BIAS IN $PM_{2.5}$ FILTER-BASED METHODS

NATIONAL AMBIENT AIR MONITORING CONFERENCE
ATLANTA, GEORGIA
AUGUST 2014

Shelly Eberly
Geometric Tools, LLC

Mike McCarthy, ShihMing Huang
Sonoma Technology, Inc.

Some Bias Basics

- Bias estimated by

$$\frac{SLTValue - PEPValue}{PEPValue} * 100$$

  - SLTValue is concentration from sampler operated by state, local, or tribal organization.
  - PEPValue is concentration from sampler operated by Performance Evaluation Program auditor.

- $PM_{2.5}$ bias Data Quality Objective (DQO):

  Average bias over three-year period should be between -10% and +10%

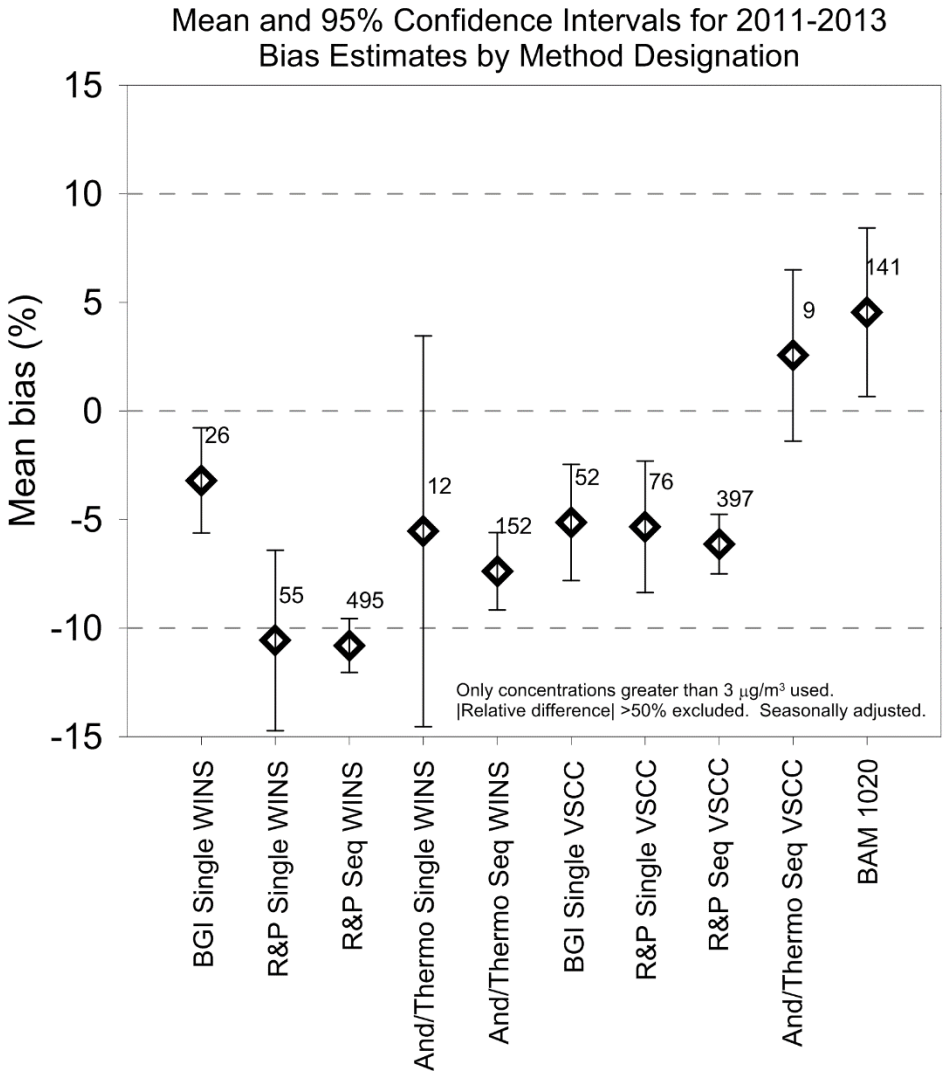
- In 2006, the number of bias pairs required within each organization changed from % of number of samplers to a fixed number, resulting in a 40% reduction in number of bias pairs.

$PM_{2.5}$ is particulate matter that is 2.5 micrometers in diameter and smaller.

Bias Questions

1. What are current levels of bias?
2. How has bias been changing over time?
3. Why did bias drop? Recap of associations presented at Denver conference 2 years ago.
4. Why did bias drop? Associations investigated over the last 2 years.

1 – What Are Current Levels of Bias?



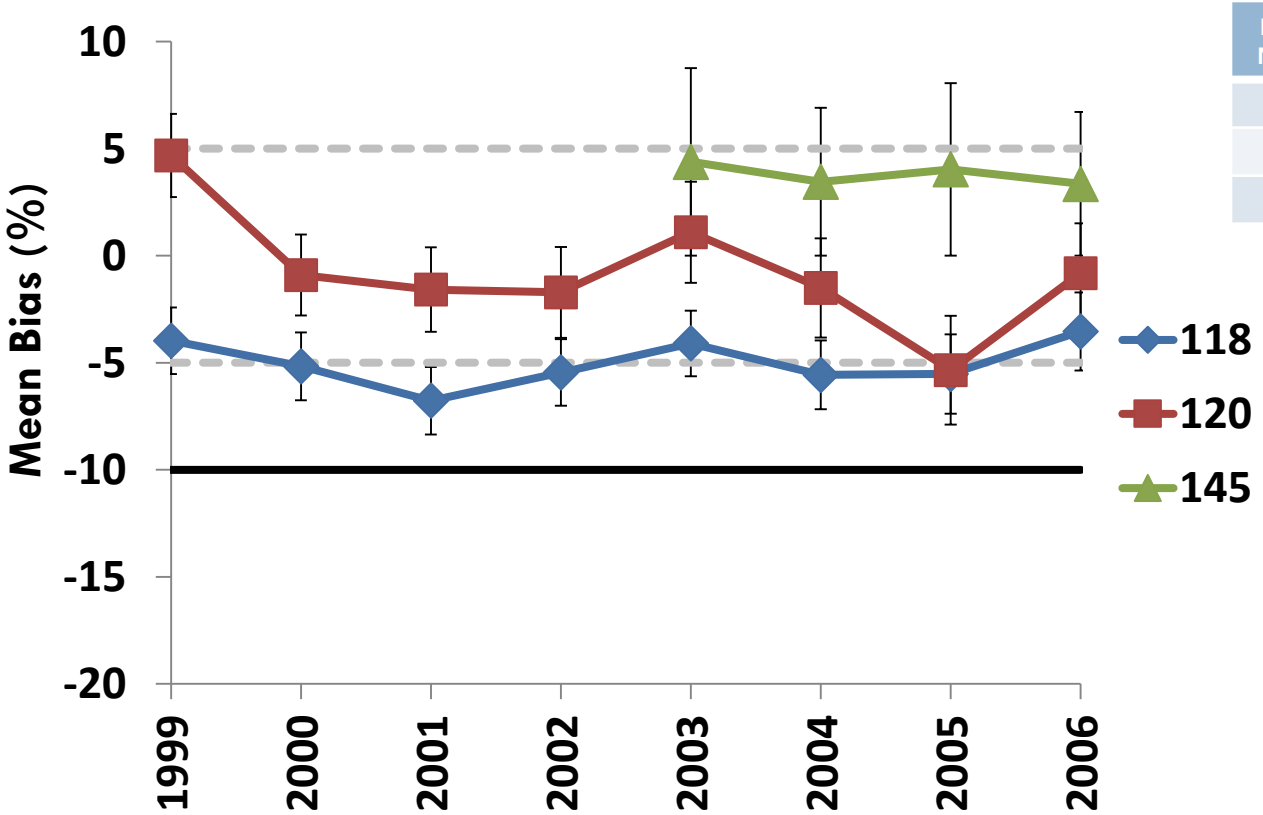
- Negative Bias means **STL conc < PEP conc**
- 2011-2013 biases mostly negative
- WINS bias generally more negative than VSCC bias

FINE PRINT
Bias adjusted for season.
Estimates based on pairs > 3 µg/m³.
Excludes pairs with |Bias| > 50%.

WINS = well-type impactor ninety-six
VSCC = very sharp cut cyclone
FEM = federal equivalent method
BAM = beta attenuation monitor
TEOM = tapered element oscillating microbalance

2 – How Has Bias Changed Over Time?

Prior to 2006, bias wiggled between -5% and +5% with no obvious trend. (Graph of three main methods.)



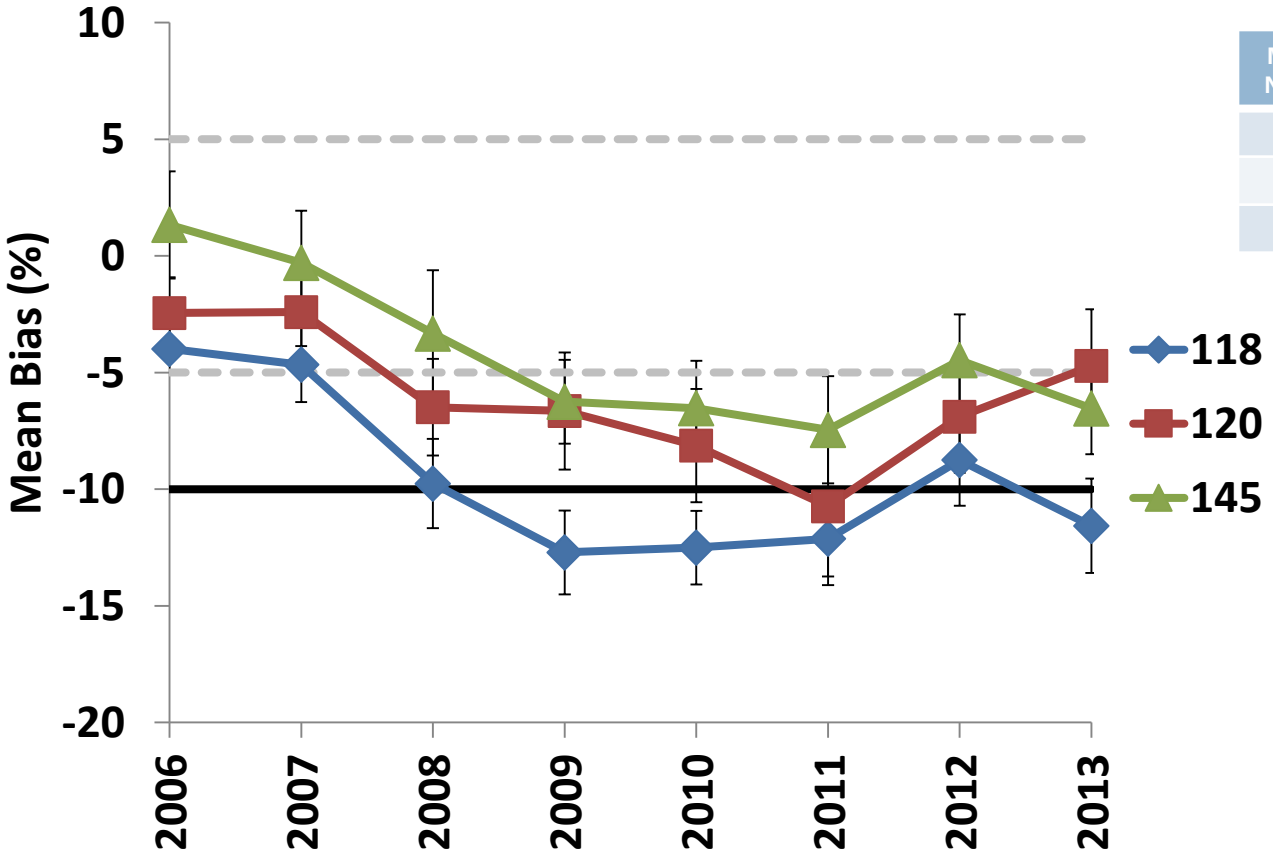
Method Number	Original Maker	Single / Sequential	WINS / VSCC
118	R&P	Sequential	WINS
120	Andersen	Sequential	WINS
145	R&P	Sequential	VSCC

FINE PRINT
Bias adjusted for PQAO and season.
Estimates based on pairs > 3 µg/m^3.
Excludes pairs with |Bias| > 50%.

