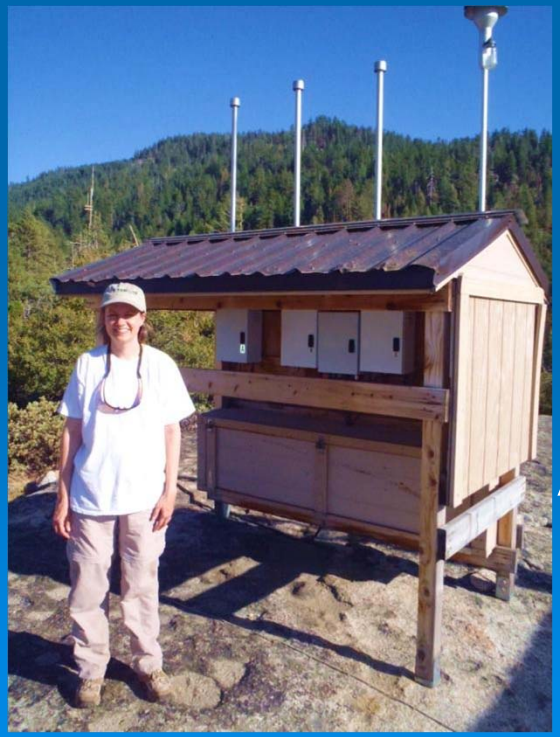
Organic Carbon Data Quality in IMPROVE and Alternate Models for the Artifact



IMPROVE Steering Committee
Columbia River Gorge
October 20, 2010
Ann M. Dillner, Warren H. White

Organic Carbon in IMPROVE

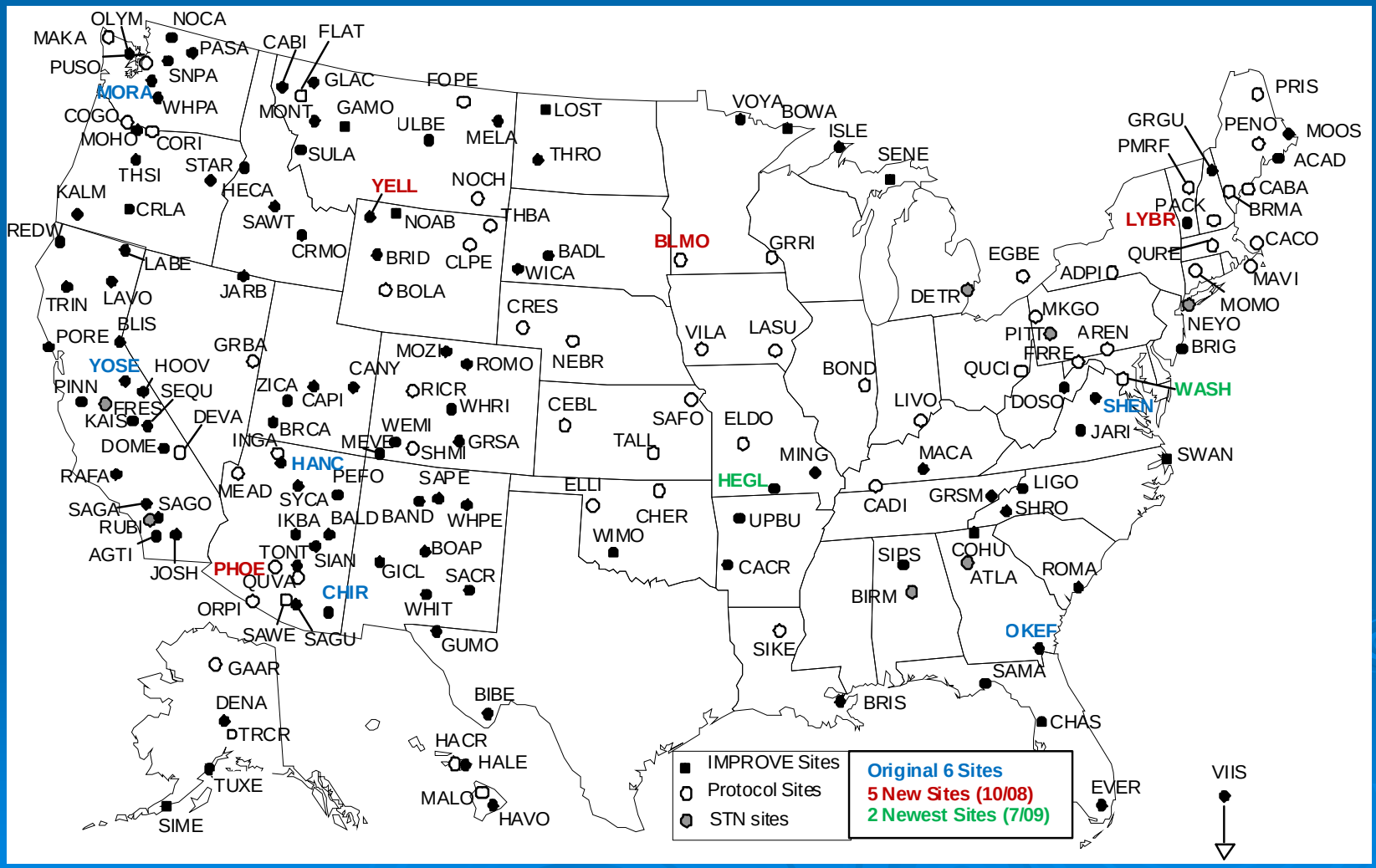
- Quartz filters are artifact-prone
- IMPROVE does not account for negative artifacts
- IMPROVE uses back filters not field blanks to artifact correct for positive artifact
- artifacts are proportionally large at low concentrations
- MDL and uncertainty not reported for OC

IMPROVE Artifact Adjustment

- Back filters collected at a few sites
- Artifacts are corrected for by subtracting the monthly median (since 6/2002) back filter OC mass from the OC mass on the front filter by OC fraction. For example,

