Optical Measurements of CSN and FRM Teflon Filters to Estimate Elemental Carbon

to Support Health Studies, PM NAAQS Implementation and Climate

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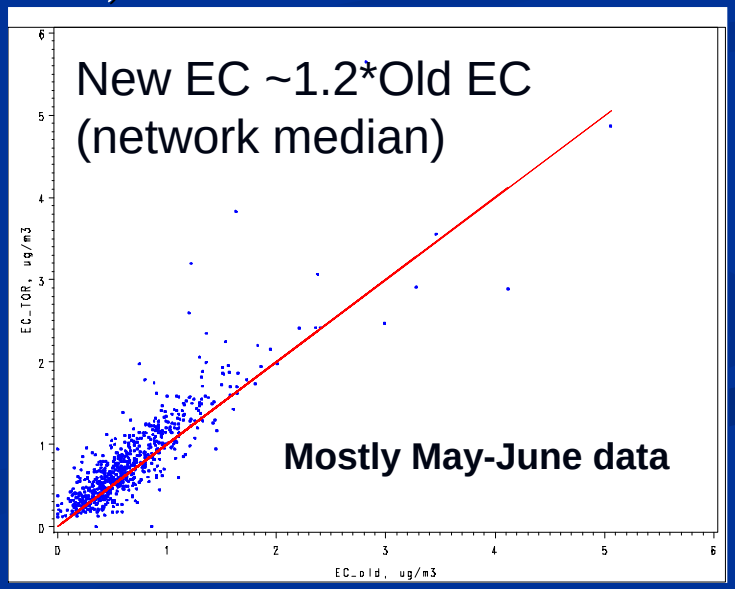
Findings

Many Benefits of Optical Measurements

- Inexpensive utilization of archived PM2.5 filters
- Can predict EC by measuring the darkness of the filters
- Better and more consistent relationship with new IMPROVE carbon method
- Opportunity to cost effectively expand our current "EC" monitoring network for
  - Health researchers
  - Climate-related purposes
  - Emission and modeling efforts
  - QA of speciation carbon

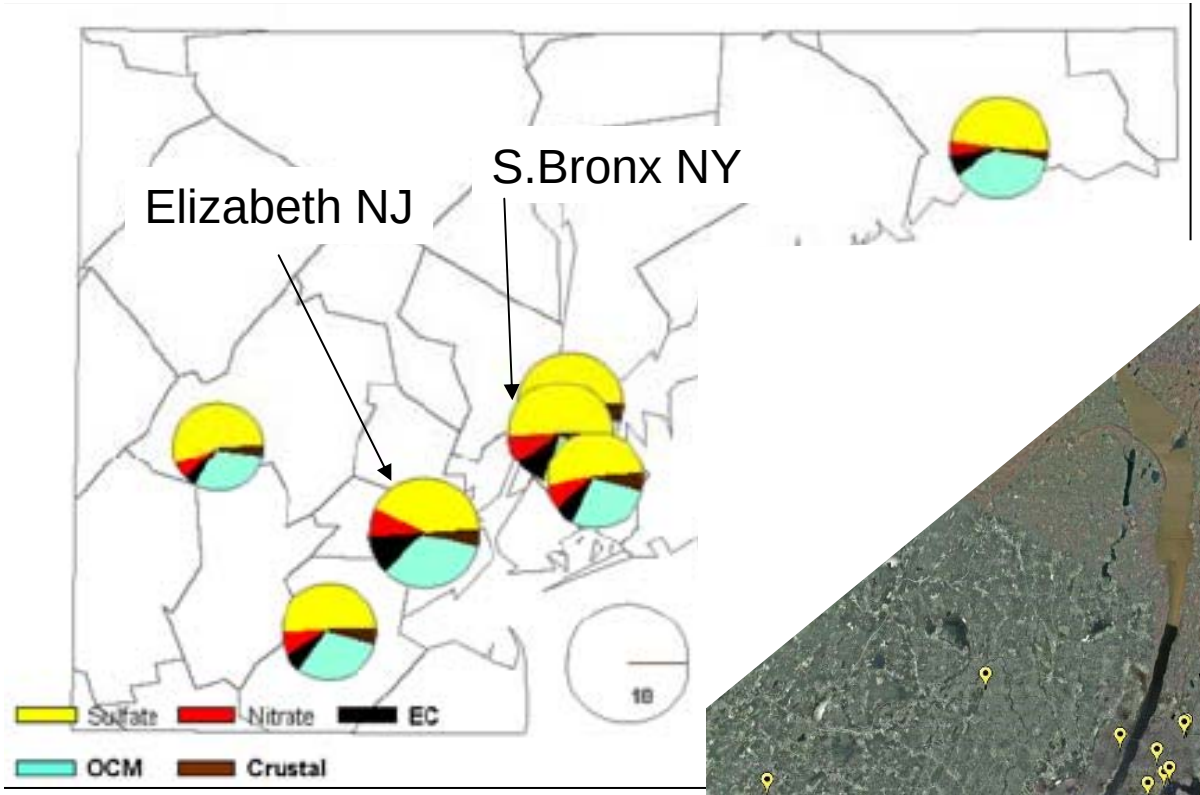
Background

- Optical measurements of filters used for decades
  - IMPROVE has been doing optical measurements for a long time (for QC of thermal EC), using HIPS
  - "British Smoke" with Reflectometer widely used in Europe
- Why is EPA now interested?
  - EPA is transitioning the OC-EC protocol from the NIOSH-type method to IMPROVE protocol (started May 2007)
  - Health community expressed concern about possible discontinuity in EPA's EC time series and recommended optical measurements to estimate EC.
    - (EPA "Health Research Workshop" – April 2008)



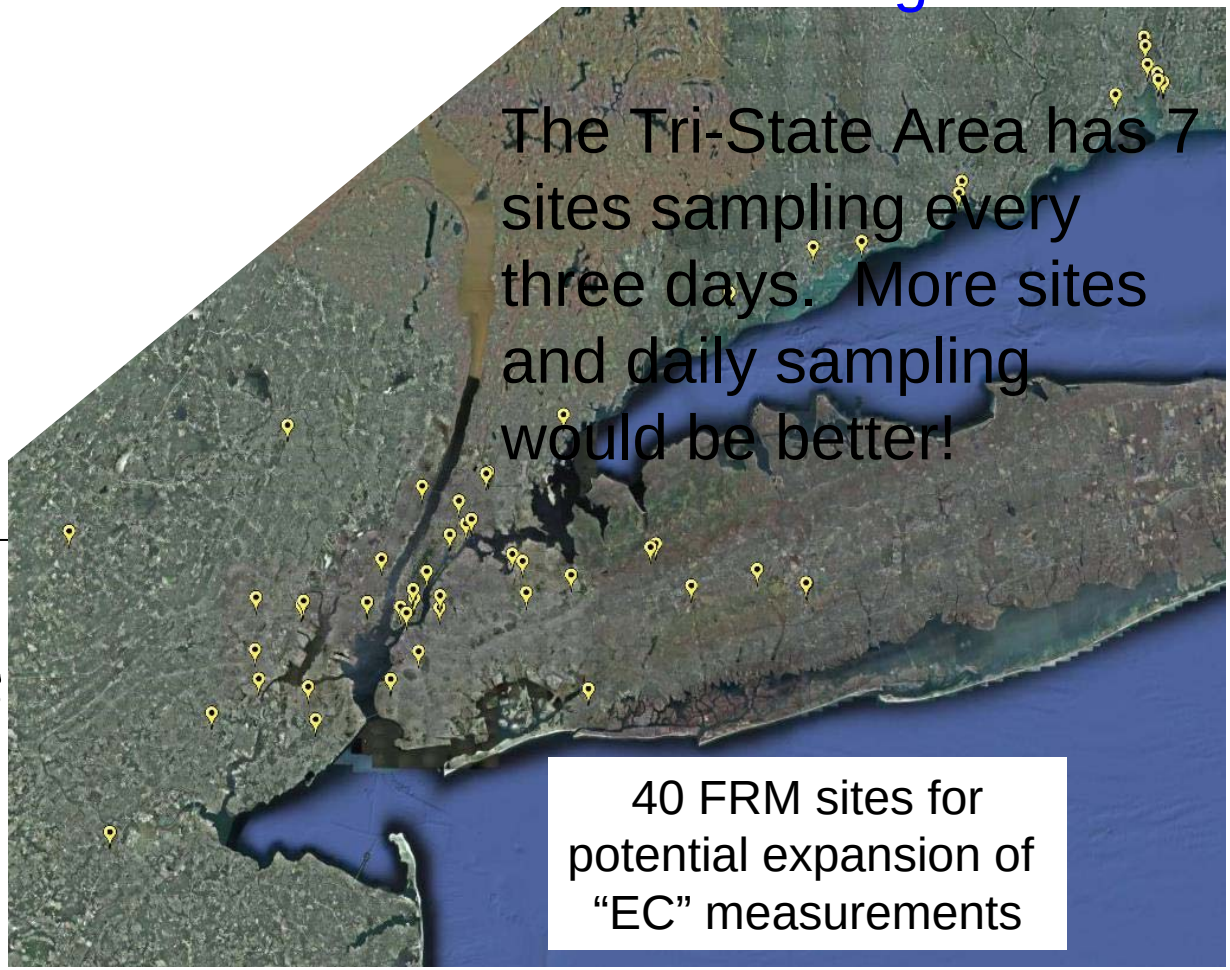
Other Motivations

- Lack of temporal and spatial detail in EPA speciation networks
  - EC has sharp gradients in urban areas
  - Everyday EC and more spatial resolution needed
- Support Health Studies and PM2.5 NAAQS Implementation
  - There are 940 PM2.5 FRM samplers which can be used to estimate EC



NYC Tri-State area

Existing Speciation Data Including EC



Optical measurements of FRM teflon filters can help increase the "EC" spatial resolution

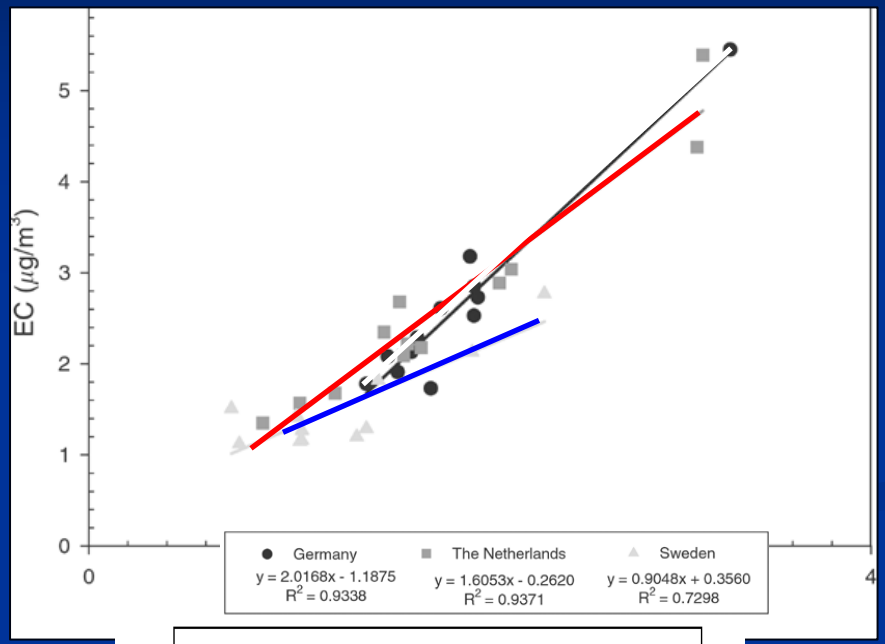
and, provide daily EC at PM2.5 sites which sample every day!

