

# Filter light transmission as a surrogate for elemental carbon: Examples from IMPROVE and other Networks

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# Motivation

- Elemental carbon (EC) linked to health effects, visibility reduction, material damage, climate change
- PM<sub>2.5</sub> Teflon filters are acquired since 1997 at over 850 locations in US to determine compliance with National Ambient Air Quality standards (NAAQS)
- Chemical speciation (with EC analysis) at relatively few sites.
- How accurately can light transmission through the filter be used to estimate EC on these filters?

# Study Objectives

- Compile data bases of consistently applied  $b_{att}$  and EC measurements.
- Examine relationships by location and season.
- Evaluate the extent to which EC can be estimated from  $b_{att}$

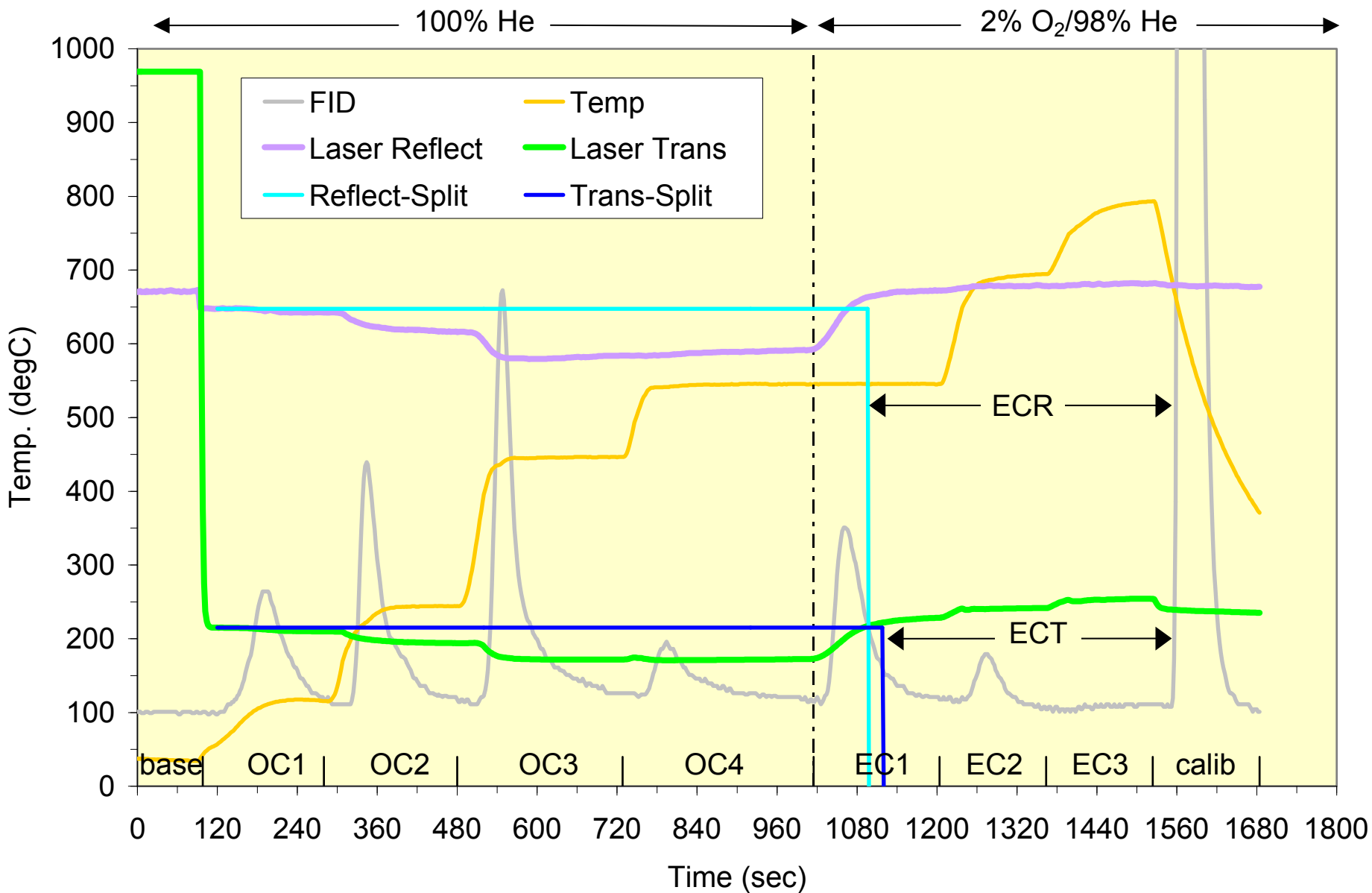
# Data Bases

| Study (Ref)                                            | Period          | Sampling Schedule                                  | Sampler Type (Flow rate) <sup>b</sup>            |
|--------------------------------------------------------|-----------------|----------------------------------------------------|--------------------------------------------------|
| Denver Brown Cloud (Watson et al., 1988) <sup>a</sup>  | 11/2/87-1/31/88 | Twice per day, every day, 0900-1600, 1600-0900 MST | PM <sub>2.5</sub> SFS (20 L/min)                 |
| Tucson Urban Haze (Watson et al., 1991a) <sup>a</sup>  | 9/23/87-1/22/90 | daily, 6am-noon, 1-7 pm                            | PM <sub>2.5</sub> SFS (20 L/min)                 |
| Phoenix Urban Haze (Watson et al., 1991b) <sup>a</sup> | 9/25/89-1/22/90 | daily, 6am-noon, 1-7 pm                            | PM <sub>2.5</sub> SFS (20 L/min)                 |
| Mexico City (Chow et al., 2002a; 2002b) <sup>a</sup>   | 2/23/97-3/22/97 | daily, 4 times/day, every 6 hours                  | PM <sub>2.5</sub> SFS (20 L/min)                 |
|                                                        | 2/23/97-3/22/97 | daily, 4 times/day, every 6 hours                  | PM <sub>10</sub> SFS (20 L/min)                  |
|                                                        | 2/23/97-3/22/97 | daily, 24 h/day                                    | PM <sub>10</sub> MiniVol (5 L/min)               |
| CRPAQS (Chow et al., 2006) <sup>a</sup>                | 12/14/00-2/3/01 | 24 hours, every day during intensives              | PM <sub>2.5</sub> SFS (20 L/min)                 |
|                                                        | 12/2/99-2/3/01  | 24 hours, every 6 <sup>th</sup> day                | PM <sub>10</sub> MiniVol (5 L/min)               |
|                                                        | 12/2/99-2/3/01  | 24 hours, every 6 <sup>th</sup> day                | PM <sub>2.5</sub> MiniVol (5 L/min)              |
| Fresno supersite (Watson and Chow, 2002) <sup>a</sup>  | 7/9/99-12/30/05 | 24 hours, every 6 <sup>th</sup> day                | PM <sub>2.5</sub> Andersen RAAS 400 (16.7 L/min) |
| IMPROVE                                                | 1988-present    | 24 hours, every third day                          | IMPROVE (22.8 L/min)                             |

