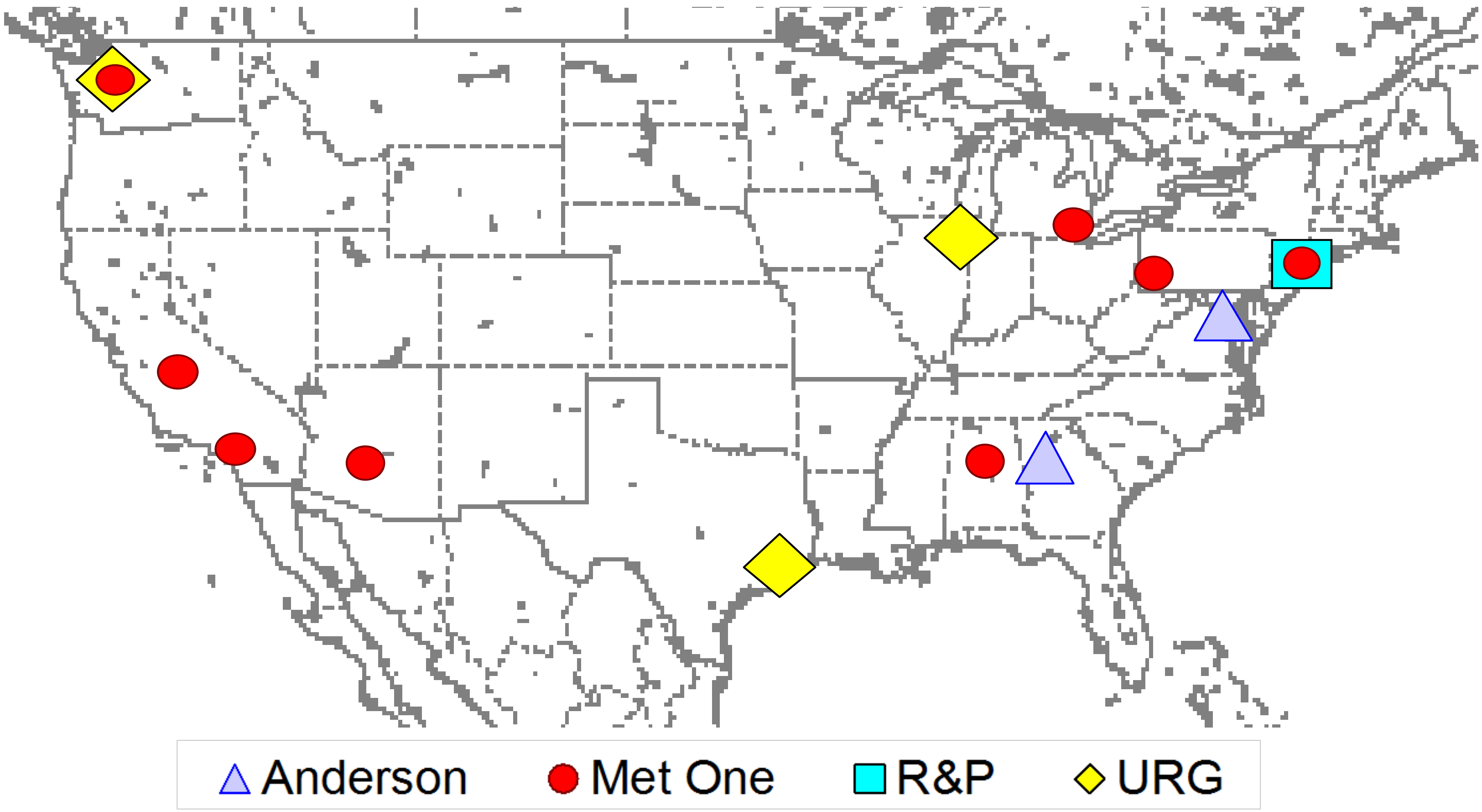
Estimating Atmospheric Scattering From Speciated PM2.5 Measurements

Sampler Intercomparison and Artifact Correction

- 1) Comparison of carbon across samplers
  - All Slides from Warren H. White, 16 April 2008 EPA workshop
- 2) Converting the CSN carbon concentrations to match IMPROVE on the average
  - Accounting for positive additive and multiplicative negative artifacts
  - Accounting for different thermal optical methods.

Comparison of IMPROVE and CSN Carbon at Collocated Sites



urban collocations of CSN and IMPROVE carbon measurements

EXPECTATION:

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

OLS REGRESSION:

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

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

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

no sampling artifact for IMPROVE EC

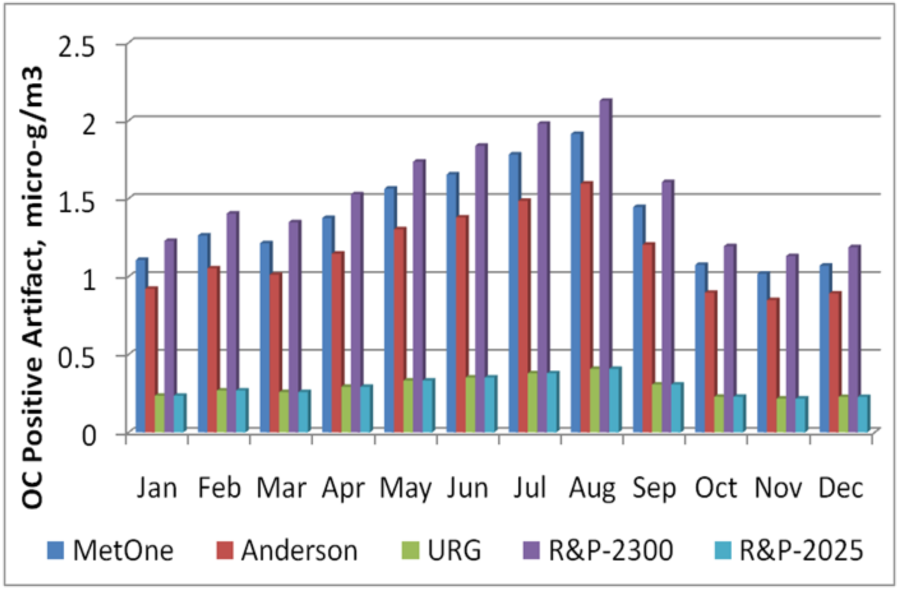
$b_{OC} = 0.22\ (+/-0.03)$

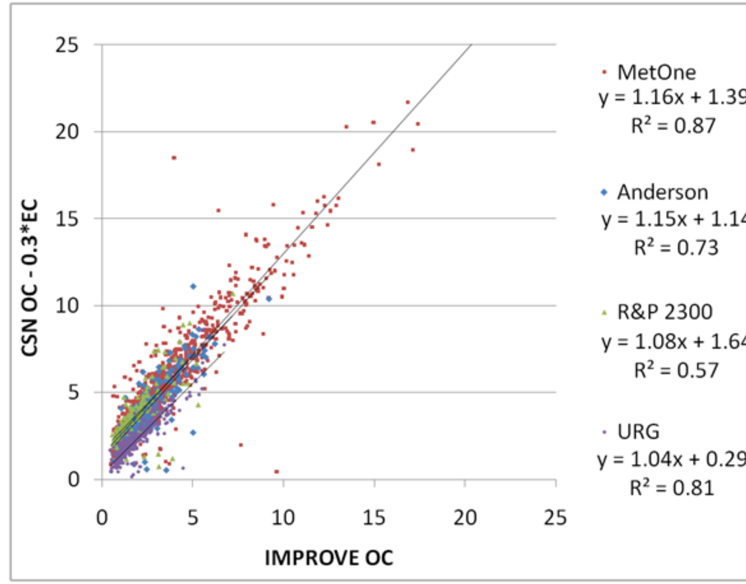
~ 20% sampling loss for IMPROVE OC

rms(e) = 0.9 ug/m^3 ($r^2 = 0.94$, n = 728)

a_{mm} → next slide

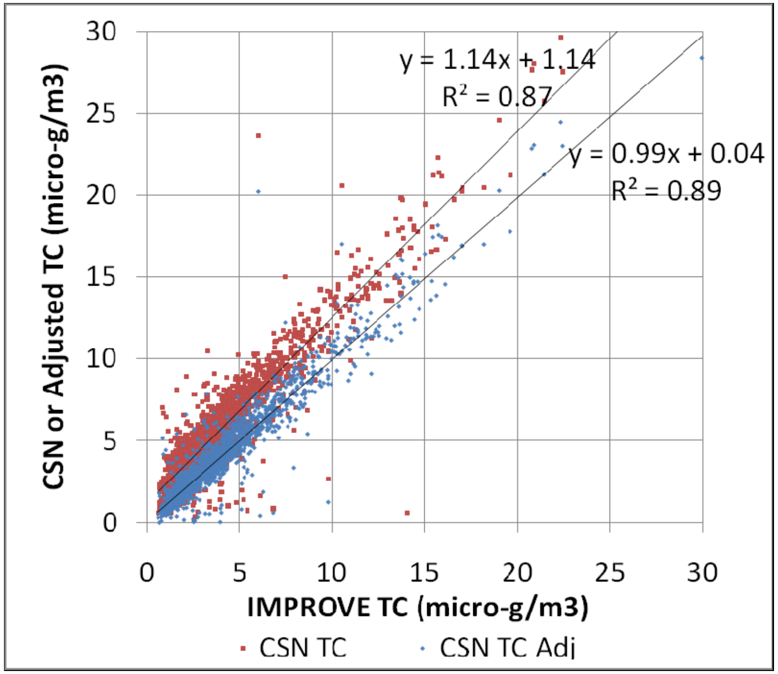
Monthly Positive Additive Artifacts

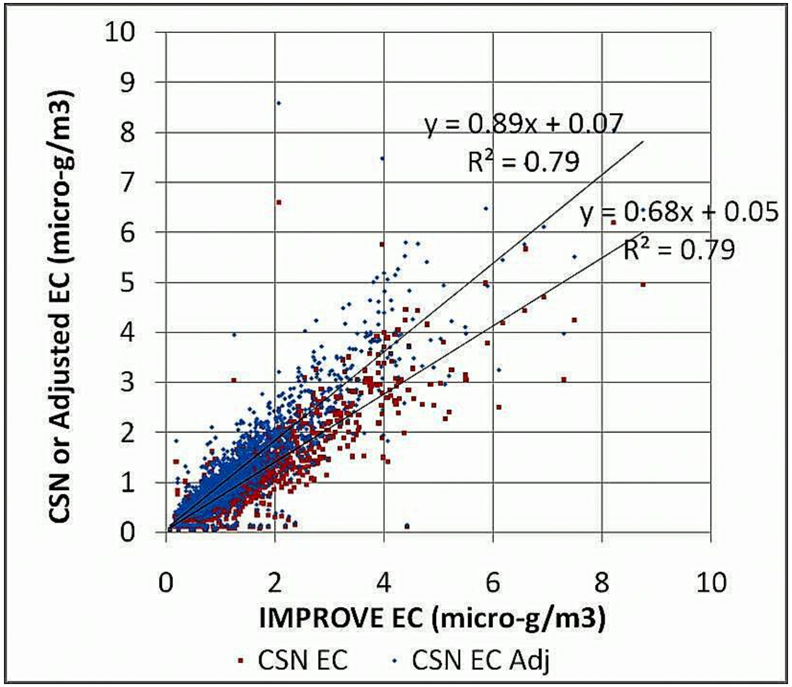




- Positive artifacts for the other were estimated by scaling the MetOne artifacts
  - For each sampler the CSN (OC – 0.3*EC) was regressed against the IMPROVE OC
  - The scalars were the ratio of the regression intercept for each sampler to the MetOne intercept
- A similar process was used to estimate the negative multiplicative artifact for each sampler

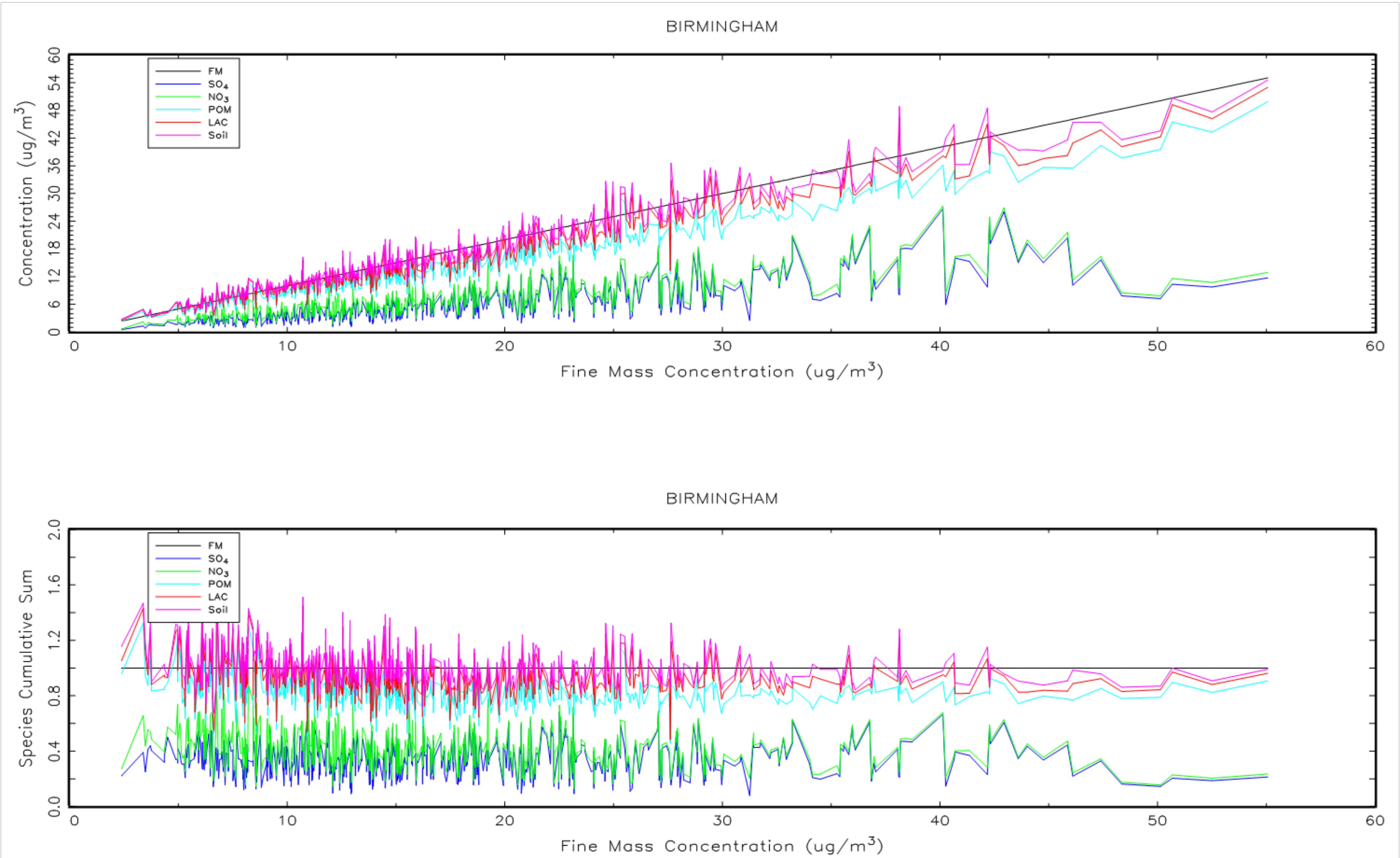
Comparison of CSN and adjusted CSN to IMPROVE Carbon





Bias Between Estimated Fine Mass and Gravimetric Fine Mass and

Bias as function of mass



Governing equations

$$FM = \left[xSO_4 + NH_4NO_3\right] f^{'}(RH_{lab}) + OCR_{oc}(lots\ \text{of stuff}) + LAC + Soil + SSf^{'}_{ss}(RH_{lab})$$

$$b_{sp} = \left[e_{xso4} xSO_4 + e_{NO3} NH_4NO_3\right] f(RH) + R_{oc} OCf_{pom}(RH) + e_{LAC} LAC + e_{soil} Soil + e_{ss} SSf_{SS}(RH)$$

- x=$(NH_4)_2SO_4/H_2SO_4$<=1.35 – lowest in summer – acidic aerosol
- $f^{'}(RH_{lab}) = \left[\frac{\rho_{mix,species}}{\rho_{species}}\right]^3 \left(\frac{D}{D_o}(RH_{lab})\right)^3$ highest in summer $(D/Do)^3 \approx 1.3$
- FM biased low because of volatilization (nitrate, SVOC, etc?)
- R_{oc}(lots of stuff) probably highest in summer months
- $f^{'}_{ss}(RH_{lab}) \approx 1.1$
- e_{xso4} and e_{nh4no3} probably highest in summer months
- $f_{pom}(RH) \approx 1.1$-1.2 – seasonal dependence ?
- $f_{ss}(RH)$ significant!

R_{oc}= ?

Mass approach

- Other= $(NH_4)_2SO_4$+NH_4NO_3+Soil+LAC+SS
- POM = FM-Other
- R_{oc}=POM vs OC (Scatter plot – average slope)

Regression approach

- FM=a_1Other+a_2OC

Seasonal Considerations

- R_{oc}(seasonal)=(FM-Other)/OC=b_o+b_1(cos(f(t))

NO_3= ?

Regression Mass approach

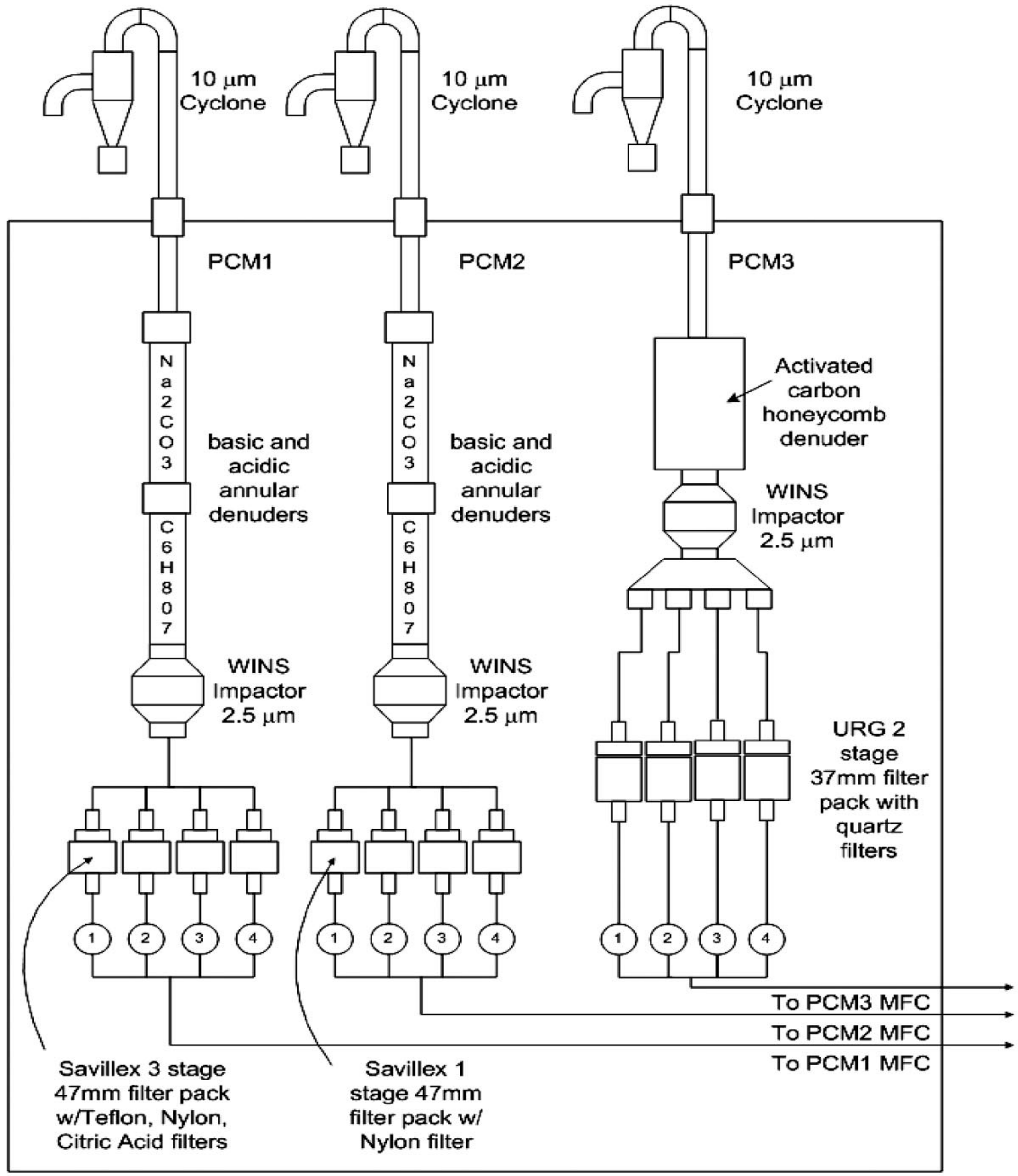
- $FM=a_1SO_4 + a_2NO_3$ (total or Teflon) f(seasonal) +…….
  - Teflon and Nylon substrates

Water= ?

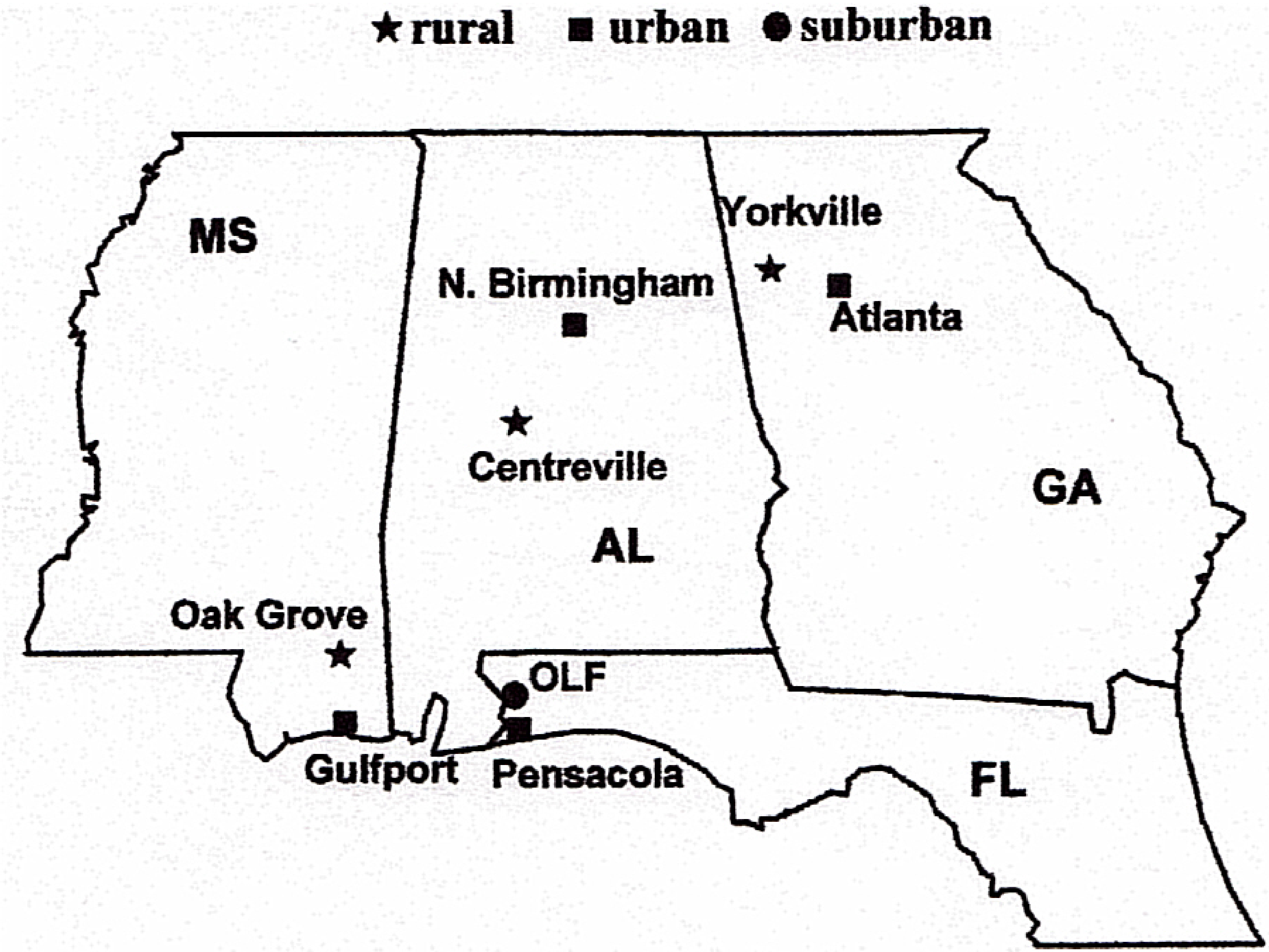
Seasonal Regression Mass approach

- $FM=a_1(SO_4 + NO_3)$ (total or Teflon) +…….