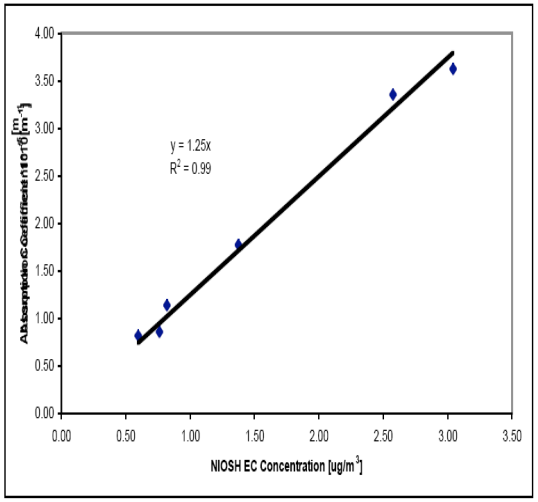
More motivations:
to better understand "black carbon" for climate

- Last week, President Signed Appropriation Bill (HR2996)
- "Not later than 18 months …. the Administrator… shall carry out and submit to Congress the results of a study on domestic and international black carbon emissions that shall include an inventory of the major sources of black carbon, an assessment of the impacts of black carbon on global and regional climate, an assessment of potential metrics and approaches for quantifying the climatic effects of black carbon emissions …..."
- EPA may need to define "BC" and must understand differences between optical and thermal methods

Optical Measurements highly correlate with "EC"

- "Smoke Stain Reflectometer" recently used with Teflon Filters
- Cyrys et. al., 2003
  - "Site-specific calibration with EC is necessary."
- Thurston et al.
  - "South Bronx Environmental Health Policy Study" (2007)
- Sometimes EC calibrated optical measurements reported as "BC"

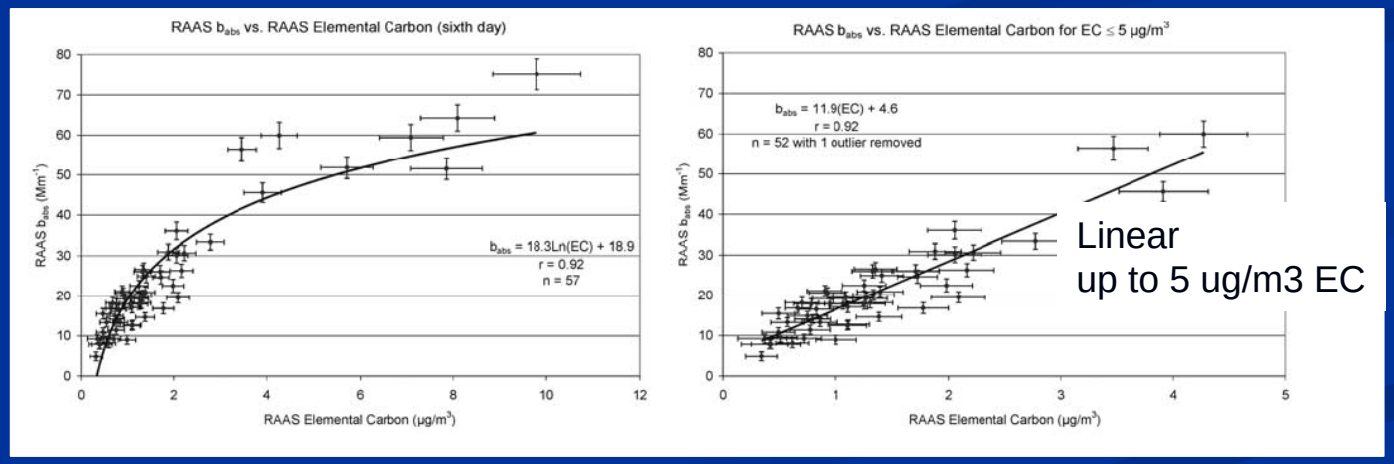




Recent OAQPS Work

- DRI study of Teflon filters (2007)*
  - To produce PM2.5 composition at 20 FRM sites without speciation data
  - "EC" using densitometer at 3 FRM-CSN sites

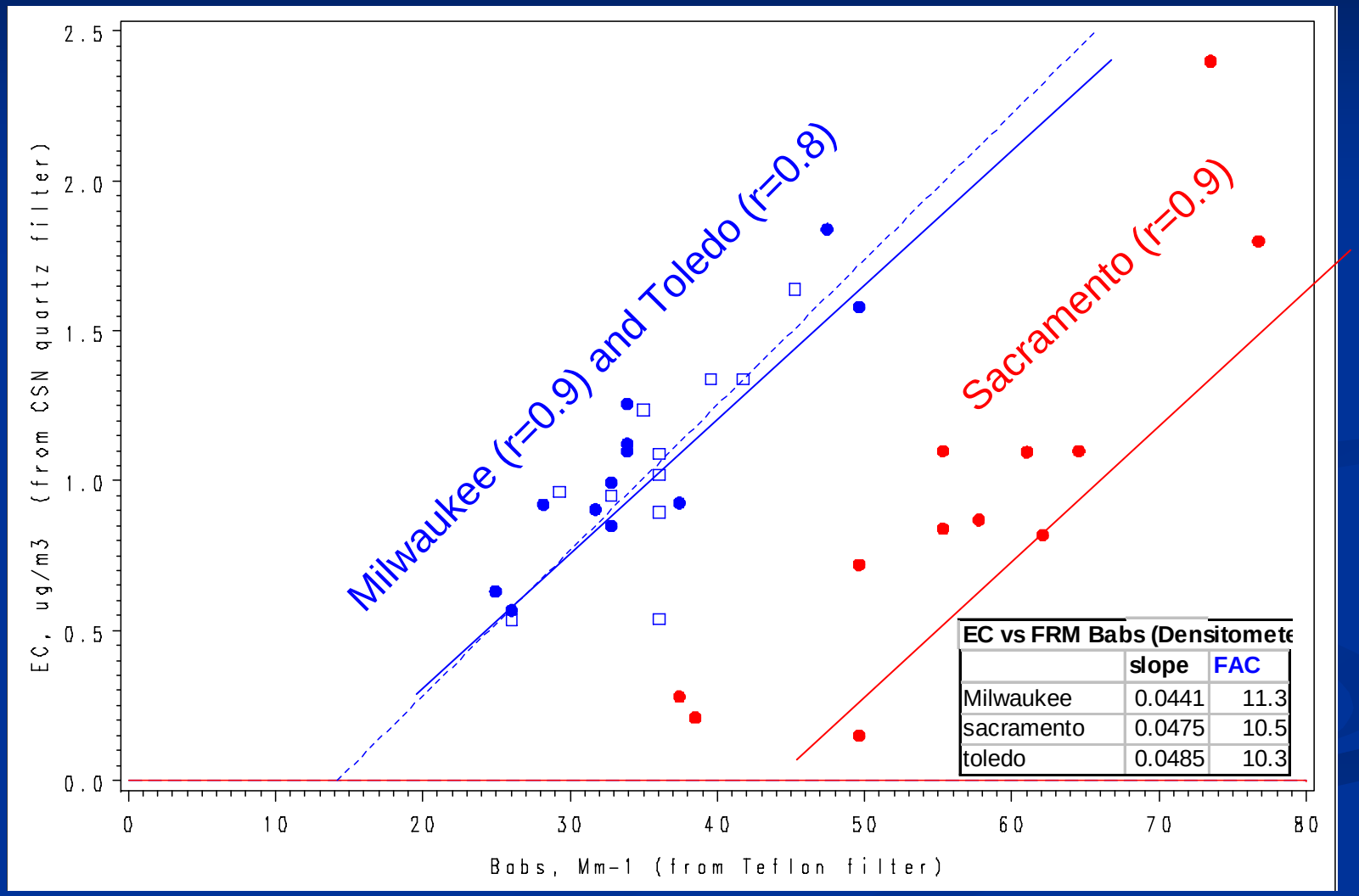
Comparison filter carbon measurements at the Fresno Supersite
John G. Watson and Judith C. Chow (2002)



* 2007 Study is posted on the PM2.5 NAAQS Designations Web Site
http://www.epa.gov/ttn/naaqs/pm/docs/available_new_speciation_data_pm2.5_naa.pdf

PILOT densitometer study (2007)

- 35 high 2004-06 FRM concentrations days
- EC is measured with the EPA NIOSH-type protocol

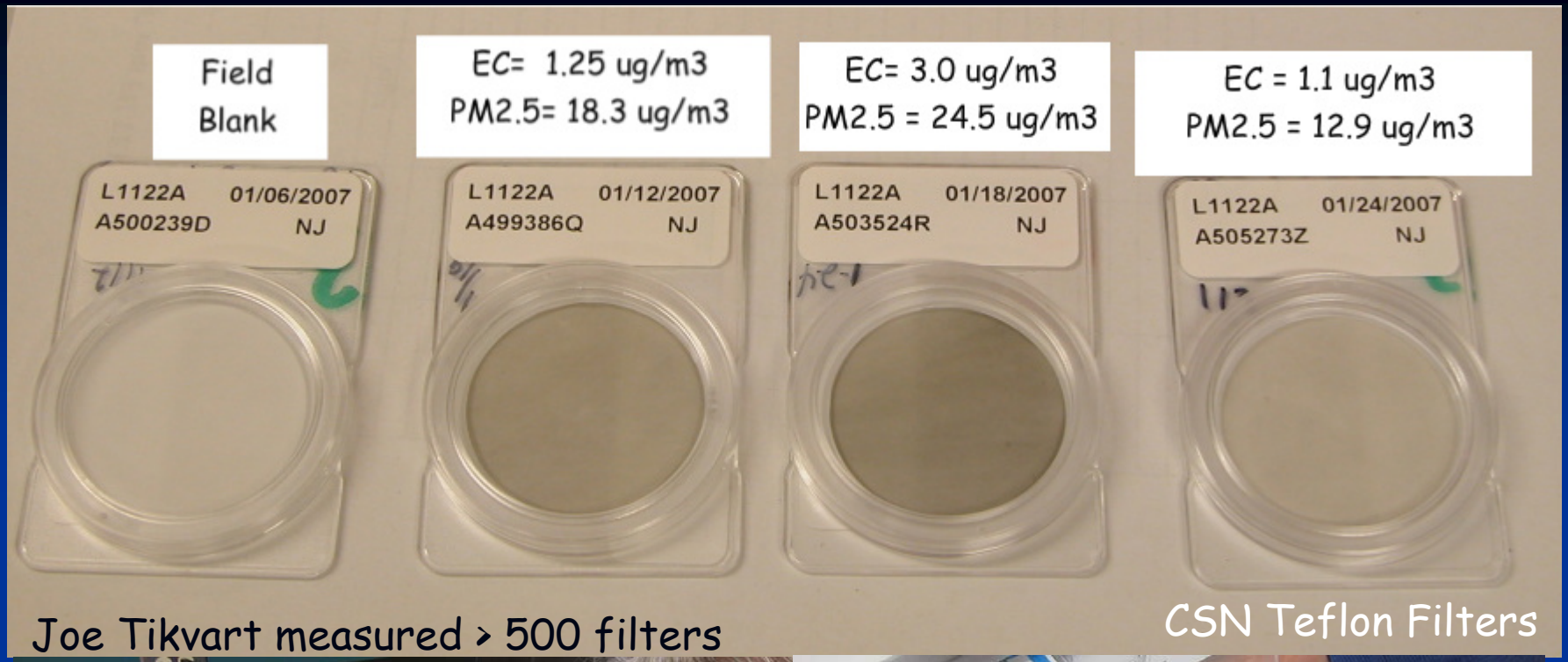


EC vs FRM Babs (Densitomete		
	slope	FAC
Milwaukee	0.0441	11.3
sacramento	0.0475	10.5
toledo	0.0485	10.3

