

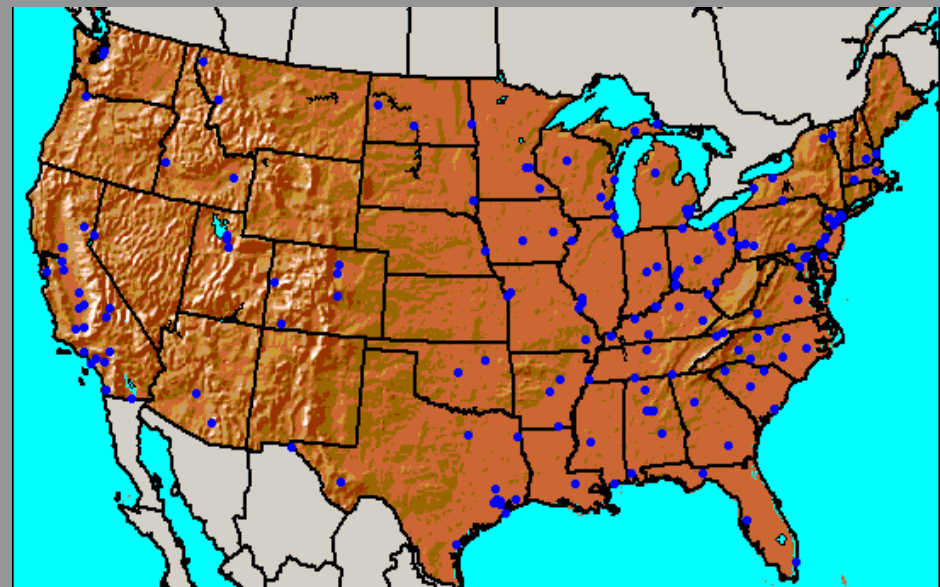
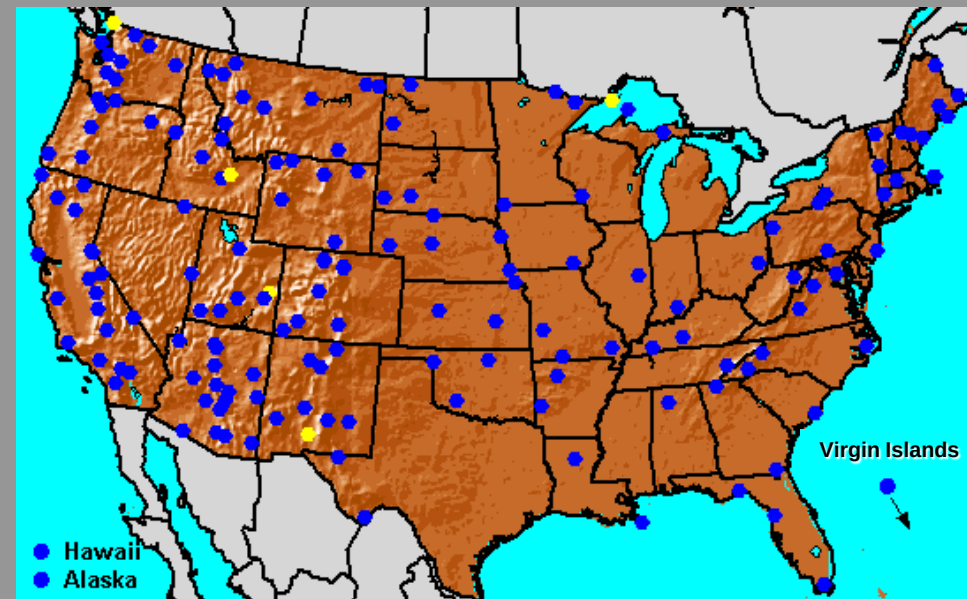
Uncertainties in PM_{2.5} Gravimetric and Speciation Measurements and What Can We Learn from Them

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Non-urban and urban PM_{2.5} networks

**Interagency
Monitoring of
PROtected Visual
Environments
(IMPROVE) Network**

**Chemical Speciation
Network (CSN)**



OBJECTIVES

- Estimate bias in some measured aerosol species.
- Estimate average bias in gravimetric PM_{2.5} measurement.
- Estimate average bias in reconstructed PM_{2.5} from measured aerosol species.
- What effect does PM_{2.5} measurement bias have on estimating atmospheric extinction?

Sampler Intercomparison and Artifact Correction

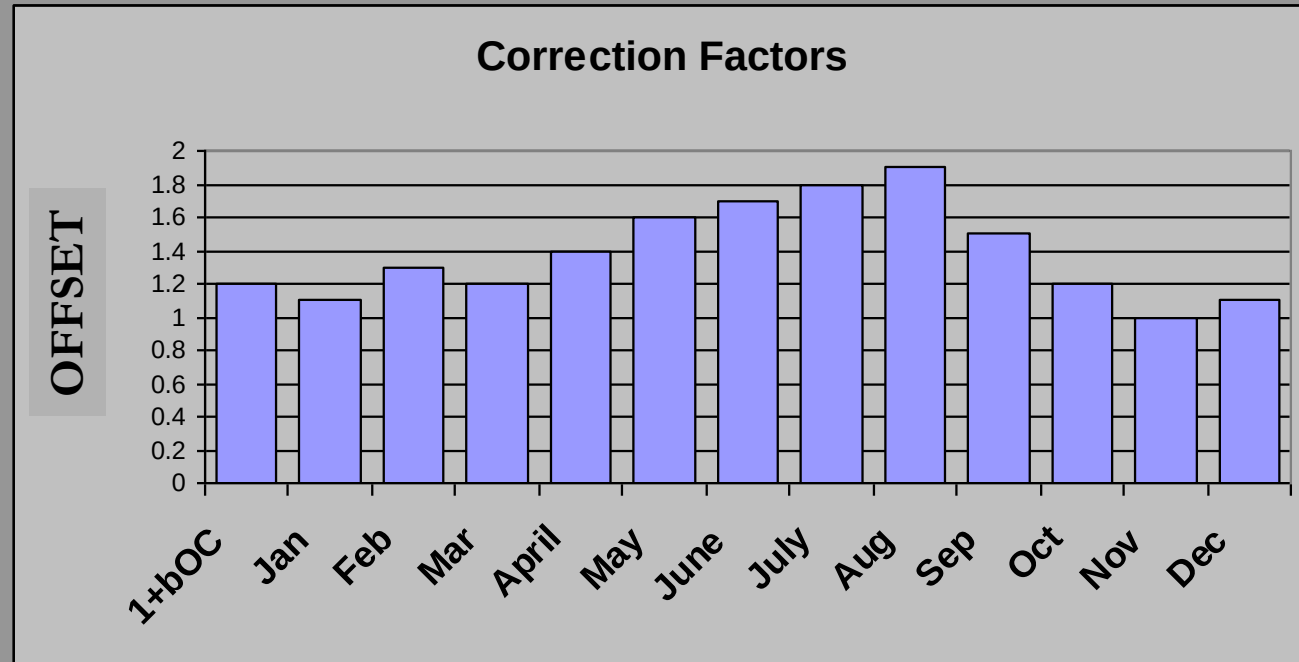
- Comparison of carbon across samplers
 - Warren H. White, 16 April 2008 EPA workshop
- Additional effort by Bret A. Schichtel

Sampler Design Characteristics

Variable					Speciation Sampler	
Network	IMPROVE	CSN	CSN	CSN	CSN	CSN
Sampler type	IMPROVE	Andersen	Met One SASS	URG MASS	R&P2300	R&P2025 sequential FRM
Number of Sites (2006)	181	18	179	6	14	22
Number of Channels	4	4	5	2	4	2
Flow Rate	22.7l/min	7.3l/min	6.7l/min	16.7l/min	10.0l/min	16.7l/min
Filter Face Velocity	107.2cm/sec	10.3cm/sec	9.5cm/sec	23.7cm/sec	14.2cm/sec	23.6cm/sec
Sampling Frequency	3 rd day	3 rd day	3 rd day	3 rd day	3 rd day/6 th day	3 rd day/6 th day
Quartz Filter Pack Configuration	Q For QBQ	QF	QF	QF	QF	QF
Quartz Filter Type	25mmPall	47mmWhatma	47mmWhatma	47mmWhatma	47mmWhatma	47mmWhatma

The multiplicative artifact ($1+b_{OC}$) and the monthly positive additive organic artifact (a) used to relate CSN and IMPROVE carbon concentrations. The units for the positive artifacts are $\mu\text{g}/\text{m}^3$ and $1+b_{OC}$ is unitless.

Variable	MetOne
α	1.3
$1+b_{OC}$	1.2
a_{Jan}	1.1
a_{Feb}	1.3
a_{Mar}	1.2
a_{Apr}	1.4
a_{May}	1.6
a_{Jun}	1.7
a_{Jul}	1.8
a_{Aug}	1.9
a_{Sep}	1.5
a_{Oct}	1.2
a_{Nov}	1



Bias Between Estimated Fine Mass and Gravimetric Fine Mass and

Governing equations

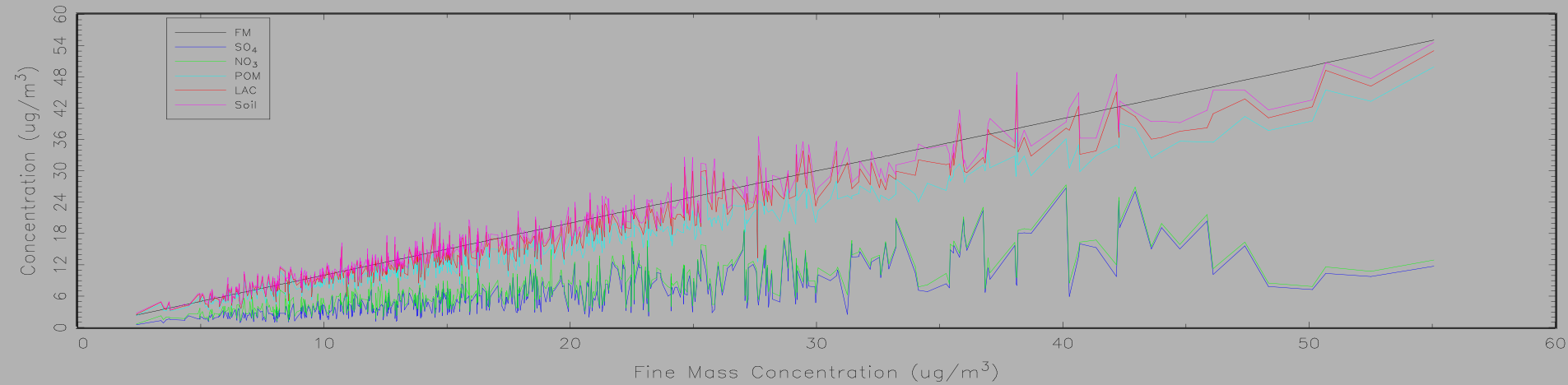
$$PM_{2.5} = [xSO_4 + NH_4NO_3] f'_{ino} (RH_{lab}) + OC R_{oc} (\text{lots of stuff}) + LAC + Soil + SS f'_{ss} (RH_{lab})$$

- $PM_{2.5}$ loss due to nitrate and SVOC volatilization
- All variable may have some spatially dependent measurement bias
- $x = (NH_4)_2SO_4/H_2SO_4 \leq 1.35$ – lowest in summer – acidic aerosol
- $f'_{ino}(RH_{lab}) = \left[\frac{\rho_{mix\ species}}{\rho_{species}} \right]^3 \left(\frac{D}{D_0} (RH_{lab}) \right)^3$ highest in summer $(D/D_0)^3 \approx 1.3$
- R_{oc} (lots of stuff) probably highest in summer months
- $f'_{ss}(RH_{lab}) \approx 1.3$
- LAC may have a multiplier

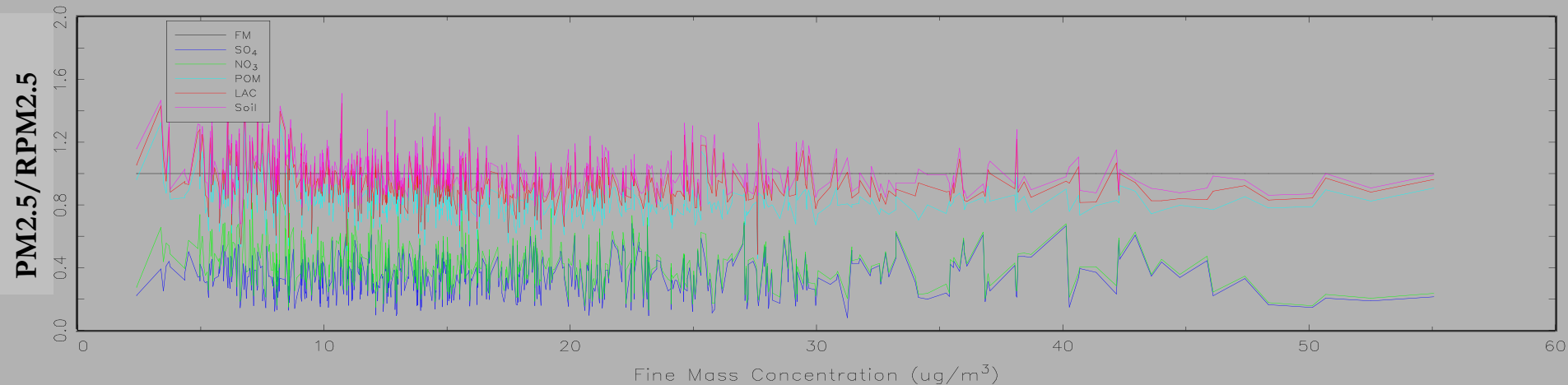
Bias as function of mass

$$\text{PM}_{2.5} = 1.375 \cdot \text{SO}_4 + 1.29 \cdot \text{NO}_3 + 1.8 \cdot \text{OC} + \text{Other}$$

BIRMINGHAM

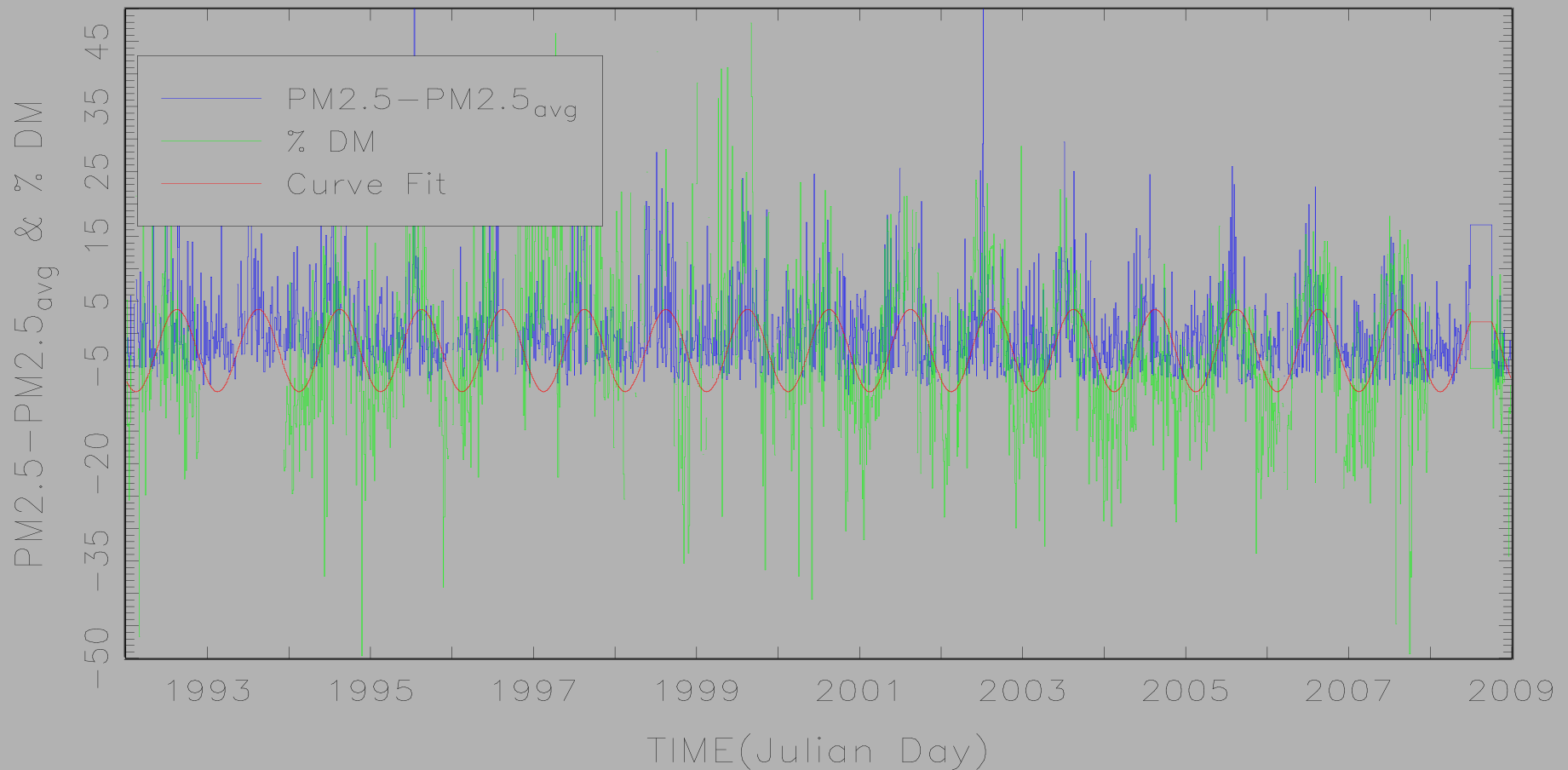


BIRMINGHAM



Temporal plot of PM2.5-PM2.5avg and the percent difference between reconstructed and gravimetric mass (Brigantine WR)

