Comparability of FRM and CSN $PM_{2.5}$ Mass

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$PM_{2.5}$ FRMs

$PM_{2.5}$ Met One SuperSASS

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Introduction:

- As part of the Chemical Speciation Network (CSN) Assessment, a recommendation is being considered to rely on the $PM_{2.5}$ FRM mass rather than the $PM_{2.5}$ CSN mass (collected on a Met One SuperSASS) at sites where both concentration measurements are performed.

- This poster identifies the differences and similarities between the two mass measurements; assesses the comparability of these measurements by grouping the data in a number of different ways; investigates the data by assessing across States, by date, with wind speed, and with nitrate; and finally investigates how sample flow affects interpreting field blank data for both mass measurement programs.

FRM/CSN Mass Assessment Background:

- $PM_{2.5}$ FRM mass is collected at nearly every CSN monitoring station
- Multiple $PM_{2.5}$ FRM makes and models are operated with either a WINS or VSCC to provide the $PM_{2.5}$ cut point.
- $PM_{2.5}$ Mass is collected in the CSN program using one channel of the Met One SASS or SuperSASS sampler
- The CSN $PM_{2.5}$ cut point is provided using a sharp cut cyclone.
- Both the $PM_{2.5}$ FRMs and CSN mass channels utilize a Teflon filter for gravimetric mass.
- Mass concentration data used in the assessment is from 2012; field blank data is from 2011-2013.
- Data were retrieved from EPA's AQS database either using Discoverer or at: http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm.

PM2.5 FRM

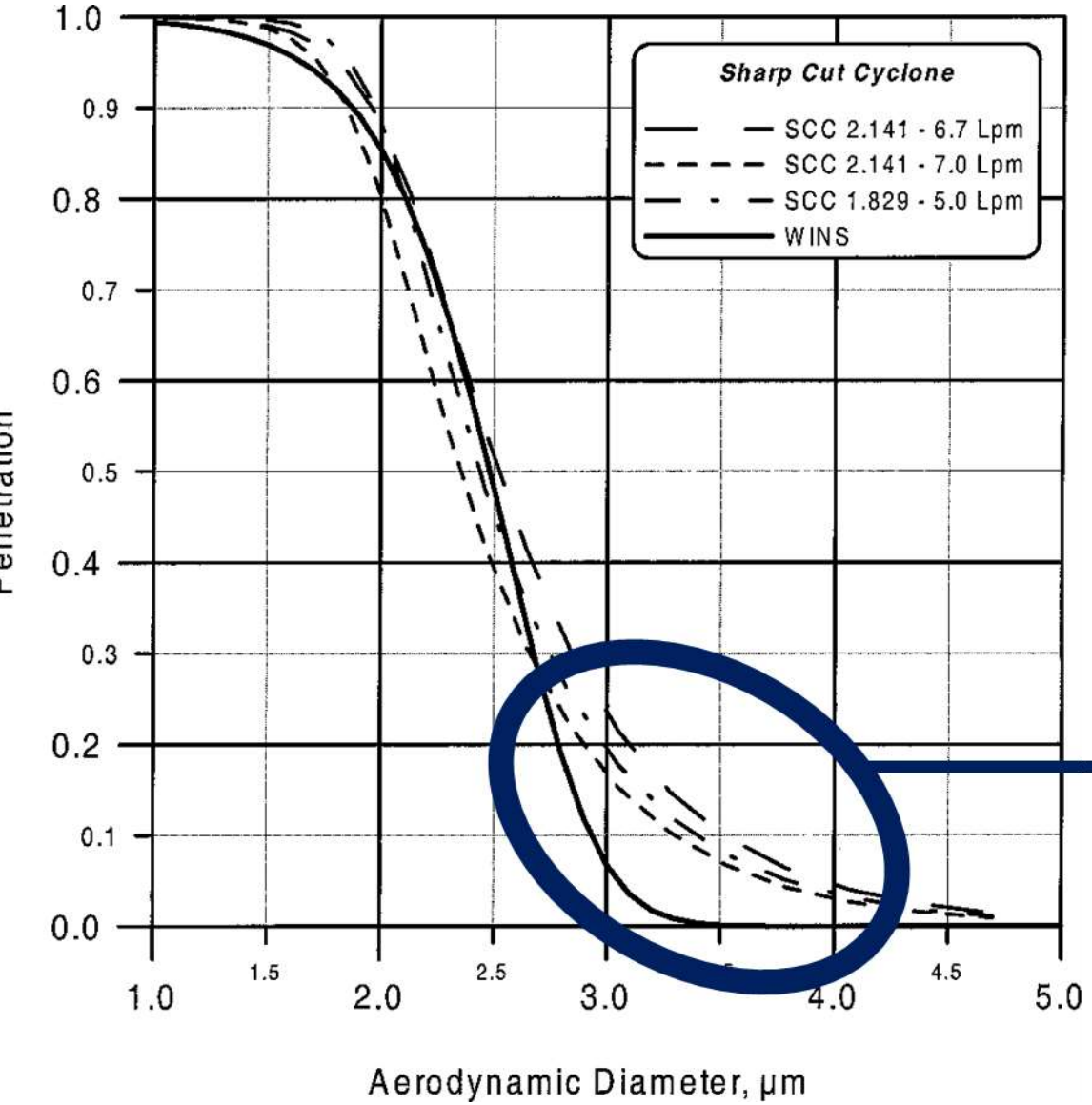
A PM10 inlet provides first stage separation, while a VSCC (or WINS, not shown) provides second stage separation. Sample flow operates at 16.7 Lpm

PM2.5 SASS/ SuperSASS

Each channel of the SASS Has a SCC.

