

Optical Absorption on IMPROVE, CSN and FRM filters

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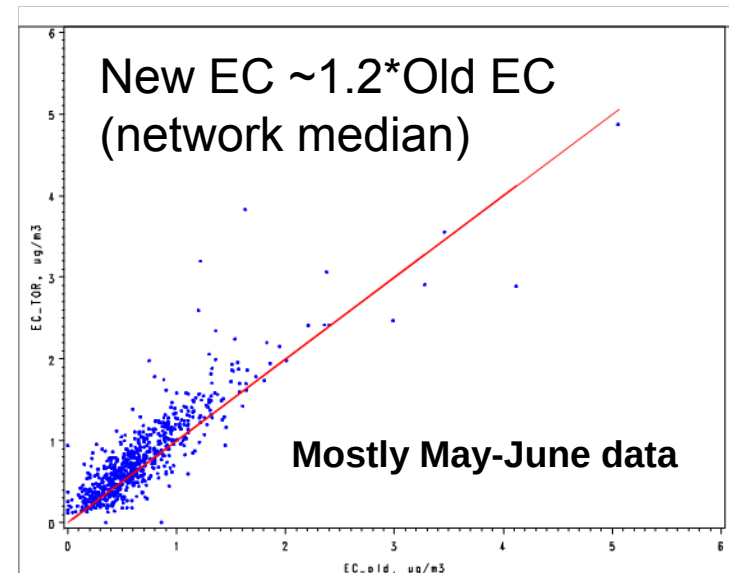
For Presentation at IMPROVE Steering Committee Meeting
Wind Caves National Park
Sept 22, 2009

Findings

- Very high correlation between measured EC and optical measurements of urban PM_{2.5} filters
- Better and consistent relationship among sites with IMPROVE carbon method compared to EPA's older NIOSH-type protocol
 - Single national relationship may be possible
- Interesting results using IMPROVE network filters

Background

- IMPROVE has been doing optical measurements for a long time (reported as Babs, Mm-1)
 - Since 1994 with HIPS
- 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.
 - (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 PM_{2.5} NAAQS Implementation
- Potential climate legislation
 - EPA to possibly identify BC sources for mitigation

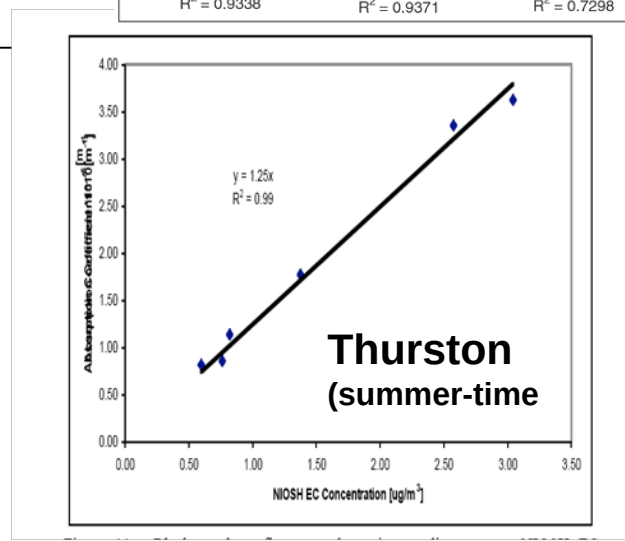
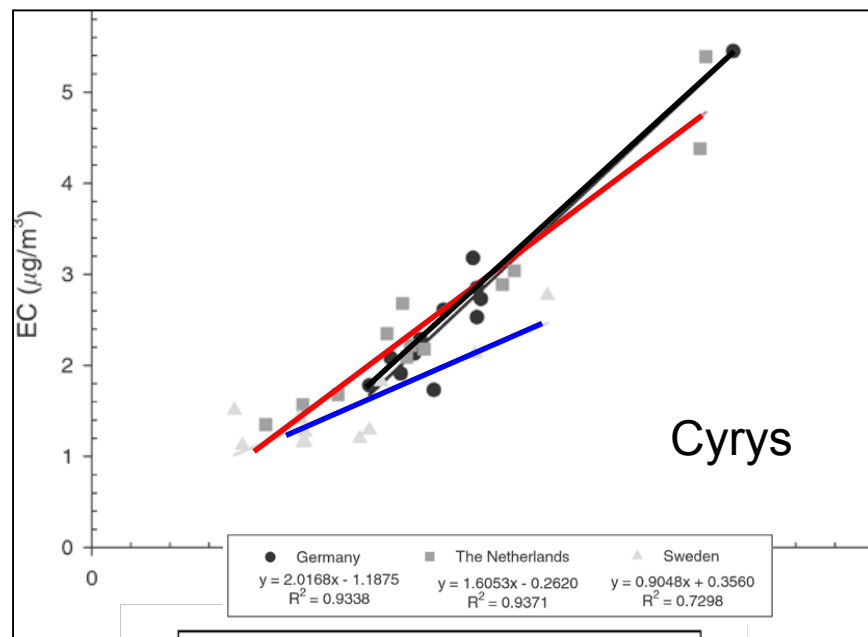
Sept 21 News:

Carper Introduces Rider on Soot Study To Interior-Environment Appropriations Bill

- Sen. Thomas Carper (D-Del.) introduced an amendment that called for an EPA study of the environmental, economic, and health impacts of soot emissions worldwide (H.R. 2996).
- The study would identify sources of soot emissions, also called black carbon, and effective control techniques; determine the public health, climate, and economic impacts of such emissions; and specify sources of funding for control technology
- Black carbon emissions are responsible for causing serious respiratory and cardiac health problems, he said. It is second only to carbon dioxide in global emissions of greenhouse gases, Carper added.

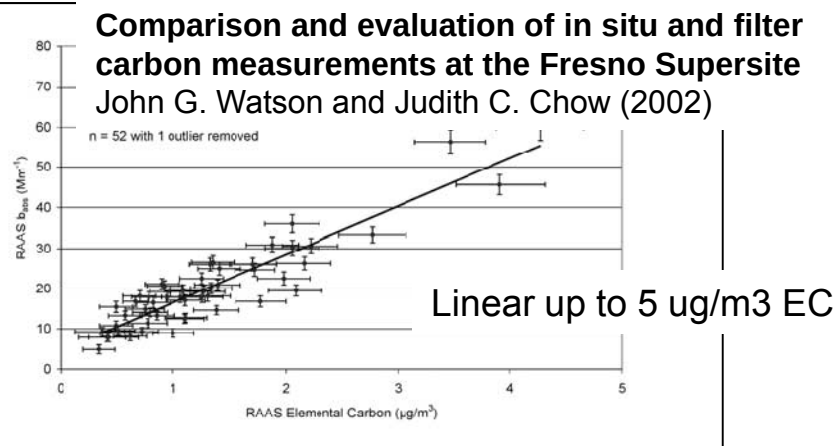
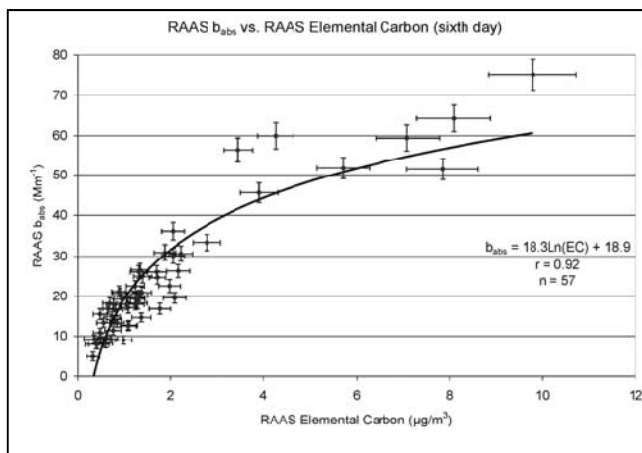
Optical Measurements highly correlate with “EC”

- A 50-year old method:
“Smoke Stain
Reflectometer,” recently
with Teflon Filters
- Cyrus 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 filter analyses including optical “EC” (2007)**
 - To produce PM2.5 composition at 20 FRM sites without speciation data
 - “BC” using densitometer at 3 FRM-CSN sites

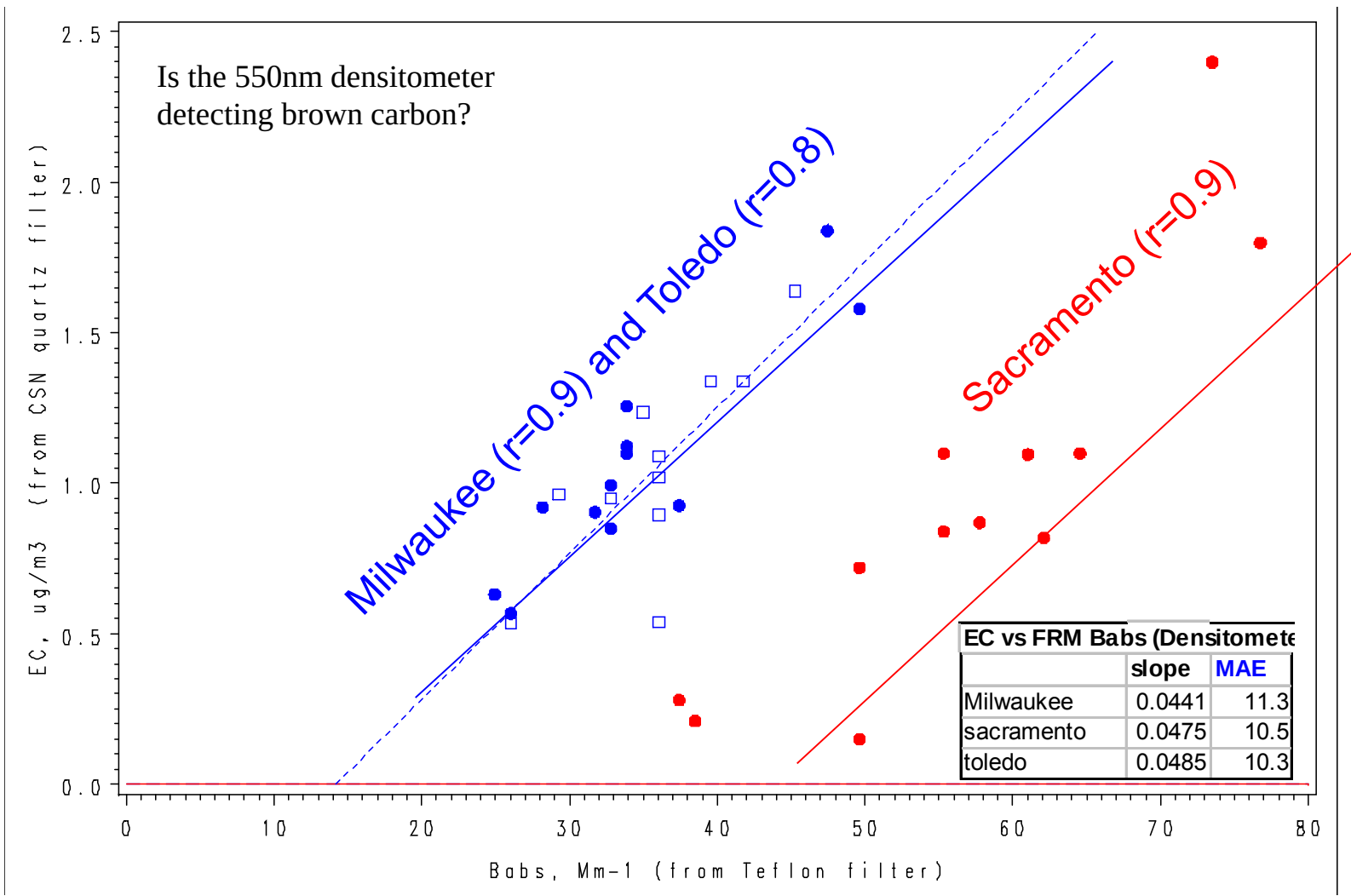


[Designations Web Site](http://www.epa.gov/ttn/naaqs/pm/docs/available_new_speciation_data_pm2.5_naa.pdf)

**http://www.epa.gov/ttn/naaqs/pm/docs/available_new_speciation_data_pm2.5_naa.pdf

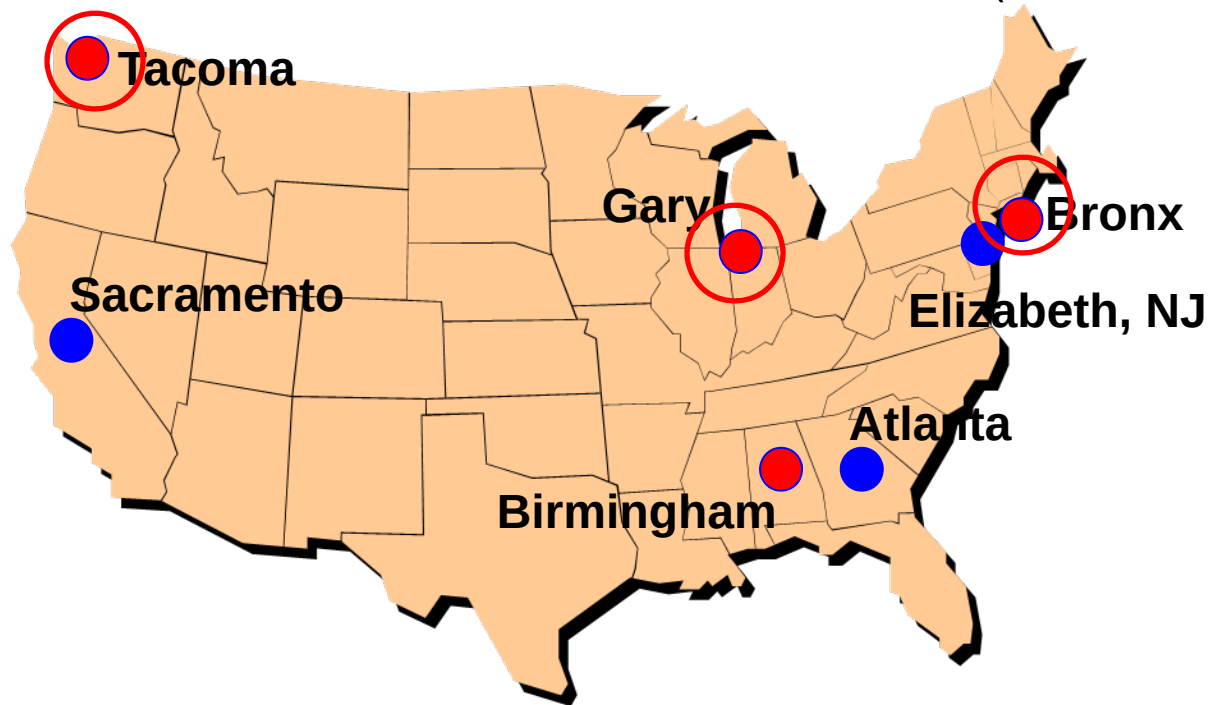
PILOT densitometer study (2007)

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



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
 - Subset of 3 sites with collocated FRM filters (16.7 LPM)

