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Class III FEMs: Performance evaluation at Queens College, New York

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INTRODUCTION

The EPA designated several new instruments as Class III Federal Equivalent Methods (FEMs) for use in $PM_{2.5}$ ambient air monitoring. This designation required high correlation and minimal additive and multiplicative biases between the FEMs and the Federal Reference Method (FRM). However, the test did not require vendors to operate their FRM's on the same sampling interval (midnight to midnight) as used by monitoring agencies for comparison to the NAAQS. The new FEMs were designed to be more cost effective than filter based sampling and to satisfy $PM_{2.5}$ monitoring data needs for comparison to air quality standards and to produce Air Quality Index (AQI) and health alerts.

The NYSDEC conducted an evaluation of the four available FEMs in Queens, NYC from January through August 2010 alongside an FRM operating on a daily schedule.

SITE

Queens NYSDEC Air Monitoring Station (**AQS: 360810124**) is at Queens College, Flushing, New York. It is a national core (NCore) site with advanced monitoring equipment (http://ncore.sonomatechdata.com). Previous summer and winter intensive studies were carried out here. It is impacted by roadway traffic from the Van Wyck and Long Island Expressways.

INSTRUMENTS

Hourly particle mass; Thermo Scientific FDMS 8500C, TEOM 1405DF and 5014i BAM. MetOne 1020 BAM. 24-hr; Thermo 2025 Federal Reference Monitor (FRM). Speciation (1 in 3 day) MetOne SAAS for inorganic and elements, URG-3000N for carbon species using IMPROVE TOR analysis.

Semi-continuous species; Thermo 5020i Sulfate Particulate Analyzer, Sunset Laboratory OC/EC carbon aerosol analyzer.
Gas; NO_x, SO_2, O_3.

FEM Evaluation –Jan-Aug 2010

8500 VerC   1405 DF   BAM 1020   5014i

Figure 1. 8500 and FRM regression fits

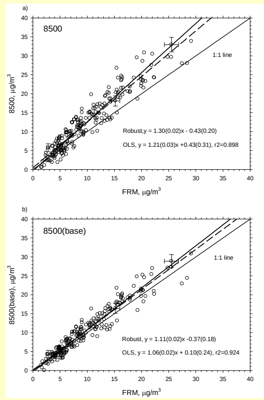


Figure 2. Time series comparison

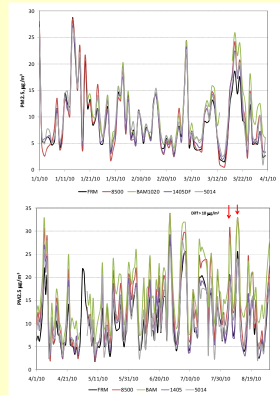


Table 1. FEM vs FRM regression coefficients.

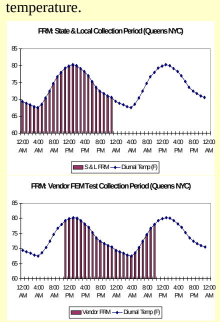
Method vs FRM	Robust		OLS		n	R2
	slope	int	slope	int		
8500	1.30	-0.43	1.21	0.42	222	0.90
8500base	1.11	-0.37	1.06	0.10	222	0.92
MetOne BAM	1.24	2.56	1.16	3.51	210	0.85
5014	0.99	1.03	0.95	1.45	224	0.89
1405DF	1.03	0.36	1.00	0.62	221	0.95
1405FEM	0.94	-0.19	0.93	-0.01	221	0.95
*1405_PM_{10}	0.96	0.53	0.94	0.82	207	0.92

*FRM PM_{10} comparison

Table 2. Mean monthly 8500-FRM differences and other parameters.

Month	8500-FRM	FRM	8500	OC	SO4	T	RH
	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	C	%
Jan	0.19	10.8	11.0	2.32	2.59	0.36	58.9
Feb	-0.16	9.05	9.09	1.55	2.06	0.85	62.0
Mar	1.21	7.56	8.77	1.93	1.54	8.54	58.6
Apr	2.73	8.06	10.7	2.00	1.92	14.0	51.3
May	2.70	9.21	10.8	2.40	2.20	18.6	57.7
Jun	4.19	12.0	16.7	3.86	3.05	24.4	58.8
Jul	3.85	12.4	16.2	3.47	3.50	27.9	53.7
Aug	4.53	10.6	15.1	3.13	2.44	25.5	59.7

Figure 3. Sample interval and temperature.



(Summer test site actual average diurnal temperatures: Ave 74° F)

Figure 4. Effect of different 24 hr sample collection intervals. State and Local (Blue) FRMs are required to operate from Midnight to Midnight. The vendor (red) FRMs operated from 11:00 am to 11:00 am.