Sharp Cut Cyclones are installed with the inlet pointed down.

Sample flow operates at 6.7 Lpm



Penetration curve of SCC From T.M Peters ET AL., AS&T, 2001

The CSN program uses the SCC 2.141 at 6.7 lpm

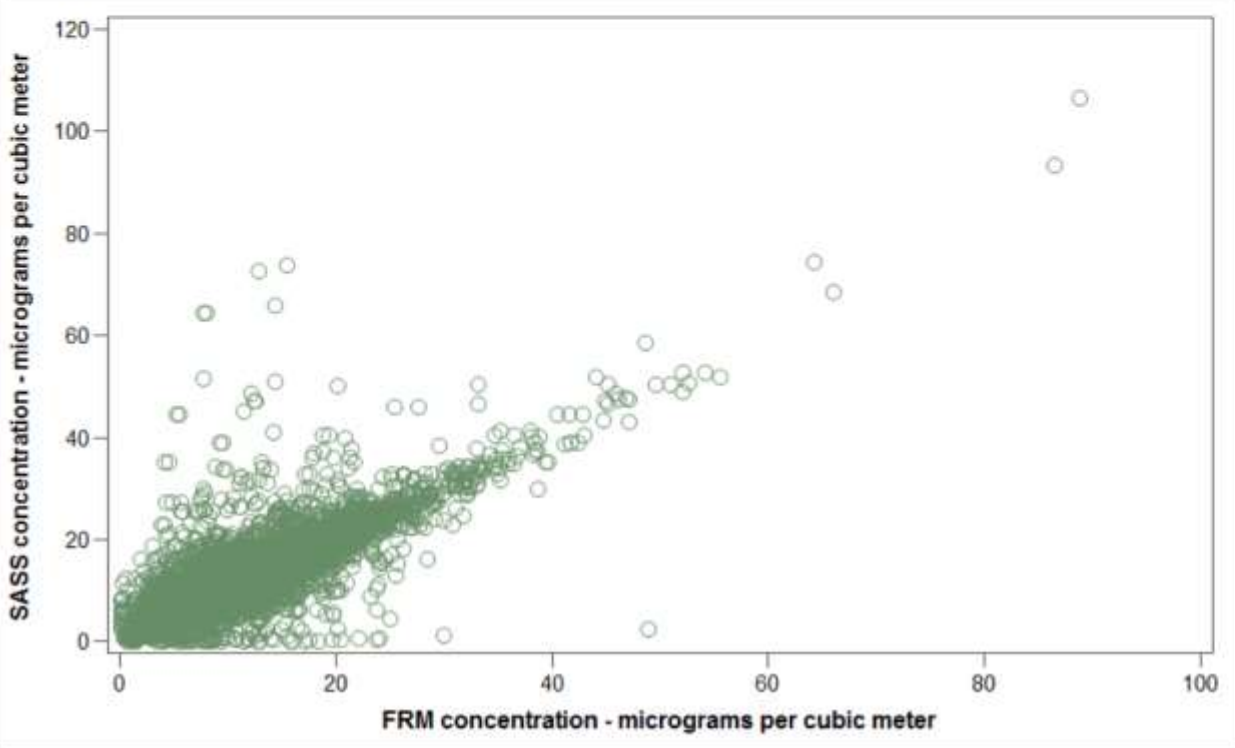
This area of the penetration curve illustrates some of the larger particles collected on the SCC, but not the WINS. (i.e., the WINS has a shaper cut than the SCC).

Comparison of Sample Collection on FRM and SASS/SuperSASS (SASS)

Sampler Element	FRM Design	SASS Design
Inlet	PM10 Size Selective Inlet	NA (nothing is in front of the SCC)
PM2.5 separation	WINS or VSCC	Sharp cut cyclone (SCC)
Flow rate	16.67 Lpm	6.7 Lpm
Flow velocity	23.4 cm/sec.	9.4 cm/sec.
Filter size	46.2 mm diameter (38.9 mm effective diameter of deposit area)	46.2 mm diameter
Flow control	Active flow control	Active flow Control
Filter media	Teflon	Teflon

Overall Summary of SASS vs FRM

Sampler	N	Mean (µg/m³)	Median (µg/m³)	5th % (µg/m³)	95th% (µg/m³)
SASS	14,991	10.4	9.3	3.4	21.0
FRM	14,991	9.6	8.5	3.0	19.6