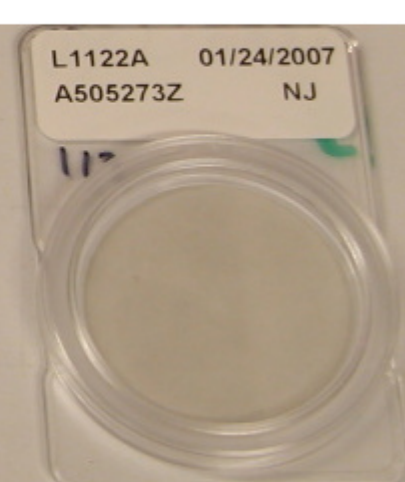


Field
Blank

EC= 1.25 ug/m³
PM_{2.5}= 18.3 ug/m³

EC= 3.0 ug/m³
PM_{2.5} = 24.5 ug/m³

EC = 1.1 ug/m³
PM_{2.5} = 12.9 ug/m³

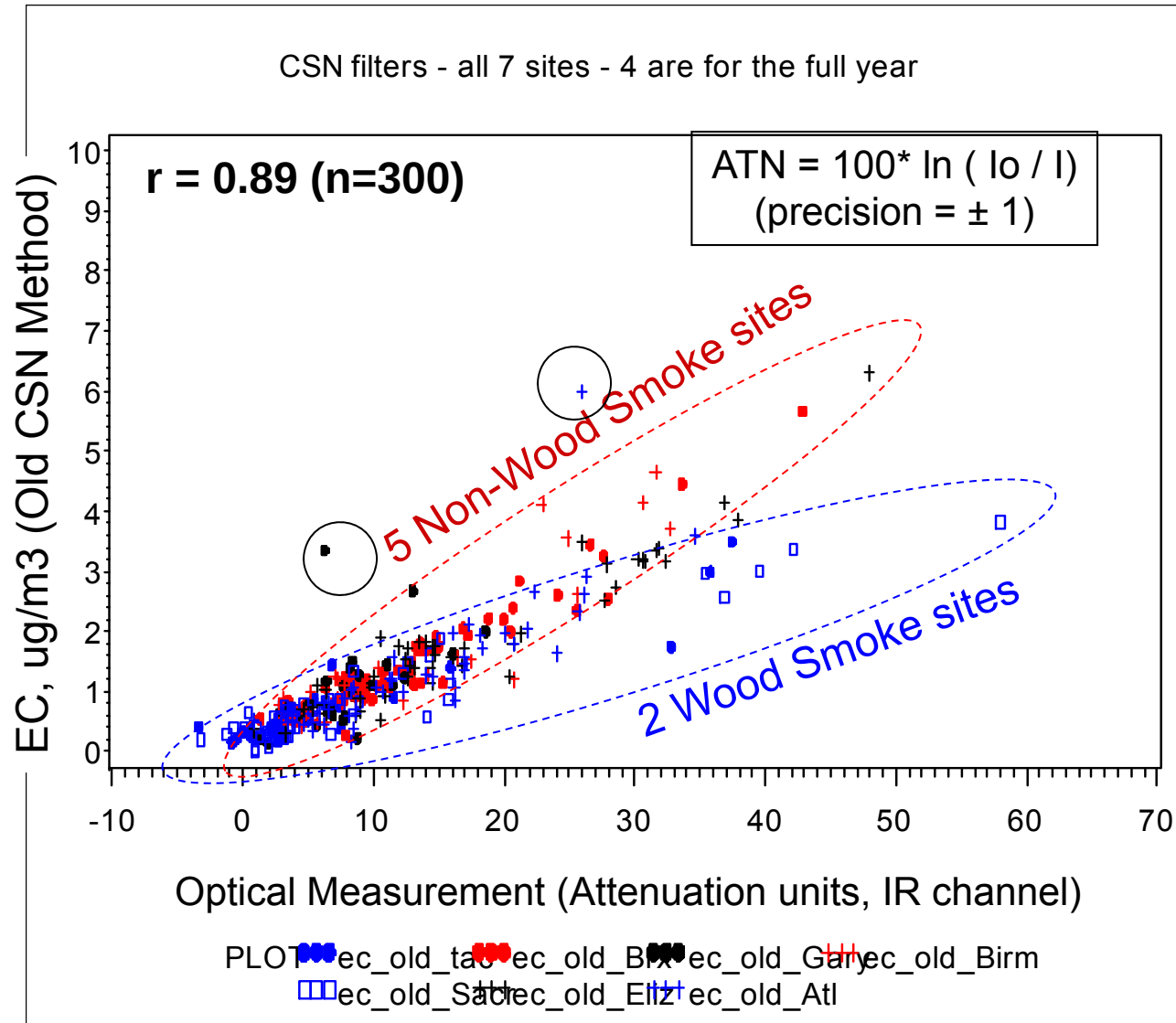


Tikvart measured > 500 filters

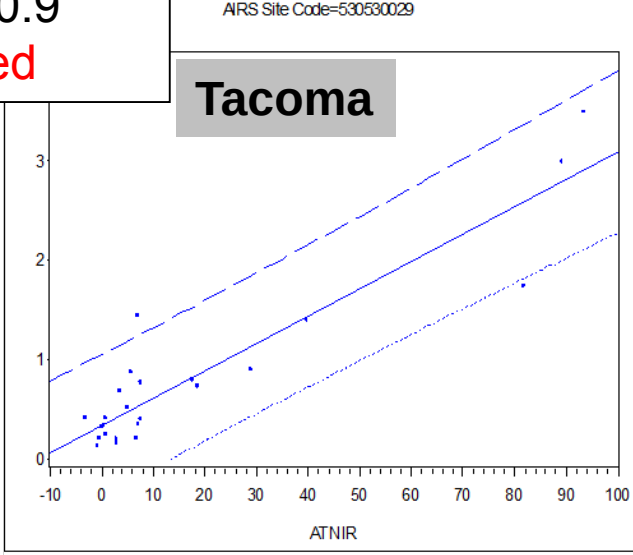
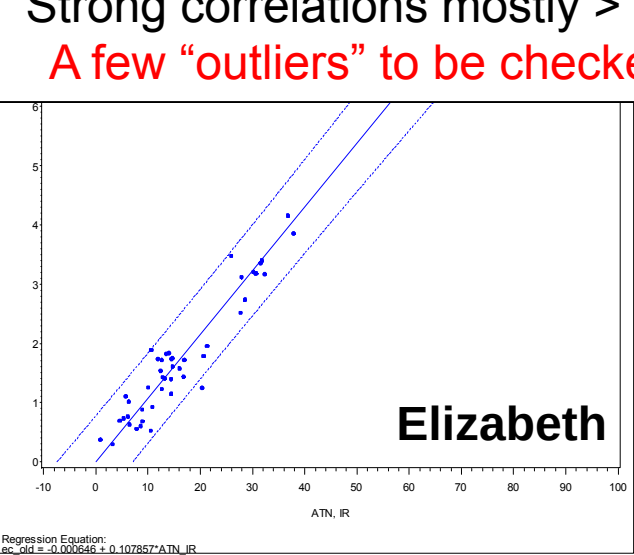
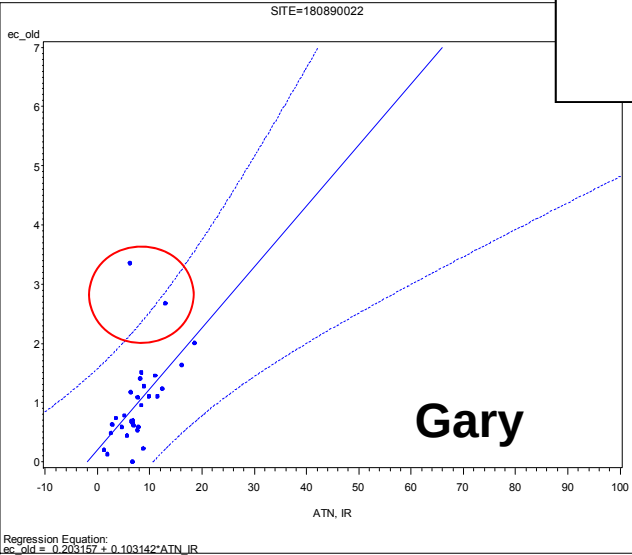
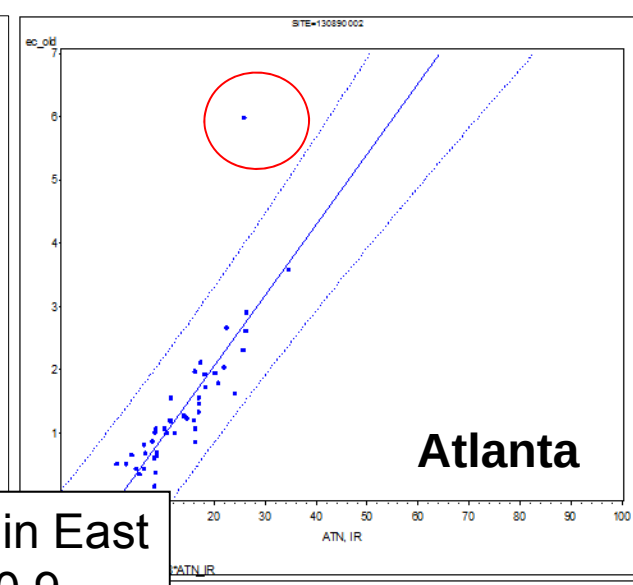
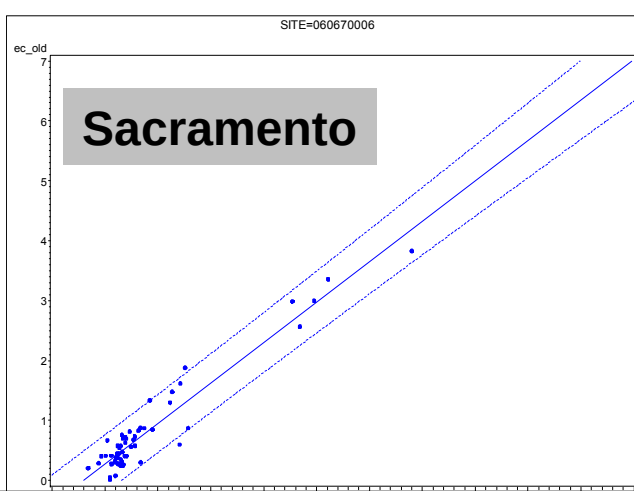
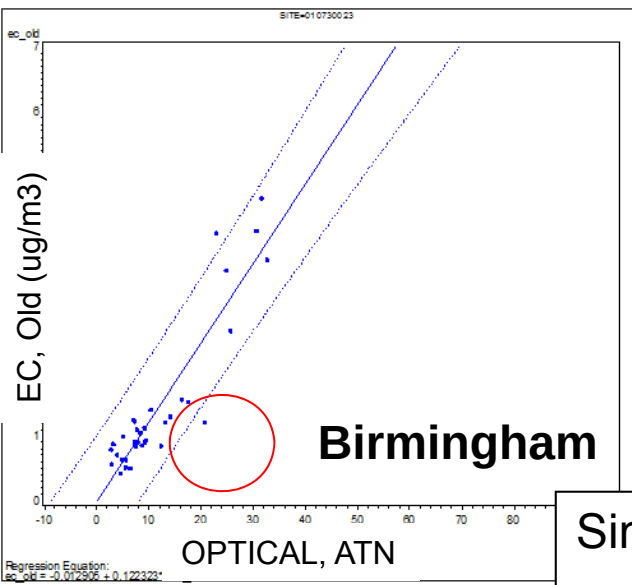
CSN Teflon Filters



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

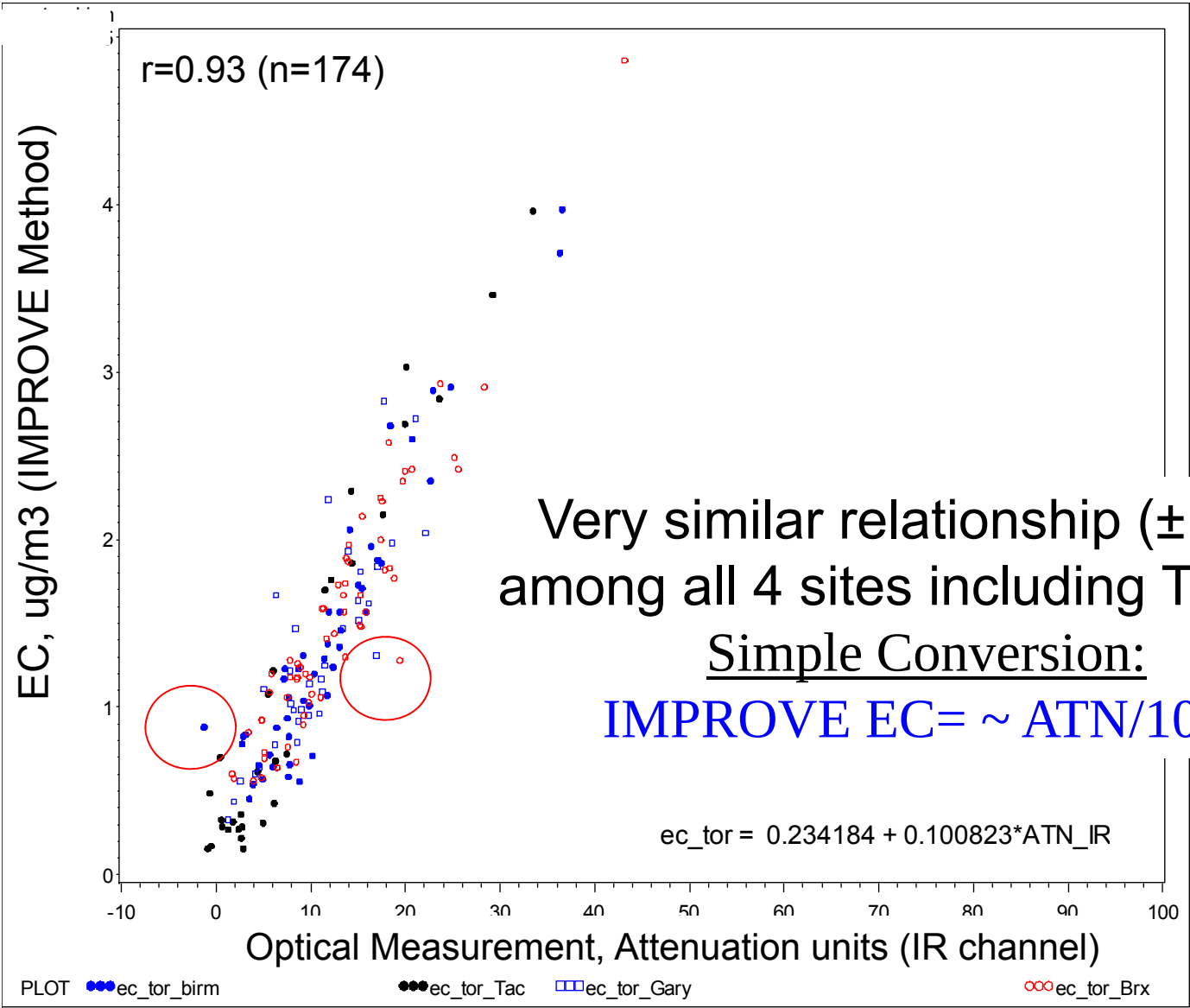


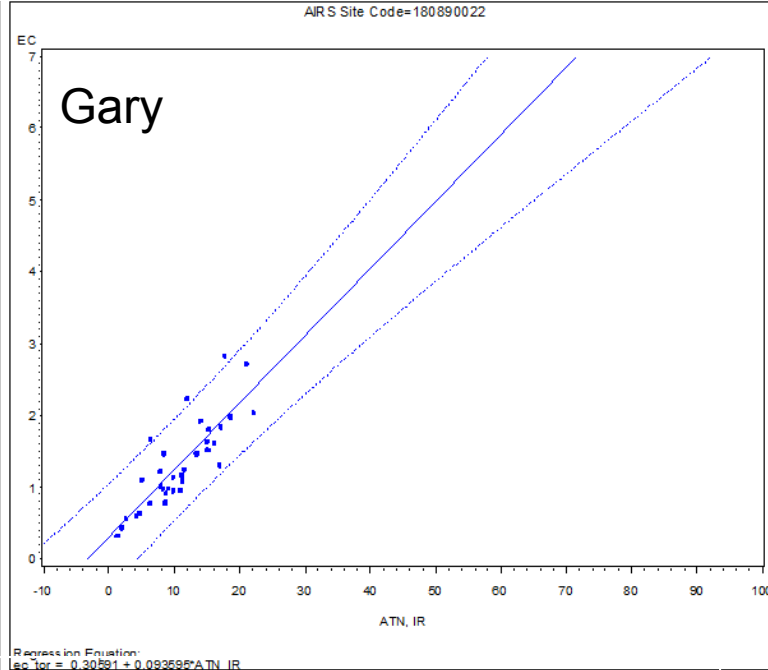
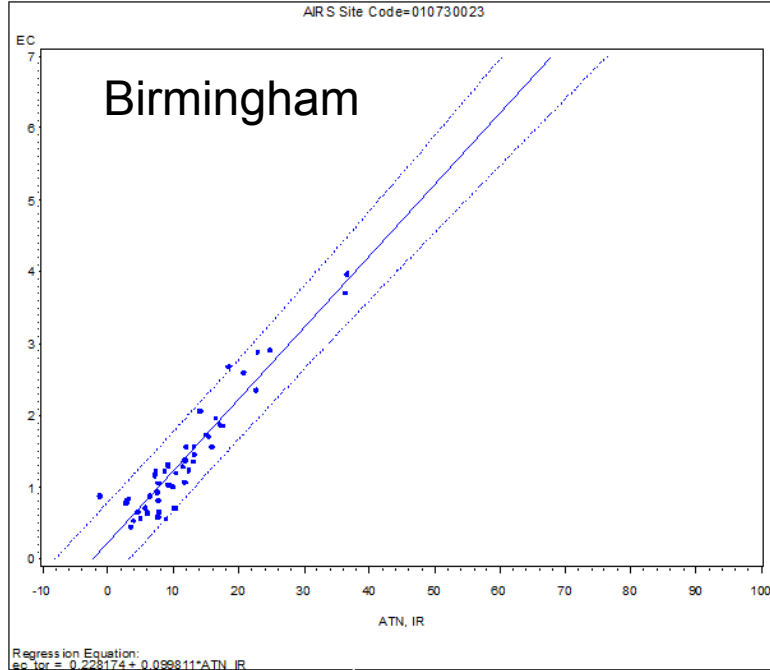
Optical attenuation vs “oldEC” varies by site wood smoke areas are different!