PQAO = primary quality assurance organization (e.g., BAAQMD)

2 – How Has Bias Changed Over Time?

From 2006 to 2009, bias dropped. Since 2009, bias held between -15% and -5%. (Graph of three main methods.)



Method Number	Original Maker	Single / Sequential	WINS / VSCC
118	R&P	Sequential	WINS
120	Andersen	Sequential	WINS
145	R&P	Sequential	VSCC

FINE PRINT

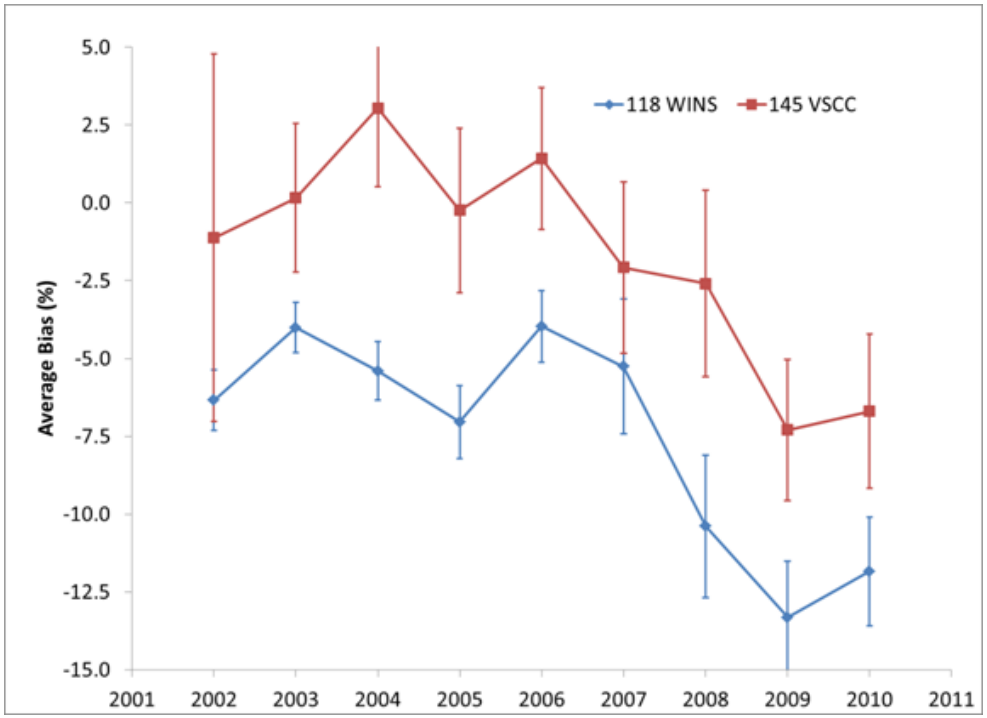
Bias adjusted for season, only.

Estimates based on pairs > 3 μg/m^3.

Excludes pairs with |Bias| > 50%.

3 – Why Did Bias Drop? Associations Investigated 2 Years Ago.

A. Does bias vary by type of separator, WINS versus VSCC? **YES for SLT,** when sufficient data to compare. In such cases, bias from WINS more negative than bias from VSCC.



Sampler Type	Method Numbers	Difference in WINS and VSCC Median Biases	Statistical Test of WINS Bias to VSCC Bias for SLT
BGI Single	116 vs. 142	-7.4 %	WINS Bias < VSCC Bias
R&P Single	117 vs. 143	-9.2 %	WINS Bias < VSCC Bias
R&P Sequential	118 vs. 145	-4.5 %	WINS Bias < VSCC Bias
Andersen Single	119 vs. 153	-0.3 %	Not significantly different.
Andersen Sequential	120 vs. 155	-6.8 %	Not significantly different. Too few observations for 155.

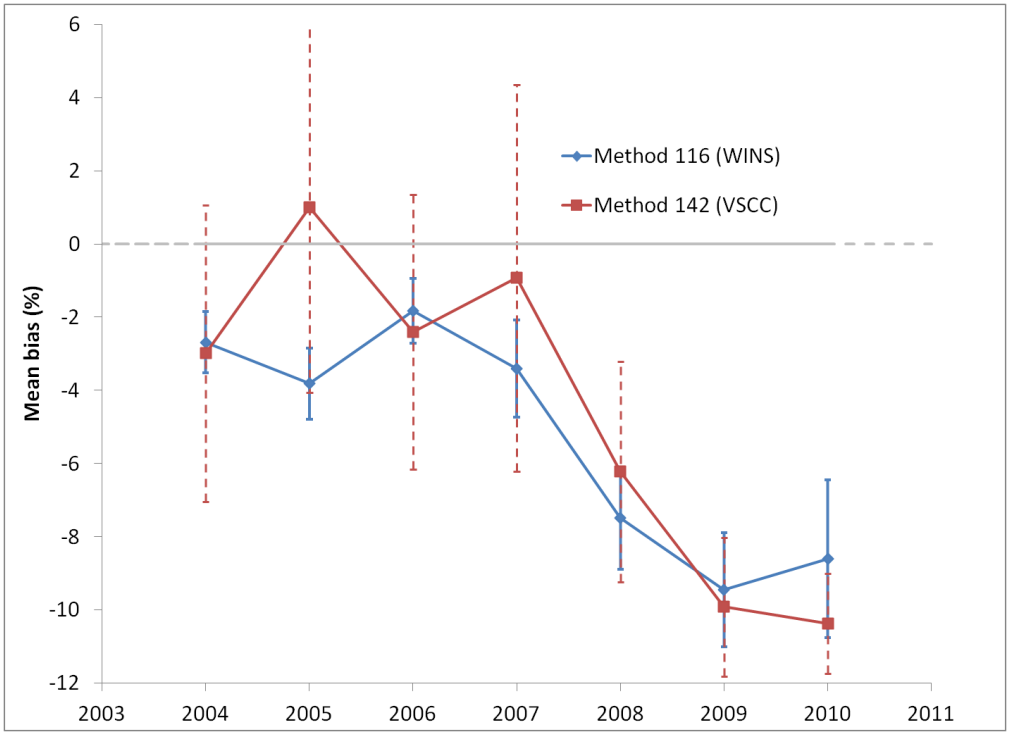
FINE PRINT

Graph is for monitor-level bias estimates, excludes pairs with |Bias| > 50%, excludes pairs <= 3 µg/m^3.

Statistical results based on Mann-Whitney Test of PQAO-season bias estimates for 2009-2010 only, excludes pairs with |Bias| > 50%, excludes pairs <= 3 µg/m^3, uses SLT methods (118,120,145) only, test at alpha=0.10.

3 – Why Did Bias Drop? Associations Investigated 2 Years Ago.

A. Does bias vary by type of separator, WINS versus VSCC?



NO for PEP. Bias does not differ by separator.

Sampler Type	Method Numbers	Difference in WINS and VSCC Median Biases	Statistical Test of WINS Bias to VSCC Bias for PEP
BGI Single	**116 vs. 142**	**0.2 %**	**Not significantly different.**

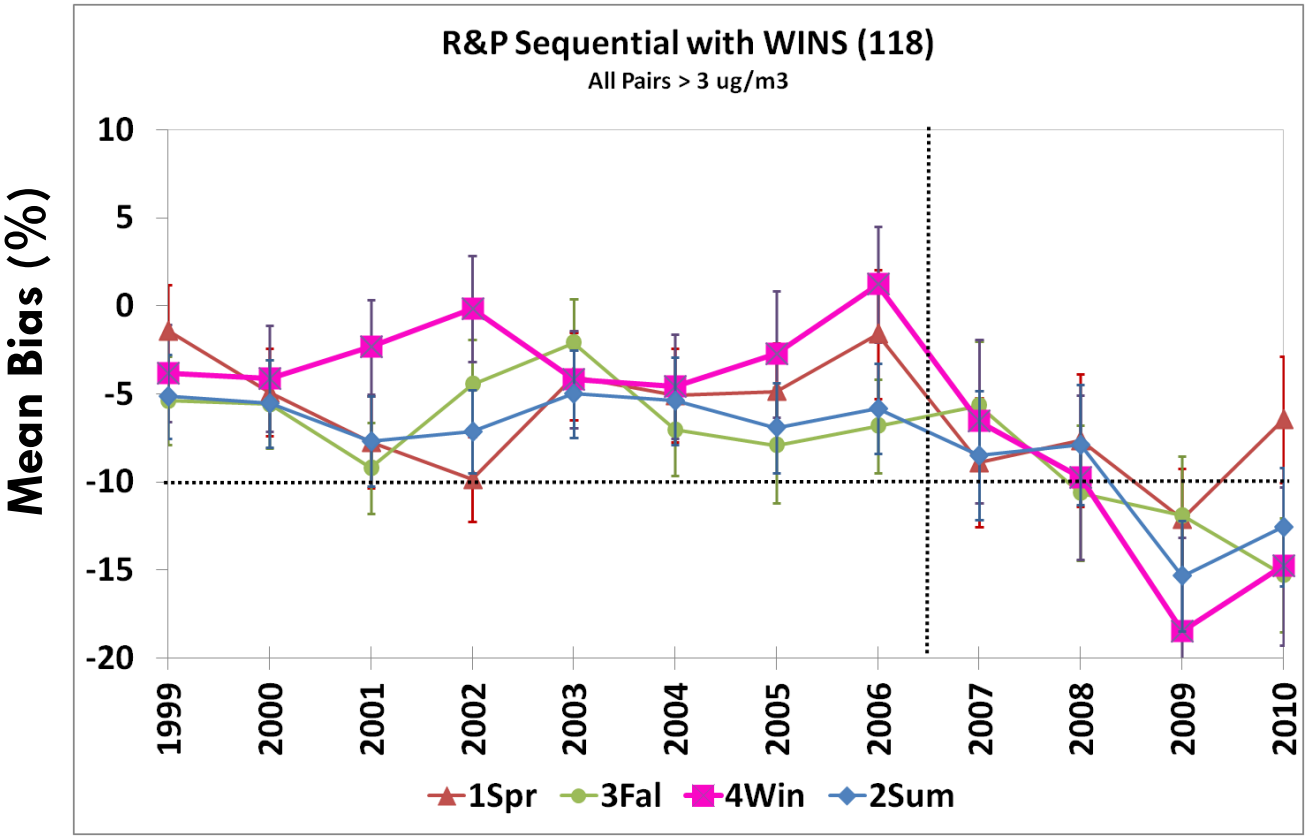
FINE PRINT

Graph is for monitor-level bias estimates, excludes pairs with |Bias| > 50%, excludes pairs <= 3 µg/m^3.