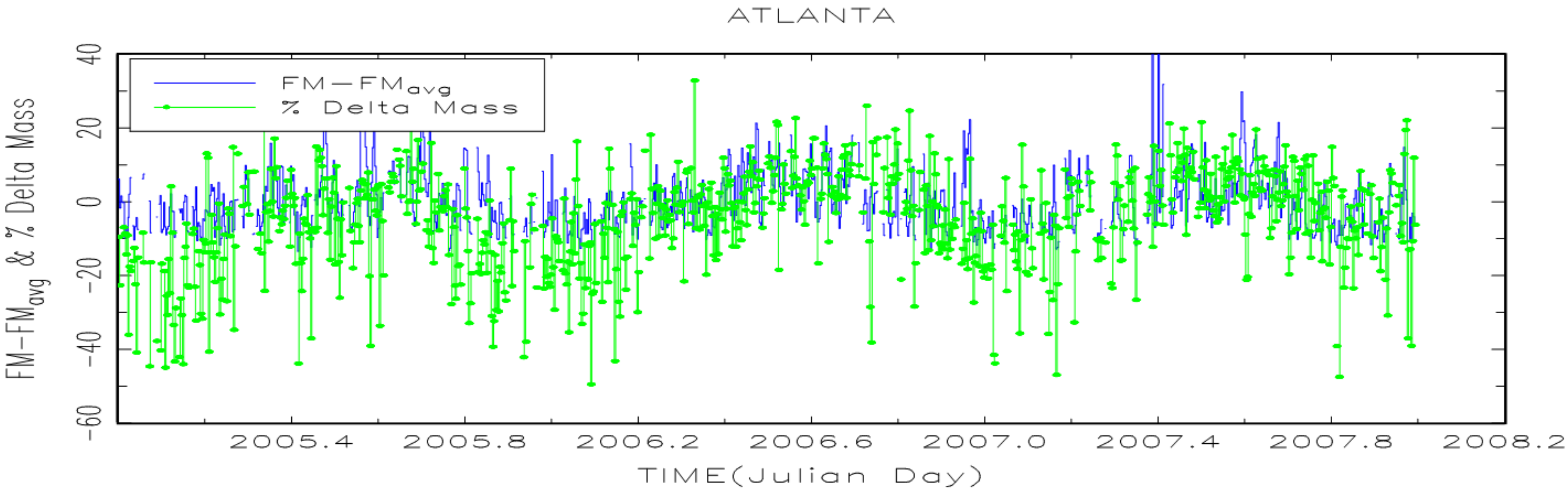
ARA Particle Composition Monitor (PCM)

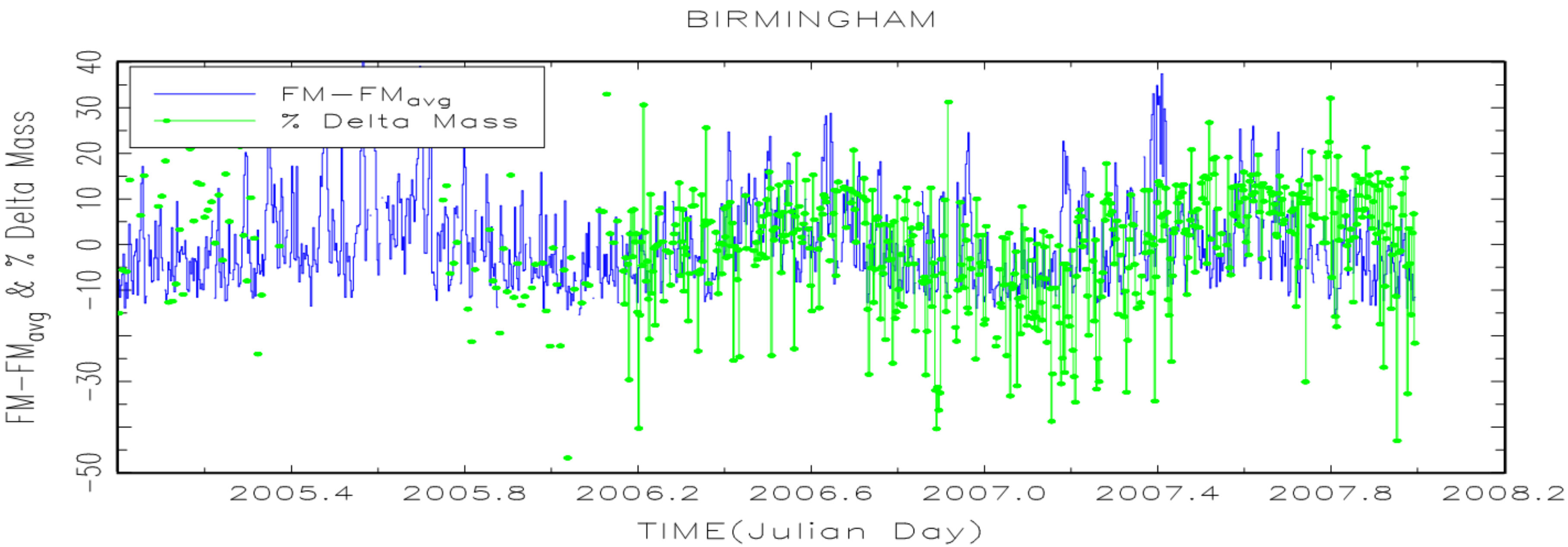


SEARCH MONITORING LOCATIONS

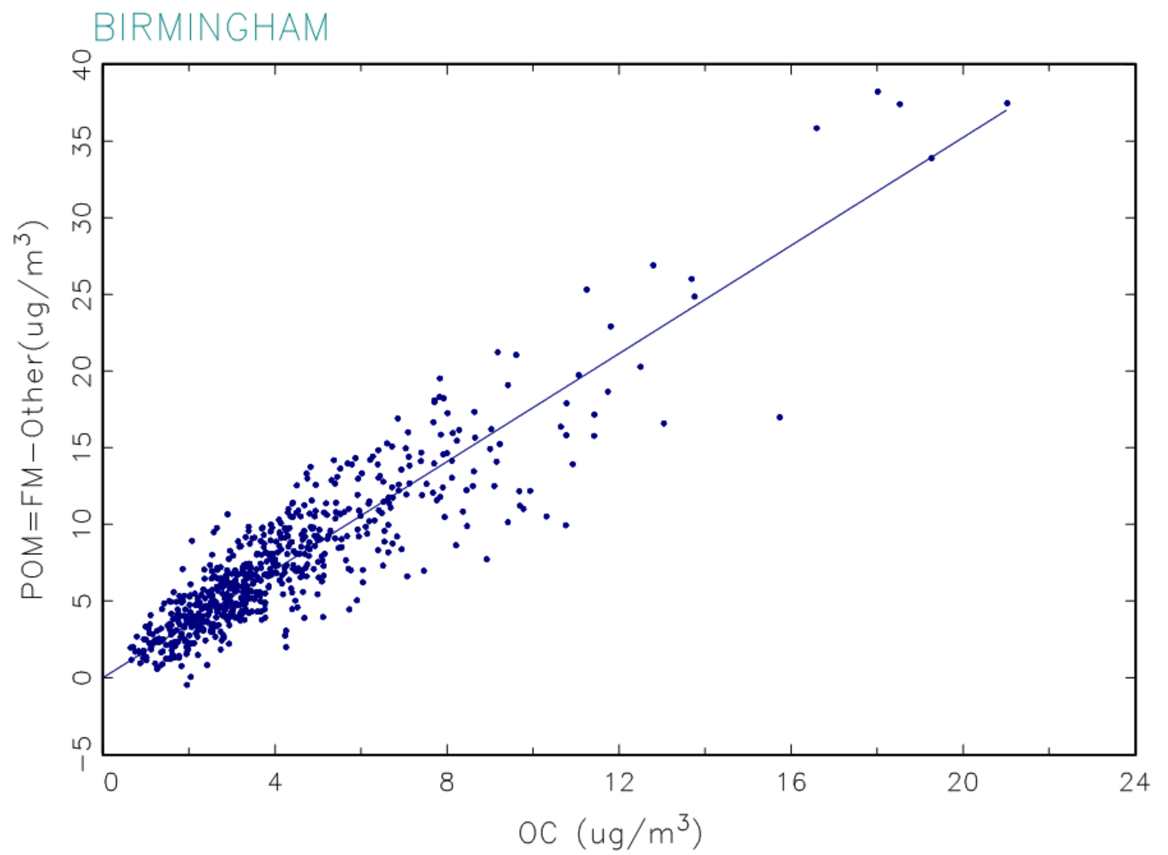


GAUSS Tue Aug 18 10:06:03 2009





POM vs OC



R2=0.81

Variable	Estimate	Standard Error	t-value	Prob >|t|
X1	1.762664	0.017235	102.274676	0.000

Seasonal Curve Fit Analysis

Roc(seasonal)=(FM-Other)/OC=bo+b1(cos(f(t))

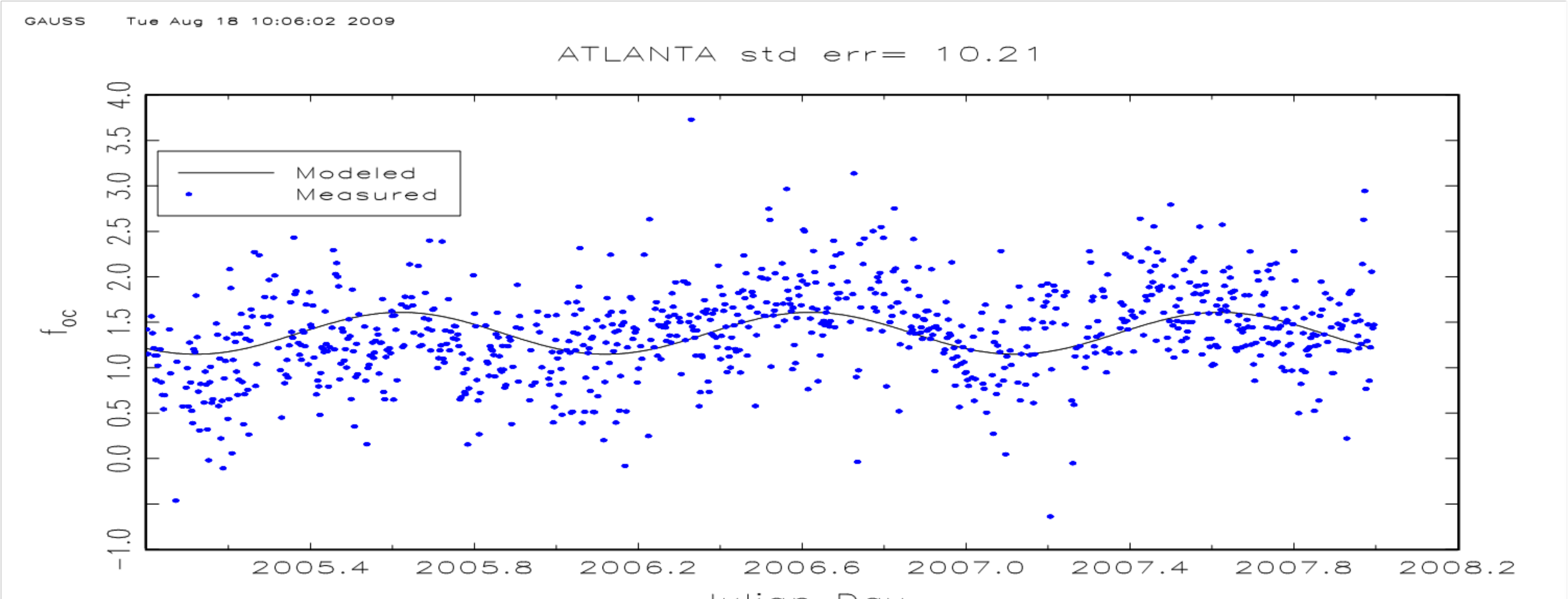
Birmingham

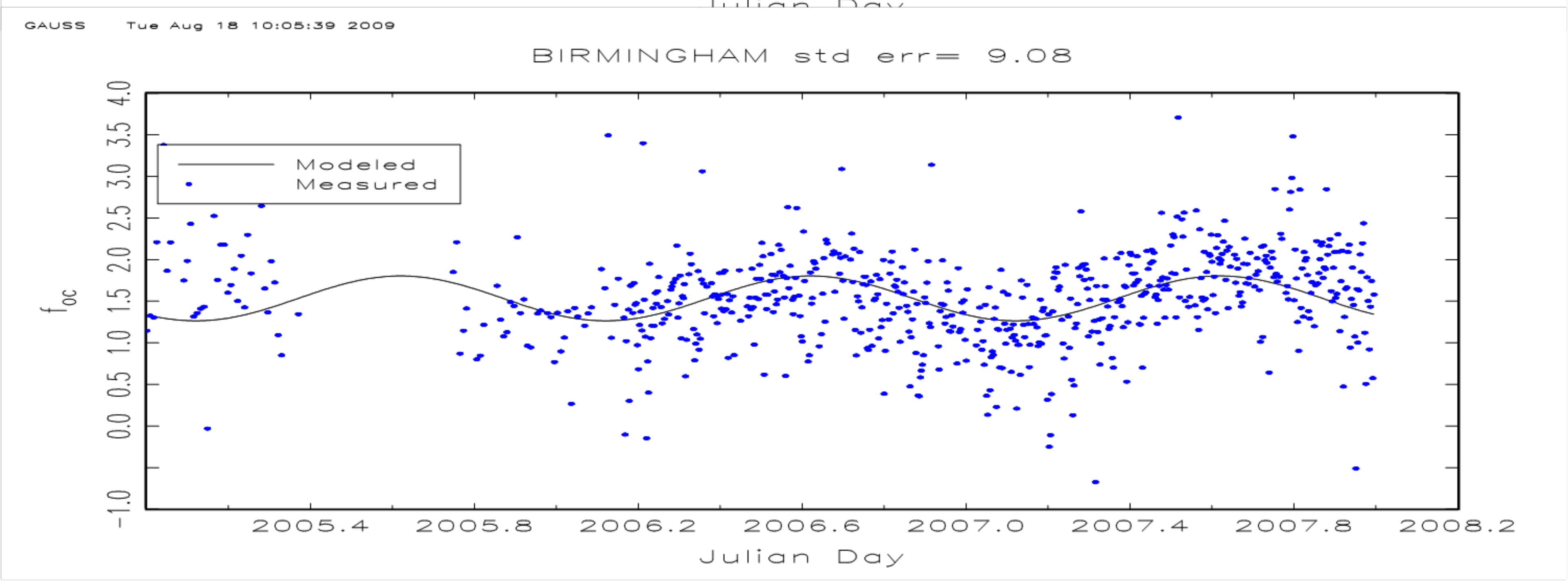
Curvefit – seasonal variablity

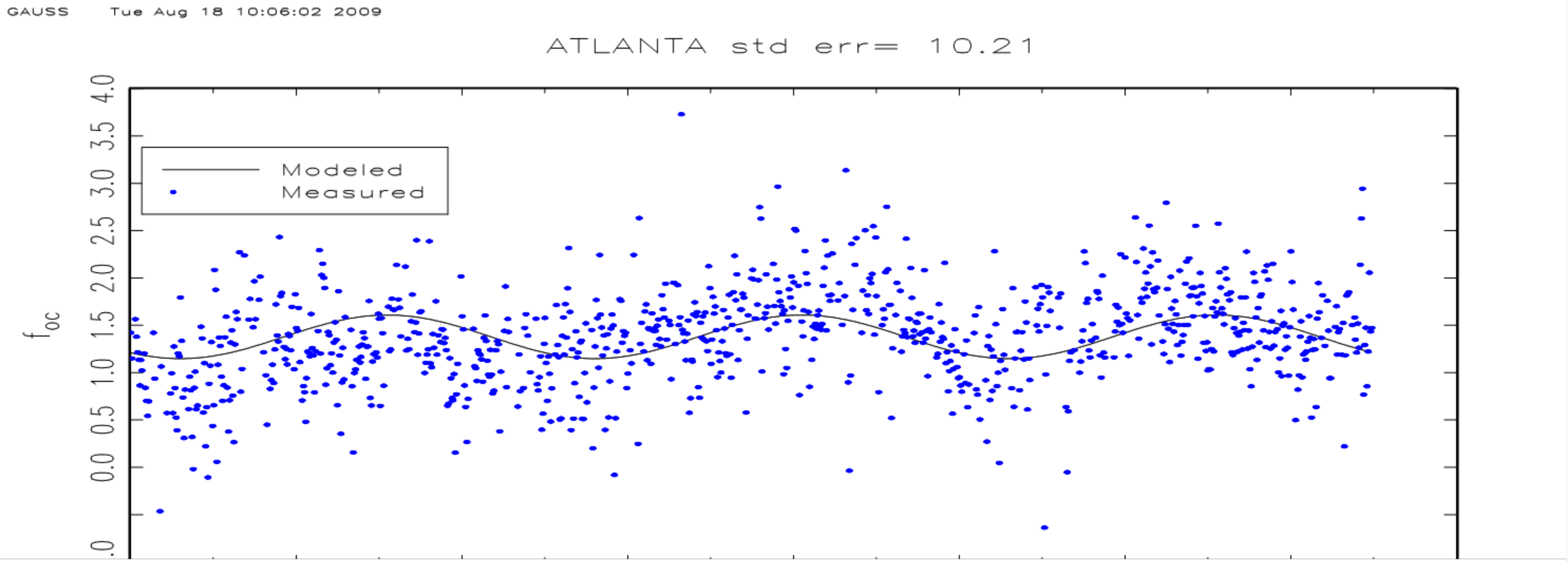
Number of cases 652

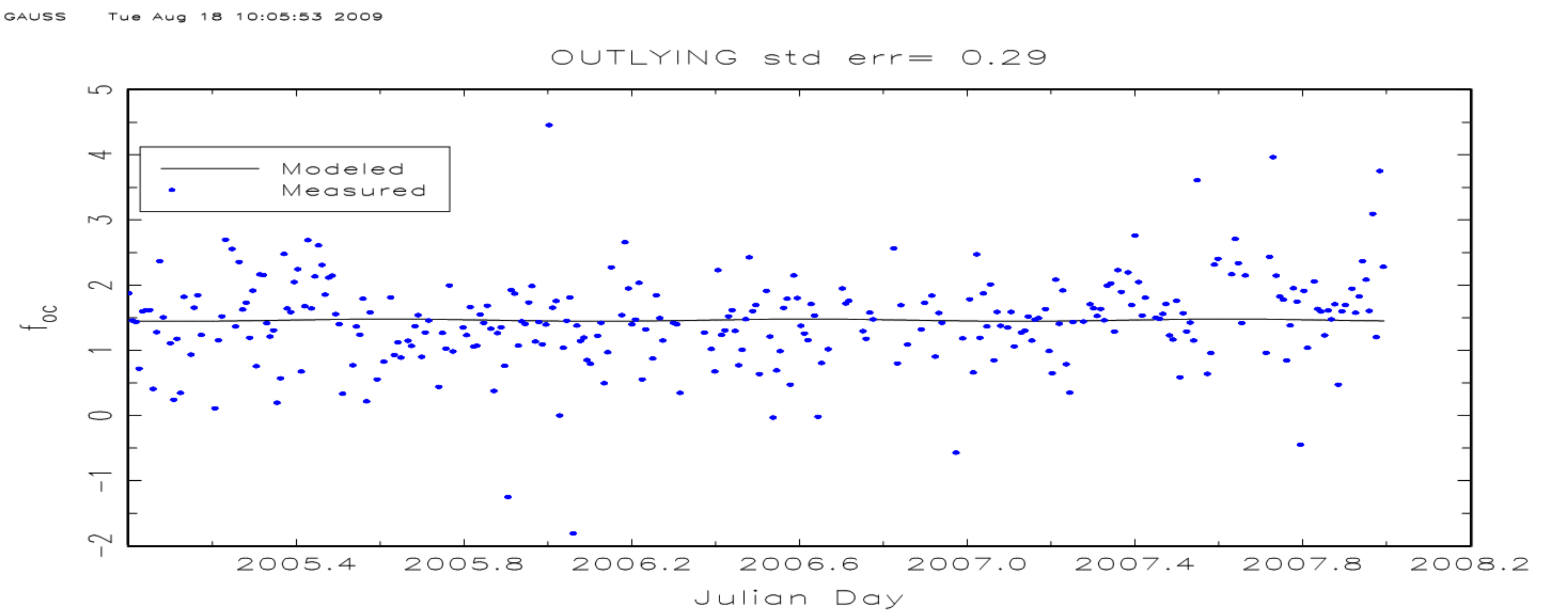
Parameters	Estimates	Std. err.	Est./s.e.	Prob.	Gradient
P01	1.524020	0.036735	41.487	0.0000	-0.000024
P02	0.619287	0.060824	10.182	0.0000	0.000014

R_{oc}=1.83


GAUSS Tue Aug 18 10:06:02 2009
ATLANTA std err= 10.21
Modeled
Measured
f_{oc}
-1.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2


GAUSS Tue Aug 18 10:05:39 2009
BIRMINGHAM std err= 9.08
Modeled
Measured
f_{oc}
-1.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
Julian Day


GAUSS Tue Aug 18 10:06:02 2009
ATLANTA std err= 10.21
Modeled
Measured
f_{oc}
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

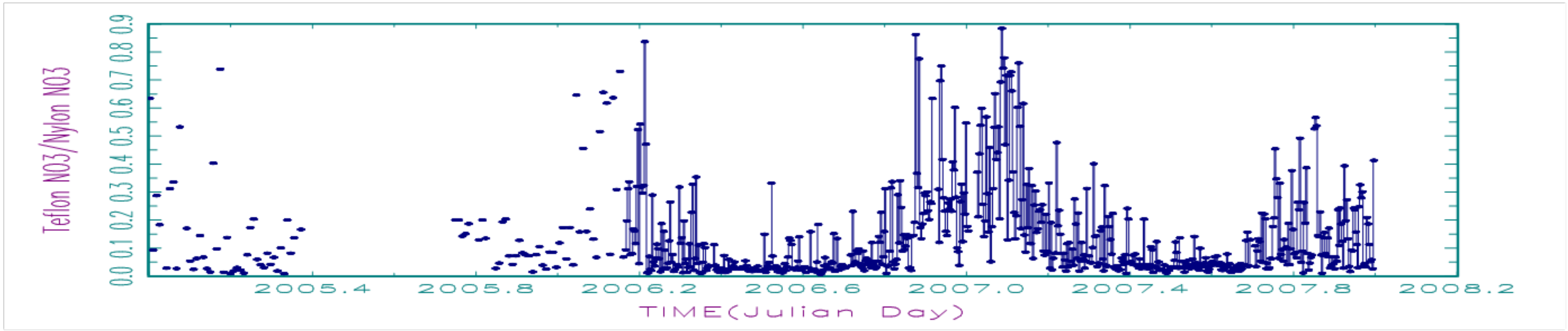

GAUSS Tue Aug 18 10:05:53 2009
OUTLYING std err= 0.29
Modeled
Measured
f_{oc}
5
4
3
2
1
0
−1
−2
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
Julian Day