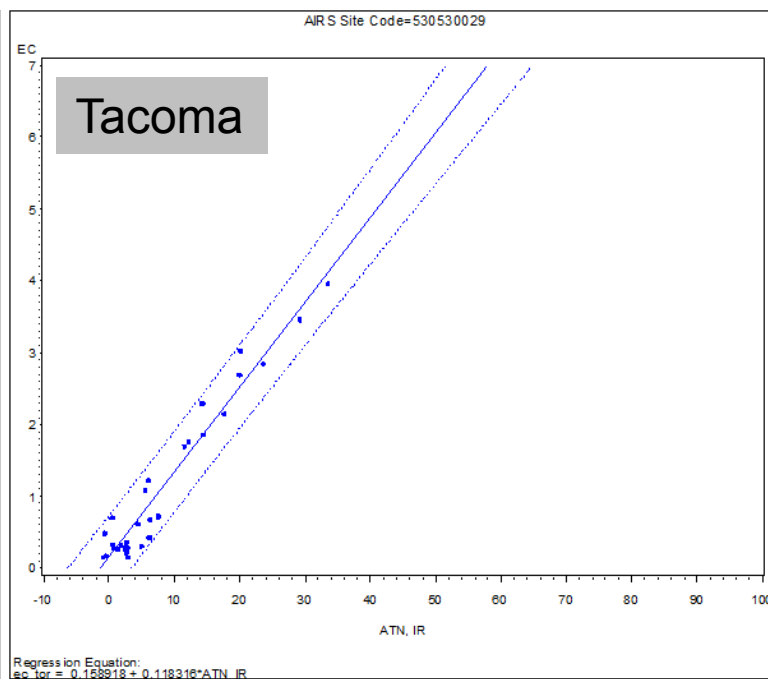
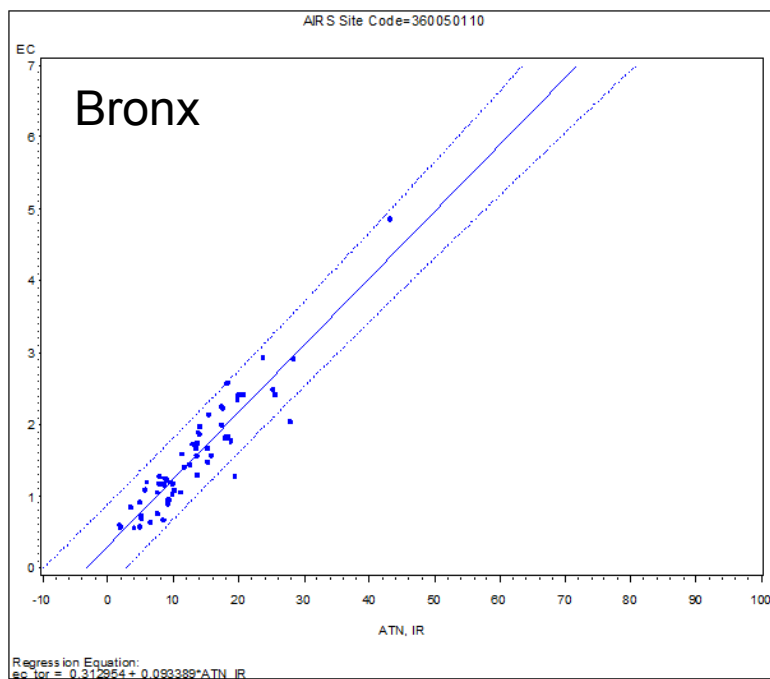
Similar site-specific relationships in East
Strong correlations mostly > 0.9
A few “outliers” to be checked

IMPROVE EC vs PM2.5 Attenuation (4 CSN sites)

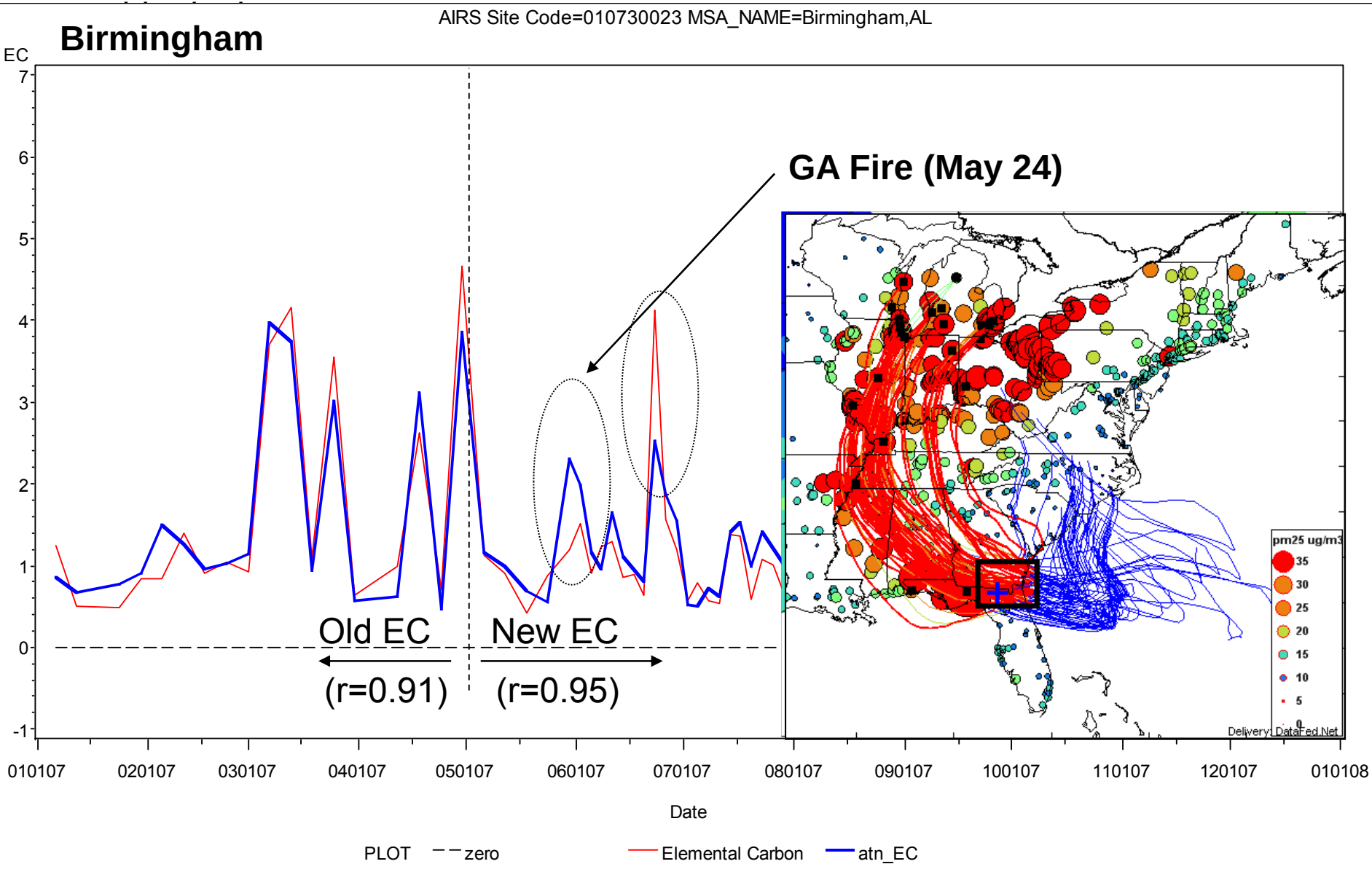




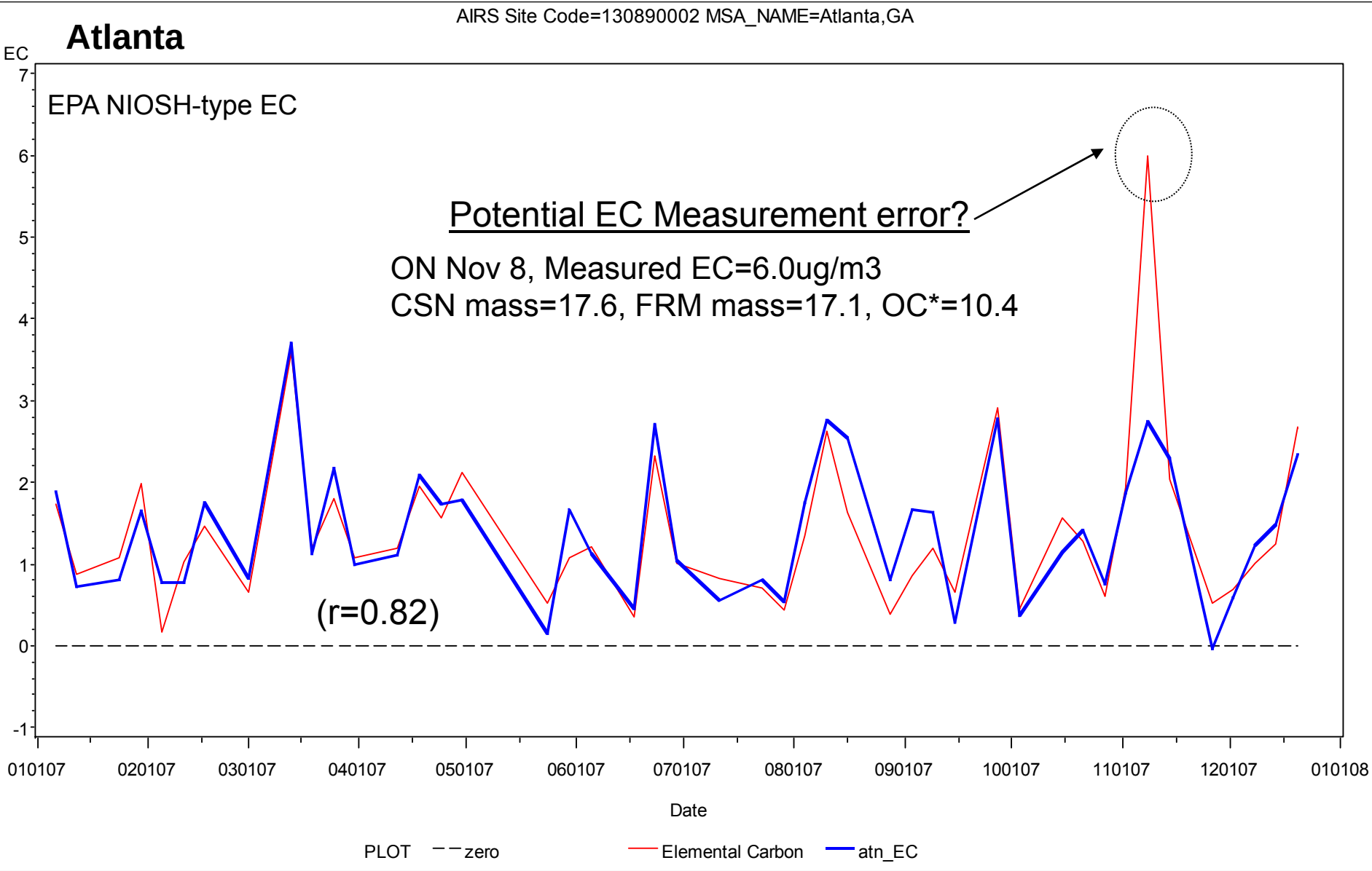
IMPROVE EC vs. Optical ATN (similar for each site)



Magee Transmissometer Study

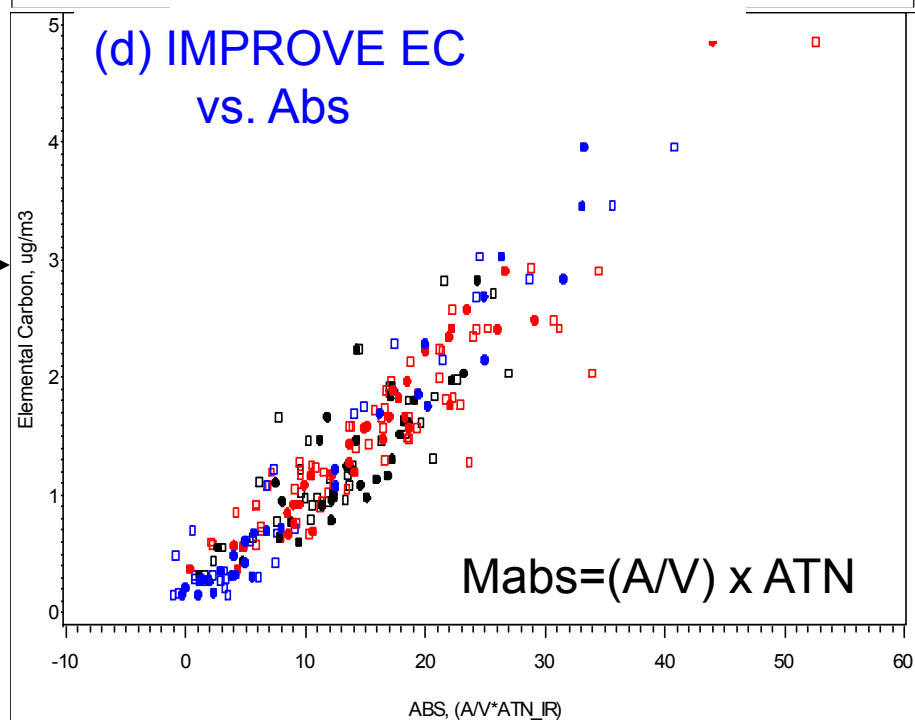
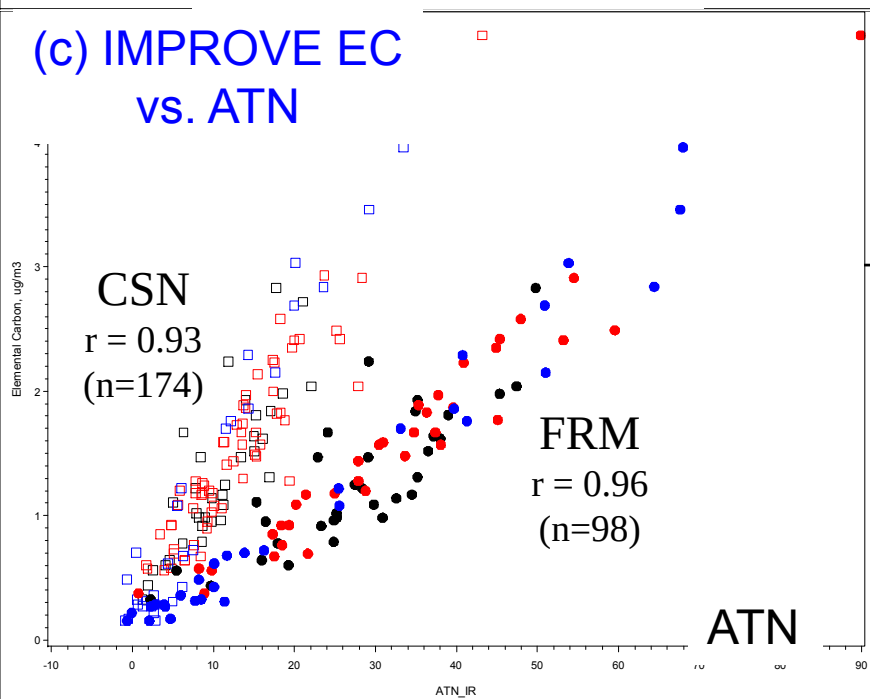
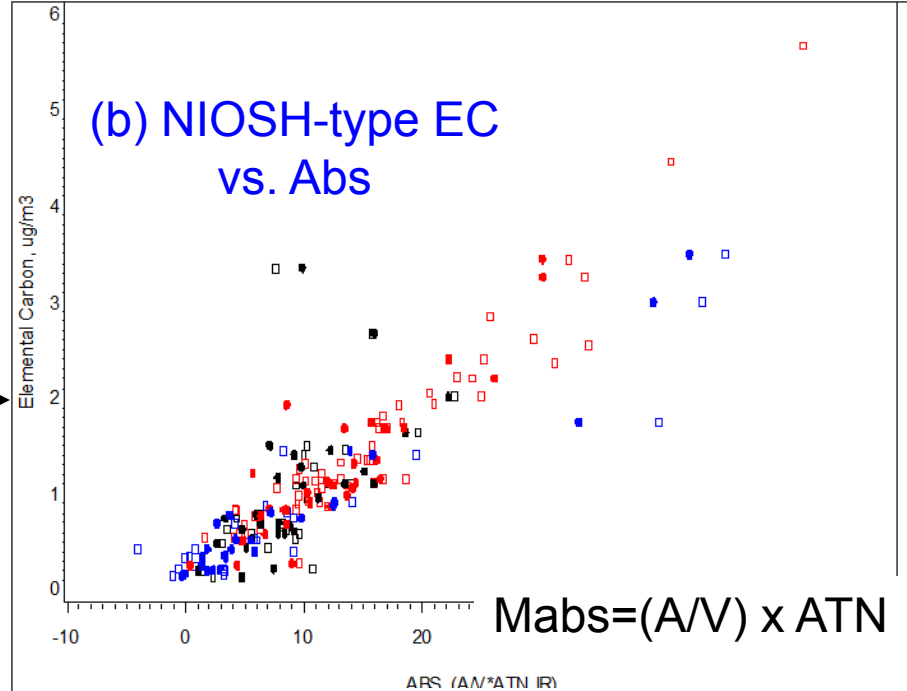
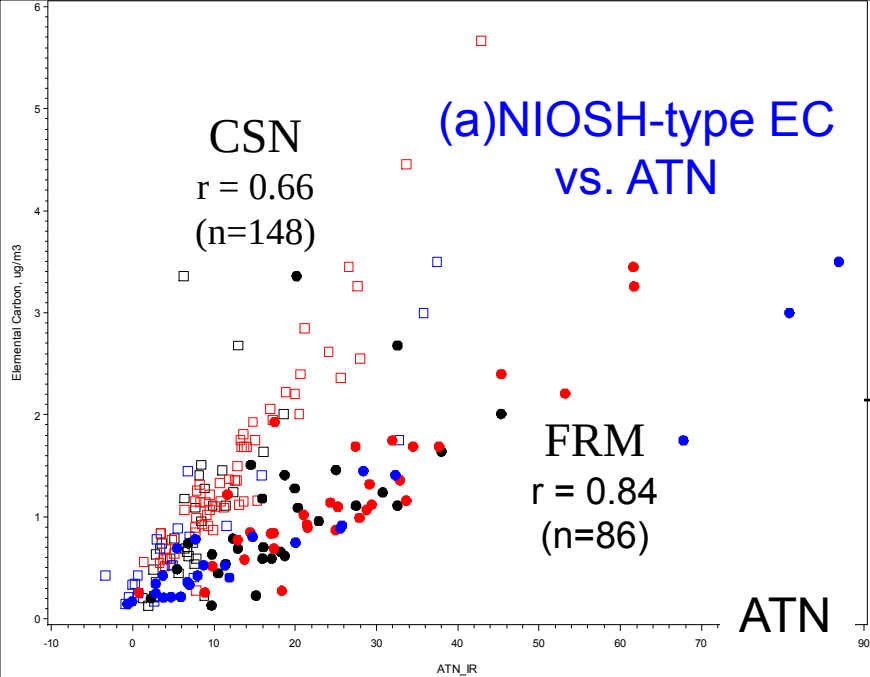