Similar filter absorption coefficients, but unexplained offset in slope

Study of Magee (OT21) Transmissometer

- Teflon filters from 7 CSN sites (6.7 LPM)
  - Representing different emission influences
  - 4 sites (●)which switched TOA protocol in May 2007
    - To permit comparisons to new EC_TOR and old EC_CSN
  - 1in6 day filters were selected per site from 2007 sampling
  - Subset of 3 sites with collocated FRM filters (16.7 LPM)

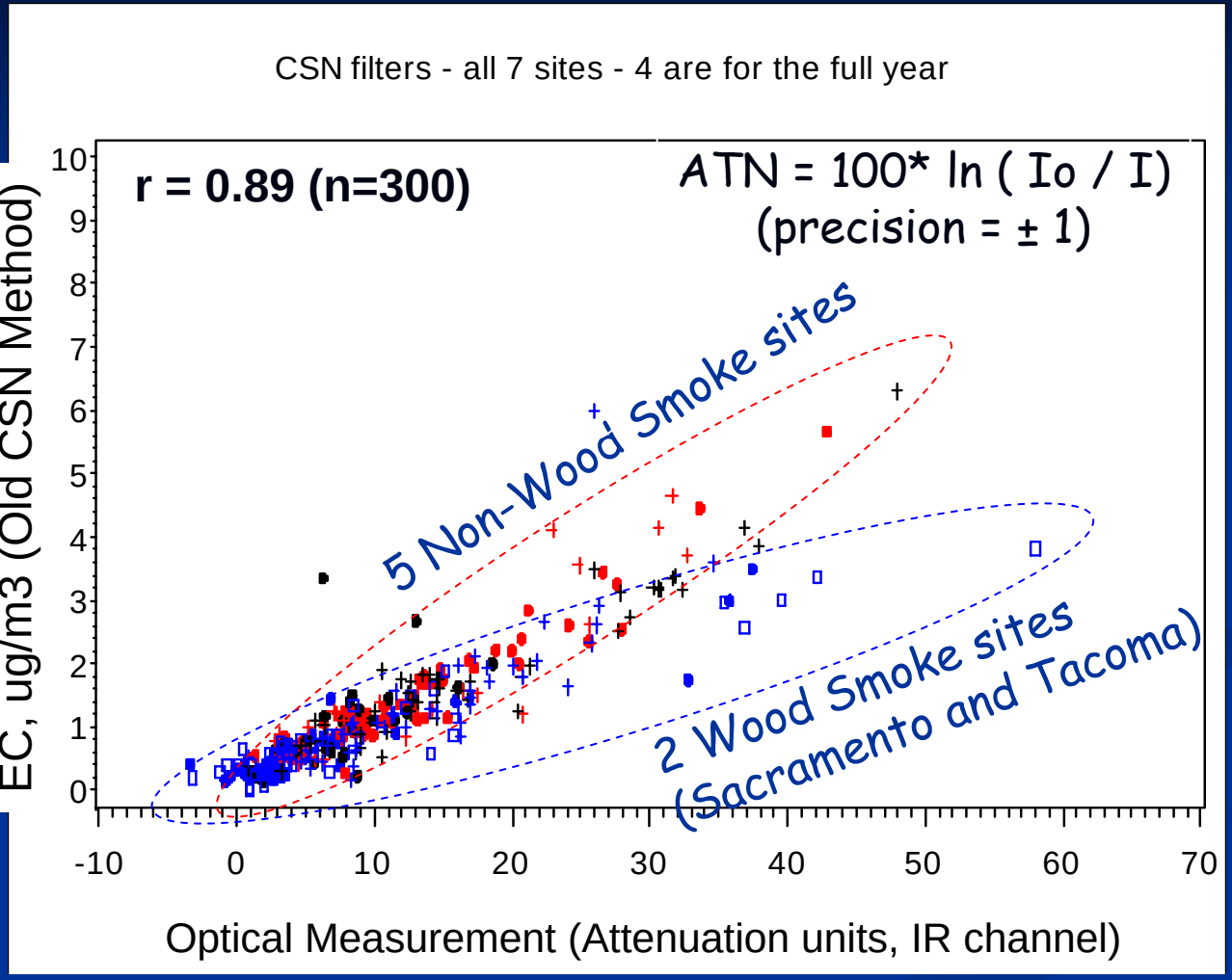


Joe Tikvart measured > 500 filters

CSN Teflon Filters

This is a non-destructive procedure

NIOSH-type EC vs. Optical Measurements (7 sites)

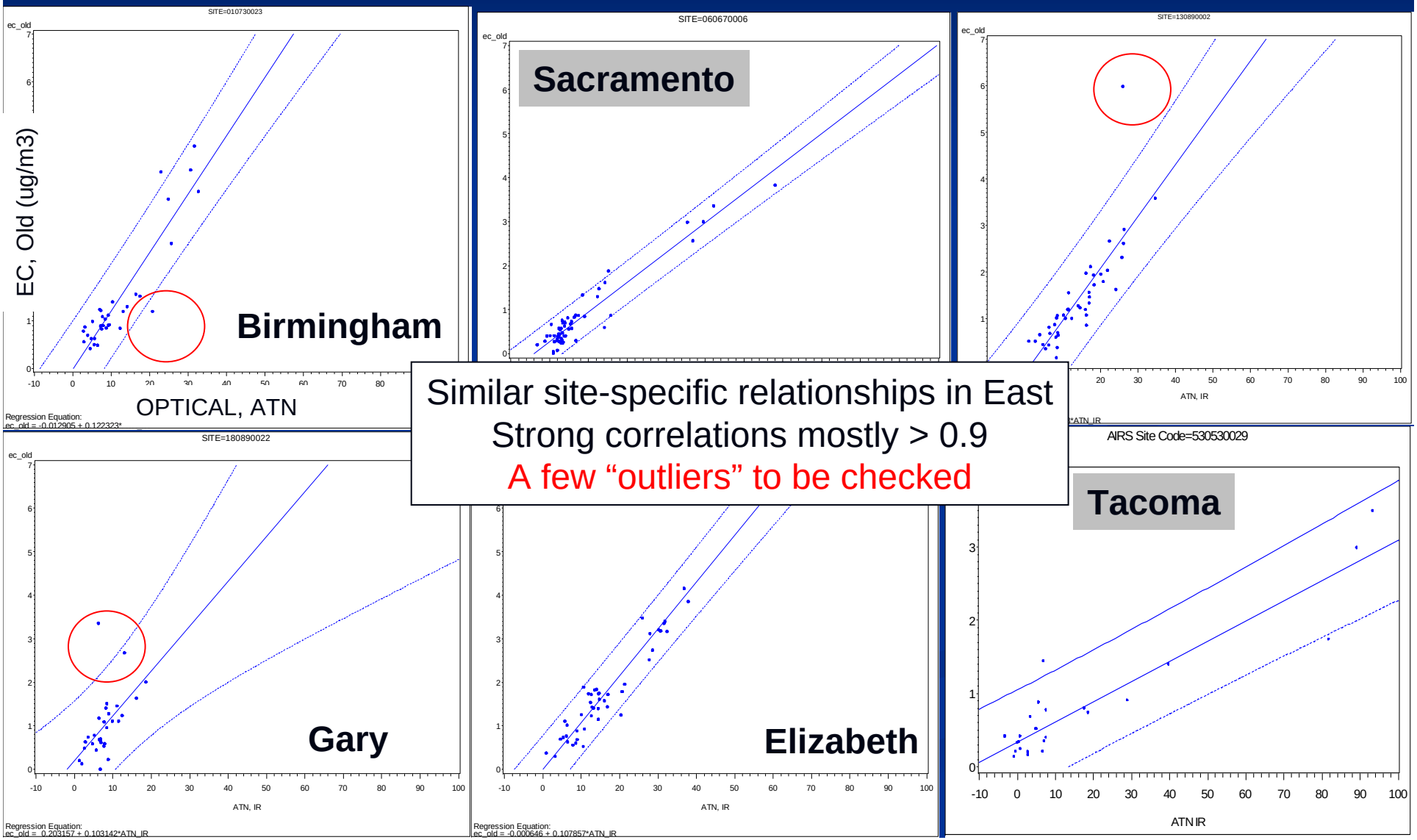


The OP21 measures at 2 wavelenths (370 and 880nm).
I only present results for the infra-red channel.

Magee Transmissometer Study

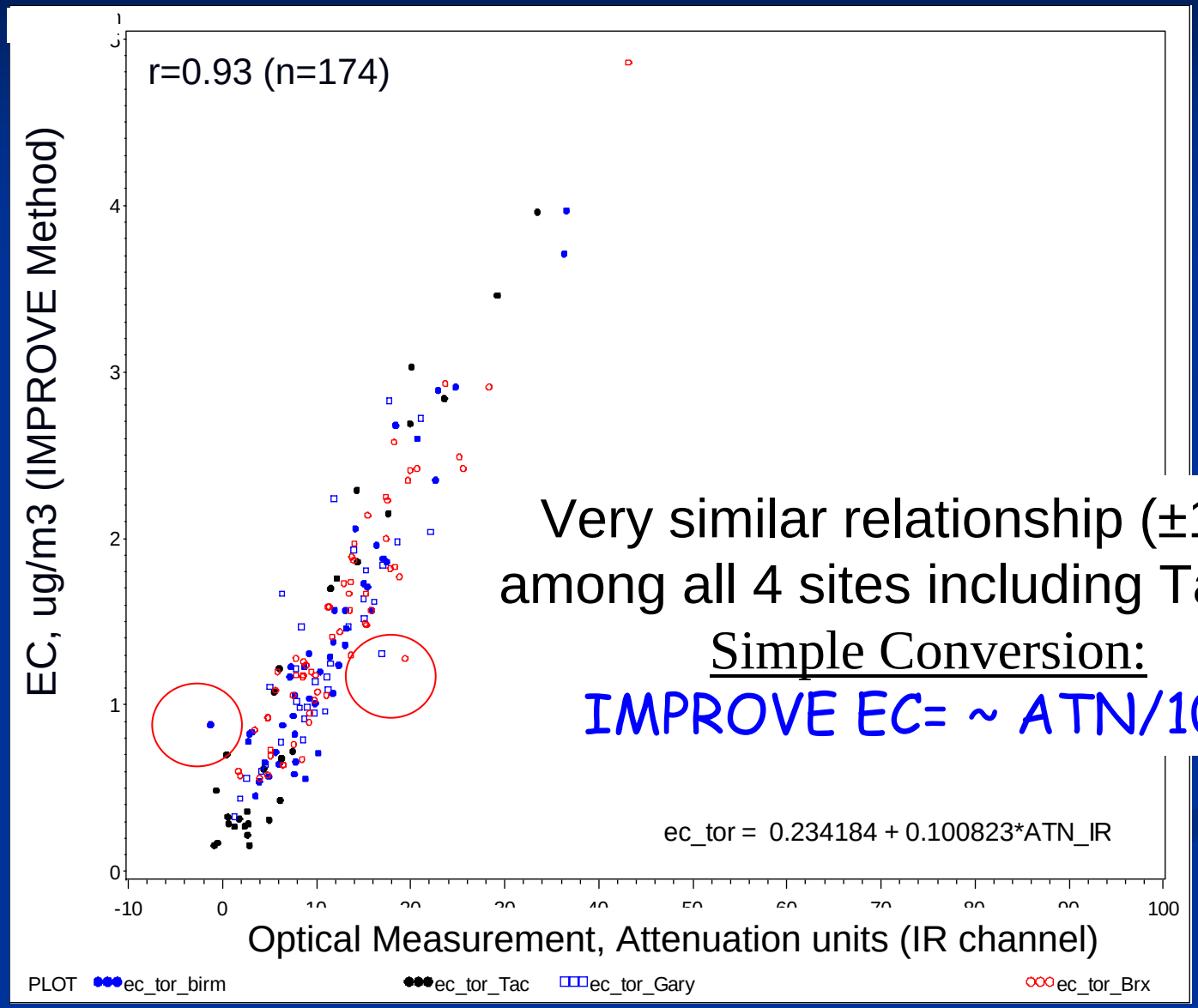
Optical attenuation vs. "old EC" varies by site

Wood smoke areas are different!