Estimated water

Birmingham $FM=a_1 Other+a_2 OC$

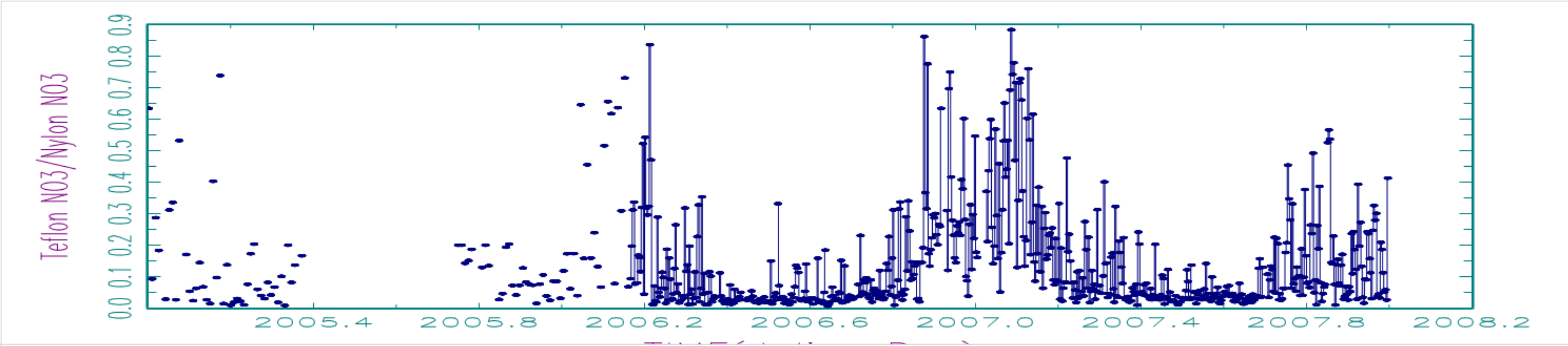
R-squared: 0.95

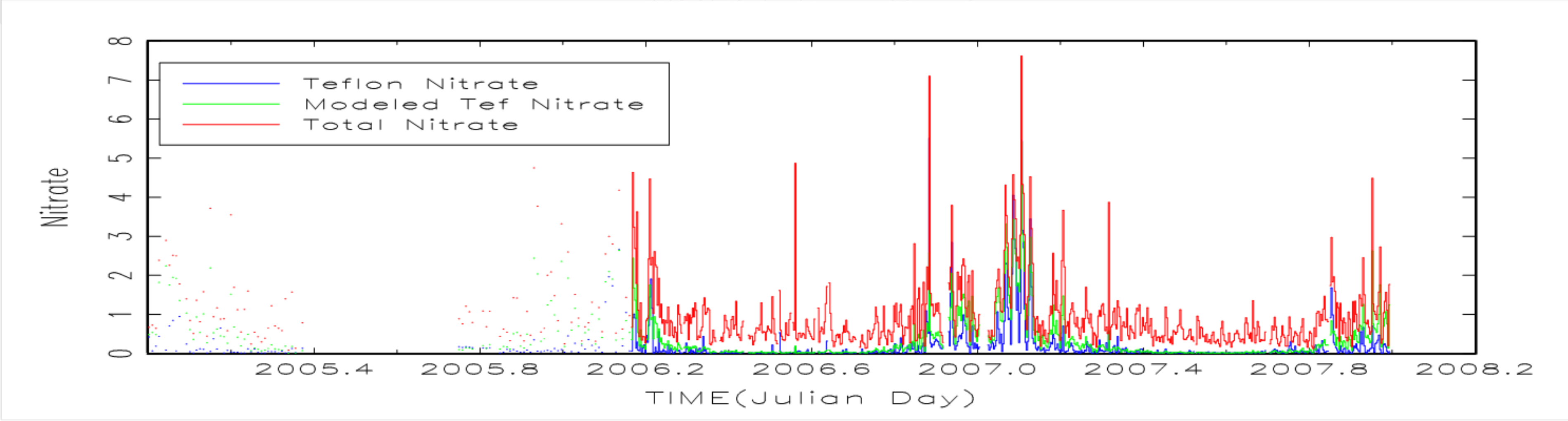
Variable	Estimate	Standard Error	t-value	Prob >|t|
OTHER	**1.112528**	0.017839	62.365958	0.000
OC	1.533060	0.040065	38.264717	0.000

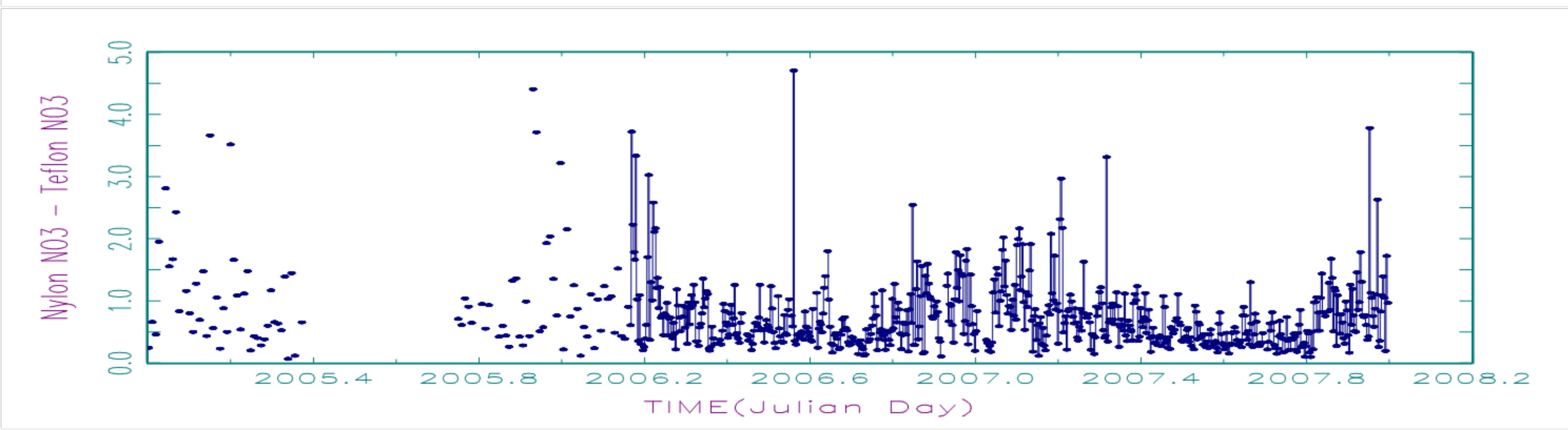


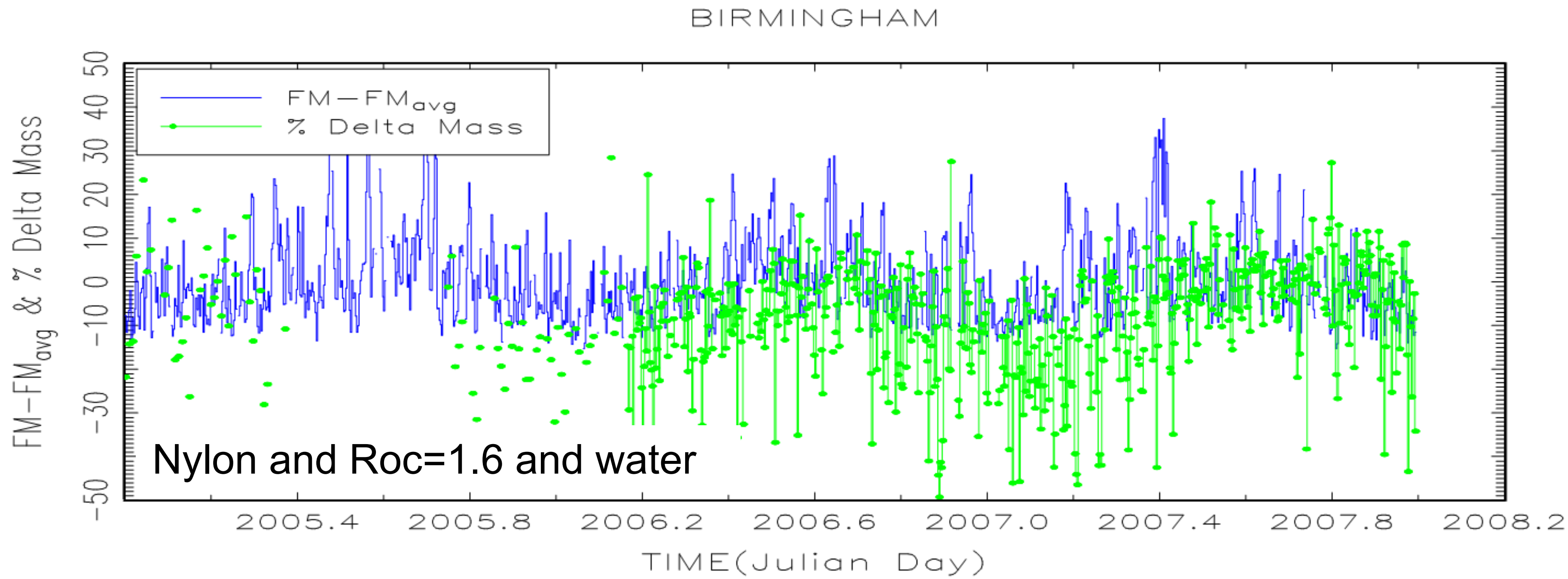
- Other= $(NH_4)_2SO_4$+NH_4NO_3+Soil+LAC+SS
- POM = FM-Other
- R_{oc}(seasonal)=(FM-Other)/OC=b_o+b_1(cos(f(t))

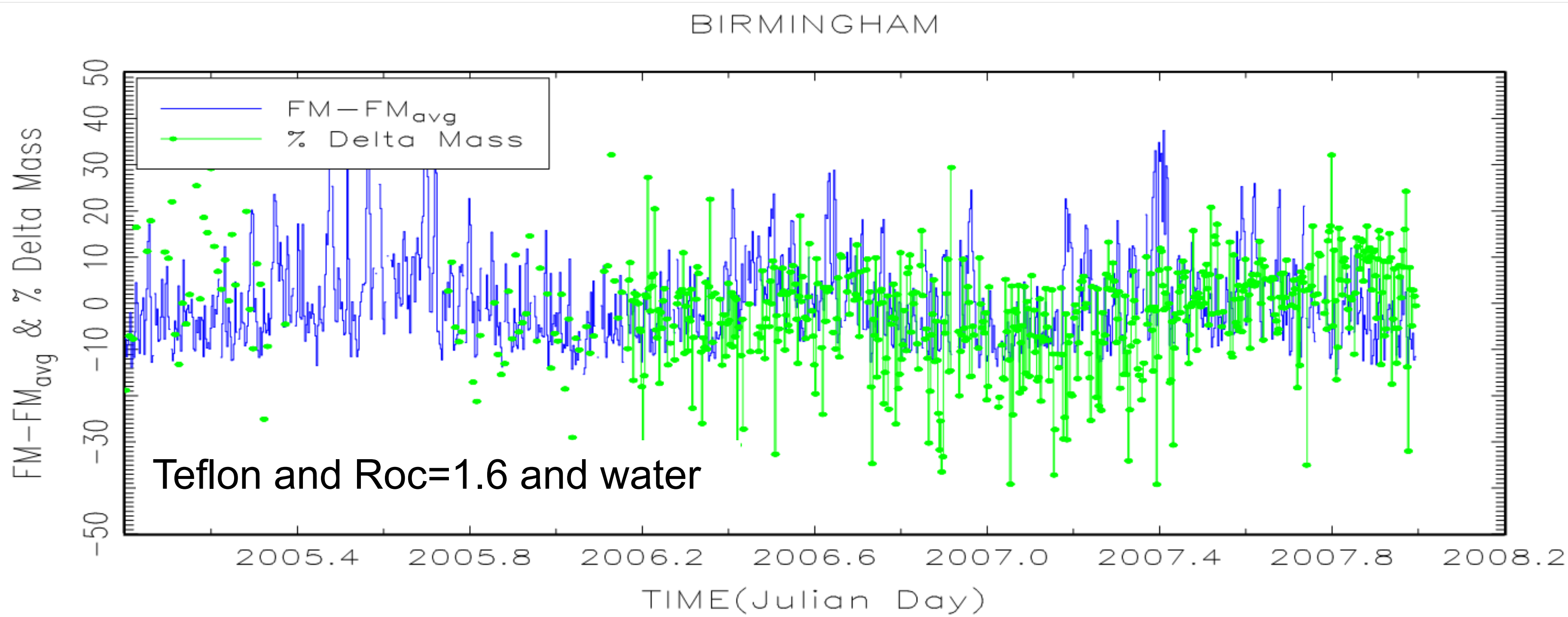
- How should nitrate volatilization affect seasonality in FM
  - Would think that FM-(NH_4NO_3+…..) is to low in summer and maybe about right in the winter – increase FM in summer serve to make the apparent seasonality in Roc even bigger

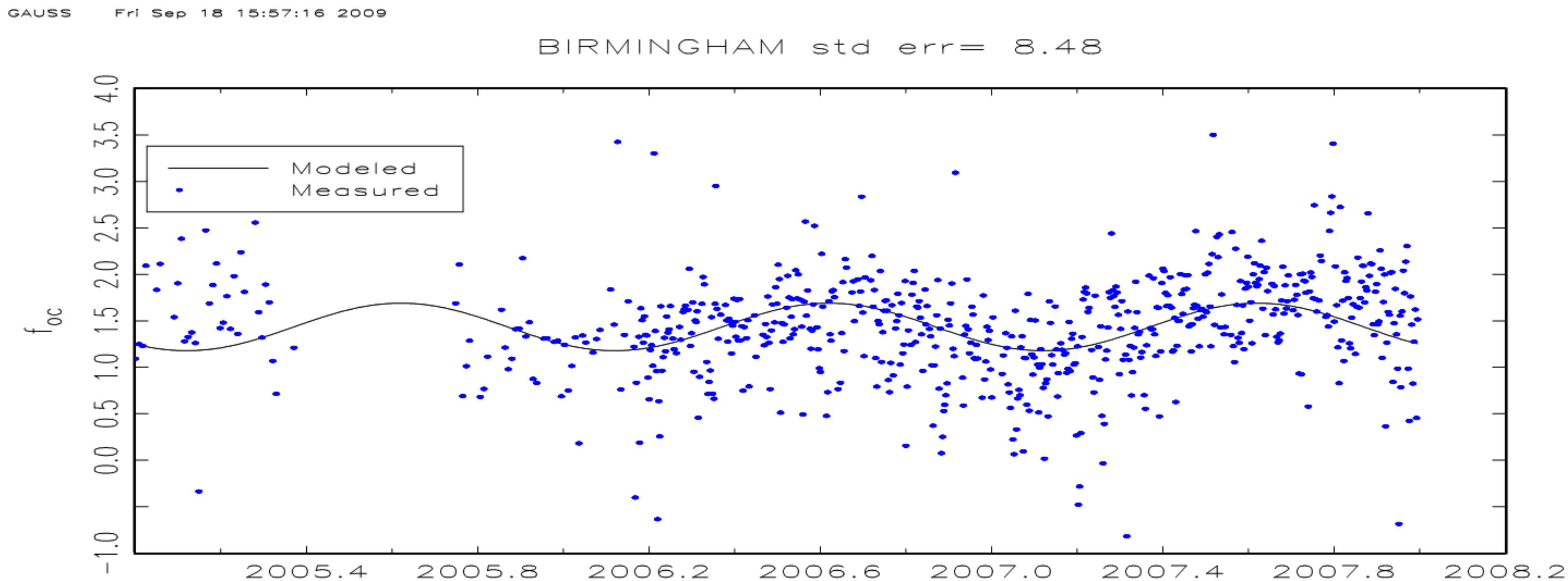

Teflon NO3/Nylon NO3
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
2005.4 2005.8 2006.2 2006.6 2007.0 2007.4 2007.8 2008.2

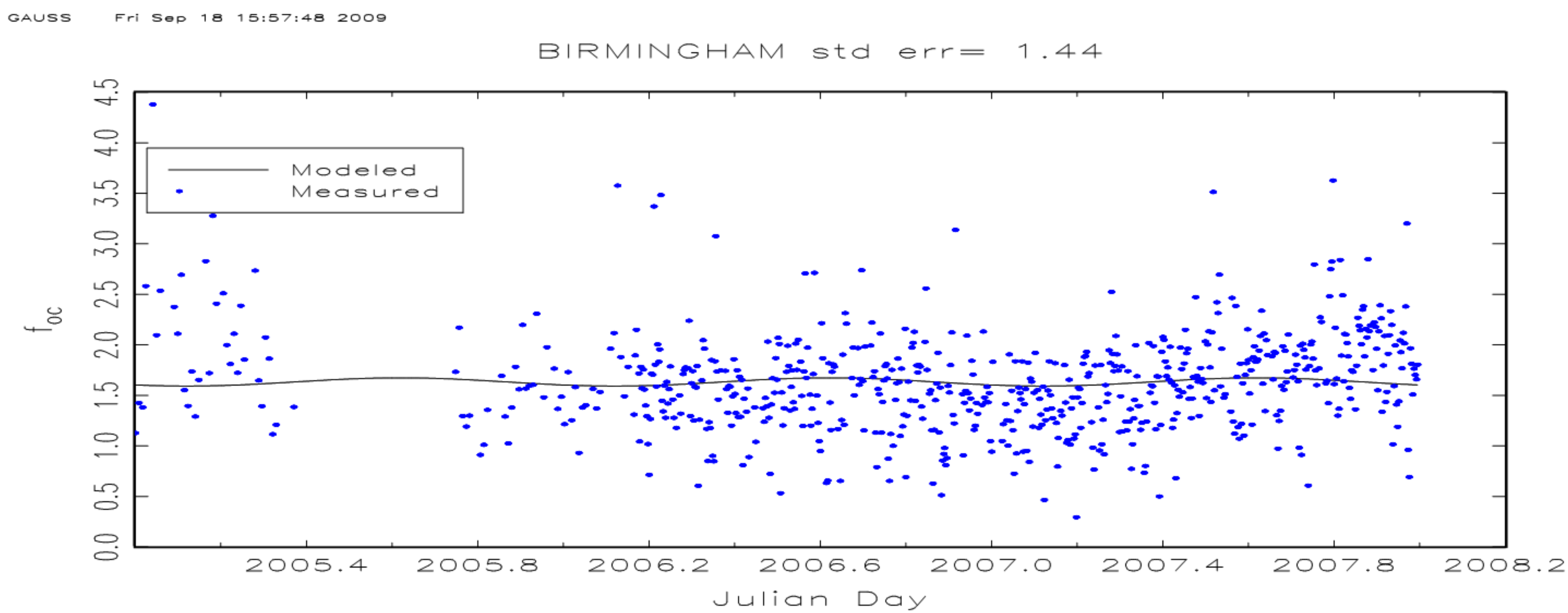

Teflon Nitrate
Modeled Tef Nitrate
Total Nitrate
Nitrate
0 1 2 3 4 5 6 7 8
2005.4 2005.8 2006.2 2006.6 2007.0 2007.4 2007.8 2008.2
TIME(Julian Day)

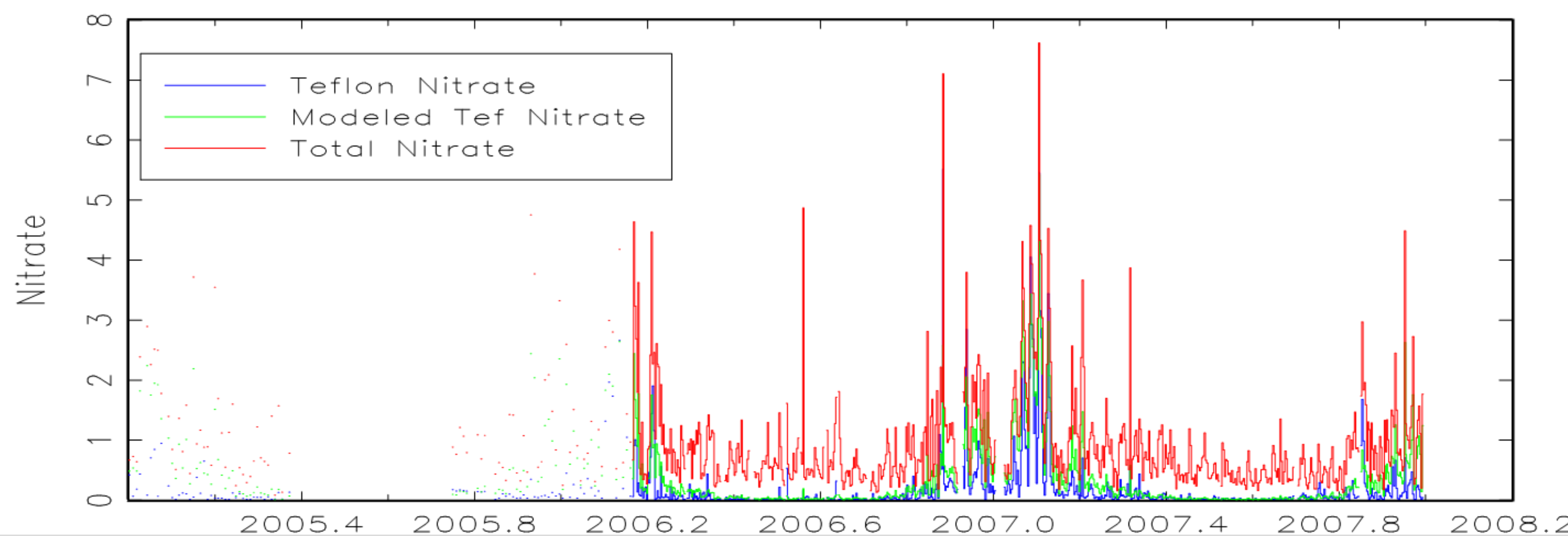

Nylon NO3 – Teflon NO3
0.0 1.0 2.0 3.0 4.0 5.0
2005.4 2005.8 2006.2 2006.6 2007.0 2007.4 2007.8 2008.2
TIME(Julian Day)