Magee Transmissometer Study

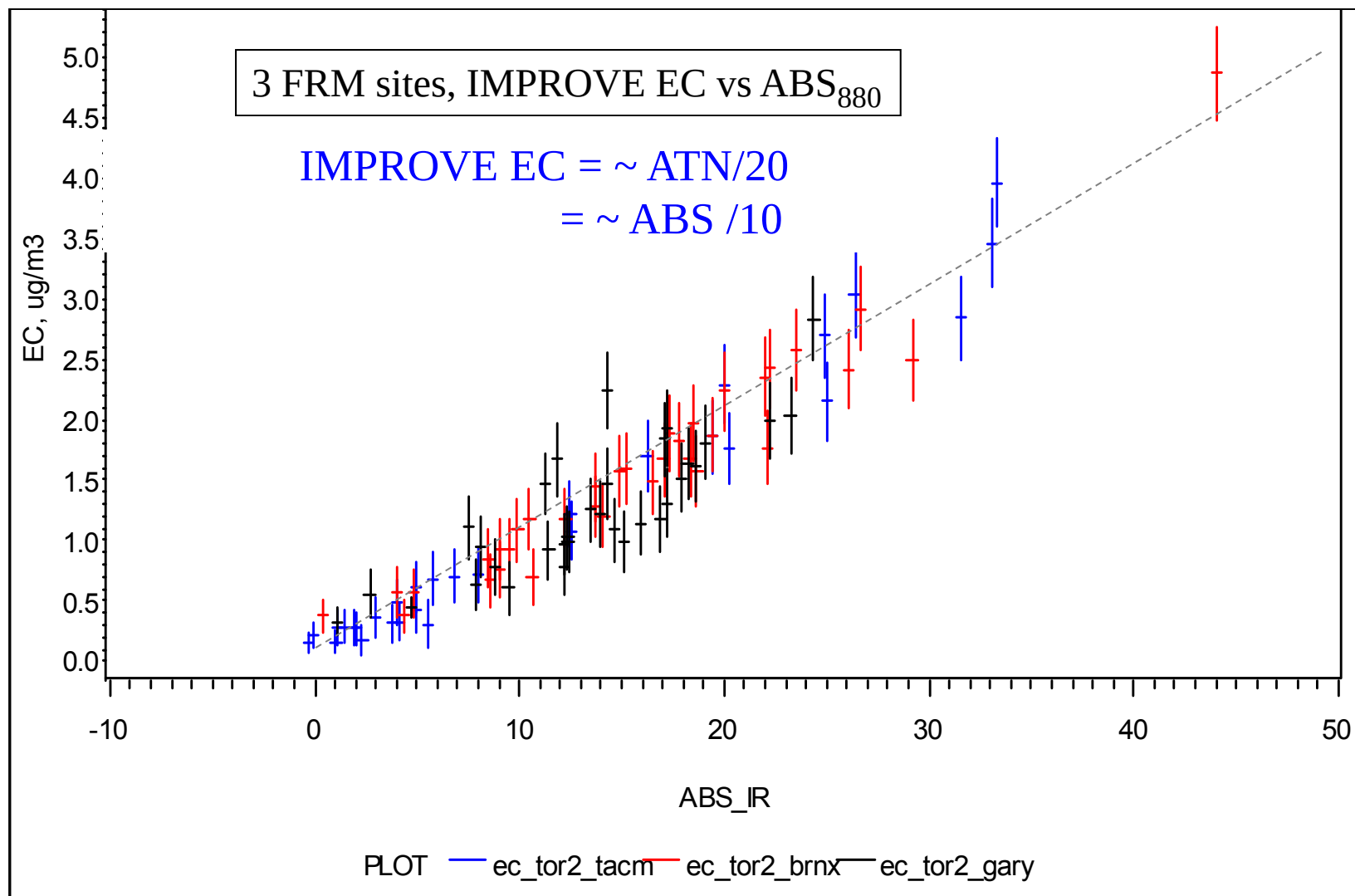


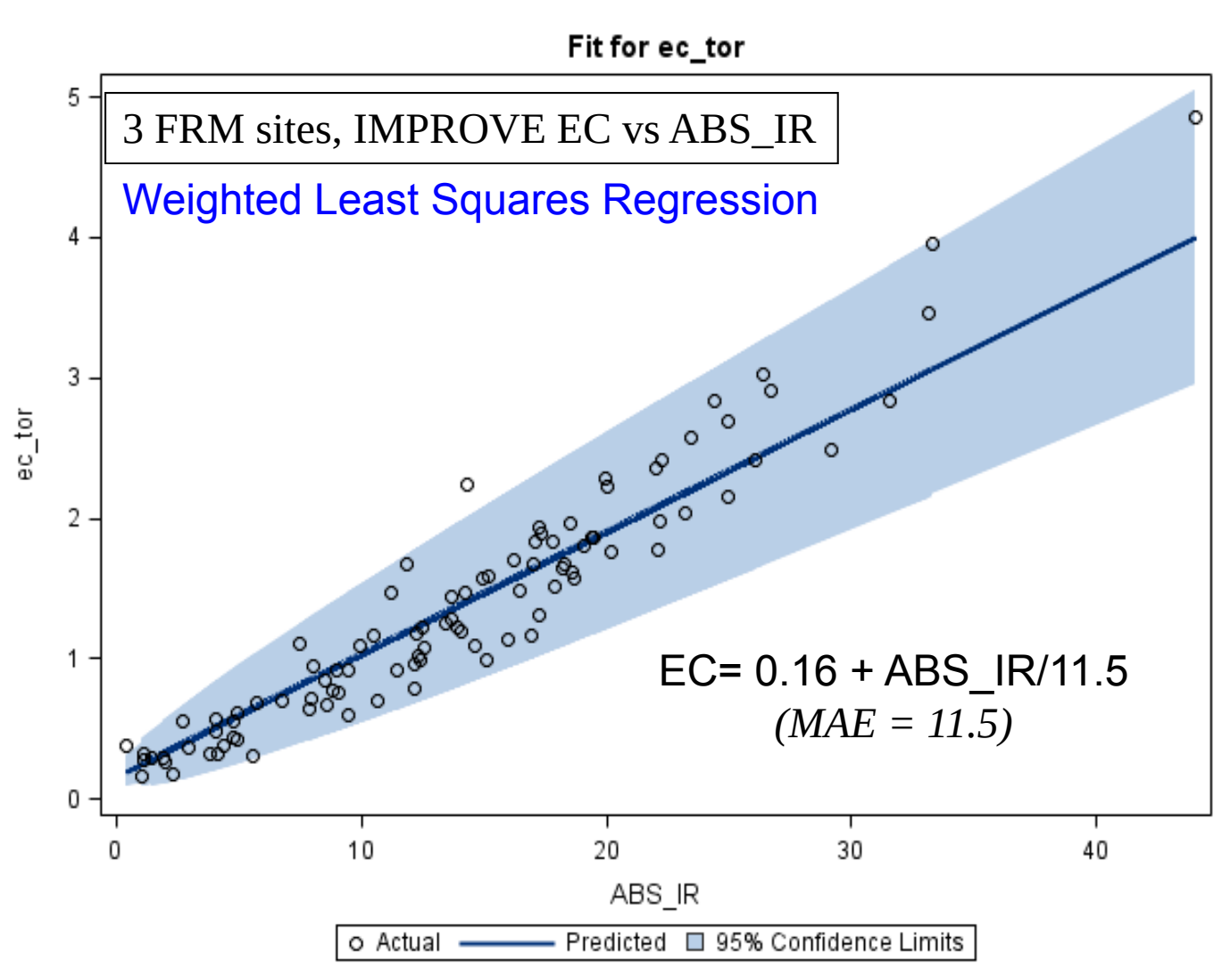
OC* is adjusted for CSN sampling artifact (i.e. blank corrected)

Now adding results
for the 3 collocated FRM sites

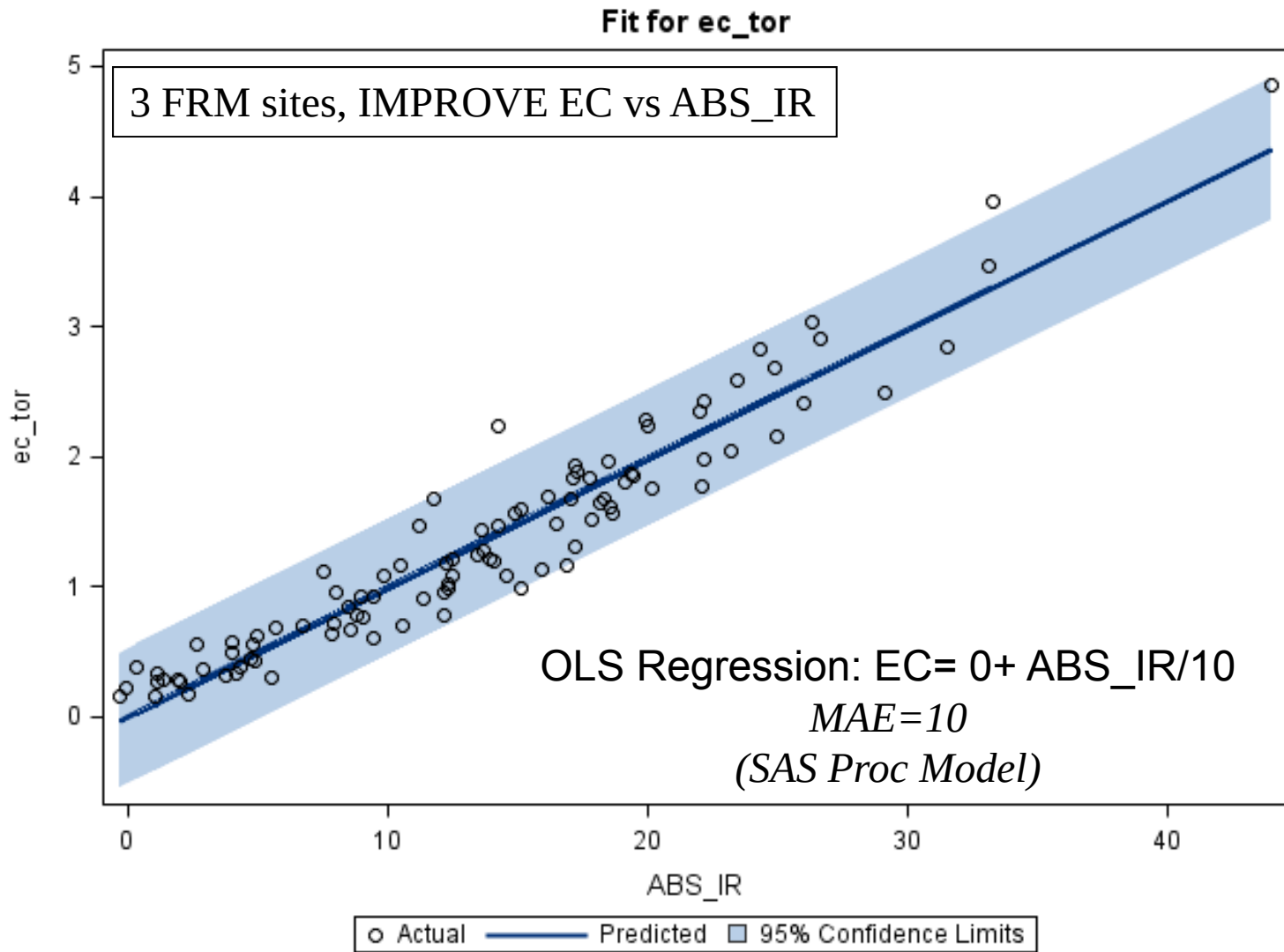


PLOT □ □ gary_c_ec_tor □ □ birm_c_ec_tor □ □ tacm_c_ec_tor ● ● gary_F_ec_tor ● ● birm_F_ec_tor ● ● tacm_F_ec_tor





$$EC_{unc} = 0.085 * \text{Log}(EC) + 0.254 \quad (\text{Mark Green, DRI})$$



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)

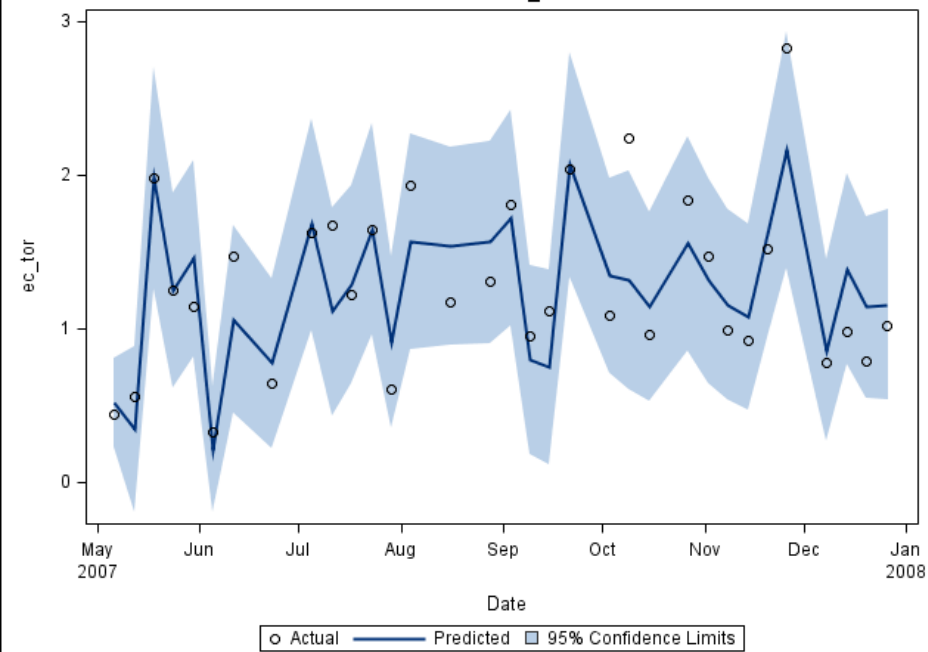
Parameter	Estimate	Std Err	t Value	Pr > t
a	0.032818	0.0672	0.49	0.6285
b	20.88619	0.9048	23.08	<.0001

R2 = 0.9417 (Bronx)

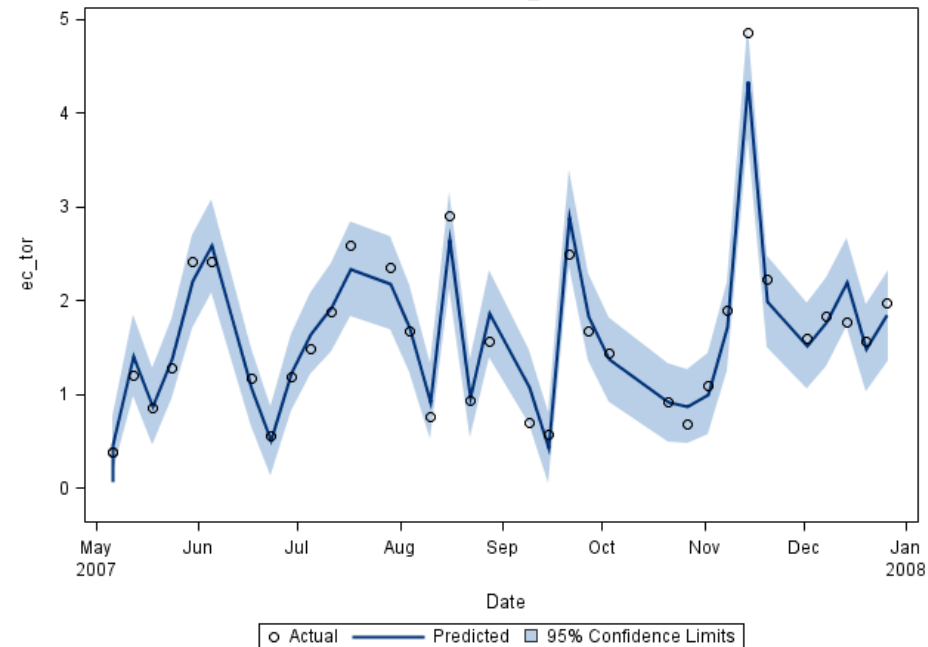
Parameter	Estimate	Std Err	t Value	Pr > t
a	0.069648	0.0374	1.86	0.0732
b	20.82608	0.7487	27.82	<.0001

R2=0.9651(Tacoma)