$\%DM = [(PM2.5 - RPM2.5) / PM2.5] * 100 = b1 + b2(\cos(f(T)))$

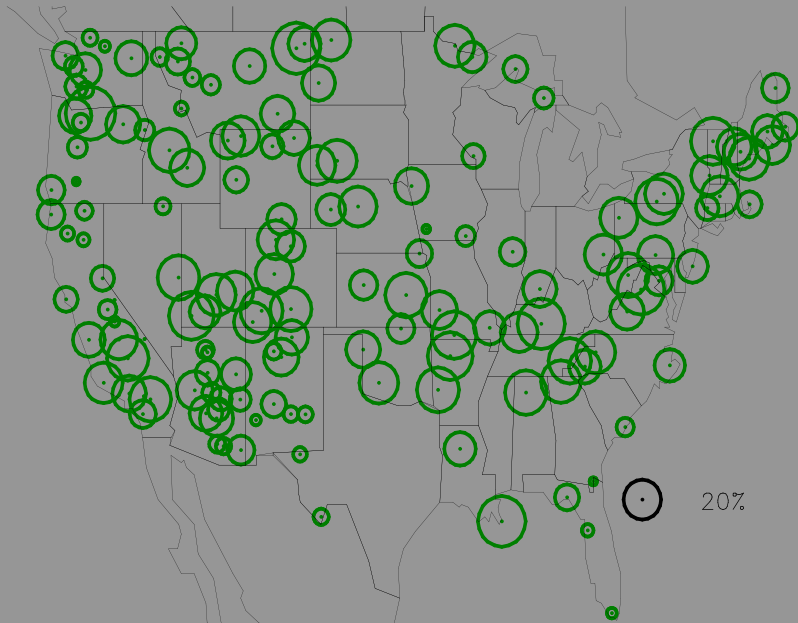


Average percent seasonal variability between reconstructed and gravimetric mass for the IMPROVE monitoring network

$$\%DM = [(PM_{2.5} - RPM_{2.5}) / PM_{2.5}] * 100 = b1 + b2(\cos(f(T)))$$

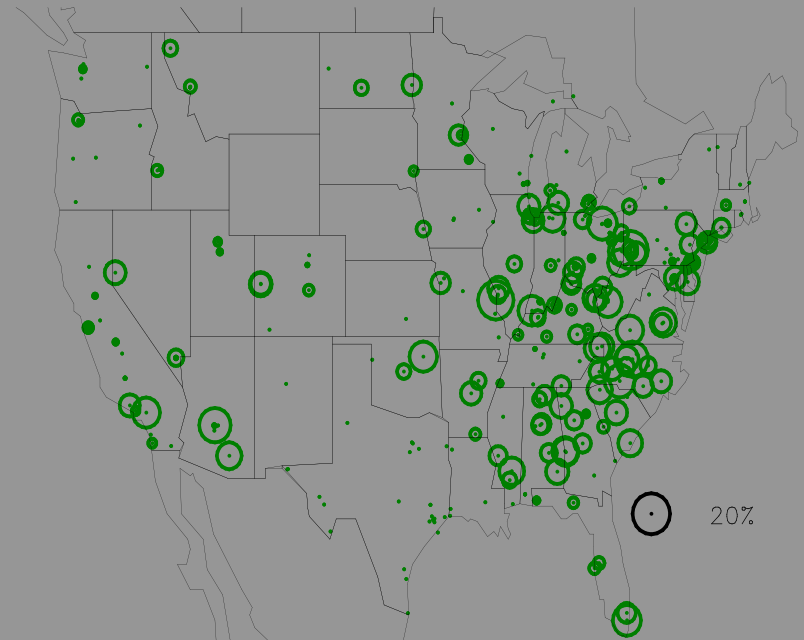
GAUSS Fri Apr 23 09:52:26 2010

% Seasonal Bias b2 (IMPROVE)



GAUSS Fri Apr 23 11:00:56 2010

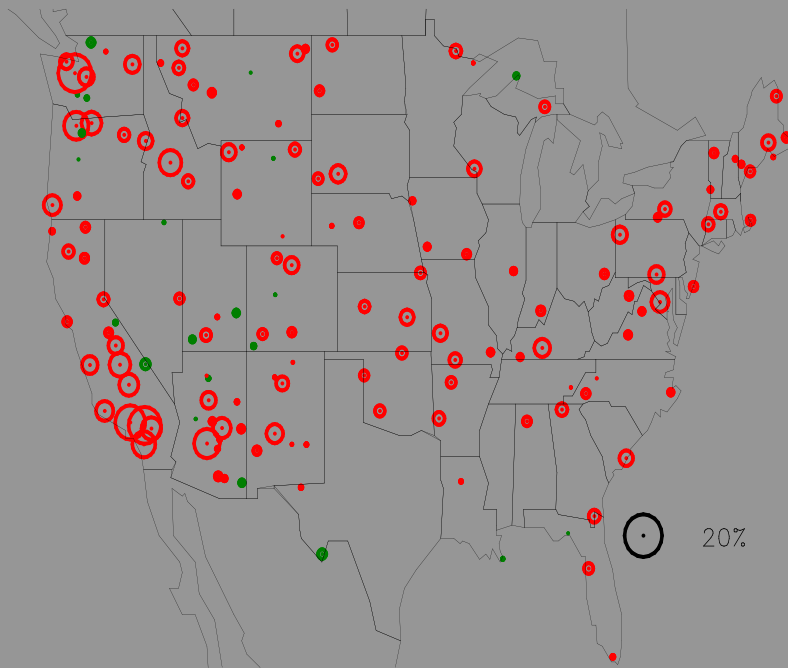
% Seasonal Bias b2 (CSN)



Average percent bias between reconstructed and gravimetric mass for the IMPROVE monitoring network. The red or green color indicates that reconstructed mass is an over or underestimate of gravimetric mass respectively.

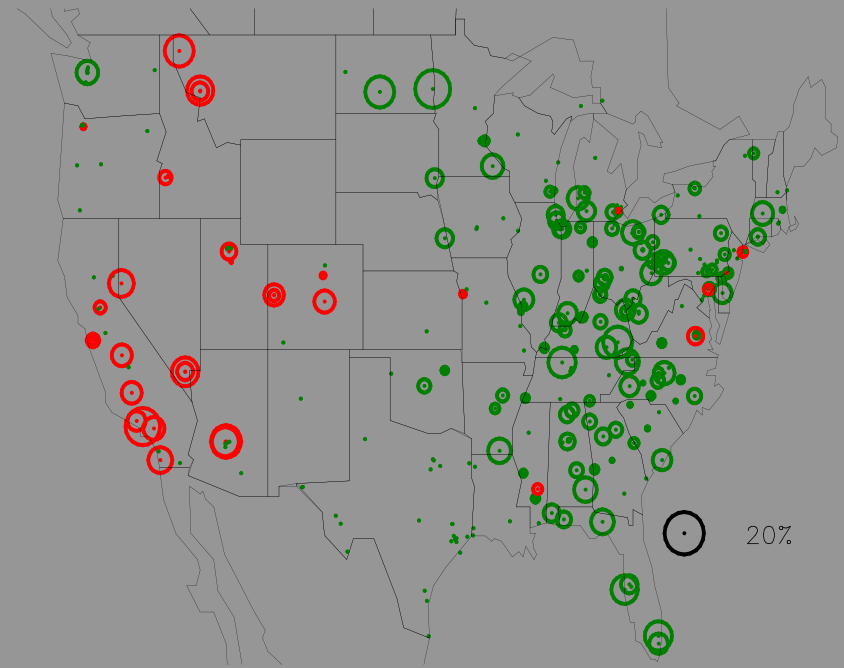
GAUSS Fri Apr 23 09:48:08 2010

Average % Bias b1 (IMPROVE)



GAUSS Fri Apr 23 10:59:25 2010

Average % Bias b1 (CSN)



Summary table of the percent seasonal variability and average bias of reconstructed versus gravimetric mass

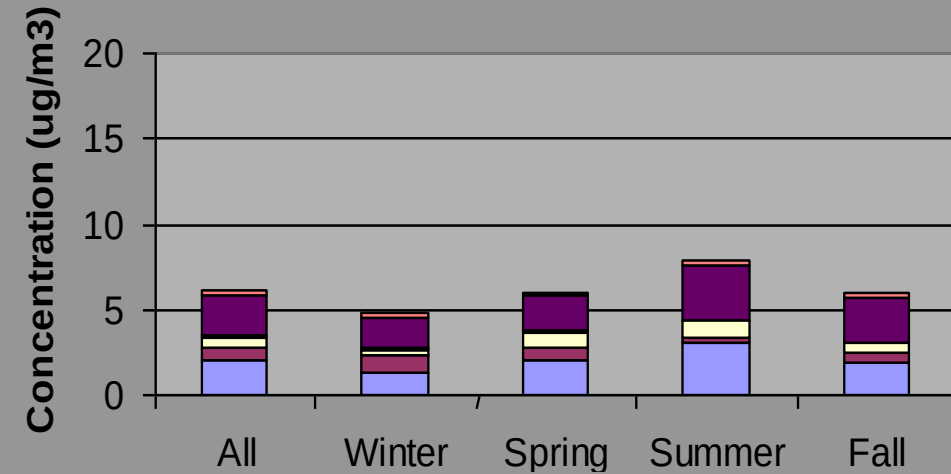
Variable	Mean	Std Dev	Min	Max	N
% Seasonal Variability (IMPROVE)	14.9	6.14	0.0	26.7	158
% Seasonal Variability (CSN)	7.6	4.51	0.0	19.0	168
AVG BIAS (IMPROVE)	-3.9	4.44	-17.9	9.4	158
AVG BIAS (CSN)	3.4	7.00	-17.7	22.7	168

Assumptions

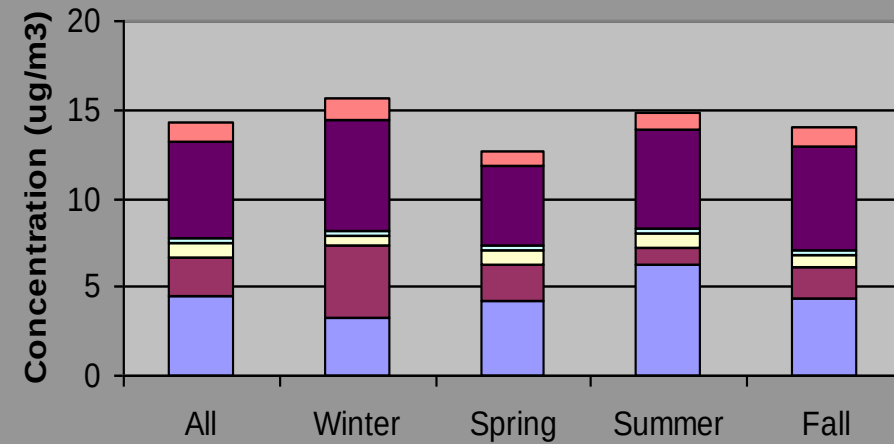
- Do not account for between sampler volatilization of SVOC's
- Comparing of CSN to IMPROVE implies SVOC loss does not affect Roc multiplier
- SVOC loss on Teflon and quartz substrates are the same
- Gravimetric mass of soil dust, sea salt, and non volatilized POM are measured without bias
- Nitrate and sulfates are measured without loss on nylon substrate and nitrate and sulfates are fully ammoniated

Stacked bar charts showing average concentrations of each species for all and seasonal data for IMPROVE, CSN suburban, and CSN urban.

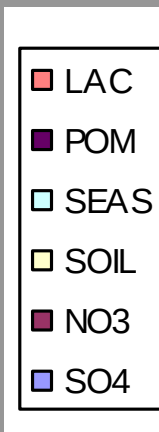
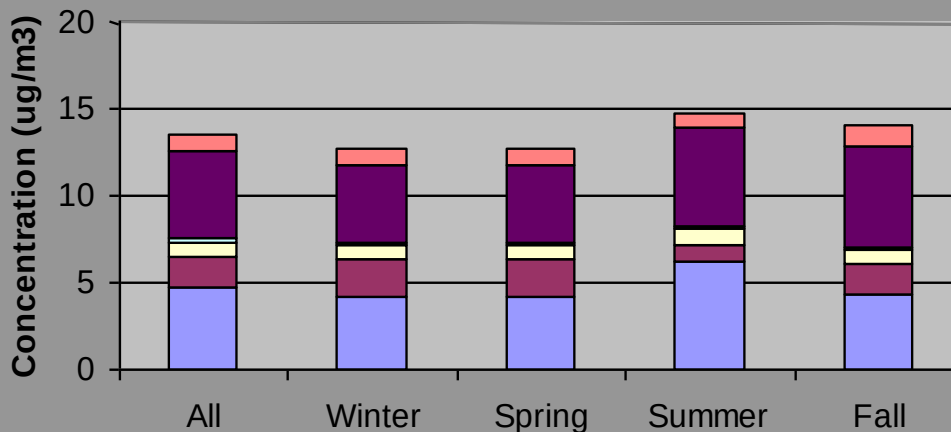
IMPROVE



STN Suburban



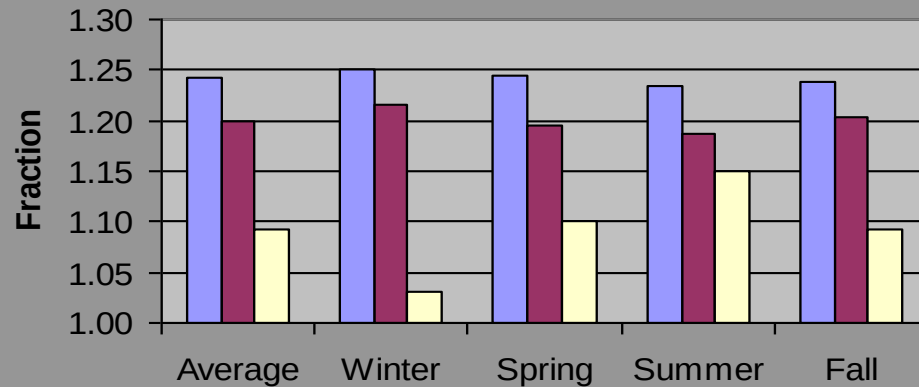
Center City



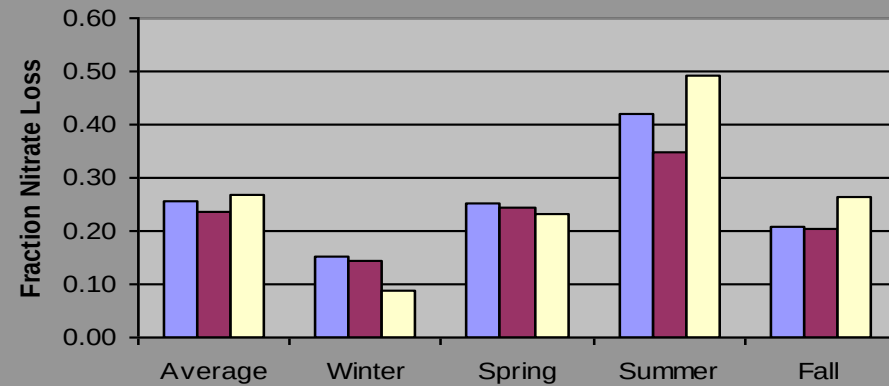
Inorganic water retention, nitrate
loss and Roc factor

$$\text{PM}_{2.5} = a_1 * 1.375 * \text{SO}_4 + a_2 * 1.29 * \text{NO}_3 + a_3 * \text{OC} + a_4 * \text{Other}$$