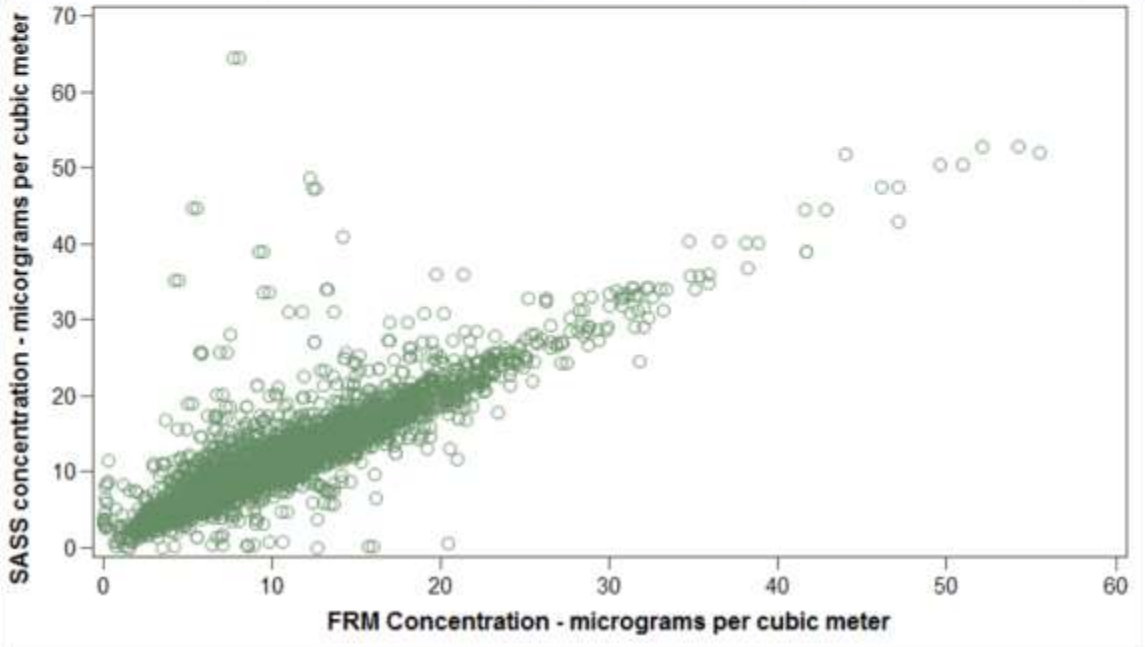
$Y = 0.96x + 1.3$

$R^2 = 0.76$

What if we only look at sites where the FRM collocated precision goal is being met?

(i.e., within a CV of 10%)

Sampler	N	Mean (µg/m³)	Median (µg/m³)	5th % (µg/m³)	95th% (µg/m³)
SASS	4,981	11.2	10.2	4.0	22.0
FRM	4,950	10.1	9.1	3.4	20.3



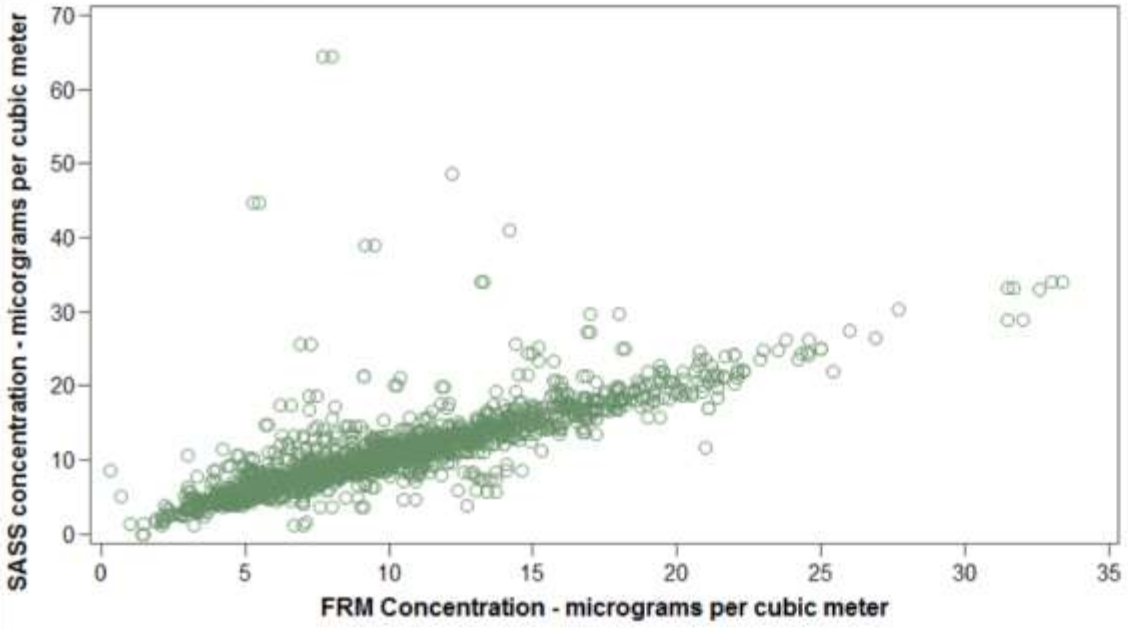
Note: sample set has a much smaller n as data pairs are limited to collocated sites. (e.g., two FRMs and at least one CSN)

$Y = 0.97x + 1.4$

$R^2 = 0.76$

What if we only look at sites where the FRM collocated precision is within 5% CV?

Sampler	N	Mean (µg/m3)	Median (µg/m3)	5th % (µg/m3)	95th% (µg/m3)
SASS	1,797	10.9	10.0	4.1	20.6
FRM	1,797	10.0	9.2	3.8	19.0



$Y = 0.94x + 1.6$

$R^2 = 0.62$

What if we exclude certain data and rerun the means and regression analysis?