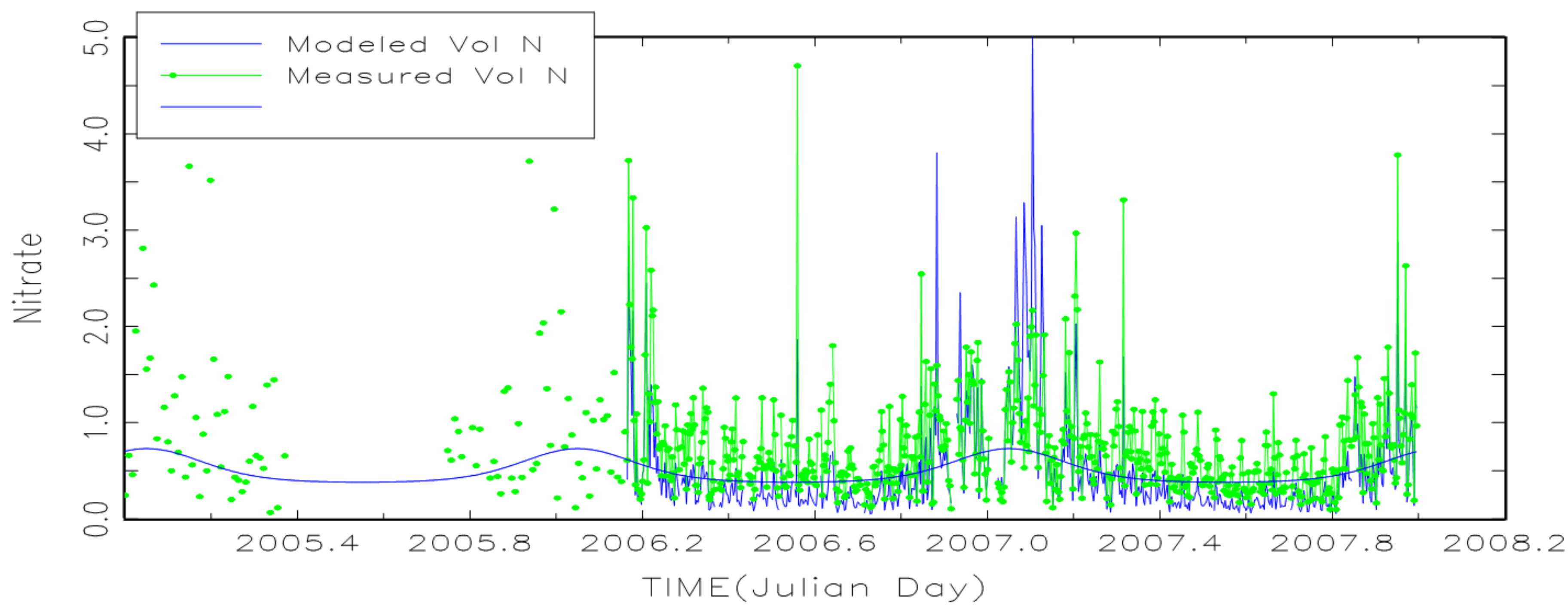

BIRMINGHAM
FM−FM$_{avg}$
% Delta Mass
FM-FM$_{avg}$ & % Delta Mass
-50
-30
-10
0
10
20
30
40
50
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
TIME(Julian Day)
Nylon and Roc=1.6 and water


BIRMINGHAM
FM−FM$_{avg}$
% Delta Mass
FM-FM$_{avg}$ & % Delta Mass
-50
-30
-10
0
10
20
30
40
50
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
TIME(Julian Day)
Teflon and Roc=1.6 and water


GAUSS Fri Sep 18 15:57:16 2009
BIRMINGHAM std err= 8.48
Modeled
Measured
f_{oc}
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2


GAUSS Fri Sep 18 15:57:48 2009
BIRMINGHAM std err= 1.44
Modeled
Measured
f_{oc}
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
Julian Day

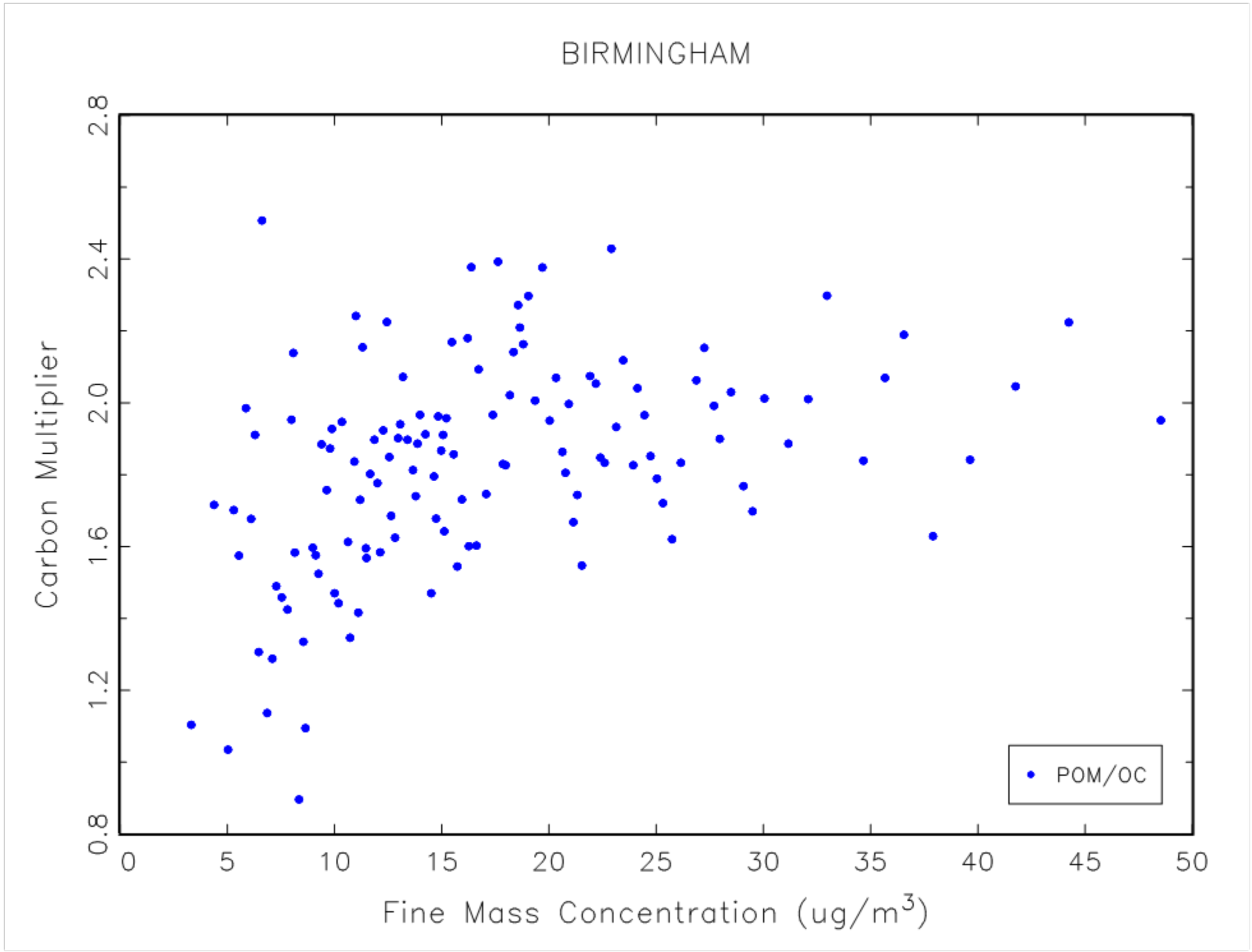

Teflon Nitrate
Modeled Tef Nitrate
Total Nitrate
Nitrate
0
1
2
3
4
5
6
7
8
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2


Modeled Vol N
Measured Vol N
Nitrate
0.0
1.0
2.0
3.0
4.0
5.0
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
TIME(Julian Day)

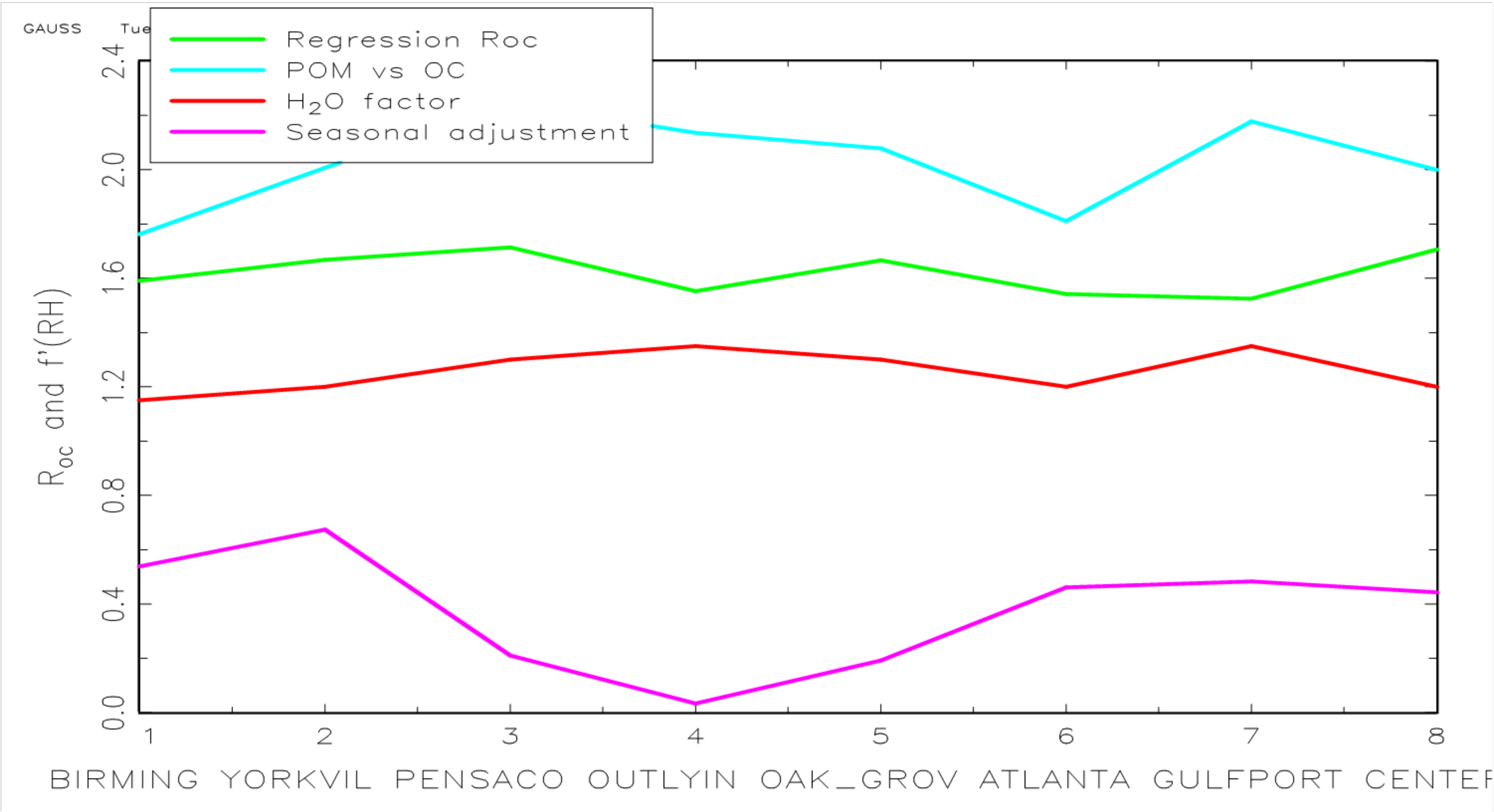
Birmingham Summary Statistics

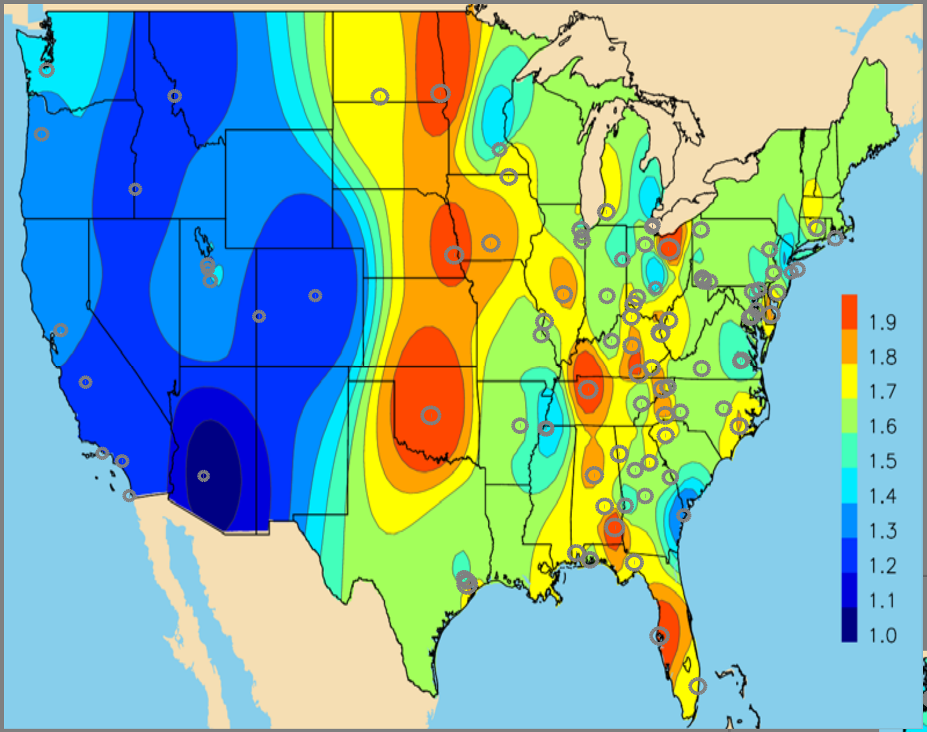
Variable	Mean	Std Dev	Variance	Minimum	Maximum	Valid
FM	17.66	9.54	90.97	2.31	57.89	1037
ASULFATE	6.24	4.43	19.62	0.50	29.58	765
ANO3	0.96	0.87	0.76	0.08	7.62	727
WATER	1.04	0.63	0.39	0.09	4.09	727
POM	5.72	3.90	15.20	0.60	30.52	772
LAC	1.85	1.54	2.37	0.12	11.77	771
SOIL	1.10	0.90	0.81	0.02	10.38	876
RH	4.97	4.05	16.41	1.00	43.94	1069
BSCAT	54.65	34.81	1211.84	5.13	224.08	1070
FACCB1	1.04	0.04	0.00	1.00	1.50	1069
FACAAB2	1.03	0.04	0.00	1.00	1.40	1069
FACCNCAL	1.00	0.03	0.00	1.00	1.64	1069
FACCONE	1.02	0.04	0.00	1.00	1.52	1069
FACCOLD	1.00	0.01	0.00	1.00	1.15	1069

R_{OC} vs FM

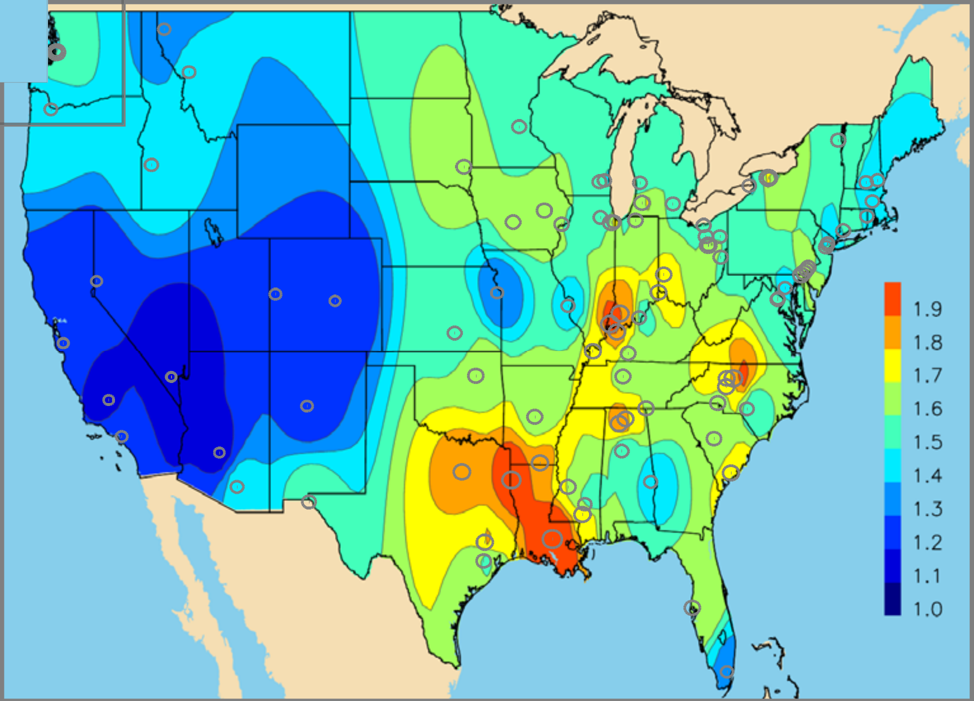

BIRMINGHAM
Carbon Multiplier
2.8
2.4
2.0
1.6
1.2
0.8
0
5
10
15
20
25
30
35
40
45
50
Fine Mass Concentration (ug/m3)
POM/OC

R_{oc} and f'(RH)

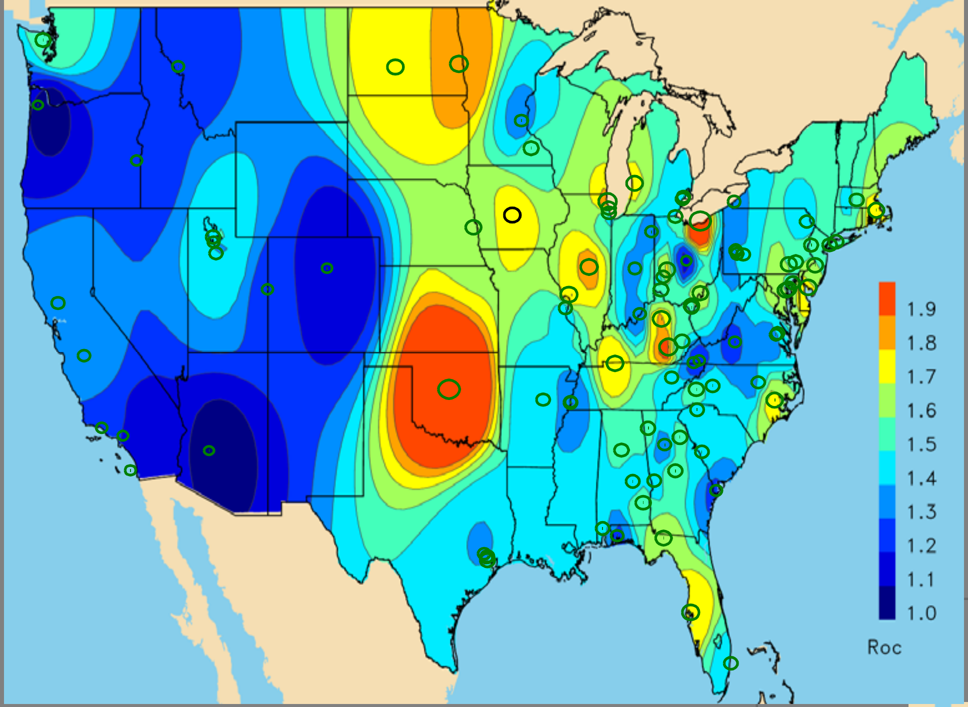

GAUSS
Tue
Regression Roc
POM vs OC
H2O factor
Seasonal adjustment
R_oc and f'(RH)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
1
2
3
4
5
6
7
8
BIRMING YORKVIL PENSACO OUTLYIN OAK_GROV ATLANTA GULFPORT CENTER