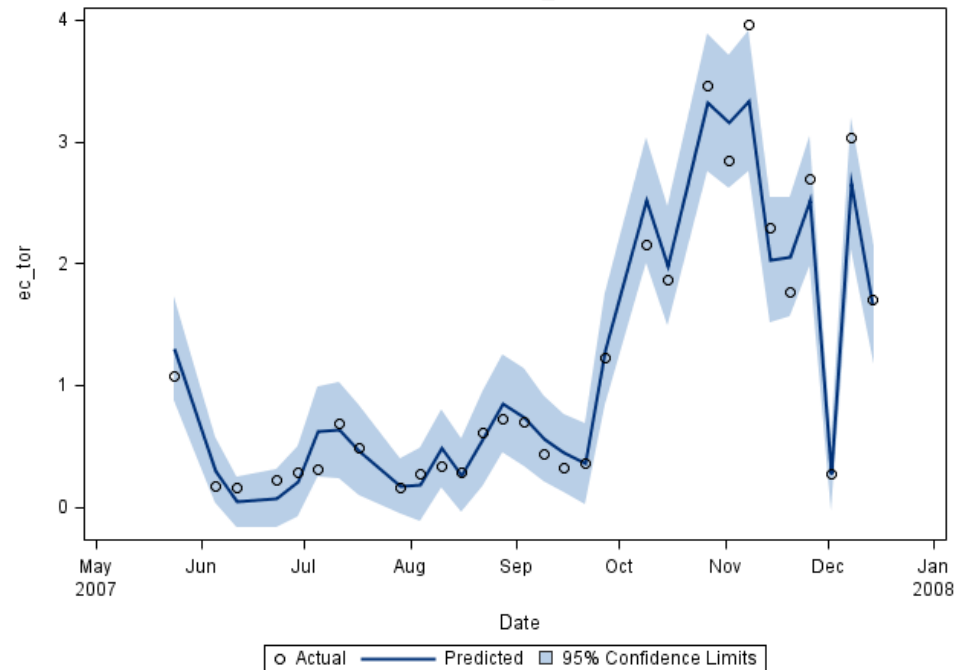
Fit for ec_tor



Fit for ec_tor



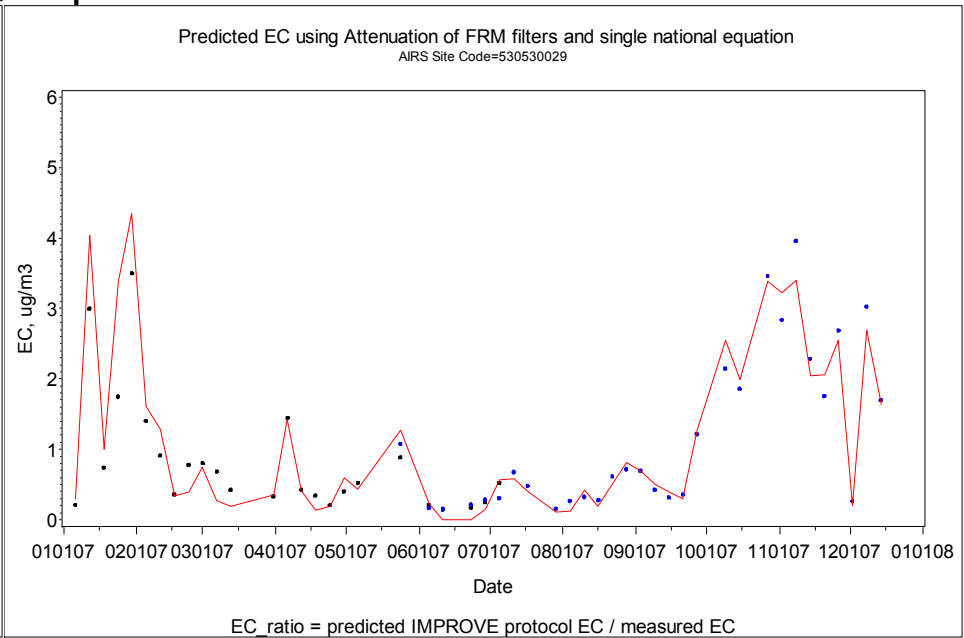
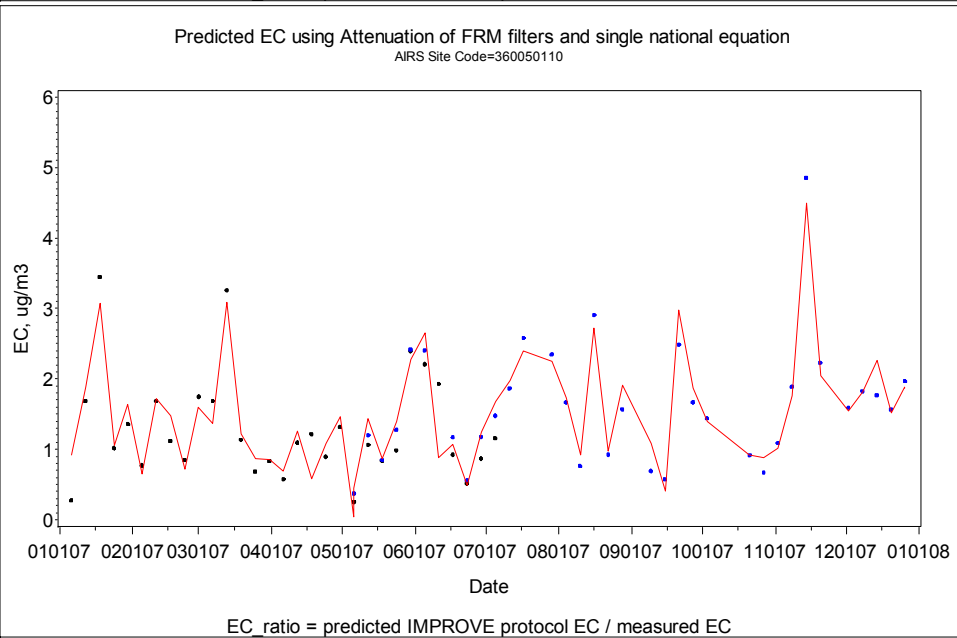
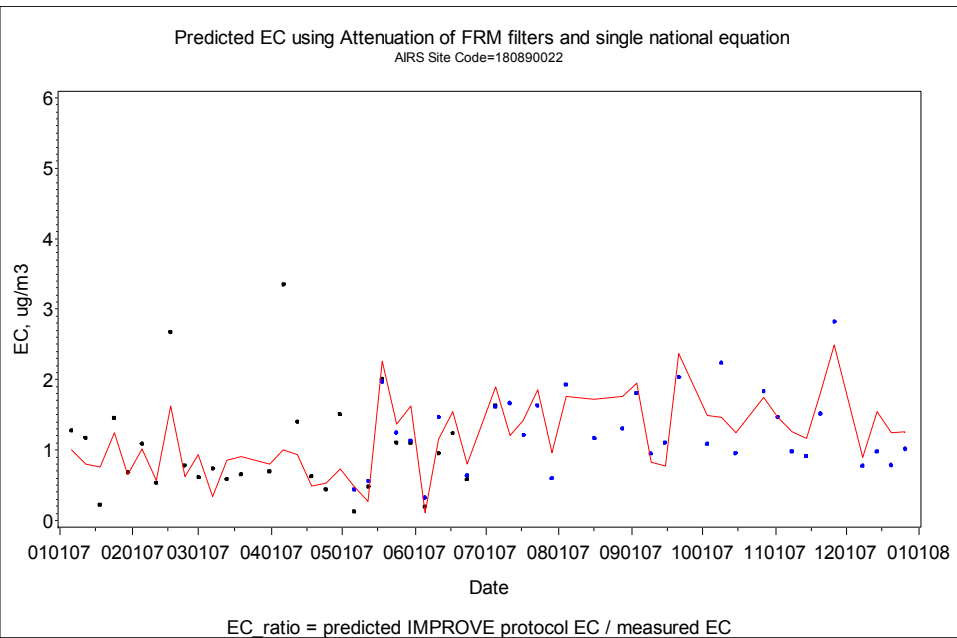
Fit for ec_tor



Estimated EC using FRM Filter Attenuation with single national equation, $EC=ATN/20$

Filter attenuation can help identify potential outliers in measured EC.

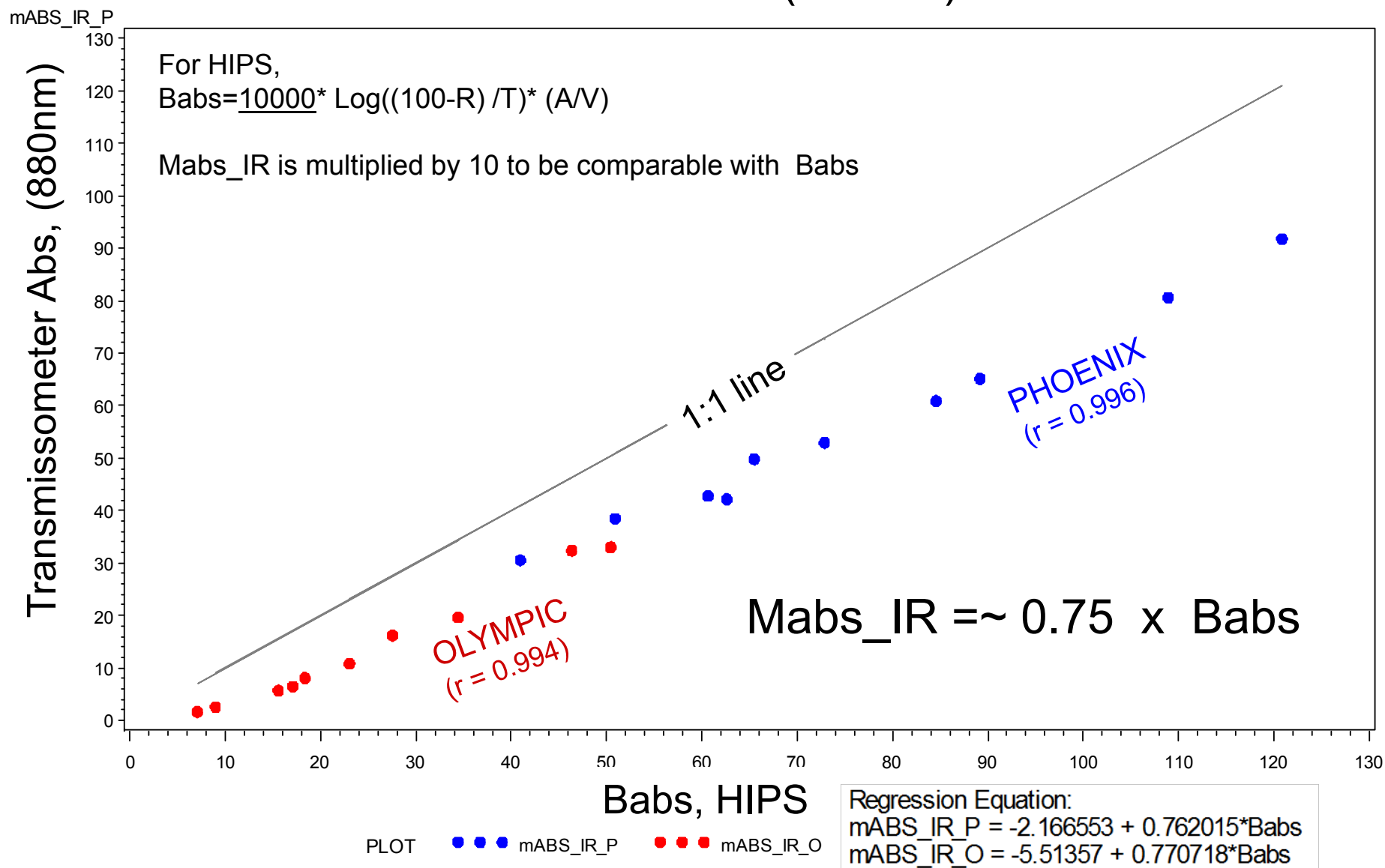
These graphs show that predicted EC tracks measured EC. **Using a single national relationship(ATN/20)** between EC and ATN, the predicted IMPROVE EC is similar to the measured EC with the old EC protocol.



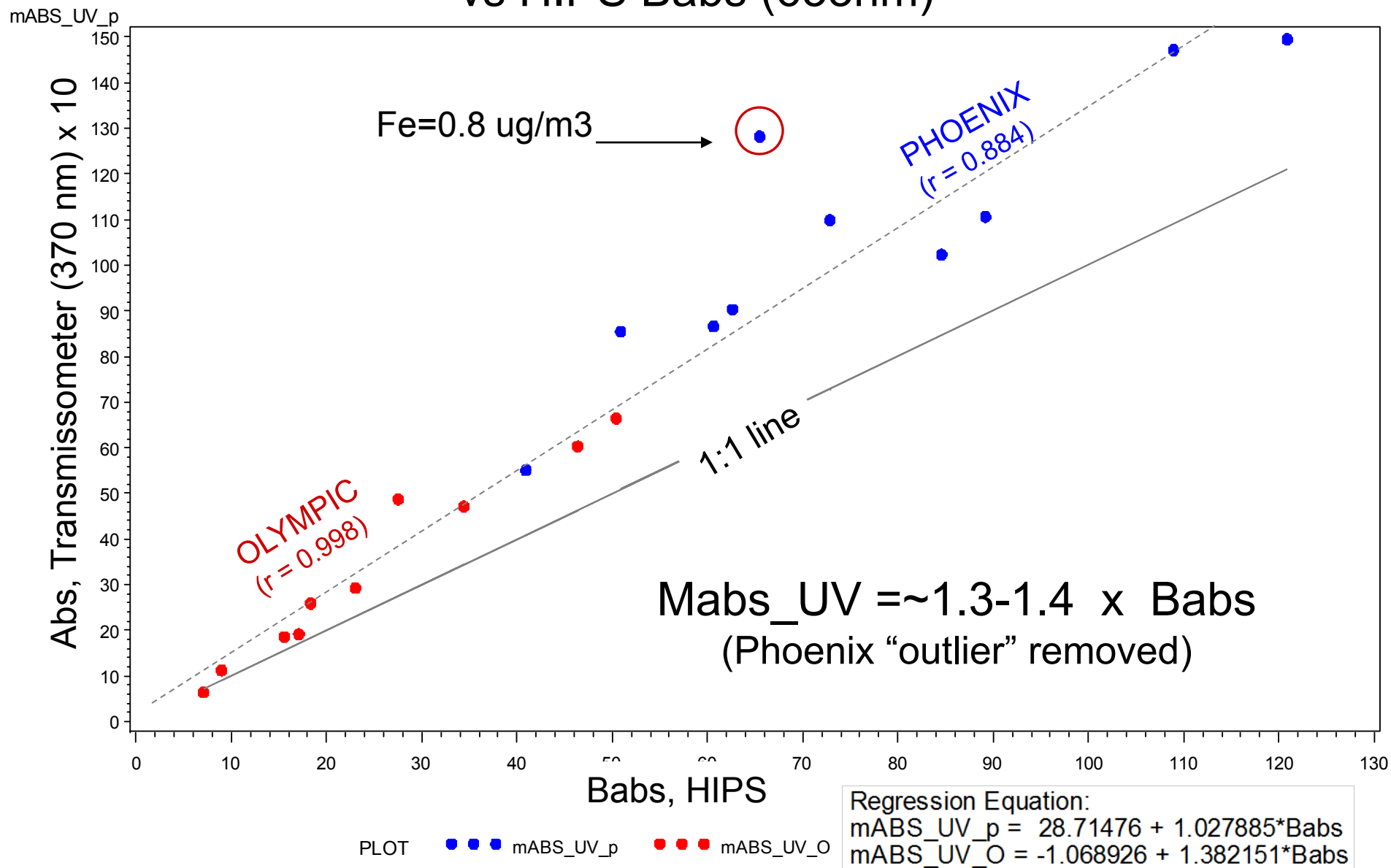
Preliminary Evaluation of Magee Transmissometer using IMPROVE PM2.5 Filters

- Comparison of Two Sites with HIPS Babs
 - OLYM
 - PHOE
- 10 PM2.5 filters each
 - QA channel
 - June-Oct 2008
- Virgin blank and field blank filters
- Magee ATN converted to Absorption
 - $(\text{Exposed Area/Volume}) = 3.53/33$
 - Multiplied by 10 to have comparable scaling to HIPS Babs

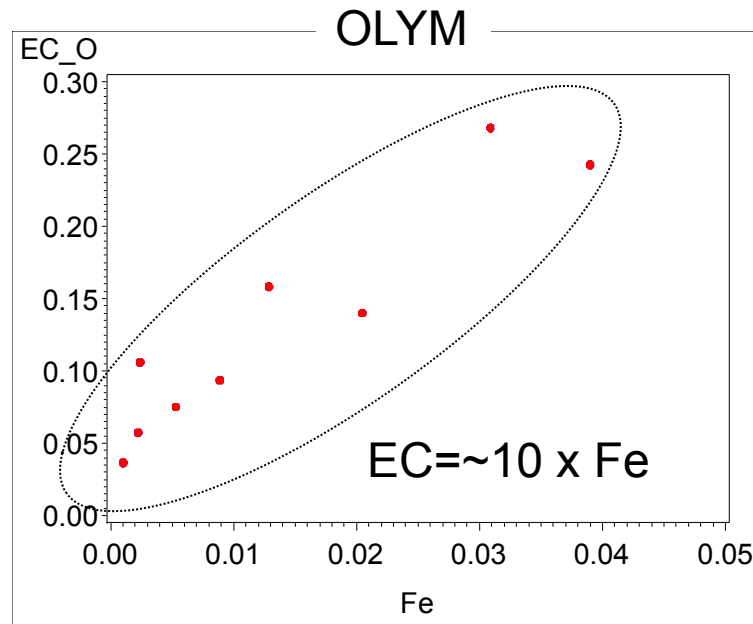
McGee Transmissometer Measured Absorption (880nm) vs HIPS Babs (633nm)



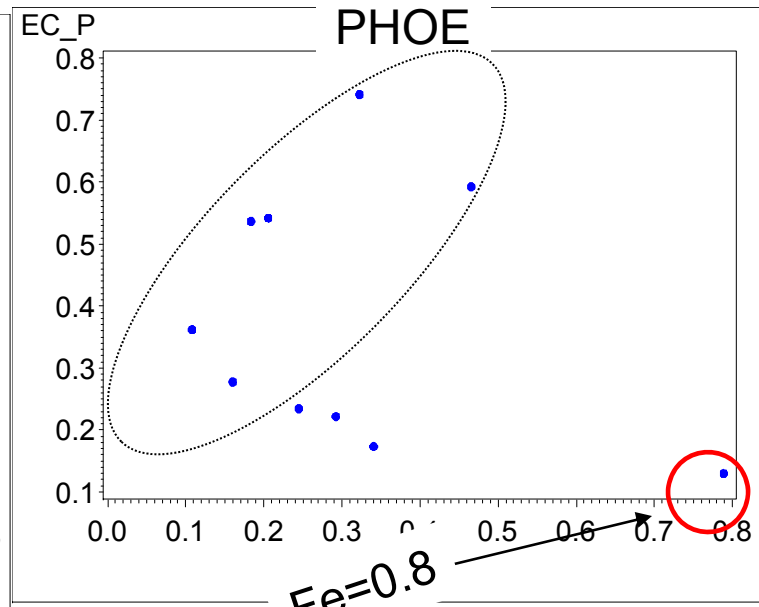
McGee Transmissometer Measured Absorption (370nm) vs HIPS Babs (633nm)