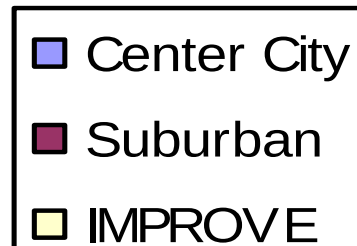
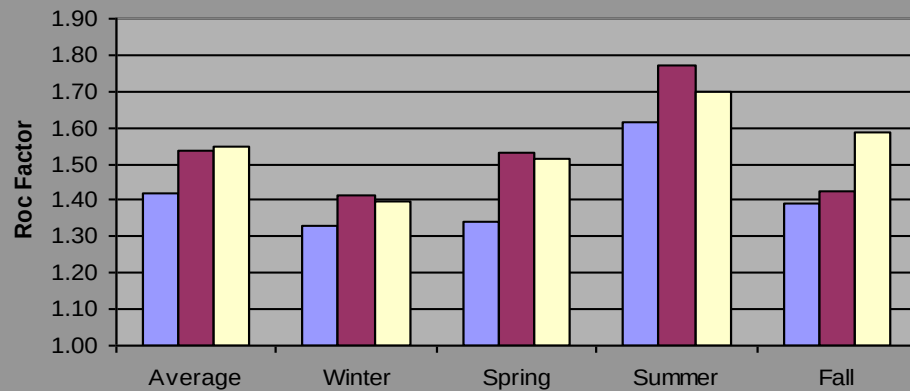
Water Fraction for Sulfate



Nitrate Loss (corrected for water)



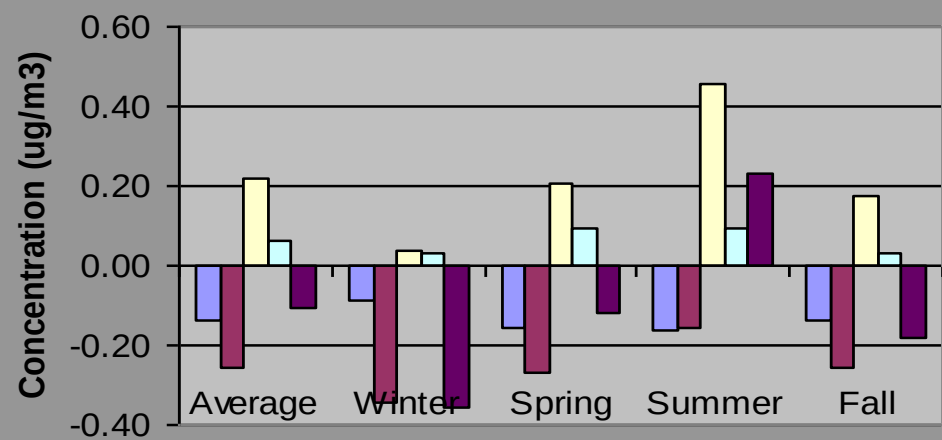
Roc Factor



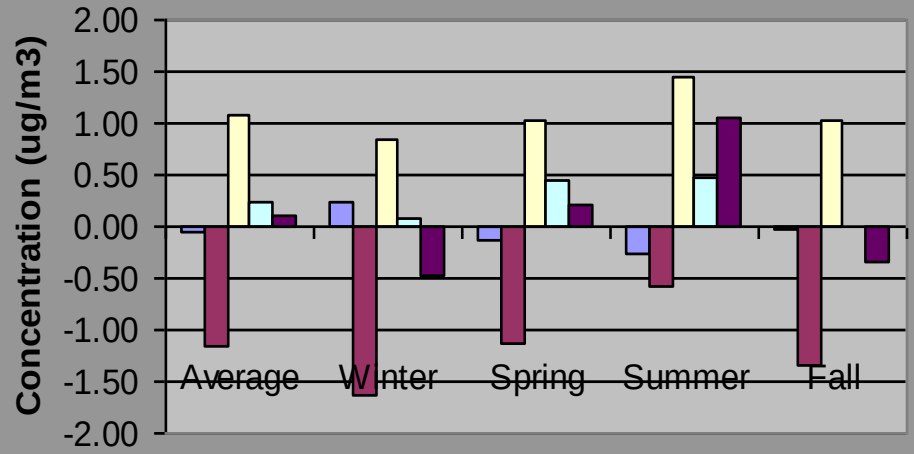
$$PM2.5-RPM2.5 = \sum_i (FM_i - RFM_i)$$

$$= (PM2.5_{SO4} - 1.375 \cdot SO_4) + (PM2.5_{NO3} - 1.29 \cdot NO_3) + (PM2.5_{POM} - 1.8 \cdot OC) + (PM2.5_{other} - Other)$$

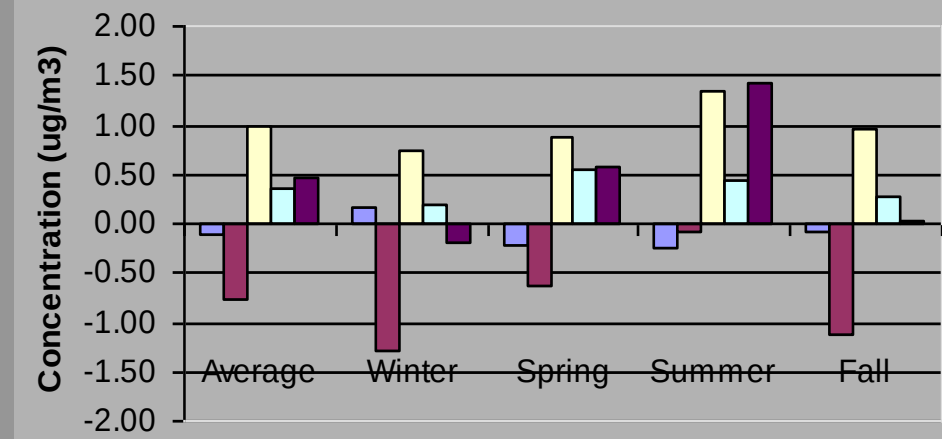
Bias IMPROVE



Bias (Center City)



Bias (Suburban)



- FMNO3-1.29*NO3
- FMPOM-1.8*OC
- FMSO4-1.375*SO4
- FMother-Other
- SUM

Assumptions for estimating gravimetric and reconstructed mass bias sans accounting for SVOC losses

- Weighing of Teflon filter includes retained water on sulfate and nitrate aerosols
- Nitrate and sulfates are measured without loss on nylon substrate
- Organic volatilization from Teflon and quartz substrates are the same
- Gravimetric mass of total carbon, soil dust, and sea salt determined without bias

Gravimetric:

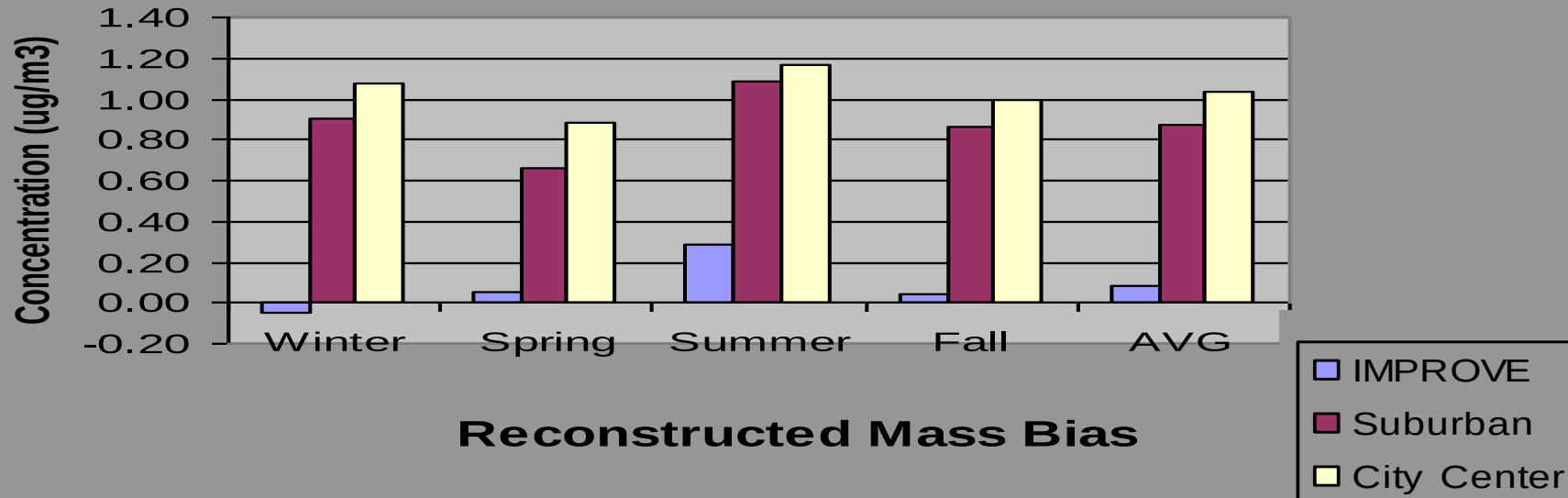
$$\text{PM}_{2.5} \text{ Bias} = (a_1 - 1) * 1.375 * \text{SO}_4 + (a_2 - 1) * 1.29 * \text{NO}_3$$

Reconstructed:

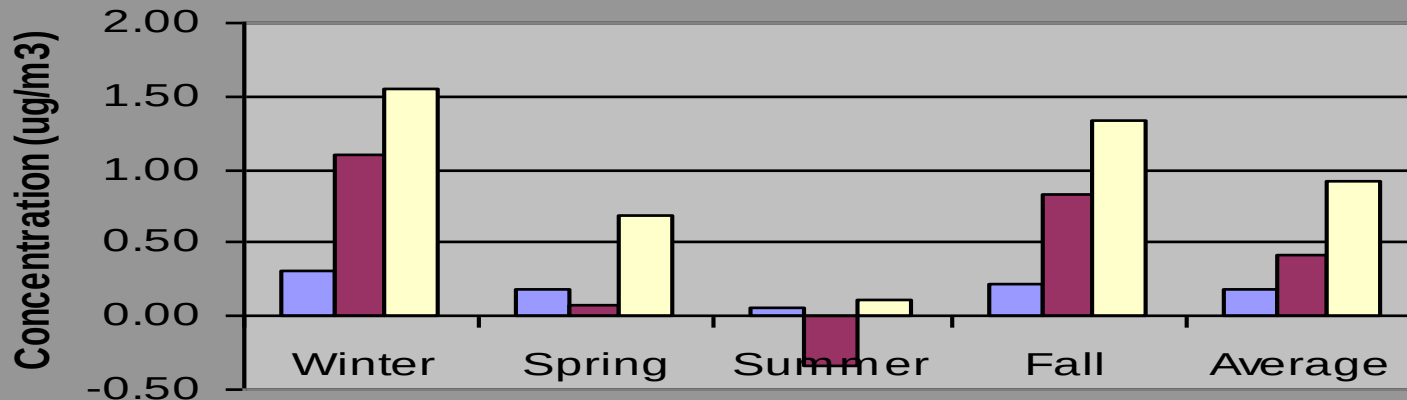
$$\text{RPM}_{2.5} \text{ Bias} = (1.8 - a_3) * \text{OC} + (1 - a_4) * \text{Other}$$

Average bias in gravimetric and reconstructed PM2.5 mass concentration for the IMPROVE and CSN datasets

FM Bias on Teflon filter

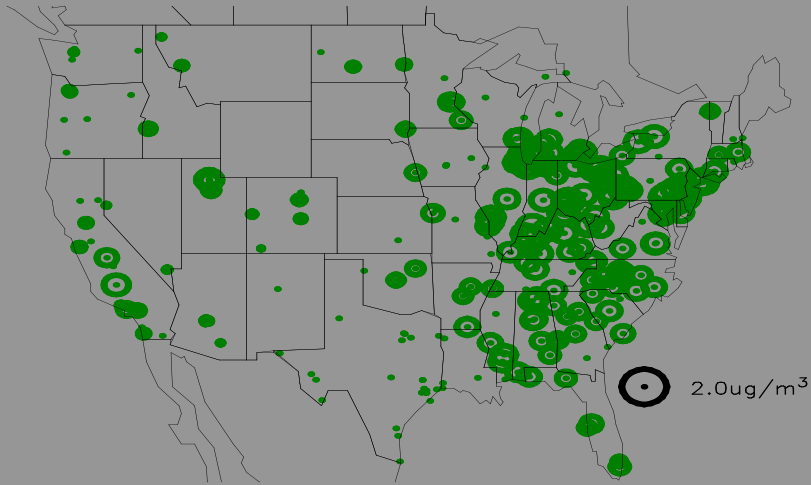


Reconstructed Mass Bias

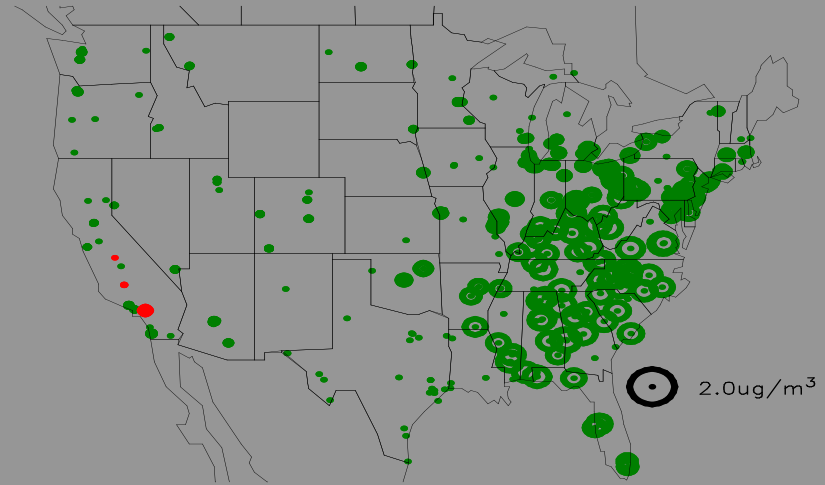


Seasonal and spatial variability in fine gravimetric mass bias for the CSN monitoring network

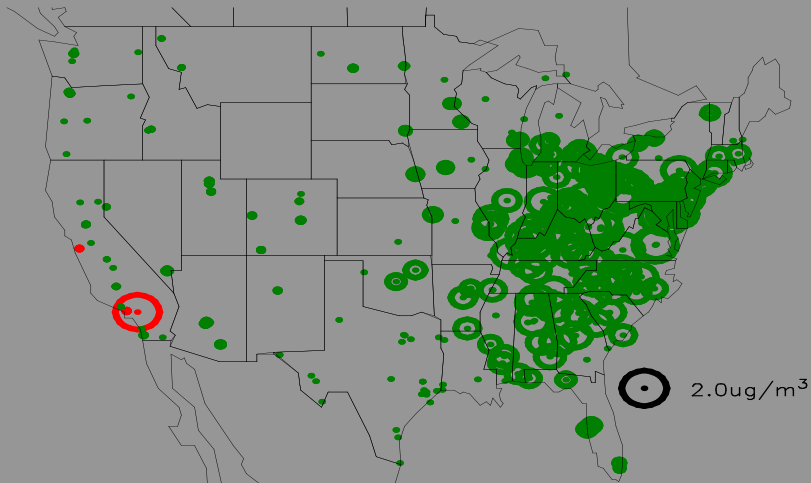
CSN Winter Gravimetric Bias



CSN Spring Gravimetric Bias

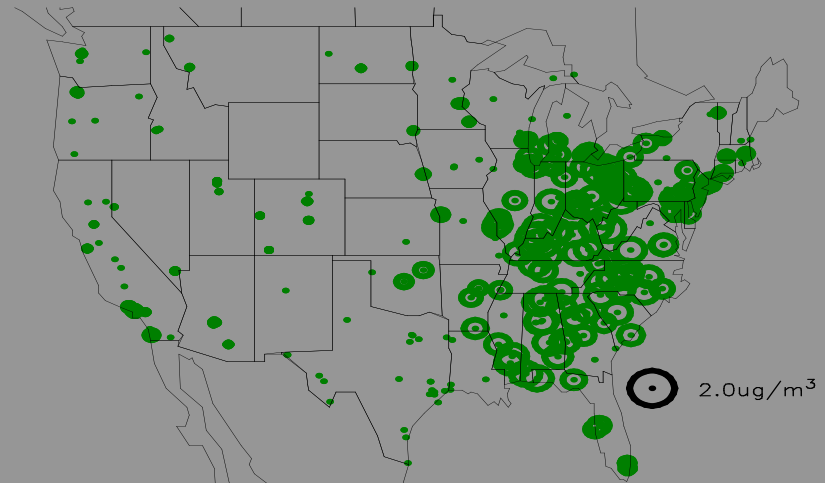


CSN Summer Gravimetric Bias



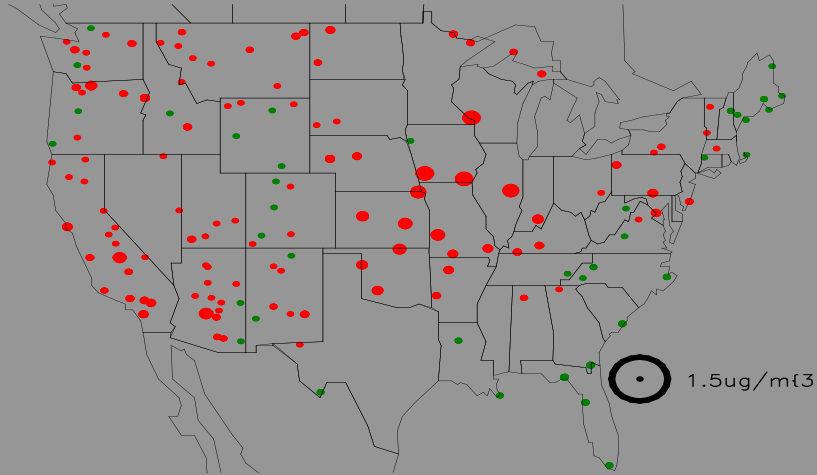
$\text{PM}_{2.5}^{\text{measured}} - \text{PM}_{2.5}^{\text{ambient}}$