- **Excluded data by:**
  - **Subtracting the SASS from the FRM, ranking the result, and taking the middle 98%, 90%, and 80% of this data set. This excludes both when the CSN mass is much higher than the FRM mass and cases where the FRM is much higher than the CSN mass (i.e., the tails of the difference).**
  - **Excluding all data where the CSN mass was identified with an "outlier " qualifier code.**

Collocated FRM/SASS dataset	N	SASS Mean ($\mu g/m^3$)	FRM Mean ($\mu g/m^3$)	Ratio of SASS to FRM	Regression equation SASS = Y FRM = X	R^2
All Data	14,991	10.4	9.6	1.08	Y = 0.96x + 1.3	0.76
1% - 99%	14,697	10.2	9.5	1.08	Y = 0.97x + 1.0	0.88
5% - 95%	13,518	10.0	9.3	1.07	Y = 0.99x + 0.8	0.94
10% - 90%	11,998	9.8	9.1	1.07	Y = 1.00x + 0.7	0.97
CSN mass excluded if "outlier"	13,894	10.6	9.8	1.08	Y = 0.97x + 1.1	0.84

Generally, as more data are excluded, the closer the slope gets to unity, the intercept improves but still stays positive, and the better the correlation squared becomes.

Looking at the worst days when the SASS was much higher than the FRM

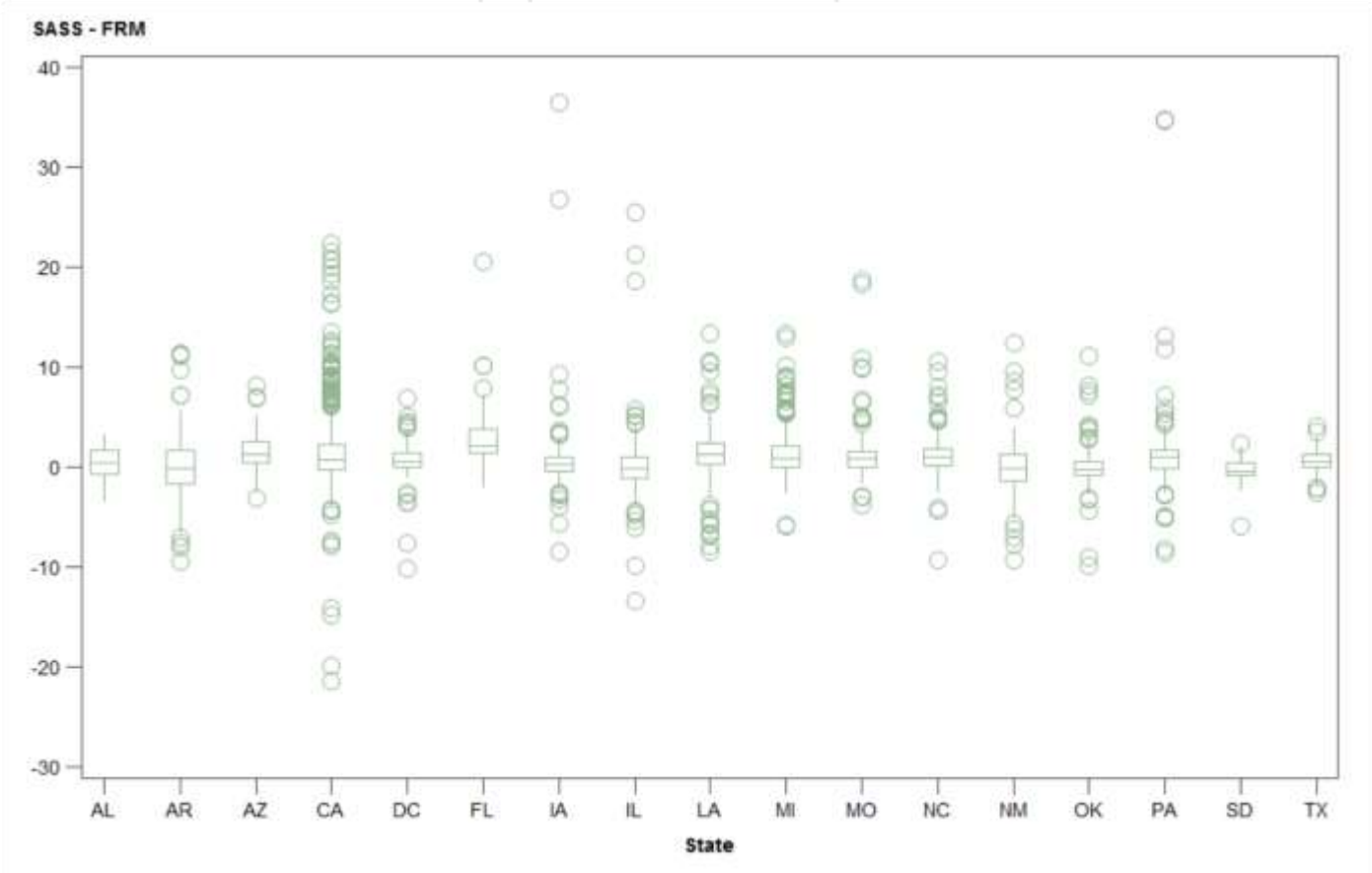
Comparing CSN mass to "reconstructed mass" appears to indicate that the CSN mass is the outlier. (e.g., CSN mass > either "reconstructed mass" or FRM mass).