# Thermal EC measurement

- EC measurements using the IMPROVE protocol – thermal optical reflectance on quartz-fiber filters
- IMPROVE- filter reflectance monitored constantly with 632 nm laser as carbon is thermally desorbed
- Charring of OC causes darkening of filter- when  $O_2$  is added at high temperature, EC and pyrolyzed OC evolve- carbon evolving after reflectance reaches it's initial value is designated EC

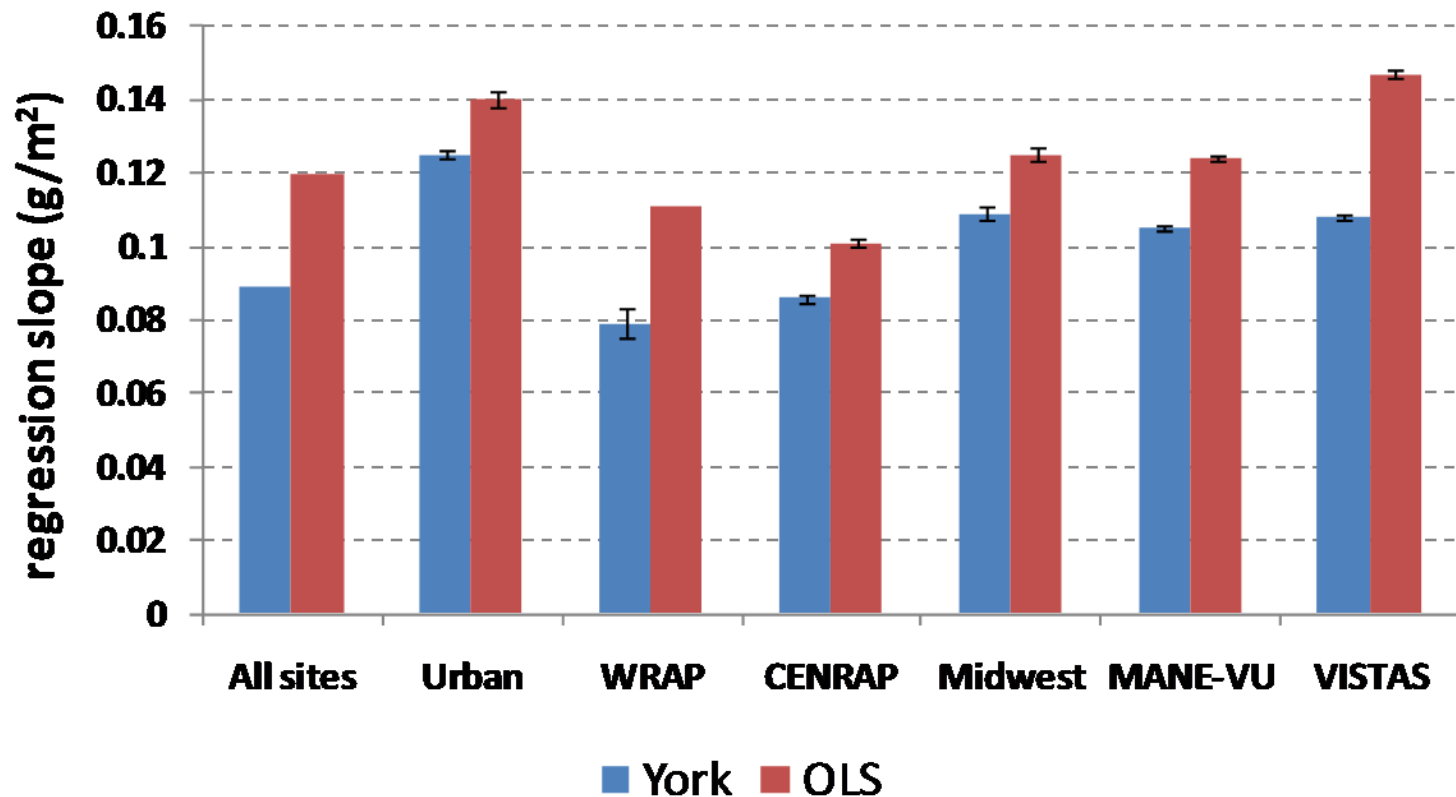
# IMPROVE Method



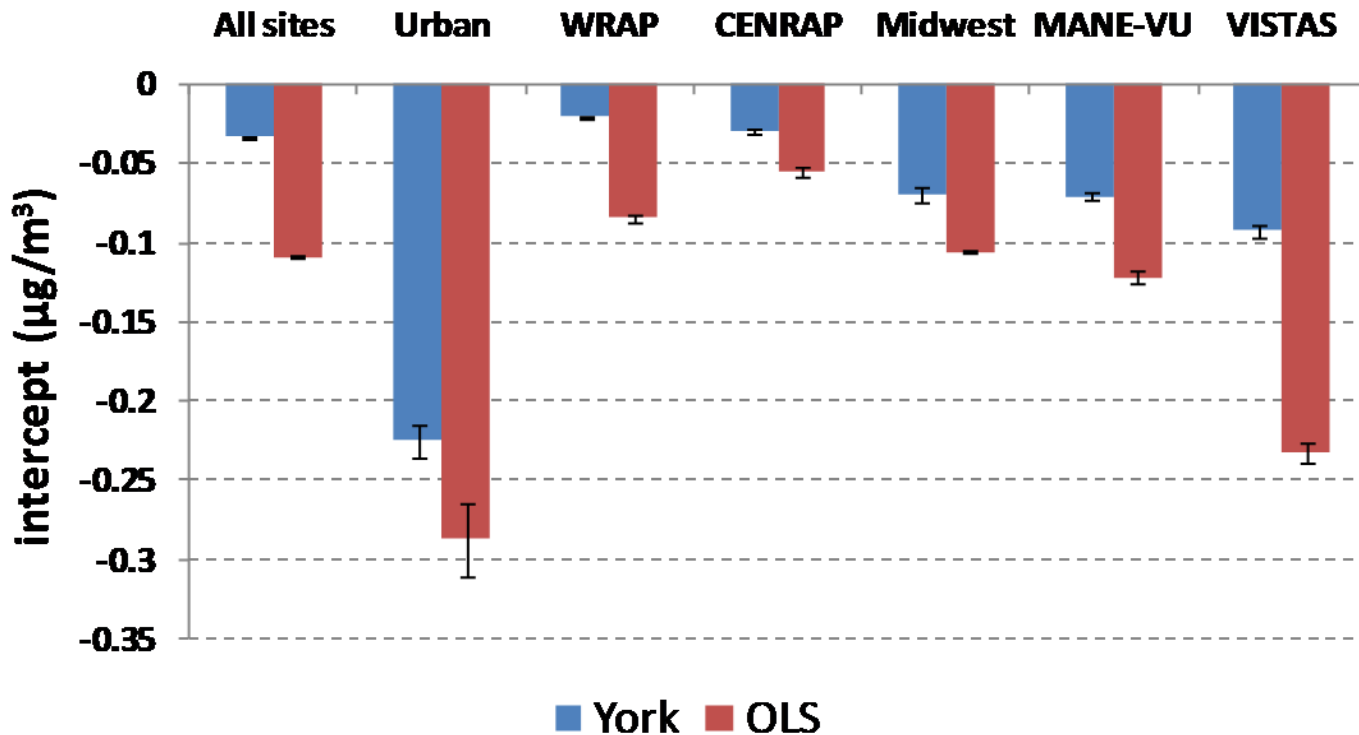
# Filter-based light absorption

- $b_{\text{att}} = (A/V) \cdot \ln(I/I_0)$
- $b_{\text{att}}$  differs from  $b_{\text{abs}}$ .  $b_{\text{att}}$  usually overestimates  $b_{\text{abs}}$  owing to multiple scattering effects of filter and sample deposit.