Statistical results based on Mann-Whitney Test of PQAO-season bias estimates for 2009-2010 only, excludes pairs with |Bias| > 50%, excludes pairs <= 3 µg/m^3, uses SLT methods (118,120,145) only, test at alpha=0.10.

3 – Why Did Bias Drop? Associations Investigated 2 Years Ago.

B. Does bias vary by season? **YES.** But most seasons trending like annual trend.



FINE PRINT

PQAO-Season bias estimates.

Estimates based on pairs > 3 µg/m^3.

Excludes pairs with |Bias| > 50%.

3 – Why Did Bias Drop? Associations Investigated 2 Years Ago.

C. Does bias vary by region of the country?
   - Not in any clear pattern.
   - Biases trended down across the nation from 2005-2007 to 2008-2010.

D. Does bias vary by $PM_{2.5}$ concentration?
   - Not clearly. Median bias is fairly stable across bias concentration ranges.
   - Spread in bias increases as concentrations decrease.

4 – Why Did Bias Drop? Associations Investigated Over the Last 2 Years.

A. Do changes in speciation of $PM_{2.5}$ play a role? As $PM_{2.5}$ concentrations come down, is the volatile fraction of $PM_{2.5}$ increasing?
   - **Appears likely.**

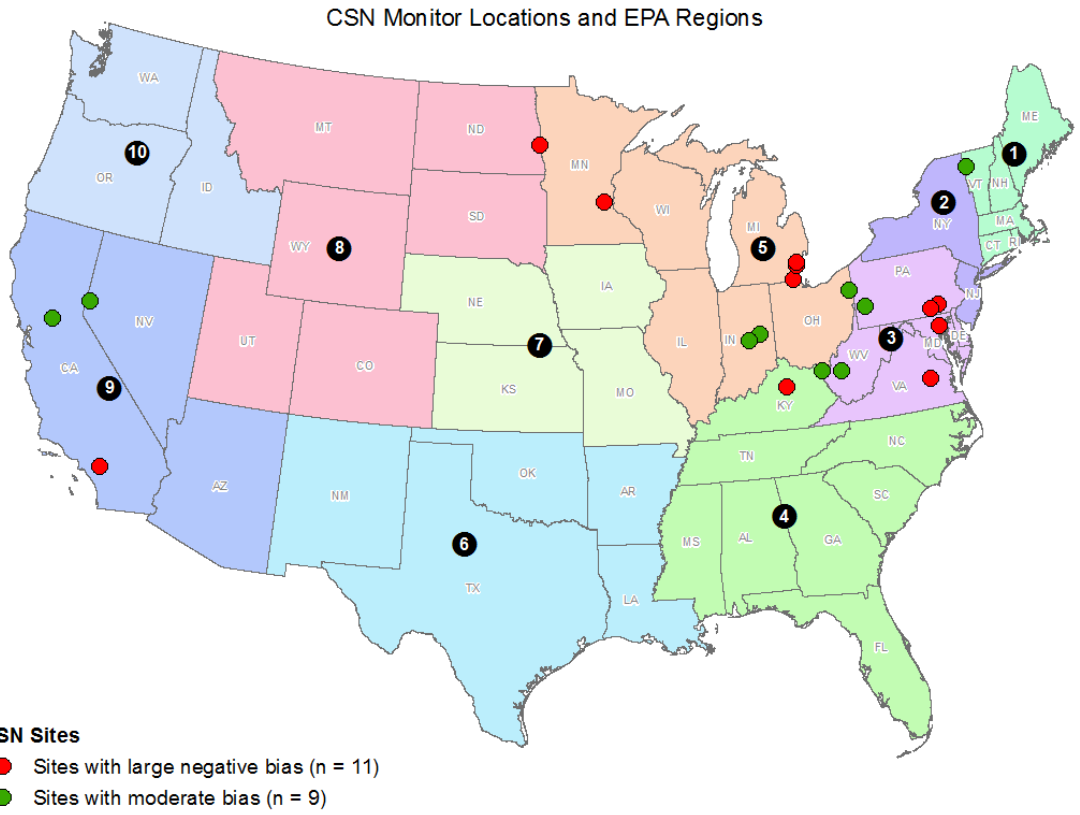
B. Can precision data give insight into bias trends?
   - **Locally, yes. Nationally, no.**

4B – Are Changes in PM Composition Contributing to Bias Trend?

- Hypothesis: Changes in the relative contributions of volatile components of PM mass may be contributing to the increasingly negative bias.
- Test: Select Chemical Speciation Network (CSN) sites near PQAOs with large negative bias and moderate bias. Are there differences in the PM composition and trends?

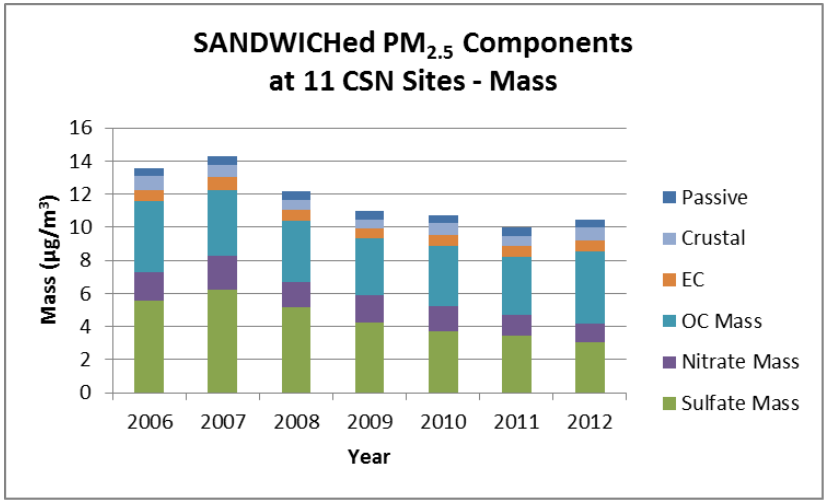
Methods: CSN – SANDWICH Data

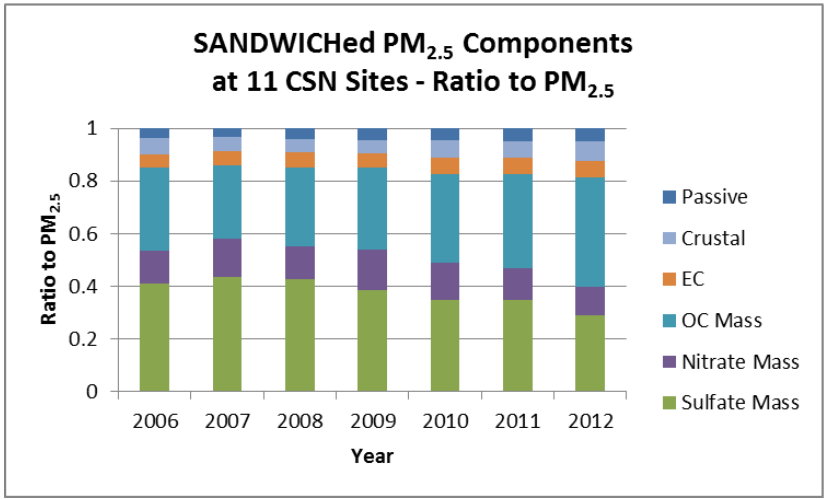
- Subset of CSN sites in PQAOs that have precise data (CV <7%).
- Compared 11 sites with large negative bias (ranked 17 to 36) to 9 sites with moderate bias (ranked 40 to 80)
  - Greater bias: bias < -10% - exceeds DQO
  - Lower bias: bias > -10% - meets DQO



