Implications of Changing Suppliers of the 46.2 mm Polytetrafluorethylene Filters Used for Low-volume, Gravimetric Measurements of Ambient Concentrations of $PM_{2.5}$, Low-volume PM-10 and Lead (Pb)

Technical Bulletin

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Implications of Changing Suppliers of the 46.2 mm Polytetrafluoroethylene Filters Used for Low-volume, Gravimetric Measurements of Ambient Concentrations of $PM_{2.5}$, Low-volume PM-10 and Lead (Pb)

1.0 **Executive Summary and Conclusions**

MTL Inc. was awarded a contract in April 2010 to supply the nation's $PM_{2.5}$, PM-10 and low-volume lead (Pb) FRM networks with 46 mm Polytetrafluoroethylene (PTFE) filters. MTL proposed to use the same filter membrane material as that used by the historical supplier (Whatman); however, MTL also proposed to use a polyfluoroalkoxy (PFA) support ring around the perimeter of the filter. It is chemically different, denser, stiffer, more incompressible, and slightly thicker than its predecessor. The new ring material will not accept conventional lettering for serial numbers, which therefore, must be printed somewhere on the filter membrane. EPA selected the option to print the serial numbers in an arc around the perimeter of the filter membrane, inside the support ring.

The EPA had 4 technical concerns about the influence of the morphological changes to the support ring and relocation of serial numbers:

- Increased incidence of leaks around filter cassettes with deleterious effect on flow rate of sampled air through the filters
- Increased incidence of jammed filter cassettes across the fleet of old R & P 2025 and newer Thermo 2025 Partisol sequential samplers that predominate the PM2.5 FRM network across the US.
- Bias in total mass measurements
- Elemental artifacts in the printing ink could affect the determination of elements by X-ray Fluorescence (XRF) or inductively couple plasma-mass spectrometry (ICP-MS).

The Ambient Air Monitoring Group of EPA, OAQPS, with several volunteer State monitoring agencies and sister EPA labs planned and conducted a pre-production testing program to determine the likelihood of any deleterious effects. MTL supplied prototype filters. The findings can be summarized as follows

- No adverse affects on average flow rates or total sample volume—were observed or recorded, and there was no reported incidence of leak check failures.
- All generations of 2025 Partisol samplers' filter exchange mechanisms performed satisfactorily in most tests. Three agencies reported no issues. One agency reported a couple of cassette shuttle jams on old R & P 2025 samplers, but the frequency was not conclusive of a filter problem.
- The gravimetric bias between Whatman and MTL filters is negligible. Mass measurements using the MTL filters from three sites with collocated samplers exhibited $<0.1\mu g/m^3$. A fourth agency's data showed a noticeable, negative bias, $-0.7\mu g/m^3$. Field- and trip-blank masses were consistent with historical data.
- Background elements on the filter were below detection limits of XRF for nearly all metals and trace elements. All were below quantification limits. EPA's ICPMS analysis of these filters has not been completed at this time.

It is concluded that the MTL filters should perform satisfactorily for gravimetric mass measurements and quantification of elements using XRF. A conclusion on expectations for ICPMS analyses is forthcoming. Agencies should note, however, that the new weight of the filters (~400 mg vs. Whatman's ~150 mg) will require labs to procure new calibration and quality control check weights and ensure their data management software accommodates the higher MTL filter mass.

2.0 Full Project Description and data analysis

2.1 Background

The PM2.5 FRM network has been supplied with Whatman 47 mm PTFE filters since initial deployment in 1998 through 2010. In April 2010, a new supply contract was awarded to MTL Corporation. MTL's product differs from the historical Whatman filters in several significant ways. Table 1 provides a comparison of the chemical and physical attributes of both. Physical requirements and performance parameters for the filters were set out in the original implementing regulations for the PM2.5 Network at 40 CFR part 50. Appendix L. A few supplementary requirements have been added through the contract specifications. Every production lot (approximately a one-year supply) of filters are evaluated by EPA for compliance with the physical and performance requirements through a set of Quality Assurance Acceptance tests for a random sampling of 0.1% of every production lot which are conducted by an independent laboratory. The acceptance test results will be posted on the Ambient Monitoring Technical Information Center of Technology Transfer Network at http://www.epa.gov/ttn/amtic/quality.html [Information will eventually be migrated to a "Monitoring Filter QA/QC" Page]