- $b_{\text{att}}$  is measured by Laser Integrating Plate Method (LIPM) and Hybrid Integrating Plate/Sphere method (HIPS) in IMPROVE and by Densitometer Integrating Plate Method (DIPM) in other networks.

**York weighted Perpendicular Least Squares (PLS) and unweighted Ordinary least Squares (OLS) regression slopes differ significantly, OLS higher slope (lower apparent absorption efficiency)**

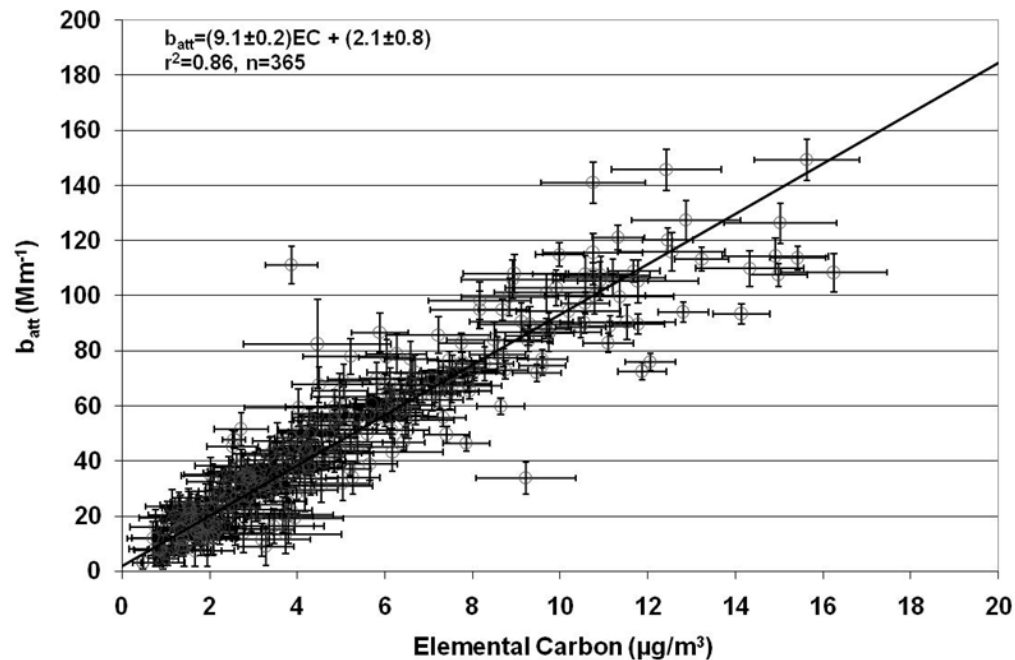


Larger negative intercept for OLS method  
(more positive  $b_{\text{abs}}$  with zero EC)

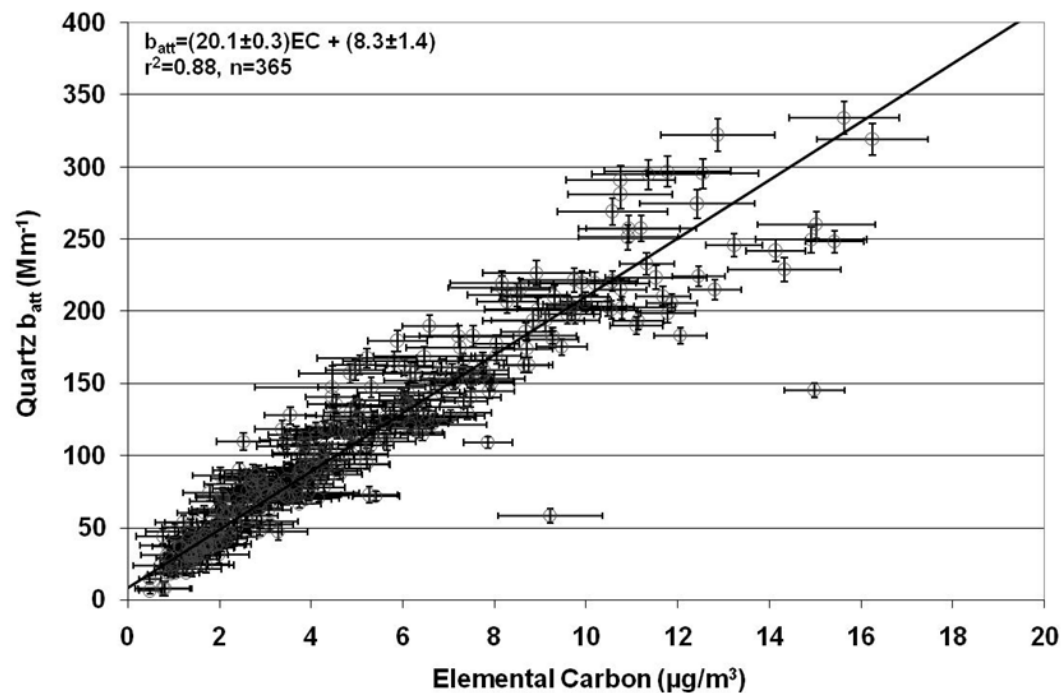


Filter substrates affect  $b_{\text{abs}}$  measurement

Denver-  $b_{\text{abs}}$  on Teflon



Denver  $b_{\text{abs}}$  on Quartz – much higher slope than Teflon and large intercept