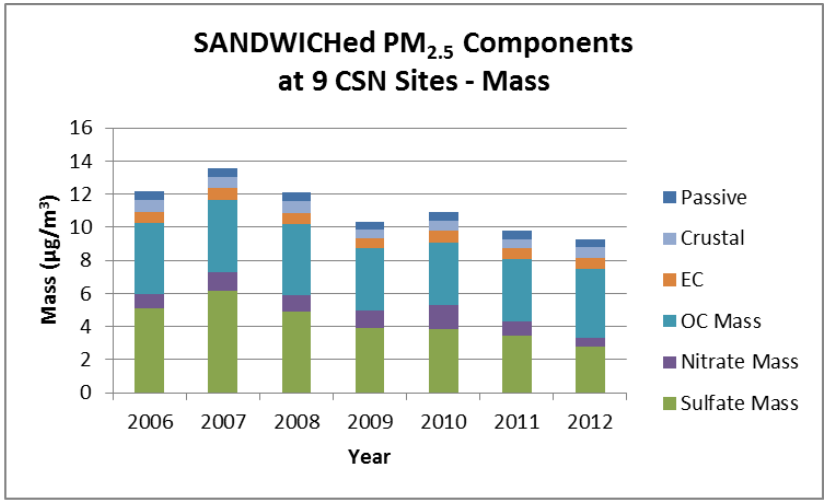
Target CSN Sites: Large vs. Small Bias

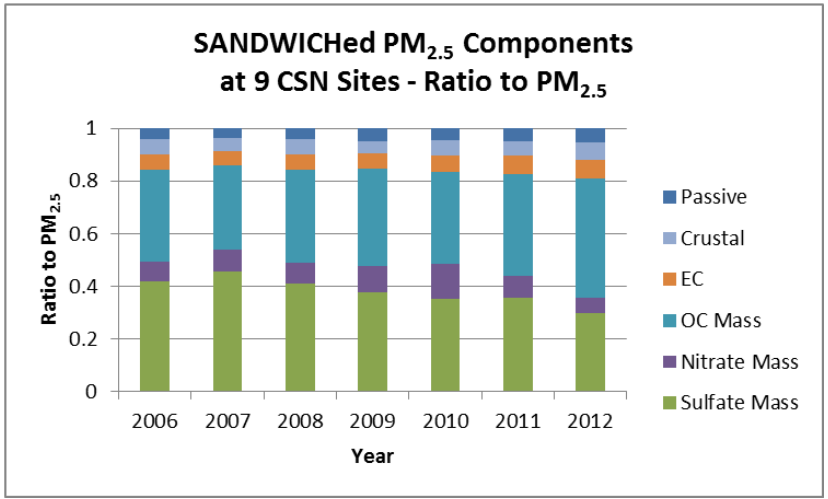
Bias < -10% - Exceeds DQO





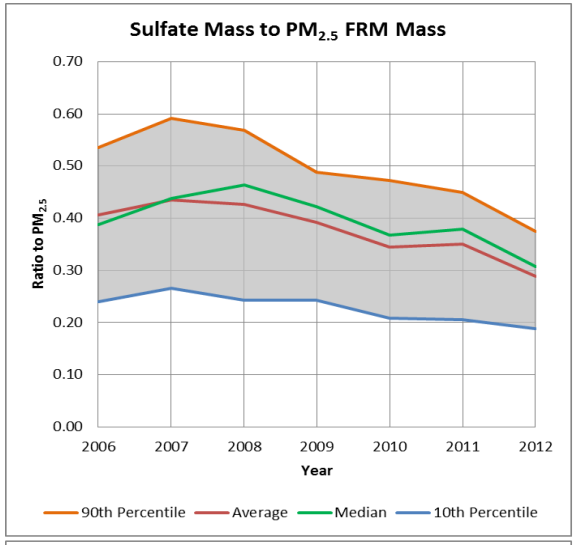
Bias > -10% - Meets DQO

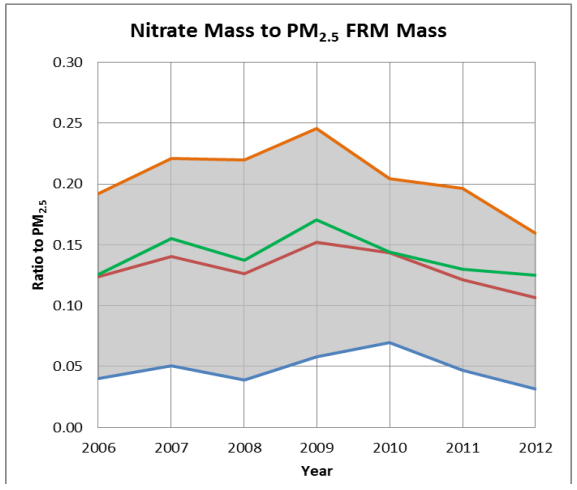




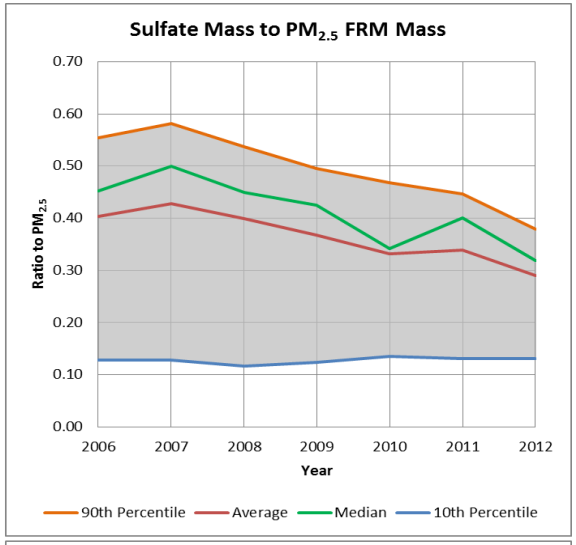
Target CSN Sites: Large vs. Small Bias

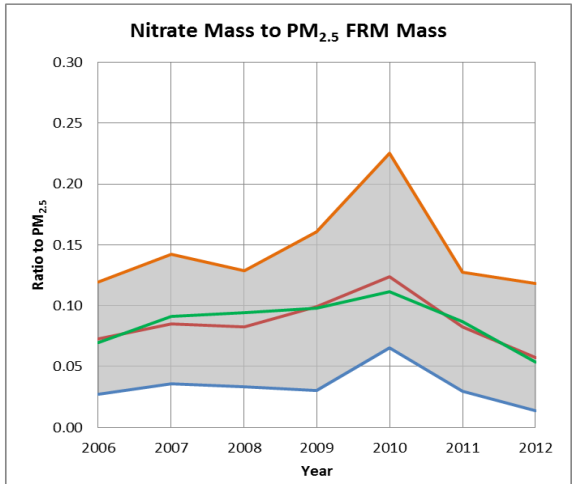
Bias < -10% - Exceeds DQO





Bias > -10% - Meets DQO

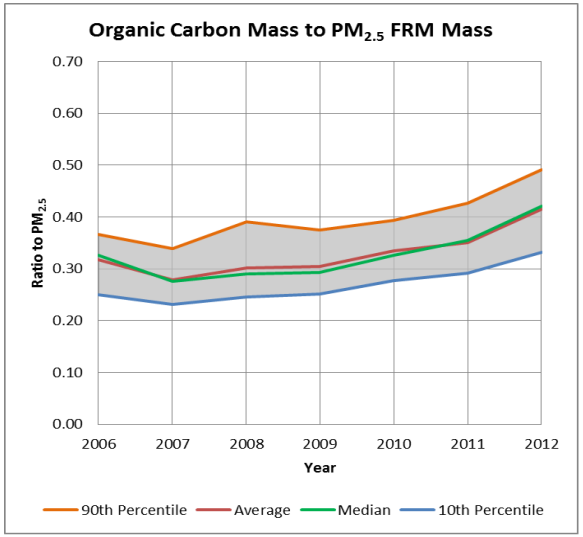


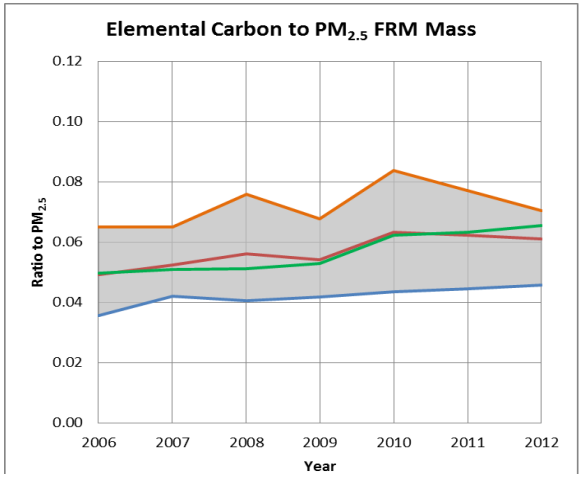


- Both groups of sites have decreasing sulfate mass.
- Sites with greater bias have a significantly higher fraction of nitrate in $PM_{2.5}$ mass.

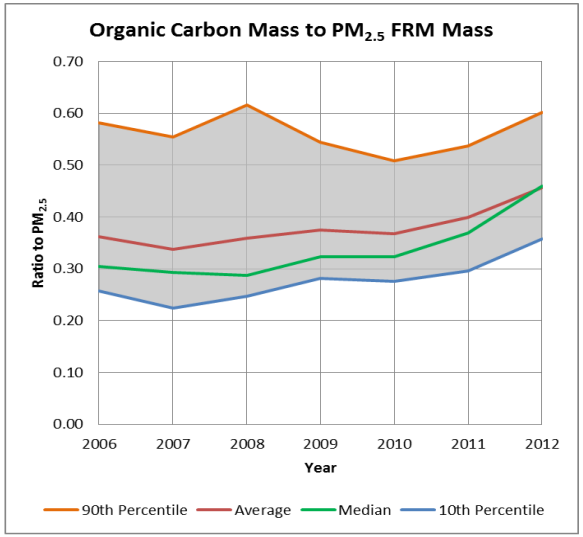
Target CSN Sites: Large vs. Small Bias

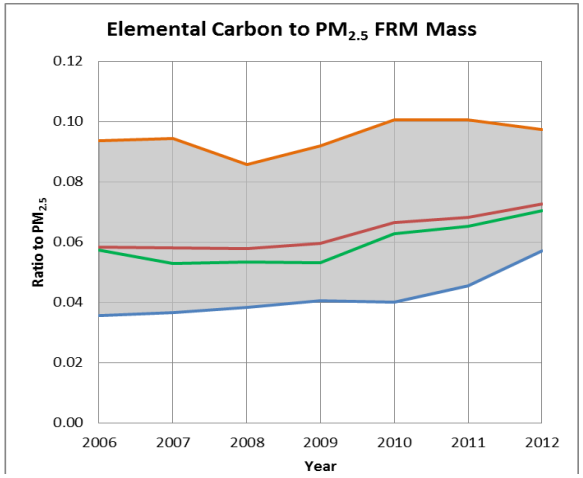
Bias < -10% - Exceeds DQO





Bias > -10% - Meets DQO

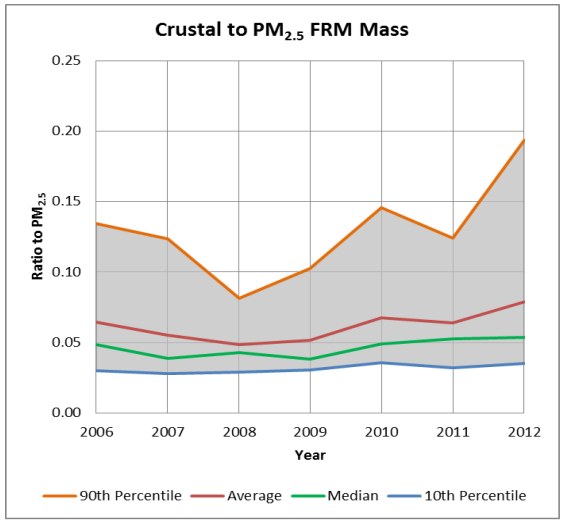


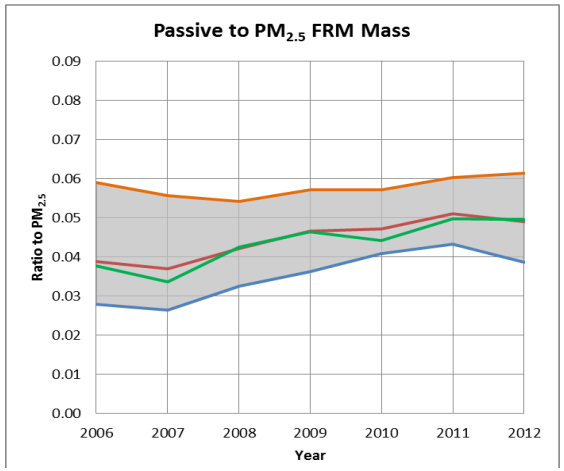


- Sites with greater bias have a slightly lower fraction of organic carbon mass.
- Trends and fractions of EC are comparable.