Table 1. Comparison of the Whatman and MTL Filter's Physical Characteristics

Characteristic	Whatman	MTL filter	Comments
Filter membrane	PTFE	PTFE	MTL claims to use the same supplier
Nominal Filter Mass	146-150 mg	400-410 mg	Increase due to new support ring material
Support Ring Chemistry	Pure Polymethyl-pentene (PMP)	Polyfluoro alkoxy (PFA)	
Support ring Flex Modulus	210,000 PSI	85,000 PSI	Goal is to eliminate the "Pringle™" effect
Support Ring Density	~0.84g/cm^3	~2.2g/cm^3	Adds substantial mass to the gross filter mass
Support ring compressibility	Not Quantified or reported	MTL claim is less than PMP	Similar to PTFE, which is the primary copolymer
Support Ring nominal avg. thickness	0.013 in 0.320 mm	0.016 in 0.394 mm	Contract specification is 0.31- 0.42 mm
Filter Identification	S/N printed on PMP ring	S/N printed on both sides of filter media	Alpha Numeric in straight line or in arc inside the PFA ring or bar code patch.
Ink chemistry	Unknown and not important since it is not on the filter	microfine particles of carbon in an aqueous suspension	Ink will not adhere to PFA
Dielectric Const.	2.1	2.1	

MTL is required by contract to furnish filters that meet the same physical requirements and performance parameters that were instituted by 40 CFR part 50 Appendix L and subsequent contract-implemented specifications. MTL's testing regimen to assure the filters will comply with all QA/QC requirements can be reviewed in MTL's Quality Assurance project Plan at http://www.epa.gov/ttn/amtic/quality.html [Information will eventually be migrated to a "Monitoring Filter QA/QC" Page]

2.2 Project scope

Notwithstanding the results of the required QC and acceptance testing, EPA had several technical concerns with the new MTL filters, some mechanical and analytical:

- Will the slightly thicker support ring exacerbate the occasional mis-feeding of filter cassettes by the shuttle mechanism in the dominant FRM samplers in the network, the R & P 2025 and the Thermo 2025 Partisol Samplers?
- Will the incompressibility and stiffness along with the thickness foster a higher incidence of leak check failures or any deleterious effect on flow through the filter?
- Will the new filters introduce a bias in the measurements of $PM_{2.5}$ compared to those made historically using the Whatman filters?
- Does the serial number printed on the actual filter membrane have a noticeable effect on the flow rate on a micro-spatial scale across the filter and therefore the interstitial velocity?
- Does the ink introduce contaminants that would have to be accounted for when the filters are analyzed for metals using XRF or ICPMS; or, if the filters are analyzed for elemental carbon?

As a result of these concerns MTL supplied EPA with preproduction prototype filters for an assessment of mechanical performance in the field, bias in gravimetric measurements and artifacts introduced by printing the ink on the filter membrane. The Ambient Air Monitoring Group of EPA, OAQPS worked with several volunteer State monitoring agencies and sister EPA labs to plan and conduct a testing program to determine the likelihood of any deleterious effects. Table 2 shows how the filters were apportioned to the monitoring Agencies that participated in the assessments and the types of tests conducted by each organization.

The chain of custody, filter pre-weighing ("taring" of blank filters) collection of filter samples, shipping and handling, and post-weighing of filters was conducted in accordance with each agency's Quality Assurance Project Plan used for the PM2.5 FRM network, or the PM2.5 Network Performance Evaluation Program as appropriate.

The MTL filters used by State agencies were deployed in collocated samplers during actual network sampling events which are reported to EPA's Air Quality System data base, and are used for determining ambient air quality design values that are compared to the national ambient air quality standard for PM2.5.

The test conducted by EPA Region 4's Science & Ecosystems Support Division Laboratory (Region 4) with gravimetric measurement support from EPA's Office of Radiation and Indoor Air' s National Air and Radiation Environmental Laboratory (NAREL), utilized six, collocated, BGI PQ200A (audit version) FRM samplers. In this test three samplers were loaded with

Whatman filters and three were loaded with MTL filters for every sampling event. The samplers that received one type of filter or the other were rotated so as to minimize any bias introduced by the samplers.