$$OC2\ (\mu g/m^3) = (OC2_{front} - OC2_{mm})/\text{air volume}.$$

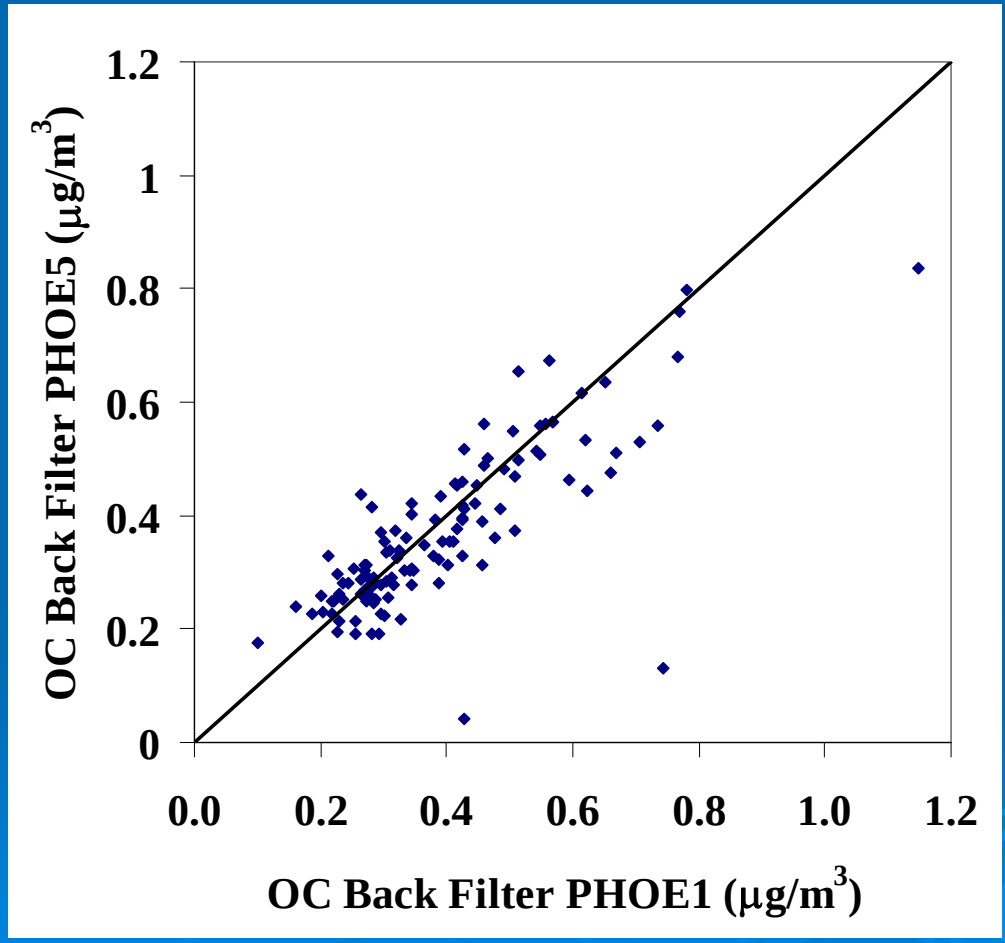
IMPROVE Carbon Back Filter Sites



Outline

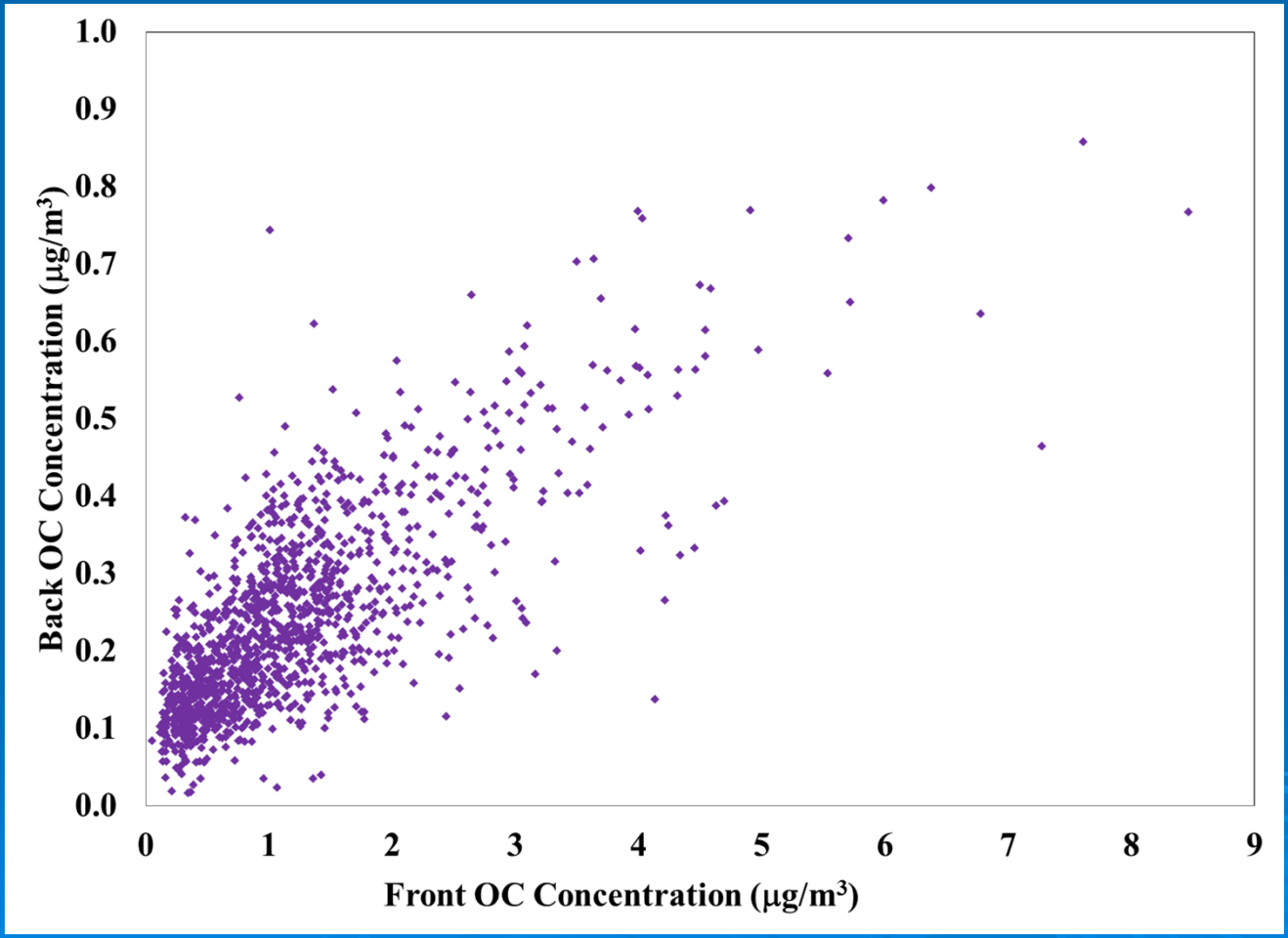
- Back filter data at 11 sites, Oct 08-Sept 09
  - Back filter concentration reproducibility
  - Impact of new sites on median
- Monthly median correction method
  - Estimate quantification limit and uncertainty
- Other models for artifact correction
- An alternate interpretation of the back filter measurement