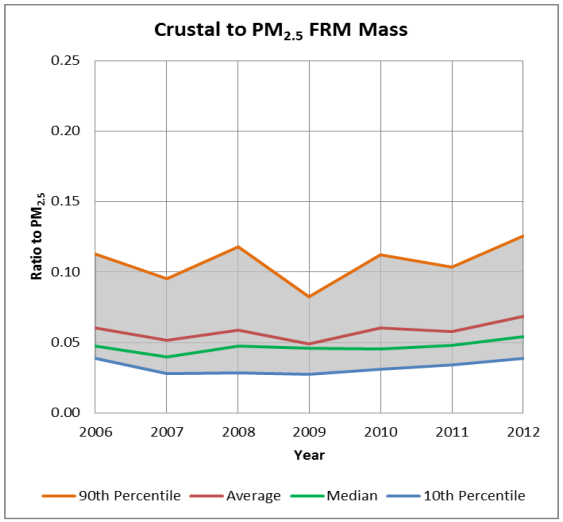
Target CSN Sites: Large vs. Small Bias

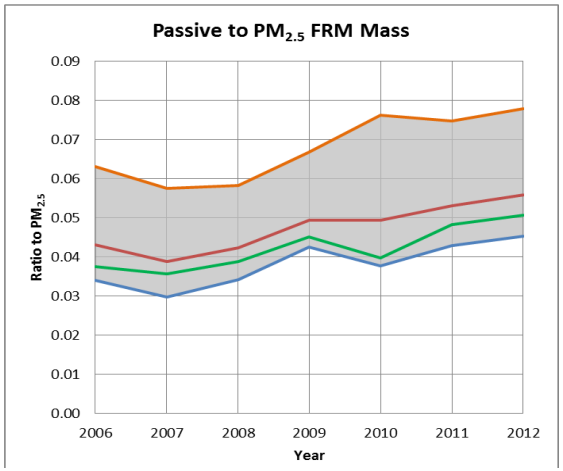
Bias < -10% - Exceeds DQO





Bias > -10% - Meets DQO

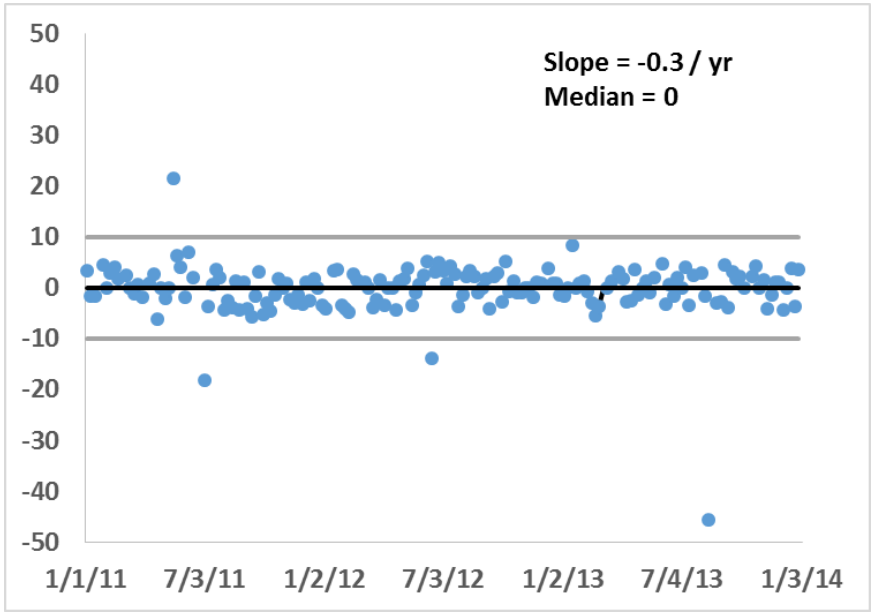


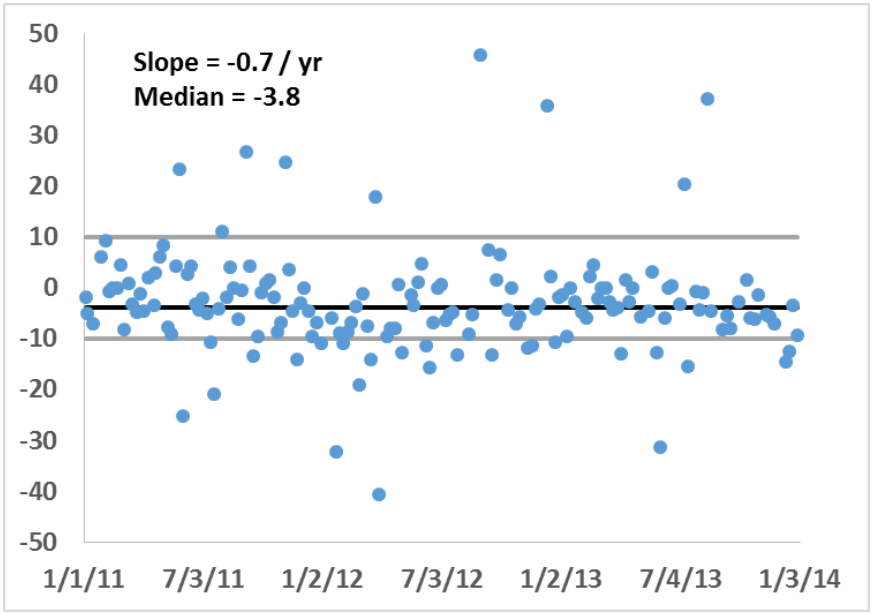


- Fractions of the crustal component are comparable.
- Fractions of the passive component are comparable.

4C – Can Precision Data Give Insights into Bias Trend?

- Using 2008-2010 precision data [200*(X-Y)/(X+Y)]:
  - Consistent relative differences suggest bias in one or both samplers.
  - Slope suggests trends in bias in one or both samplers.





Ideal: tight, slope ~ 0, median ~ 0.

Bias: tight, slope ~ 0, horizontal ~ -4%.

Black line shows Median Relative Difference (%).

4C – Can Precision Data Give Insights into Bias Trend?

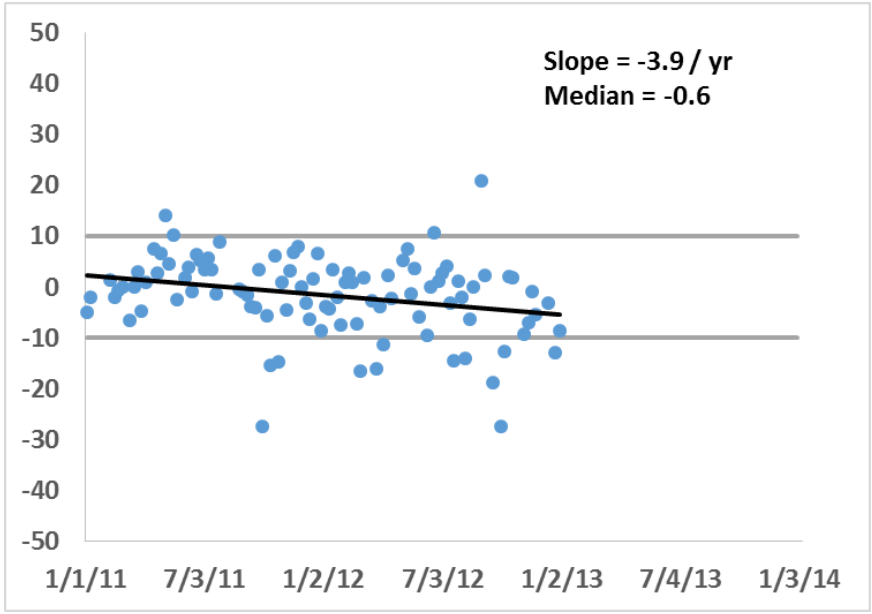
- At the NATIONAL level, the range of site-level annual median relative differences suggests minimal site-level bias
  - Central value (median) approximately 0% for most method-year combinations.
  - 5^{th} – 95^{th} percentiles approximately -5% to +5%.
- At the SITE level, a few sites have |annual median relative differences| > 15% (based on 30 or more pairs). Most involve Method 170 (Met-One BAM).

4C – Can Precision Data Give Insights into Bias Trend?

Method	Year	# Collo Pairs	# Collo Sites	5th Ptile (% Rel Diff)	Median (% Rel Diff)	95th Ptile (% Rel Diff)
117 w/ 117	2011	184	4	-5%	-2%	1%
	2012	255	6	-3%	0%	3%
	2013	92	2	-5%	-1%	2%
118 w/ 118	2011	2929	51	-4%	0%	6%
	2012	3026	47	-5%	-1%	2%
	2013	2903	49	-4%	0%	5%
120 w/ 120	2011	836	16	-5%	0%	4%
	2012	715	14	-3%	0%	5%
	2013	511	10	-2%	0%	3%
145 w/ 145	2011	2758	35	-2%	0%	2%
	2012	2885	36	-4%	-1%	4%
	2013	2847	39	-4%	0%	2%
170 w/ 170 (small sample size)	2011	622	2	-19%	-9%	0%
	2012	754	3	-8%	2%	6%
	2013	1097	4	-11%	12%	33%

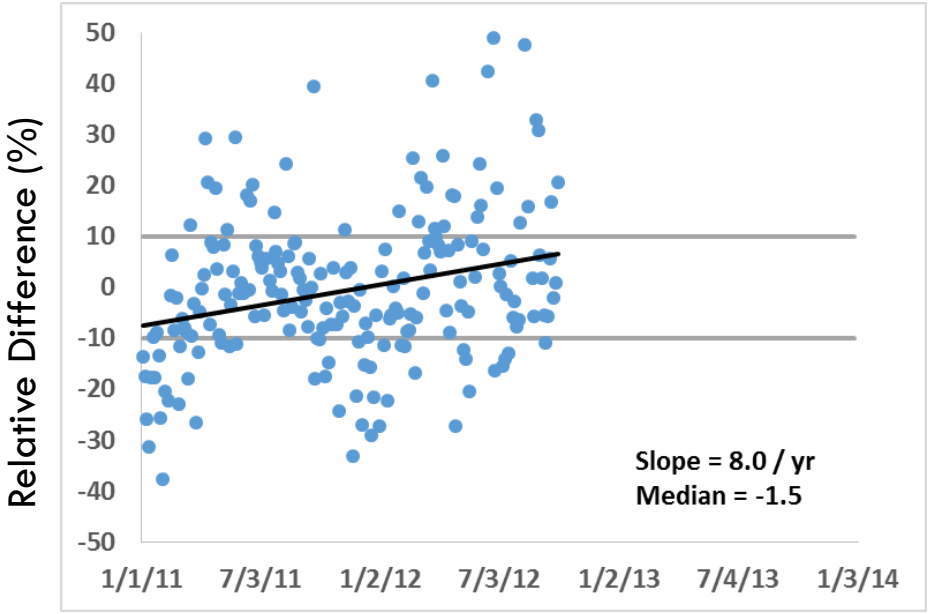
Excludes low concentrations (=< 3 $\mu g/m^3$). Percentiles taken over annual median relative differences for site-years with at least 30 pairs. Median used to reduce impact of outliers.

