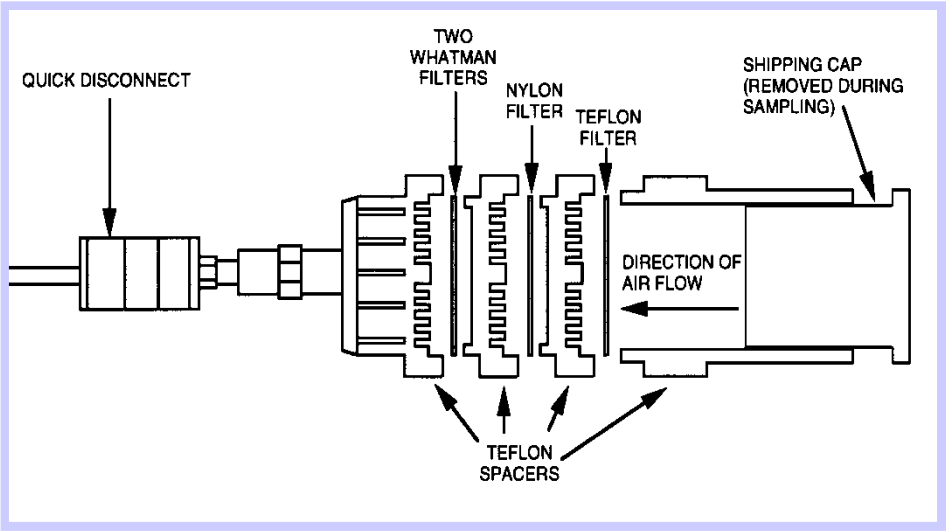
# Clean Air Status and Trends Network (CASTNET)



## NTN NV05
## Great Basin National Park




## CASTNET CTH110
## Connecticut Hill, NY




# CASTNET Filter Pack

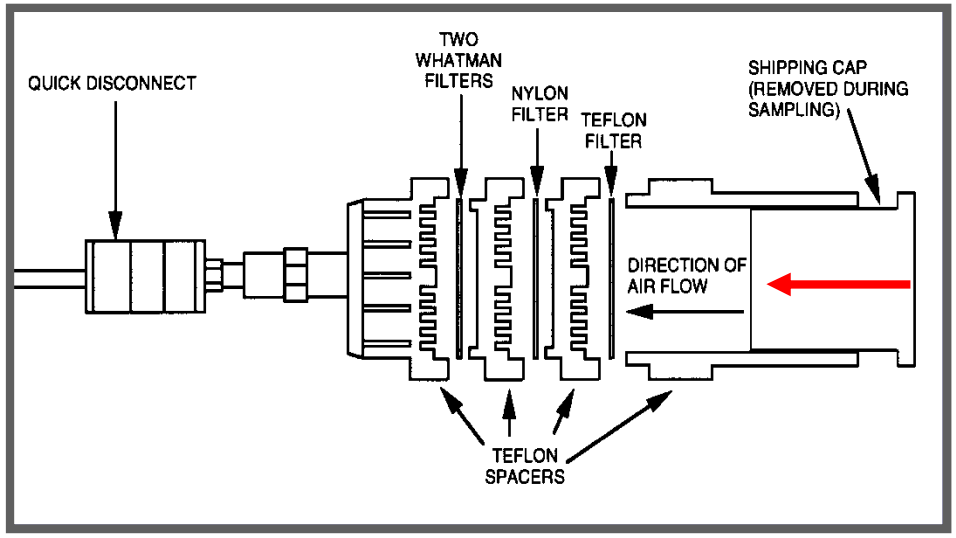


*Images provided by U.S. EPA's Clean Air Status and Trends Network*

# Clean Air Status & Trends Network (CASTNET)

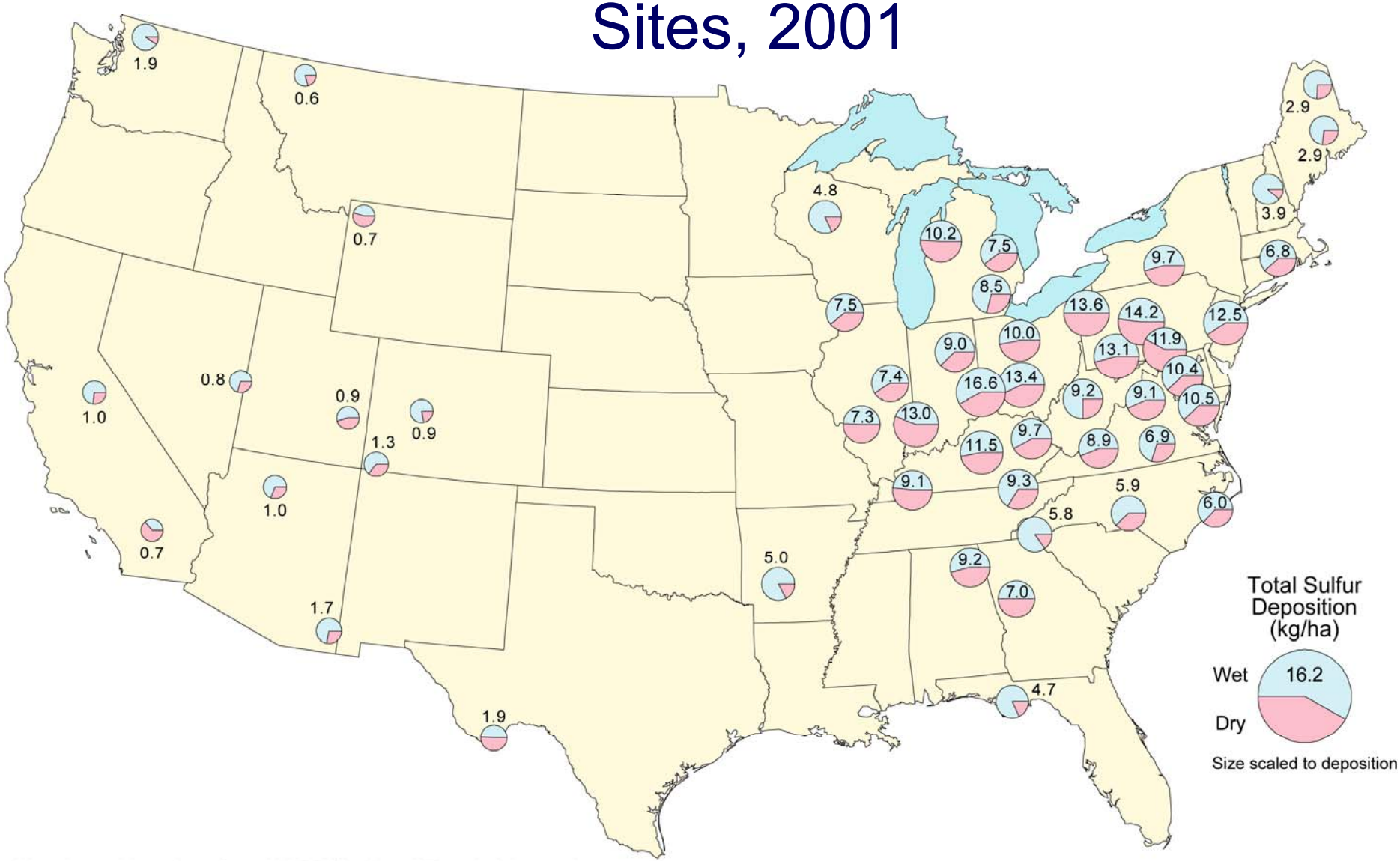
- Weekly 3-stage filter pack samples
  - Teflon filter: particulate sulfate and nitrate
  - Nylon filter: nitric acid, sulfur dioxide
  - Impregnated cellulose: sulfur dioxide

## CASTNET Filter Pack

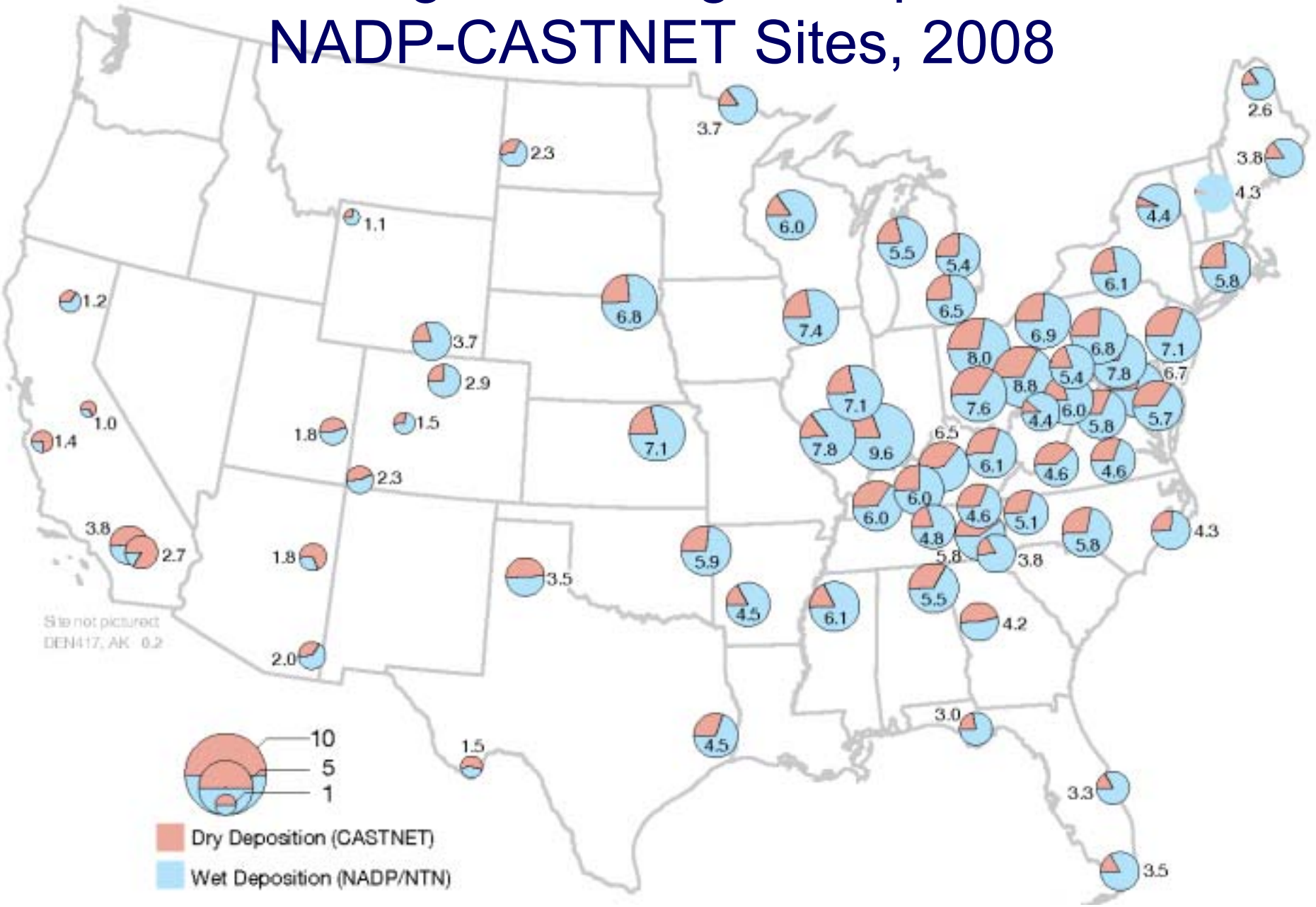

*Images provided by Clean Air Status and Trends Network (U.S. EPA)*

# Total Sulfur Deposition at NADP-CASTNET Sites, 2001

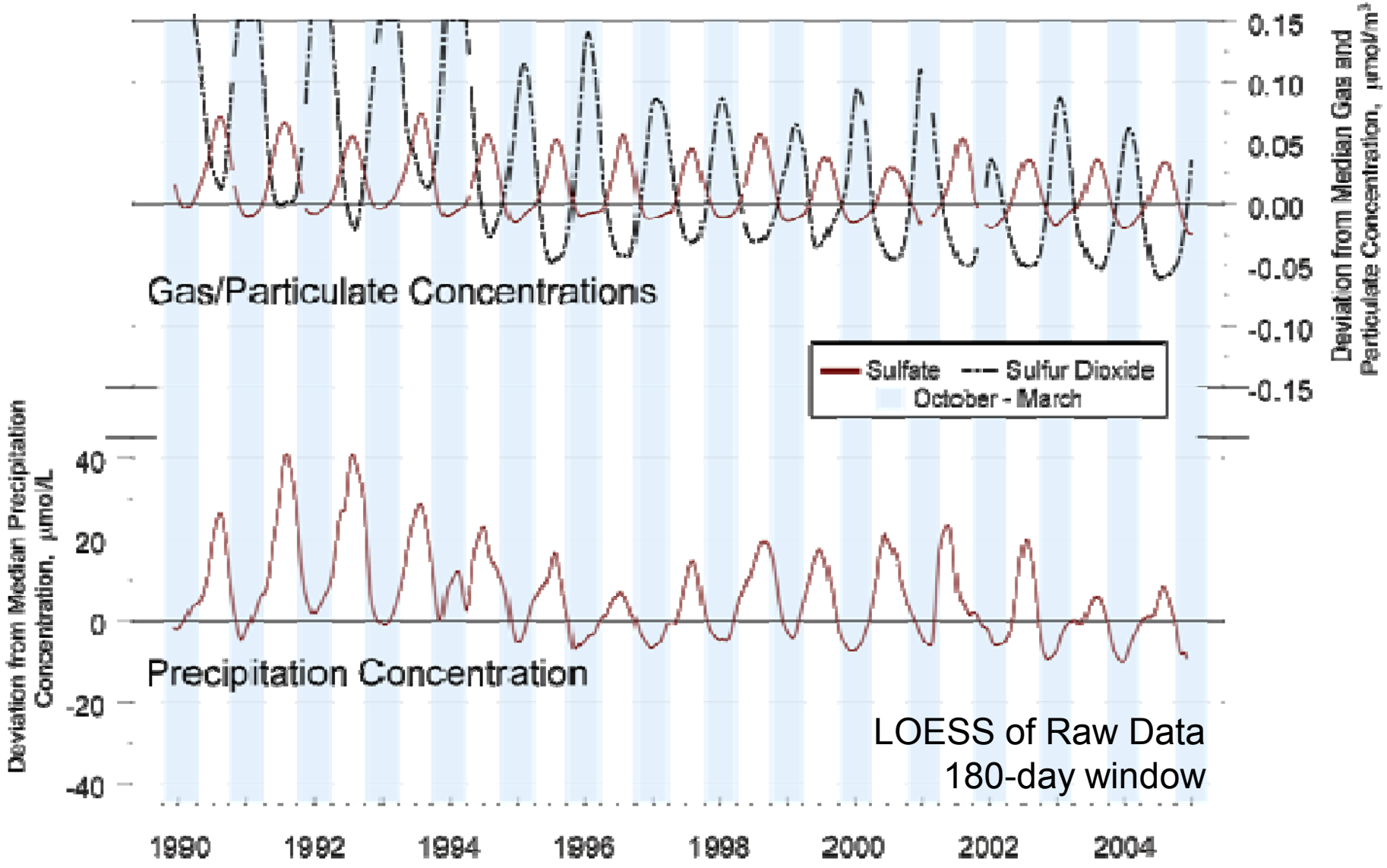



Wet deposition data from NADP/National Trends Network
Dry deposition data from Clean Air Status and Trends Network