# Comparable results from DIPM and LIPM for Denver Brown Cloud Study

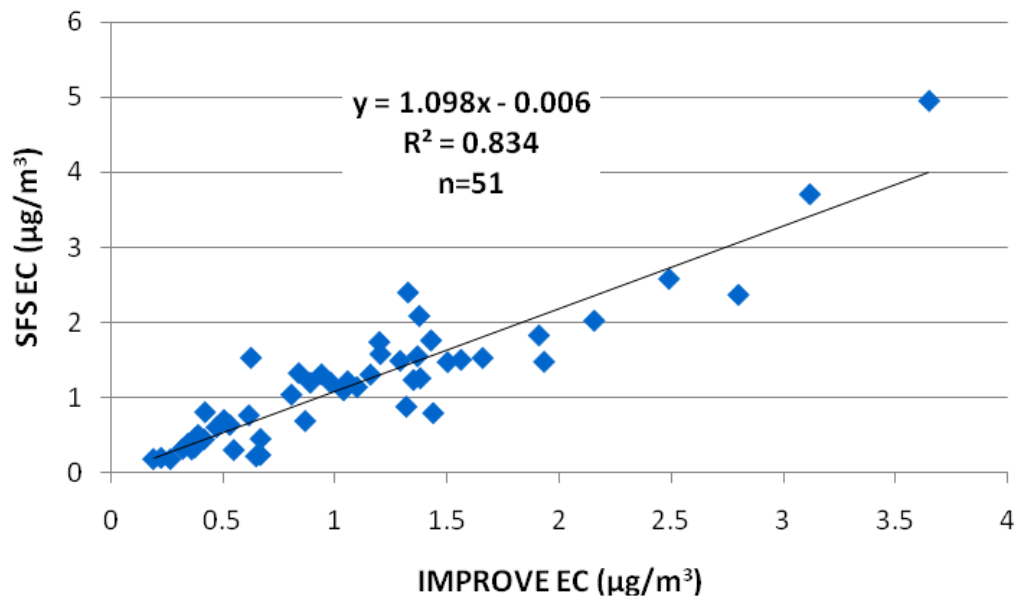
Table 6-6

Comparison of Filter Light Absorption  
Measurements with UC Davis

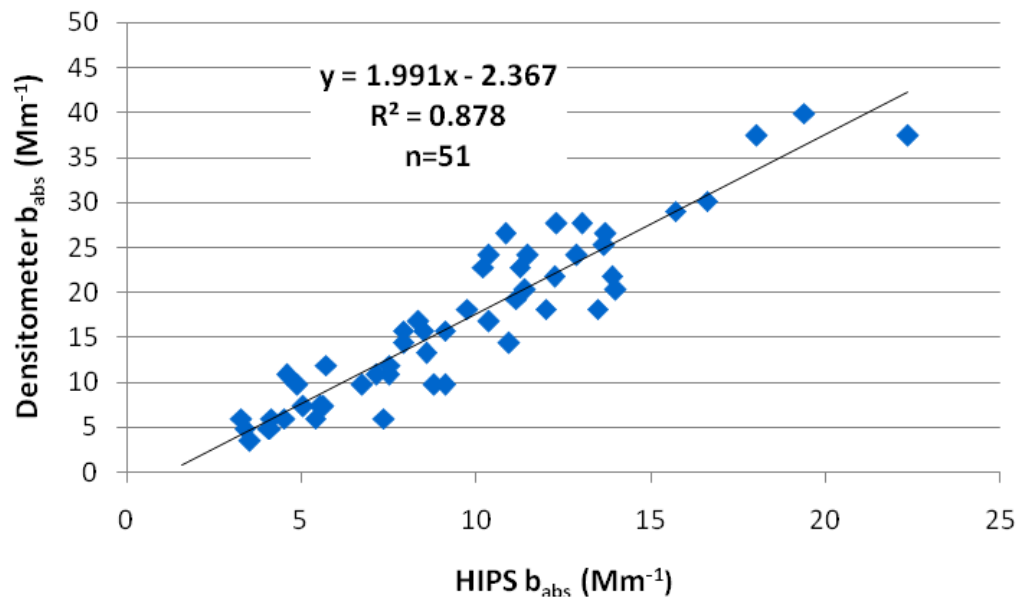
| <u>Filter Absorption in <math>\text{Mm}^{-1}</math> and Ratios</u> |                        |                          |                        |                        |                          |  |
|--------------------------------------------------------------------|------------------------|--------------------------|------------------------|------------------------|--------------------------|--|
| <u>Teflon Filters</u>                                              |                        |                          | <u>Quartz Filters</u>  |                        |                          |  |
| <u>DRI<sup>a</sup></u>                                             | <u>UCD<sup>b</sup></u> | <u>Ratio<sup>c</sup></u> | <u>DRI<sup>a</sup></u> | <u>UCD<sup>b</sup></u> | <u>Ratio<sup>c</sup></u> |  |
| 56.92                                                              | 69.23                  | 0.822                    | 126.73                 | 120.03                 | 1.056                    |  |
| 94.99                                                              | 111.12                 | 0.855                    | 219.39                 | 214.37                 | 1.023                    |  |
| 70.11                                                              | 79.55                  | 0.881                    | 150.34                 | 157.08                 | 0.957                    |  |
| 46.68                                                              | 59.76                  | 0.781                    | 127.54                 | 127.54                 | 1.000                    |  |
| 90.23                                                              | 101.32                 | 0.890                    | 201.24                 | 191.21                 | 1.052                    |  |
| 108.17                                                             | 132.59                 | 0.816                    | 320.17                 | 306.48                 | 1.045                    |  |
| 113.15                                                             | 130.34                 | 0.868                    | 247.98                 | 239.94                 | 1.034                    |  |
| Mean                                                               | 82.89                  | 97.70                    | 199.06                 | 193.81                 | 1.024                    |  |
| Std. Dev.                                                          |                        | 0.037                    |                        |                        | 0.032                    |  |