Table 2. Testing of MTL Prototype filters by State Monitoring Agency Labs and EPA

Monitoring Agency	Type of Assessment	Number of filter pairs	Service Laboratory	Samplers or equipment
South Carolina	Complete Sampler performance and Gravimetric comparison between Whatman and MTL filters	9 parings 1 Field Blank	South Carolina	R & P 2025 Partisol Sequential (2 collocated)
Florida	Complete Sampler performance and Gravimetric comparison between Whatman and MTL filters	8 pairings 1 Field Blanks 1 Lab Blank	Florida	New and old Thermo Fisher 2025 Partisol Sequential (2 collocated)
Utah Division of Air Quality	Complete Sampler performance and Gravimetric comparison between Whatman and MTL filters	10 MTL Filters provided	Utah	Thermo Fisher 2025 Partisol Sequential (2 collocated)
GA DNR	Complete Sampler performance and Gravimetric comparison between Whatman and MTL filters; with daily sampling	14 pairings, 2 Field Blanks	US EPA ORIA, NAREL	New Thermo Fisher 2025 Partisol Sequential (2 collocated)
US EPA Region 4 Lab	Field testing of bias using BGI PQ200A single channel PM2.5 FRM sampler	33 pairings, 9 Field Blanks 3 Trip Blanks	US EPA ORIA, NAREL	6 BGI PQ200A samplers, 3 of each filter per event
US EPA	XRF Analysis of blank MTL filters some with and some without Serial numbers printed on edge of filter media inside the support ring; Also included Blank Whatmans w/ serial numbers on support rings	10 MTL w/ SN 8 MTL w/o SN 10 Whatmans w/SN on Ring	US EPA, ORD, NERL	Kevex

Since the objective was to compare mass loading of the filters, there was one deviation from the national PM2.5 operating procedure allowed—the 24-hour sampling period was started at mid morning to facilitate more convenient daily filter retrieval and reloads. Another important aspect of this test was collection of several field blanks. This was designed to determine if the static charge properties of the MTL filter would increase the propensity to collect passive contaminants.

Blank (clean and unexposed) MTL filters were subjected to XRF Analyses by the EPA's Office of Research and Development, National Exposure Research Laboratory (NERL), Research Triangle Park, NC. The objective was to determine if the filters contain background levels of trace elements that would interfere with XRF analyses of filters used for $PM_{2.5}$, PM-10 or low-volume lead (Pb) measurements. MTL filters with and without alphanumeric serial numbers were analyzed. To provide additional "control" results, the NERL also analyzed a set of Whatman PTFE filters that are the same production type (with the PMP support ring marked with serial numbers) as has been used historically in the $PM_{2.5}$ monitoring network. The NERL utilized a Kevex™ energy dispersive x-ray spectrometer for these analyses. The Kevex™ was selected because it uses the largest diameter excitation beam of all commercial XRF instruments. It is still not clear that the beam is wide enough to impinge on the MTL serial numbers printed on the perimeter of the exposed membrane; however, it was concluded that the Kevex™ represents the highest probability of exposure and inclusion of the ink in the analysis.

2.3 Summary of Test Results

Table 3. Summary of the analyses of the data reported by the State Agencies and EPA labs and reports of mechanical problems or flow rate issues

Assessment \ Agency	South Carolina	Florida	Utah	Georgia	EPA Region 4	EPA ORD NERL
Bias Test	0.49%	0.23%	Satisfactory	-6.9%*	-0.9%**	NA
Mechanical Problems, (Leakage/flow) Reported	2 shuttle jams on R &P 2025; no leaks	None on R & P and Thermo 2025s; no leaks	None on Thermo 2025; no leaks	None on Thermo 2025; no leaks	None on BGI PQ200A no leaks	NA
XRF back-ground trace elements	NA	NA	NA	NA	NA	Non-detectable; inconclusive‡

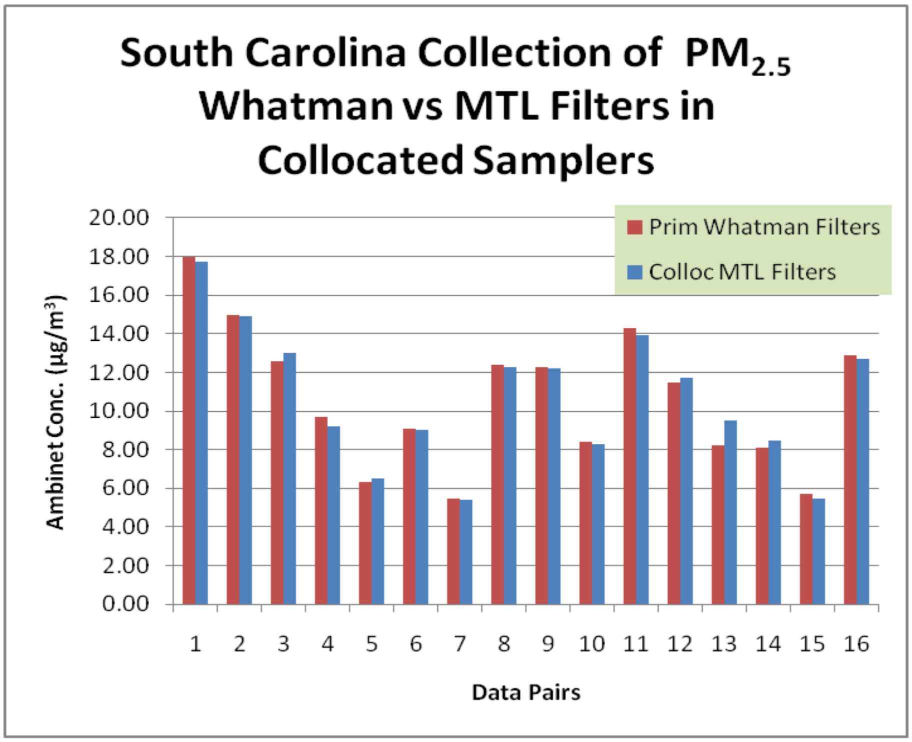
* The Results from Georgia could have been influenced by the fact that a separate lab (USEPA, NAREL) analyzed the MTL filters.
** A separate 2-sigma uncertainty test suggested that all Whatman-MTL data pairs exhibited indistinguishable results.
‡ The XRF instrument in this test utilizes the largest diameter excitation beam of all commercial units, but it may not have impinged on the printed serial numbers on the perimeter of the filter membrane. The possible introduction of elements to unexposed filters via the serial number in this position could not be assessed.