OC Concentrations for Collocated Back Filters at PHOE

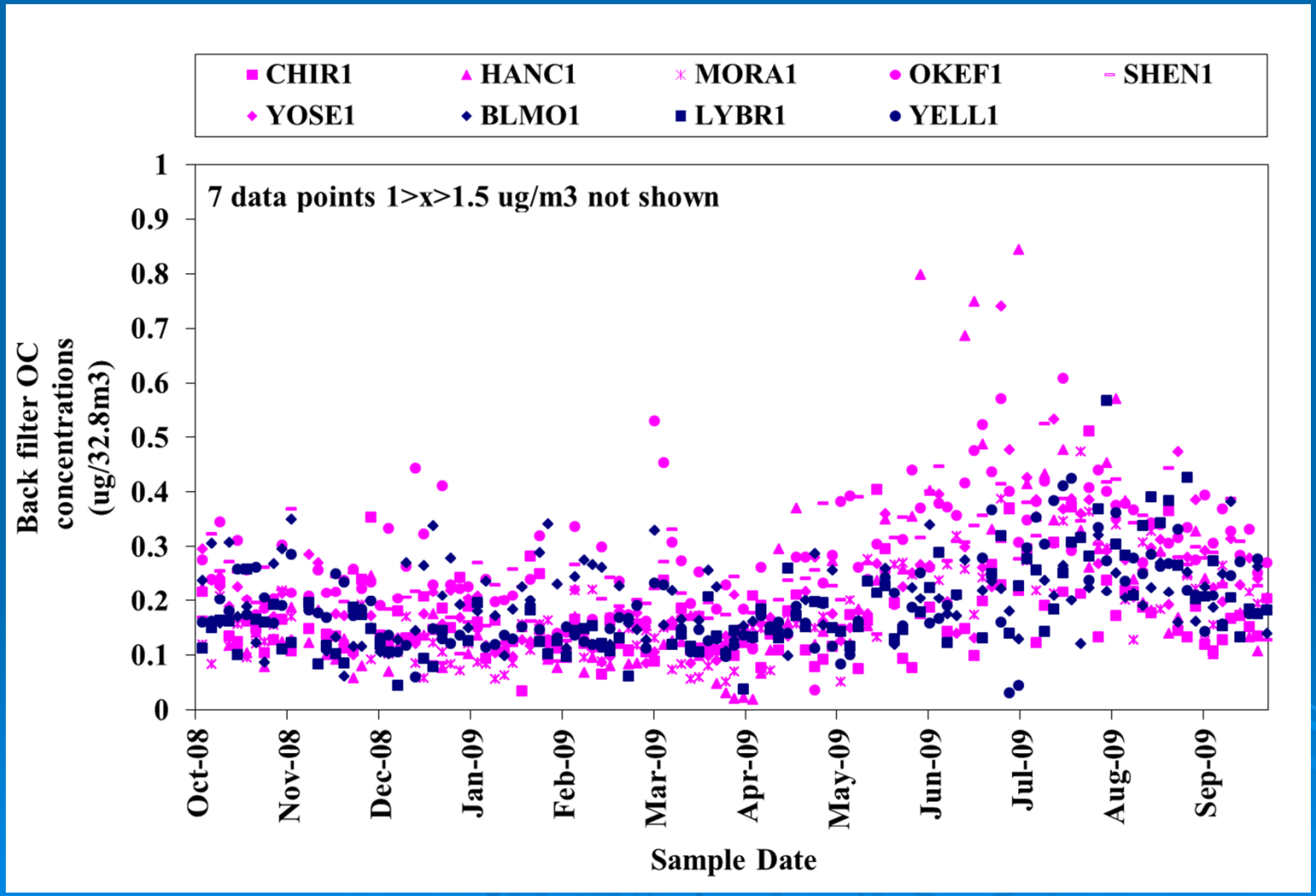


Front vs. Back OC

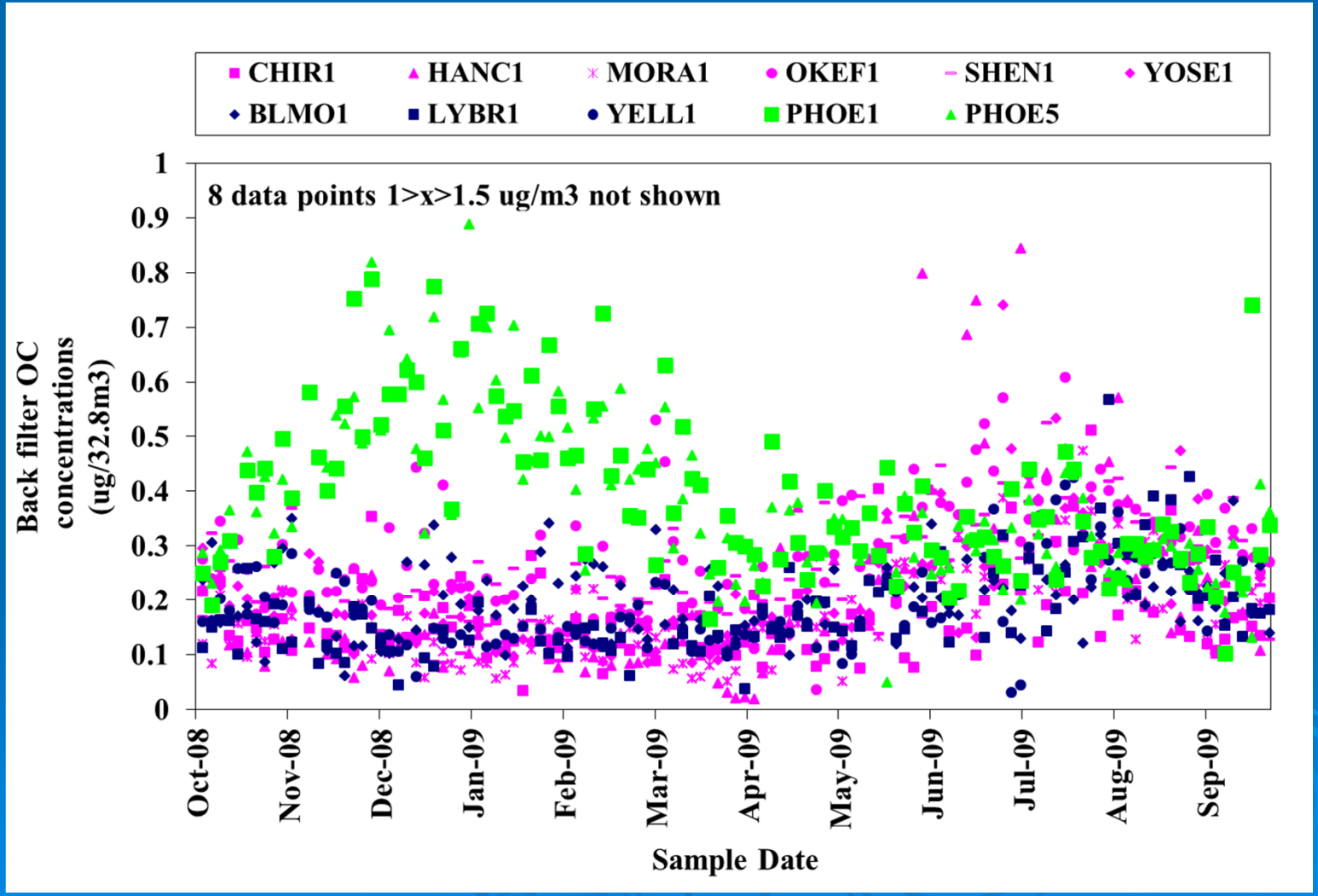
(highest 1% of data excluded from figure)