POM vs OC suburban

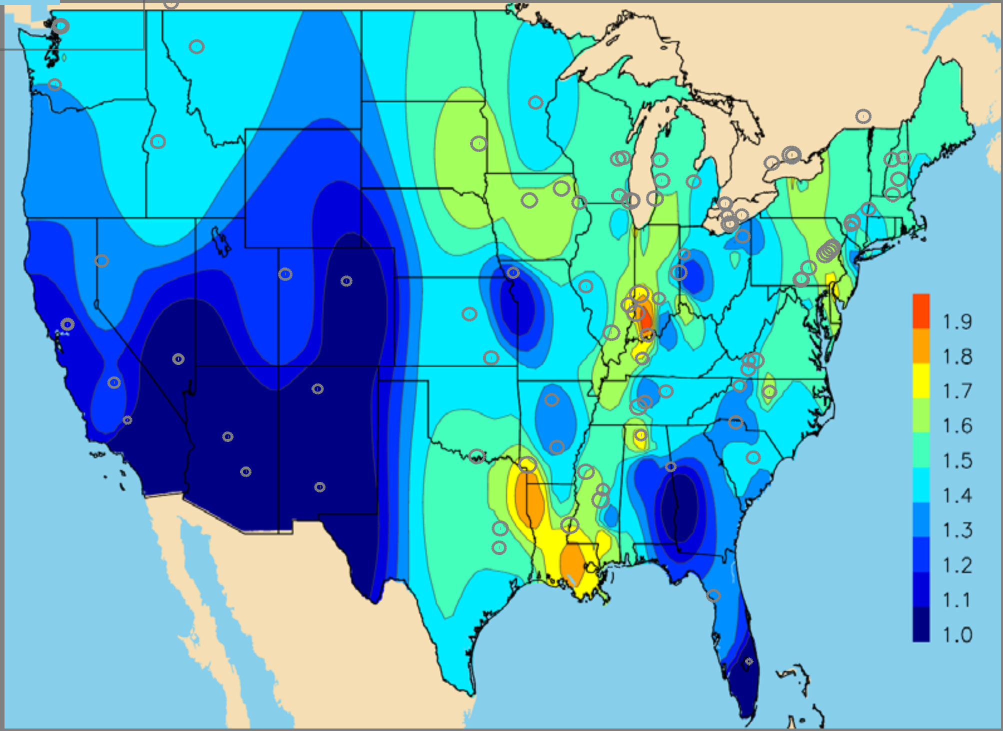


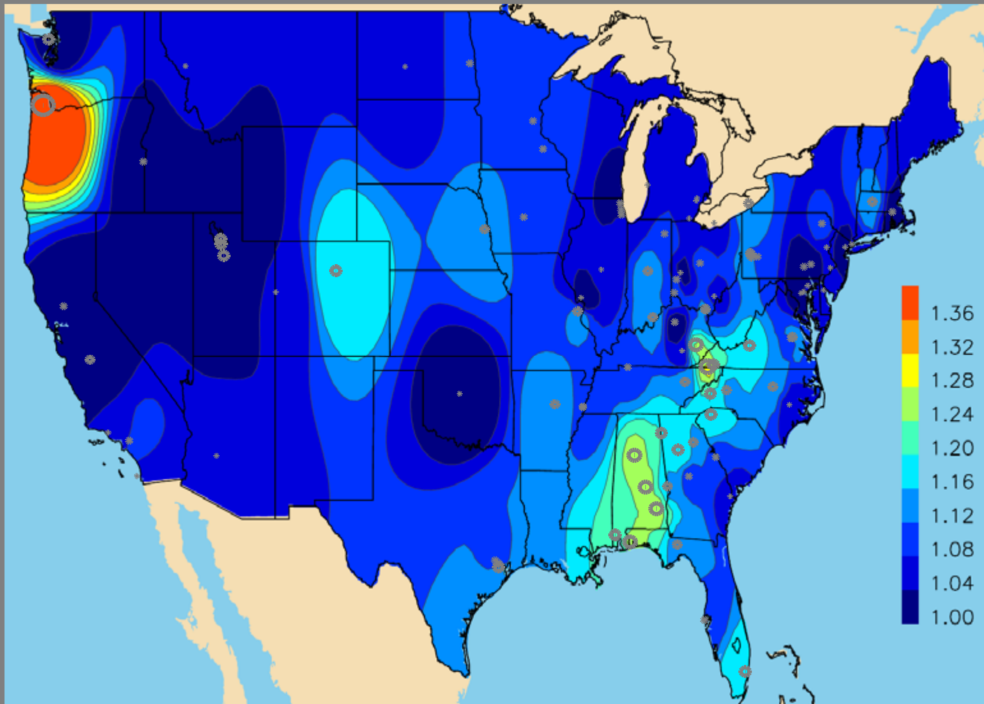
POM vs OC urban



Regression Suburban

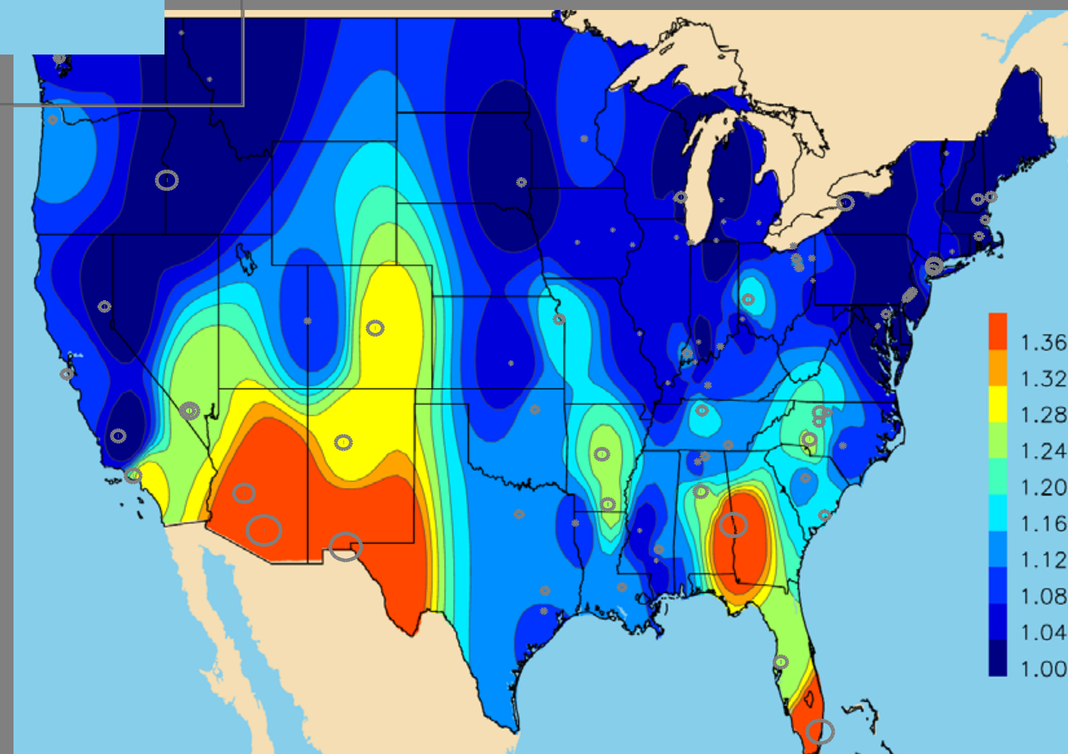
Regression urban



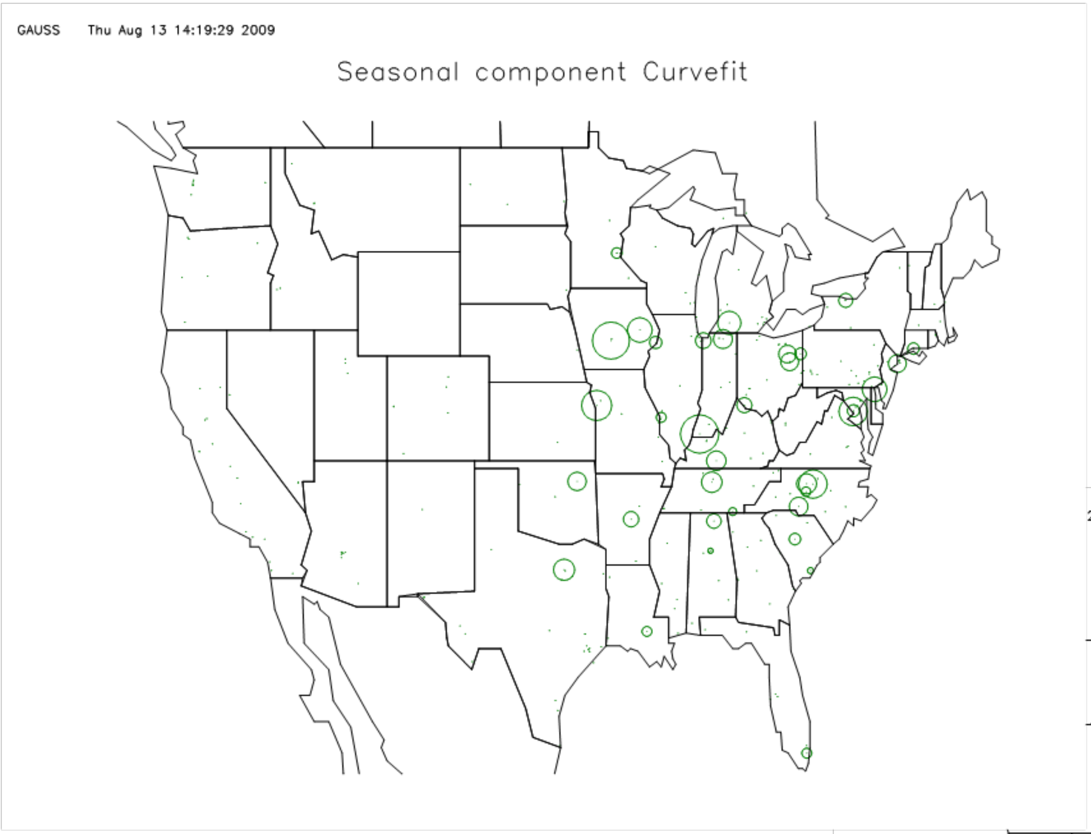


Water Suburban

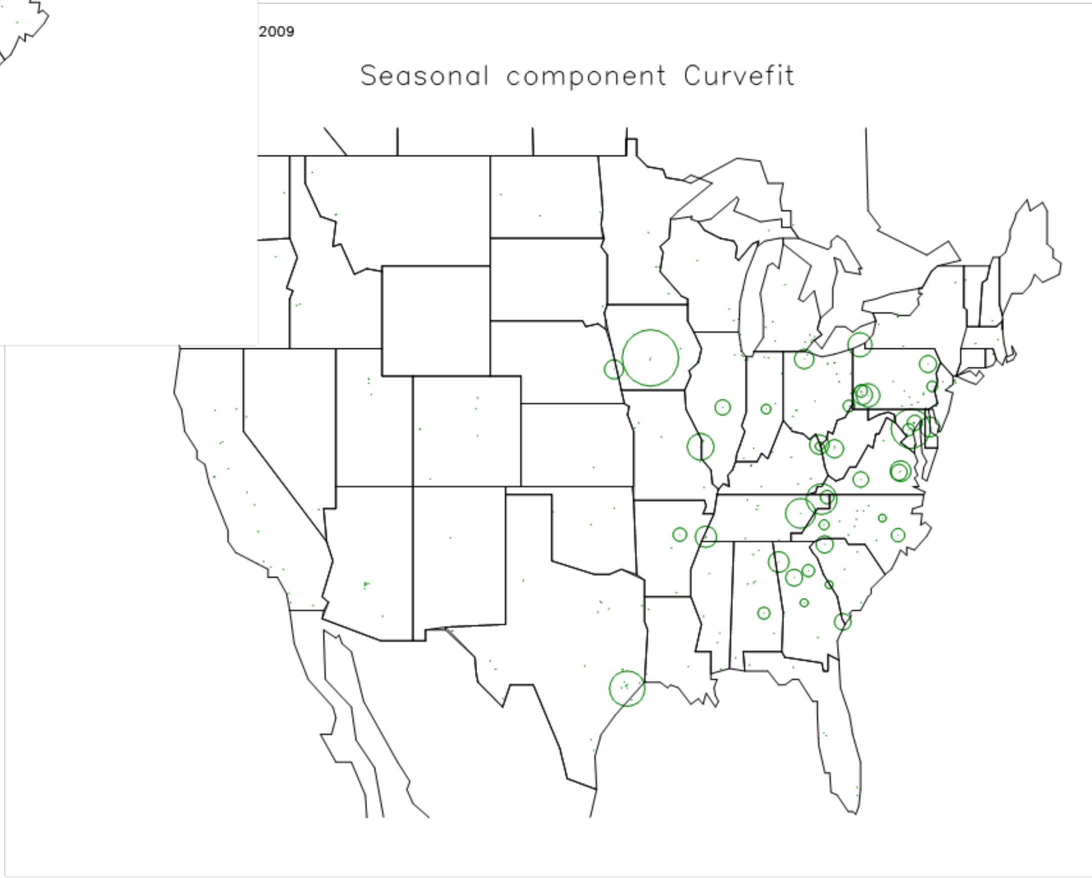
Water Urban



Urban seasonal modulation after correction for water max =1+1

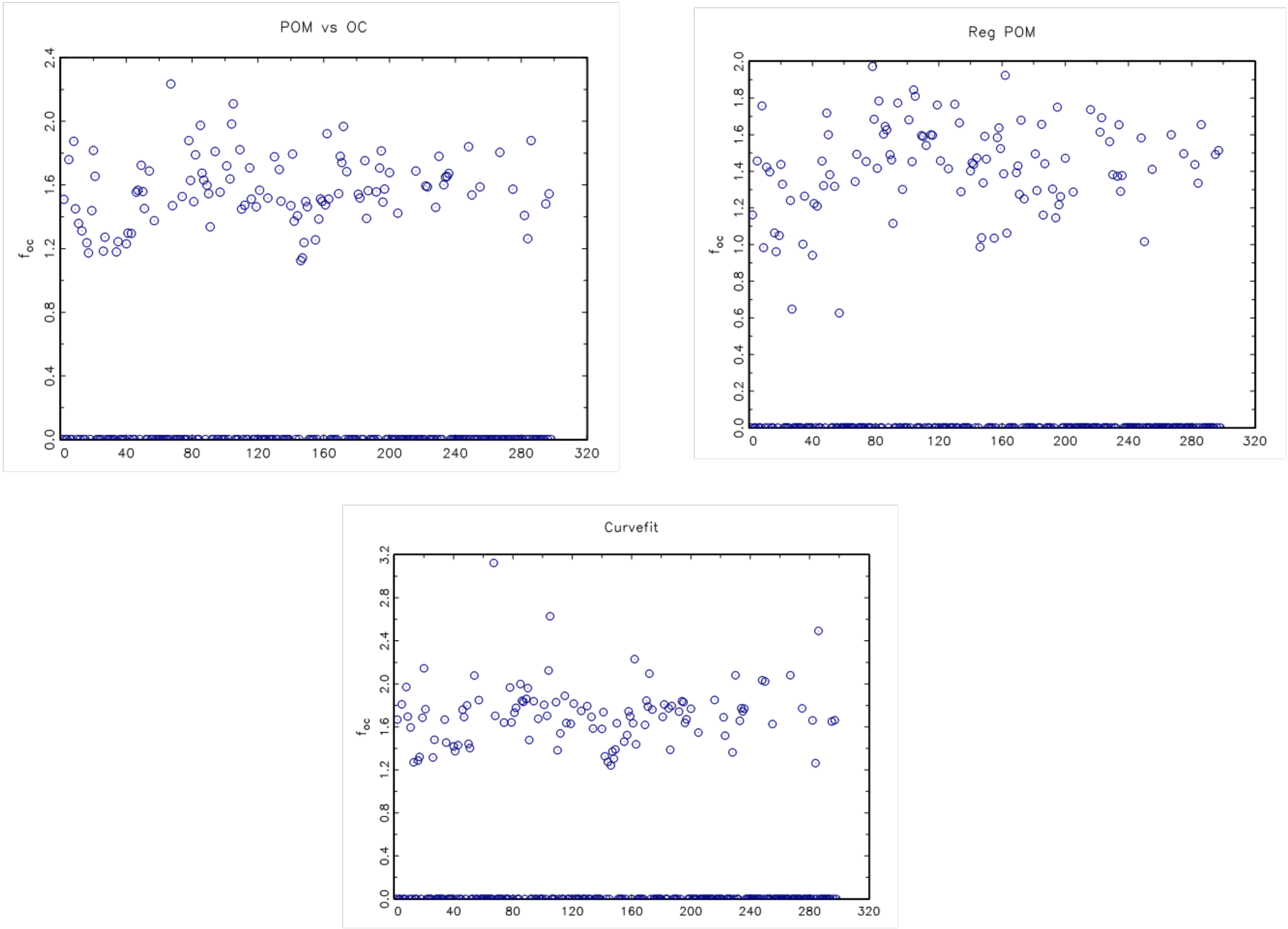


City Center

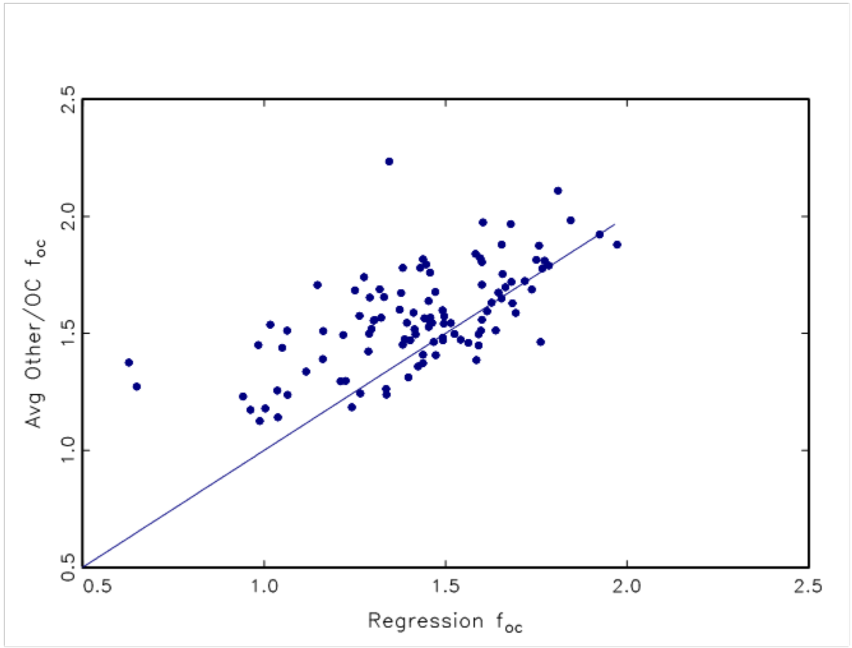


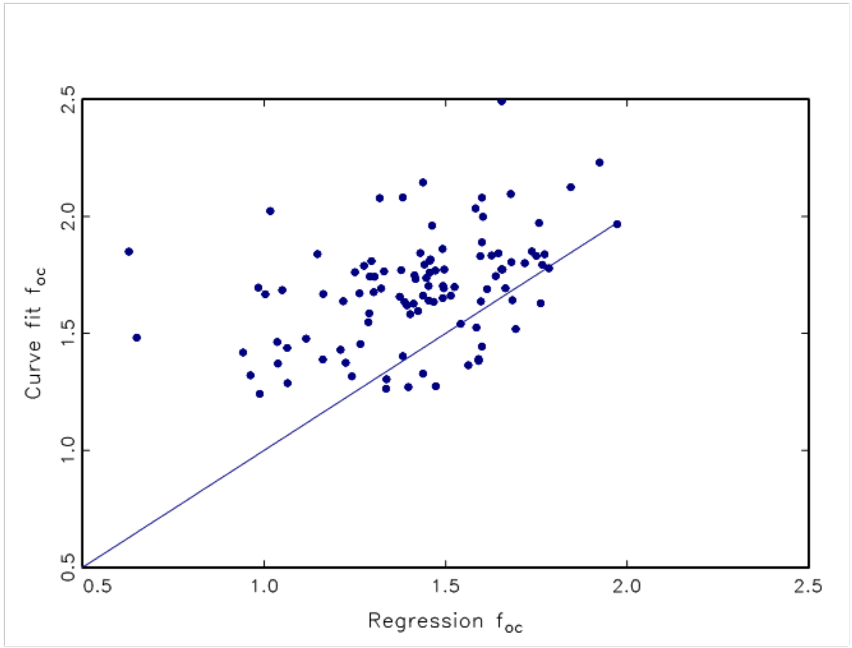
Suburban

R_{oc} vs STN Urban sites for different estimates



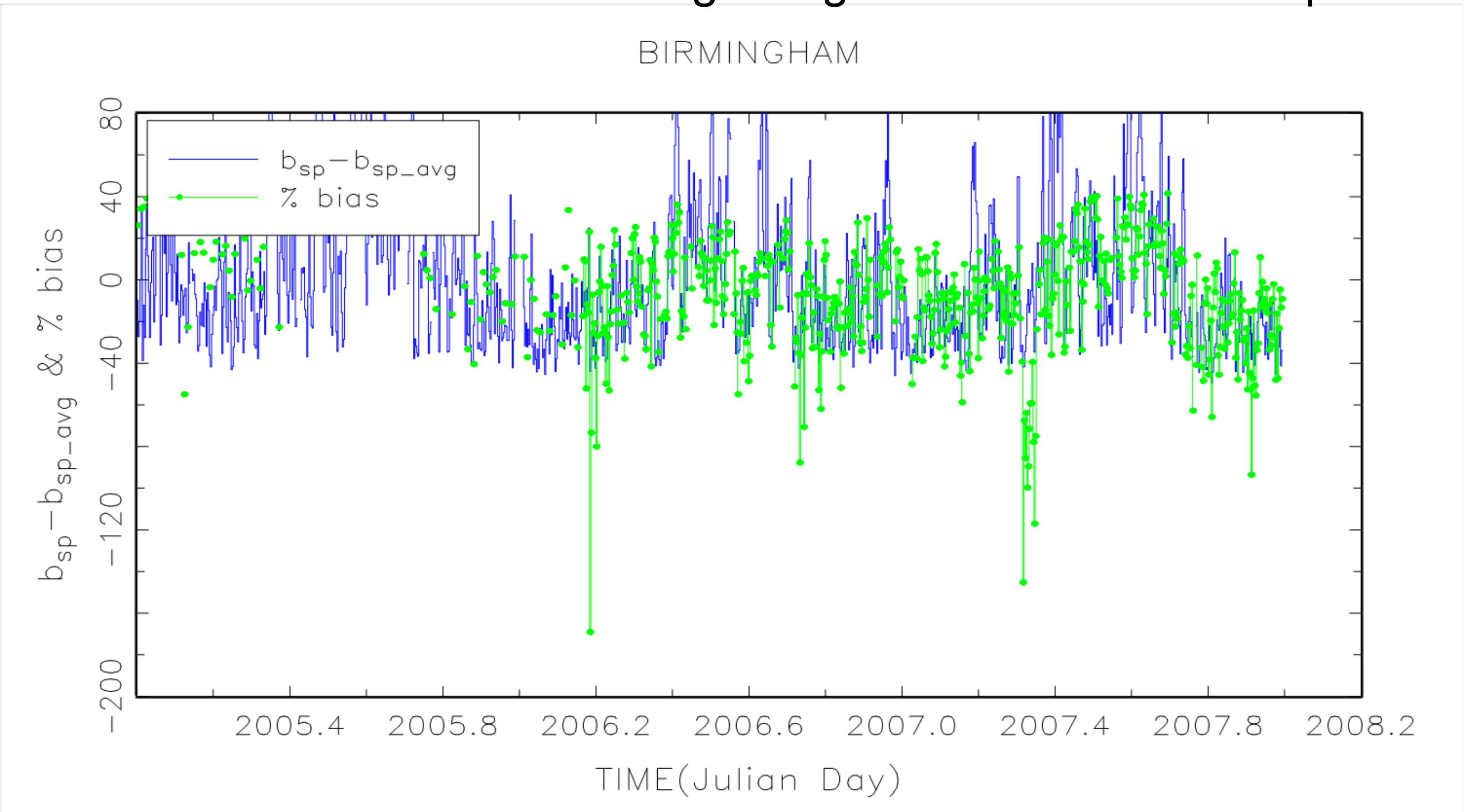
R_{oc} estimates compared with each other





Scattering Estimations

Bias in reconstructed scattering using the old IMPROVE equation

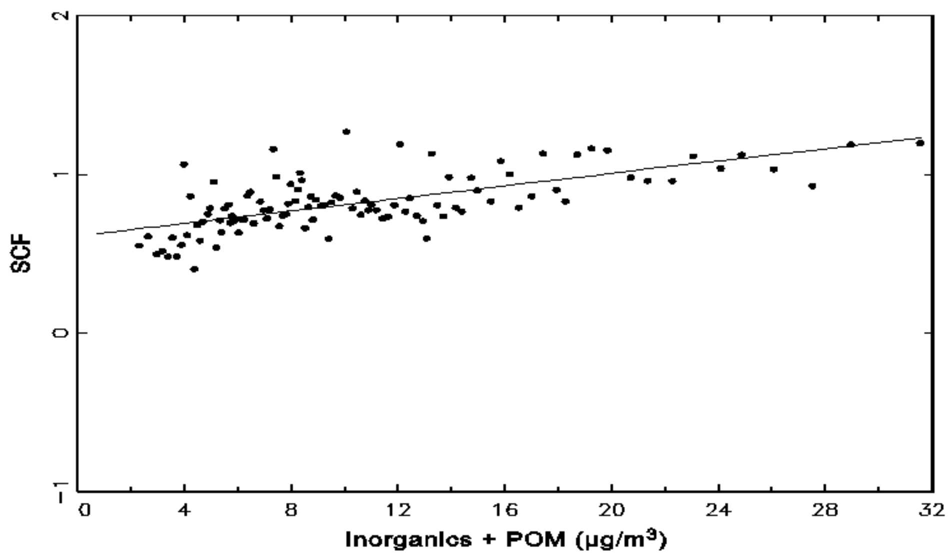


Scattering Estimation Equations

$b_{mix}=b_{open}-b_{CM}-b_{soil}-b_{SS}$ =

$c1\{3.0f(RH)AS[(NH_4)_2SO_4 + NH_4NO_3] + 3.81[POM]\}$

$$SCF = \frac{b_{mix}}{b_{mix\_est}} = \frac{b_{open} - b_{CM} - b_{soil} - b_{SS}}{c_1\{3.0\,f(RH)_{AS}[(NH_4)_2SO_4 + NH_4NO_3] + 3.81[POM]\}}$$



M_{mix}=[(NH4)2SO4]+ [NH4NO3]+[POM]),

$$M_{mix} = [(NH_4)_2SO_4] + [NH_4NO_3] + [POM]),$$

$$SCF = b_o + b1[M_{mix}]$$

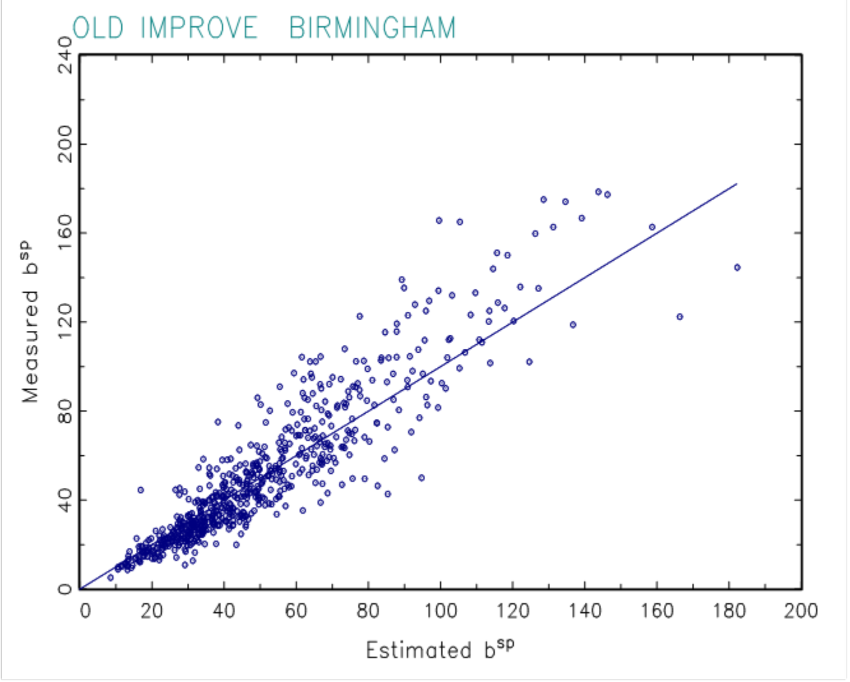
$$b'_{mix\_est} = SCF'(M_{mix})c_1\{3.0f(RH)\ [(NH_4)_2SO_4 + NH_4NO_3] + 3.81[POM]\}$$