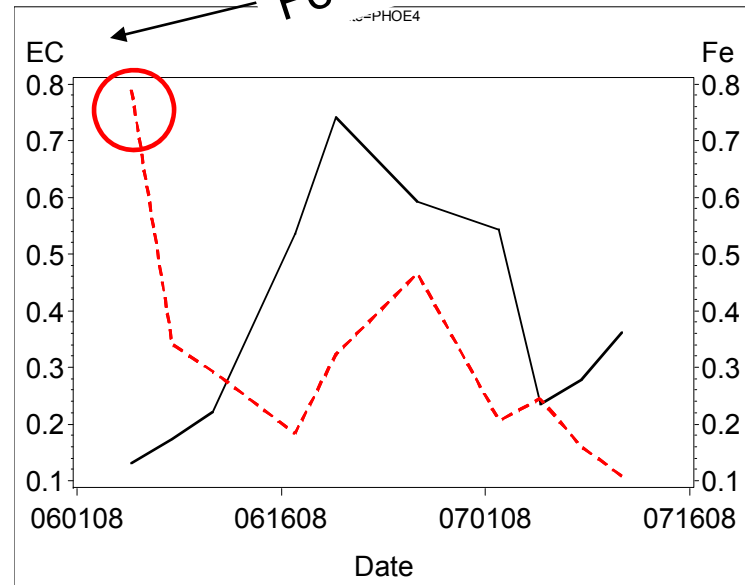
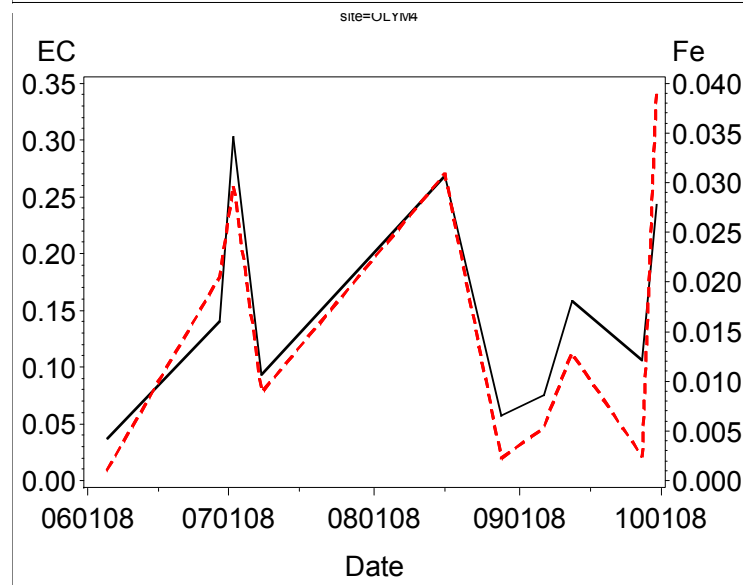
Confounding Influence of Iron?



site=OLYM4



site=PHOE4

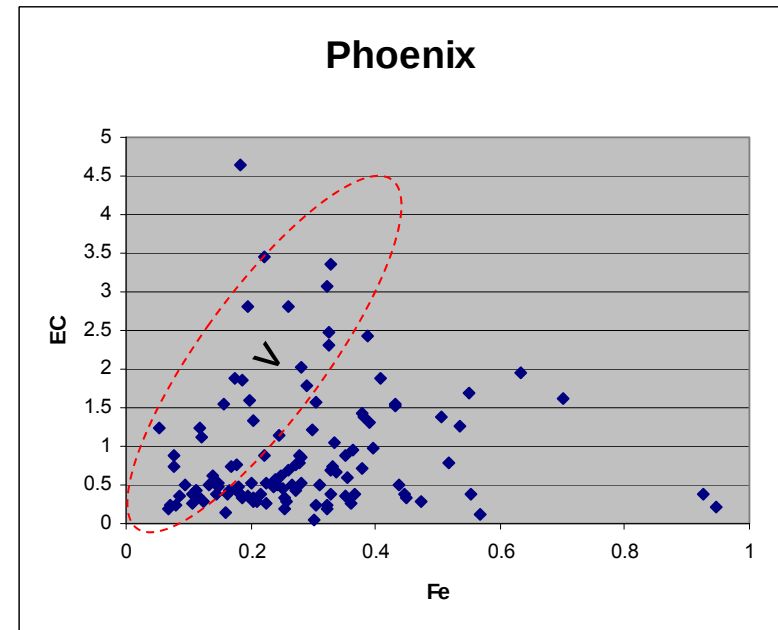
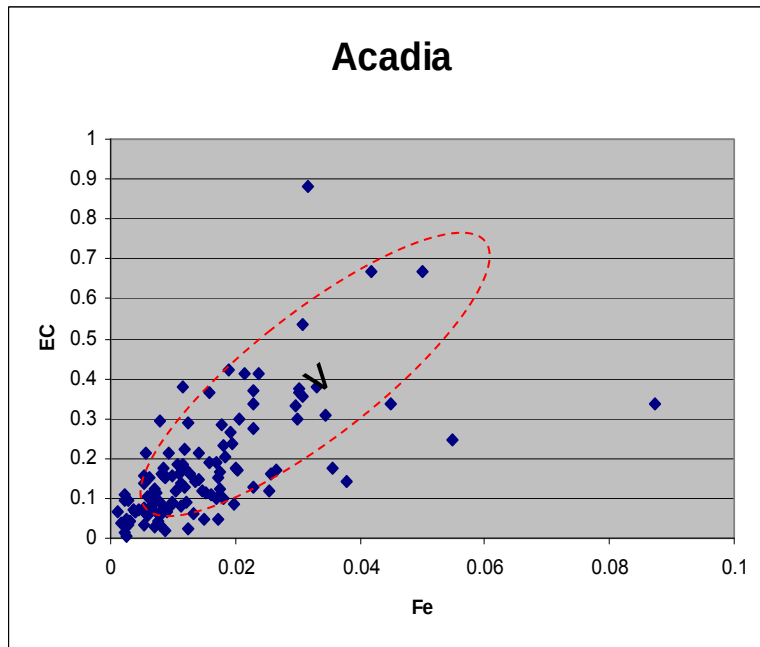
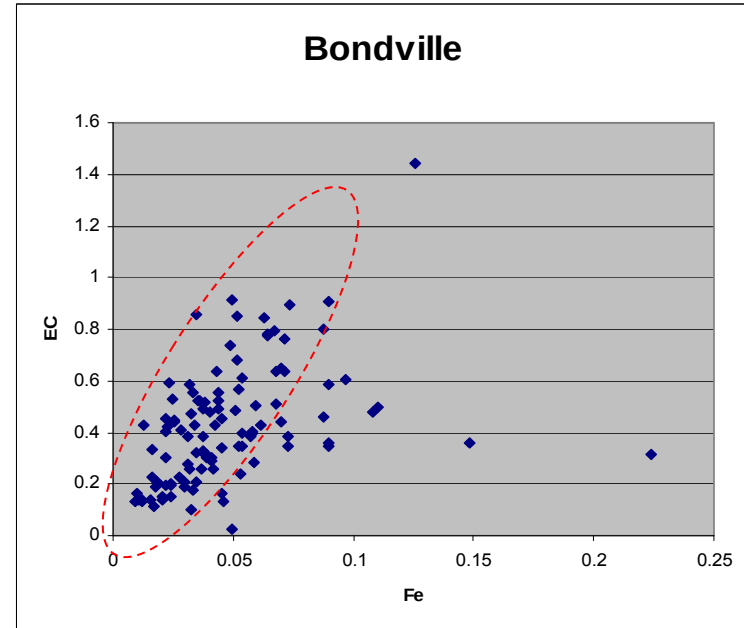
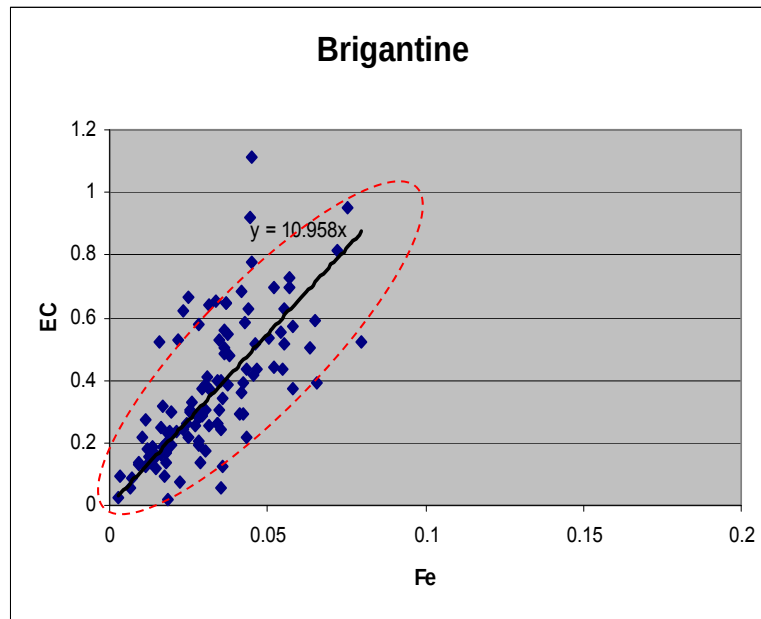


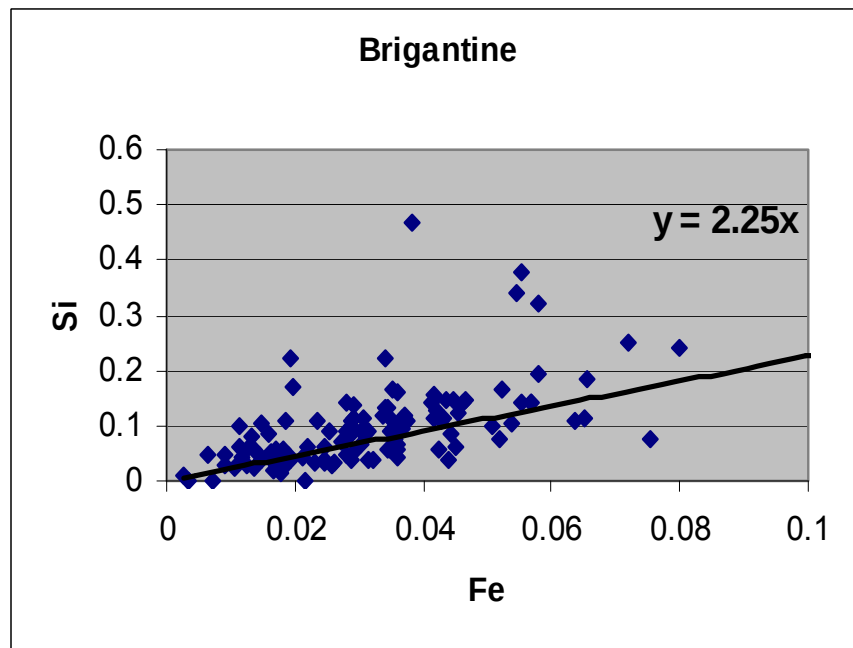
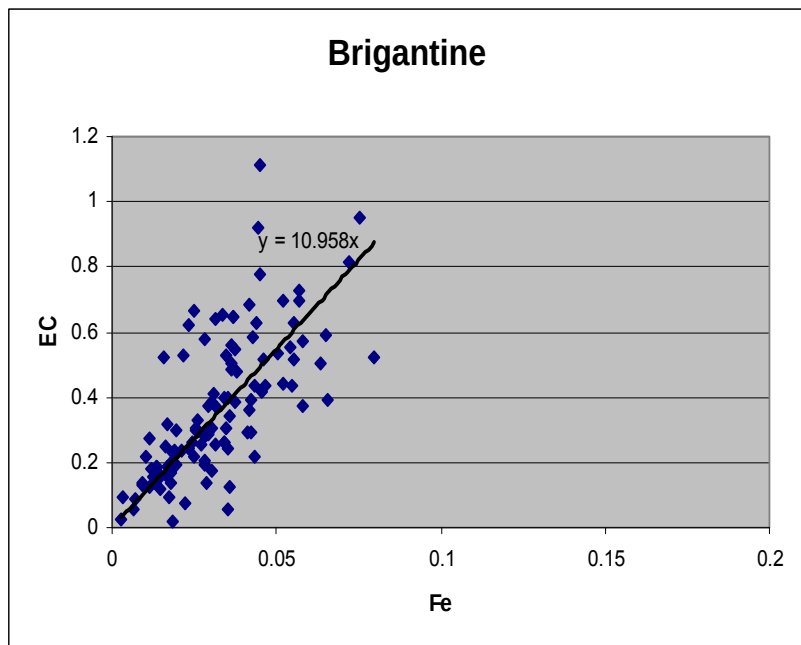
Frank Hubris about Iron

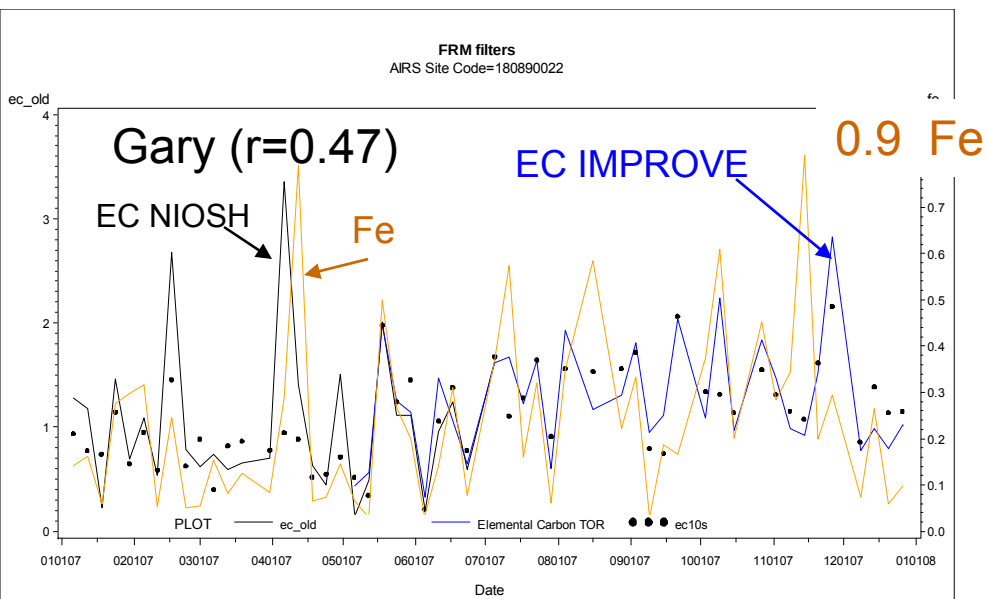
Food for Thought

- There are multiple emission sources
 - Ubiquitous urban(regional) aerosol
 - Mobile sources (brakes, fuel additives)
 - Fine Soil (urban and regional)
 - Industrial (local urban)
- Possibly different Iron oxides
 - Different absorption efficiencies
- Iron Oxides influence the pyrolosis of OC
 - EC is underestimated according to K.Fung
- Changes EC-derived MAE
- Iron Oxides in Soil
 - Goethite (α -FeOOH): yellowish brown
 - Hematite (α -Fe₂O₃): bright red
 - Lepidocrocite (γ -FeOOH): bright orange
 - Maghemite (γ -Fe₂O₃): red to brown.
 - Ferrihydrite (5Fe₂O₃*9H₂O): reddish brown
- Other
 - **Iron(II) oxide**, also known as **ferrous oxide**,(black)

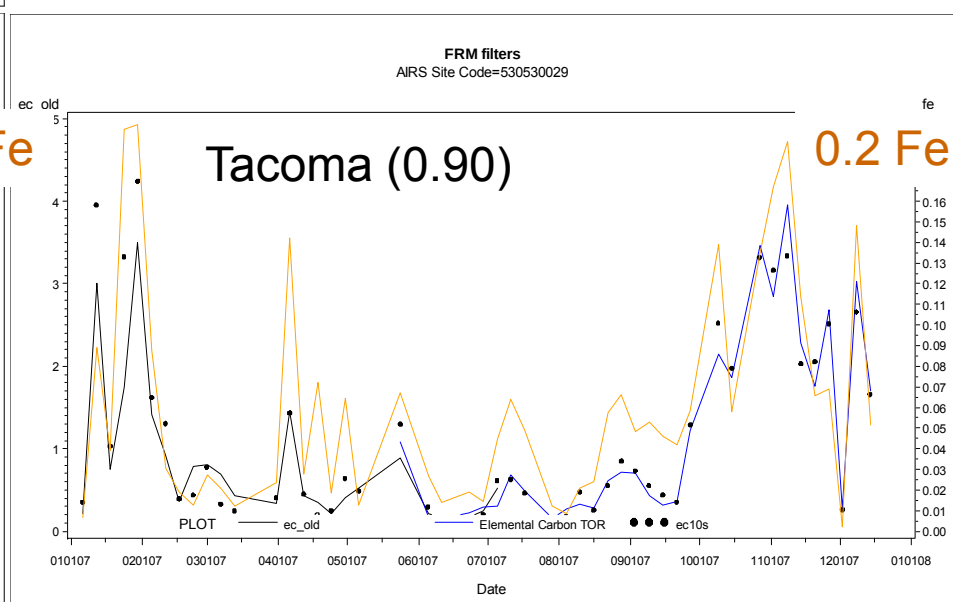
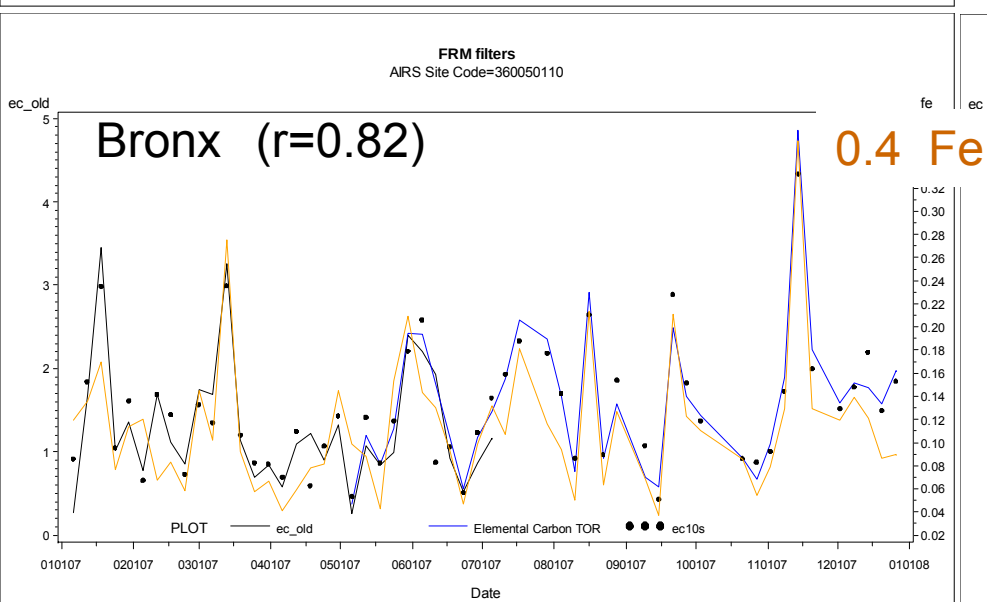
Varying Relationships between EC and Fe







Urban Fe & IMPROVE EC Correlations
Gary, $r=0.47$
Bronx, $r=0.82$
Tacoma, $r=0.90$ } Typical urban emissions