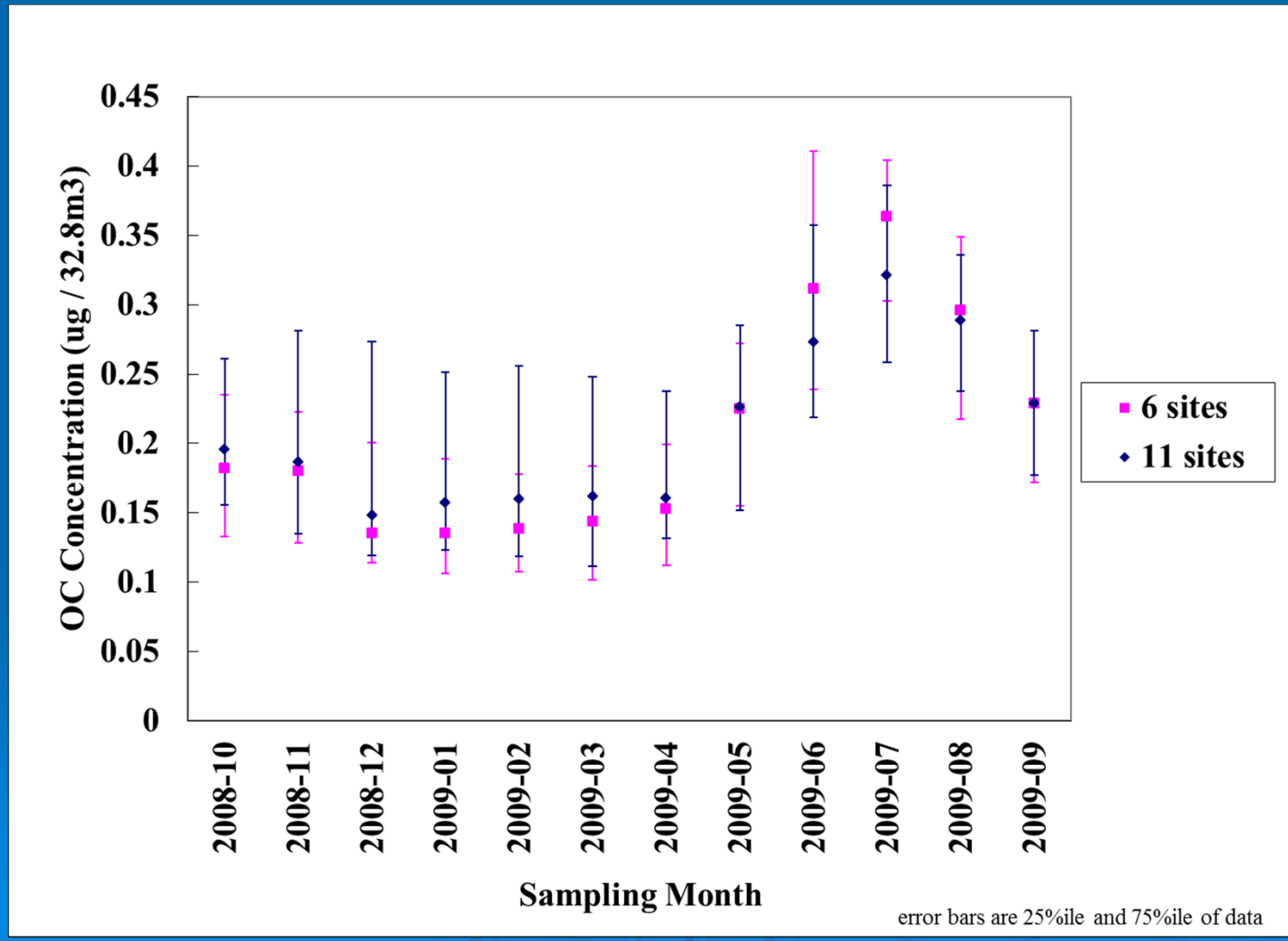
Back filter data without PHOE1 and PHOE5