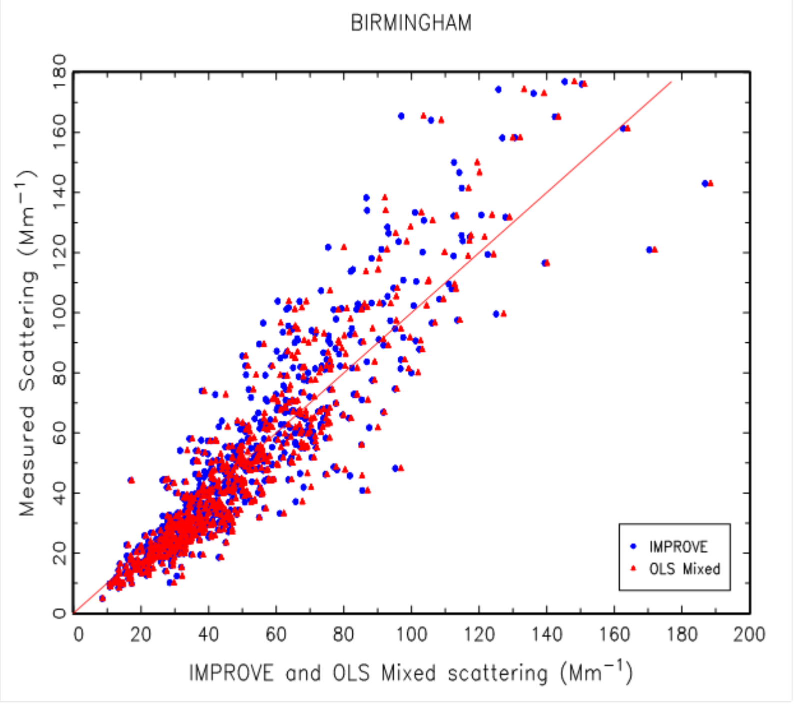
New inorganic and organic mass-adjusted specific mass scattering efficiencies are calculated using:

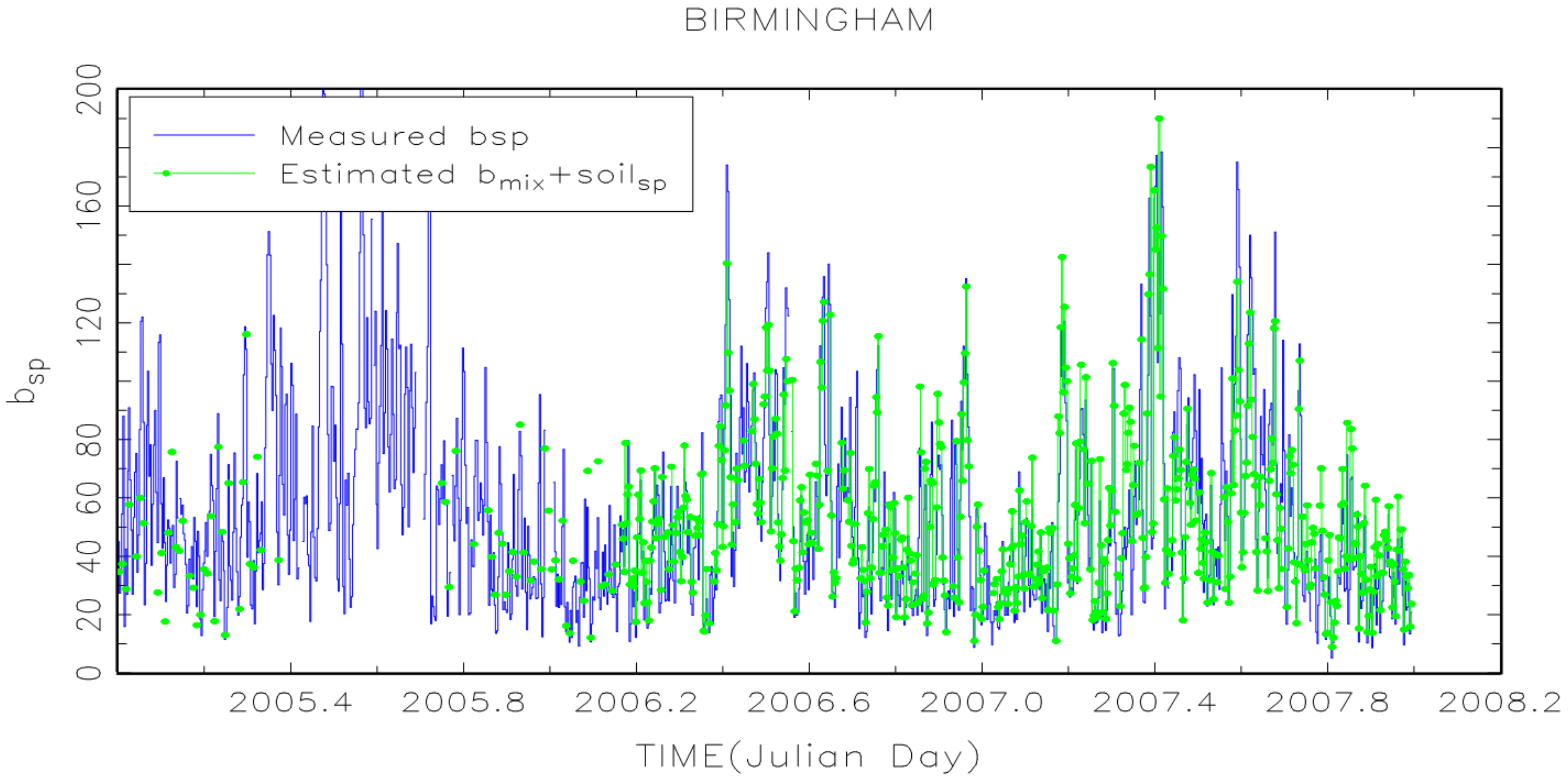
$\alpha'i_{norg} = 3.0c_1 \cdot SCF'(M_{mix})$ and

$\alpha'_{org} = 3.81c_1 \cdot SCF'(M_{mix})$.

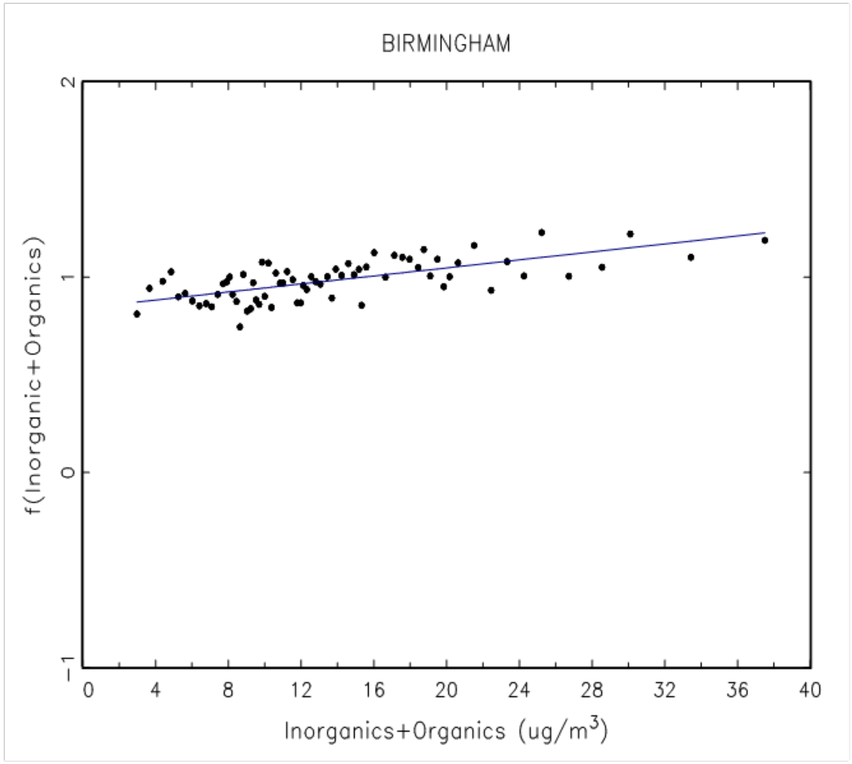
Old IMPROVE equation vs measured b_{sp} and MIXED model vs measured b_{sp} (Corrected for R_{oc} seasonal)

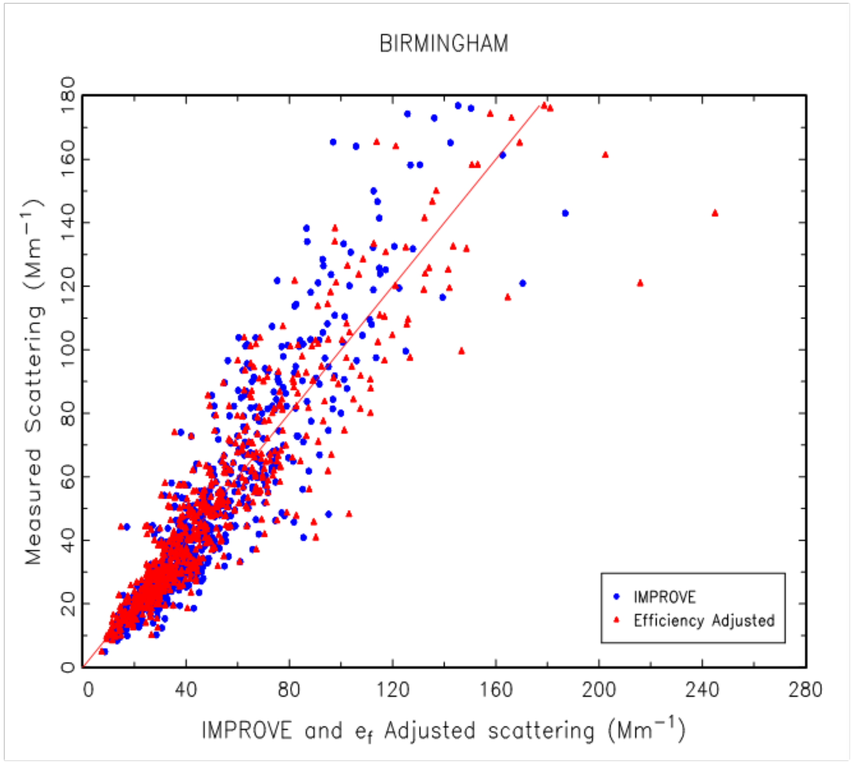




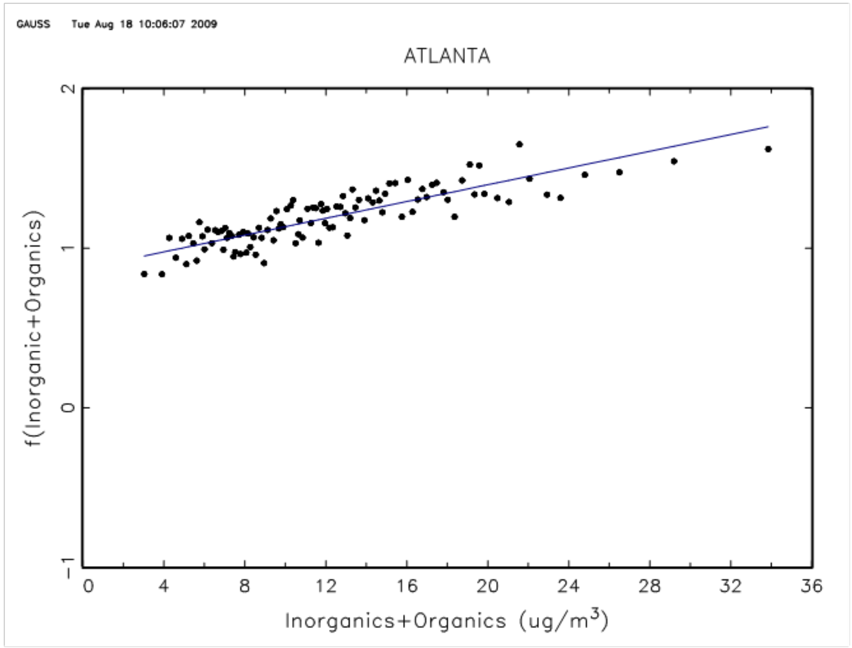

BIRMINGHAM
Measured bsp
Estimated $b_{mix}+soil_{sp}$
b_{sp}
0
20
40
60
80
120
160
200
2005.4
2005.8
2006.2
2006.6
2007.0
2007.4
2007.8
2008.2
TIME(Julian Day)

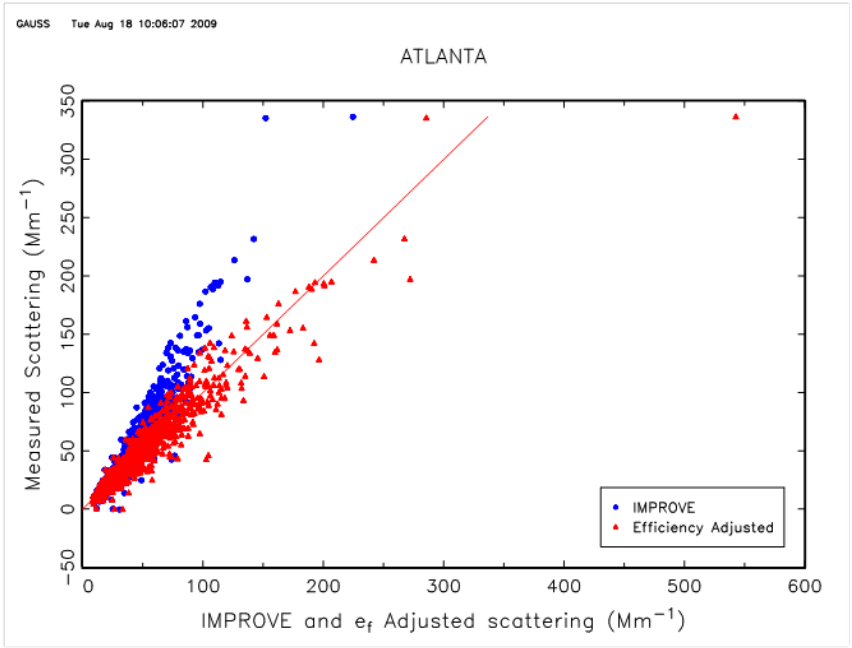
SCF vs inorganics+organic mass and resulting estimated b_{sp} vs measured b_{sp}





SCF vs inorganics+organic mass and resulting estimated b_{sp} vs measured b_{sp}





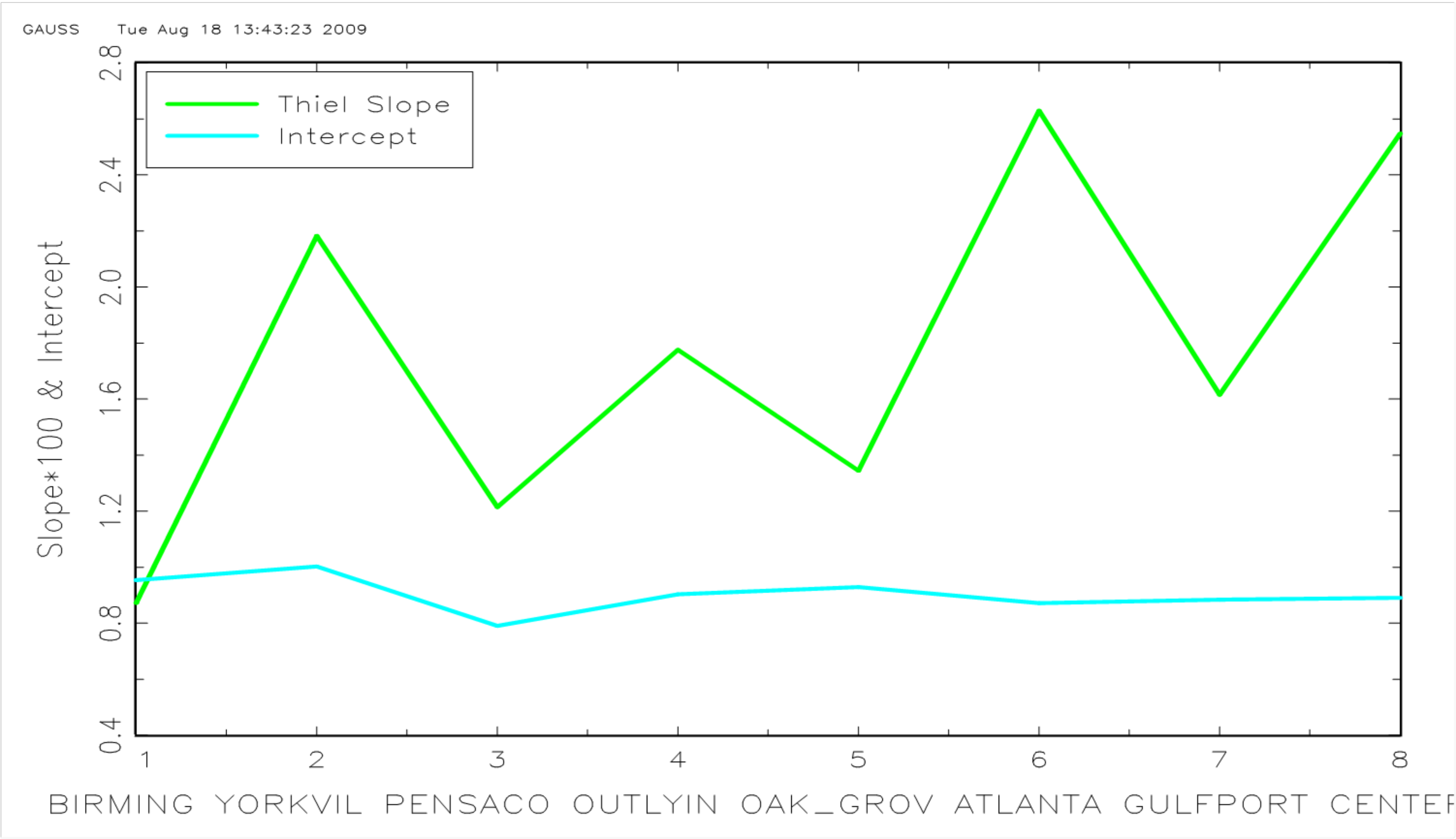
Mass scattering efficiency statistics

- Sulfate and Nitrate
- Meanl= 2.889
- Mean= 2.964
- Meanu= 3.015
- Organic
- Meanl= 3.668
- Mean= 3.764
- Meanu= 3.829

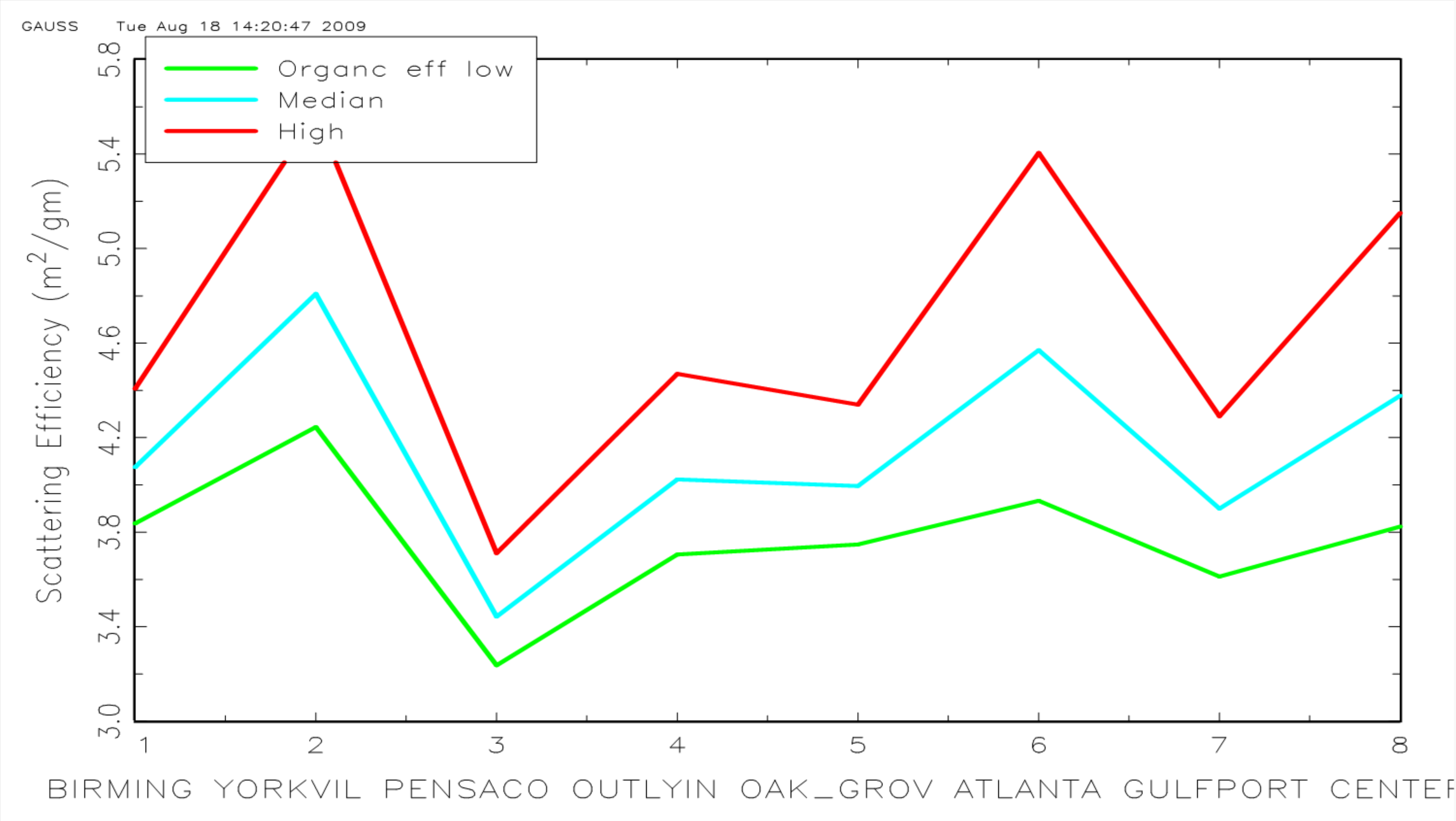
- Thiel Regression Results
- Intercept= 0.842
- Slope= 0.010
- Significance= 0.000