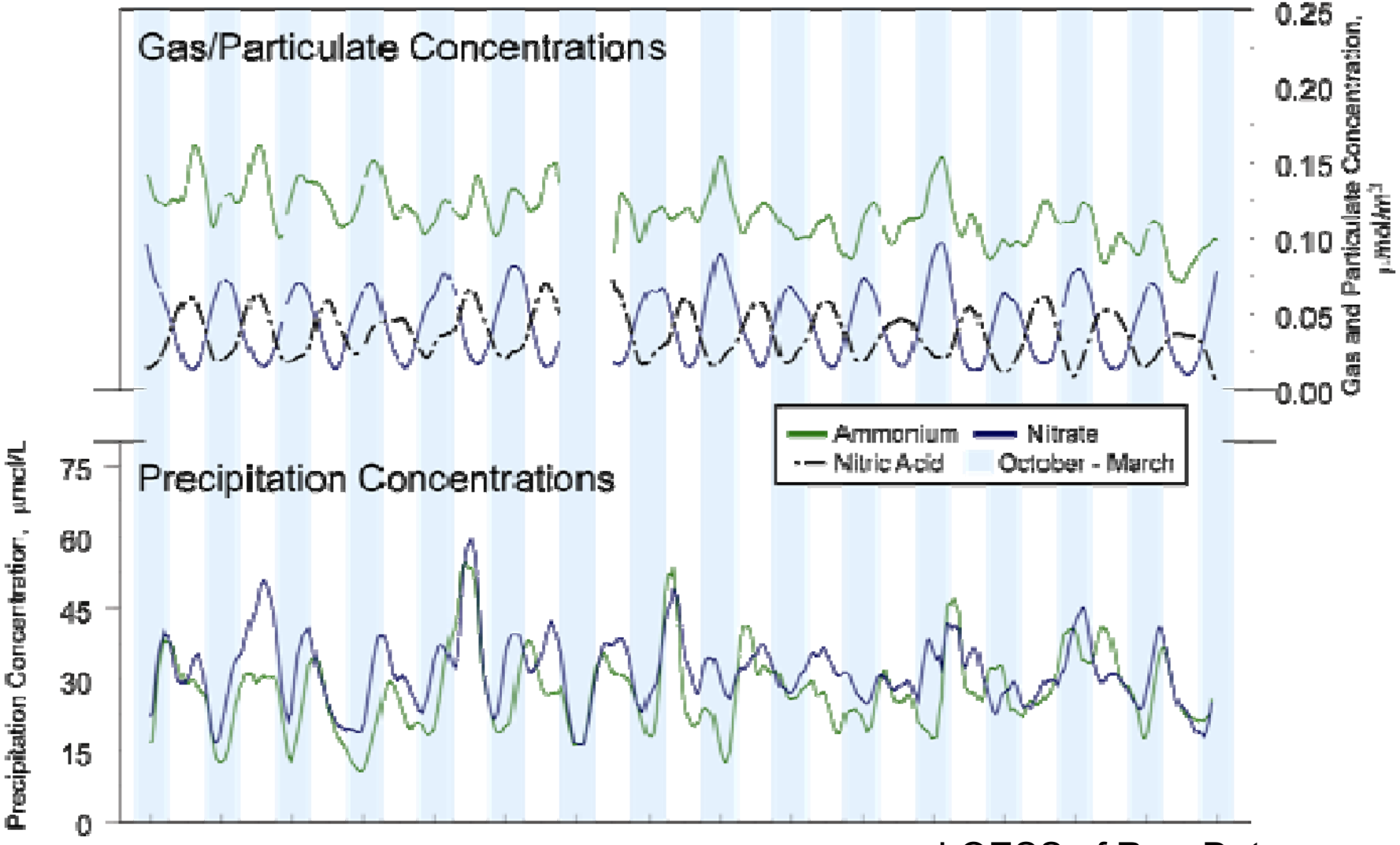
# Total Inorganic Nitrogen Deposition at NADP-CASTNET Sites, 2008



# Sulfur Dioxide, Particulate Sulfate, and Precipitation Sulfate
# Tucker County, WV (WV18)

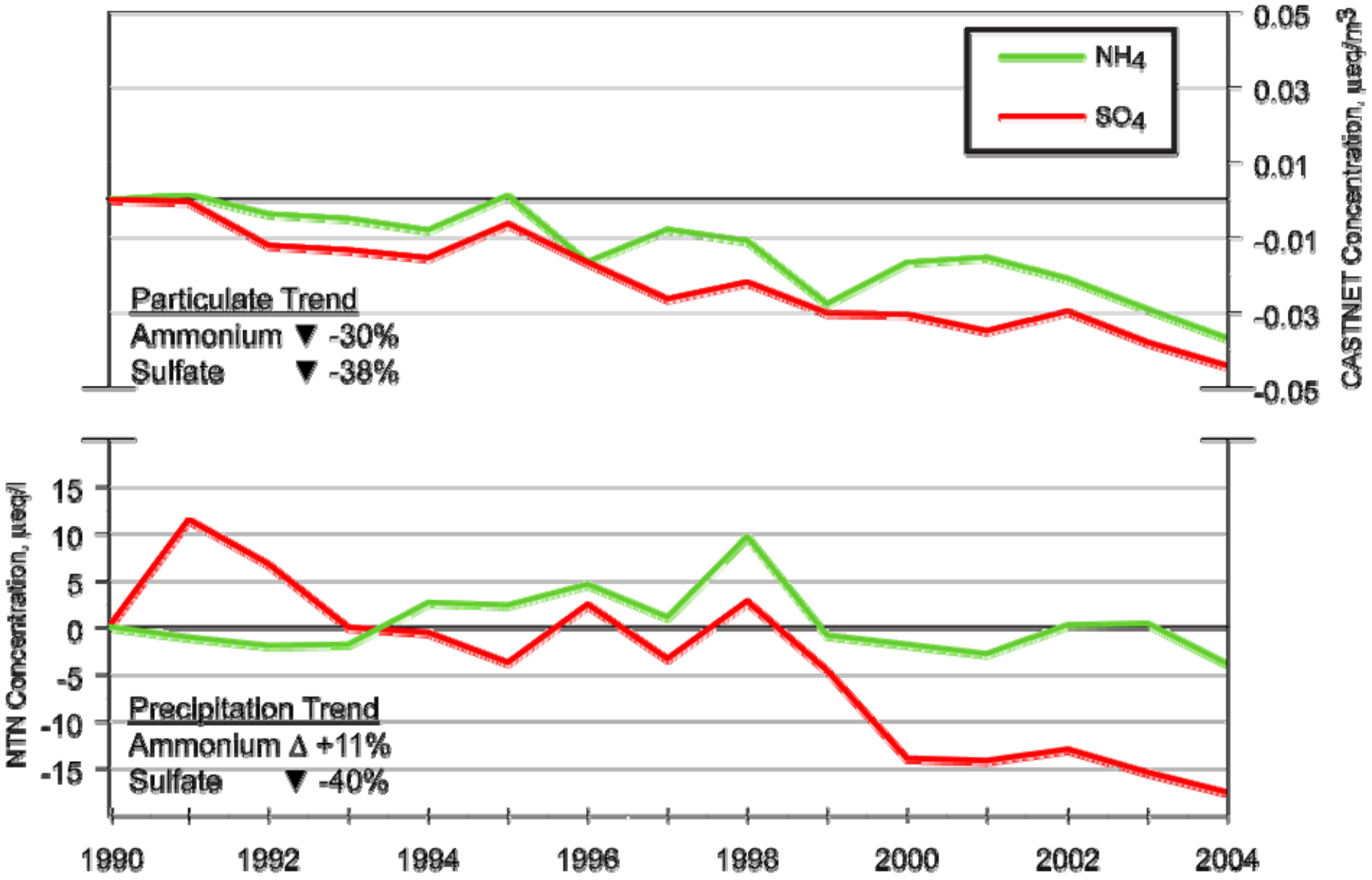


# Ammonium, Nitrate, and Nitric Acid Concentrations
# Bondville, IL (IL11)

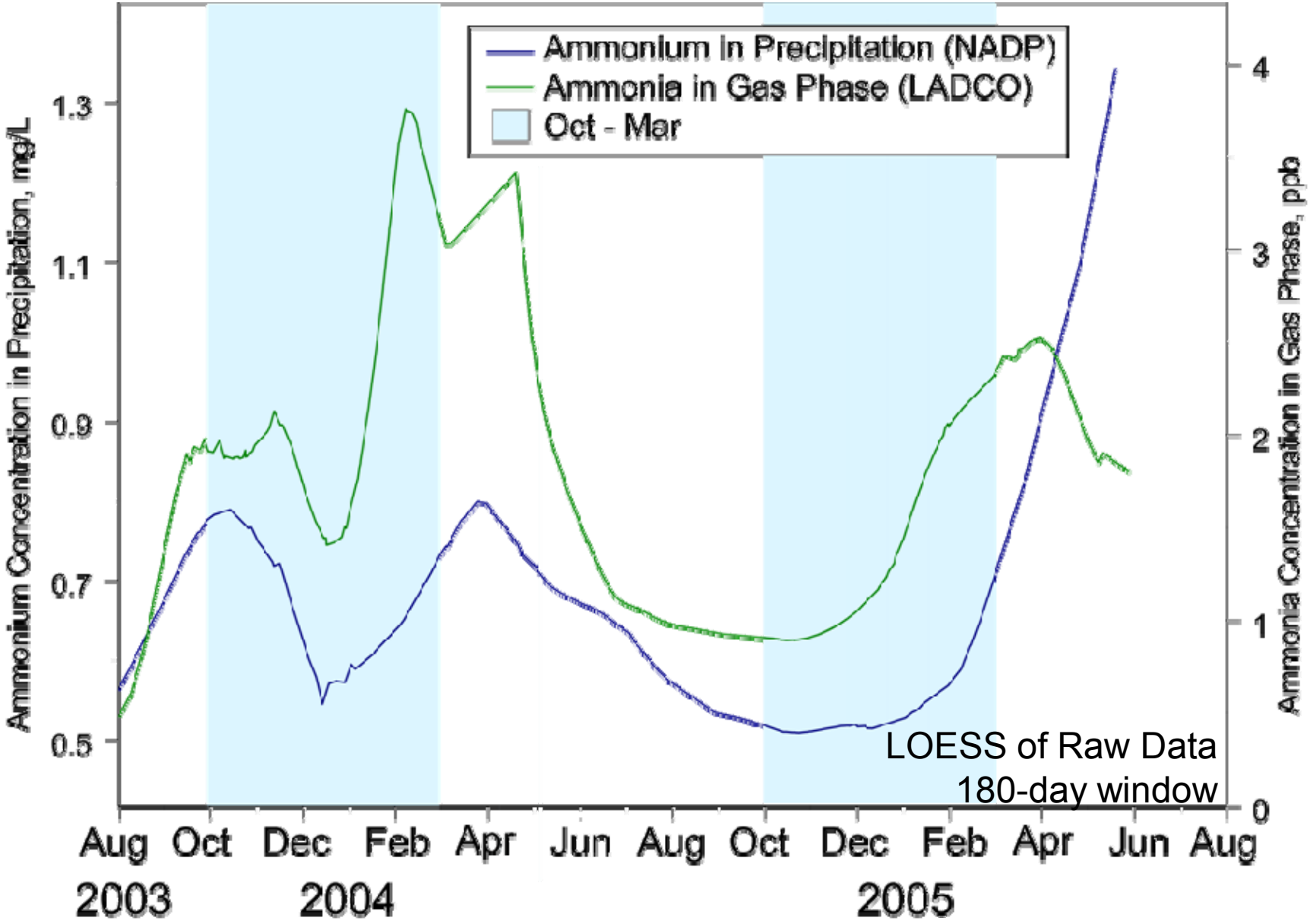



LOESS of Raw Data
180-day window

# Ammonium vs. Sulfate Trends
# Bondville, IL



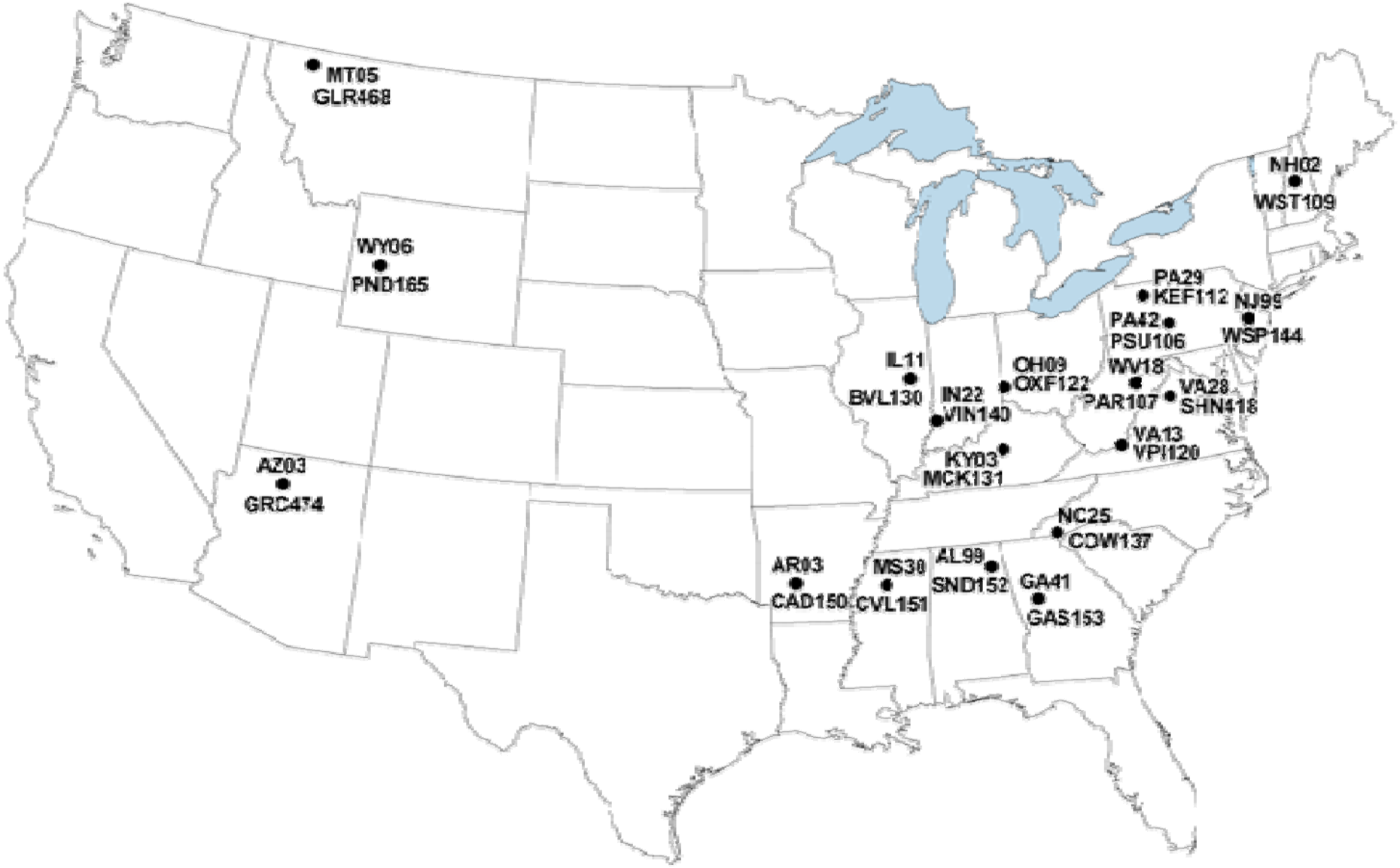
# Ammonia vs. Ammonium Concentrations
# Bondville, IL