Similar site-specific relationships in East
Strong correlations mostly > 0.9
A few "outliers" to be checked

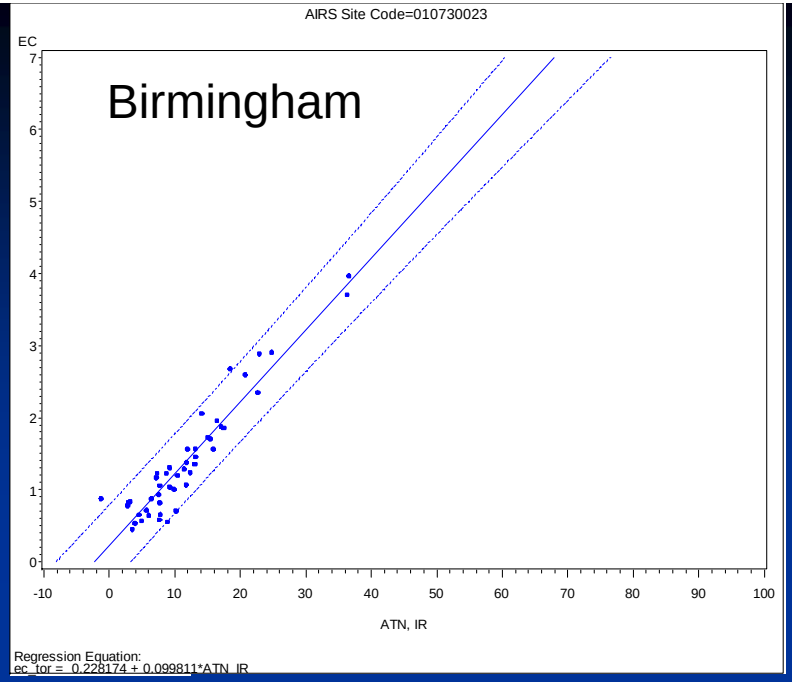
IMPROVE EC vs. Filter Attenuation (4 CSN sites)

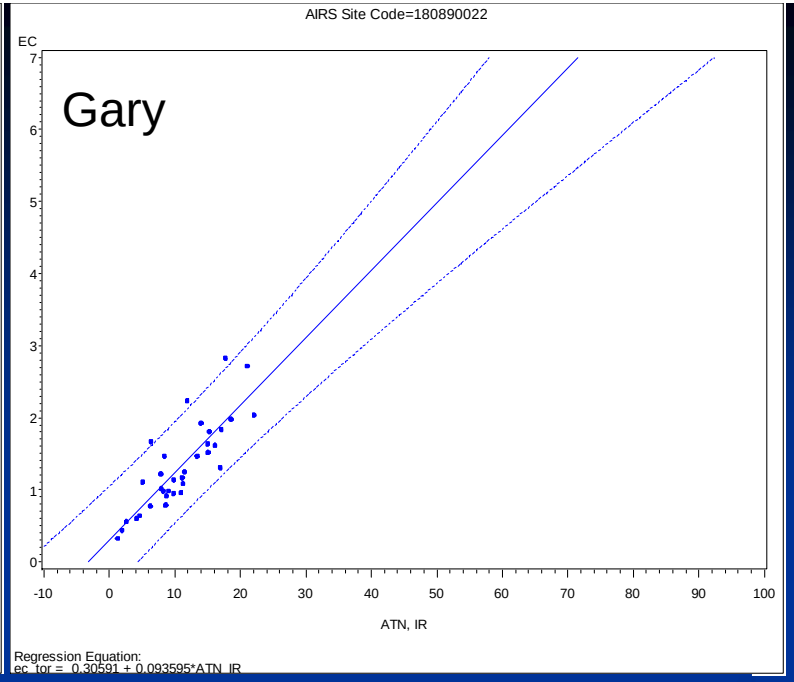


Very similar relationship (±10%) among all 4 sites including Tacoma

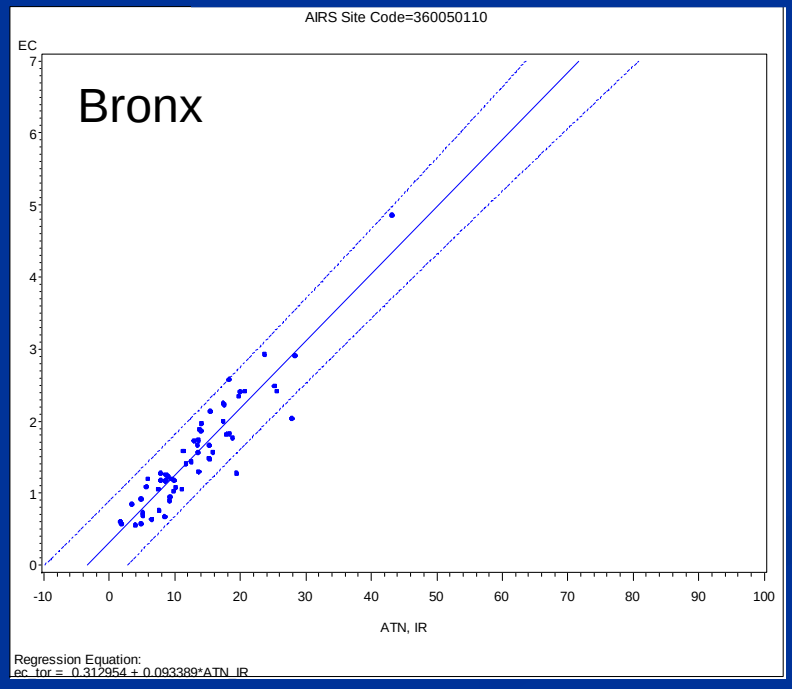
Simple Conversion:

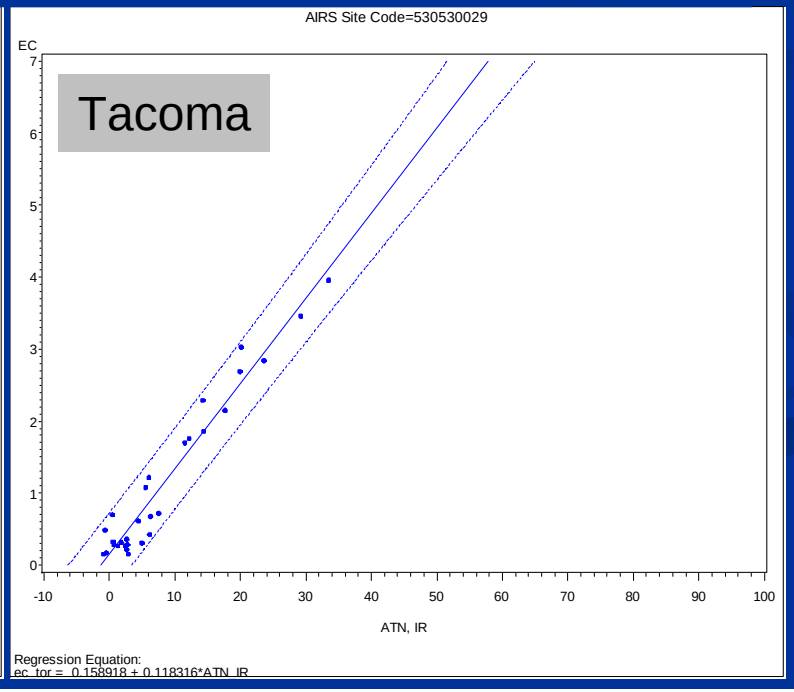
IMPROVE EC= ~ ATN/10 !!



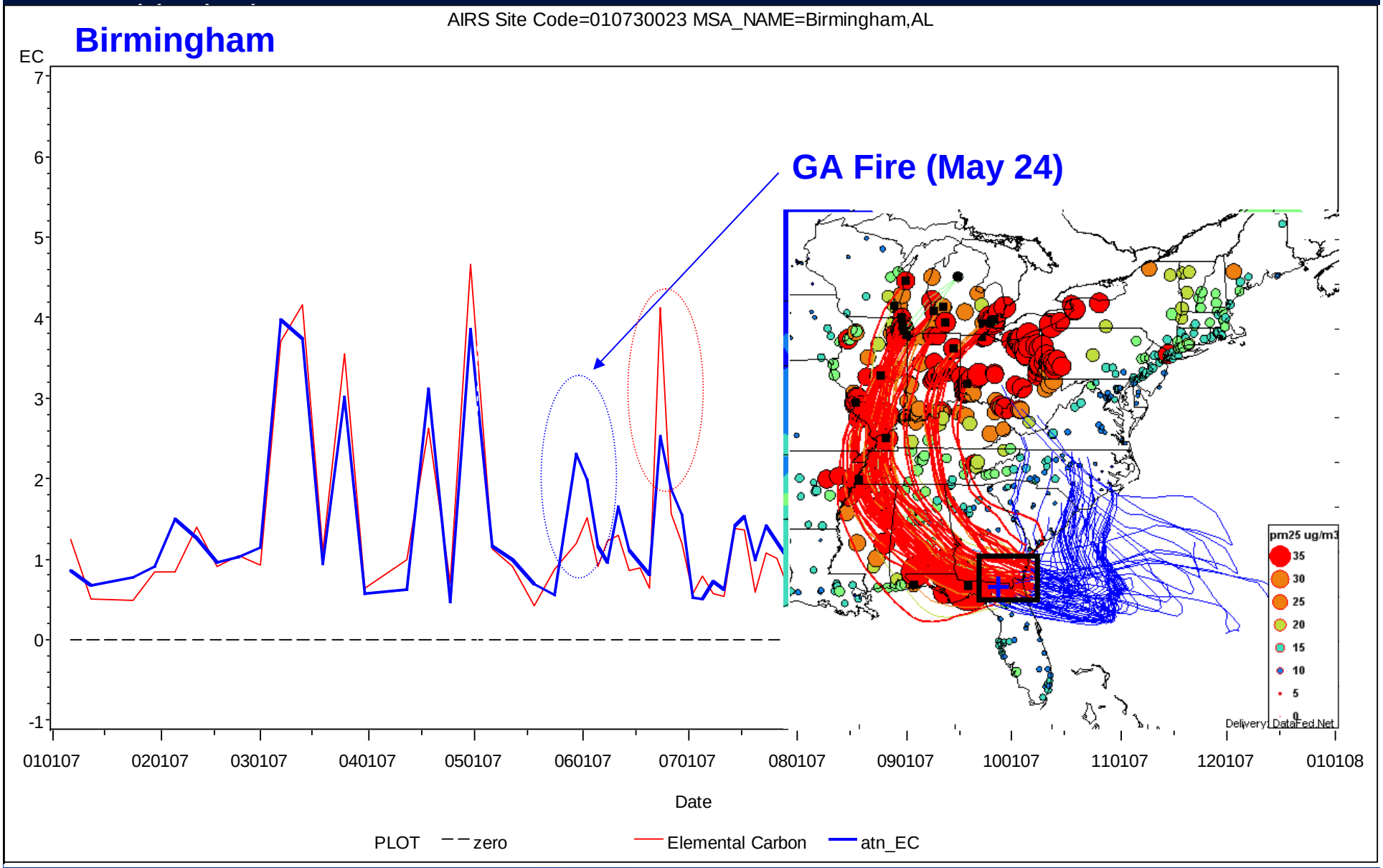


IMPROVE EC vs. Optical ATN (similar for each site)