4C – Can Precision Data Give Insights into Bias Trend?



Precision suggesting possible downward trend in bias.

Precision shows oscillations with possible upward trend in bias.
Larger positive relative differences in summer, larger negative relative differences in winter (Method 181).



Review of patterns in precision at site level valuable in assessing quality of $PM_{2.5}$ system.

Black line shows slope in Median Relative Difference (%).

Puzzling/Outstanding Questions

- Why did biases drop in 2006-2010?
- Why are almost all methods producing negative biases since 2007?
  - Prior to 2007, some methods positive, some negative.
- What other associations are useful and possible to investigate?
  - Are exposed filters sitting longer before retrieval and is that impacting bias?
  - Does time since WINS impactor last cleaned impact bias?
  - Are ambient temperatures changing and is that contributing to changes in bias?
  - Other ideas?

Who's Behind the Curtain

- EPA
  - Mike Papp
  - Dennis Crumpler
  - Greg Noah
  - Tim Hanley
  - Robert Coats

- STI
  - Bryan Penfold

Sonoma Technology, Inc.

Slides for Reference as Needed

$PM_{2.5}$ Sampler Methods and Models

Method Number	Original Maker	Single / Sequential / Continuous	Model	WINS / VSCC
116	BGI	Single	PQ200	WINS
117	R&P	Single	2000	WINS
118	R&P	Sequential	2025	WINS
119	Andersen	Single	RAAS2.5-100	WINS
120	Andersen	Sequential	RAAS2.5-300	WINS
142	BGI	Single	PQ200	VSCC
143	R&P	Single	2000	VSCC
145	R&P	Sequential	2025	VSCC
155	Andersen	Sequential	RAAS2.5-300	VSCC
170	Met-One BAM	Continuous	BAM-1020	VSCC
181	Thermo Sci. TEOM	Continuous	TEOM 1400a	VSCC

Does Bias Vary by Season?

YES. 2008-2010 biases show strong seasonality. Summer has most negative bias. Winter usually has least negative bias.

Method Number	Maker	Single / Sequential	WINS / VSCC	Season	Bias (%)	90% Confidence
118	R&P	Sequential	WINS	Spring	-9.2 %	±2 %
				Summer	-12.2 %	±2 %
				Fall	-12.8 %	±2 %
				Winter	-14.0 %	±3 %
120	Andersen	Sequential	WINS	Spring	-9.3 %	±3 %
				Summer	-11.4 %	±3 %
				Fall	-7.1 %	±3 %
				Winter	-2.0 %	±3 %
145	R&P	Sequential	VSCC	Spring	-4.8 %	±3 %
				Summer	-10.5 %	±3 %
				Fall	-5.1 %	±3 %
				Winter	-3.0 %	±3 %

FINE PRINT

PQAO-Season bias estimates.

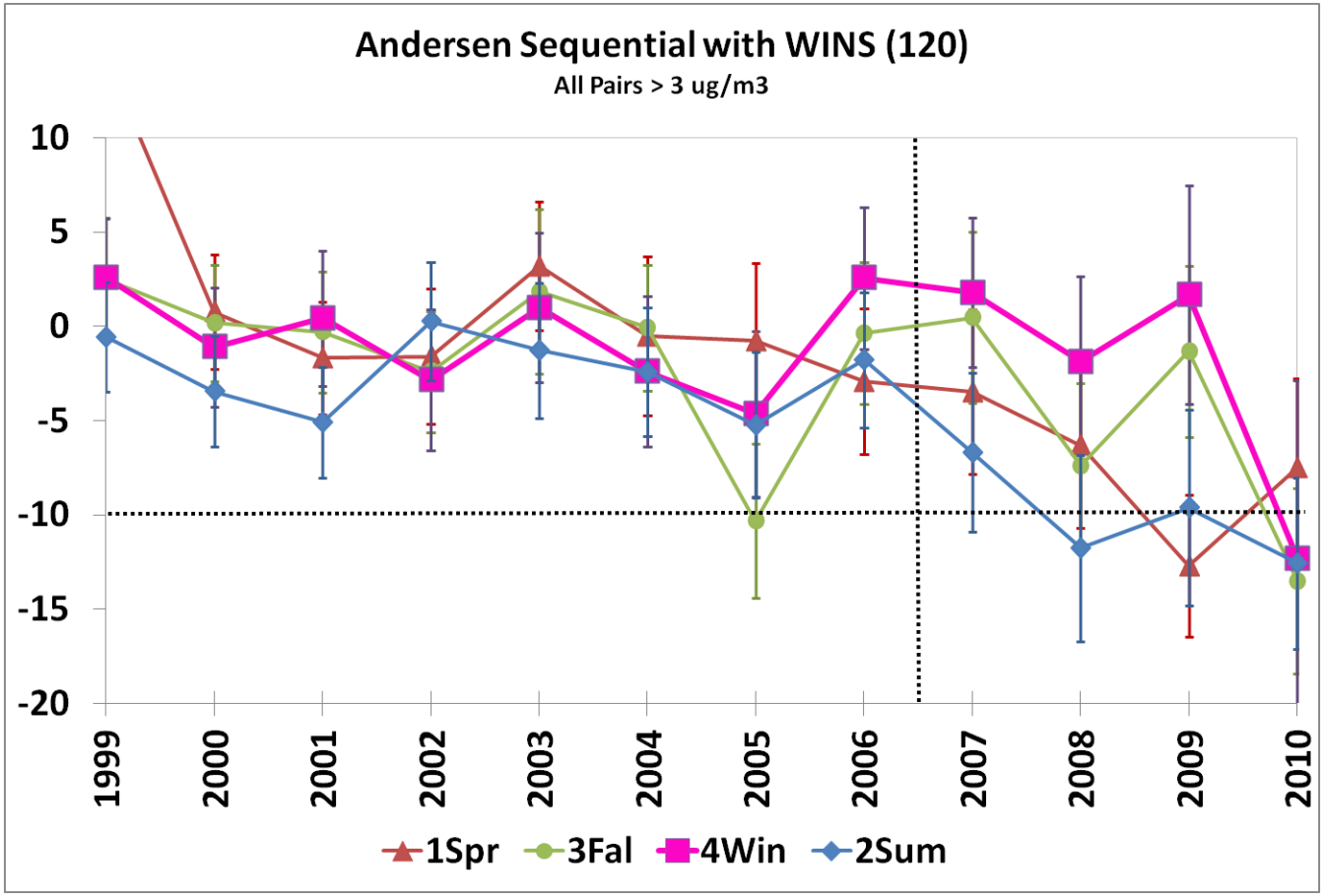
Estimates based on pairs > 3 $\mu g/m^3$.

Excludes |% diff| > 50%.

Excludes SLTValues = 0 $\mu g/m^3$.

Has Bias Been Changing Over Time by Season?

YES. All seasons trending down, starting in 2007.



FINE PRINT

PQAO-Season bias estimates.

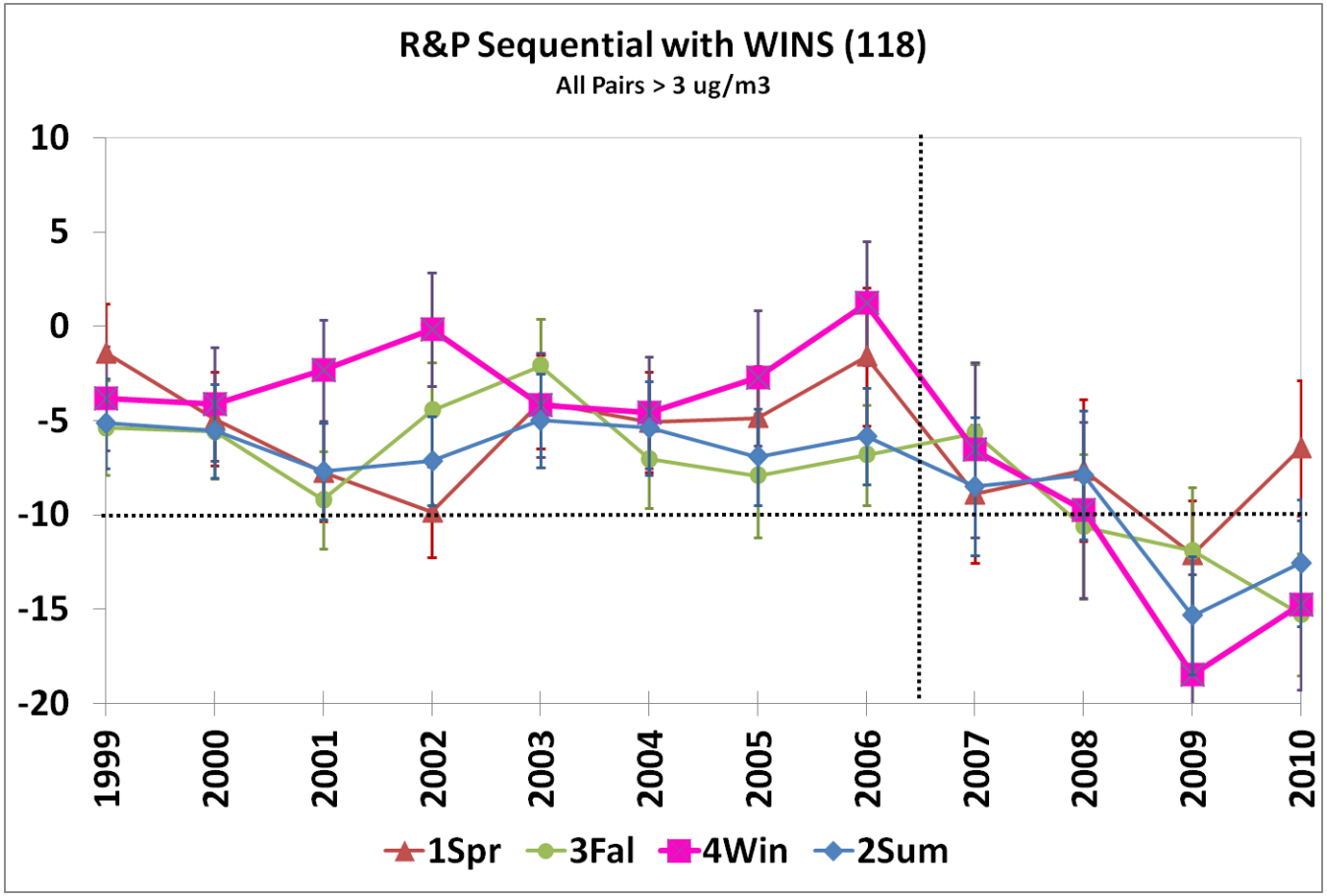
Estimates based on pairs > 3 µg/m^3.