# Comparing Trends in Wet and Dry Deposition

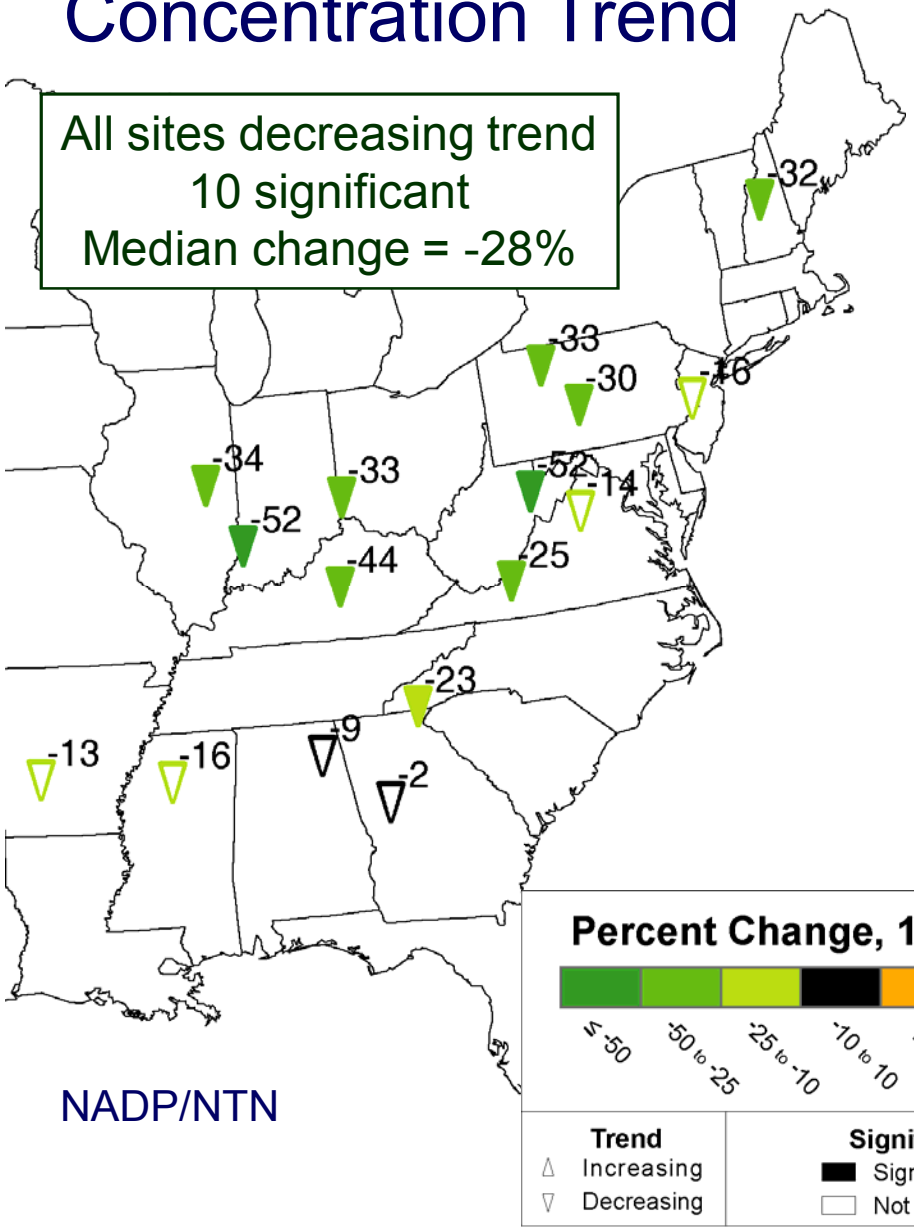
- Data from 19 collocated (< 10 km) wet and dry deposition monitoring sites, 1990 to 2004
- Wet deposition from precipitation concentrations (NADP/NTN)
  - Ammonium, sulfate, nitrate
- Dry deposition from gas and particulate concentrations (CASTNET)
  - Particulate ammonium, sulfate, and nitrate
  - Gas phase sulfur dioxide and nitric acid

# Collocated Sites Evaluated



# Precipitation Sulfate Concentration Trend

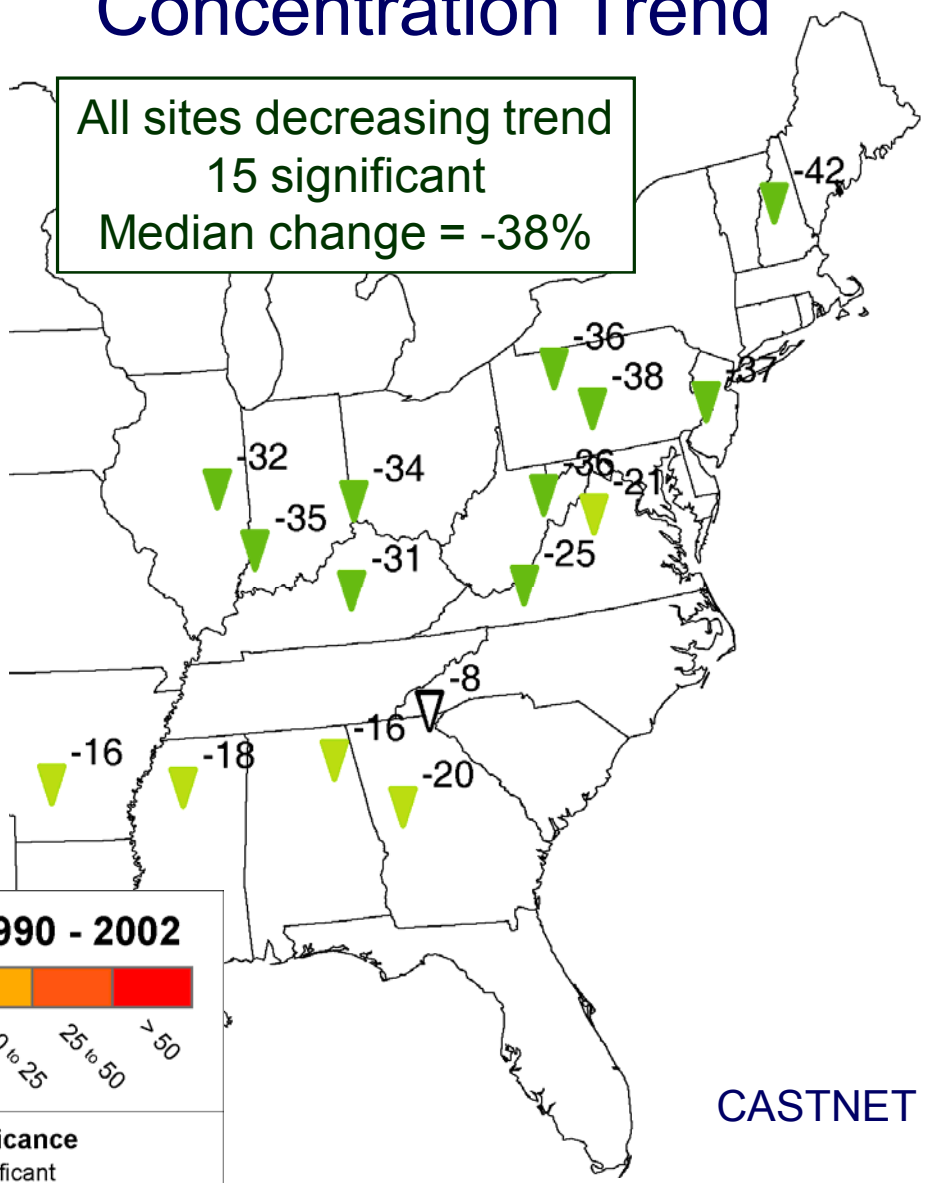
All sites decreasing trend
10 significant
Median change = -28%




NADP/NTN

# Particulate Sulfate Concentration Trend

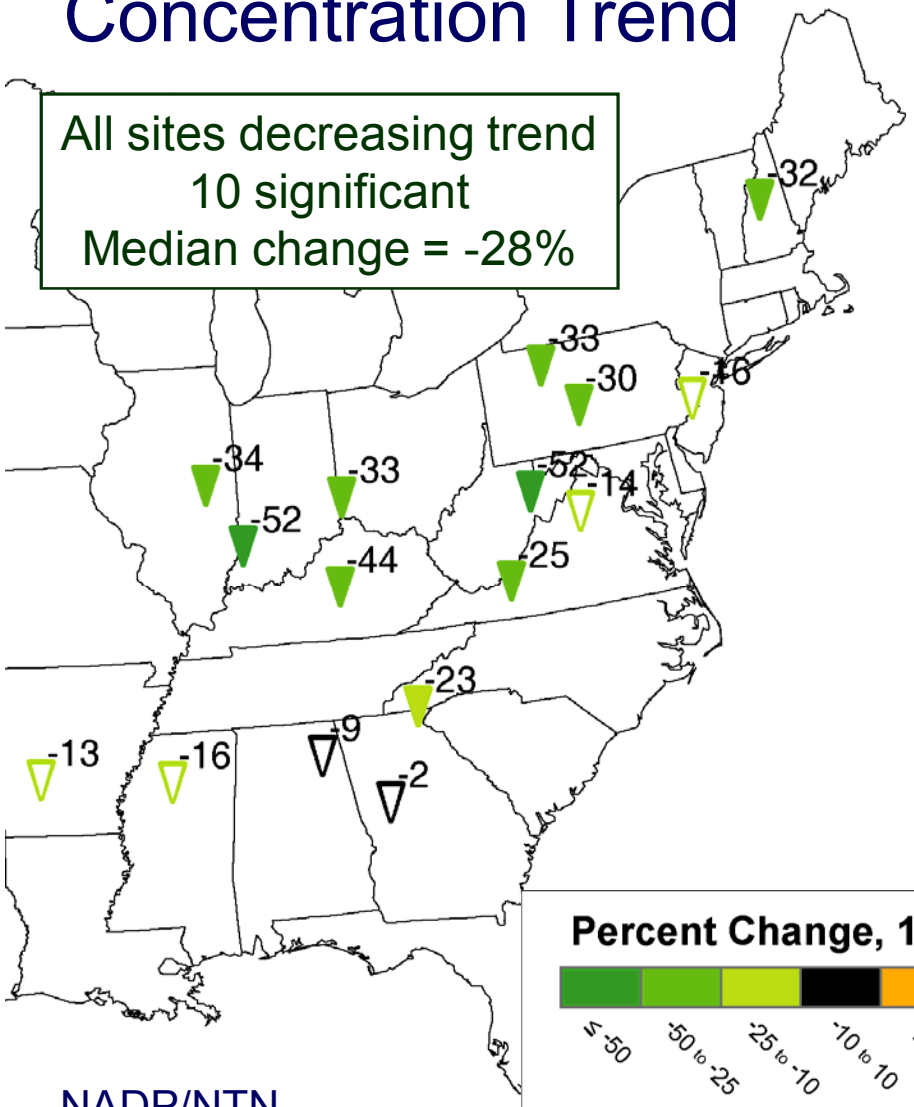
All sites decreasing trend
15 significant
Median change = -38%




CASTNET

# Precipitation Sulfate Concentration Trend

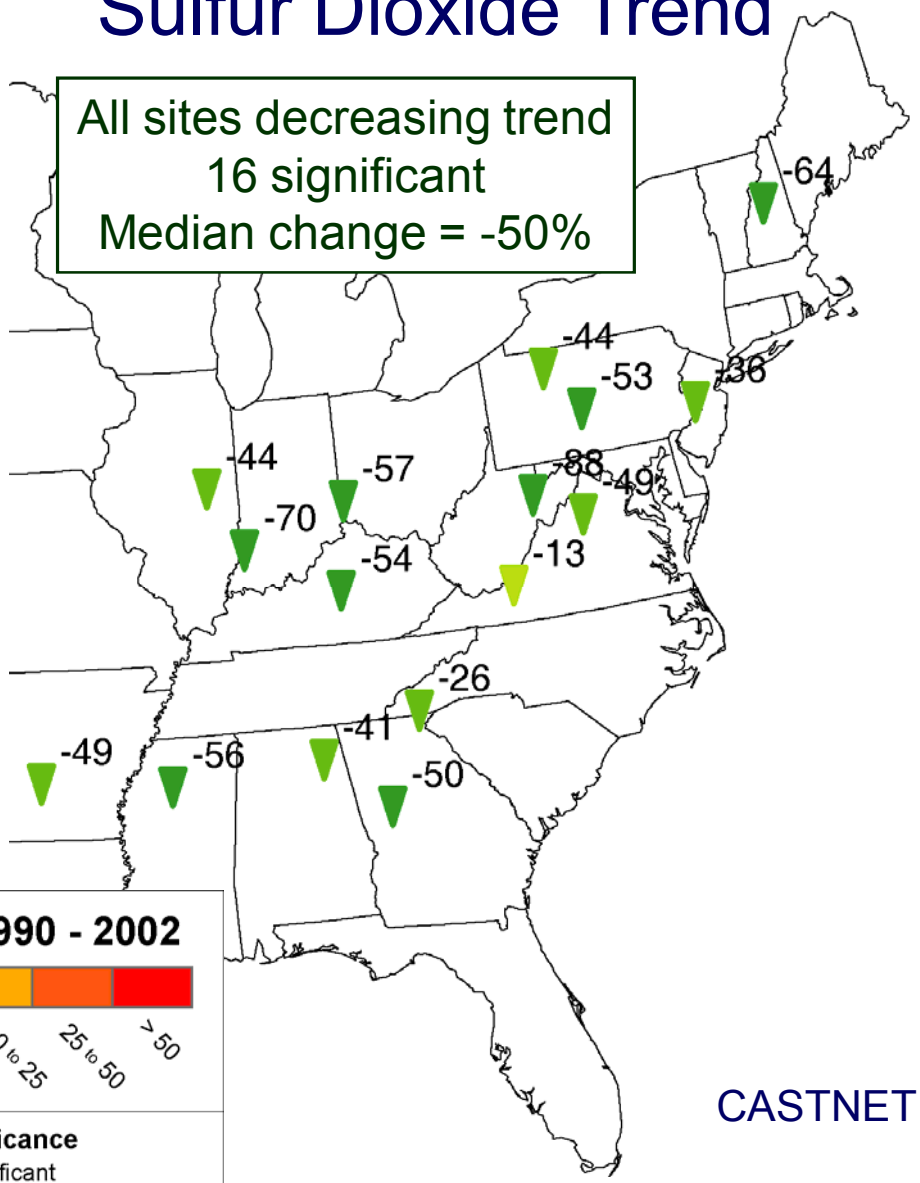
All sites decreasing trend
10 significant
Median change = -28%