SASS – FRM	SASS	FRM	State	Date	Site ID	Reconstructed Mass	Notes
56.8	64.5	7.7	KS	9/30/2012	201730010	7.6	Collocated FRM measured 8.0 on same day
51.5	65.9	14.4	IL	9/6/2012	171190024	Only a few XRF soil species detected. Sulfate flagged as outlier (very low 0.04); OC flag BA.	32 FRMs operating on this day in the State ranging from 4 to 24 ug/m3. CSN value not likely valid.
39.4	44.7	5.3 Primary 5.5 Collo.	TN	6/2/2012	470654002	No carbon reported for this sample*. OC flag AN. Soil and ion conc. was not unusually high.	27 sites in TN and majority within 4 ug/m3 of FRM on this day. CSN not likely valid
36.5	48.7	12.2	IA	9/3/2012	191630015	10.7	19 FRMs in Iowa on this day and all within 4 ug/m3 of the 12 ug/m3. CSN not likely valid
34.8	47.2	12.4 Primary 12.6 Collo.	PA	7/26/2012	420030008	9.5	29 Sites in Pennsylvania and all measured within 4 ug/m3 of FRM on this day. CSN not likely valid.
31	35.2	4.2 Primary 4.5 Collo.	FL	10/30/2012	120730012	4.1	29 Sites in Florida and the majority measured within 4 ug/m3 of FRM on this day. CSN not likely valid.

"Reconstructed mass" is: soil + ammonium nitrate + ammonium sulfate + 1.6*OC + EC;
soil = 2.2(AL) + 2.42(Fe) + 1.63(Ca) + 2.49(Si) + 1.94(Ti).
ammonium nitrate = 1.29 * nitrate; ammonium sulfate = 4.125 * sulfur

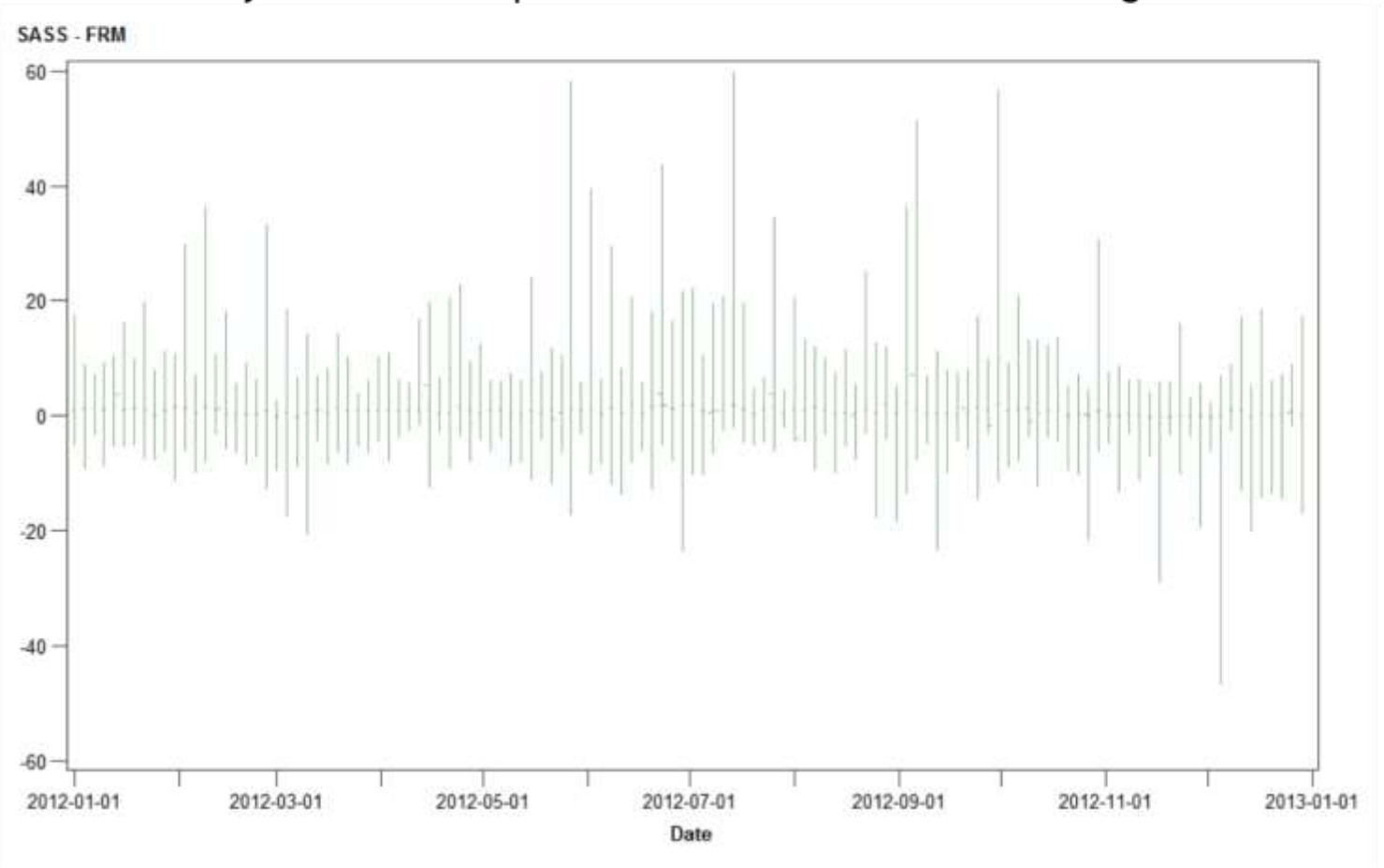
Box and whisker plots of the difference between SASS and FRM difference by State