All back filter data



Monthly Median Back Filter Concentrations

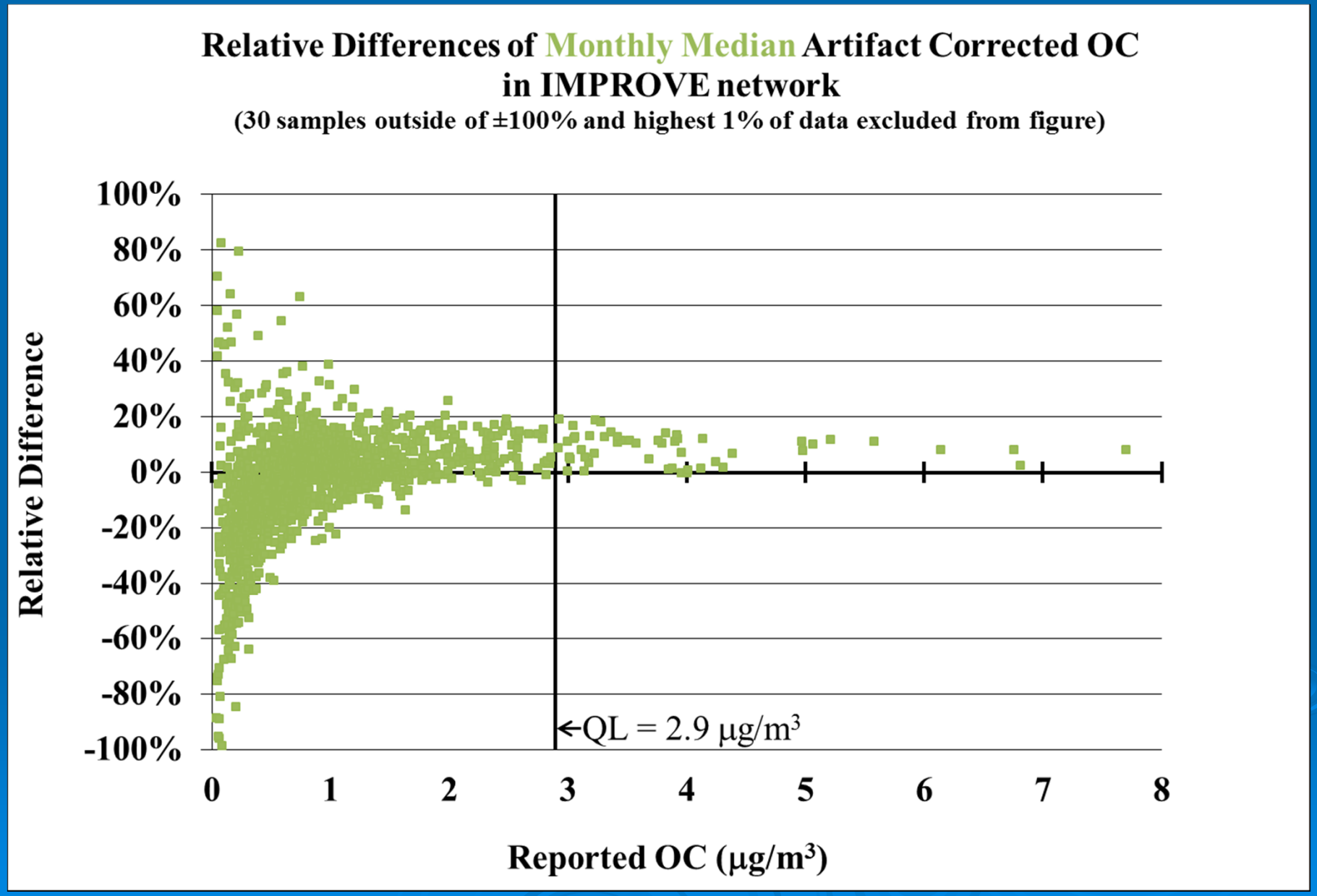


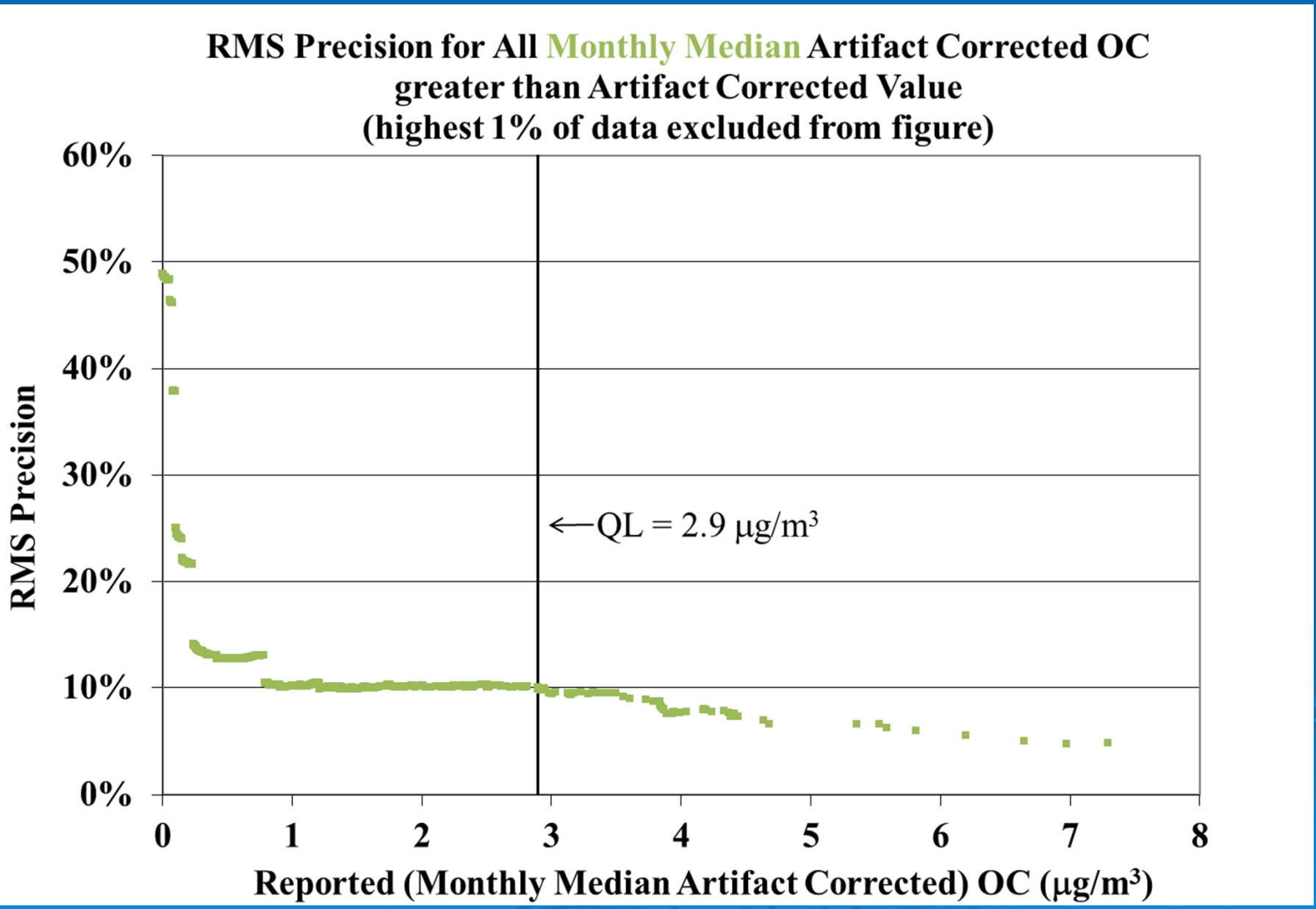
Estimating Quantitative Limit for OC with Monthly Median Artifact Correction

- One year of data
- 11 sites with back filters
- For each sample calculate
  - Sample specific OC, best estimate
    - OC_{ss} = (front – back)/air volume
  - Monthly median corrected OC
    - OC_{mm} = (front – $back_{mm}$)/(air volume)
    - $Back_{mm}$ = median from 10 other sites
    - This is the method used for most sites in IMPROVE for the carbon fractions

Estimating Quantitative Limit for OC with Monthly Median Artifact Correction

- Relative difference $= \left(\frac{OC_{mm} - OC_{ss}}{OC_{ss}}\right) * 100\%$
- Relative RMS Precision $= \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{(OC_{mm})_i - (OC_{ss})_i}{(OC_{ss})_i}\right)^2}$
  - n = all samples greater than or equal to OC_{ss}
- Quantification Limit (QL)
  - Defined as artifact adjusted OC concentration above which the precision is less than 10%.


Relative Differences of Monthly Median Artifact Corrected OC in IMPROVE network
(30 samples outside of ±100% and highest 1% of data excluded from figure)
Relative Difference
100%
80%
60%
40%
20%
0%
-20%
-40%
-60%
-80%
-100%
←QL = 2.9 µg/m3
0
1
2
3
4
5
6
7
8
Reported OC (µg/m3)