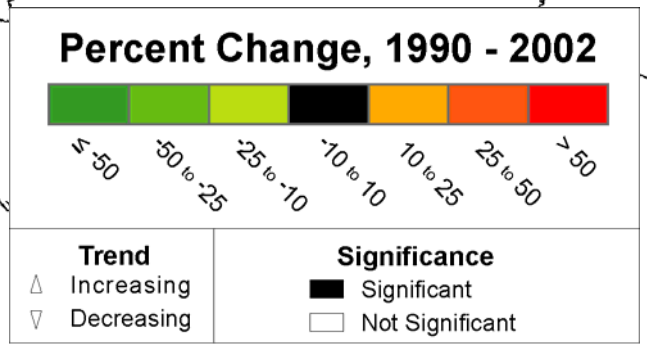

NADP/NTN

# Gas Phase Sulfur Dioxide Trend

All sites decreasing trend
16 significant
Median change = -50%

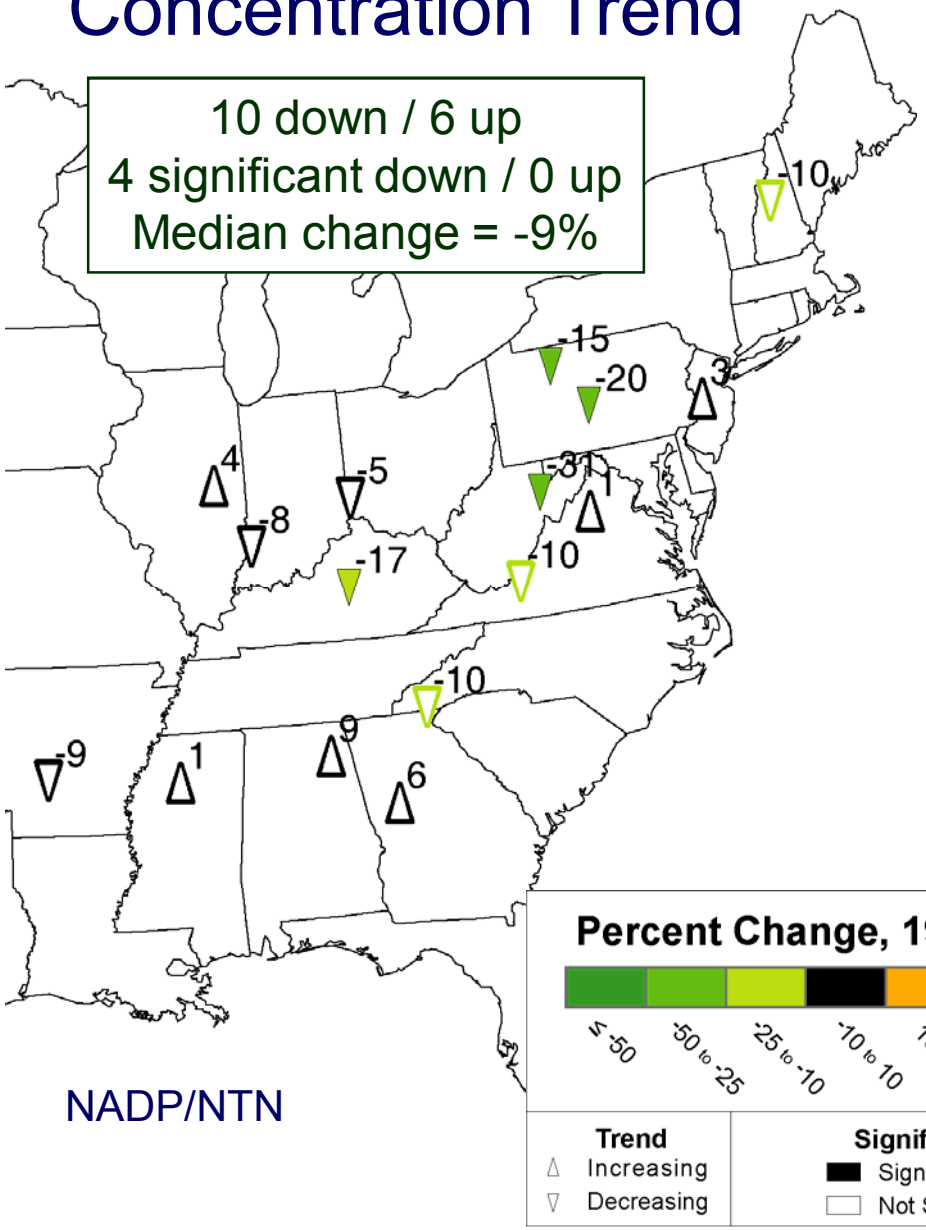



CASTNET



# Precipitation Nitrate Concentration Trend

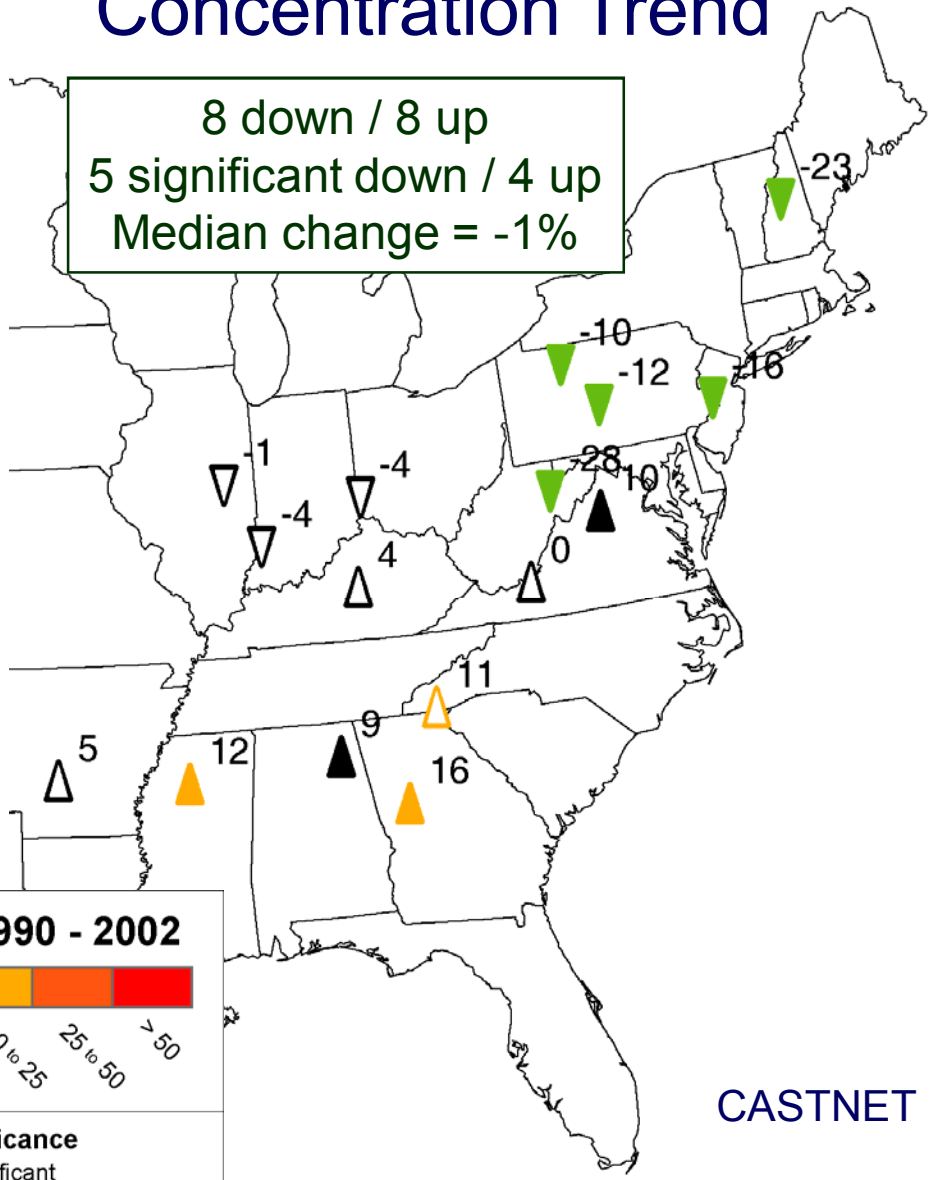
10 down / 6 up
4 significant down / 0 up
Median change = -9%




NADP/NTN

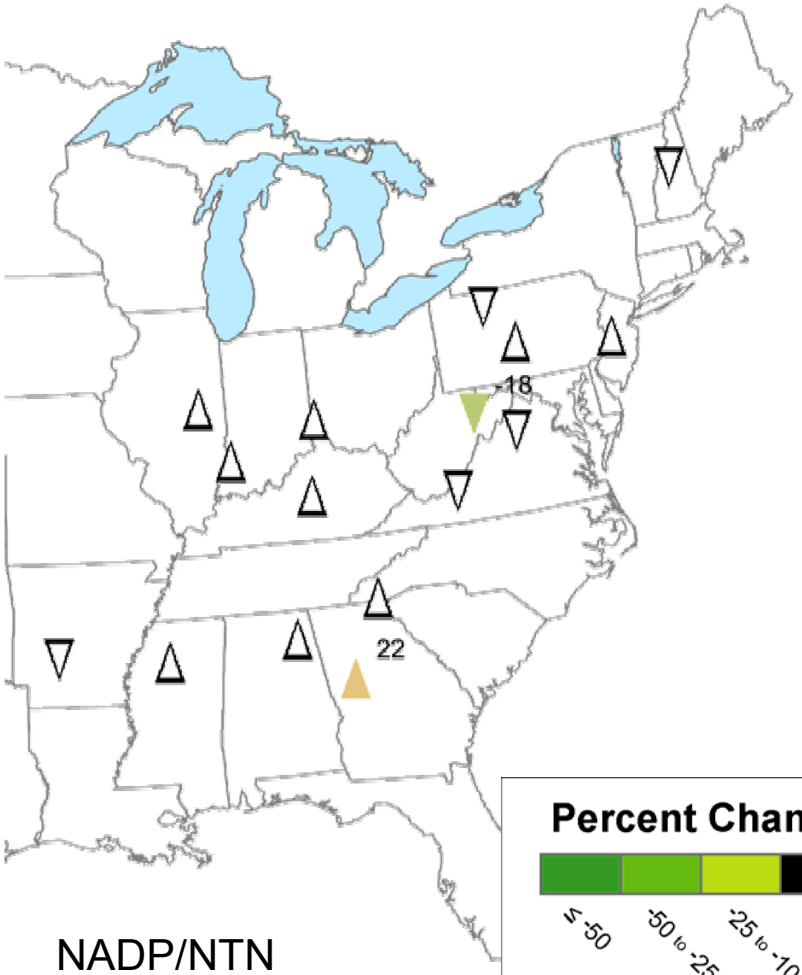
# Particulate Nitrate Concentration Trend