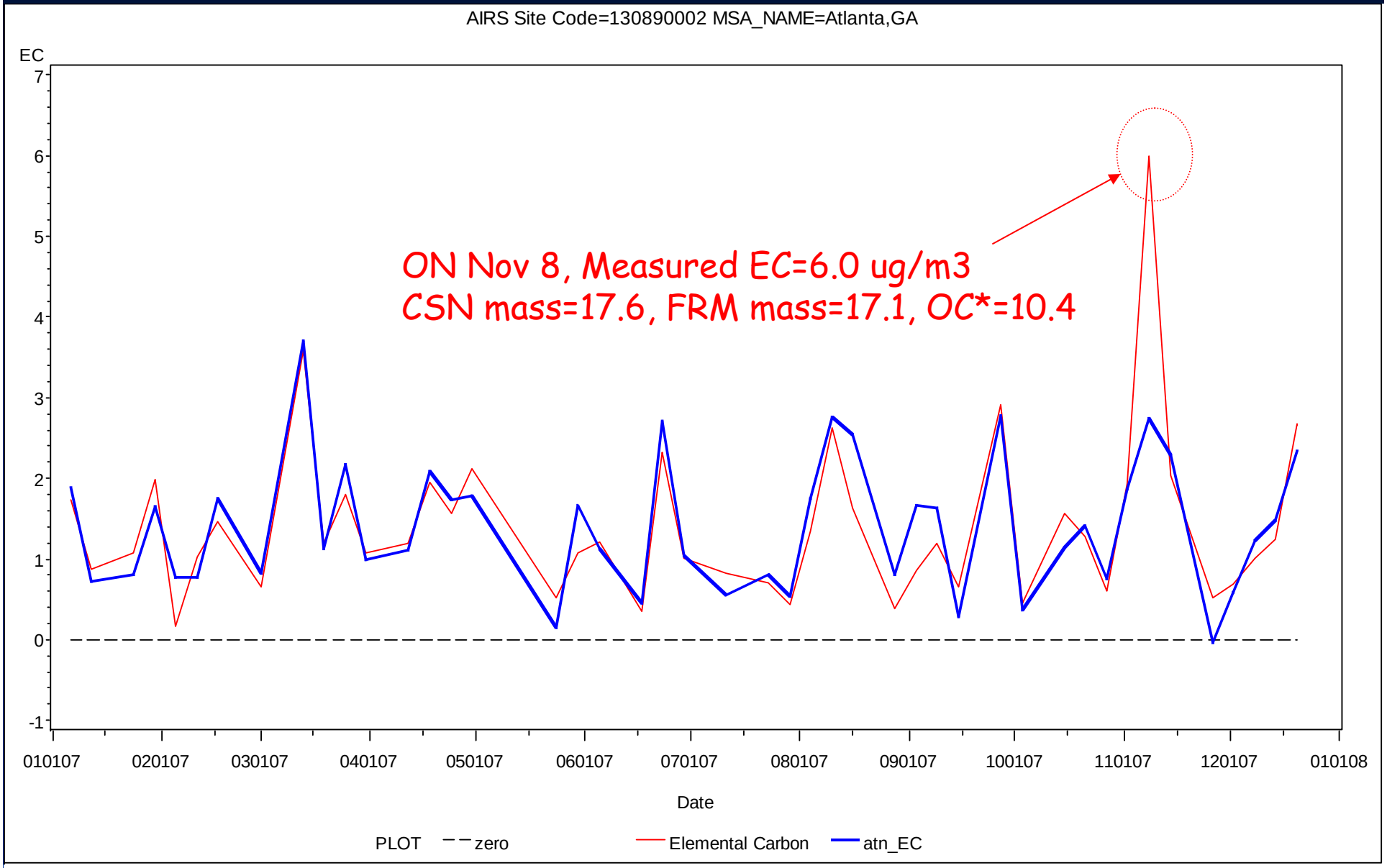




Magee Transmissometer Study



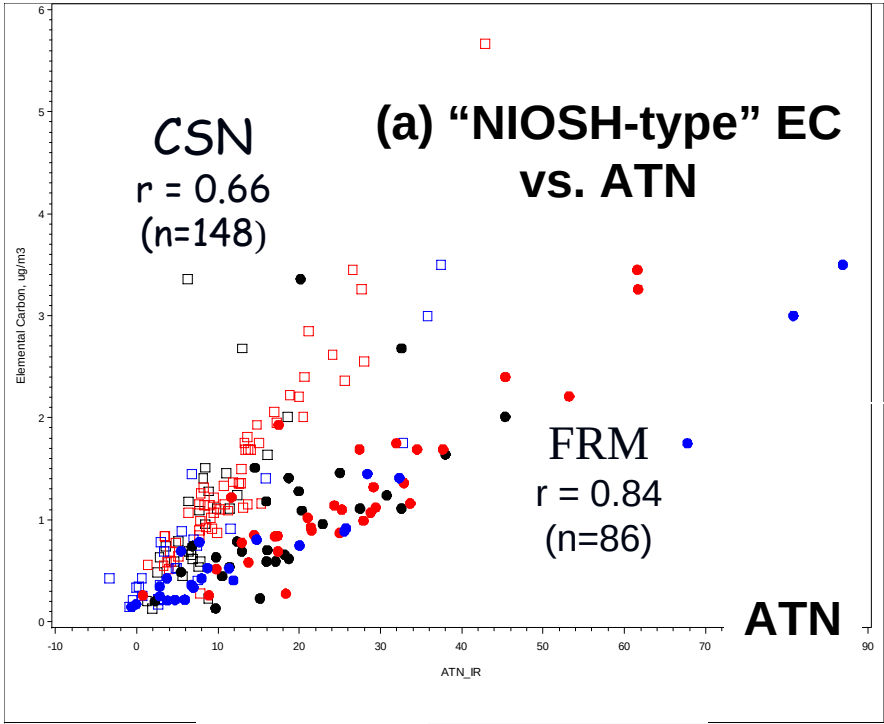
Magee Transmissometer Study

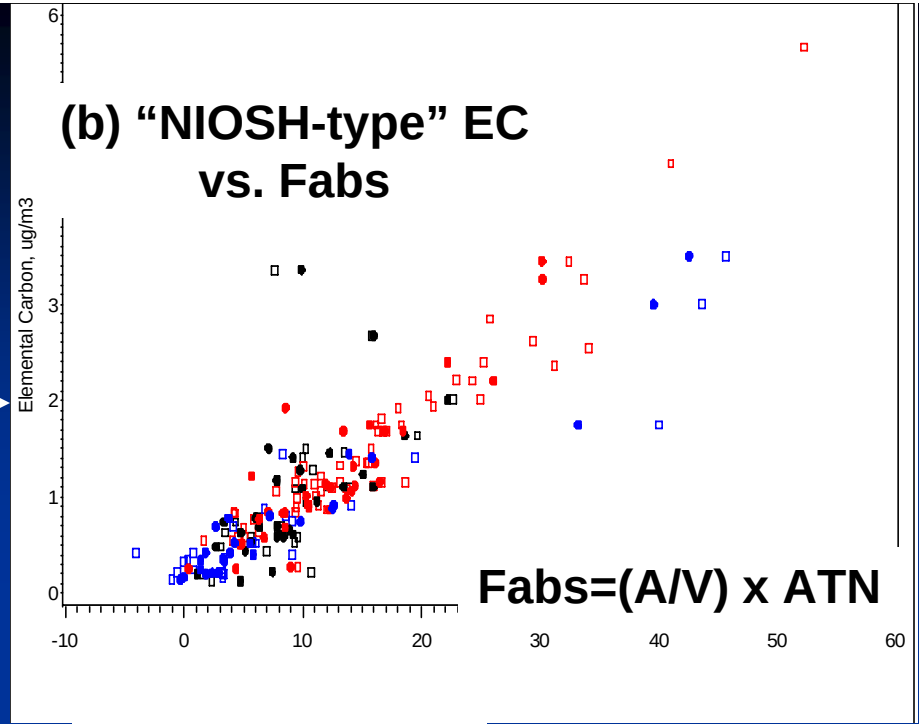


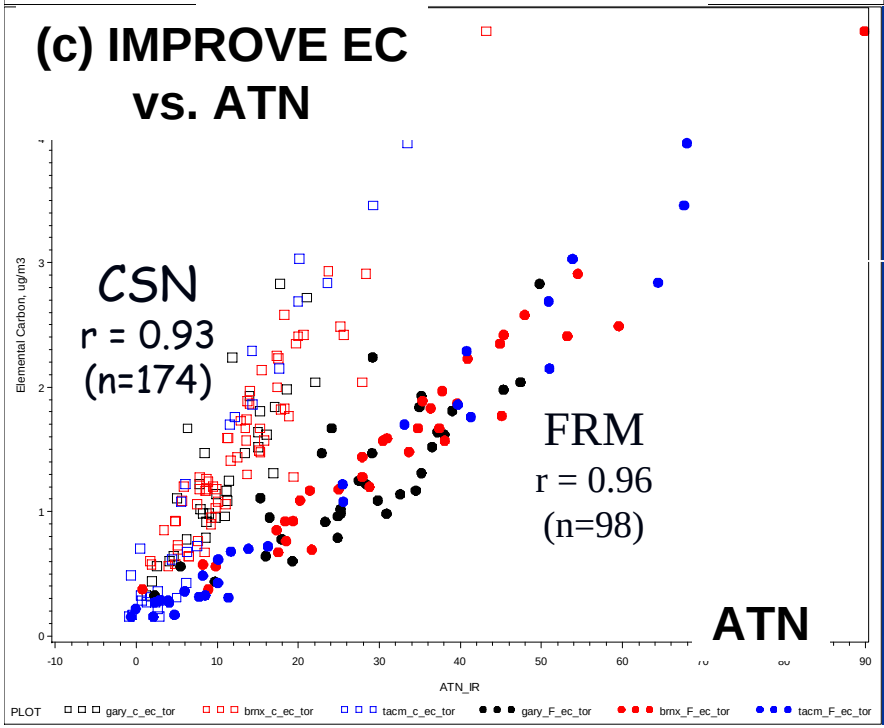
OC* is adjusted for CSN sampling artifact (i.e. blank corrected)