**HIPS half DIPM  
measurements at  
Fresno (non-wavelength  
corrected)**

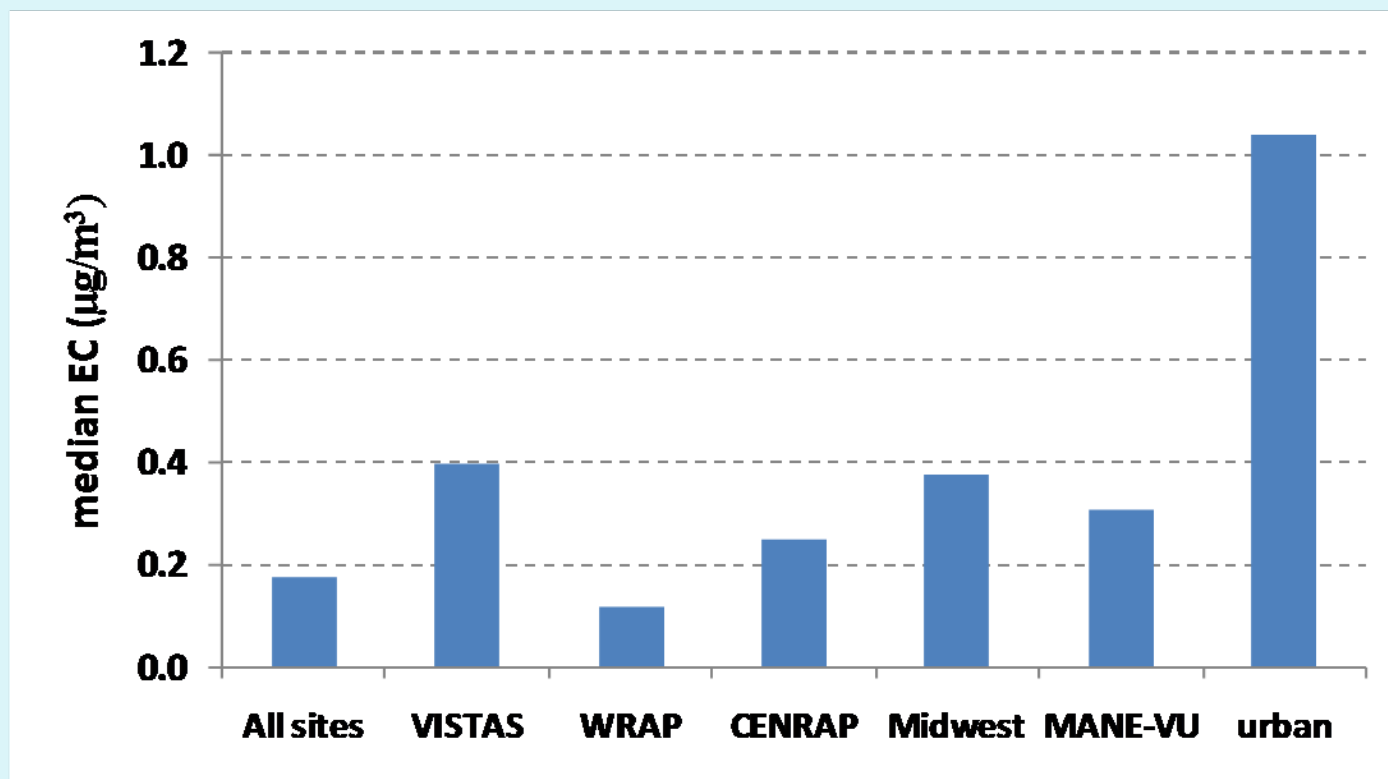
**Fresno –co-located SFS  
and IMPROVE samplers  
TOR EC compares well**