Mass Absorption Efficiency, m^2g^{-1}

Magee Transmissometer (880nm)

EC Protocol	IMPROVE Network (based on limited summer data)		CSN / FRM Networks	
	OLYM	PHOE	WS	Non-WS
IMPROVE_A (TOR)	14	10	10-11	10-11
EPA NIOSH-type (TOT)	-	-	13-16	10-12

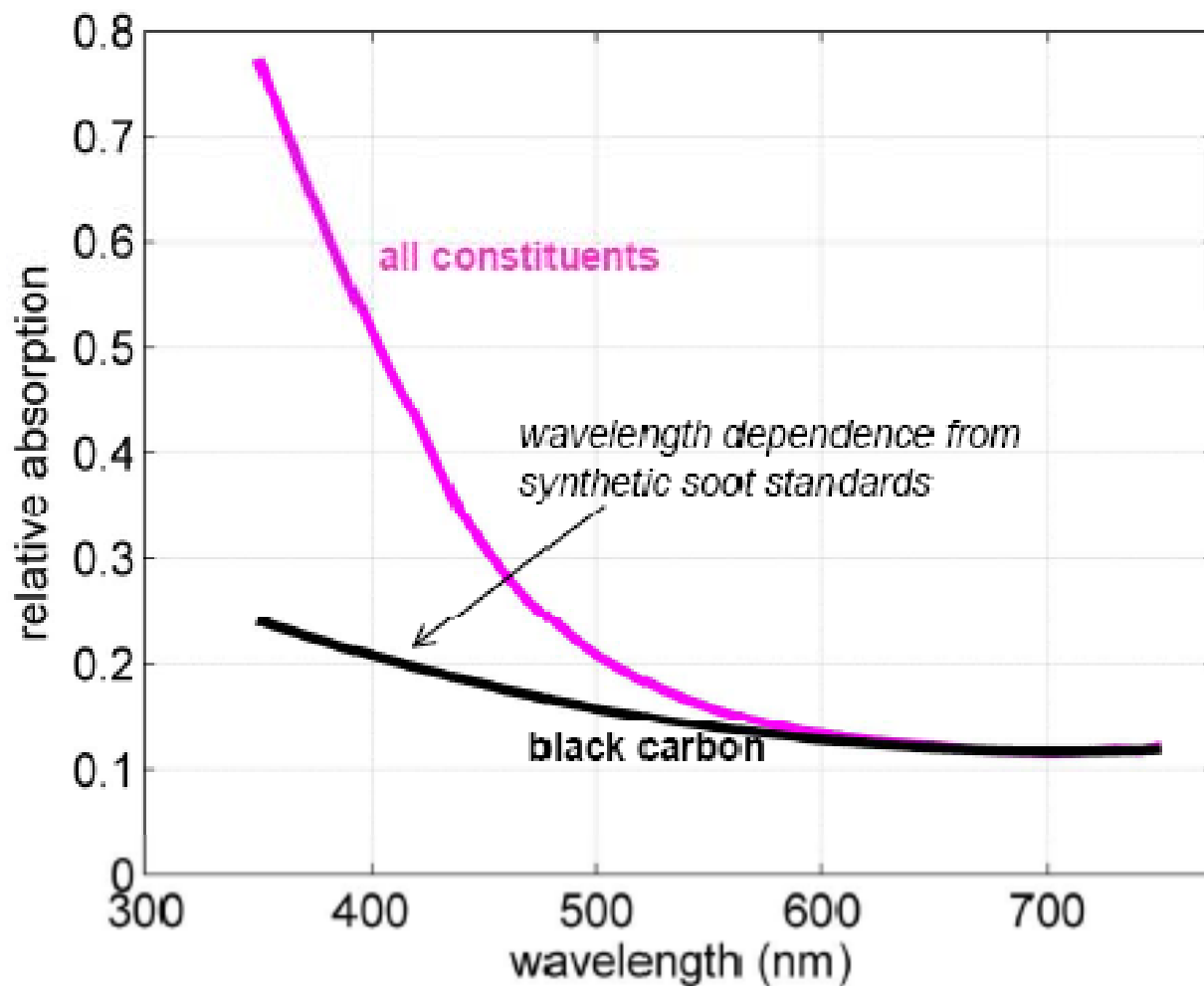
Note: $\text{Mabs_IR (880nm)} = \sim 0.75 * \text{Babs (HIPS, 633nm)}$

Summary

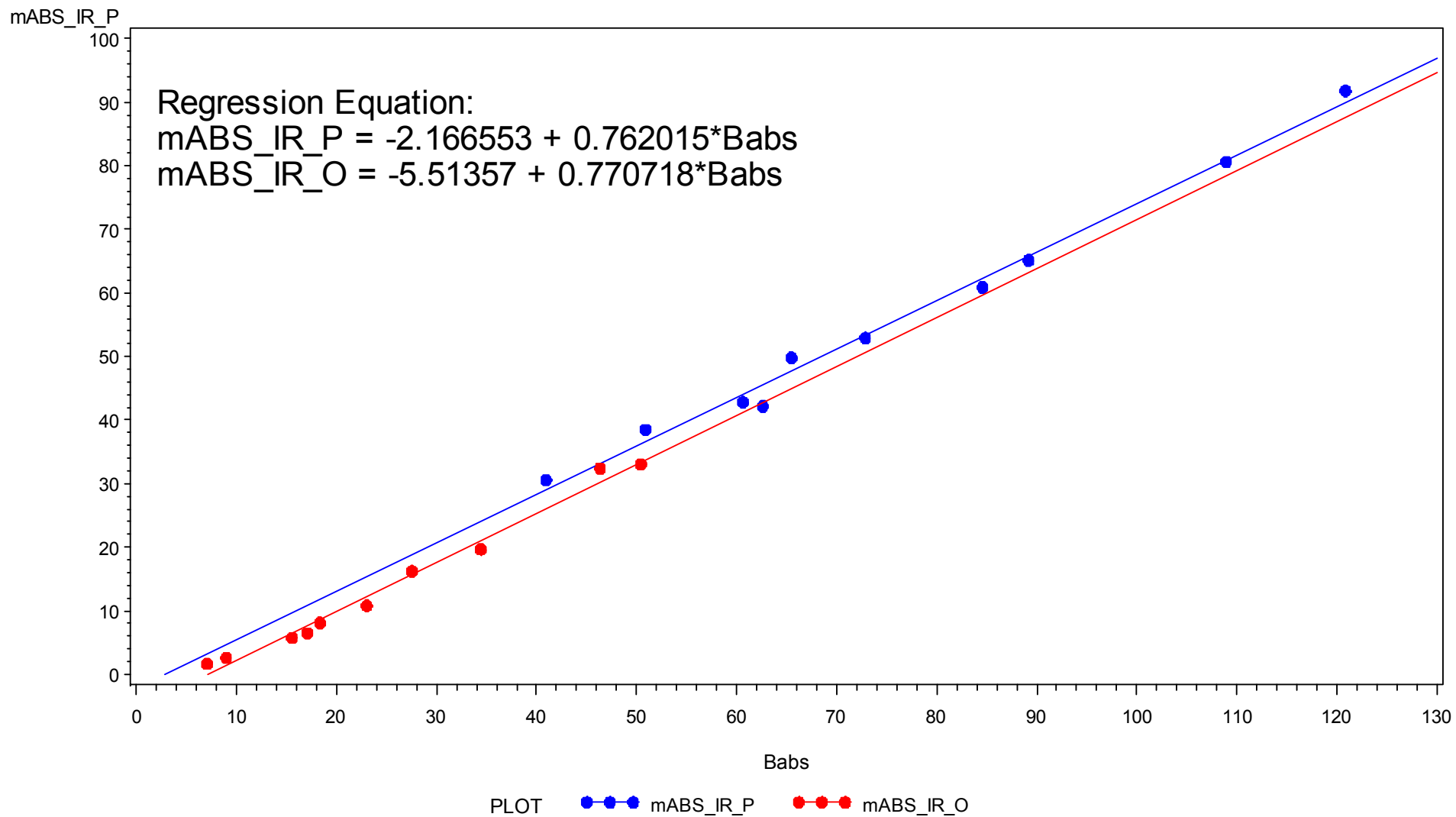
- Optical absorption is dependent on
 - Wavelength
 - Thermal Optical Protocol
 - Filter material (teflon vs quartz)
 - Fe concentrations
 - warrants further study
- EPA is pursuing optical measurements

Extra slides

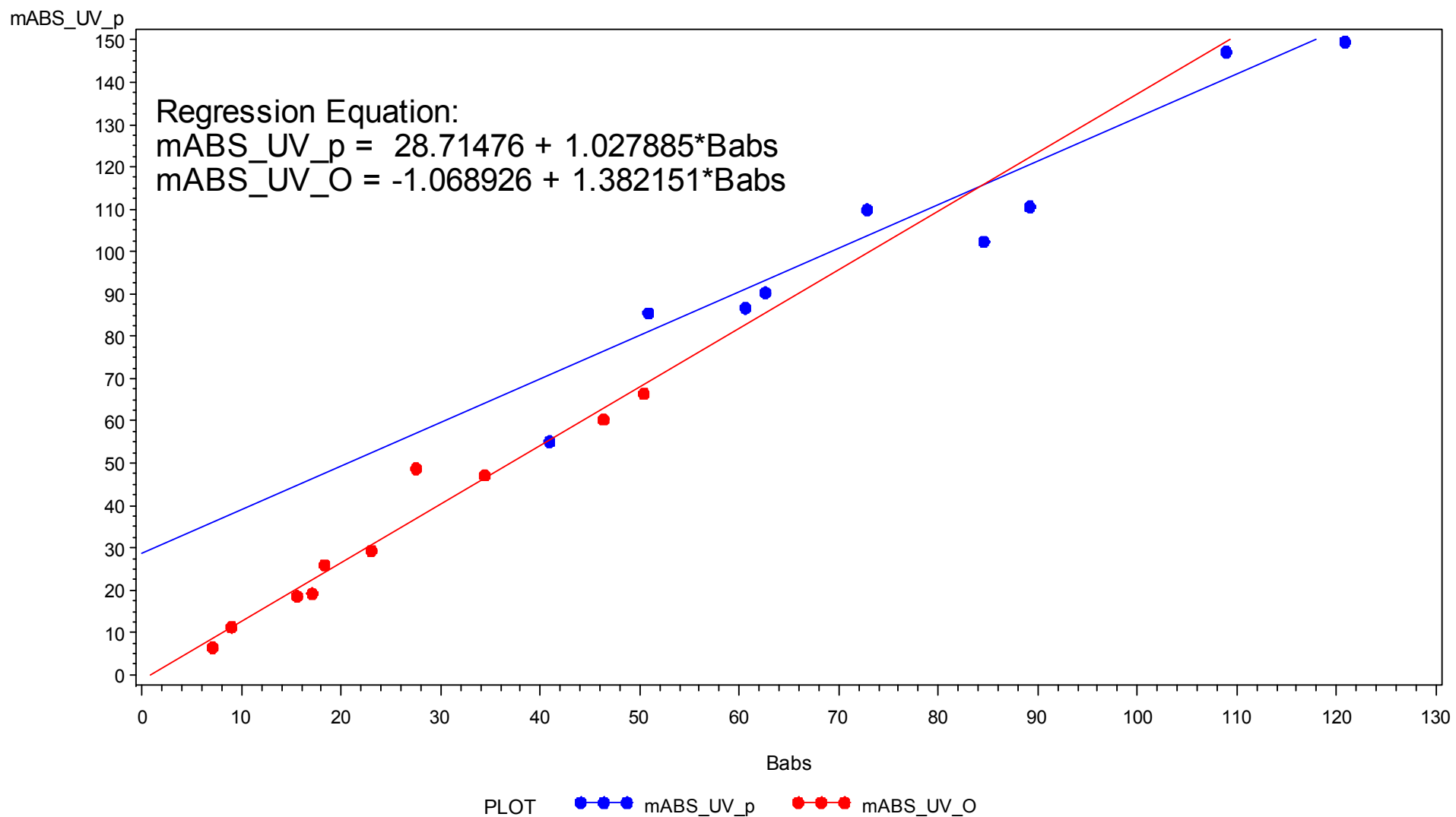
	(Area/Volume)	
<u>CSN</u>	<u>FRM</u>	<u>IMPROVE</u>
1.22	0.49	0.11



Grenfell et. al. *Workshop on BC in Snow, NPI*, August 2009

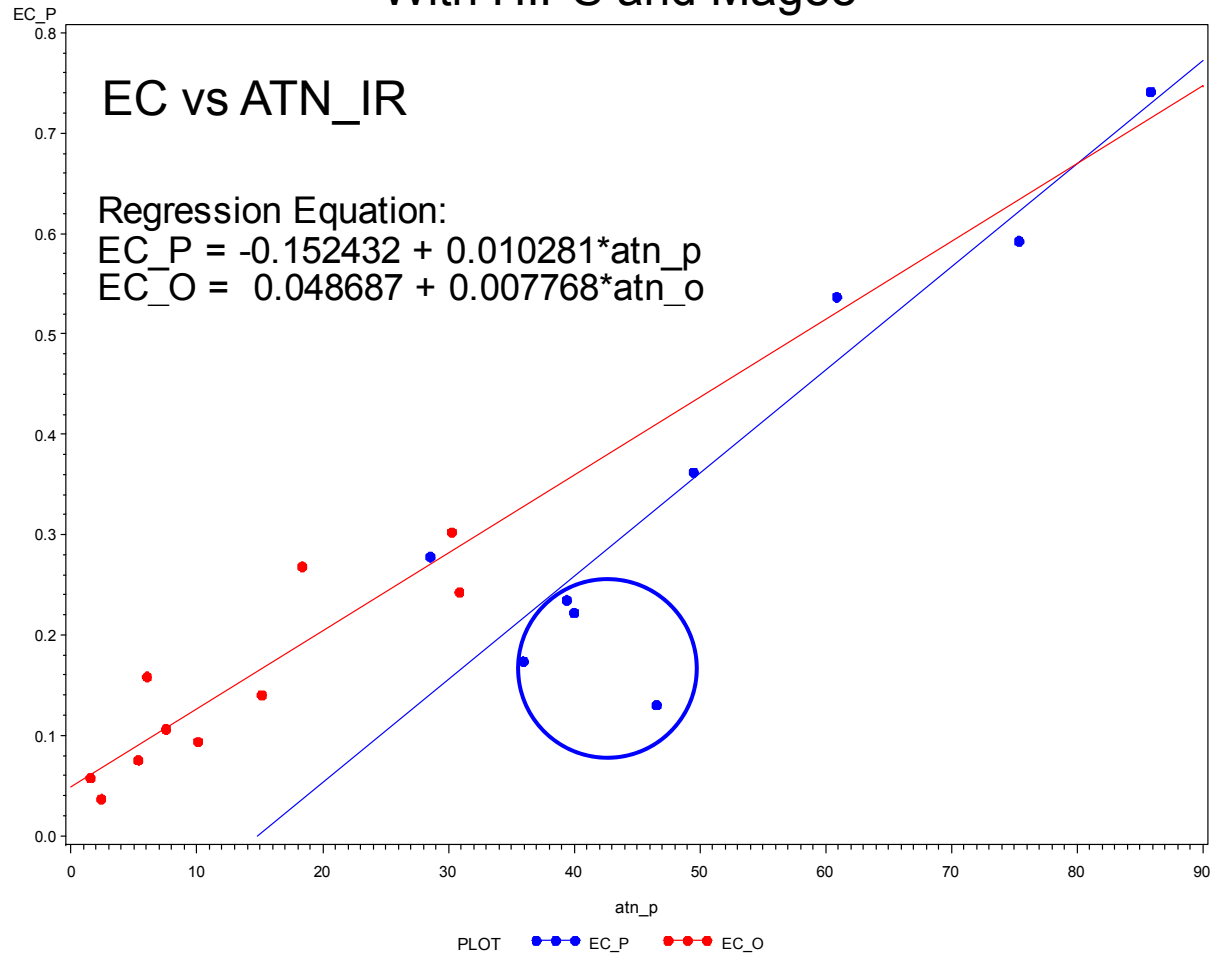


Regression Equation:
 $mABS_IR_P = -2.166553 + 0.762015 \cdot Babs$
 $mABS_IR_O = -5.51357 + 0.770718 \cdot Babs$

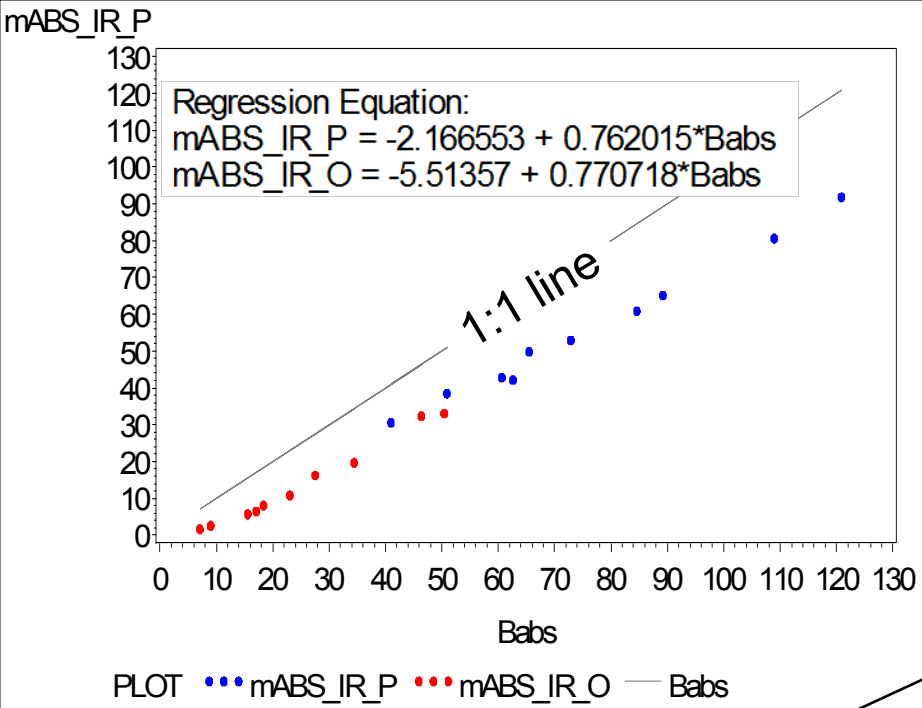


Regression Equation:
 $mABS_UV_p = 28.71476 + 1.027885 \cdot Babs$
 $mABS_UV_O = -1.068926 + 1.382151 \cdot Babs$