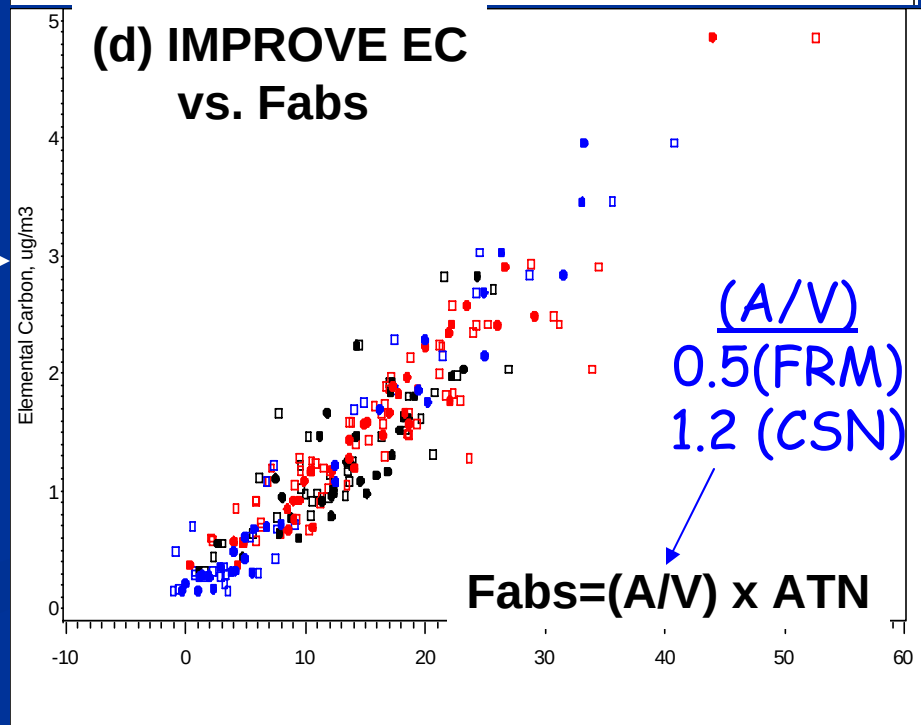
Now adding results for the 3 collocated FRM sites

We will normalize CSN and FRM filter attenuation for their different sampler flow rates and 24-hr sample volumes


(a) "NIOSH-type" EC vs. ATN
CSN
r = 0.66
(n=148)
FRM
r = 0.84
(n=86)
ATN
Elemental Carbon, ug/m3
ATN_IR

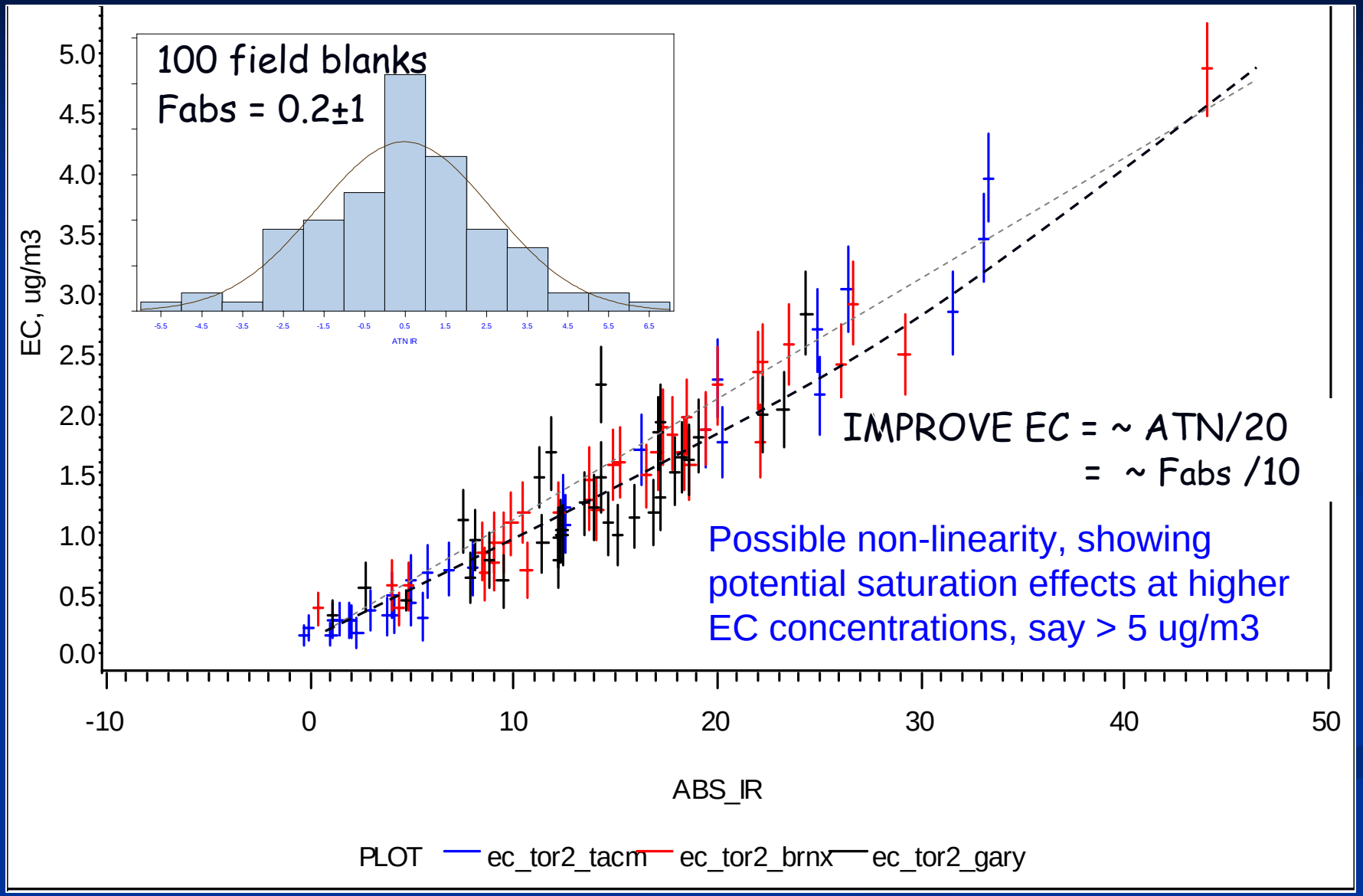

(b) "NIOSH-type" EC vs. Fabs
Fabs=(A/V) x ATN
Elemental Carbon, ug/m3

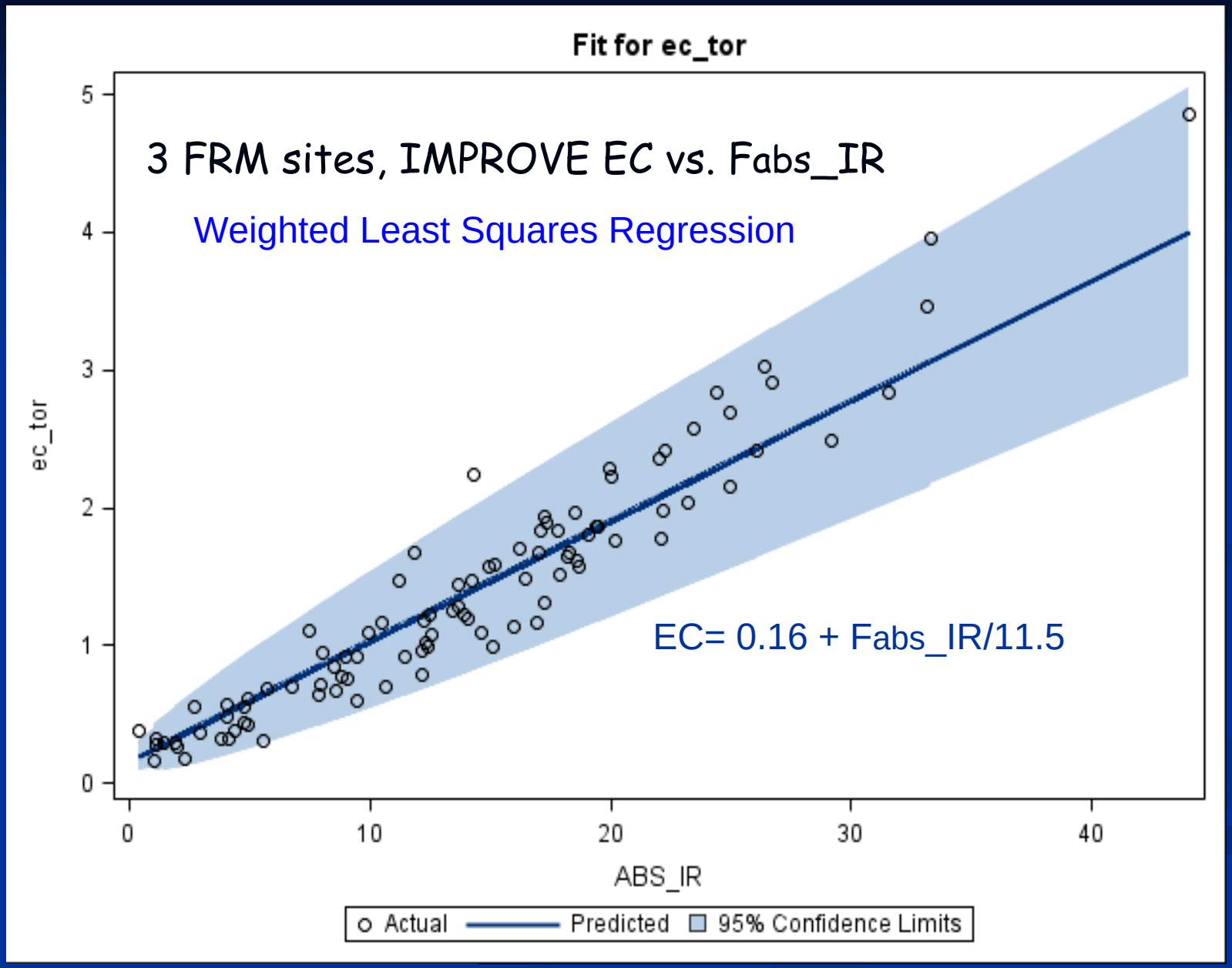

(c) IMPROVE EC vs. ATN
CSN
r = 0.93
(n=174)
FRM
r = 0.96
(n=98)
ATN
Elemental Carbon, ug/m3
ATN_IR
PLOT
gary_c_ec_tor
bmx_c_ec_tor
tacm_c_ec_tor
gary_F_ec_tor
bmx_F_ec_tor
tacm_F_ec_tor


(d) IMPROVE EC vs. Fabs
(A/V)
0.5(FRM)
1.2 (CSN)
Fabs=(A/V) x ATN
Elemental Carbon, ug/m3