CSN Fall Gravimetric Bias

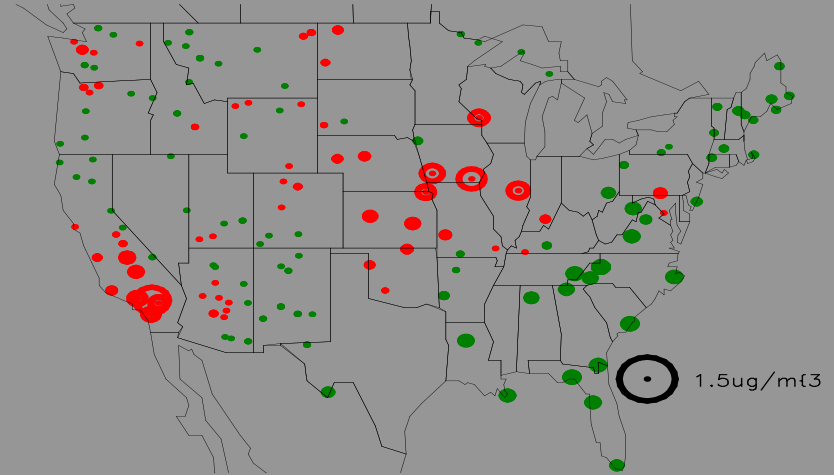


Seasonal and spatial variability in fine gravimetric mass bias for the IMPROVE monitoring network

IMPROVE Winter Gravimetric Bias

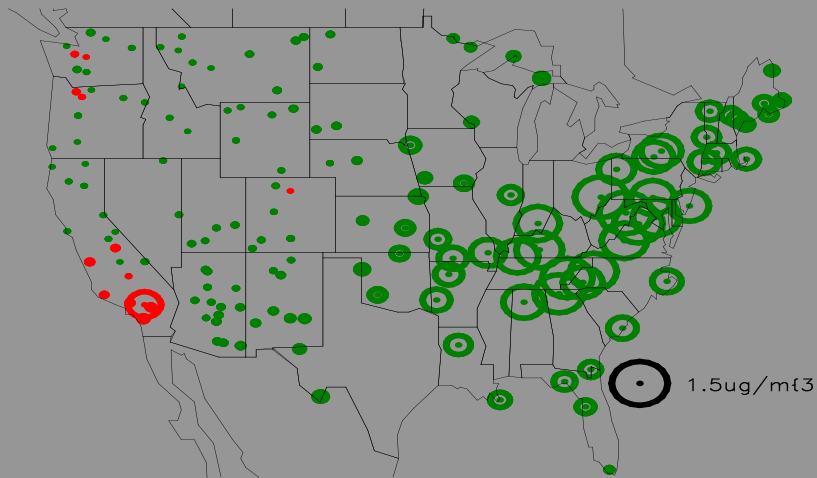


IMPROVE Spring Gravimetric Bias

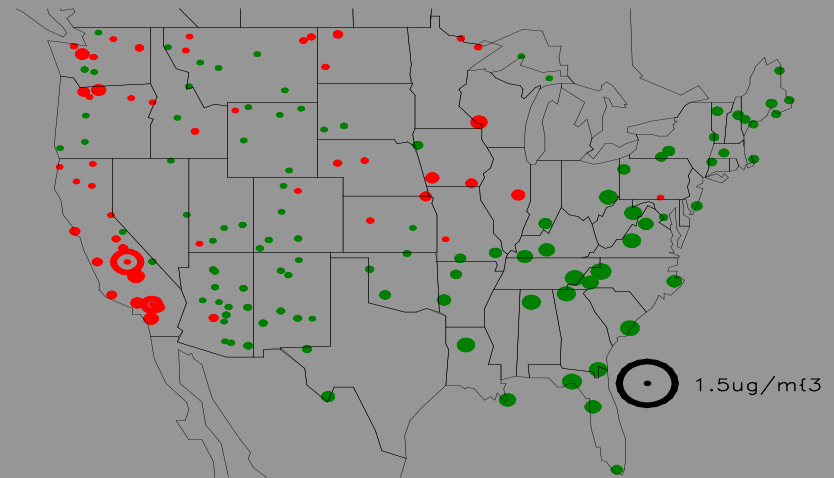


$PM_{2.5}_{measured} - PM_{2.5}_{ambient}$

IMPROVE Summer Gravimetric Bias

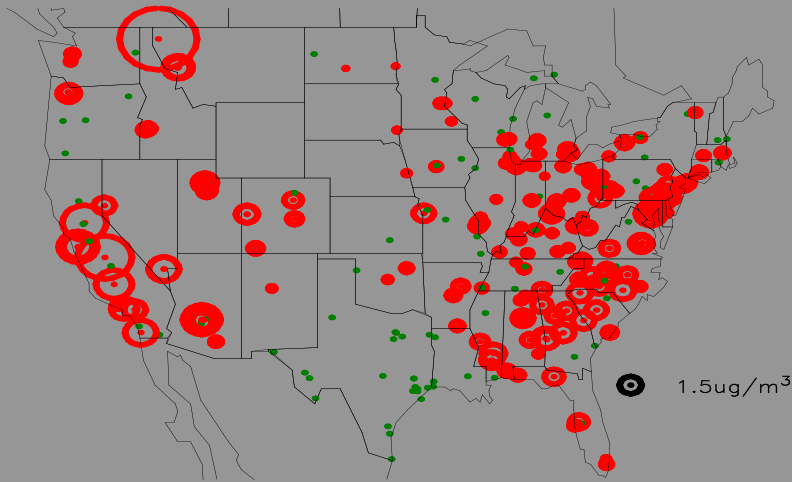


IMPROVE Fall Gravimetric Bias

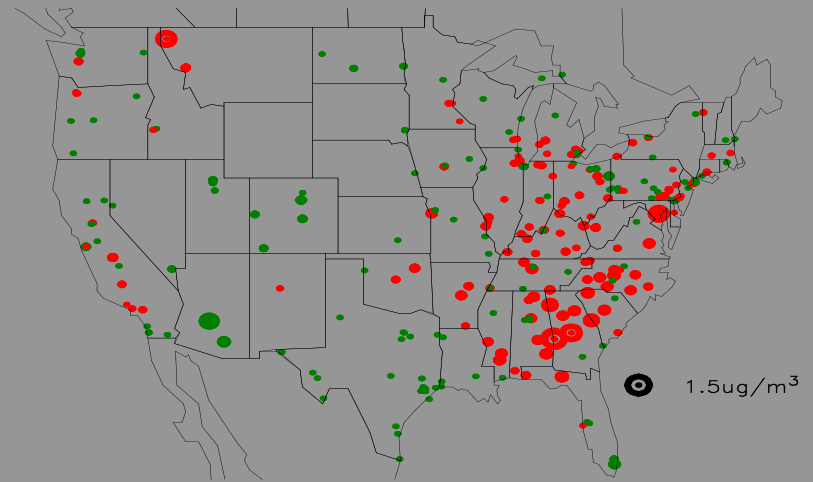


Seasonal and spatial variability in reconstructed mass bias for the CSN monitoring network.

CSN Winter Reconstructed Bias

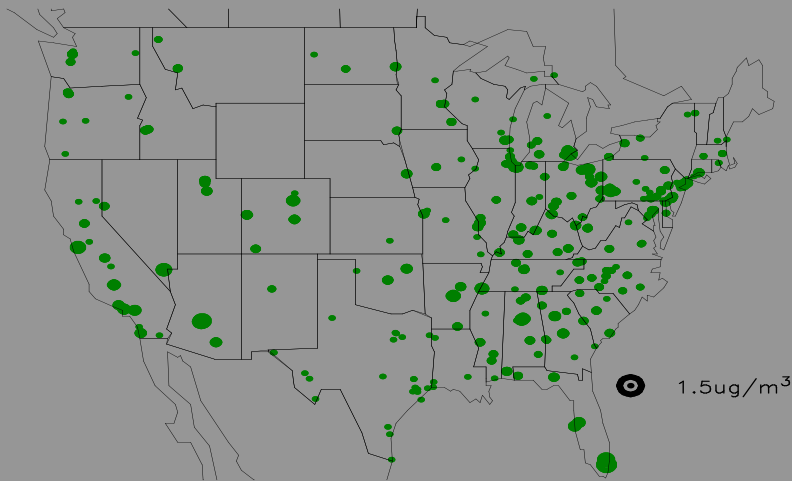


CSN Spring Reconstructed Bias

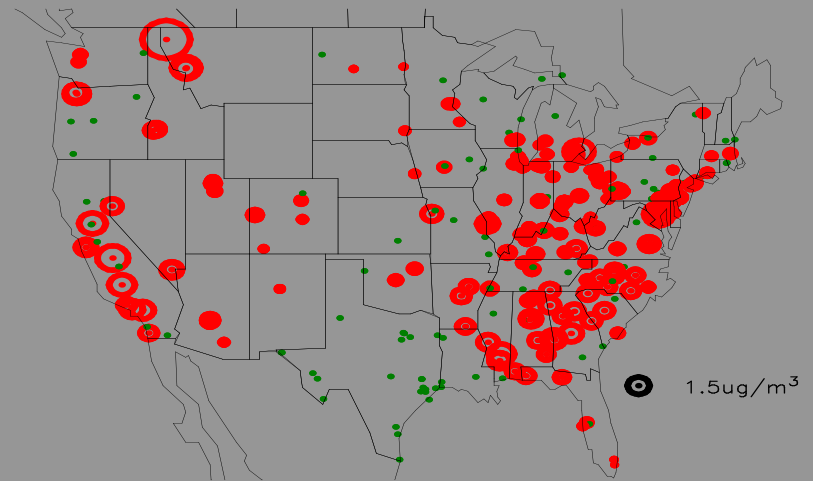


$PM_{2.5_{measured}} - PM_{2.5_{reconstructed}}$

CSN Summer Reconstructed Bias

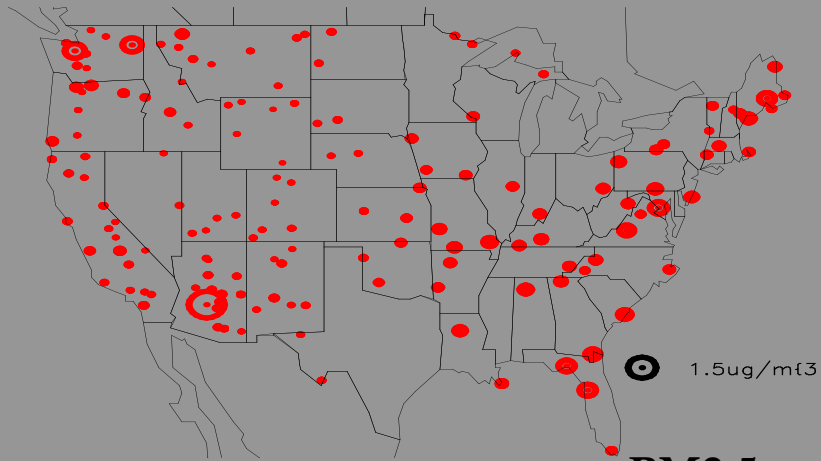


CSN Fall Reconstructed Bias

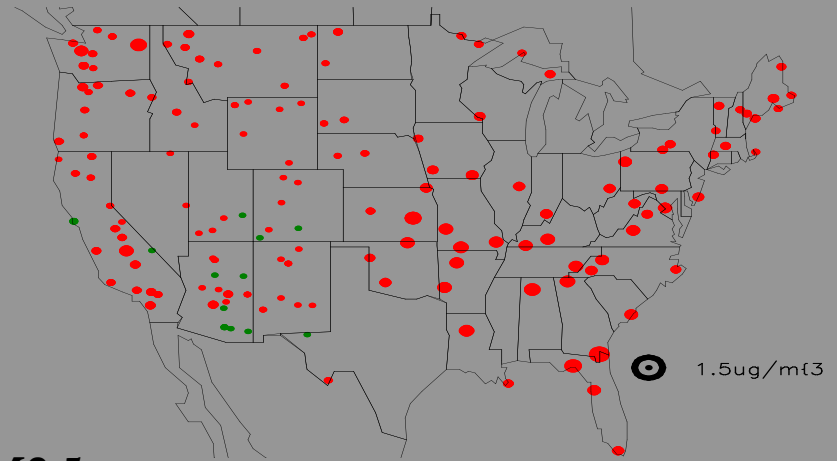


Seasonal and spatial variability in reconstructed mass bias for the IMPROVE monitoring network

IMPROVE Winter Reconstructed Bias

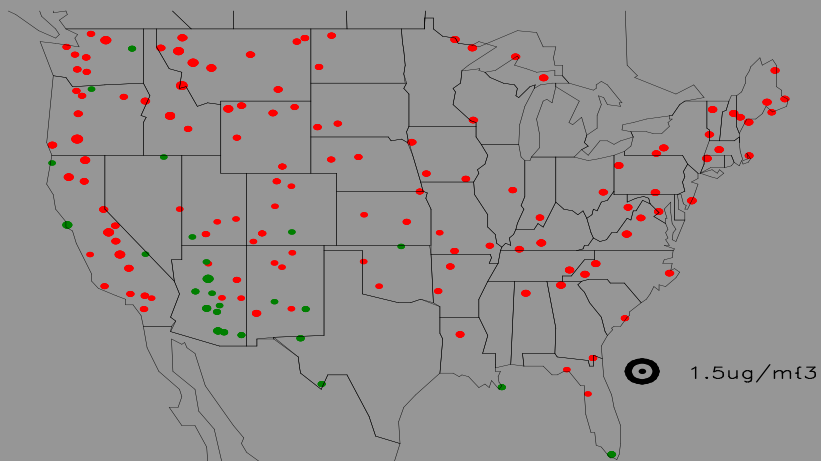


IMPROVE Spring Reconstructed Bias

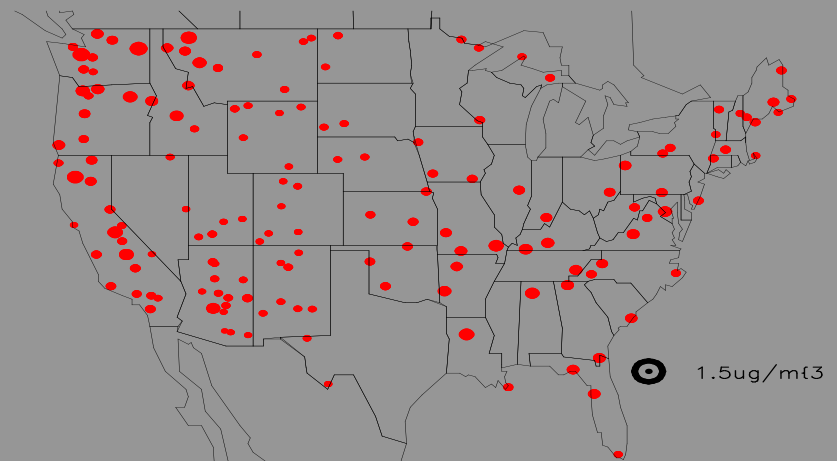


$PM_{2.5_{measured}} - PM_{2.5_{reconstructed}}$

IMPROVE Summer Reconstructed Bias



IMPROVE Fall Reconstructed Bias



SUMMARY

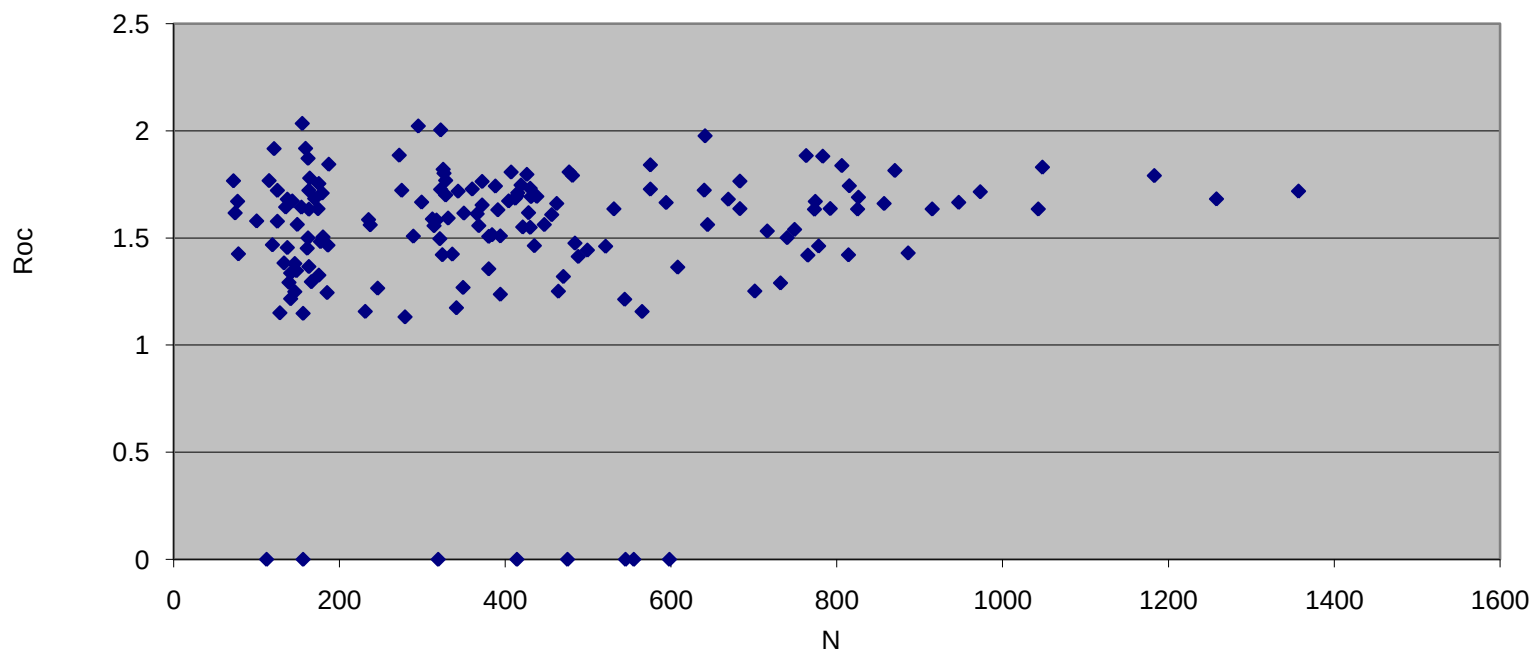
- Approximately 20% of OC is volatilized in the IMPROVE sampling system
- The Roc factor (POM/OC) has a seasonal dependence that varies from about 1.4 in the winter to 1.6-1.8 in the summer
- Urban/suburban Roc factors may be marginally higher than rural factors
- Nitrate volatilization from the Teflon substrates vary from about 10% in the winter to 35-40% in the summer
- There doesn't appear to be a systematic difference in nitrate volatilization between CSN and IMPROVE monitoring sites
- About 20% of inorganics species mass is retained water