Excludes |% diff| > 50%.

Excludes SLTValues = 0.

Has Bias Been Changing Over Time by Season?

For Method 118, winter trending down fastest.



FINE PRINT

PQAO-Season bias estimates.

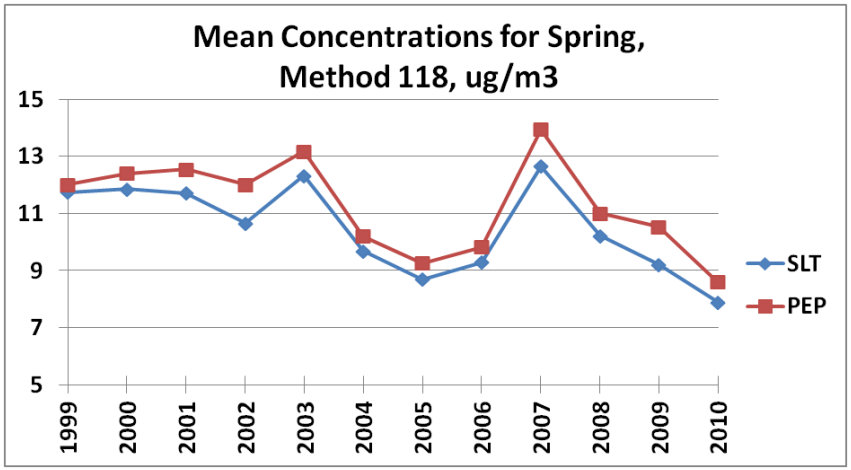
Estimates based on pairs > 3 µg/m^3.

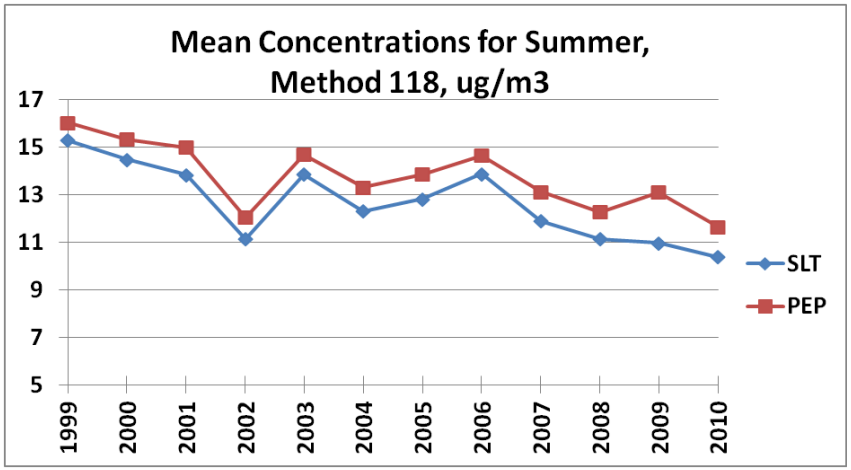
Excludes |% diff| > 50%.

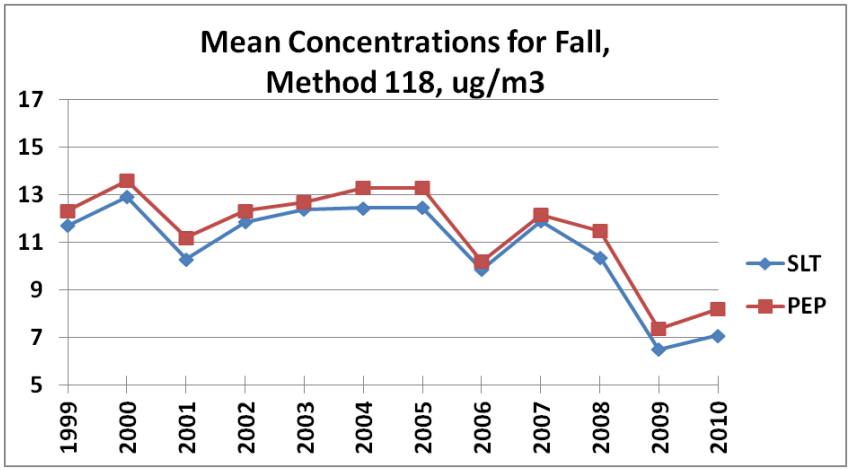
Excludes SLTValues = 0.

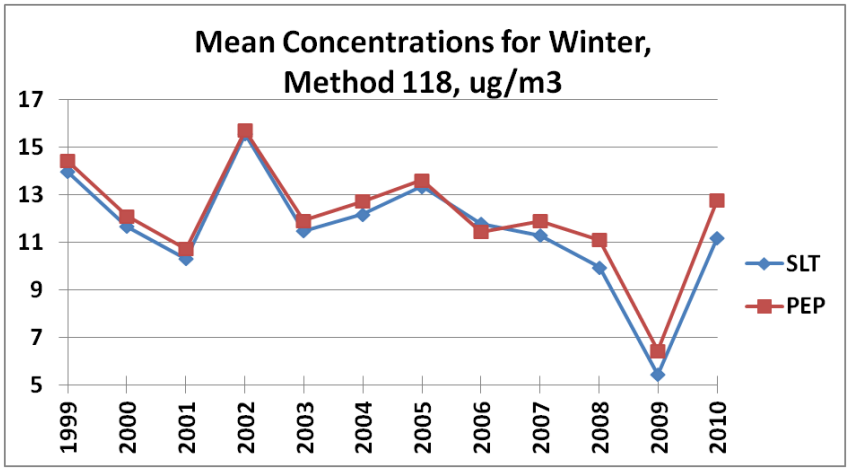
A Closer Look at Bias by Season Over Time for Method 118

For Method 118, in 2007-2008, the spread between SLT and PEP increased in all seasons and has not returned to pre-2007 levels.









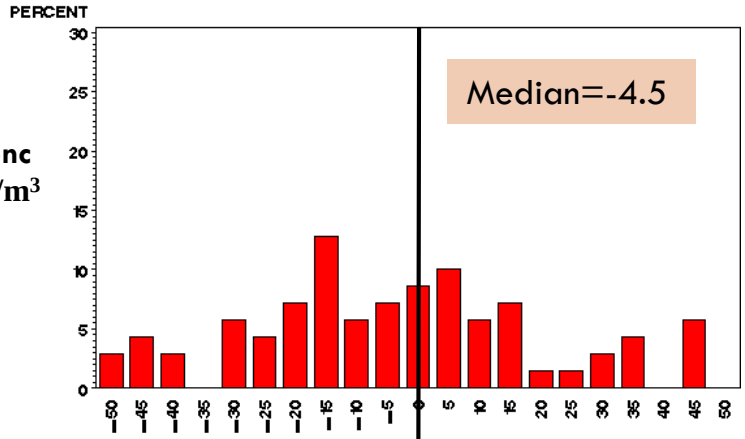
Does Bias Vary by $PM_{2.5}$ Concentration?

- The role of $PM_{2.5}$ concentrations appears minimal; it does not appear to explain the more recent trends in negative bias.
- **Spread** of bias decreases as concentration increases.
- However, **central tendency (median)** does depend on years analyzed.
  - Bias data from 2004-2006 suggest no association between $PM_{2.5}$ concentration and bias.
    - Median bias distributed similarly for various $PM_{2.5}$ concentration bins.
  - Bias data from 2008-2010 suggest no or limited association between $PM_{2.5}$ concentration and bias.
    - Median bias closer to 0 $\mu g/m^3$ for concentrations > 12 $\mu g/m^3$.
    - However, below 12 $\mu g/m^3$, there is no association between $PM_{2.5}$ concentration and bias.

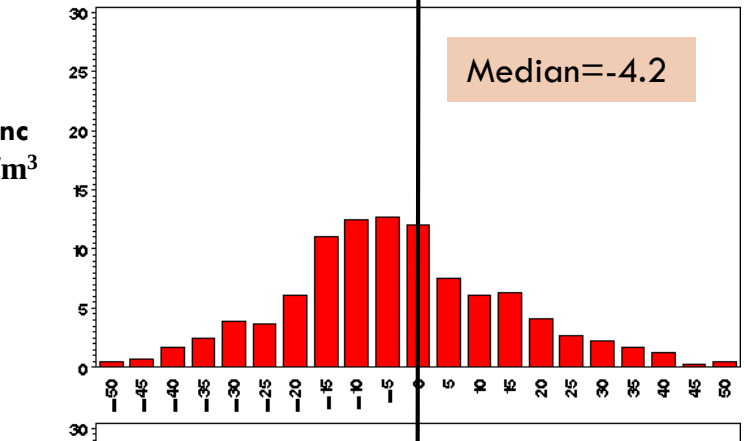
FINE PRINT
Monitor-level bias estimates.
Excludes |% diff| > 50%.
Excludes SLTValue=0.