No noticeable pattern of states with similar differences

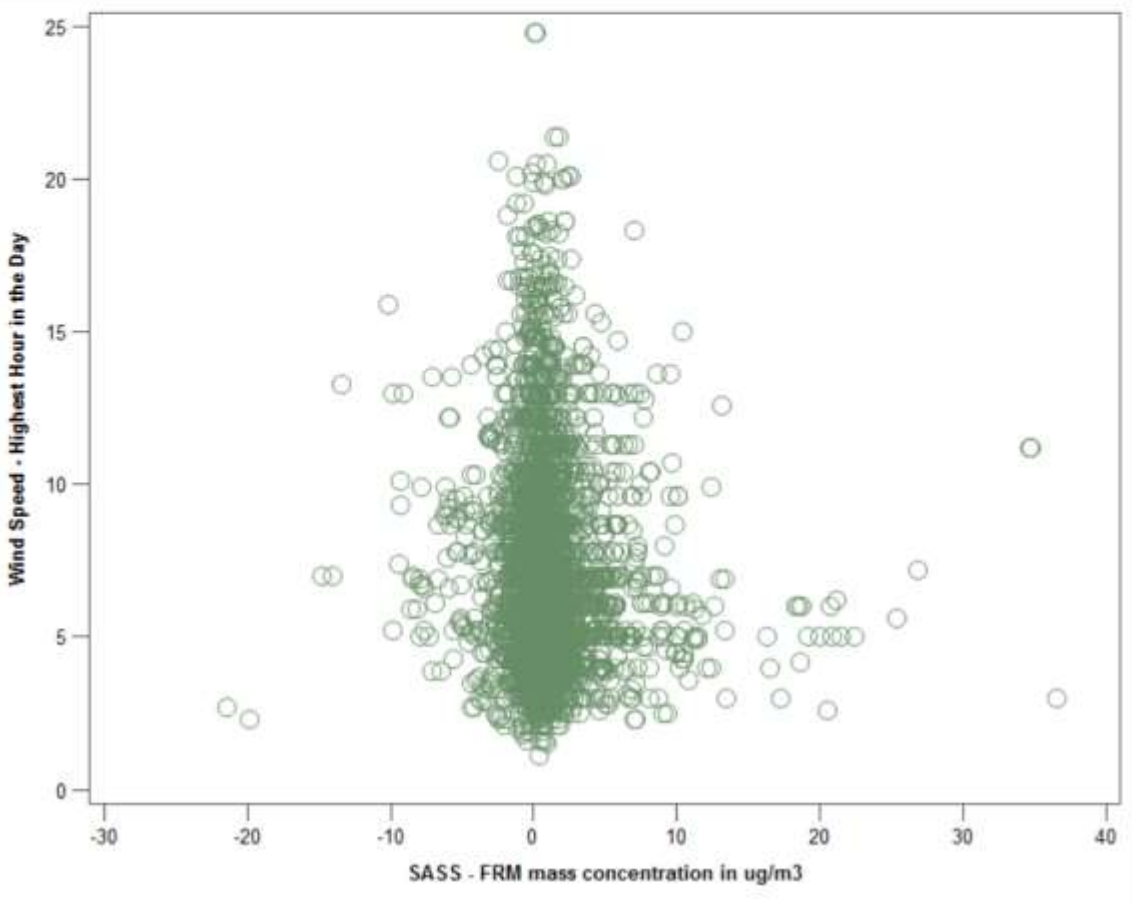


High-Low of (SASS- FRM) Boxplot by Date

Seasons may have some impact on whether differences are high or low.