8 down / 8 up
5 significant down / 4 up
Median change = -1%



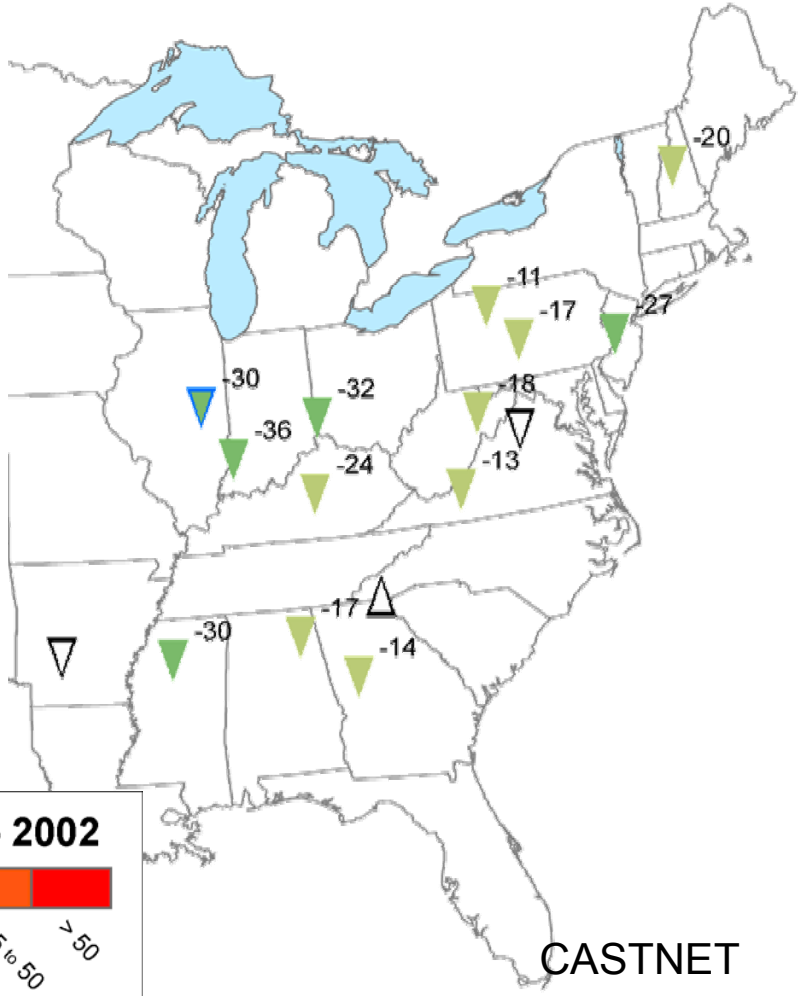

CASTNET

# Precipitation Ammonium Concentration Trend

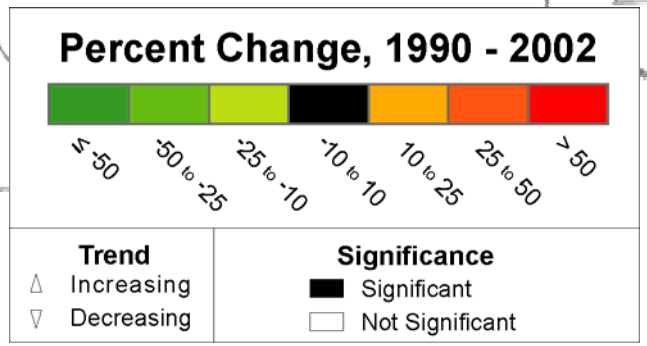



NADP/NTN

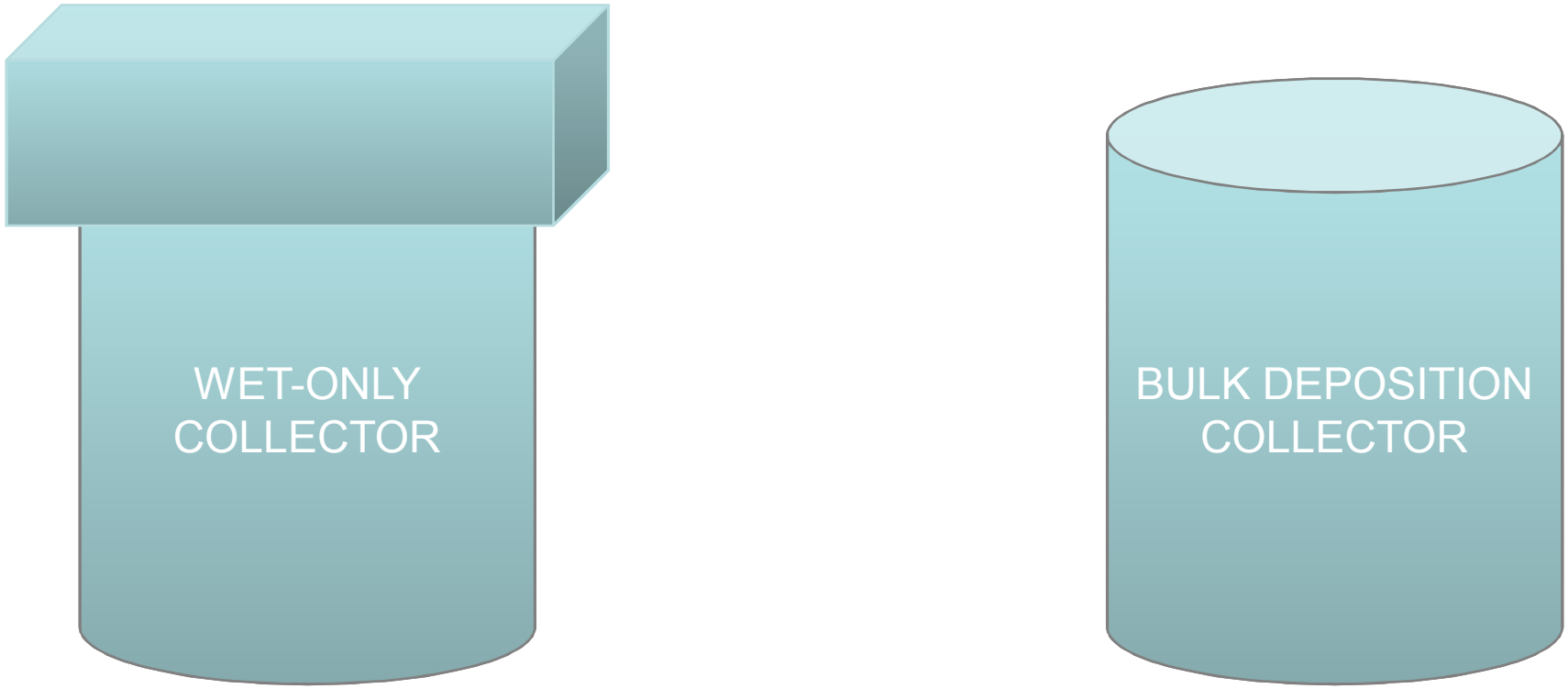
# Particulate Ammonium Concentration Trend




CASTNET

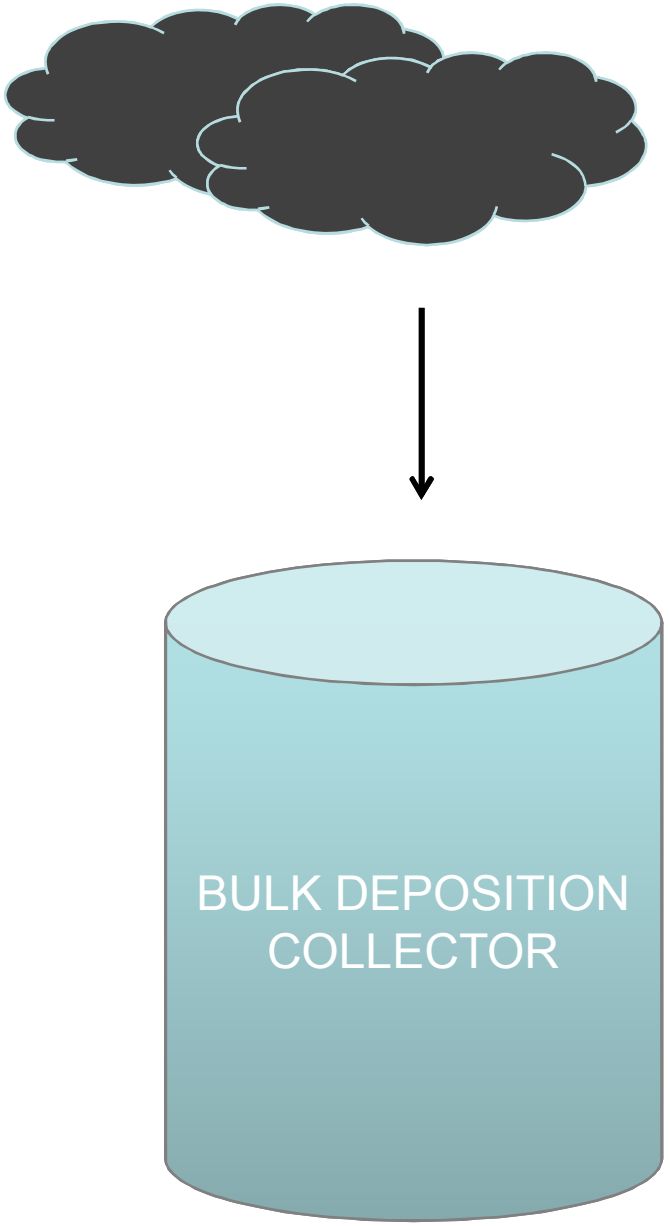


# Why Wet-Only Deposition?



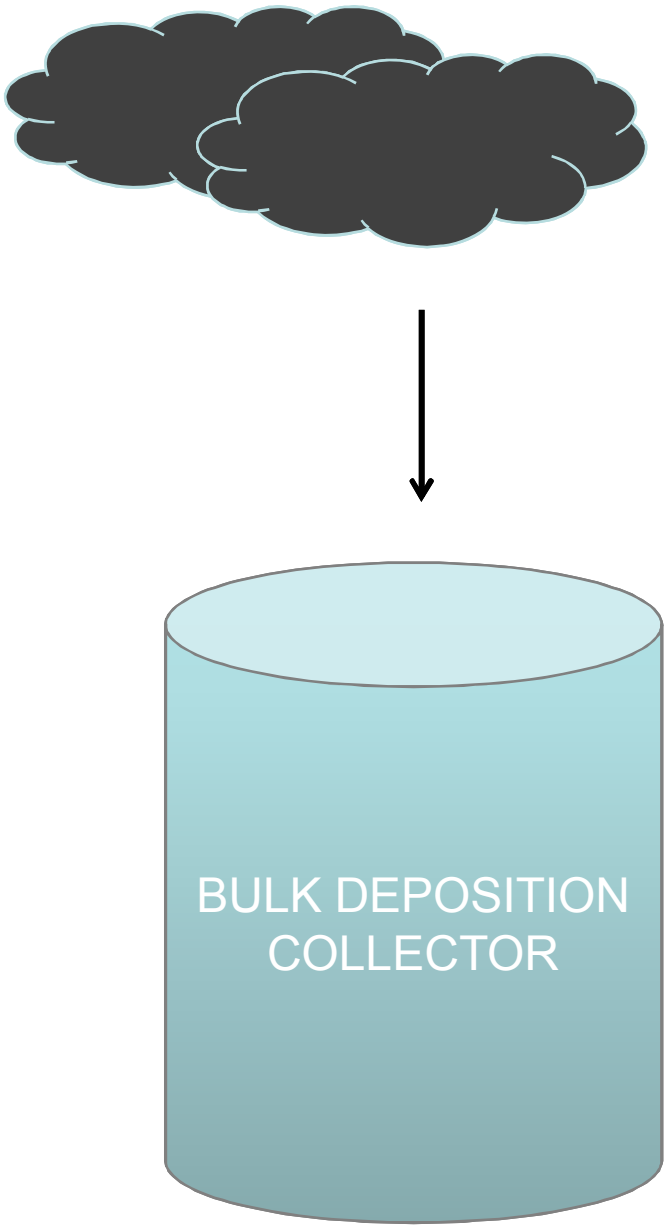
Can’t we just measure bulk deposition to measure total deposition?

TOTAL = WET + DRY



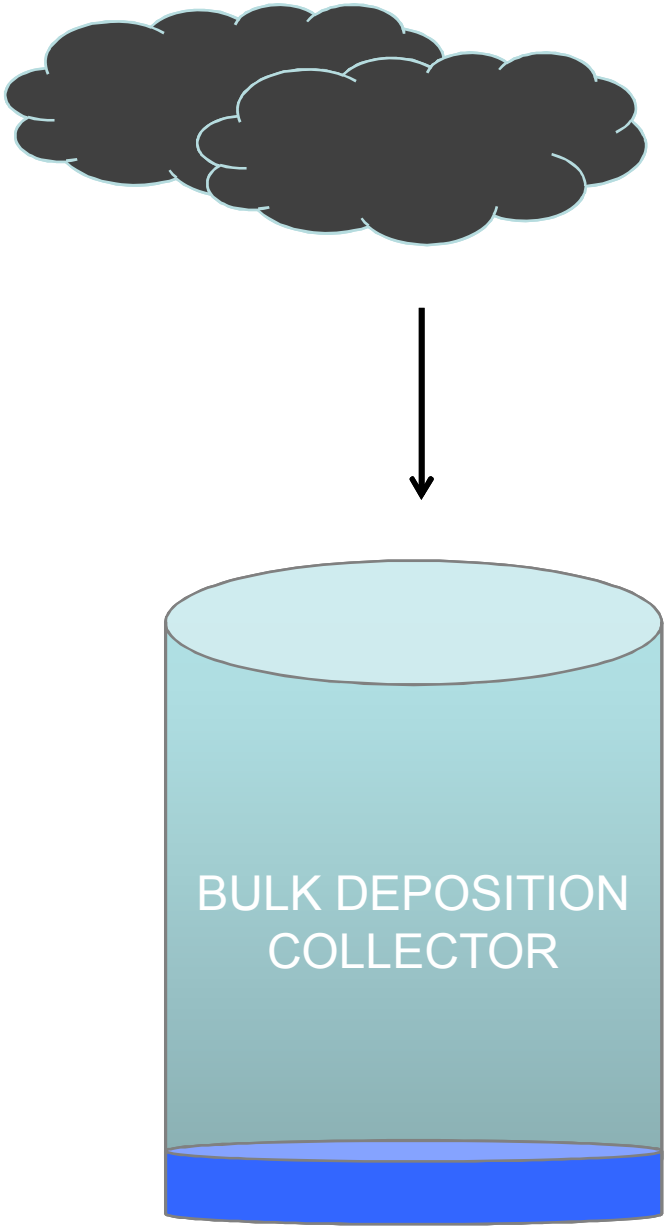
UNKNOWS:

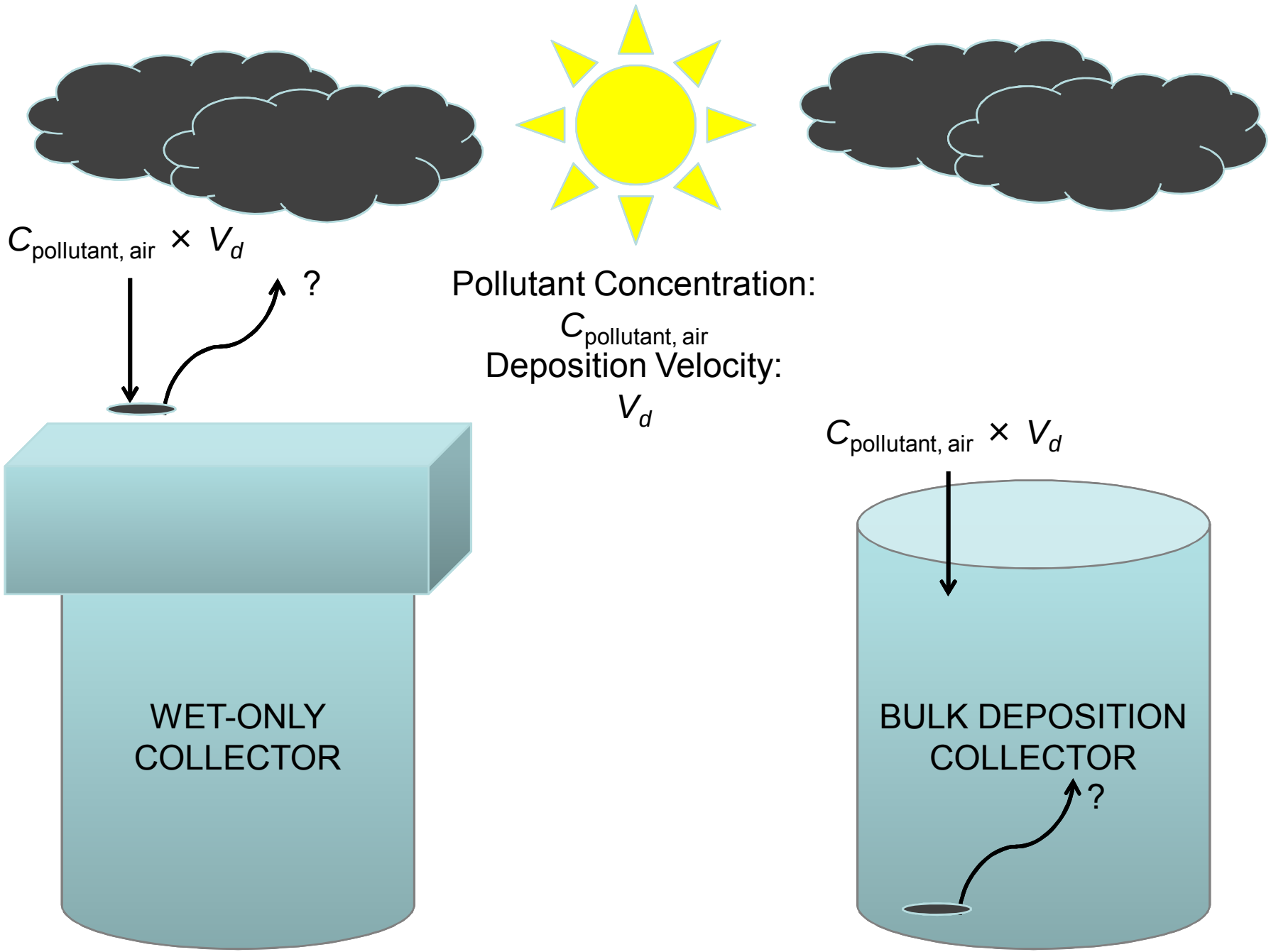
- Capture efficiency of surrogate surface?
- Reemission/volatilization of pollutants?