SUMMARY (Cont)

- Bias between PM_{2.5} gravimetric and reconstructed mass is lowest (negative) in winter and highest (positive) in summer
- This bias is primarily driven by assuming a constant Roc factor and retained water by inorganic species
- Gravimetric PM_{2.5} in CSN network is biased high by one to two $\mu\text{g}/\text{m}^3$ in most the east and during the summer biased low by about two $\mu\text{g}/\text{m}^3$ in southern California
- IMPROVE reconstructed mass is biased high during all seasons but highest in winter. During summer it is biased low in the desert southwest

END

N vs FM-LAC



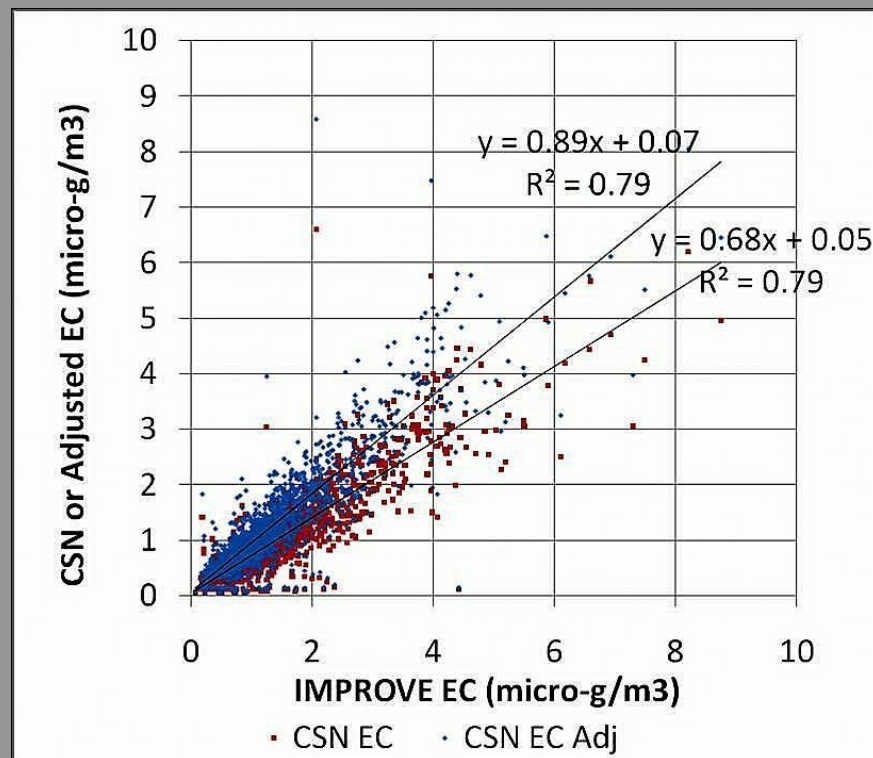
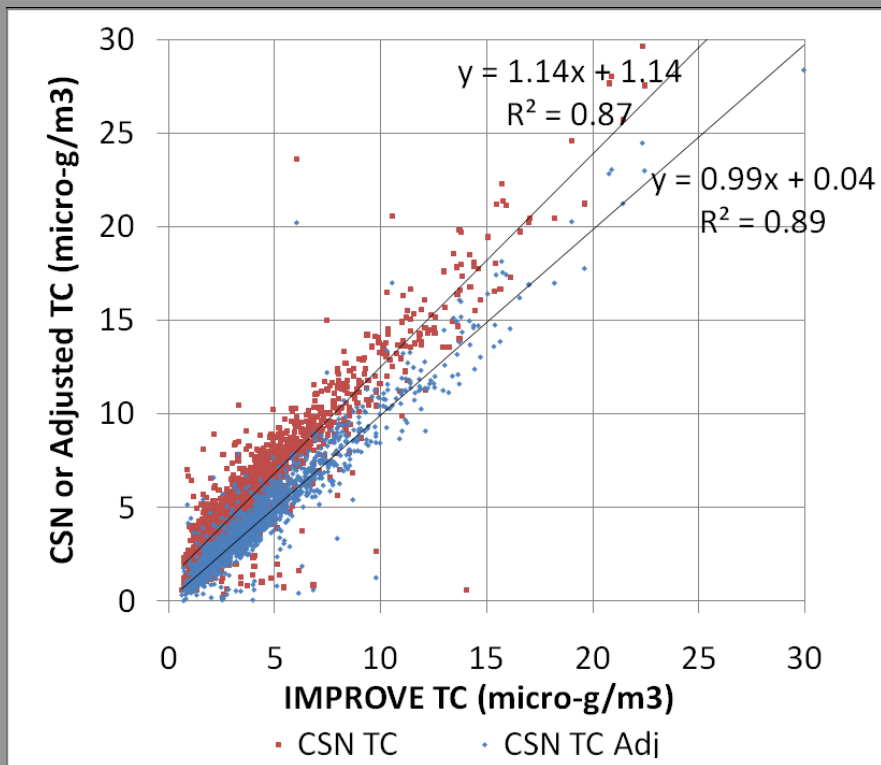
Neighborhood- and Urban-Scale Monitoring Objectives

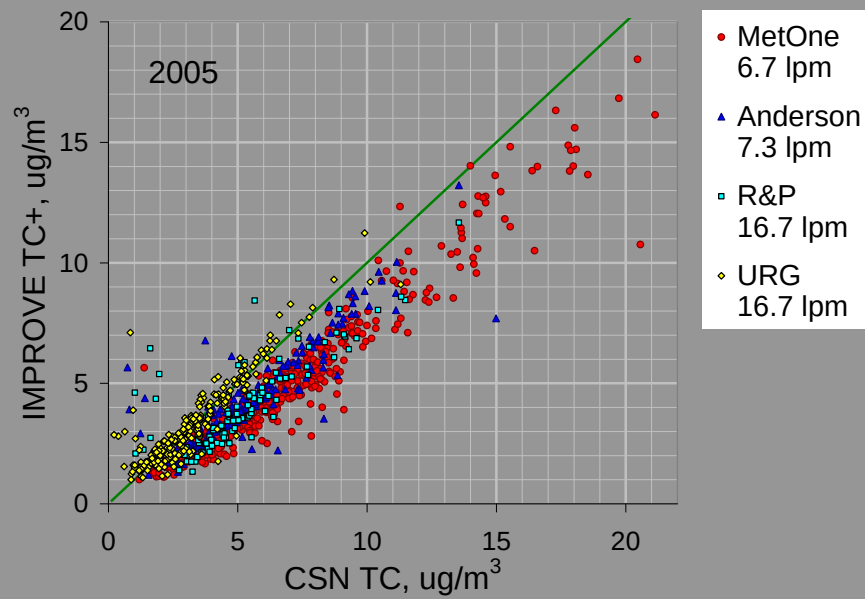
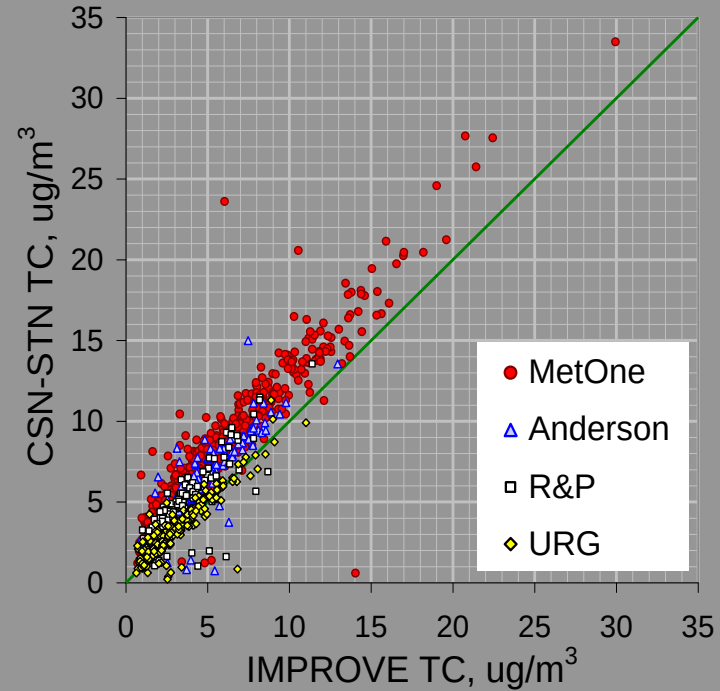
- Determine compliance with air quality standards
- Validation of regional scale models
- Assess source/receptor relationships
- Evaluate health, radiative, and ecological effects

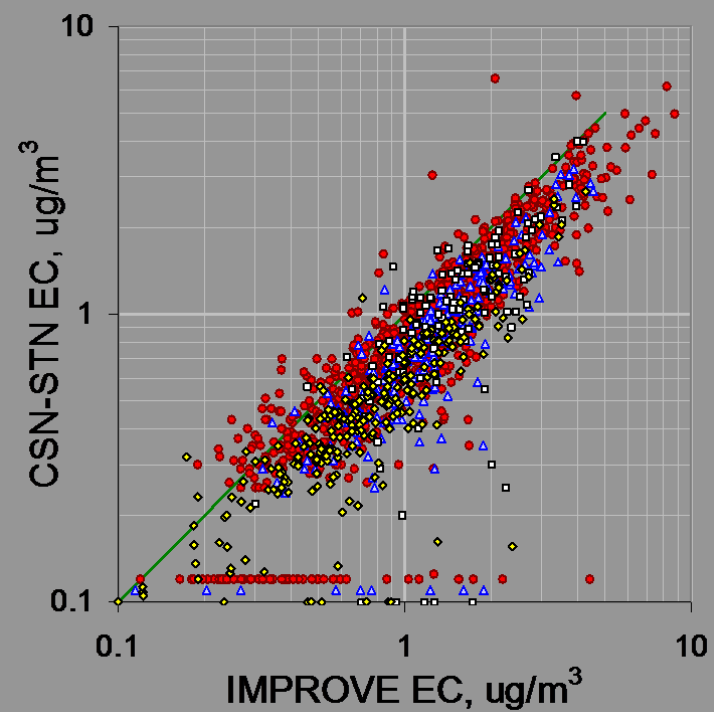
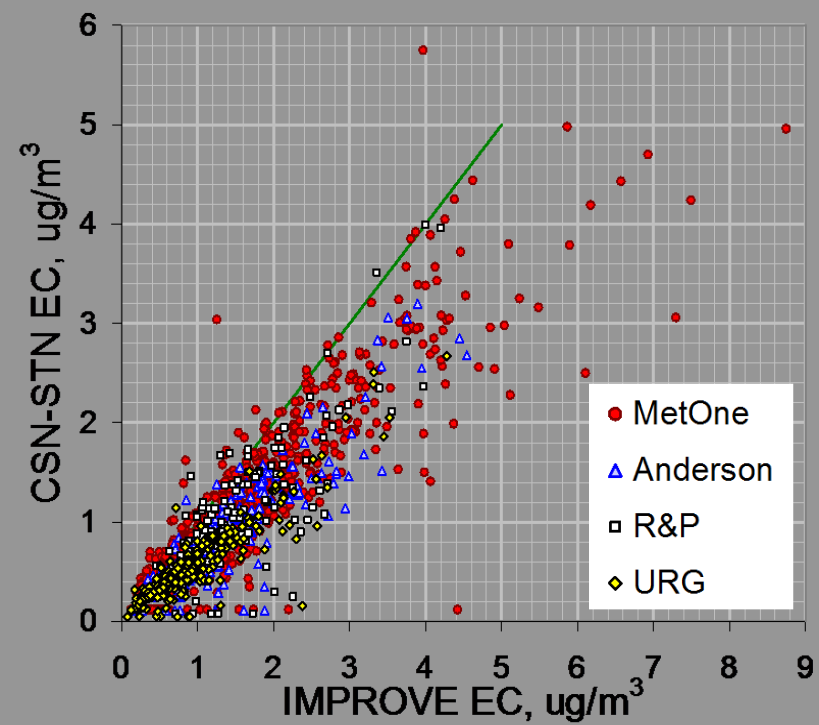
IMPROVE Monitoring Objectives

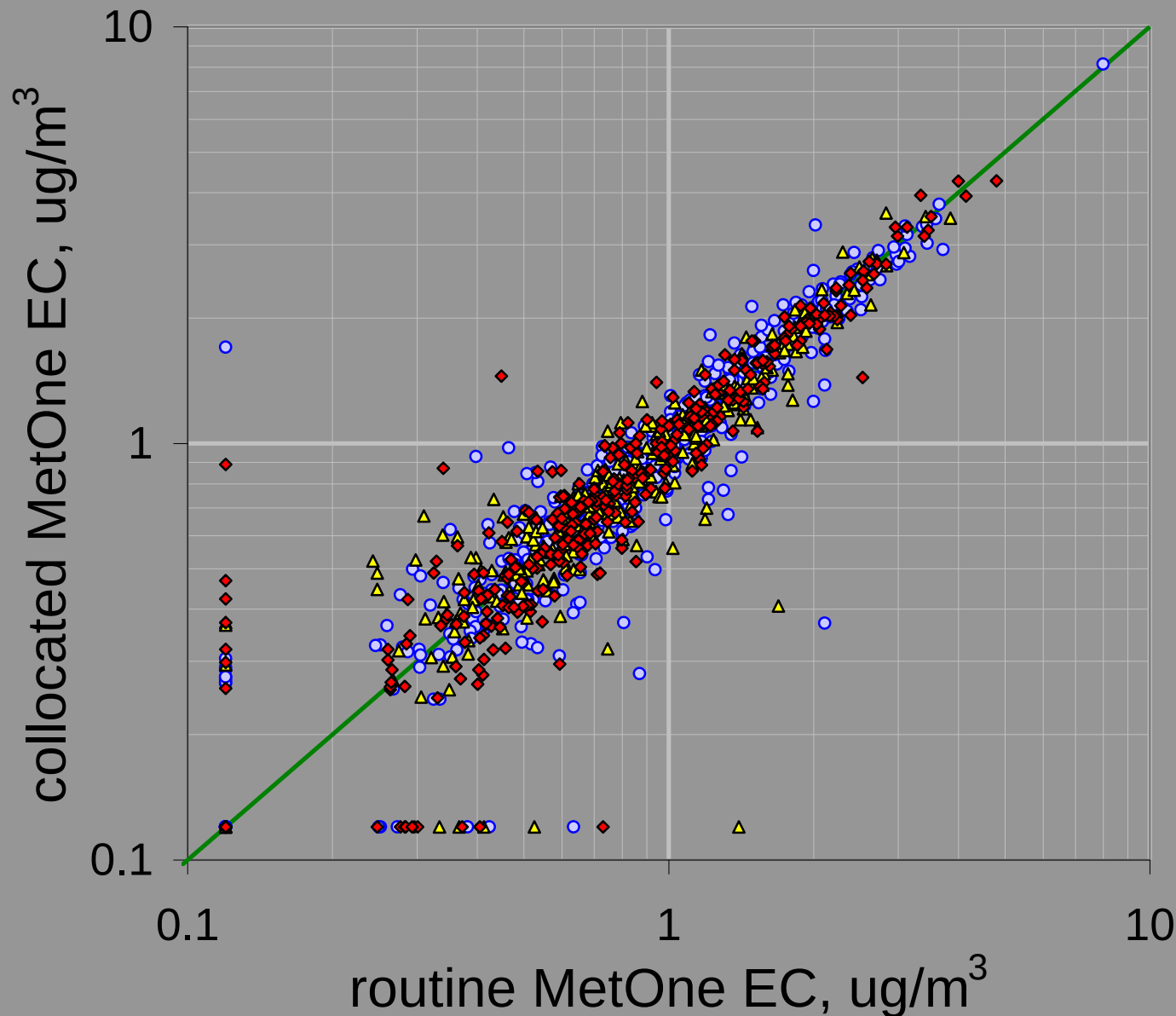
- Tracking long term temporal changes in visibility (extinction)
- Assess source/receptor relationships
- Serve as a regional backdrop for special studies and understanding non urban background
- Used for regional modeling validation studies

Comparison of CSN and adjusted CSN to IMPROVE Carbon









- 2003-4
- △ 2005
- ◆ 2006

Considerably more scatter is observed in routine CSN measurements by collocated MetOne samplers, particularly in the earlier years.