**DIPM  $b_{att}$  and HIPS  $b_{abs}$   
well correlated but  
densitometer  $b_{abs}$  about  
twice as high**

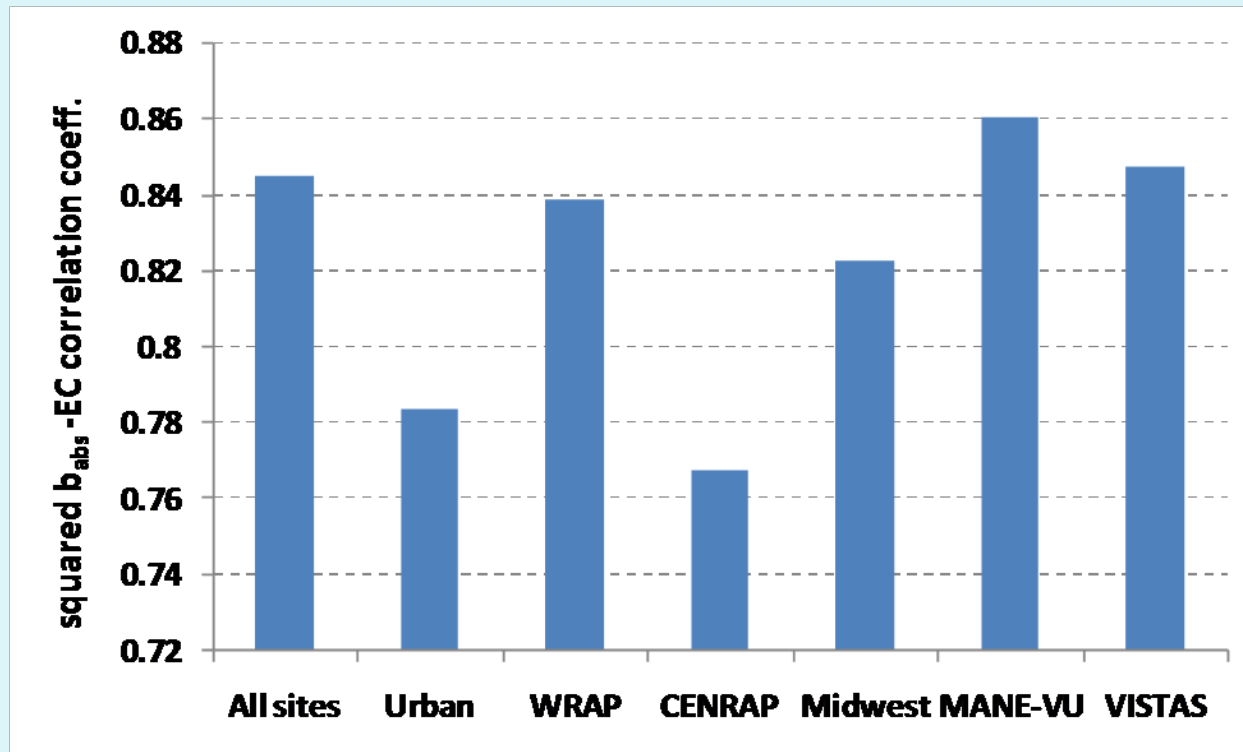


## 2005-2006 EC levels by planning region

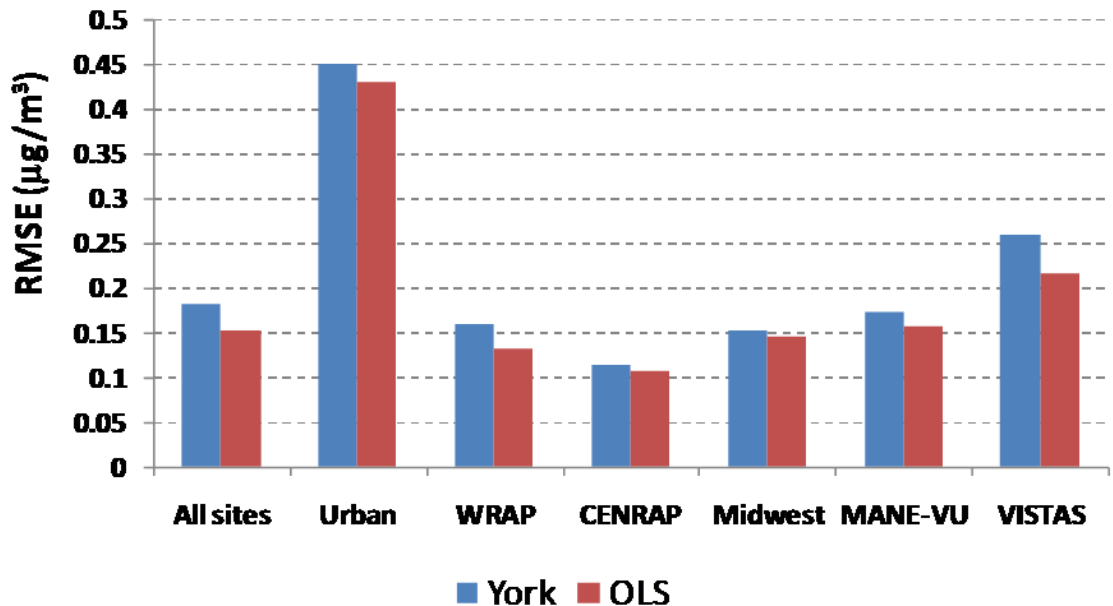


Urban IMPROVE sites had highest EC levels, WRAP sites lowest

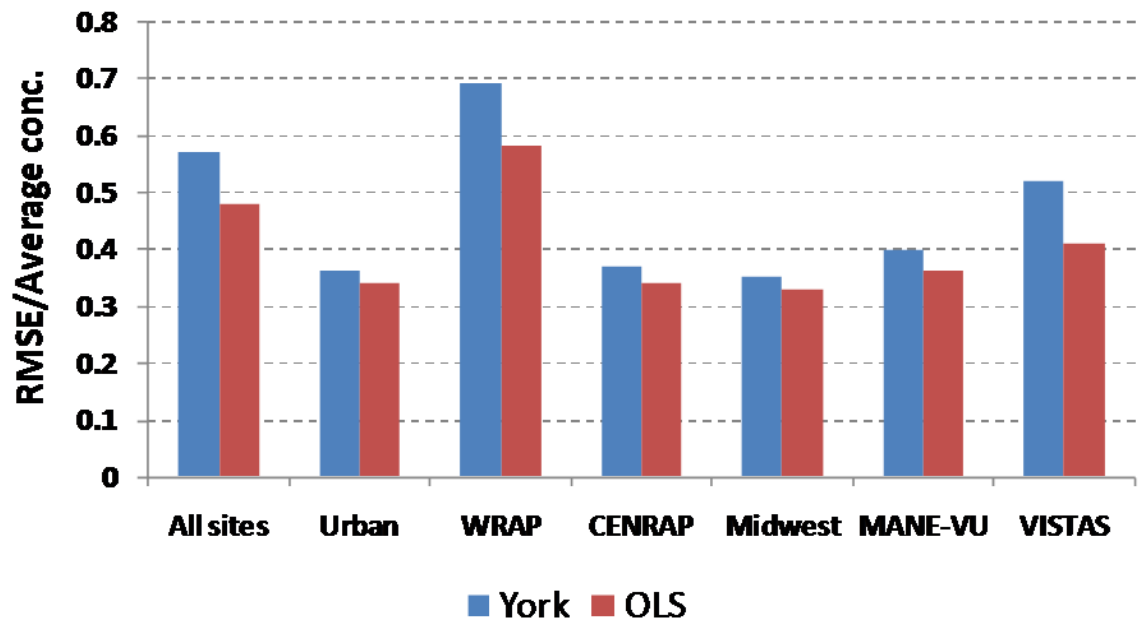
Squared correlation coefficients ( $R^2$ ) between  $b_{abs}$  and EC range from 0.77 at CENRAP sites to 0.86 for MANU-VU sites- network wide  $R^2=0.84$



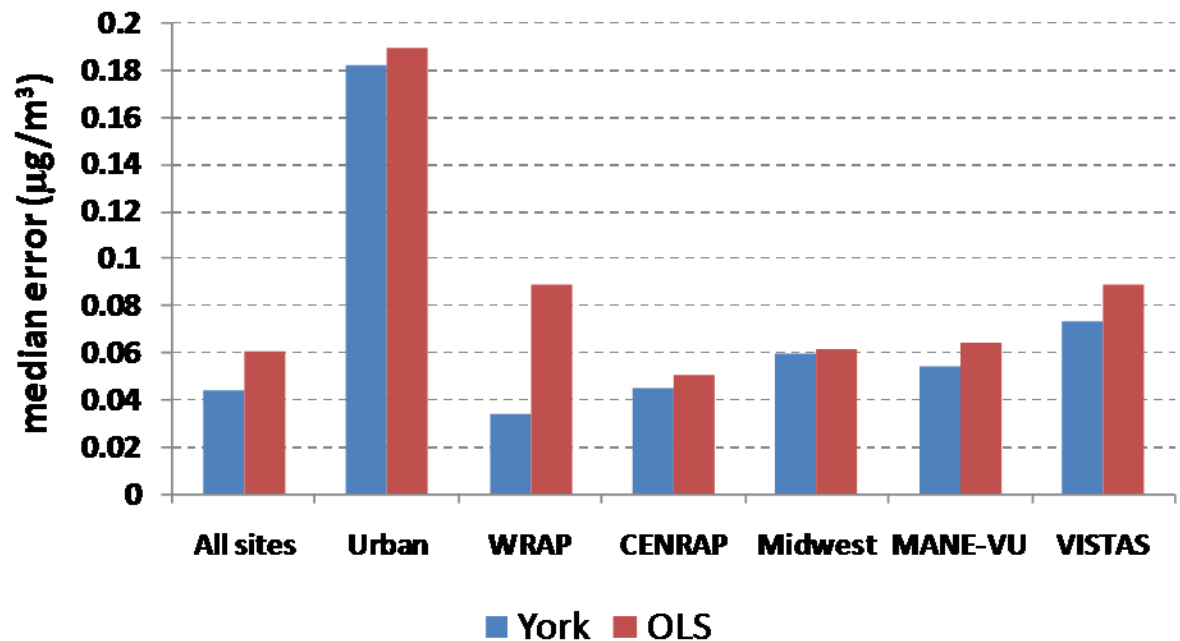
RMS error greater for York PLS regression than OLS regression