UNKNOWS:

- Capture efficiency of surrogate surface?
- Reemission/volatilization of pollutants?
- Gas capture and partitioning in water surface?
- Evaporation?

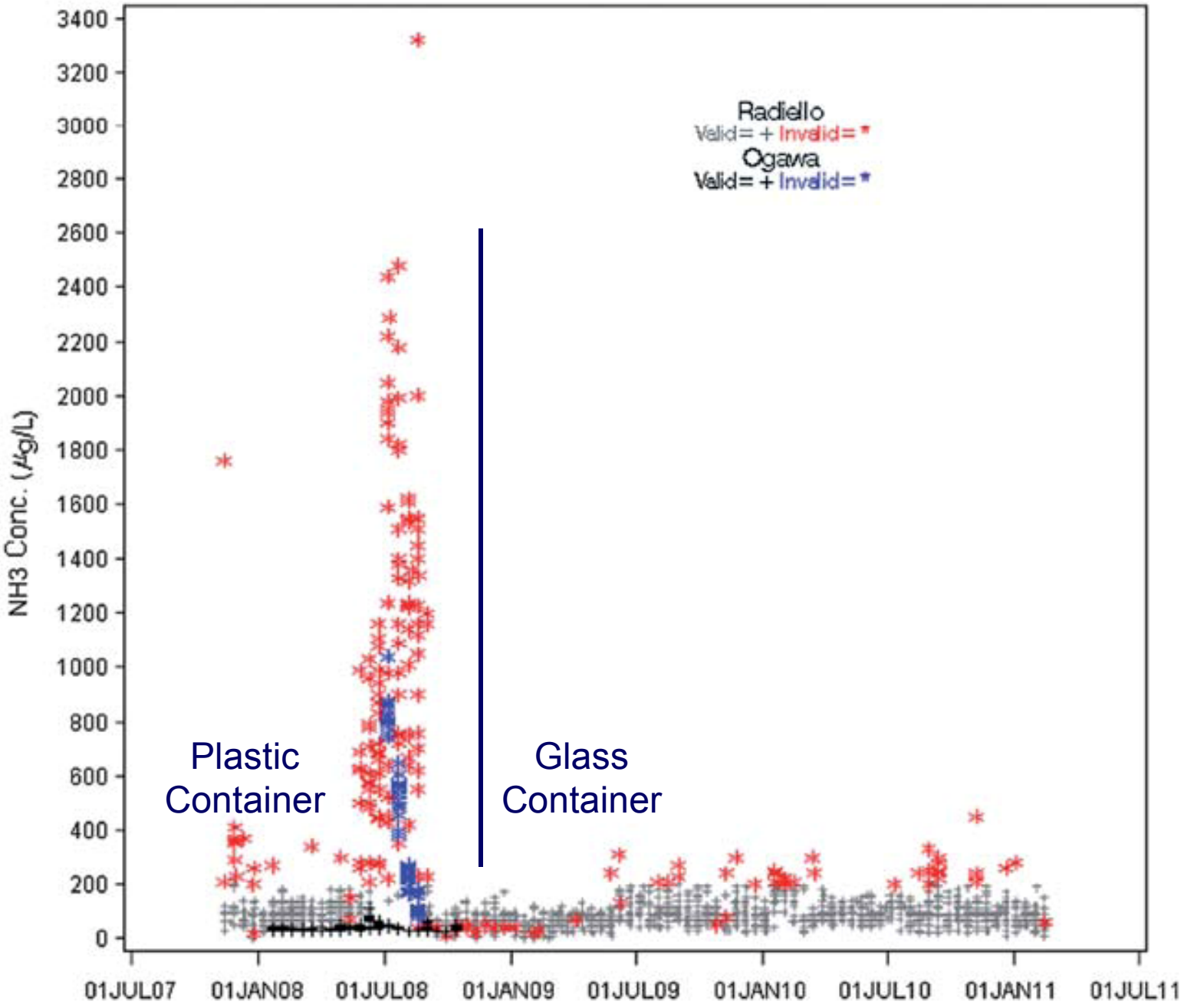


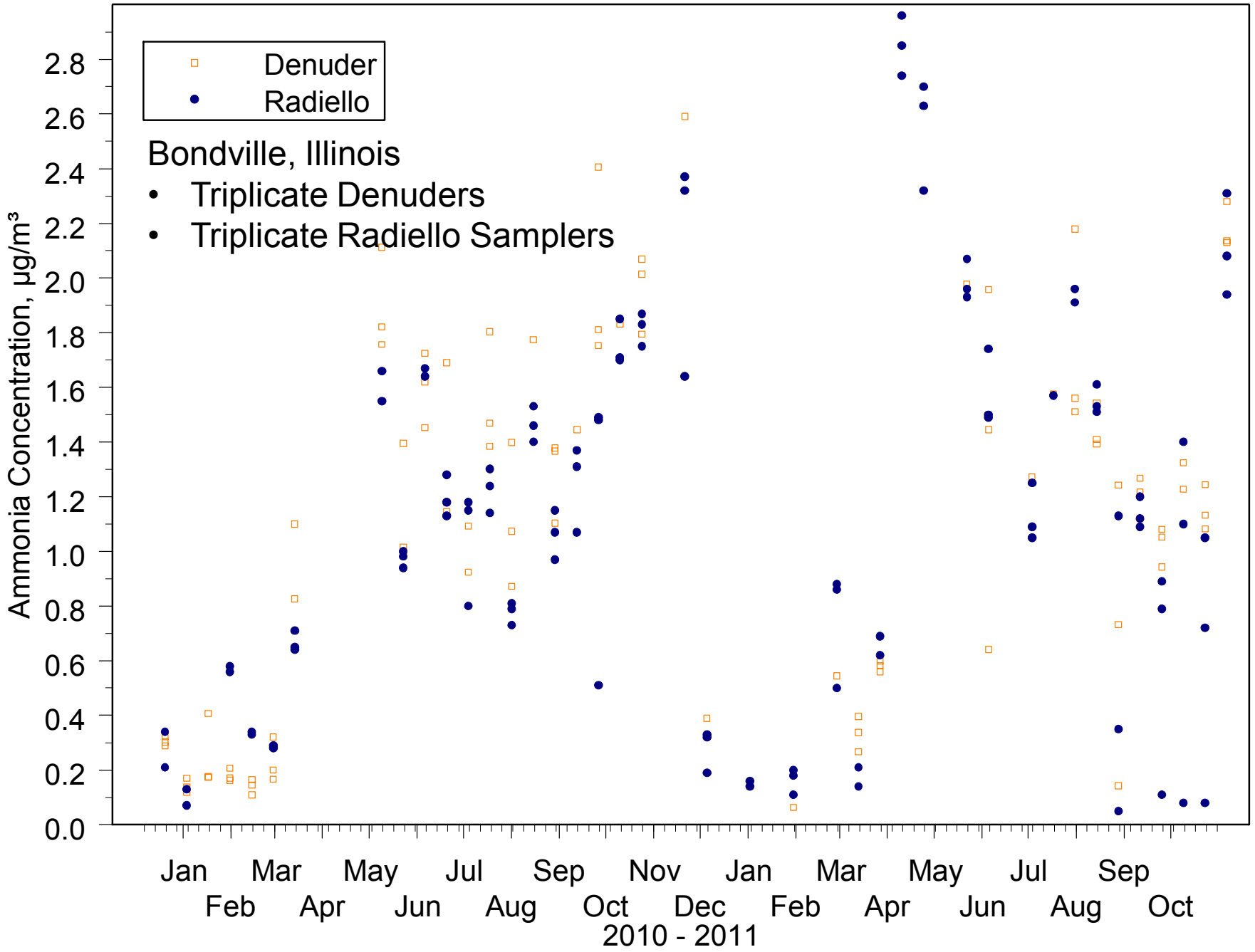

$C_{pollutant,\ air} \times V_d$
?
Pollutant Concentration:
$C_{pollutant,\ air}$
Deposition Velocity:
$V_d$
WET-ONLY
COLLECTOR
$C_{pollutant,\ air} \times V_d$
BULK DEPOSITION
COLLECTOR
?

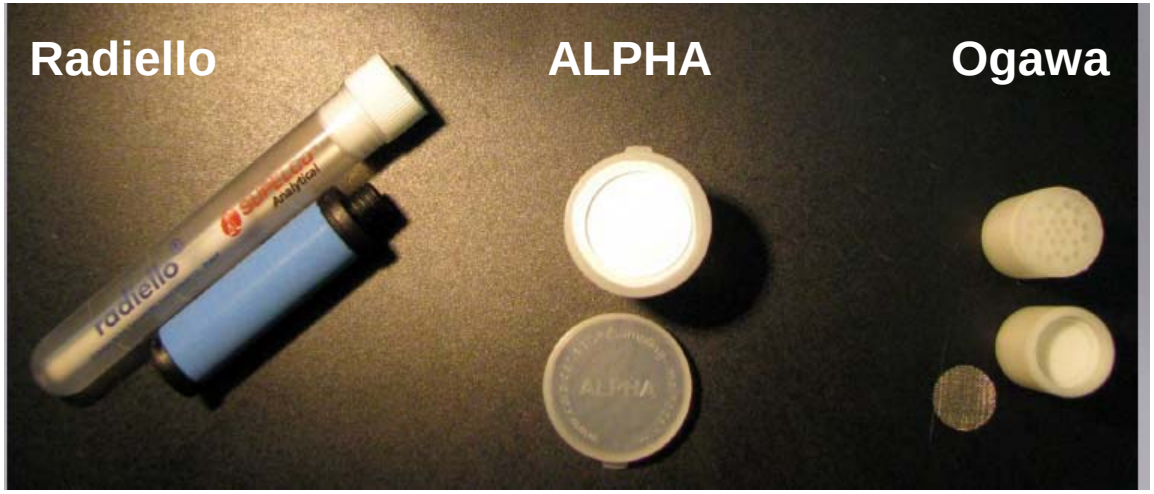
# Some Remarks about Passive Air Samplers

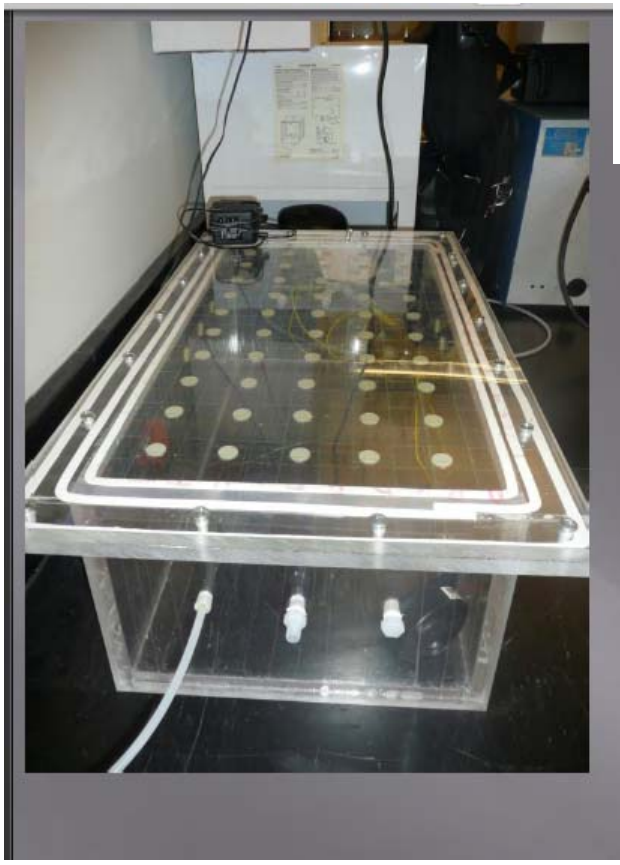
# Good Practices for Passive Air Samplers

- Must run blanks (laboratory and travel)
- Triplicate samples are best to assess variability
- Should compare passive measurements with a reference method (e.g., denuder, or a continuous analyzer)


Radiello
Valid = + Invalid = *
Ogawa
Valid = + Invalid = *
NH3 Conc. (µg/L)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Plastic Container
Glass Container
01JUL07
01JAN08
01JUL08
01JAN09
01JUL09
01JAN10
01JUL10
01JAN11
01JUL11


Denuder
Radiello
Bondville, Illinois
• Triplicate Denuders
• Triplicate Radiello Samplers
Ammonia Concentration, µg/m³
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
2010 - 2011



## CHAMBER STUDY PRELIMINARY DATA
## (Please do not cite)

| | ALPHA | Ogawa | Blue Radiello |
|---|---|---|---|
| Mean Concentration (µg/m³) | 15.49 | 15.54 | 11.87 |
| Bias (µg/m³) | +1.88 | +1.92 | -1.75 |
| Standard Deviation (µg/m³) | 1.36 | 1.44 | 0.32 |
| Travel Blank (µg/m³) | 0.40 | 0.45 | 0.22 |

Test Conditions

- Concentration = 13.62 µg/m³
- 99th percentile concentration of AMoN

# Action Research.ILLINOIS

College of Fine and Applied Arts | University of Illinois at Urbana-Champaign

- **Action Research.Illinois**
- **ESLARP**
- **Metro East Citizens Air Project**
  - Contact Information
  - Resources
  - Criteria Pollutants and Your Health
  - Toxics and Your Health
  - Events and News
- Illinois Global Action Research

Outreach Weekend Registration

Check out the Action Research.Illinois Blogspot!

## *Spotlight . . .*

**Martin Wolske receives 2011 Library Journal Teaching Award**

*Enriching young minds through community engagement*

## Metro East Citizens Air Quality Project

**The Metro East Citizens Air Quality Project** aims to promote community-based efforts to address air pollution by empowering community members as citizen scientists with the knowledge and skills to advocate for improved air quality in their neighborhoods.

This community oriented project will integrate citizen engagement and education programs, monitoring, and research over the next three years. We will focus on drawing awareness at the neighborhood level to the health risks associated with air pollution, while providing citizens with the tools to address local air quality and public health concerns.