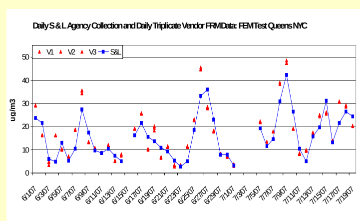


Figure 5. Ordered grouping of 8500-FRM difference versus OC, 8500ref mass and temperature.

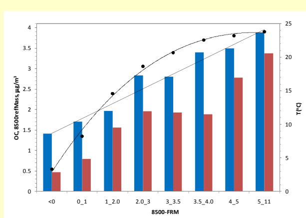
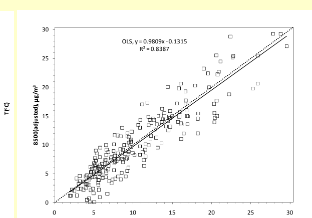


Figure 6. Comparison of FRM mass and 8500 adjusted mass based on non-linear temperature fit. Dotted line is 1:1.



RESULTS

Figure 1 shows the linear fits for the FDMS (a) 8500 and (b) 8500base mass with the FRM. The 8500 total mass measures higher than the FRM (average 20-30%) because it has a chilled filter (4°C) to collect semi-volatile material. The base mass is the non-volatile fraction and is within 6-11% of the FRM. Table 1 shows a summary of the comparisons for all the other FEMs. Similar to the 8500 the MetOne BAM also measures higher than the FRM (16-24%) but has a large positive intercept (background interference issues) and a lower R^2. The Thermo 5014i BAM has a long heated inlet to control sample RH, but the 5014i filter temperature can reach 40°C which leads to evaporative losses. Note that the 1405DF also has a chilled filter to collect semi-volatile material but on average it agrees or measures lower (~6%) than the FRM ($PM_{2.5}$ and PM_{10} shown).

The time series comparison in Figure 2 shows that the methods tend to agree better from Jan to Mar when the atmosphere is colder and drier. Table 2 shows the mean monthly difference (8500-FRM) was close to zero in Jan and Feb but increased to ~4 µg/m³ in Jun-Aug. The daily 8500-FRM difference exceeded 10 µg/m³ on Aug 5th, 9th and 11th (arrows in Figure 2). On these days maximum ambient temperatures reached 33-34°C in the early afternoon. Hourly data shows that most of the particle loading occurred prior to or near peak ambient temperatures. Continuous instruments collect and record particle material on an hourly basis and therefore semi-volatile material captured during the cold part of the day is not lost to evaporative processes later in the day when peak ambient temperatures are likely to occur. Figure 3 shows that the FRM midnight to midnight collection exposes the filter to the highest evaporative losses during peak ambient temperatures when the sample is at a relatively high loading. Using a 11:00 am to 11:00 am collection interval exposes the filter to the highest ambient temperature before much of the mass has been collected. Figure 4 shows a comparison of the Vendor FRMs (V1-V3) versus the State & Local (S&L) NYSDEC operated FRM during the Queens study period. The vendor FRMs use an 11am to 11am sample interval and measure more mass on high pollution days when the proportion of volatile mass is likely higher.

Figure 5 shows that the 8500-FRM difference is correlated with the 8500ref mass or volatile fraction (R=0.78) and ambient temperature (0.69) and moderately with organic carbon (0.58). With the transition from the cold to warm season, a larger proportion of the volatile mass lies in the organic fraction as the nitrate fraction decreases. The effect of temperature on the FRM's ability to retain volatile particle mass is non-linear and is affected by when the mass is collected on the filter relative to the daily peak ambient temperature. Using this relationship with temperature we can estimate the evaporative loss from the FRM filter. Figure 6 compares the FRM with the 8500 total mass adjusted downward by the amount lost. The agreement is reasonable, slope close to 1 and zero intercept, but there is considerable scatter, R^2 is 0.84. Factors other than temperature such as the nature of the volatile material and when it is collected on the FRM filter in relation to ambient temperature also affect evaporative losses.

Summary

Comparison of four different FEM methods with the FRM revealed method and season dependent differences. Agreement was best during the colder months, Jan and Feb, and worst during the warmer months, Jun-Aug. Individual daily differences of above 10 µg/m³ were observed between the FRM and the Thermo 8500C or MetOne BAM. The differences are mainly due to evaporative losses from the FRM filter which is exposed to high ambient temperatures particularly during the warm season on high pollutant days. An alternative 24hr sample collection and post filter conditioning would reduce the FRM losses. Although the FEM's provide data which is more beneficial for Health and Air Quality Alerts, the large biases will cause problems for long term trends analysis and epidemiology studies as well as potential issues for comparison to air quality standards. Finally, the long term reliability of the new more complex FEM instrumentation has to be evaluated prior to their use in a $PM_{2.5}$ monitoring network.