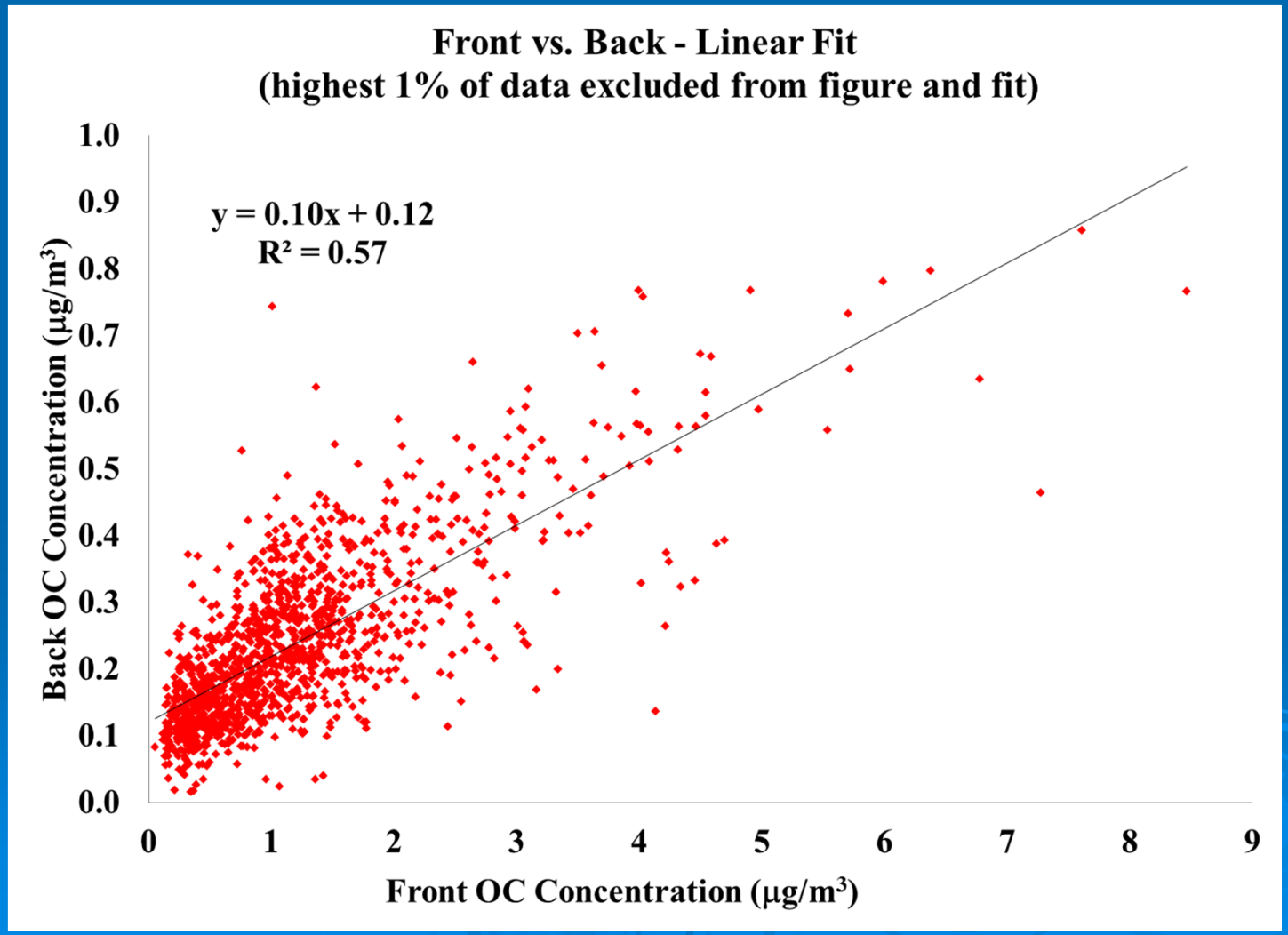

RMS Precision for All Monthly Median Artifact Corrected OC
greater than Artifact Corrected Value
(highest 1% of data excluded from figure)
RMS Precision
60%
50%
40%
30%
20%
10%
0%
←QL = 2.9 µg/m³
0
1
2
3
4
5
6
7
8
Reported (Monthly Median Artifact Corrected) OC (µg/m³)

Monthly Median Corrected OC

- Reported Concentrations
  - Biased low at low concentrations
  - Biased high at high concentrations
- QL (precision = 10%) = 2.9 $\mu g/m^3$
  - 13% of data above QL
  - Bias in quantifiable data is 8.5%

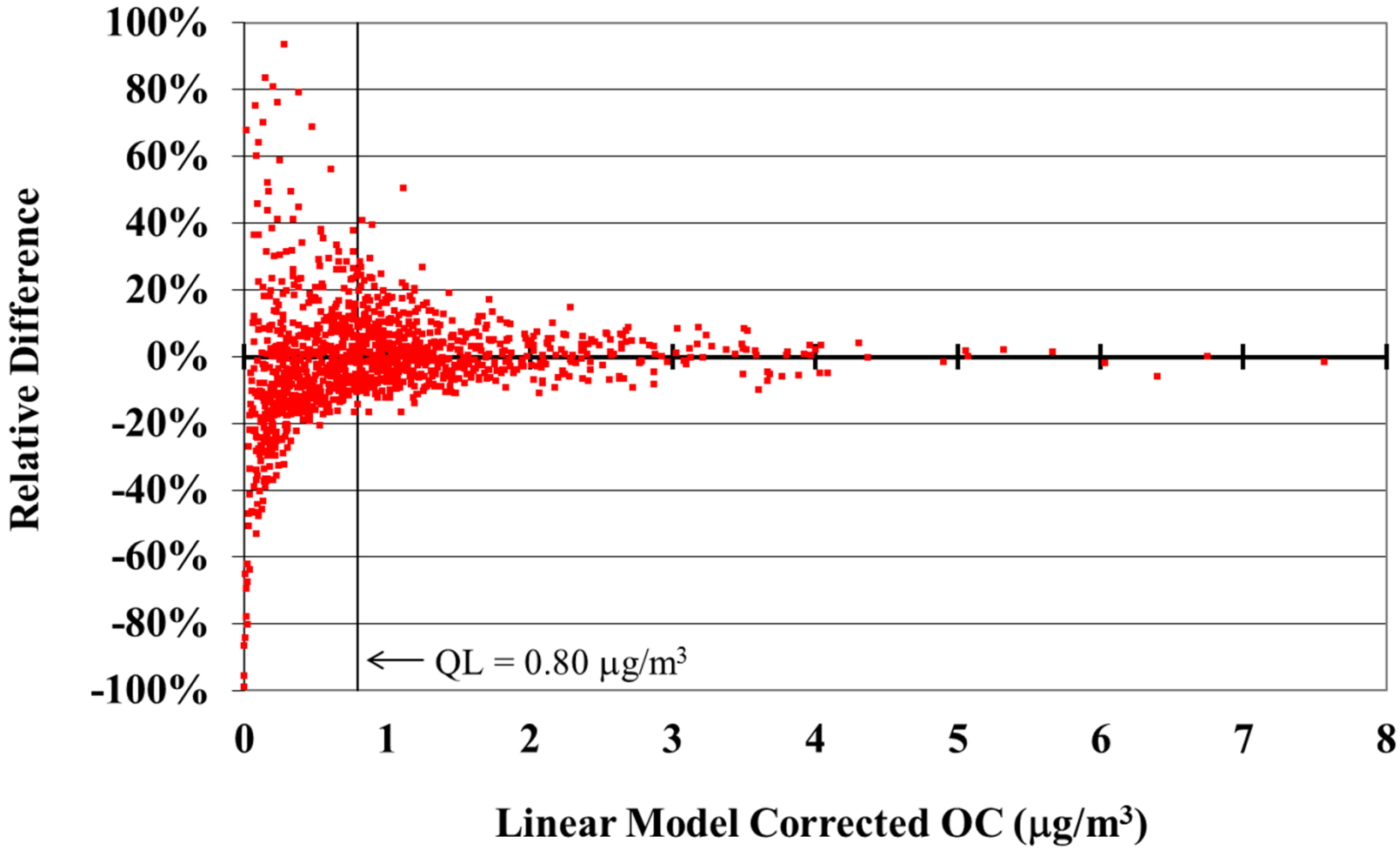
Can we do better?