**Long Term Project Goals**

At the end of three years, our project aims to:

- Establish a solid foundation for citizen activism that will sustain the project as a community led 501(c)3 organization.
- Foster working relationships with citizens and government representatives working on air pollution issues in the Metro East.
- Contribute to joint community/state initiatives to address air quality and public health.
- Contribute to reductions in local impacts to those at risk populations.

---

**Sign up for daily air quality alerts!**

EnviroFlash provides air quality information such as forecasts and action day notifications via email for your area of interest. Sign-Up

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***Click here to be added to a listserve to receive AirNews relevant to the Metro East Area***

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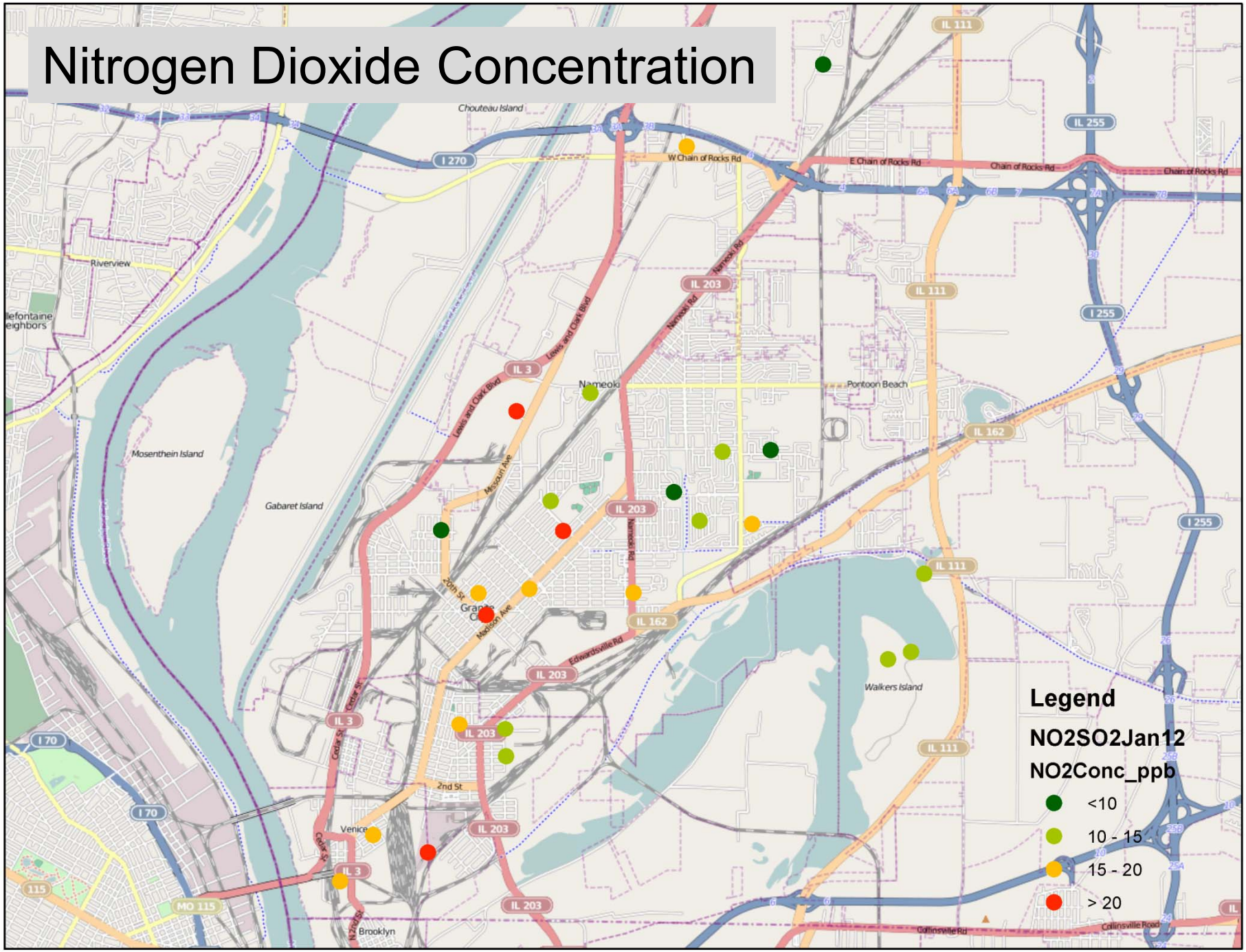
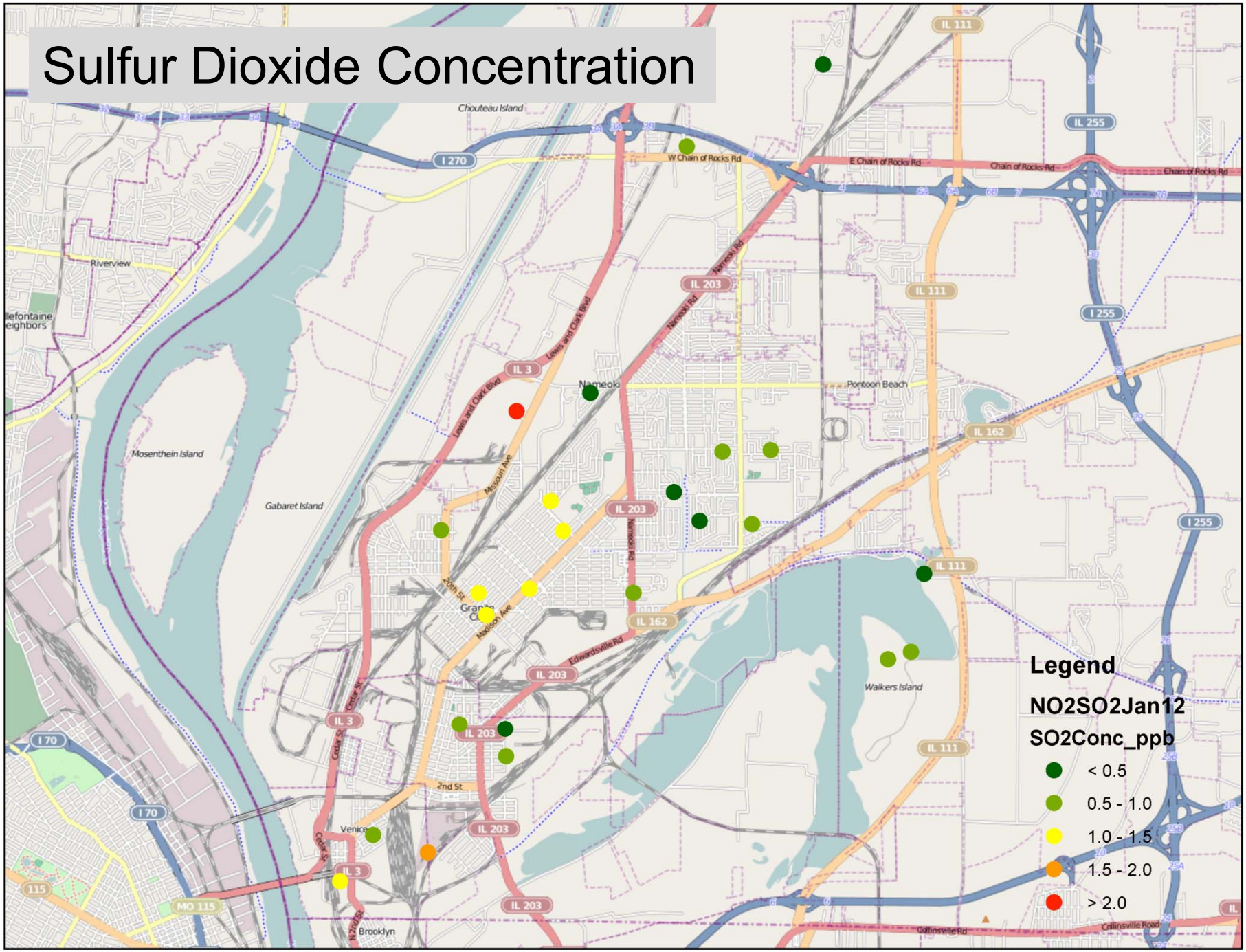
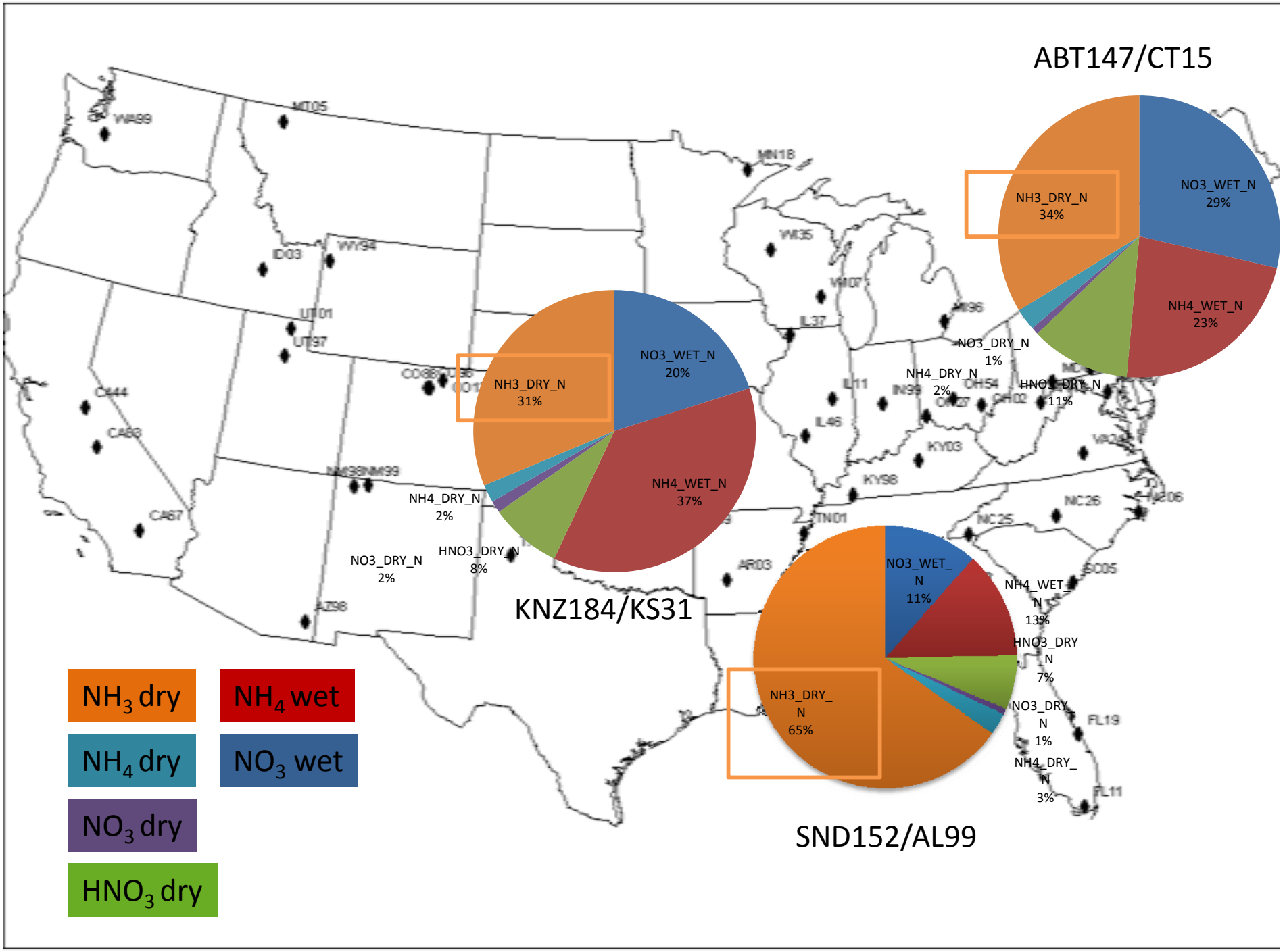
# Nitrogen Dioxide Concentration