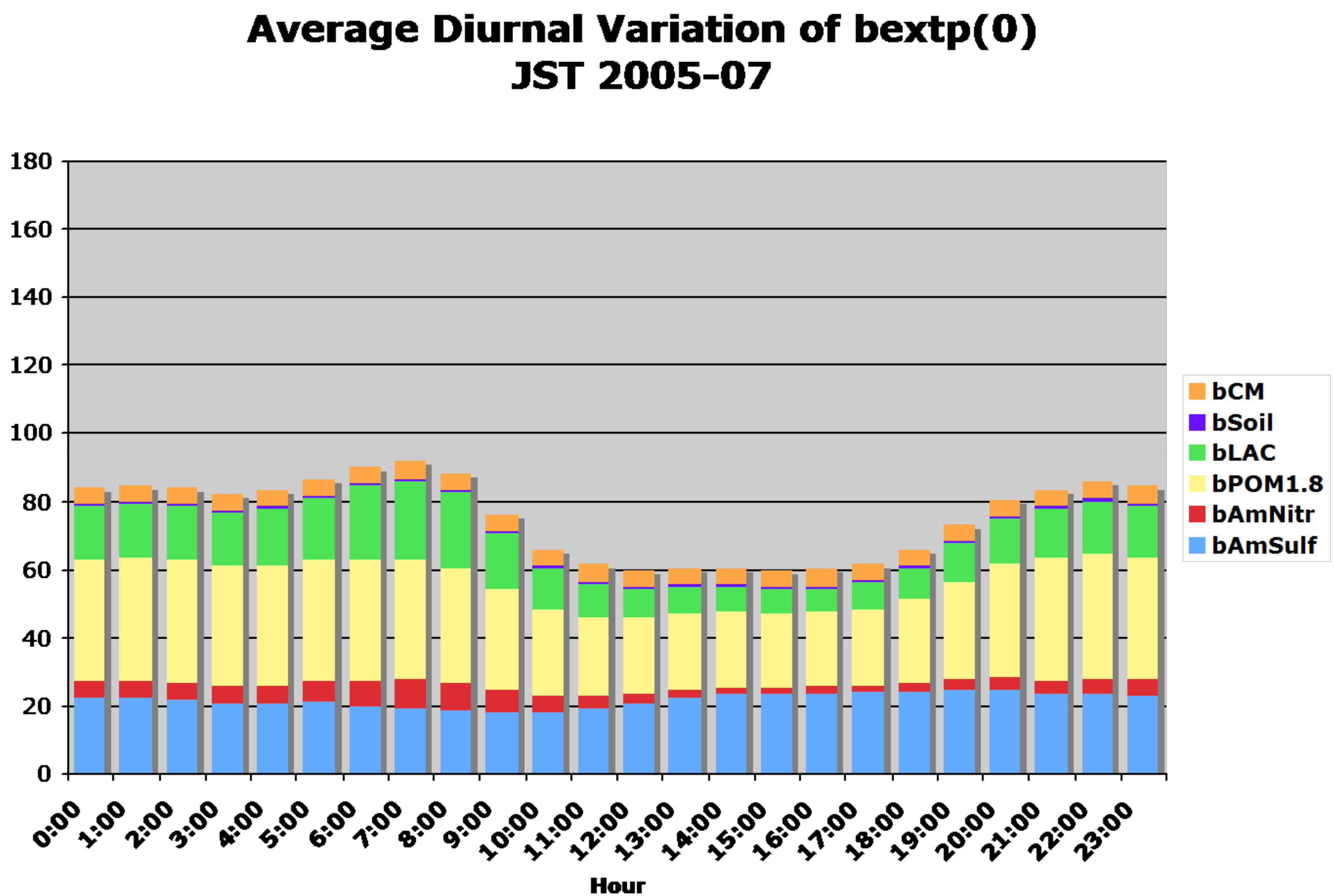
Variable	Mean	Std Dev	Variance	Minimum	Maximum	Valid	Missing
F(MASS)	1.0004	0.2564	0.0658	0.3642	2.6904	642	452
EFFS	2.9637	0.2299	0.0529	2.5983	4.0650	698	396
EFFOC	3.7639	0.2920	0.0853	3.2998	5.1626	698	396

Thiel Slope and Intercept

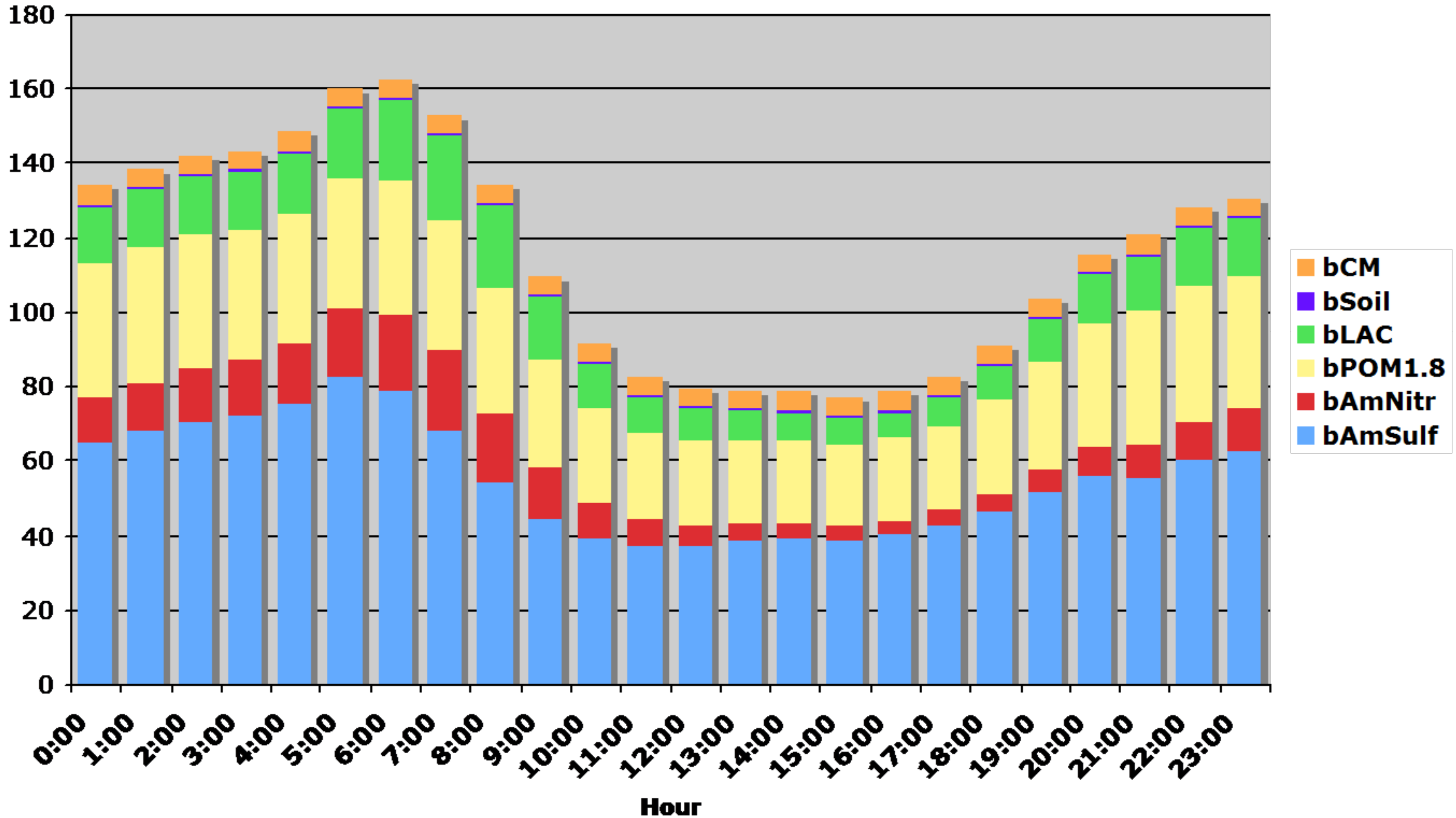


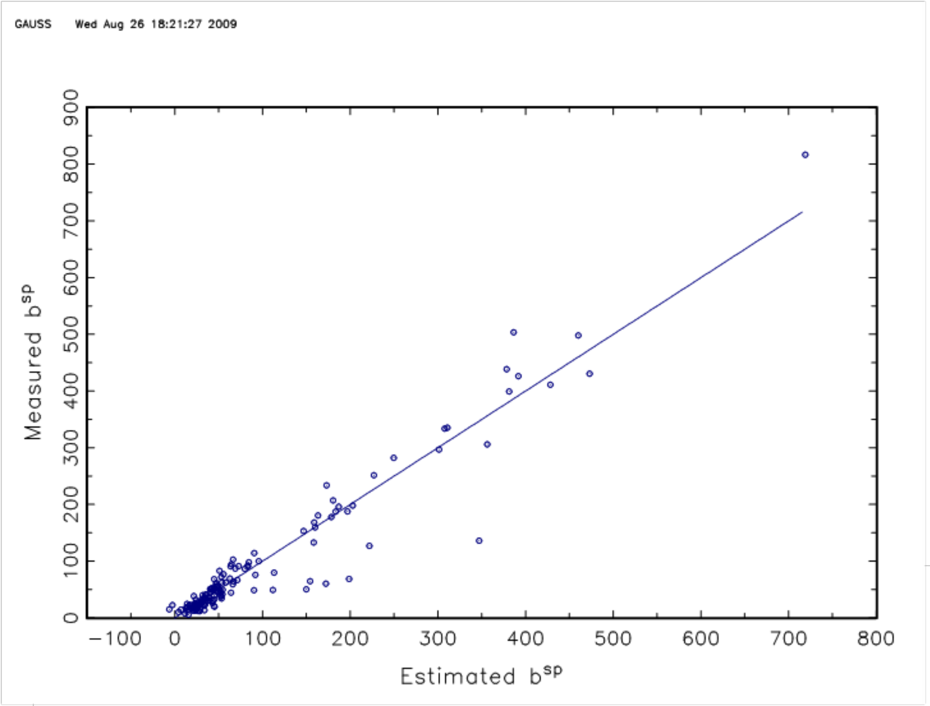
Mass Scattering Efficiencies

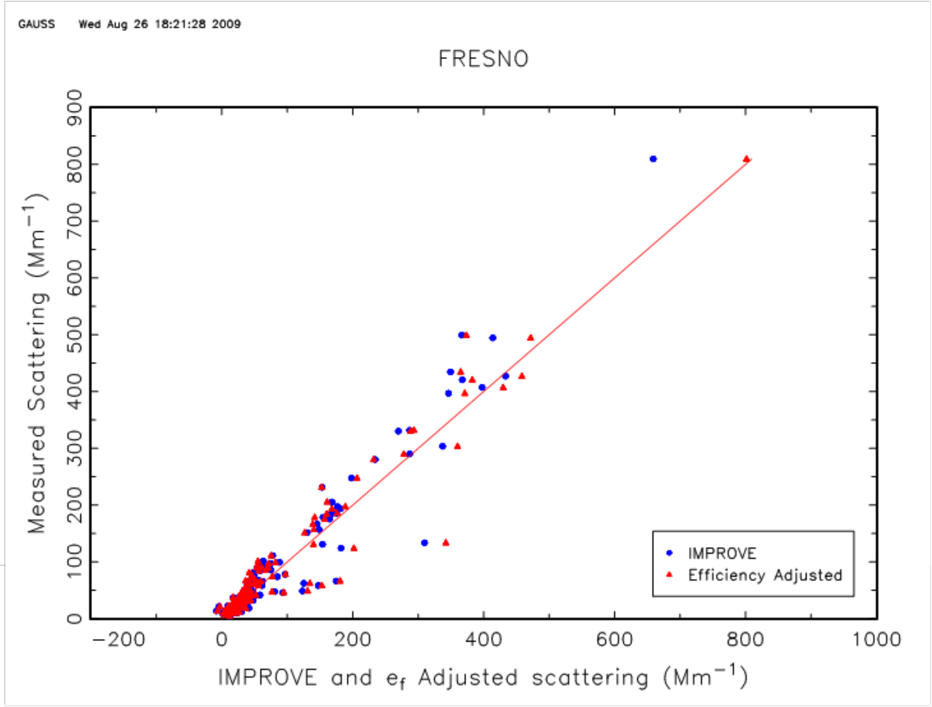


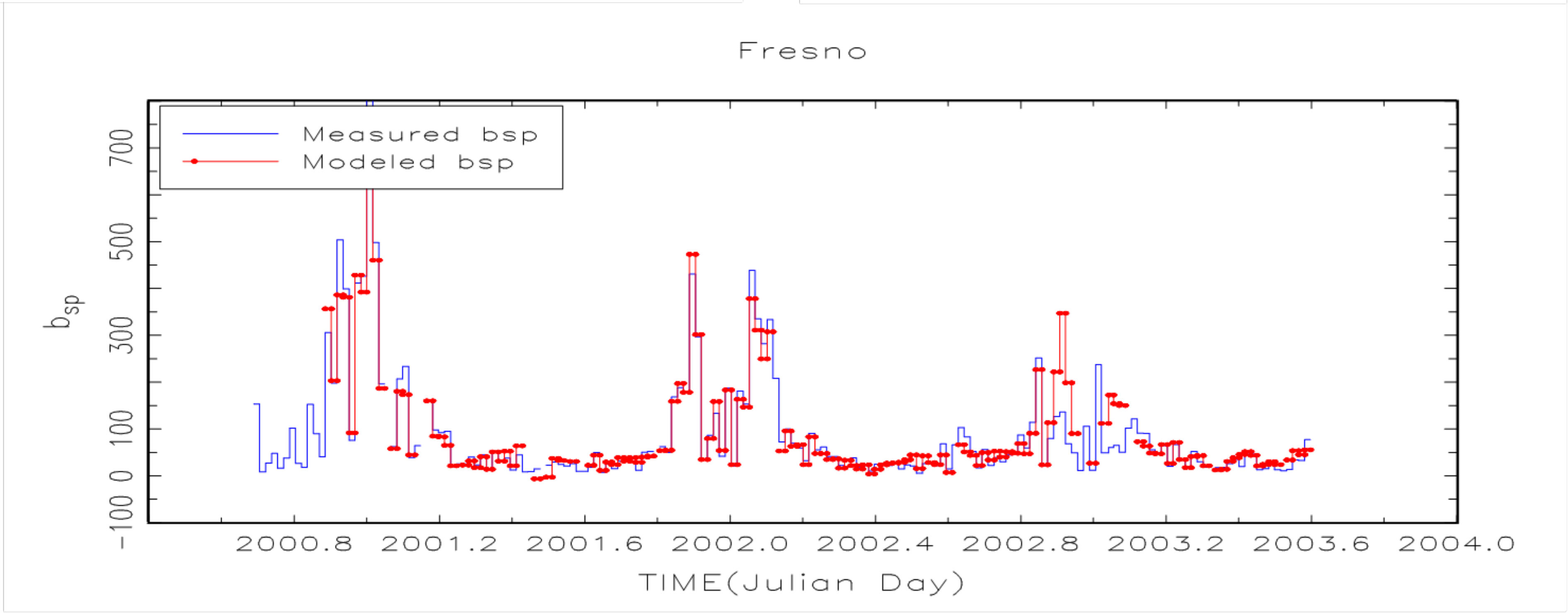

Average Diurnal Variation of bextp(0)
JST 2005-07
180
160
140
120
100
80
60
40
20
0
0:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
21:00
22:00
23:00
Hour
bCM
bSoil
bLAC
bPOM1.8
bAmNitr
bAmSulf

Average Diurnal Variation of bextp(RH)
JST 2005-07

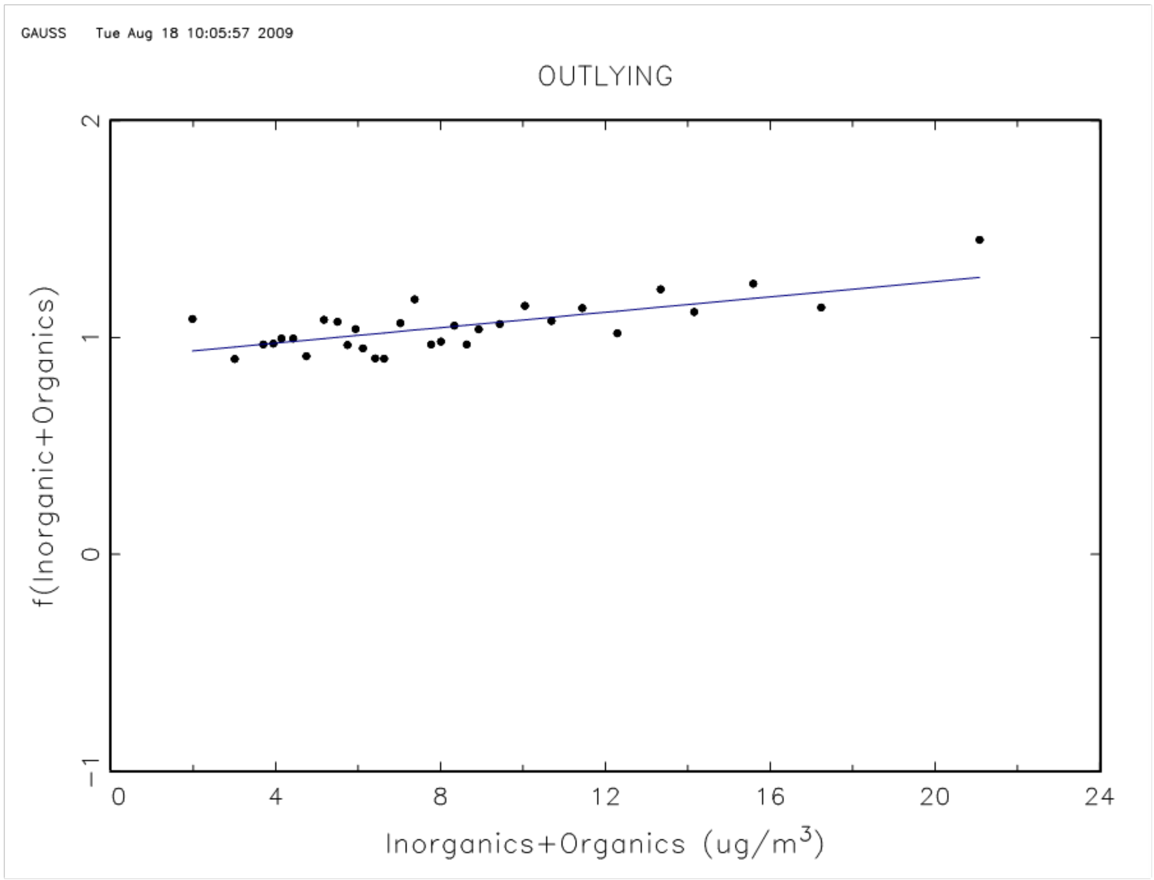


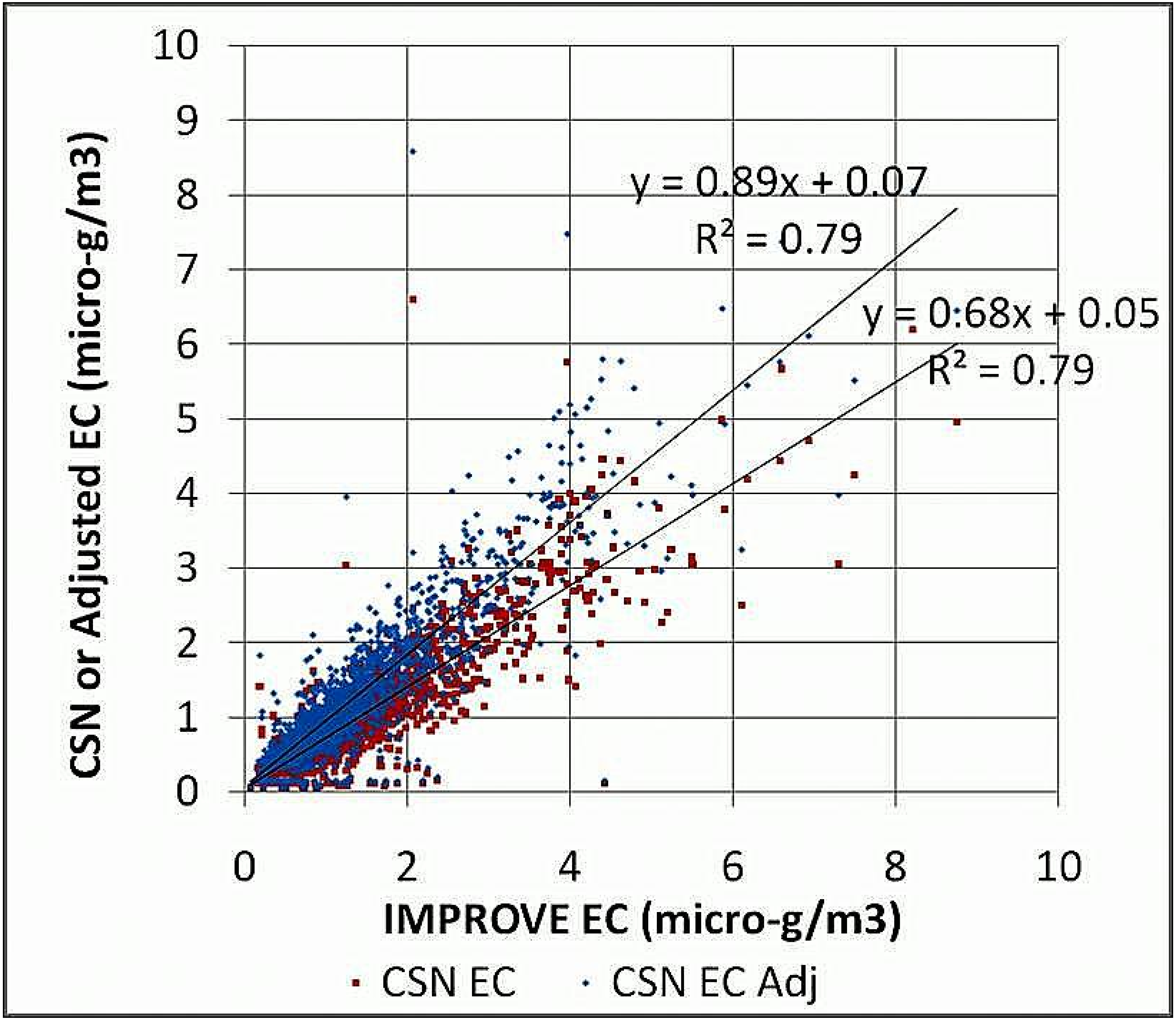

GAUSS Wed Aug 26 18:21:27 2009
Measured b^{sp}
Estimated b^{sp}


GAUSS Wed Aug 26 18:21:28 2009
FRESNO
Measured Scattering (Mm^{-1})
IMPROVE and e_f Adjusted scattering (Mm^{-1})
IMPROVE
Efficiency Adjusted

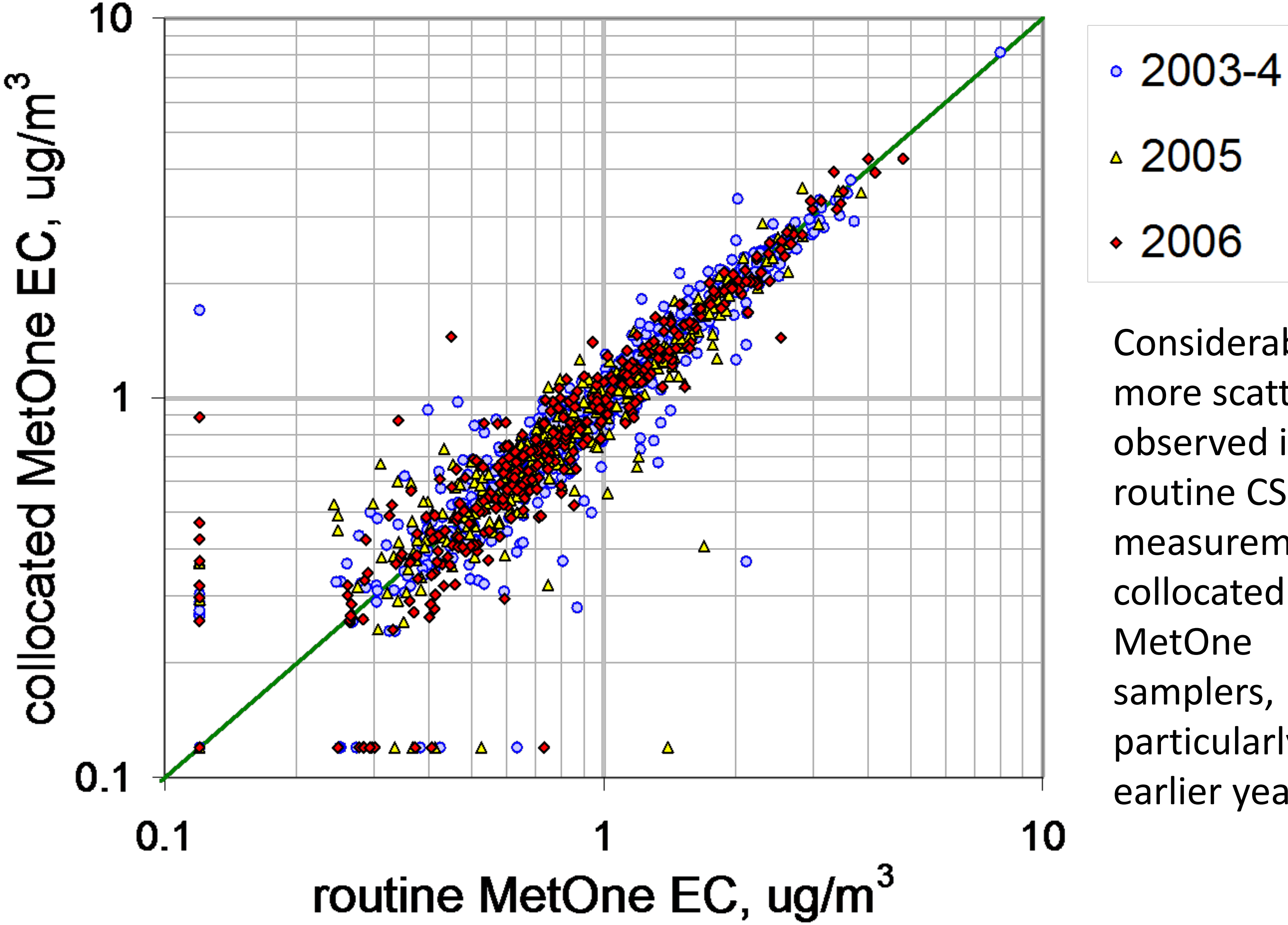

Fresno
Measured bsp
Modeled bsp
b_{sp}
TIME(Julian Day)