Other Models: Use relationship between front and back filter



Relative Differences of Linear Model Artifact Corrected OC in the IMPROVE Network

(22 samples outside of ±100% and highest 1% of data excluded from model and figure)



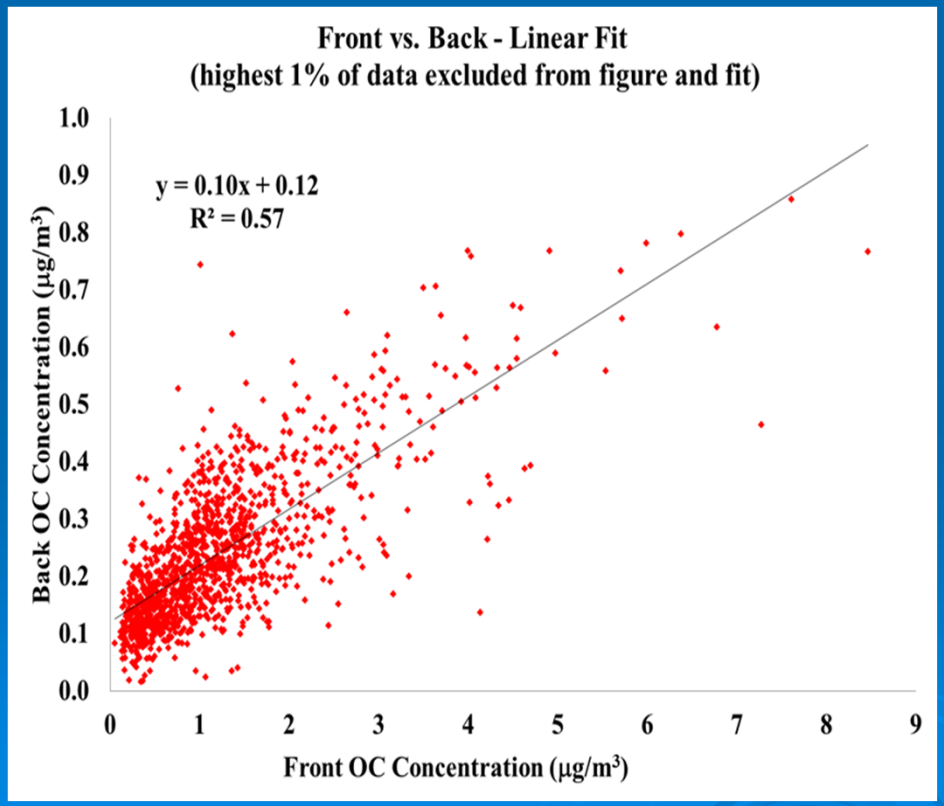
Summary of Models for Artifact Correction

	Monthly Median	Linear (99% of data used in fit)
Quantifiable Limit (QL, μg/m^3)	2.90	0.80
% of data above QL	13%	48%
bias in data above QL	8.3%	0.02

Alternate Interpretation of Artifact

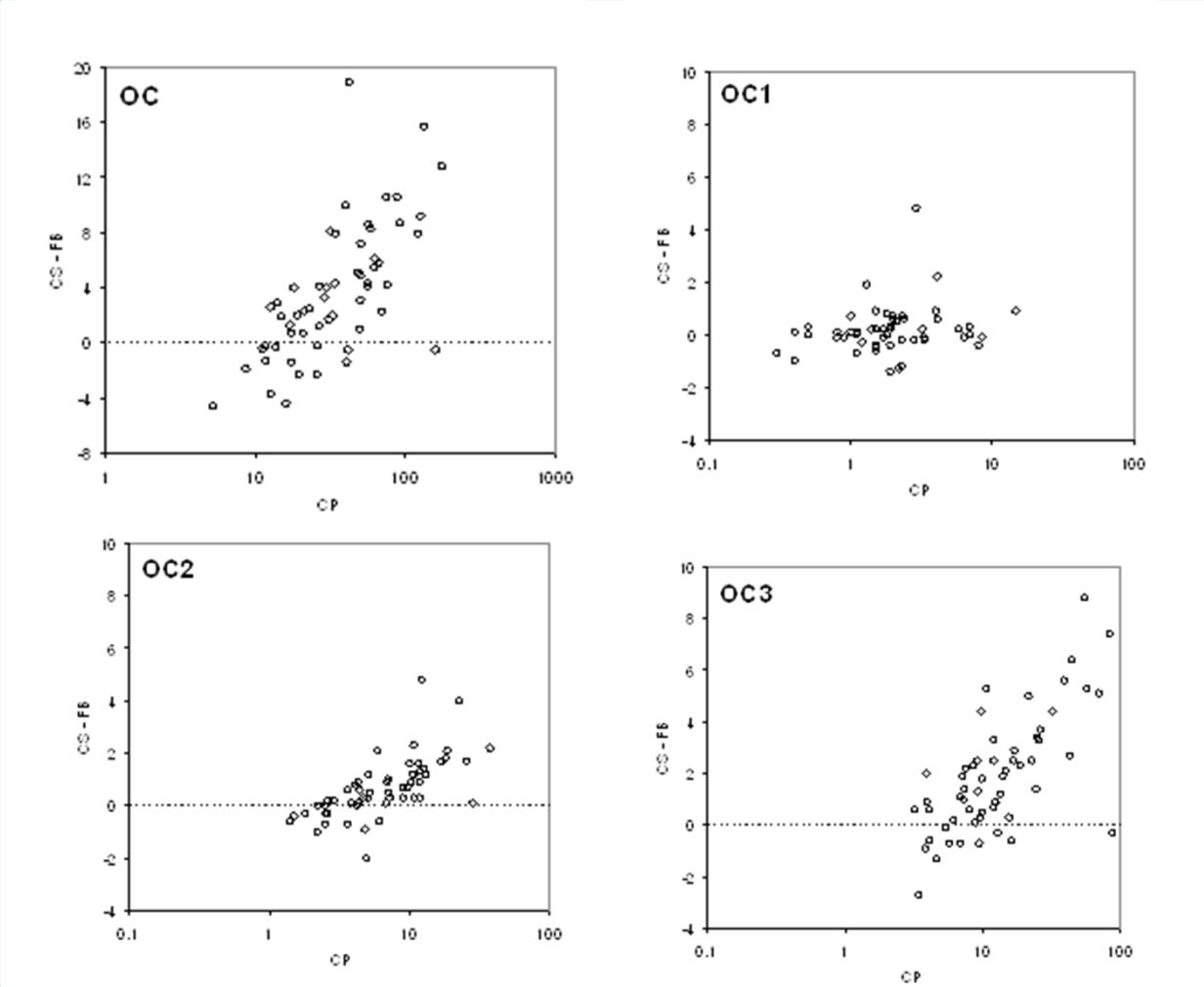
Back = 0.1 X Front + 0.12

Linear relationship between front and back



- Additive term = positive artifact (gas adsorption)
- Multiplicative term = negative artifact (blow off from the front filter)
- Artifact =negative – positive
- Artifact = 0.1 X Front - 0.12