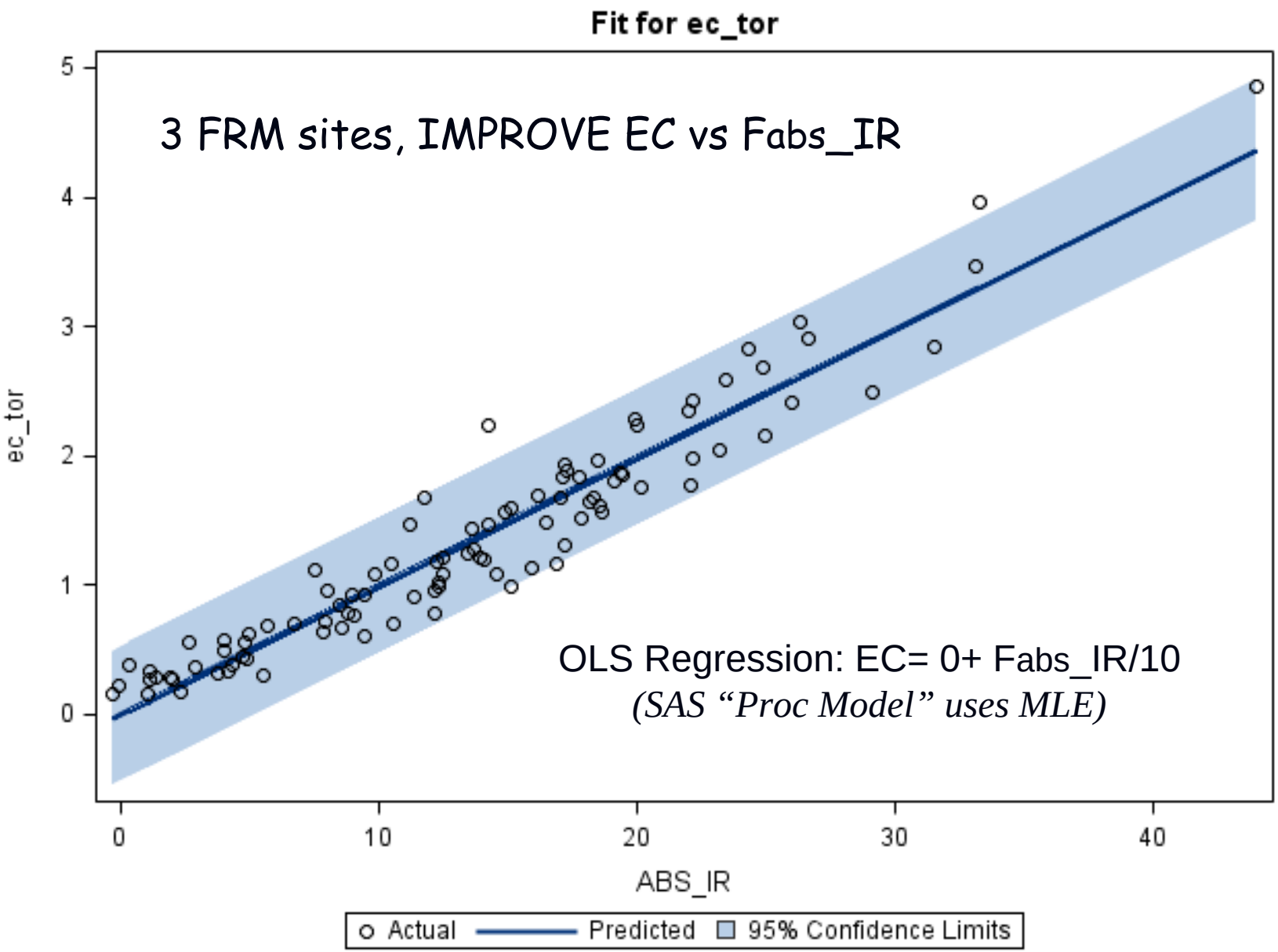
3 FRM sites, IMPROVE EC vs. Optical Measurements

Filter absorption (Fabs) is <u>much</u> more precise than thermal EC

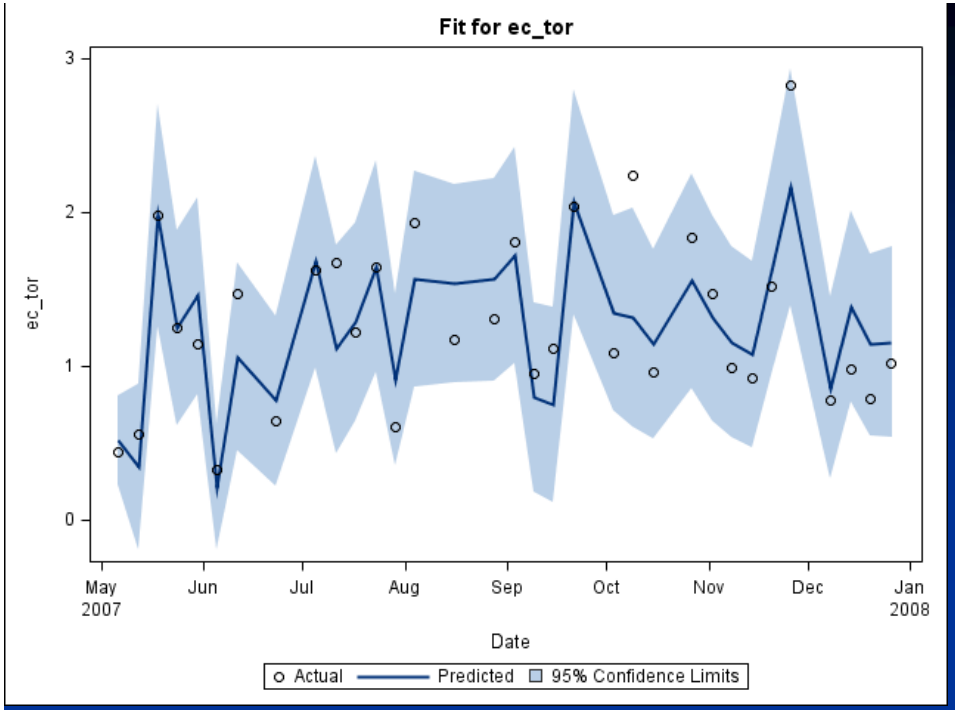




EC_unc
= **0.085** *Log(EC) + **0.254** (Mark Green, DRI)


Fit for ec_tor
3 FRM sites, IMPROVE EC vs Fabs_IR
OLS Regression: EC= 0+ Fabs_IR/10
(SAS "Proc Model" uses MLE)
ec_tor
ABS_IR
0
1
2
3
4
5
0
10
20
30
40
Actual
Predicted
95% Confidence Limits

Site Specific Relationships



Parameter	Estimate	Std Err	t Value	Pr > |t|
a	0.120029	0.1021	1.18	0.2488
b	24.37738	2.3294	10.46	<.0001

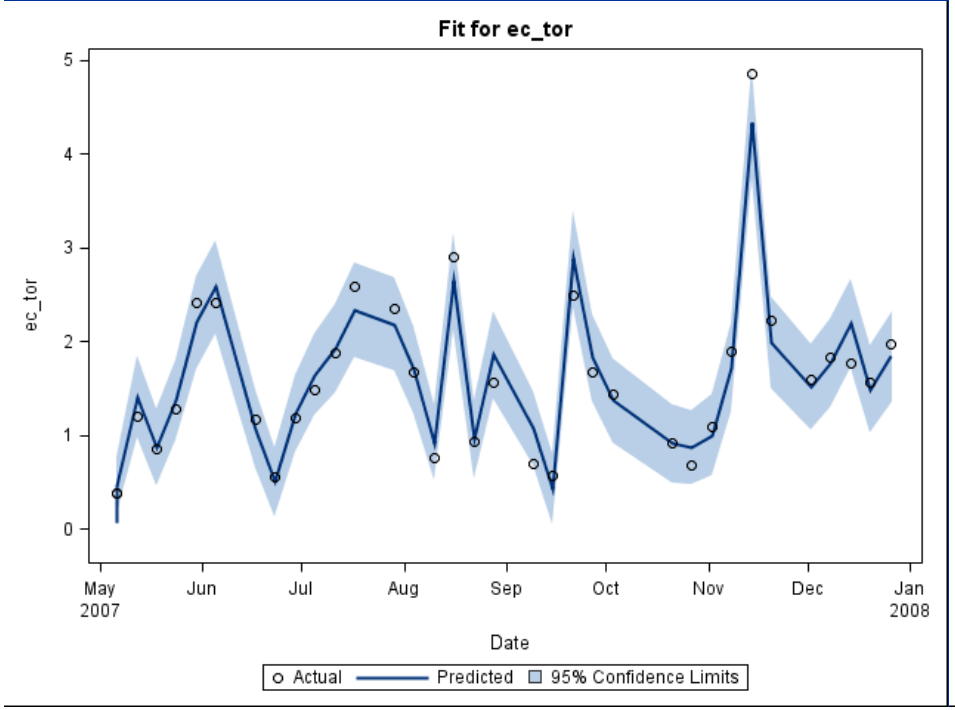
R2=0.7793(Gary)

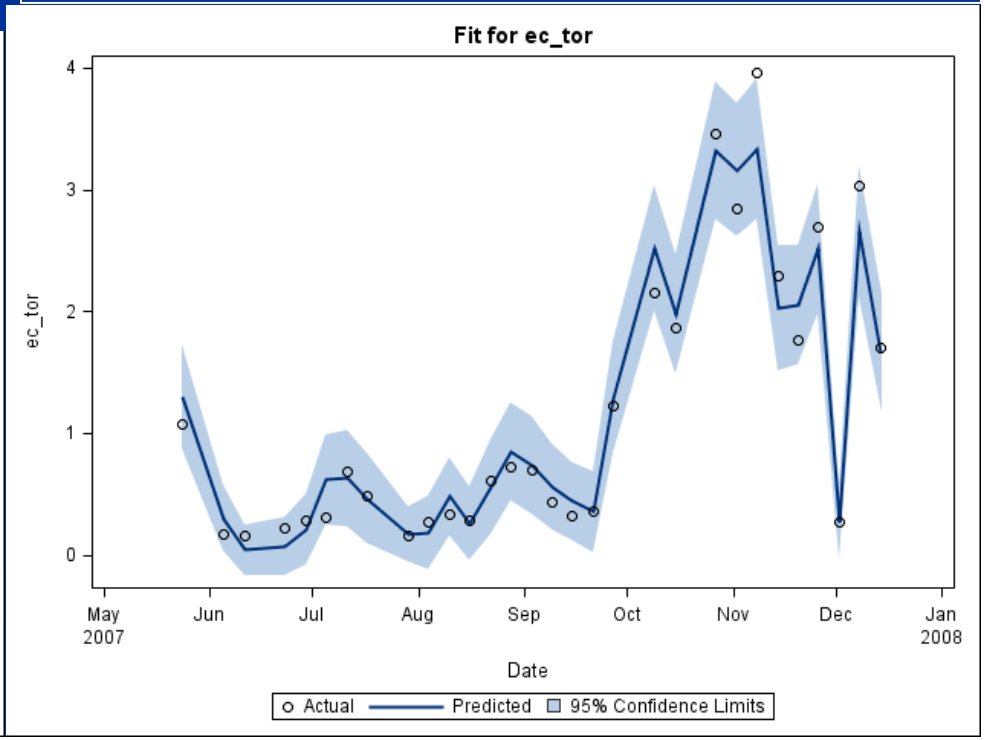
Parameter	Estimate	Std Err	t Value	Pr > |t|
a	0.032818	0.0672	0.49	0.6285
b	20.88619	0.9048	23.08	<.0001

R2 = 0.9417 (Bronx)

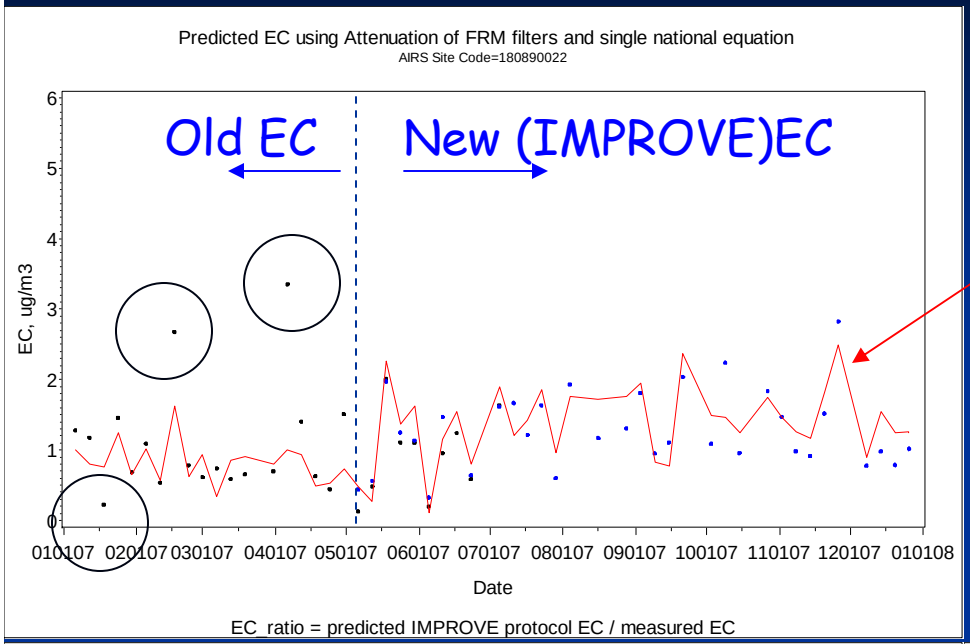
Parameter	Estimate	Std Err	t Value	Pr > |t|
a	0.069648	0.0374	1.86	0.0732
b	20.82608	0.7487	27.82	<.0001