Data are from Bakersfield,* Boston,* Cleveland,* New Brunswick* and Rubidoux.
* **Not** collocated with IMPROVE

EXPECTATION:

$$[TC]^{CSN} = [EC]^{IMP} + (1+B^{IMP*})[OC]^{IMP} + A^{CSN}/V_{MetOne}$$

OLS REGRESSION:

$$[TC]^{CSN} = (1+b_{EC})[EC]^{IMP} + (1+b_{OC})[OC]^{IMP} + a_1 + \dots + a_{12} + e$$

2005-6 observations at 7 MetOne sites (excluding Phoenix):

$$b_{EC} = 0.008 (+/-0.05)$$

no sampling artifact for IMPROVE EC

$$b_{OC} = 0.22 (+/-0.03)$$

~ 20% sampling loss for IMPROVE OC

$$rms(e) = 0.9 \text{ ug/m}^3 \quad (r^2 = 0.94, n = 728)$$

$a_{mm} \rightarrow$ next slide

EC – the short story:

- $\varepsilon_{IMP} \cong 0$, $\varepsilon_{IMP} = artifact_adj$
- $IMP_{new} \cong \alpha CSN$, $\alpha > 1$
- $CSN_{\phi} \cong CSN_{\varphi}$, $\phi \neq \varphi$ samplers
- EC has little to no positive artifact for both IMPROVE and CSN
- Multiplicative bias between CSN and IMPROVE that is sampler independent

TC – the short story:

$$\varepsilon_{IMP} = artifact_adj$$

$$IMP_{new} \cong \lambda (CSN - \theta), \quad \lambda < 1, \theta > 0$$

$$CSN_{\phi} \neq CSN_{\varphi}, \quad \phi \neq \varphi \text{ samplers}$$

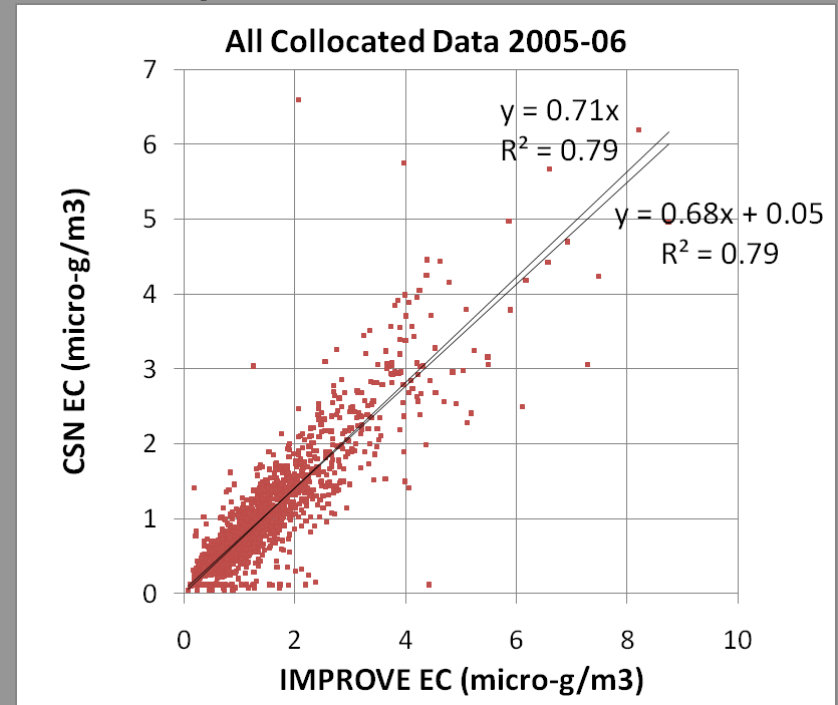
Relating IMPROVE and CSN EC

Making CSN look like IMPROVE

- Recall

- EC has little to no positive artifact for both IMPROVE and CSN
- CSN and IMPROVE have a multiplicative bias that is sampler independent

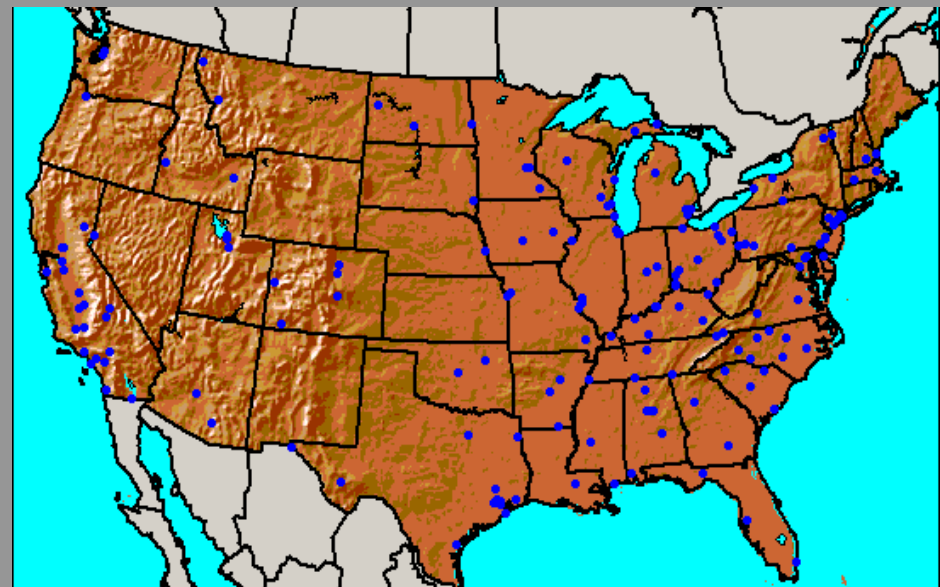
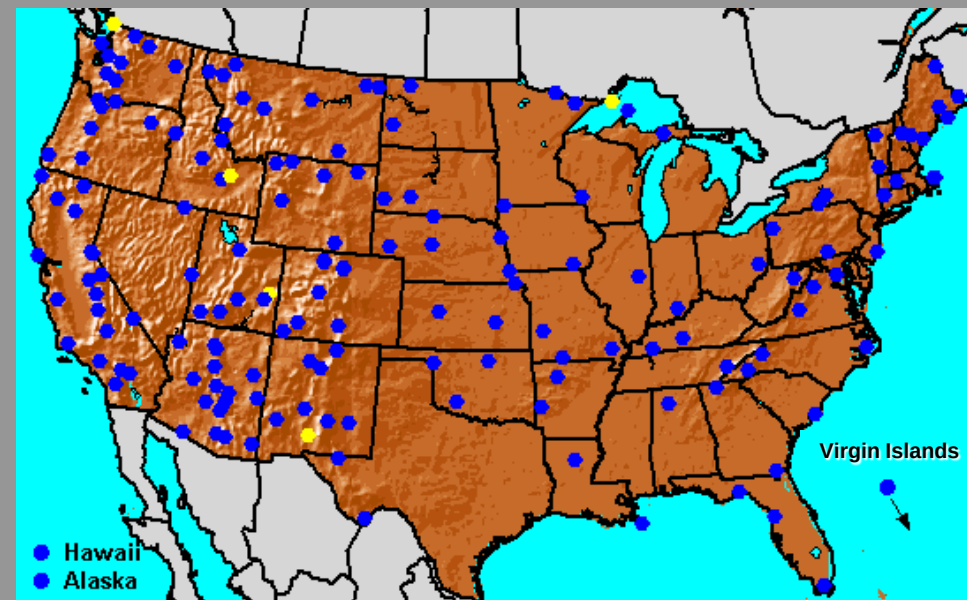
- $EC_{IMP} = \alpha * EC_{CSN}$
- $\alpha \sim 1.3$