Percent Bias from 2004-2006

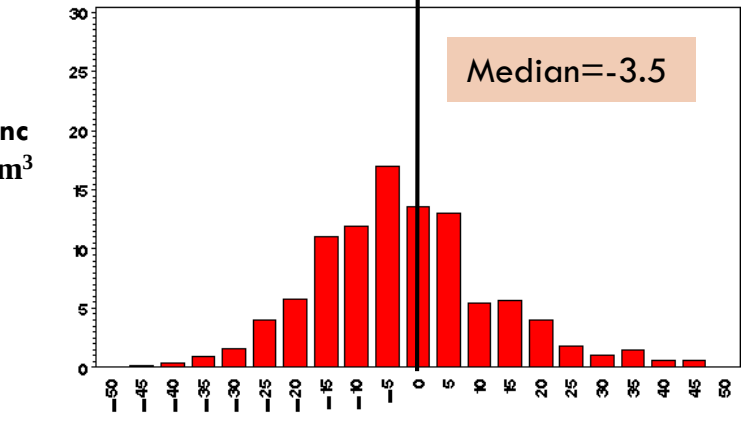
PEP Conc
0-3 µg/m^3



PEP Conc
3-6 µg/m^3

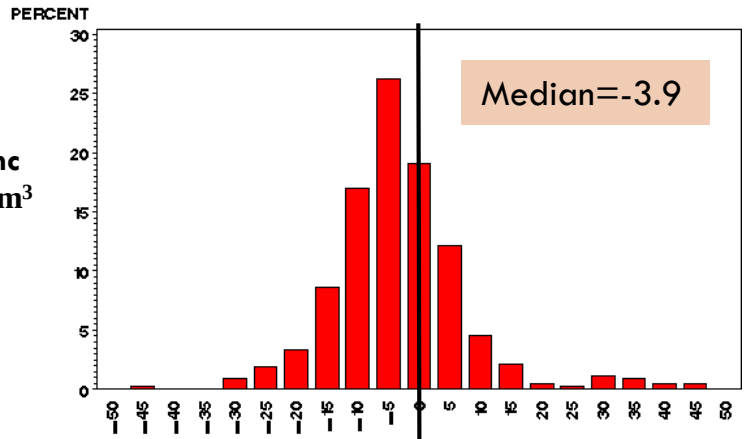


PEP Conc
6-9 µg/m^3

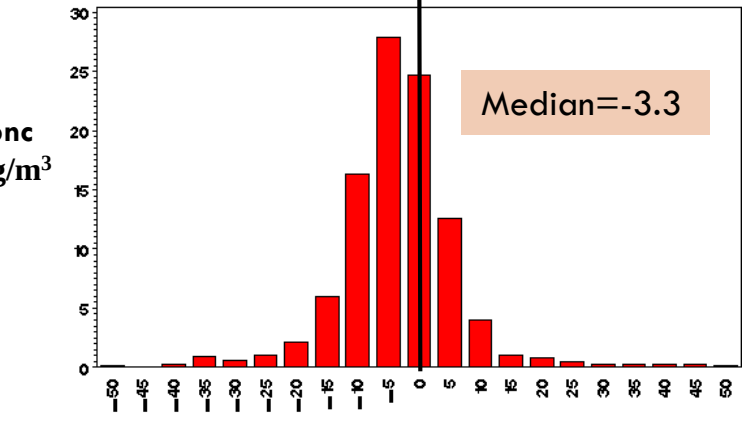


Percent Bias from 2004-2006

PEP Conc
9-12 µg/m^3

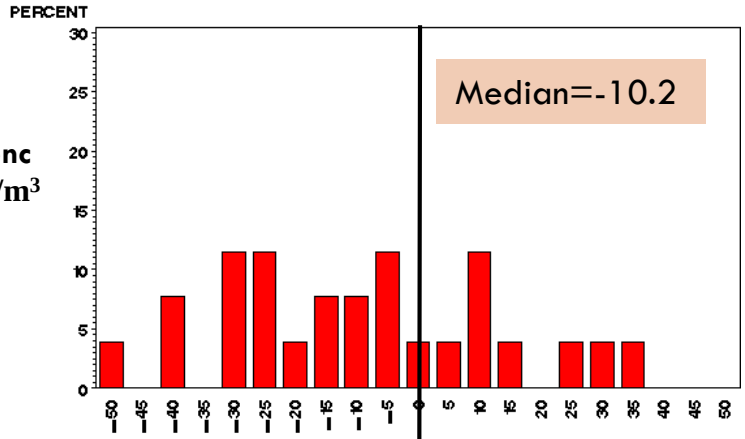


PEP Conc
> 12 µg/m^3

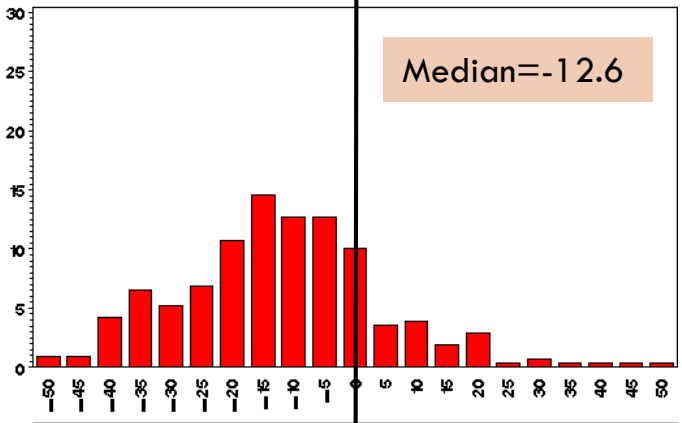


Percent Bias from 2008-2010

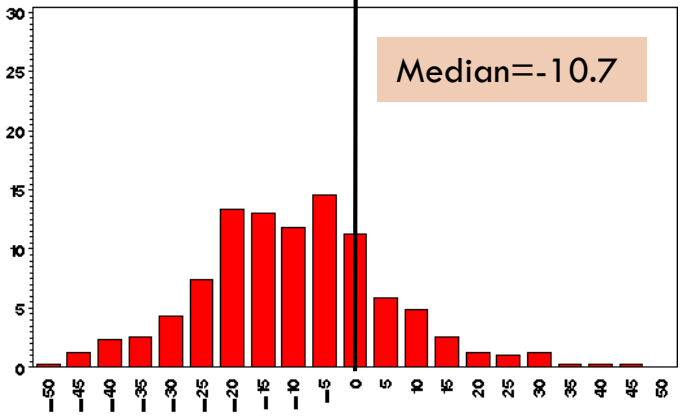
PEP Conc
0-3 µg/m^3



PEP Conc
3-6 µg/m^3

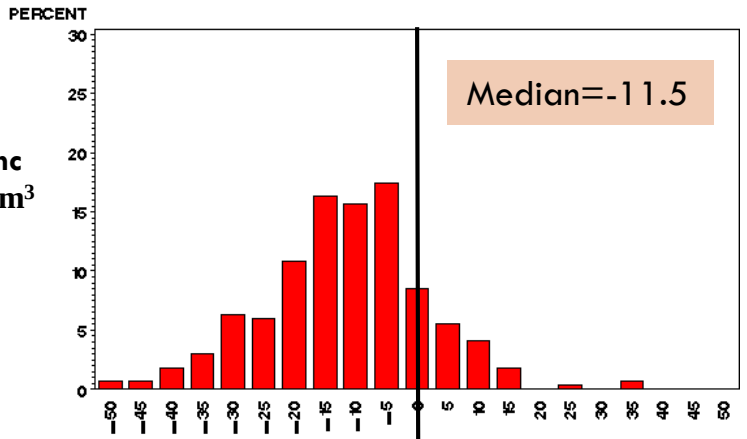


PEP Conc
6-9 µg/m^3

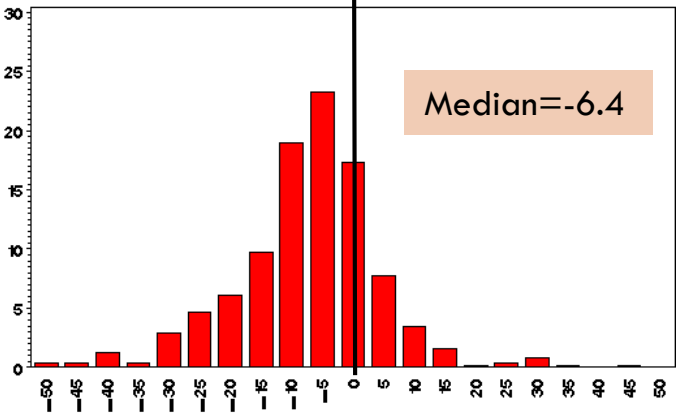


Percent Bias from 2008-2010

PEP Conc
9-12 µg/m^3

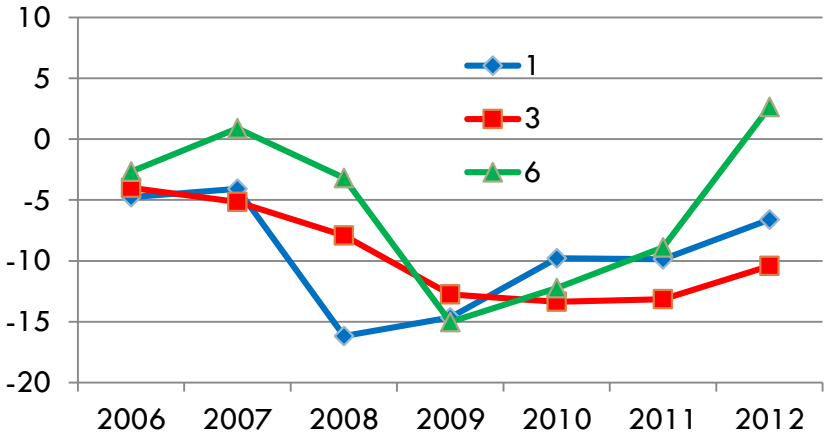


PEP Conc
> 12 µg/m^3

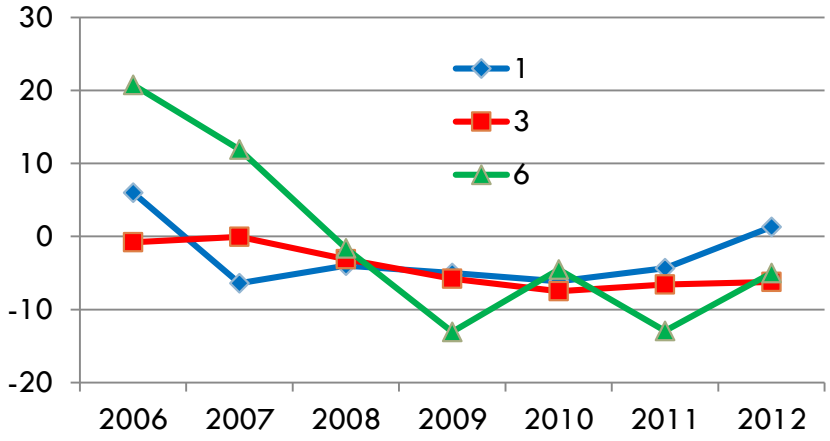


Does Sampler Cleaning Affect Bias?

Draft Bias **R&P Seq, WINS**, AQS Code for 1-in-1, 1-in-3, and 1-in-6 Sampling



Draft Bias for **R&P Seq, VSCC**, AQS Code for 1-in-1, 1-in-3, and 1-in-6 Sampling



- If cleaning theory is right, expect bias to be ordered such that 1-in-1 lowest, 1-in-6 highest, and 1-in-3 in the middle for WINS. No pattern expected in VSCC.
- Approximately see this ordering for 2006-2008.
- Not seeing this for 2009-2012
  - 1-in-1 bias above 1-in-3 since 2009 for R&P.
  - 1-in-6 bias sometimes lowest and sometimes highest for And Seq with WINS.

Draft Bias for **And Seq, WINS**, AQS Code for 1-in-1, 1-in-3, and 1-in-6 Sampling