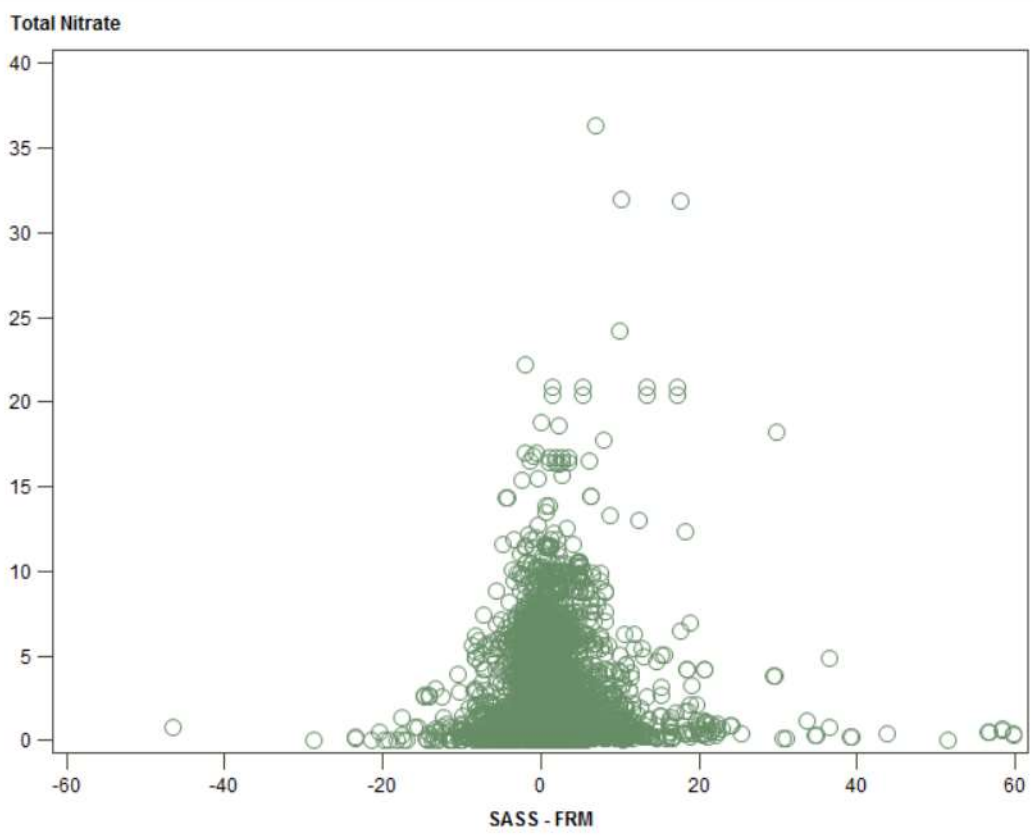


What if we examine hourly wind speed versus difference between the SASS and FRM mass concentration?



If we had many more values in the top right part of the chart it would indicate high SASS mass values with a high bias compared to the FRM are related to high wind days; however, that is not the case.

What is we examine nitrate versus difference between SASS and FRM mass concentration?



High nitrate days do appear to have some impact on the bias of the SASS.

Summary of Relationships between CSN and FRM mass

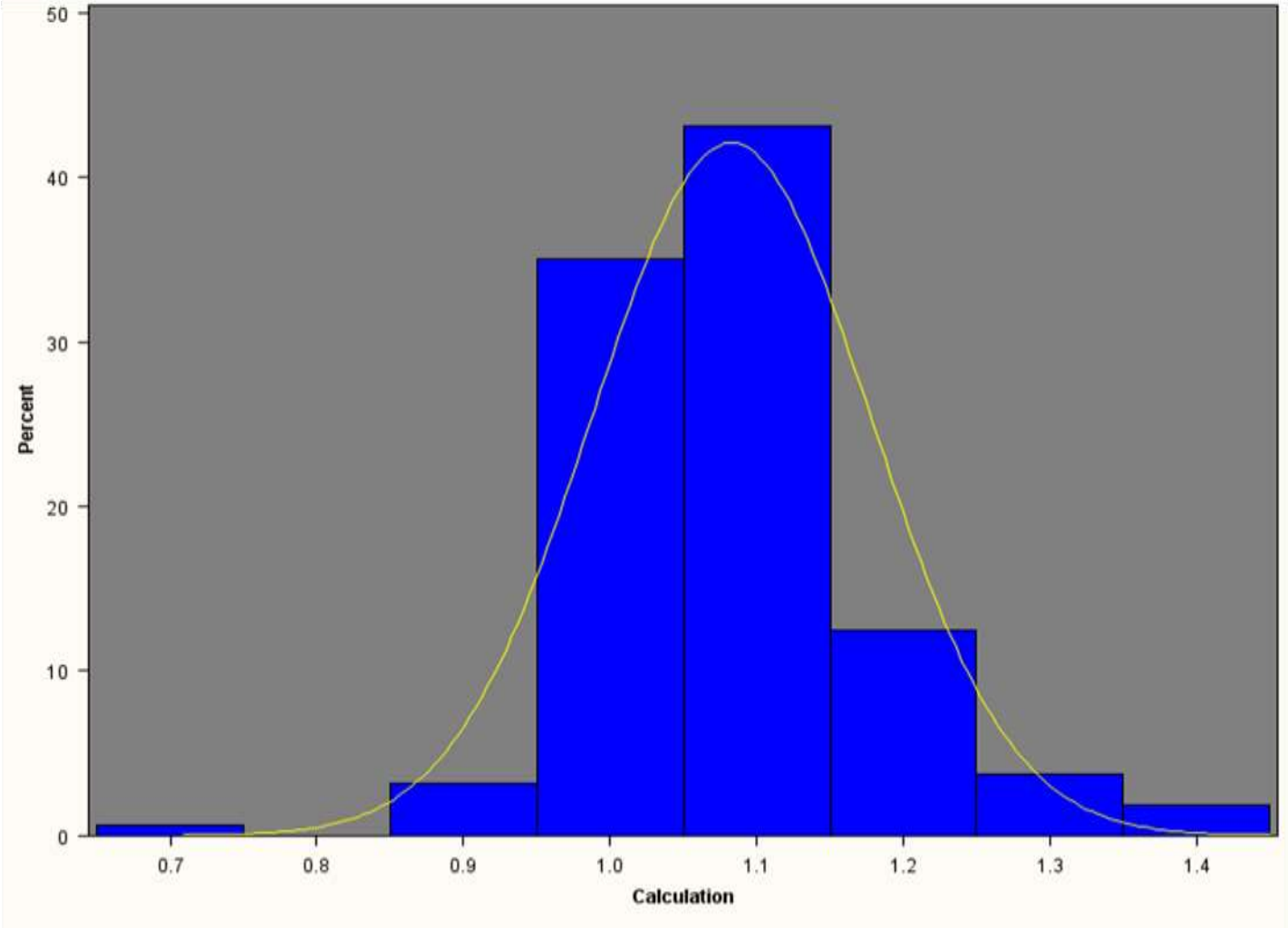
Collocated FRM/SASS dataset	N	SASS Mean (µg/m³)	FRM Mean (µg/m³)	Ratio of SASS to FRM	Regression equation	R^2
All Data	14,991	10.4	9.6	1.08	Y = 0.96x + 1.3	0.76
1% - 99%	14,697	10.2	9.5	1.08	Y = 0.97x + 1.0	0.88
5% - 95%	13,518	10.0	9.3	1.07	Y = 0.99x = 0.8	0.94
10% - 90%	11,998	9.8	9.1	1.07	Y = 1.00x + 0.7	0.97
CSN mass excluded if "outlier"	13,894	10.6	9.8	1.08	Y = 0.97x + 1.1	0.84
Where FRM CV <=10%	4,843	11.2	10.2	1.10	Y = 0.97 + 1.4	0.76
Where FRM CV<=5%	1,752	10.9	10.0	1.09	Y = 0.94 + 1.6	0.62