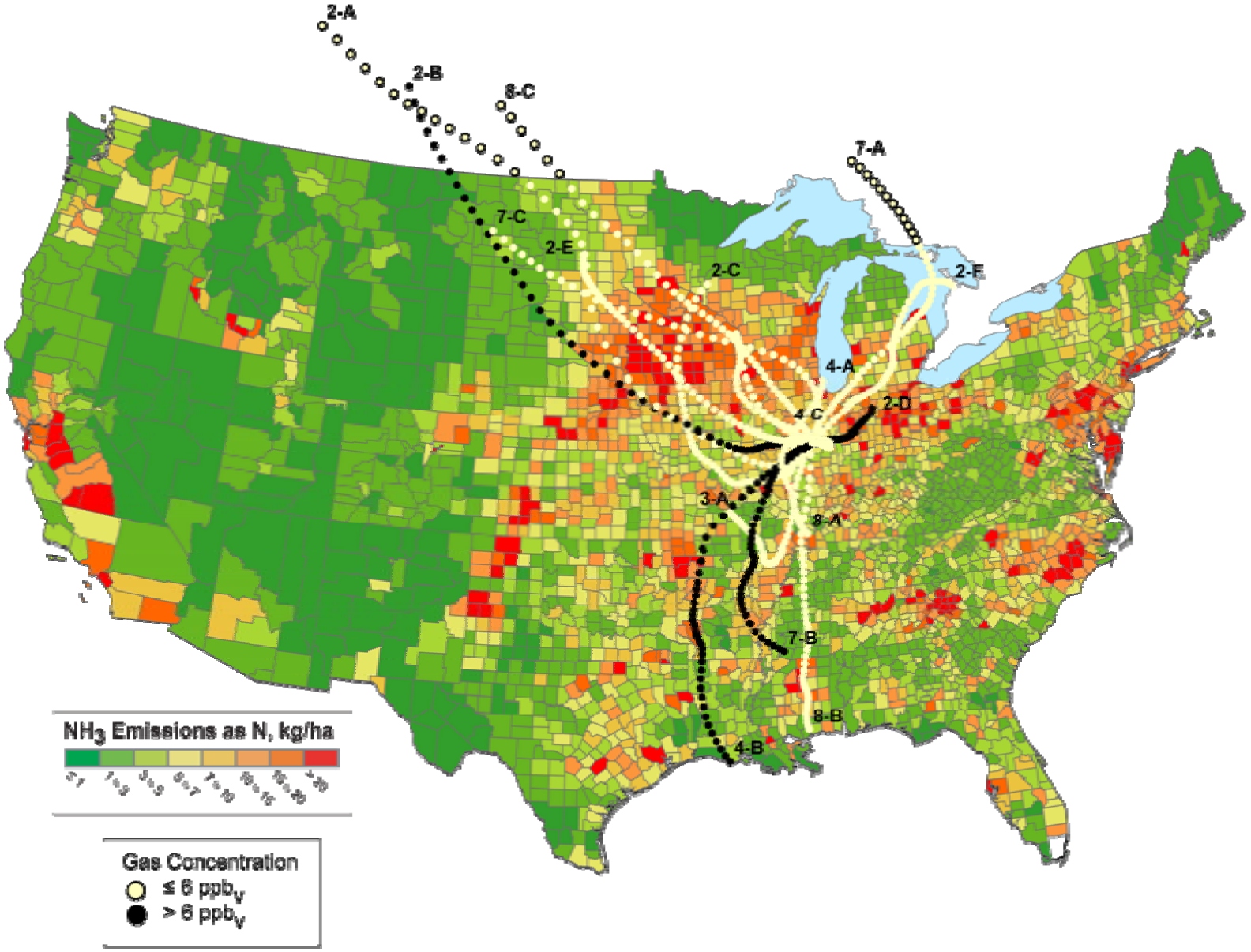
# Sulfur Dioxide Concentration



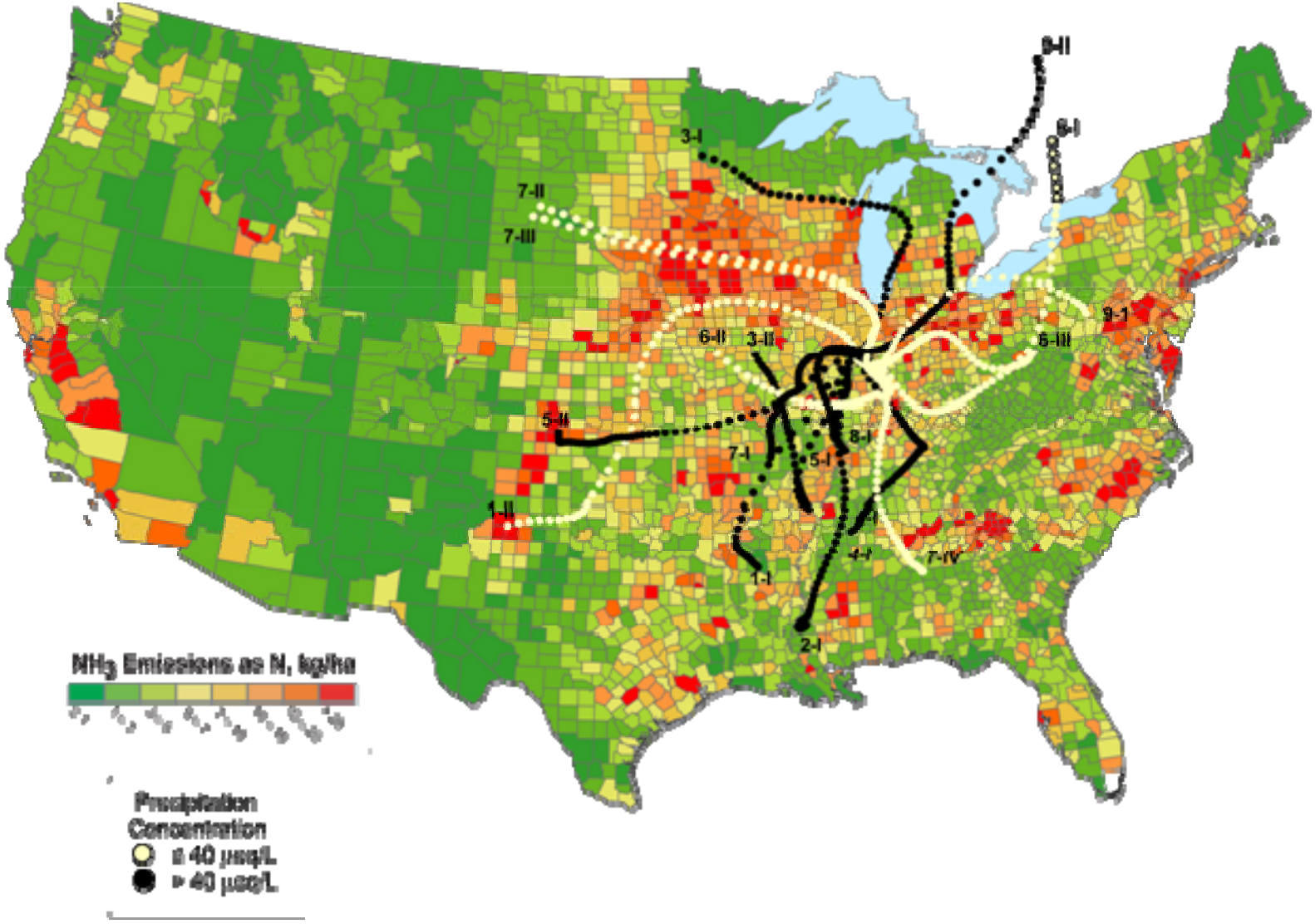

ABT147/CT15
NH3_DRY_N 34%
NO3_WET_N 29%
NH4_WET_N 23%
NO3_DRY_N 1%
NH4_DRY_N 2%
HNO3_DRY_N 11%
KNZ184/KS31
NH3_DRY_N 31%
NO3_WET_N 20%
NH4_WET_N 37%
NH4_DRY_N 2%
NO3_DRY_N 2%
HNO3_DRY_N 8%
SND152/AL99
NH3_DRY_N 65%
NO3_WET_N 11%
NH4_WET_N 13%
HNO3_DRY_N 7%
NO3_DRY_N 1%
NH4_DRY_N 3%
NH3 dry
NH4 wet
NH4 dry
NO3 wet
NO3 dry
HNO3 dry

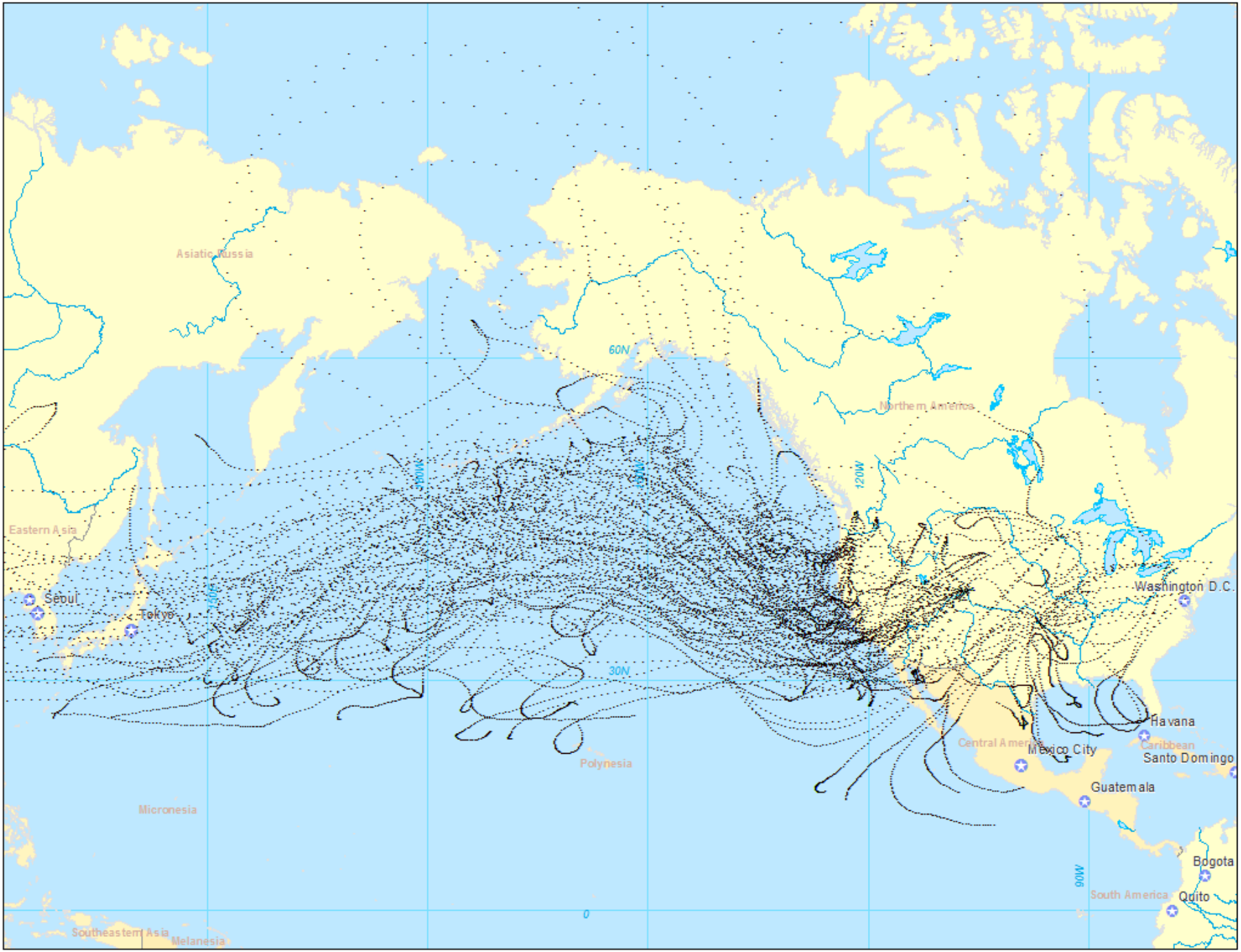
# Trajectory Analysis Examples

# Back Trajectories – Daily Ammonia Gas Events

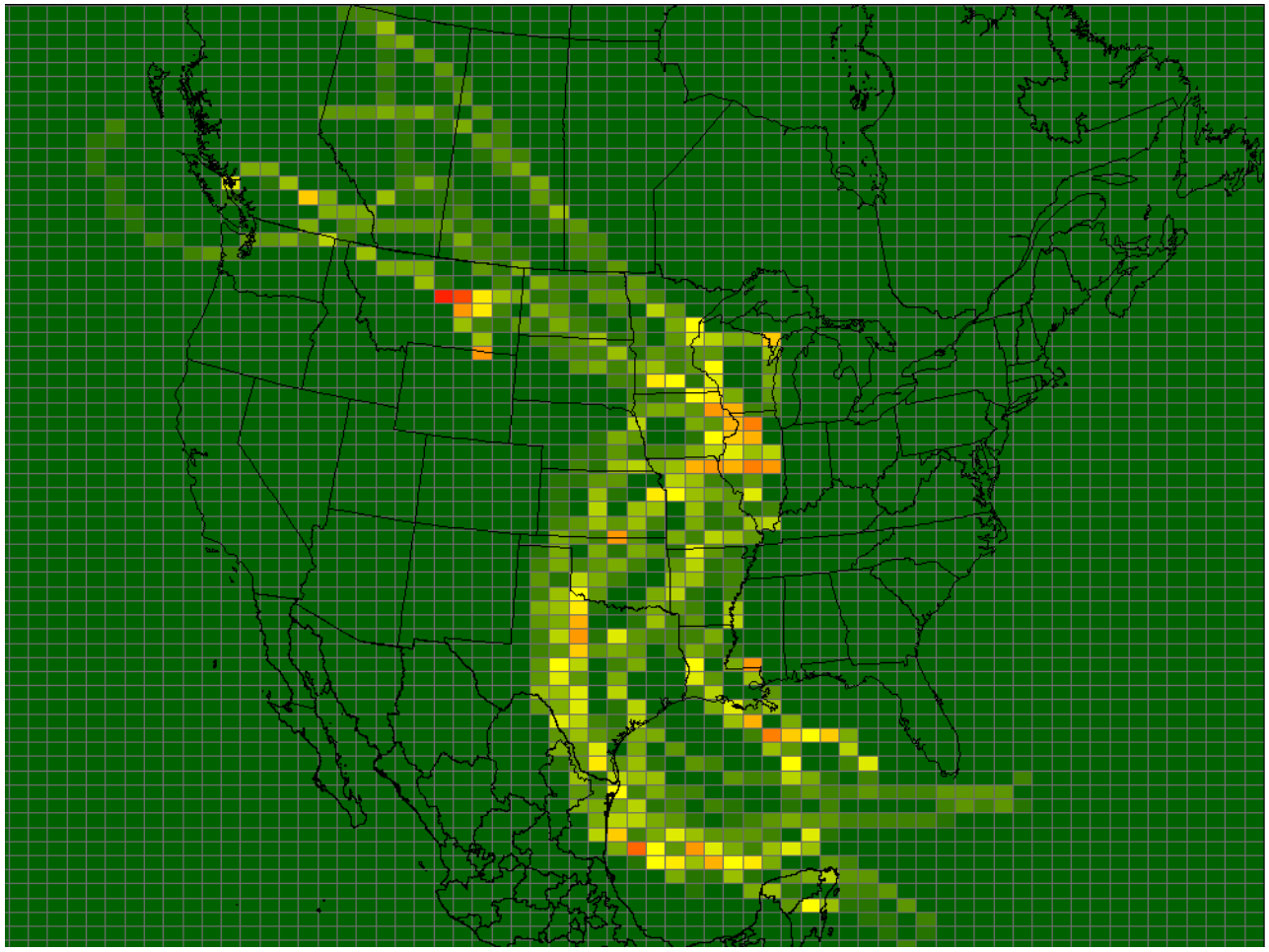


# Back Trajectories – Precipitation Events




Asiatic Russia
60N
Northern America
120W
Eastern Asia
Seoul
Tokyo
Washington D.C.
30N
Havana
Caribbean
Central Amer
Mexico City
Santo Domingo
Polynesia
Guatemala
Micronesia
90W
Bogota
South America
Quito
0
Southeastern Asia
Melanesia

# GIS Analysis



# ARL
## Air Resources Laboratory
Conducting research and development in the fields of air quality, atmospheric dispersion, climate, and boundary layer

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- READY
  - READY News
  - Transport & Dispersion
    - Get/Run HYSPLIT >>
    - Volcanic Ash
    - Transfer Coefficient Matrix for Fukushima Daiichi
    - Short-Range Ensemble Dispersion Forecasts
    - Gaussian Plume Model
    - Balloon Flight Forecasting Tools
  - Current & Forecast Meteorology
    - North America

## HYSPLIT - Hybrid Single Particle Lagrangian Integrated Trajectory Model

The HYSPLIT model can be run interactively on the READY web site or installed on a PC (Mac) and run using a graphical user interface (GUI).

### HYSPLIT-WEB (Internet-based)

- Run HYSPLIT Trajectory Model
- Run HYSPLIT Dispersion Model
- Run HYSPLIT for Volcanic Ash
- Spain HYSPLIT
- HYSPLIT for National Weather Service Forecast Offices (NOAA employees only)

### PC Windows-based HYSPLIT

- Download Public (unregistered) Version
- Download Registered Version (registration required)
- Graphical Utilities
- Meteorological Data Conversion Utilities

### HYSPLIT-compatible Meteorological Data

### 2012 PC HYSPLIT Workshop

A 3 day HYSPLIT workshop will be given June 26 - 28, 2012 in Silver Spring, Maryland. The workshop will focus on the use of the recently updated version 4.9 of the model and its PC Graphical User Interface (GUI). Details and registration instructions can be found at: http://www.ertcorp.com/HYSPLIT/.

# For more information….

http://nadp.isws.illinois.edu
clehmann@illinois.edu

National Atmospheric
Deposition Program