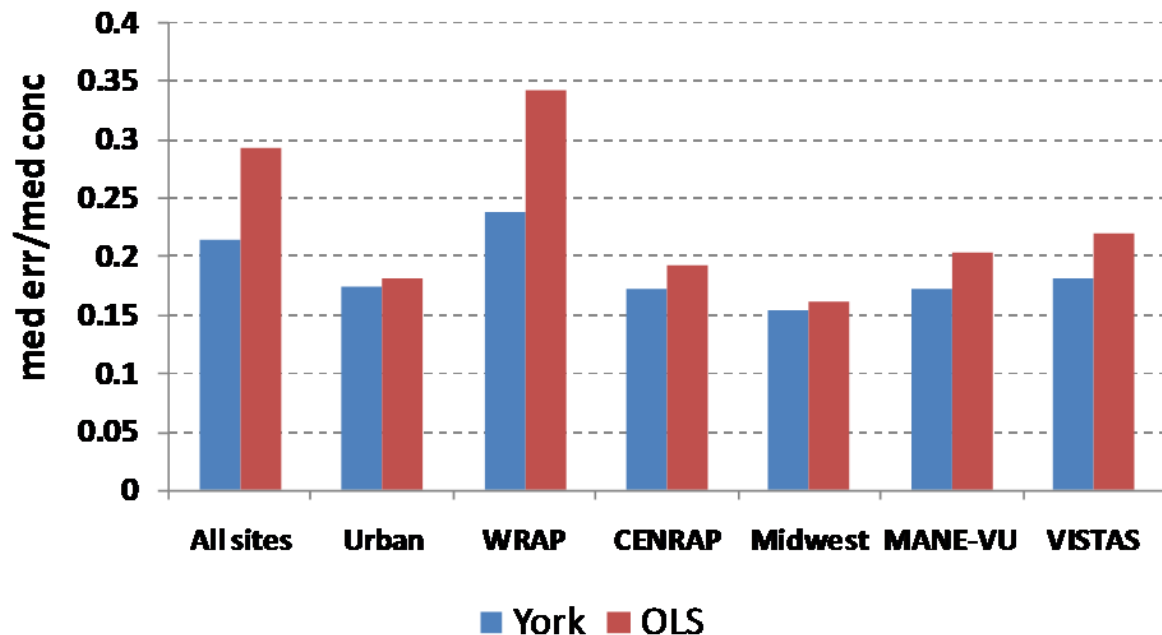
RMS error ranges from 30-70% of average concentration



Median errors less for the York PLS regression than OLS regression -weighting by uncertainty, which is proportional to concentration ( $R^2=0.58$ ) reduces influence of high values

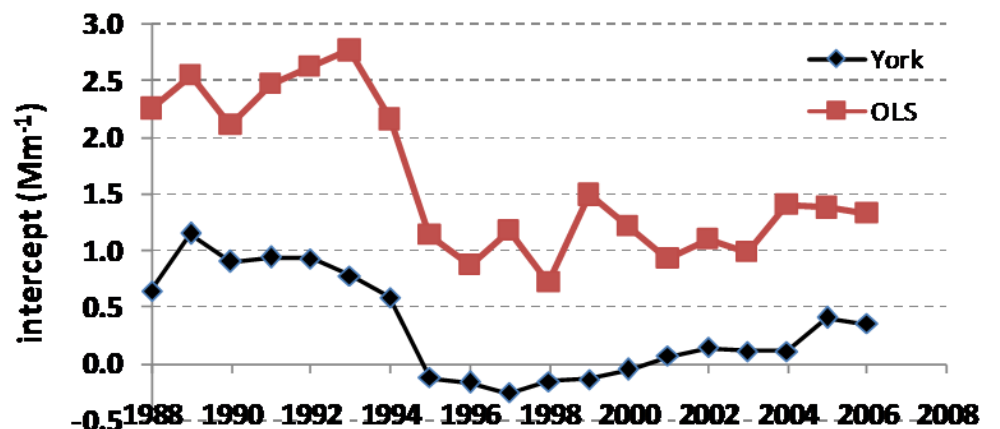
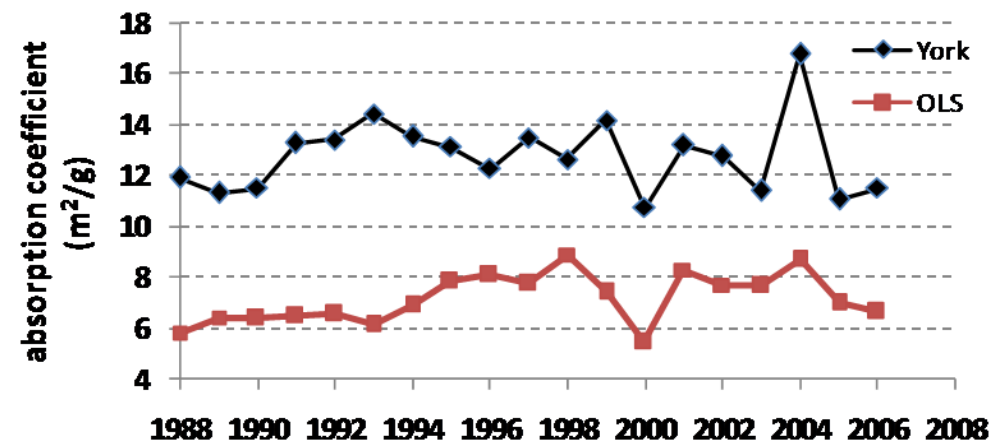
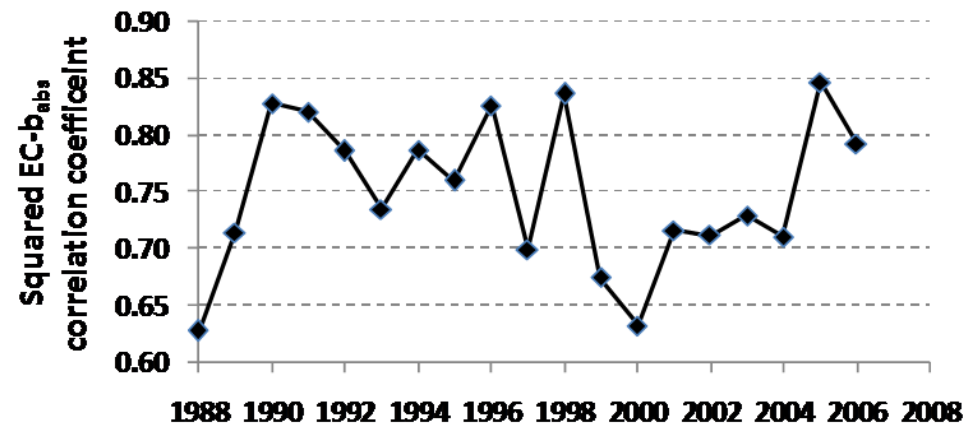


Median errors 15-25% of median concentration for York, 15-35% for OLS



For IMPROVE,  $R^2$  increased first few years. Substantial difference for PLS and OLS slopes and intercepts

Very high apparent  $\sigma_{abs}$  in 2004 probably due to oxygen leak (too little EC)



Intercept change ~ same time as change to HIPS in 1994

Equations for estimating PM<sub>2.5</sub> elemental carbon (EC) based on DIPM ( $b_{att}$ ) measurements at Denver, Mexico City<sup>a</sup> and the Fresno, CA, Supersite. The slope is the inverse of the light absorption efficiency ( $1/\sigma_{abs}$ ). Values in bold are for York regression; values in parentheses are ordinary least squares.