Regardless of how we look at the data, the regression equation essentially tells us the same story:

- The slope is approaching 1
- The intercept is positive; meaning the SASS has a positive offset relative to the FRM
- The ratio of the SASS to FRM is fairly consistent.

Note: Part 53 Performance FEM criteria are met for multiplicative bias (slope) and additive bias (intercept), but not for correlation.

Histogram of Ratio of SASS to FRM concentration by site (All Data)



Lets examine how Field Blanks may affect the Intercept

- Differences in field blank contamination (FB concentration/volume of flow for routine sample) will result in an additive bias (intercept) between the CSN and FRM. This is due to field blank concentrations being mostly consistent across all collected samplers rather than a function of the collected aerosol.

- Field blank contamination is exacerbated on the CSN mass as the volume of flow collected is substantially less than that of an FRM.
  - CSN Teflon channel operates at 6.7 lpm = 9.6 m^3 of air collected
  - FRM operates at 16.7 lpm = 24.0 m^3 of air collected

- Even if the field blank concentration were the same, its overall effect is 2.5 more pronounced on the CSN channel than an FRM
  - Example: consider if the FRM and CSN programs both had field blank concentrations of 6 micrograms.
    - CSN: 6 µg/9.6 m^3 = 0.63 µg/m^3
    - FRM: 6 µg/24.0 m^3 = 0.25 µg/m^3

- Therefore, at this concentration, which is very good, the difference in volume alone means that 0.38 µg/m^3 more additive bias is associated with CSN mass program.

What differences do we actually see in Field Blank contamination between CSN MASS and the FRM?

CSN Field Blanks

(via national contract)

Year	N	Mean (µg/m³)	Std Dev. (µg/m³)	Median (µg/m³)
2011	550	0.65	0.73	0.50
2012	539	0.86	0.77	0.70
2013	531	0.67	0.76	0.50
Total/ Avg.	1620	**0.73**	0.76	**0.60**
What if we don't consider volume?				
Total/ Avg.	1620	7.0	7.3	5.8

FRM Field Blanks

(all FRM FBs in AQS 88101)

Year	N	Mean (µg/m³)	Std Dev. (µg/m³)	Median (µg/m³)
2011	14405	0.24	1.73	0.21
2012	14545	0.31	3.95	0.21
2013	13456	0.22	1.64	0.17
Total/ Avg.	42405	0.26	2.69	0.21
What if we don't consider volume?				
Total/ Avg.	42405	6.2	64.6	5.0

- Mean (µg/m³): 0.73 - 0.26 = 0.47 µg/m³
- Median (µg/m³): 0.60 - 0.21 = 0.39 µg/m³

- Therefore, using data from 2011 – 2013, ~0.4 µg/m³ of contamination is associated with the differences in field blanks and flow rates.

Conclusions:

- FRM and CSN mass compare favorably on most days.
  - For entire 2012 collocated dataset, slope (multiplicative bias) and intercept (additive bias) meet Part 53 requirements for approval of class II methods
- Excluding the tails of the difference between the FRM and CSN mass appears to result in a slope approaching unity, but a remaining positive intercept (SASS higher than FRM).
- Wind speed shows no apparent relationship in explaining errors in the mass collected on the CSN mass.
- High nitrate days appear to have a mild impact on the CSN mass measuring slightly more than the FRM mass.
- Differences in the volume collected between the CSN and FRM samplers result in explaining a portion of the error in the intercept
- Reconstructed mass compared to FRM mass is a suitable approach to QC the CSN data.
- Since CSN mass and FRM mass are very similar and the FRM mass is the regulatory measurement, we recommend relying on the FRM mass as the mass measurement at CSN sites.