R2=0.9651(Tacoma) These coeff not normalized for Volume



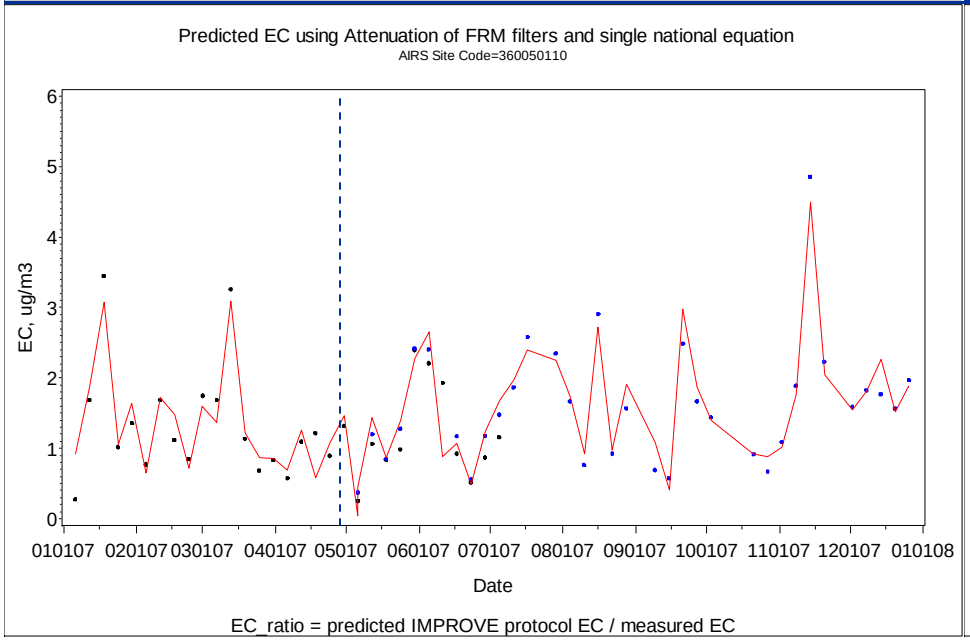


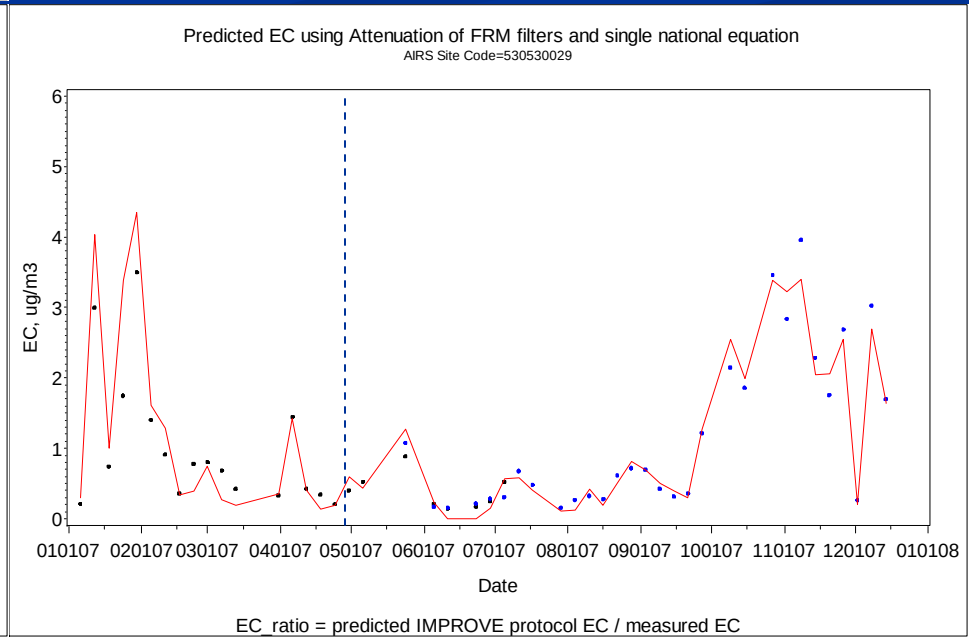
Estimated EC using FRM Filter Absorption with single national equation, EC=Fabs/10



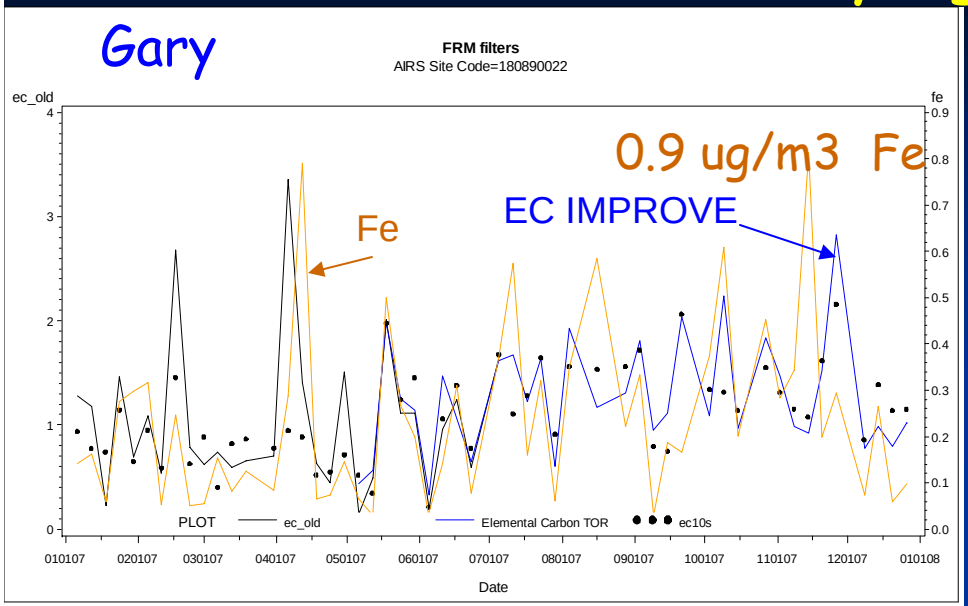
These graphs show that predicted new EC with single equation tracks the IMPROVE measurements among sites

Fabs/10 can help identify potential outliers in measured EC.





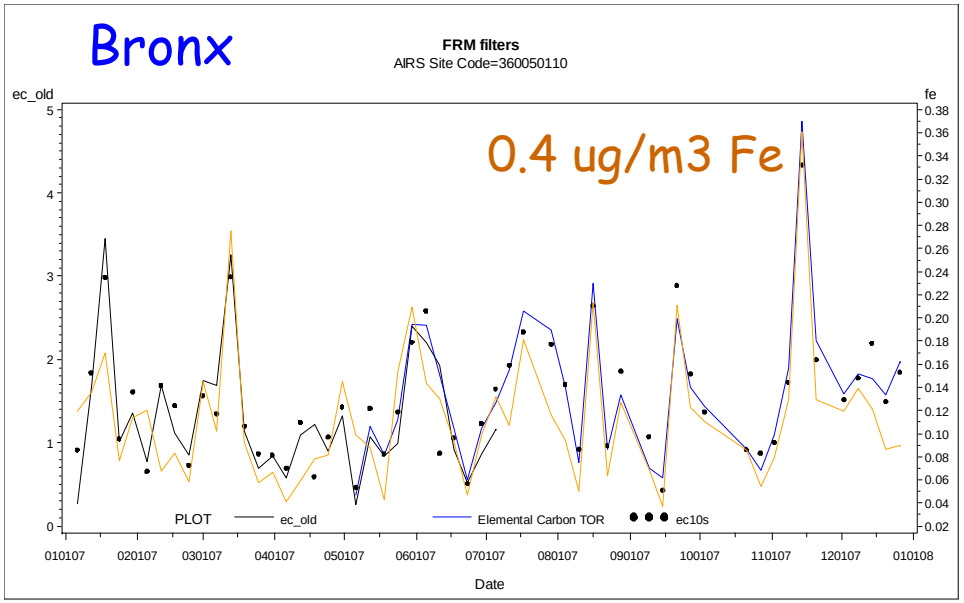
EC is not the only light absorbing aerosol

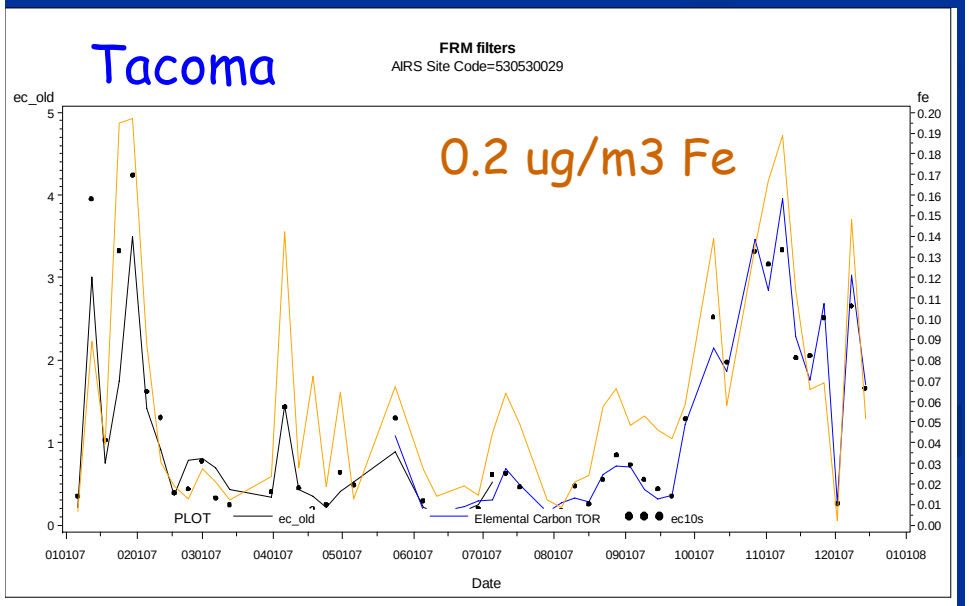


Iron can also be important !
It <u>may</u> affect measured EC

Urban Fe & IMPROVE EC Correlations
Gary, r=0.47
Bronx, r=0.82
Tacoma, r=0.90

With typical mobile dominated urban emissions





PM2.5 Attenuation Coefficients (Teflon Filters)

using Magee Transmissometer (880nm)

Carbon Protocol	CSN / FRM Networks	
	Wood Smoke	Non-WS
IMPROVE_A (TOR)	10-11 m^2g^{-1}	10-11 m^2g^{-1}
EPA "NIOSH-Type" (TOT)	13-16 m^2g^{-1}	10-12 m^2g^{-1}

These numbers for teflon filters suggest aerosol and carbon-protocol specific differences in PM2.5 absorption

Summary and Next Steps

- Optical filter absorption is dependent on many factors
  - Wavelength
  - Thermal Optical Protocol
  - Filter material (teflon vs quartz)
  - Fe concentrations
    - warrants further study
- These measurements can help estimate EC without speciation sampling and help QA thermal OC-EC
- EPA is pursuing analysis of archived filters and potential incorporation into CSN and FRM networks
  - Can help provide daily EC and higher spatial resolution
  - Will be closing coordinating with State/local agencies

We can't do this without YOU!