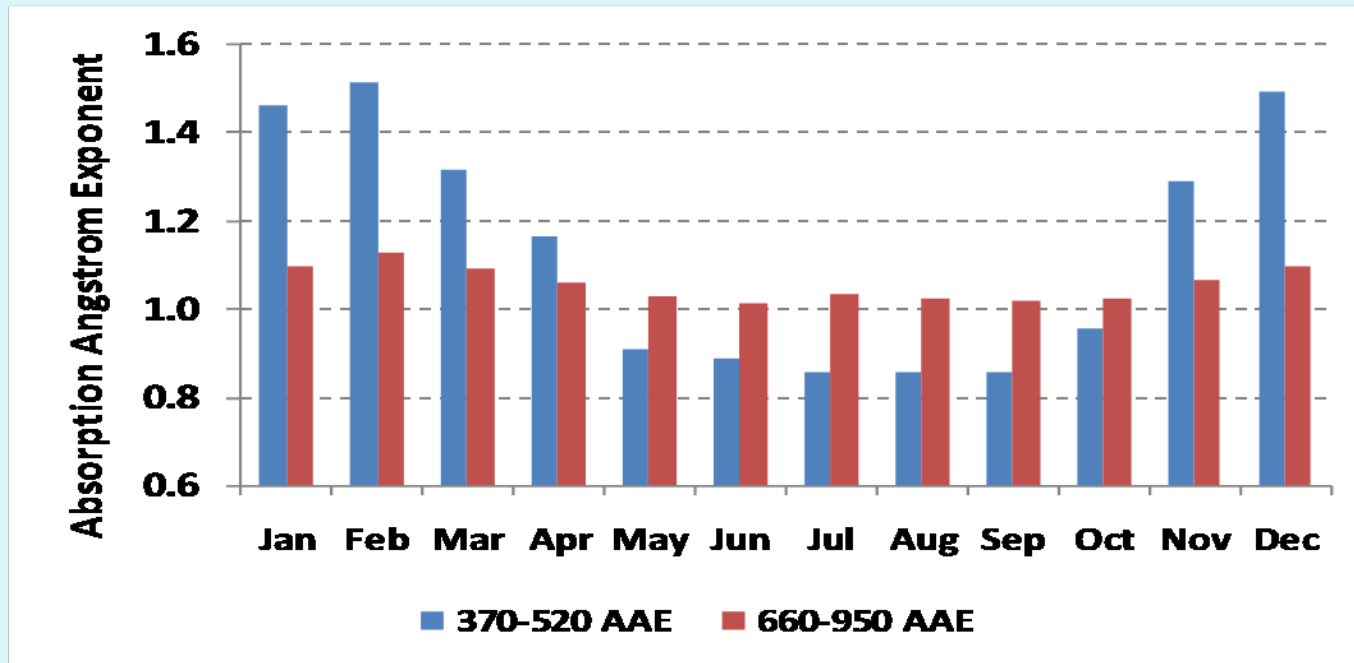
| Data set            | Average EC/ $b_{att}$ | Slope (g/m <sup>2</sup> )             | Intercept (ug/m <sup>3</sup> )         | R <sup>2</sup> | RMS <sup>b</sup> error (ug/m <sup>3</sup> ) | Average Conc. (ug/m <sup>3</sup> ) | RMS error/ Average Concentration |
|---------------------|-----------------------|---------------------------------------|----------------------------------------|----------------|---------------------------------------------|------------------------------------|----------------------------------|
| Denver (n=365)      | <b>0.104</b>          | <b>0.110± 0.001</b><br>(0.101± 0.002) | <b>-0.229± 0.058</b><br>(0.117± 0.122) | 0.926          | <b>1.40</b> (1.28)                          | 4.87                               | <b>0.29</b><br>(0.26)            |
| Mexico City (n=260) | <b>0.086</b>          | <b>0.098±0.002</b><br>(0.095±0.002)   | <b>-0.661±0.090</b><br>(-0.627±0.163)  | 0.907          | <b>2.05</b> (1.34)                          | 6.39                               | <b>0.32</b><br>(0.21)            |
| Fresno (n=350)      | <b>0.081</b>          | <b>0.092± 0.002</b><br>(0.118± 0.003) | <b>-0.472± 0.038</b><br>(-0.838±0.075) | 0.833          | <b>1.07</b> (0.71)                          | 1.84                               | <b>0.58</b><br>(0.38)            |

For IMPROVE, there is small seasonal variation relationships

| <b>Data set</b><br><b>IMPROVE</b><br><b>2005-2006<sup>b</sup></b> | <b>Average</b><br><b>EC/Average</b><br><b>b<sub>att</sub></b> | <b>Slope (g/m<sup>2</sup>)</b>      | <b>Intercept</b><br><b>(ug/m<sup>3</sup>)</b> | <b>R<sup>2</sup></b> | <b>RMS<sup>b</sup></b><br><b>error</b><br><b>(ug/m<sup>3</sup>)</b> | <b>Average</b><br><b>Conc.</b><br><b>(ug/m<sup>3</sup>)</b> | <b>RMS error/</b><br><b>Average</b><br><b>Concentration</b> |
|-------------------------------------------------------------------|---------------------------------------------------------------|-------------------------------------|-----------------------------------------------|----------------------|---------------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| Winter<br>(n=8,165)                                               | <b>0.094</b>                                                  | <b>0.094±0.001</b><br>(0.123±0.000) | <b>-0.026±0.001</b><br>(-0.096±0.002)         | 0.883                | <b>0.183</b><br>(0.152)                                             | 0.32                                                        | <b>0.57</b><br>(0.48)                                       |
| Spring<br>(n=8,882)                                               | <b>0.081</b>                                                  | <b>0.083±0.001</b><br>(0.115±0.001) | <b>-0.045±0.001</b><br>(-0.110±0.002)         | 0.832                | <b>0.164</b><br>(0.136)                                             | 0.26                                                        | <b>0.63</b><br>(0.52)                                       |
| Summer<br>(n=7,483)                                               | <b>0.091</b>                                                  | <b>0.086±0.001</b><br>(0.119±0.001) | <b>-0.026±0.002</b><br>(-0.114±0.003)         | 0.777                | <b>0.195</b><br>(0.168)                                             | 0.36                                                        | <b>0.53</b><br>( 0.47)                                      |
| Autumn<br>(n=7,844)                                               | <b>0.093</b>                                                  | <b>0.089±0.001</b><br>(0.122±0.001) | <b>-0.003±0.001</b><br>(0.108±0.004)          | 0.857                | <b>0.193</b><br>(0.156)                                             | 0.35                                                        | <b>0.56</b><br>(0.45)                                       |

York regression results in bold, OLS in parentheses

Brown carbon is evident at the Fresno supersite where light transmission was measured continuously at several wavelengths



Fresno has enhanced light absorption at shorter wavelengths in winter

Absorption angstrom exponent =  $-\ln(\text{babs}_{\lambda_1}) / \ln(\text{babs}_{\lambda_2}) / \ln(\lambda_1 / \lambda_2)$

# Conclusions

- Filter light attenuation is reasonably correlated with IMPROVE EC, regardless of the filter transmission method.
- $b_{\text{att}}$ -EC relationships differ among filter transmission methods, but they are consistent over space and time for the same method.
- EC can be estimated from  $b_{\text{att}}$  within  $\pm 20\%$  at urban concentrations.
- OLS regression gives lower RMS error, but greater median errors than weighted PLS regressions.