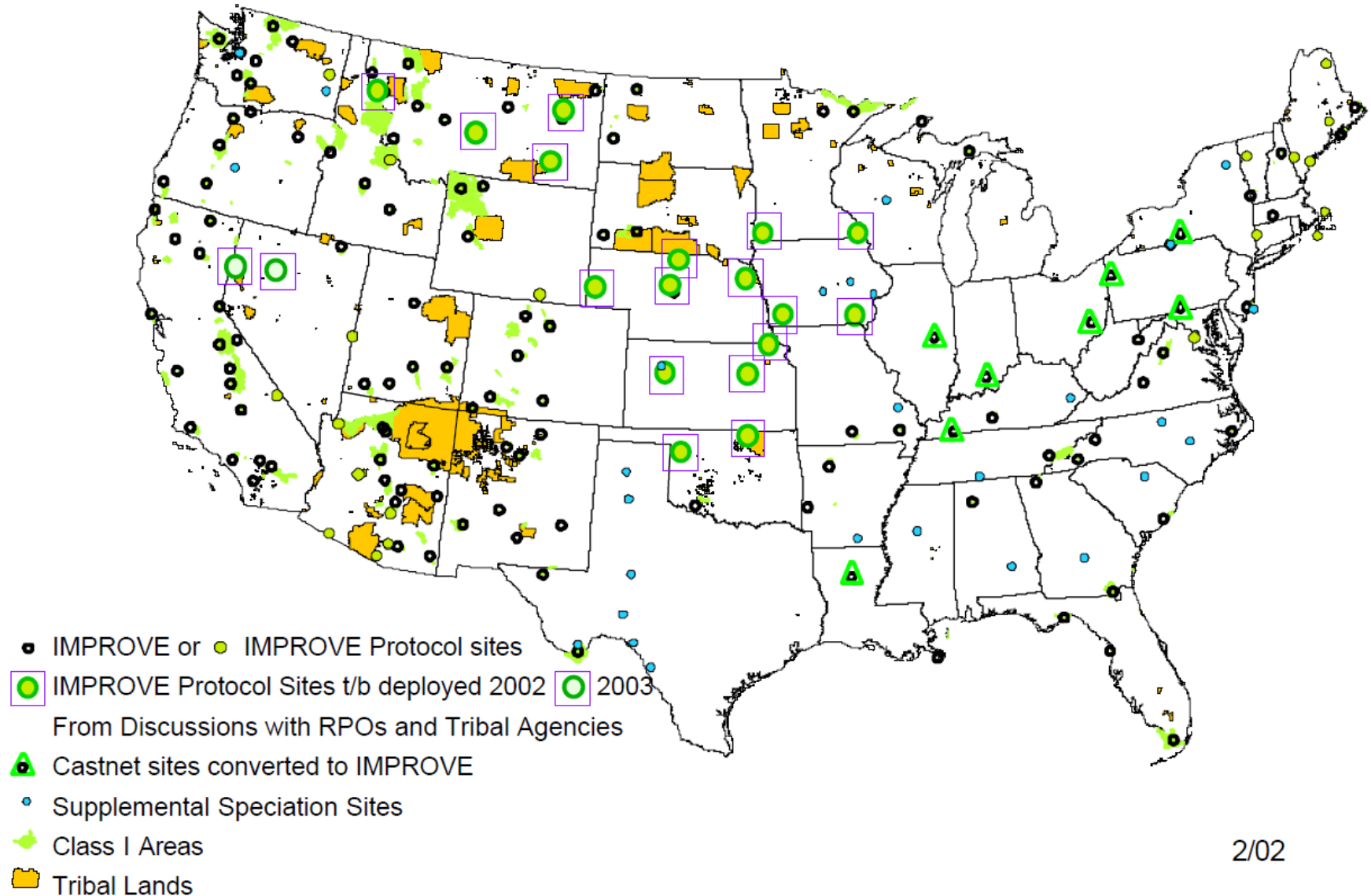
Non-urban and urban PM_{2.5} networks

**Interagency
Monitoring of
PROtected Visual
Environments
(IMPROVE) Network**

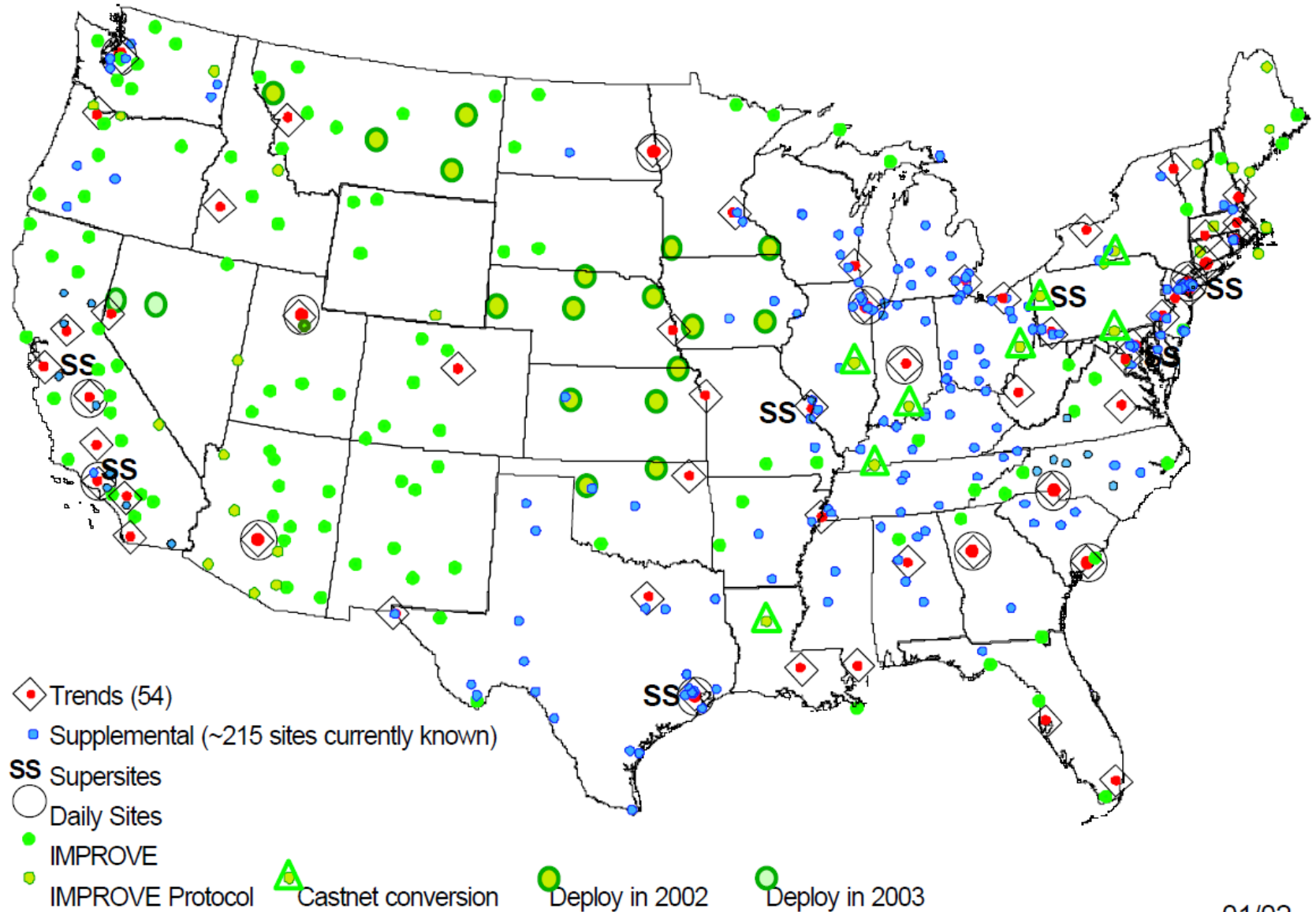
**Chemical Speciation
Network (CSN)**



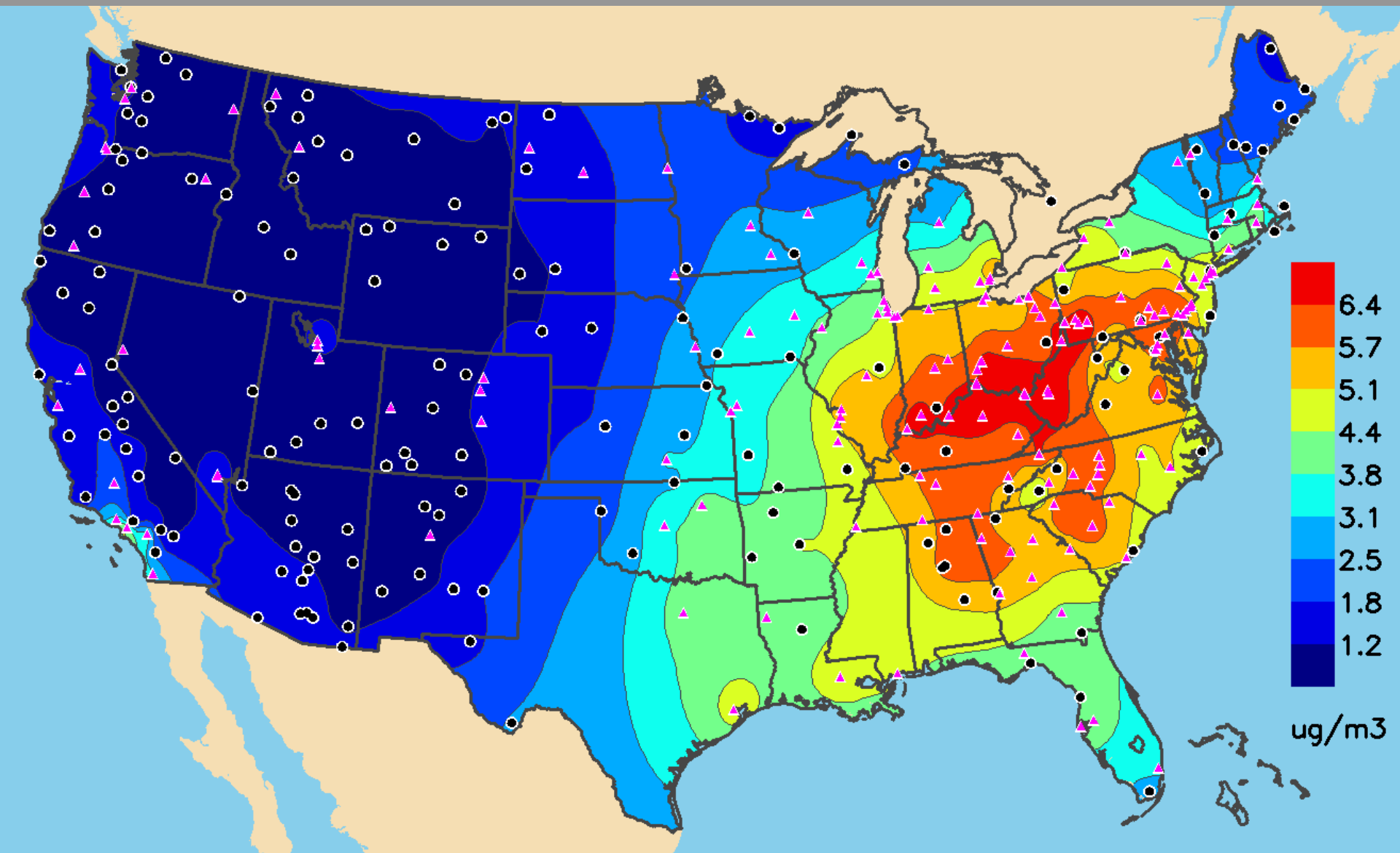
Current/Planned IMPROVE, IMPROVE Protocol & Rural Supplemental PM_{2.5} Speciation Sites



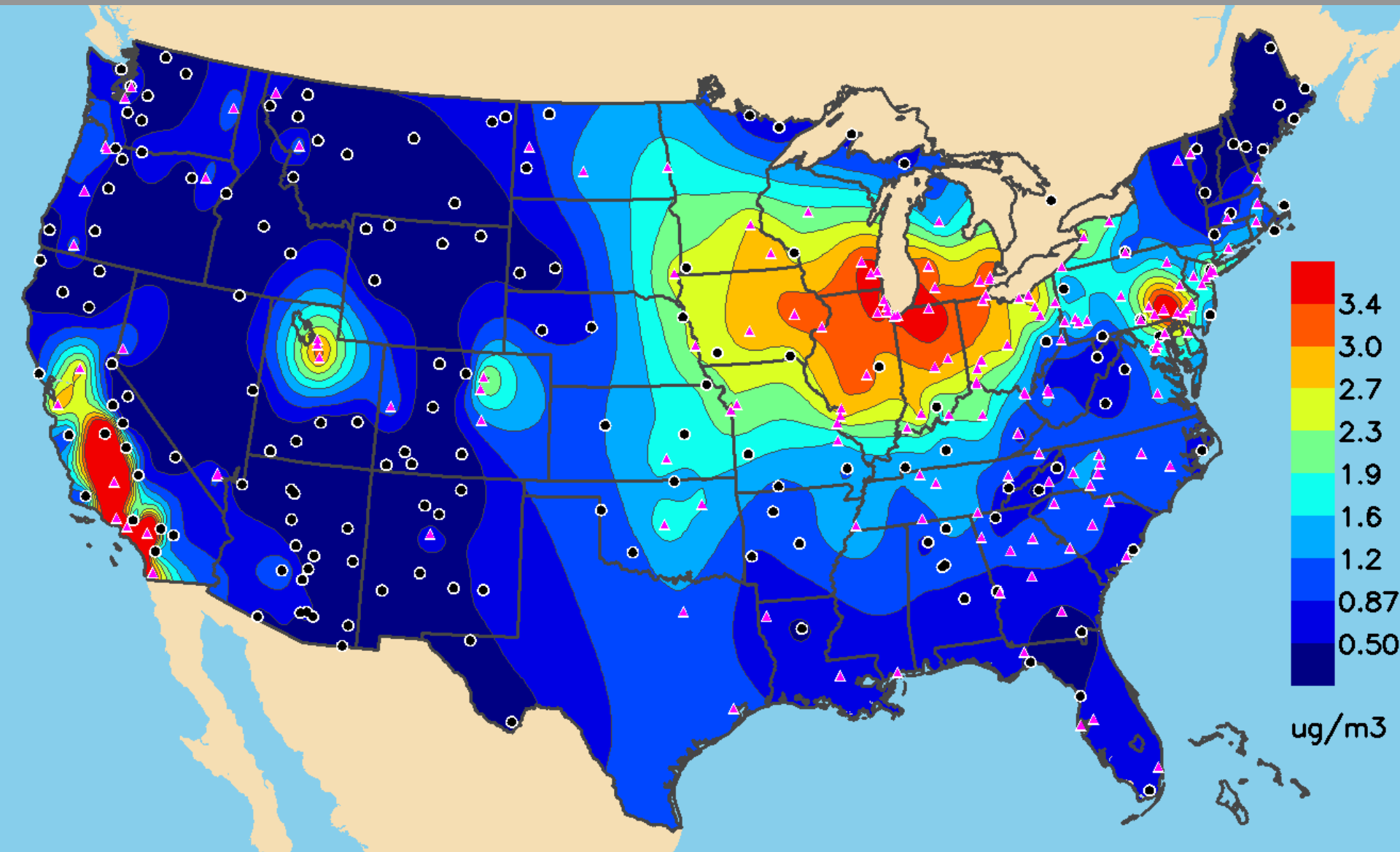
Current/Planned Urban & Rural PM_{2.5} Speciation Networks