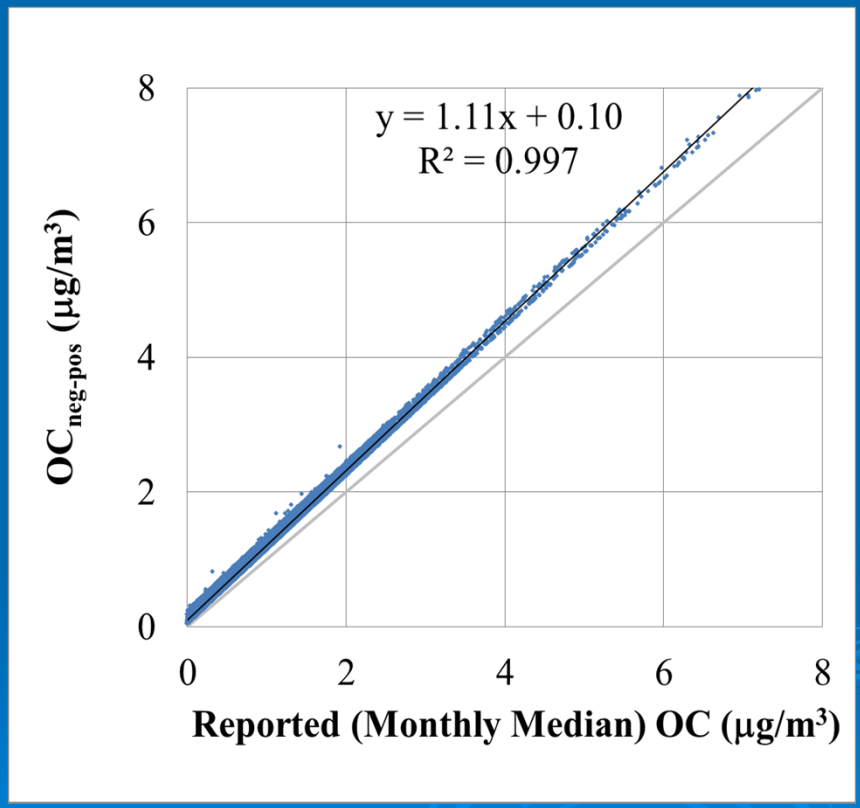
Carbon Fractions – samples with front, back and field blanks



Analysis courtesy of Jay R. Turner, May 2006

Application of Interpretation

- Oct 08-Sept09 IMPROVE data
- All sites
- $OC_{Neg\text{-}Pos}$ = Front + (0.1 X Front – 0.12)

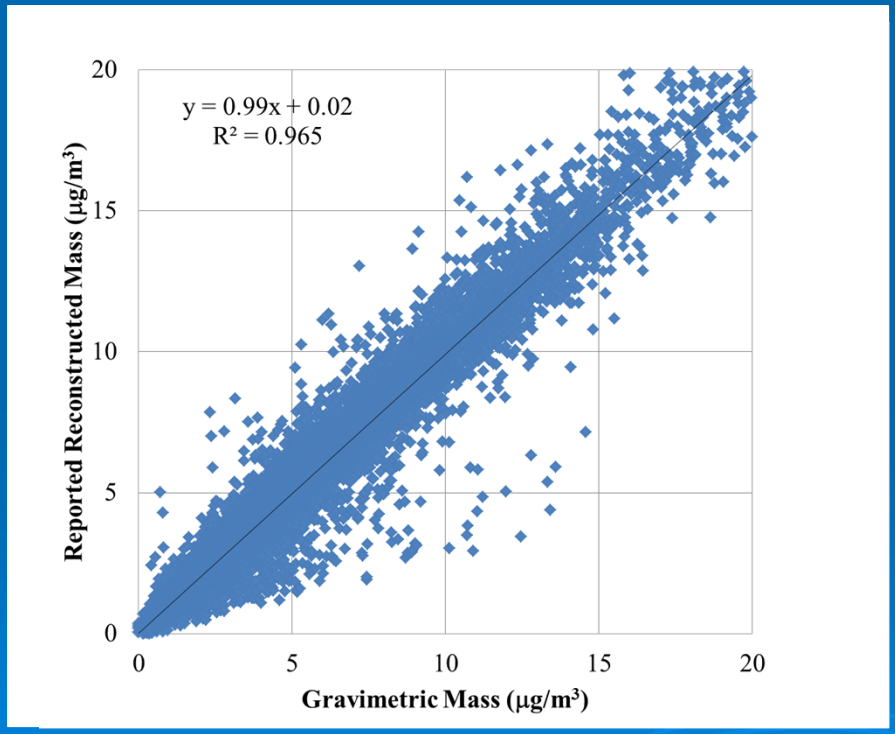


- Compare reconstructed masses using OM/OC=1.8

Comparison of Reconstructed Mass

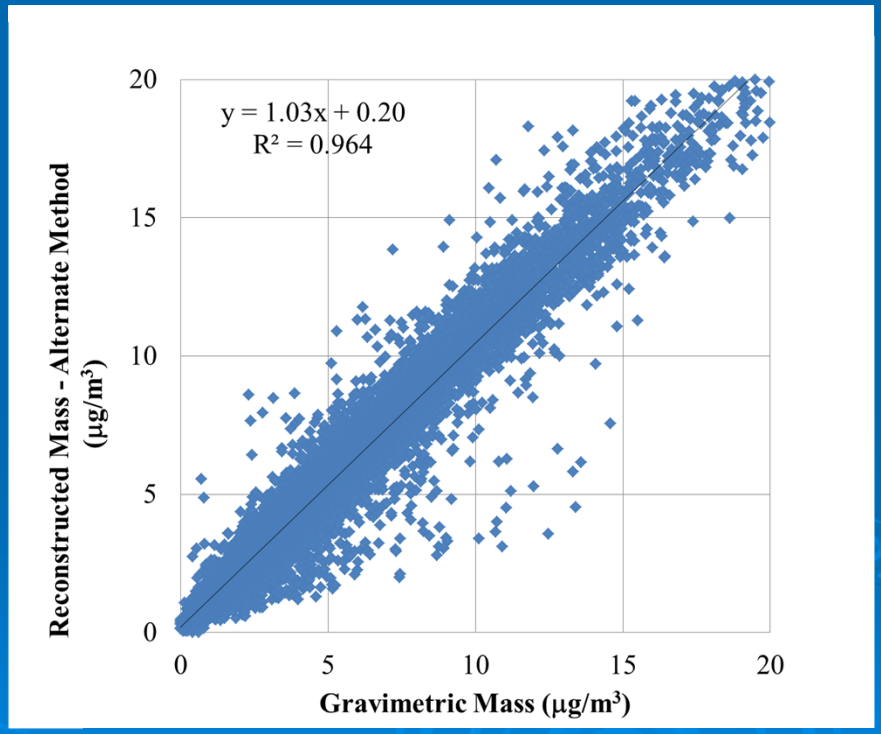
Reported

(highest 1% of data excluded from figure)



Alternate Method

(highest 1% of data excluded from figure)



Conclusions

- New sites narrow seasonal variation
- Monthly median model gives OC measurements that are biased
- Front vs. back filter model provides:
  - Lower quantification limit
  - More quantifiable data
  - No bias
- Linear model invites alternate conceptual model for the back filter measurement

IMPROVE Artifact Correction Timeline

- Time line for sites
  - Prior to 1995 – 4 sites
  - 1995 – 2001 - 4 sites
    - Grand Canyon, MORA, SHEN, YOSE
  - 2001 - August 1, 2008, 6 sites
    - HANC, MORA, SHEN, YOSE, CHIR, OKEF
  - By end of September, 2008, 11 sites, including both PHOE sites
  - May 1, 2009, 12 sites - HEGL
  - July 1, 2009, 13 sites – WASH
- Artifact Correction
  - Prior to June 1, 2002 – quarterly median
  - June 1, 2002 to current – monthly median