END


GAUSS Tue Aug 18 10:05:57 2009
OUTLYING
f(Inorganic+Organics)
2
1
0
−1
0
4
8
12
16
20
24
Inorganics+Organics (ug/m3)



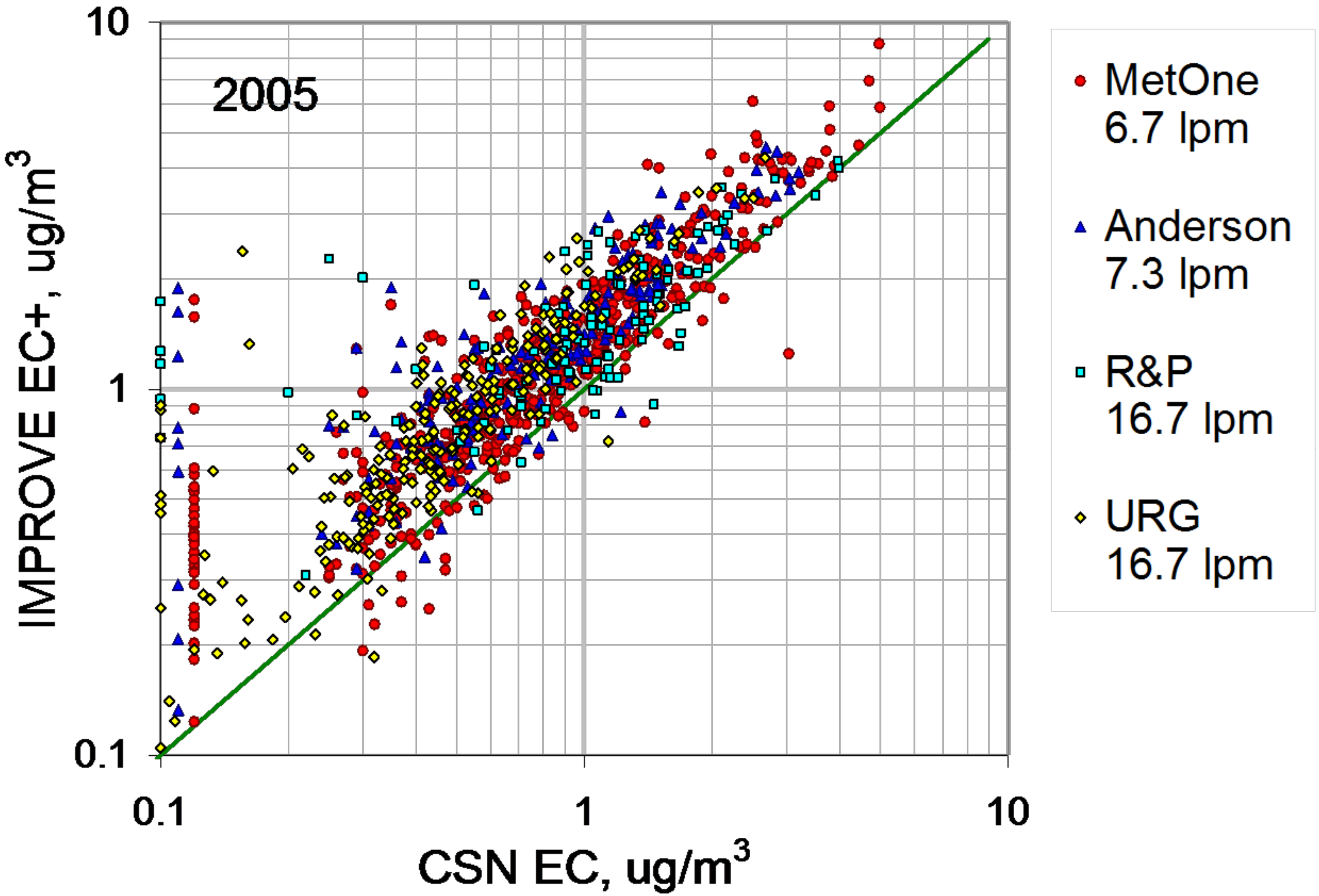
CSN or Adjusted EC (micro-g/m3)
IMPROVE EC (micro-g/m3)
y = 0.89x + 0.07
R² = 0.79
y = 0.68x + 0.05
R² = 0.79
CSN EC
CSN EC Adj
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10



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



- The EC difference between CSN and IMPROVE shows little dependence on the CSN sampler, suggesting that it is mainly analytical.
- The bias is rather uniform in the log-log plot indicating it is dominated by multiplicative errors

EC – the short story:

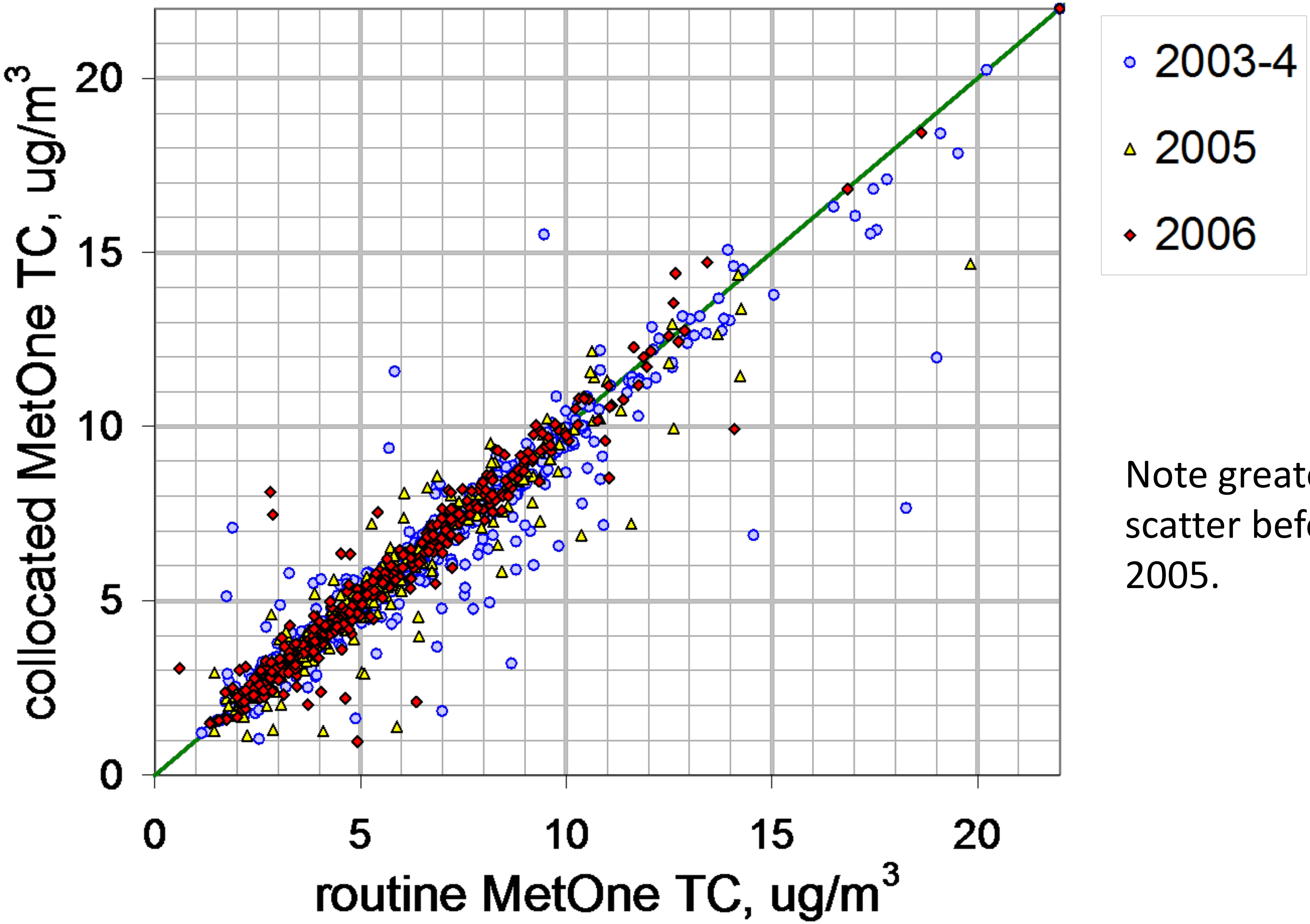
- $\varepsilon_{IMP} \cong 0, \quad \varepsilon_{IMP} = artifact\_adj$

- $IMP_{new} \cong \alpha CSN, \quad \alpha > 1$

- $CSN_{\phi} \cong CSN_{\varphi}, \quad \phi \neq \varphi \;\; samplers$

- EC has little to no positive artifact for both IMPROVE and CSN

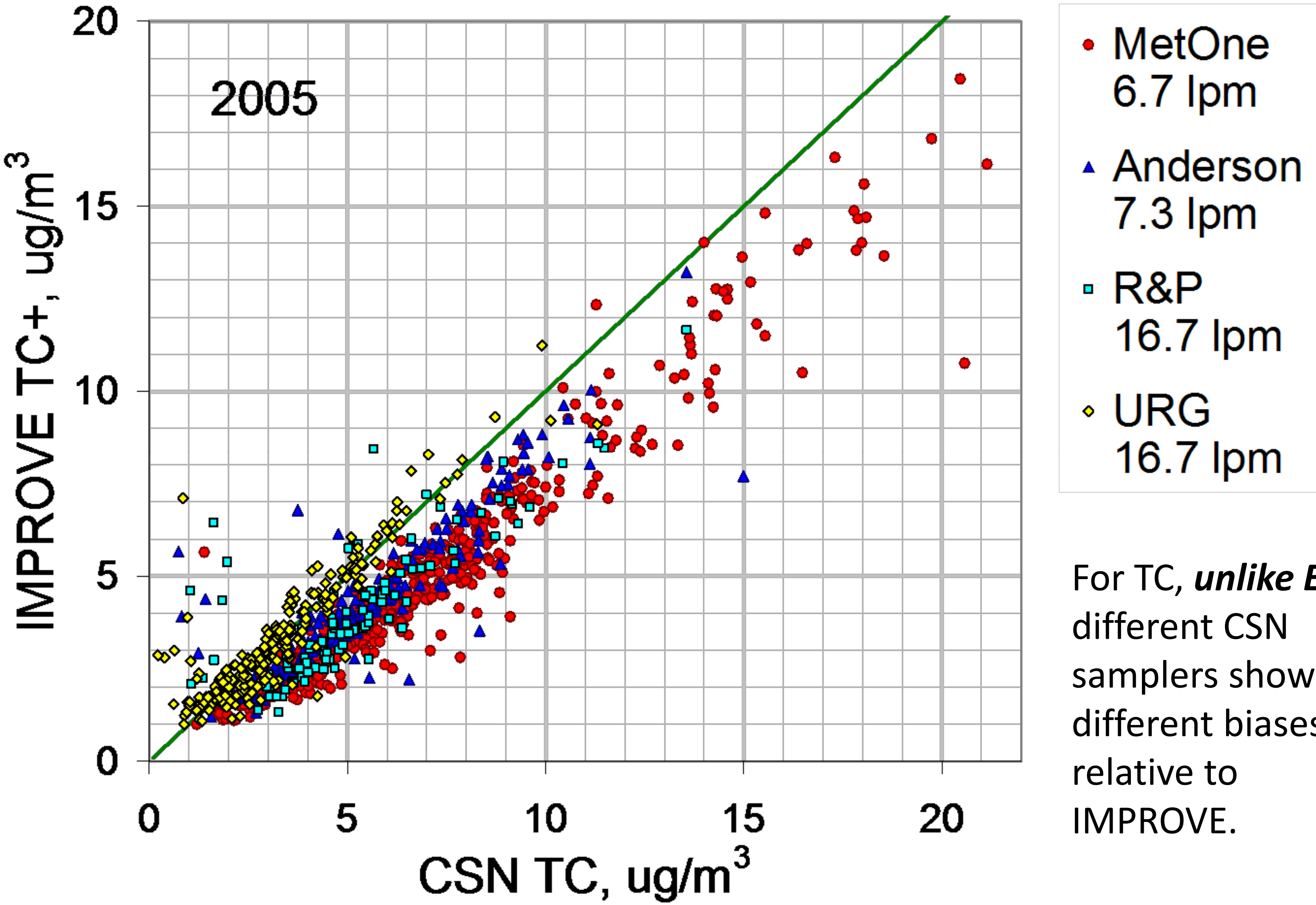
-Multiplicative bias between CSN and IMPROVE that is sampler independent



Note greater scatter before 2005.

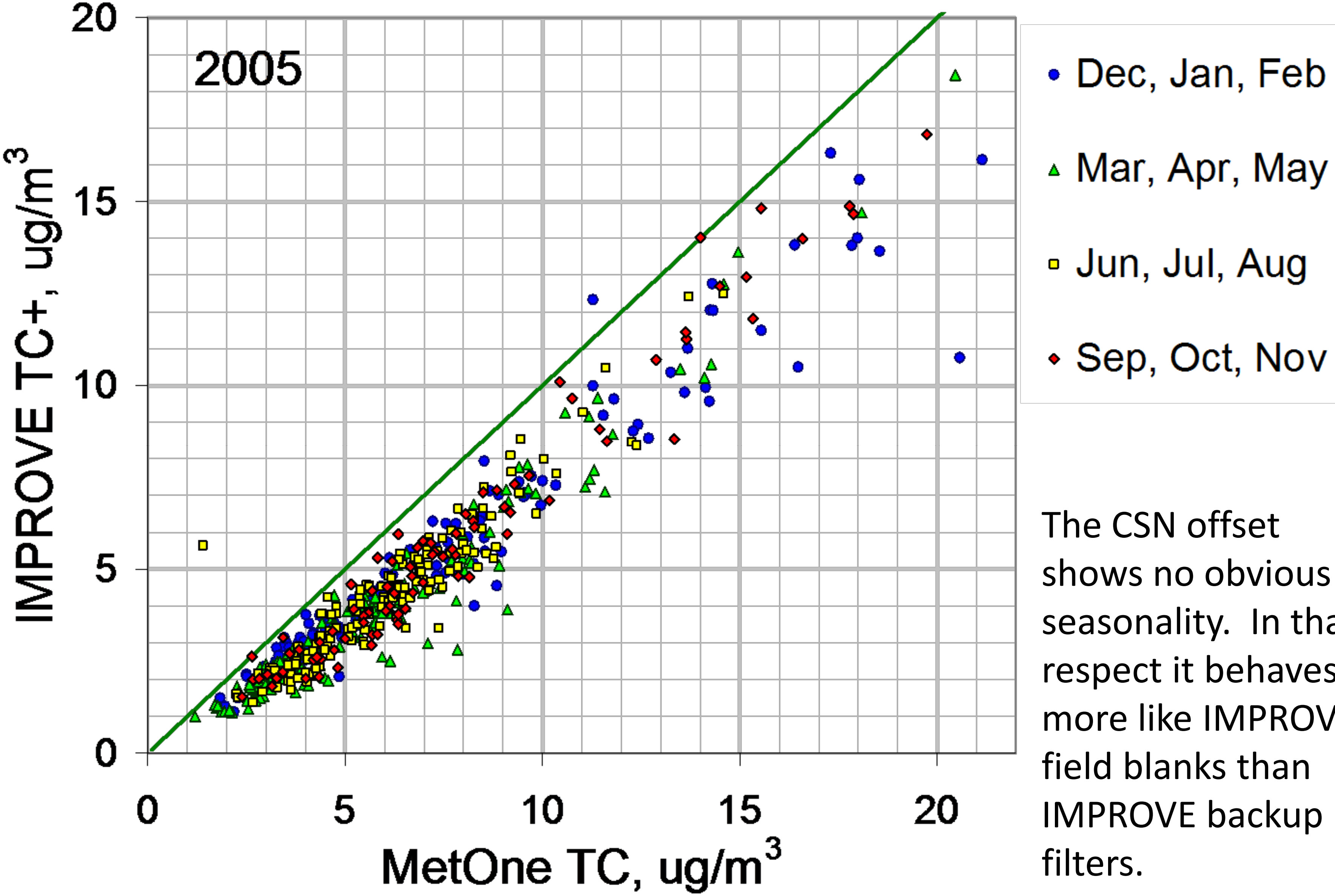
Data are from Bakersfield,* Boston,* Cleveland,* New Brunswick* and Rubidoux.

* ***Not*** collocated with IMPROVE

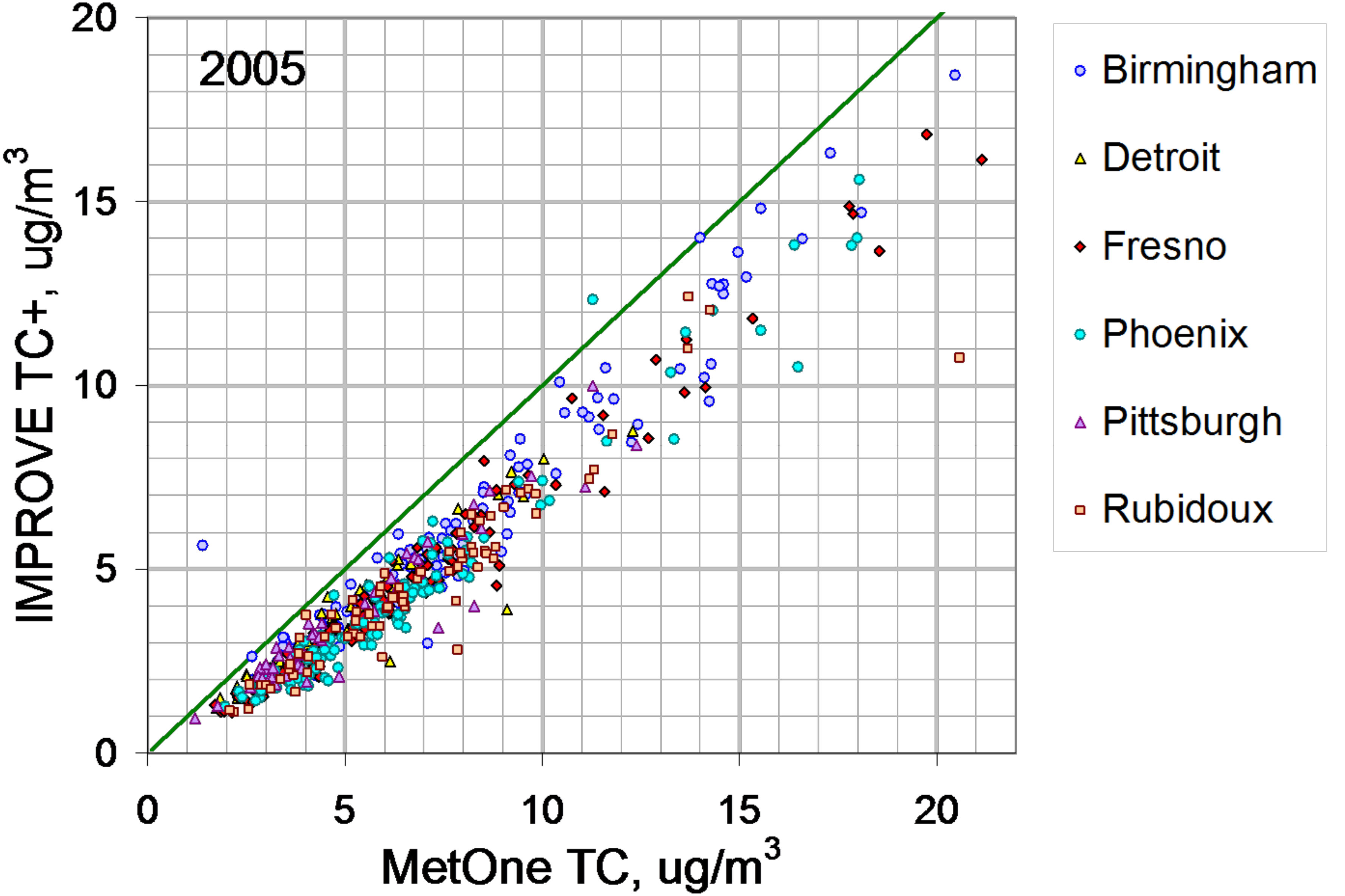


For TC, ***unlike EC***, different CSN samplers show different biases relative to IMPROVE.

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



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


2005
IMPROVE TC+, ug/m3
MetOne TC, ug/m3
0
5
10
15
20
Birmingham
Detroit
Fresno
Phoenix
Pittsburgh
Rubidoux

TC – the short story:

$$\varepsilon_{IMP} = artifact\_adj$$

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

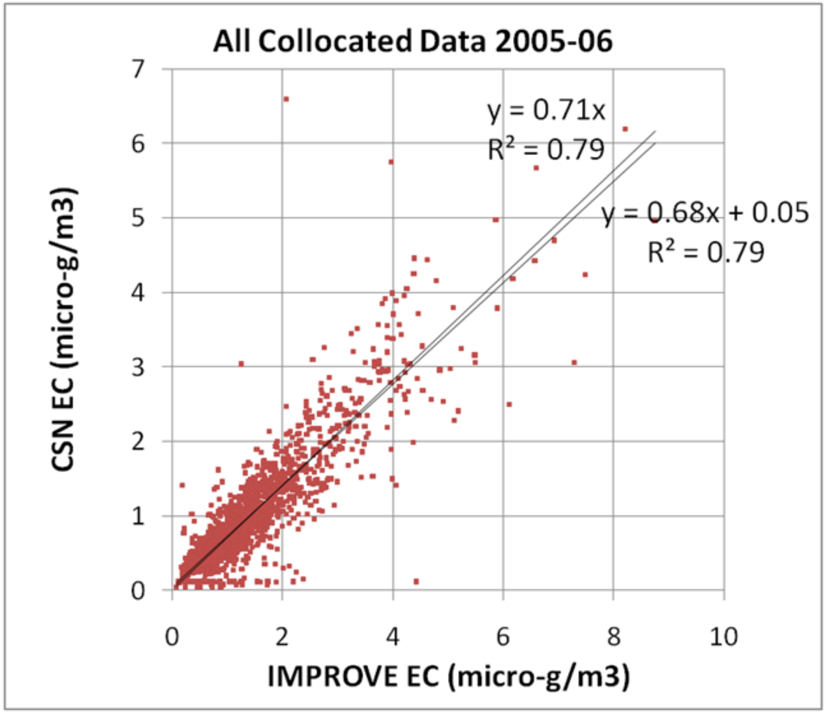
$$CSN_{\phi} \neq CSN_{\varphi}, \quad \phi \neq \varphi \ \ samplers$$

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

- $EC_{IMP} = \alpha * EC_{CSN}$
- $\alpha \sim 0.3$



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
  - 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

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