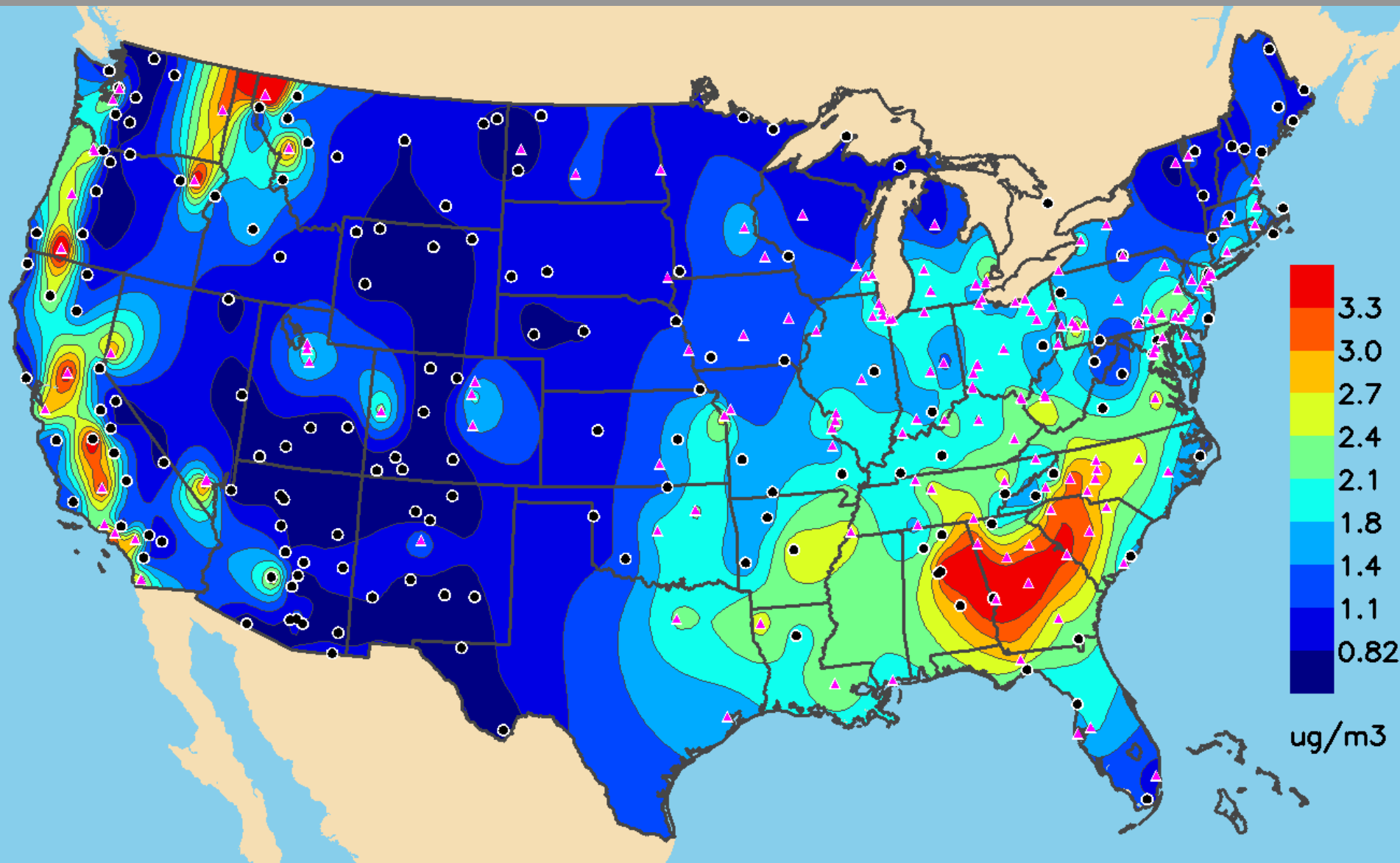
Ammonium Sulfate



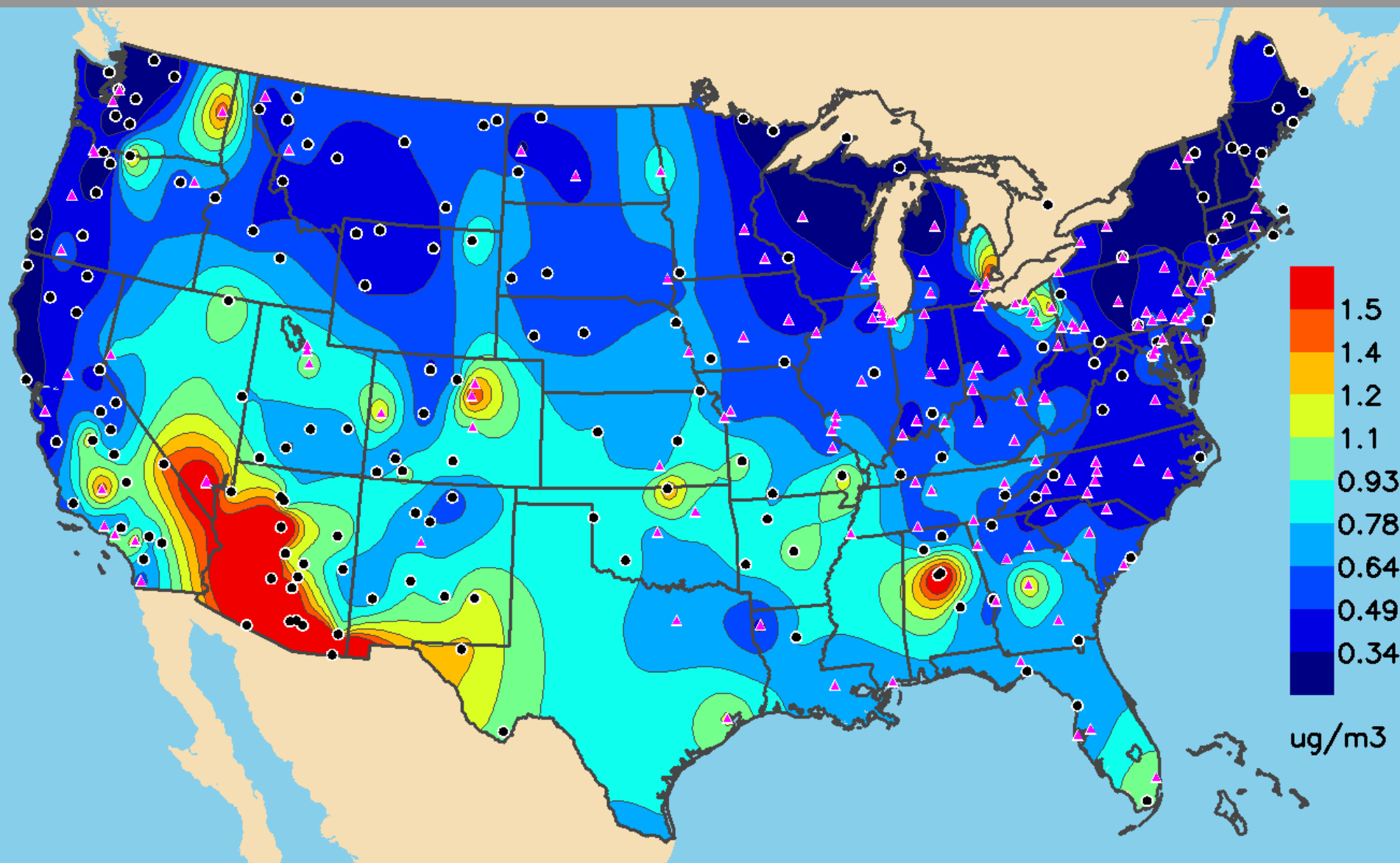
Ammonium Nitrate



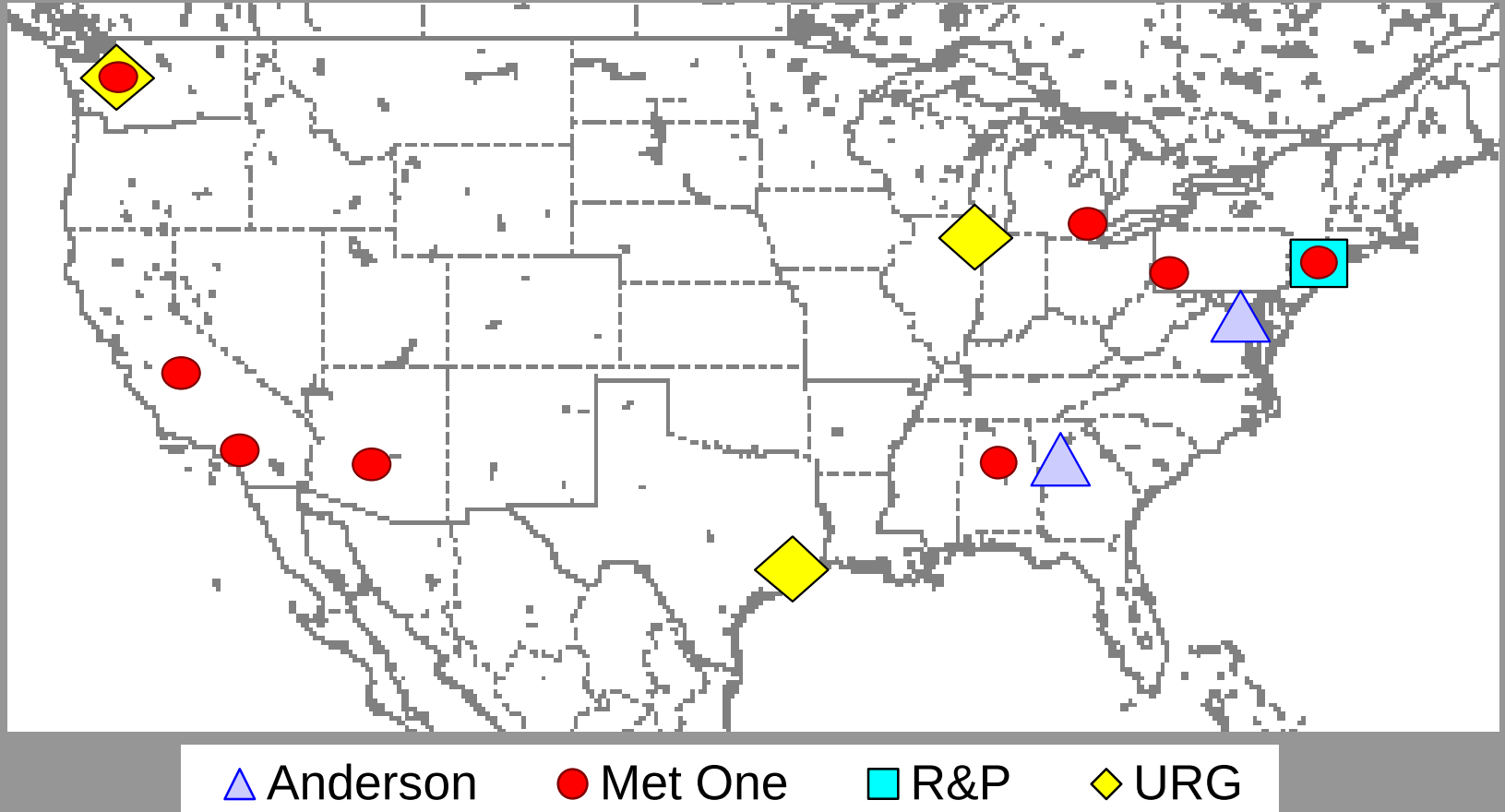
Organic Carbon



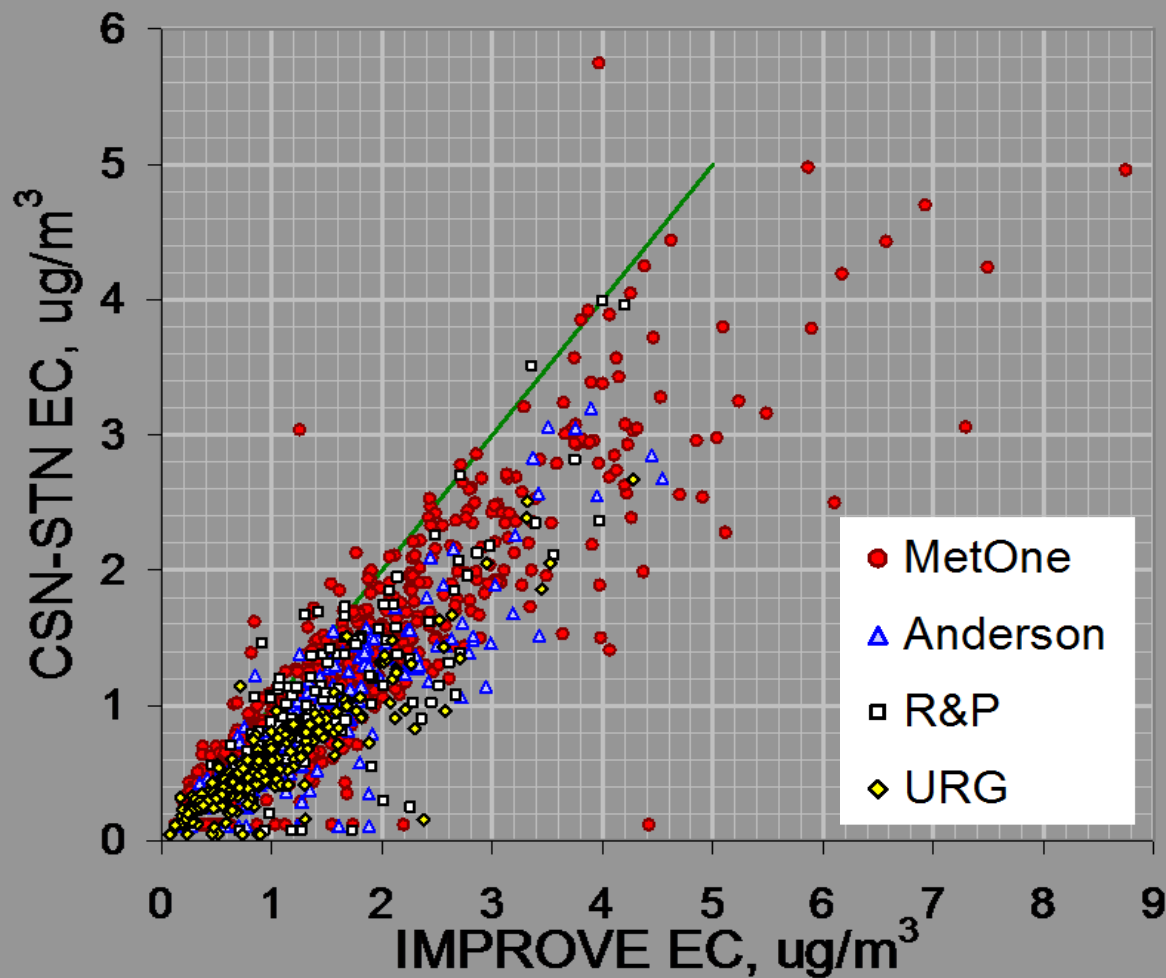
Fine Soil



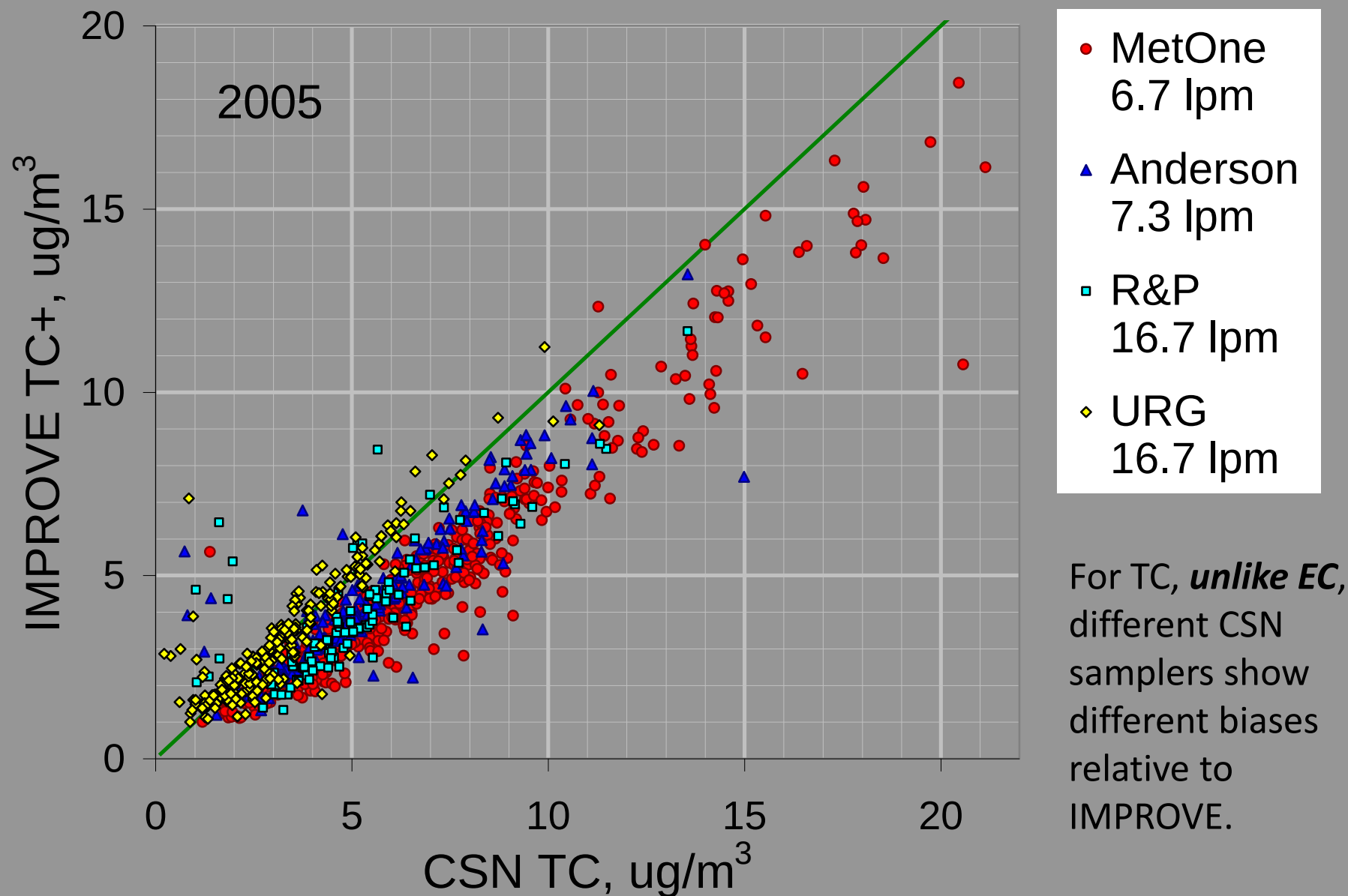
Comparison of IMPROVE and CSN Carbon at Collocated Sites



urban collocations of CSN and IMPROVE carbon measurements⁴⁶

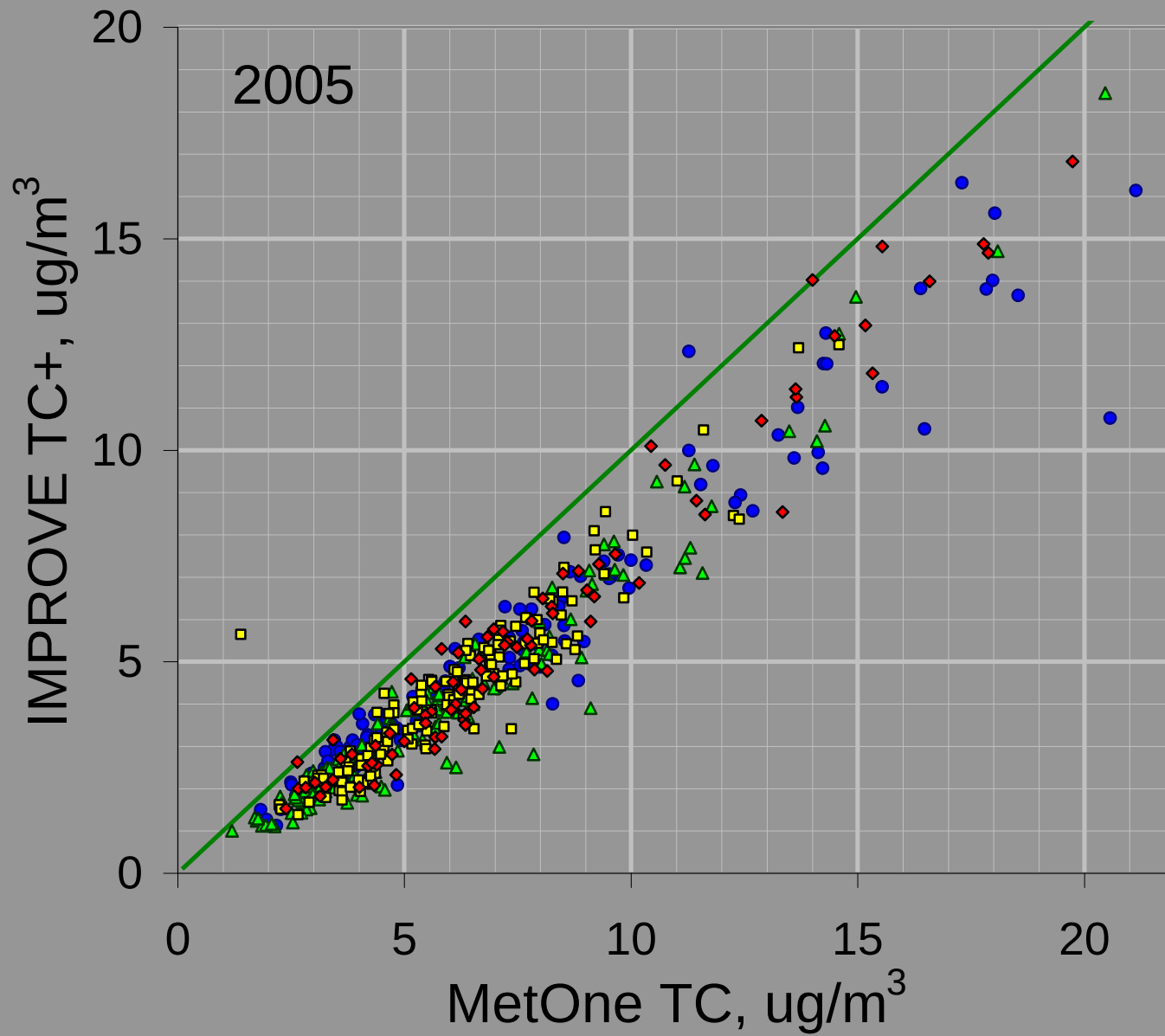


- The EC difference between CSN and IMPROVE shows little dependence on the CSN sampler, suggesting that it is mainly analytical.
- IMPROVE:TOR (DRI) – CSN: TOT(NIOSH)



Note that the CSN offset is **not** determined simply by flow rate.

2005



- Dec, Jan, Feb
- ▲ Mar, Apr, May
- Jun, Jul, Aug
- ◆ Sep, Oct, Nov

The CSN offset shows no obvious seasonality. In that respect it behaves more like IMPROVE field blanks than IMPROVE backup filters.

2005

IMPROVE TC+, $\mu\text{g}/\text{m}^3$

MetOne TC, $\mu\text{g}/\text{m}^3$

- Birmingham
- △ Detroit
- ◆ Fresno
- Phoenix
- △ Pittsburgh
- Rubidoux

PM_{2.5} Federal Reference Methods (FRMs)



Andersen RAAS
Thermo Fisher
Scientific, formerly
Andersen Instruments,
Smyrna, GA



BGI PQ-200
BGI, Inc., Waltham, MA



Partisol Sampler
Thermo Fisher Scientific,
formerly Rupprecht &
Patashnick, Albany, NY



URG MASS
URG Corp.,
Raleigh, NC

Speciation Monitors (EPA Speciation Network)



Mass Aerosol Sampling System (MASS)
URG Corporation, Raleigh, NC



Reference Ambient Air Sampler (RAAS)
Andersen Instruments, Smyrna, GA



Spiral Aerosol Speciation Sampler (SASS)
Met One Instruments, Grants Pass, OR



Interagency Monitoring of Protected Visual
Environments (IMPROVE) Sampler
Air Resource Specialists, Ft. Collins, CO



Other Speciation Monitors



Partisol 2300 Speciation Sampler
Rupprecht & Patashnick, Albany, NY

Dual Channel
Sequential Filter Sampler
and Sequential Gas Sampler
Desert Research Institute, Reno, NV



Dichotomous Virtual Impactor
Andersen Instruments, Smyrna, GA

Paired Minivols
Airmetrics, Inc., Springfield, OR



URG 3000N
Speciation Sampler
*URG Corporation,
Raleigh, NC*



Dichotomous Partisol-Plus Sampler
Rupprecht and Patashnick, Albany, NY

Relating IMPROVE and CSN TC

Making CSN look like IMPROVE

- Recall
 - Measured TC has a positive OC artifact.
 - IMPROVE corrects for the artifact but CSN does not
 - IMPROVE TC has a negative multiplicative artifact due loss of OC from high face velocities (FV)
 - IMPROVE FV = 107.2 cm/s
 - CSM MetOne FV = 9.5 cm/s
 - Assume CSN negative artifact is 0

- Then

$$[TC]^{IMP} = [TC] - B^{IMP}[OC]$$

B - multiplicative artifact

$$[TC]^{CSN} = [TC] + A^{CSN}/V_{MetOne}$$

A/V – additive artifact

- Combine

$$[TC]^{CSN} = [TC]^{IMP} + B^{IMP}[OC] + A^{CSN}/V_{MetOne}$$

Comparison of regression and ratio method for estimating Roc

- Other= $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{NO}_3 + \text{Soil} + \text{LAC} + \text{SS}$
- POM = FM-Other
- $R_{\text{oc}} = (\text{FM} - \text{Other}) / \text{OC}$