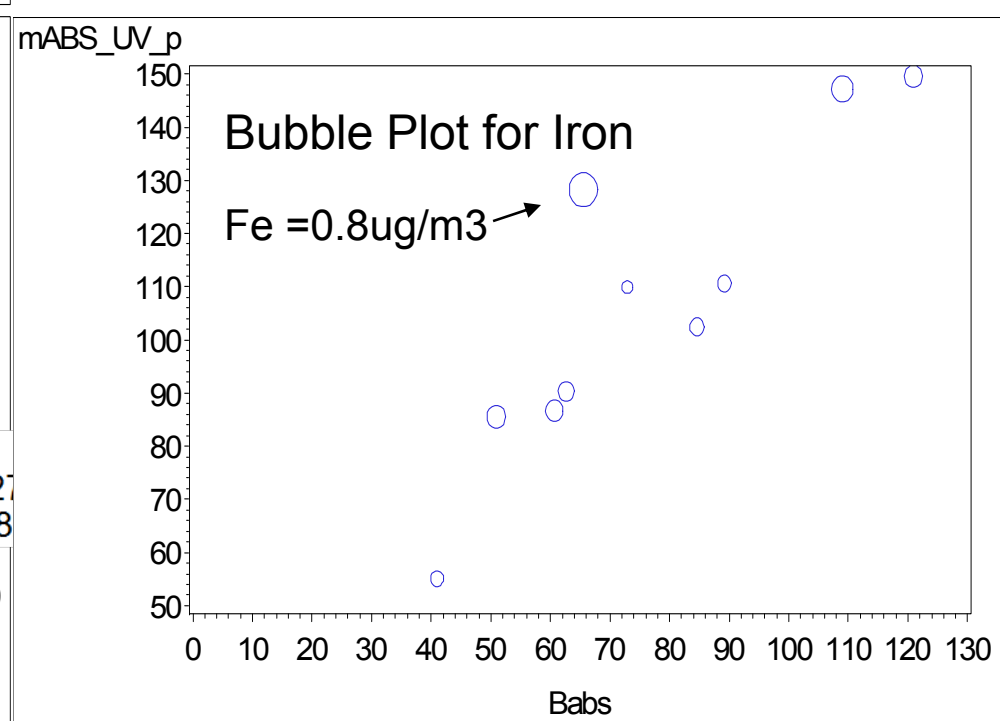
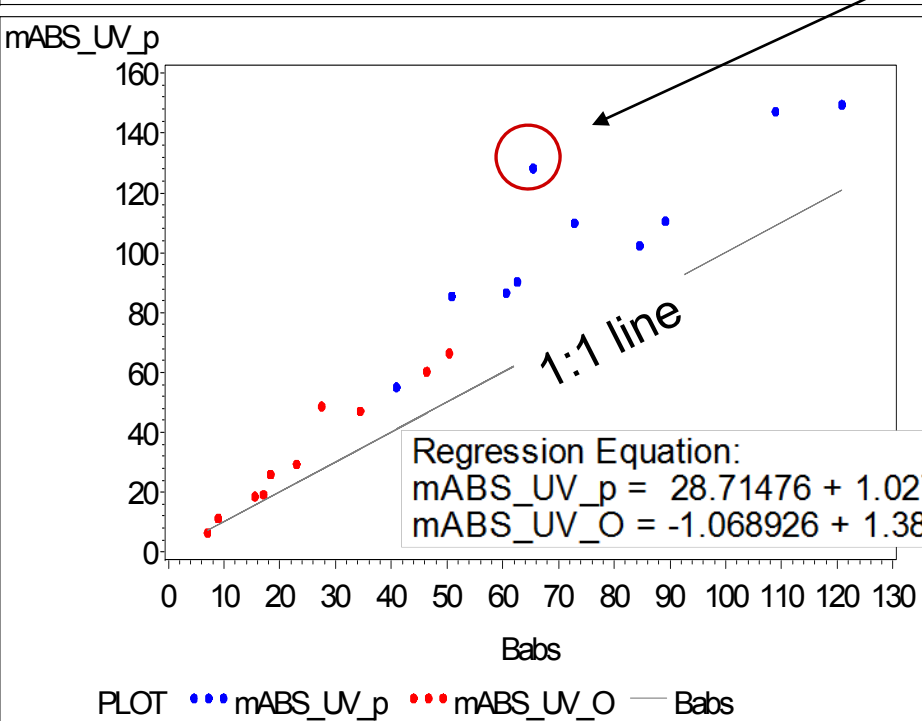
Relatively high Phoenix attenuation on some days With HIPS and Magee



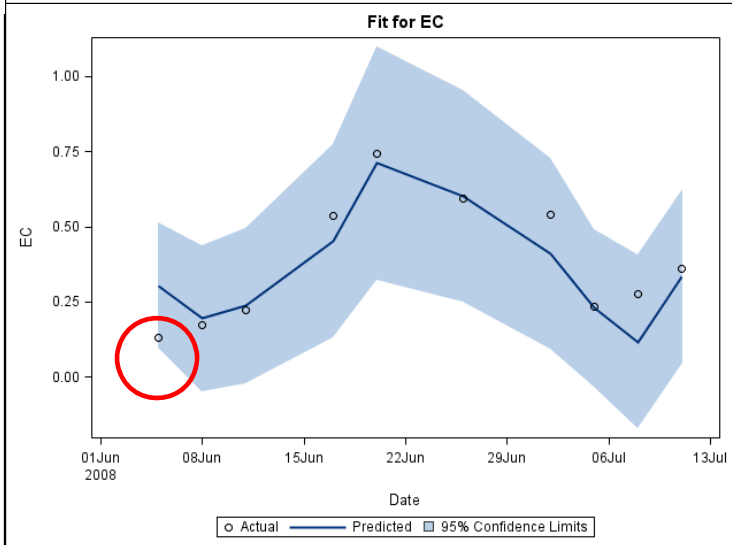
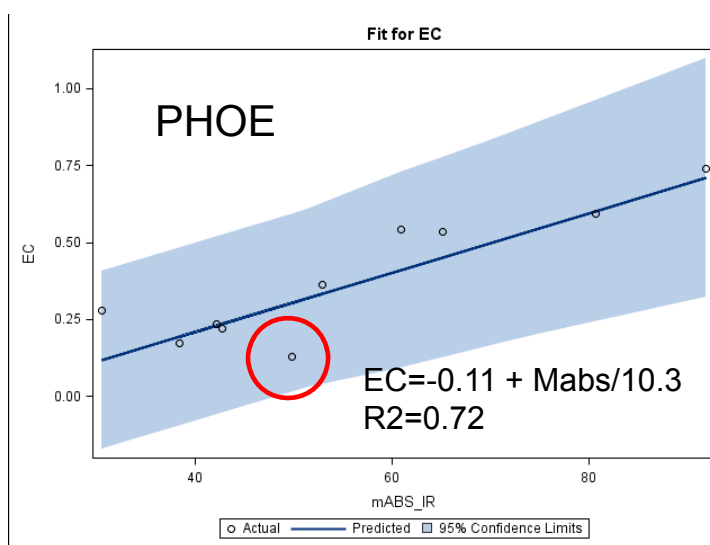
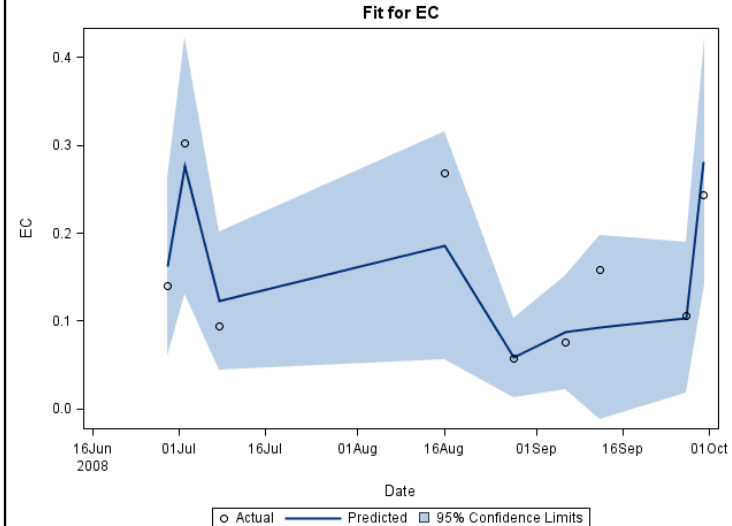
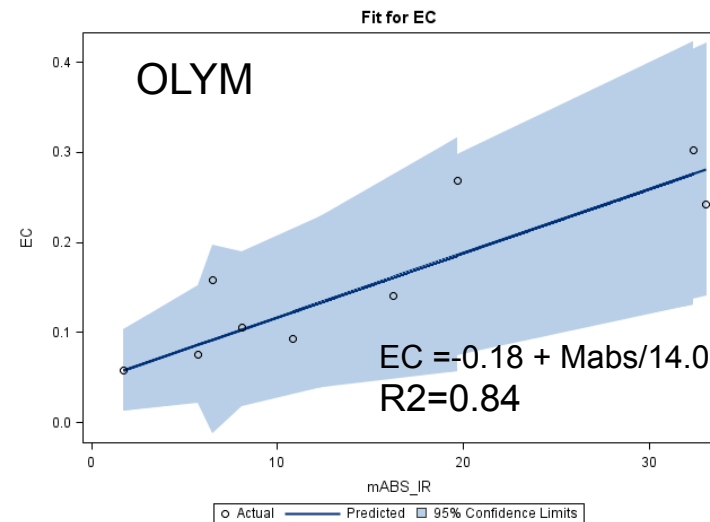
Regression Equation:
 $EC_P = -0.152432 + 0.010281 \cdot atn_p$
 $EC_O = 0.048687 + 0.007768 \cdot atn_o$



Note: more variability between
Mabs_UV and Babs for Phoenix



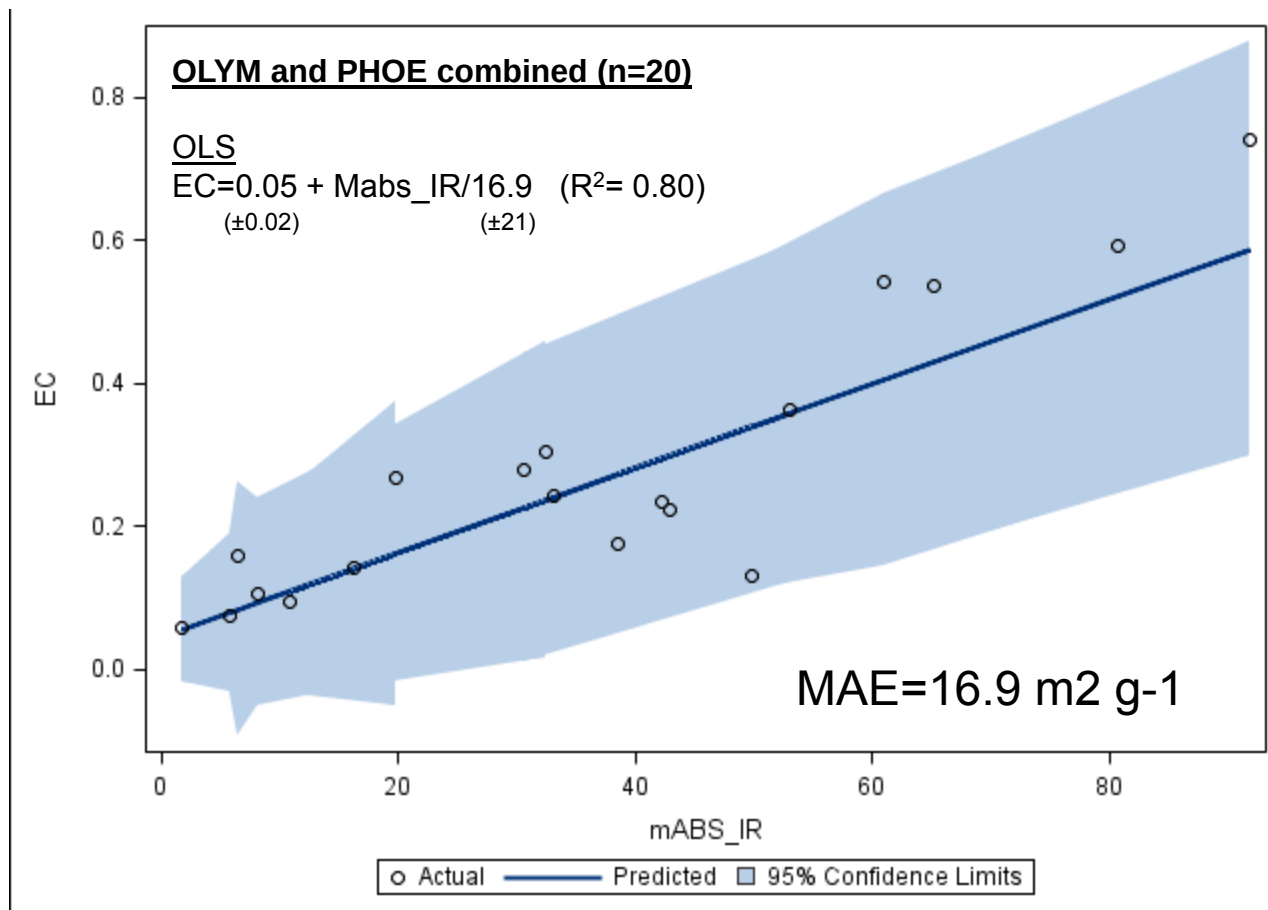
To Predict EC from Mabs_{IR}: Confidence Limits



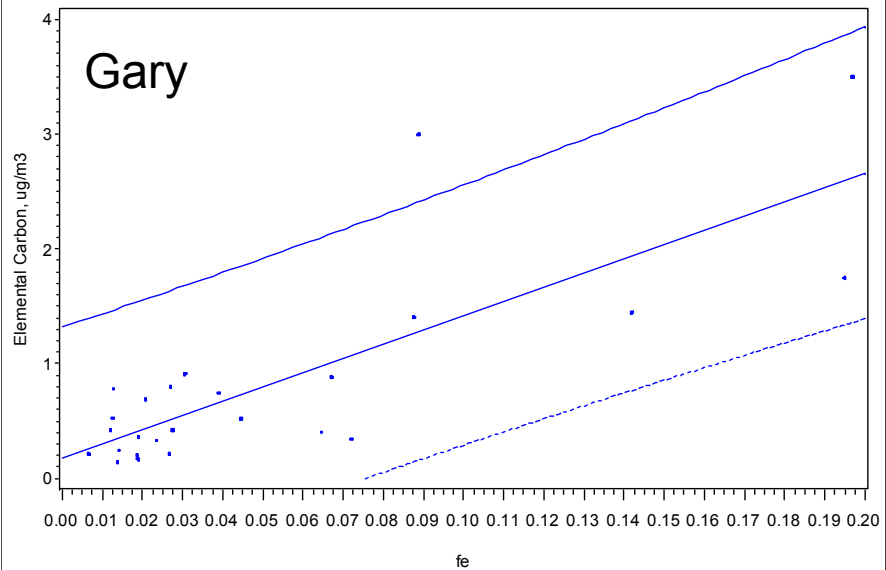
Note: Using Weighted LS (with $\sigma = 0.085 * \text{Log}(\text{EC}) + 0.254$, from Mark Green, DRI)

OLYM: EC = $-0.18 + \text{Mabs}/14.0$ (R²=0.84) → Mass Absorption Efficiency = $14 \text{ m}^2 \text{ g}^{-1}$

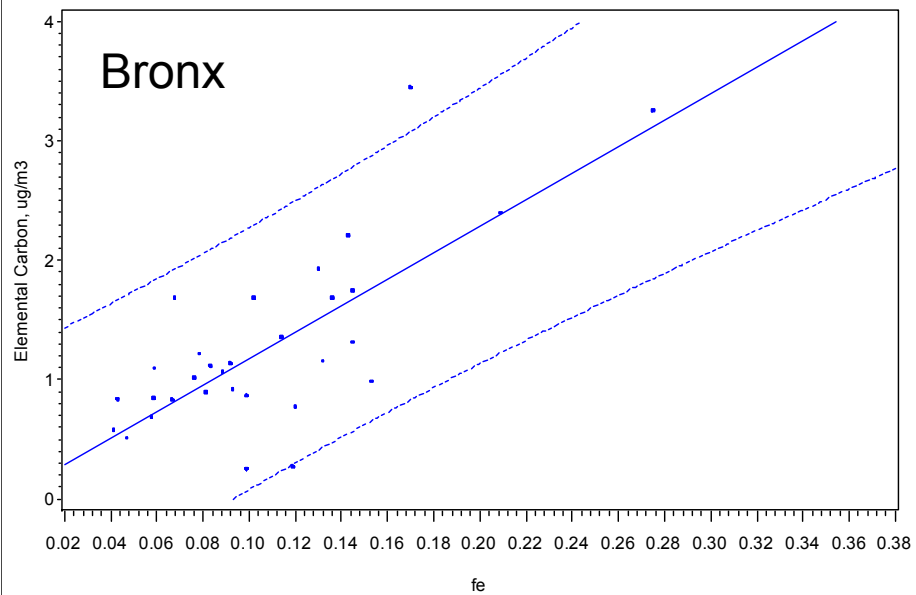
PHOE: EC = $-0.11 + \text{Mabs}/10.3$ (R²=0.72) → MAE = $10 \text{ m}^2 \text{ g}^{-1}$



AIRS Site Code=530530029



AIRS Site Code=360050110



AIRS Site Code=530530029