Below are charts that illustrate the data collected by the participating agencies and laboratories. Reported concentrations have been calculated exactly as they are for the national network results—by dividing the mass gain of the filter by the sampler's recorded, sample air volume. Bias in each data set has been calculated using the statistical metric specified in 40 CFR part 58 Appendix A, Section 4. An Excel version of this tool called the Data Assessment Statistical Calculator (DASC) can be accessed at EPA - TTN - AMTIC Quality Indicator Assessment Reports. In the DASC tool the "Audit" values are taken to be the results from the Whatman filters since they are the control values for the tests. It is important to realize that the data quality objective for bias across the US is ± 10% and precision between collocated samplers expressed as a coefficient of variation should be within ± 10%. The raw data is included in

Appendix 1. The report of the collocation study in Athens by EPA, ORIA/NAREL and the XRF analysis report by ORD/NERL are posted on AMTIC at http://www.epa.gov/ttn/amtic/quality.html [Information will eventually be migrated to a "Monitoring Filter QA/QC" Page].

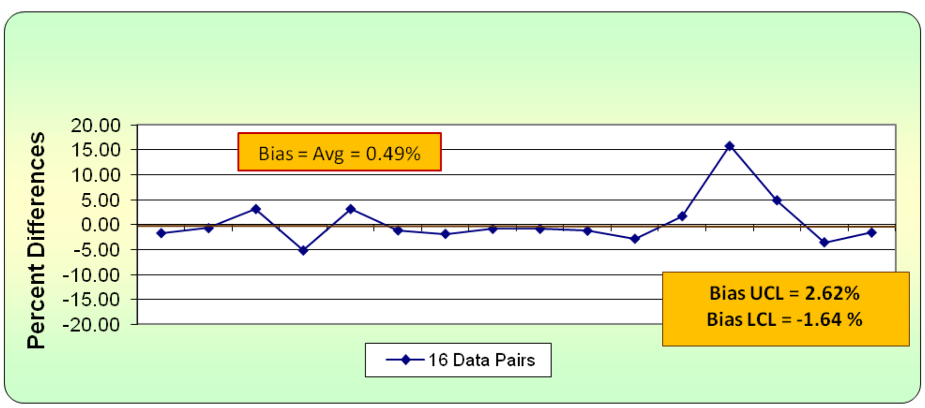
2.4 Detailed Data Analyses and Findings:

South Carolina



The average difference in concentration measured on the paired filters from South Carolina was 0.02 µg/m^3, and the standard deviation was 0.43 µg/m^3. There was one data pair (#13) that may have been an outlier, exhibiting a difference of 1.30 µg/m^3, but there was no disqualifying information. Figure 2. Illustrates The DASC tool bias calculation. The bias, the mean of the percent difference data all the data pairs was 0.49%.

Figure 1. South Carolina PM2.5 collected on Whatman and MTL Filters in Collocated R & P 2025 Partisol Samplers.



The upper and lower (95%) confidence limits were 2.73% and -1.76%, respectively. The bias for South Carolina's data set was clearly within the acceptance criteria specified in 40 CFR Part 58 Appendix A.

Figure 2. DASC tool analysis of South Carolina's Whatman vs. MLT Collocated $PM_{2.5}$ Data

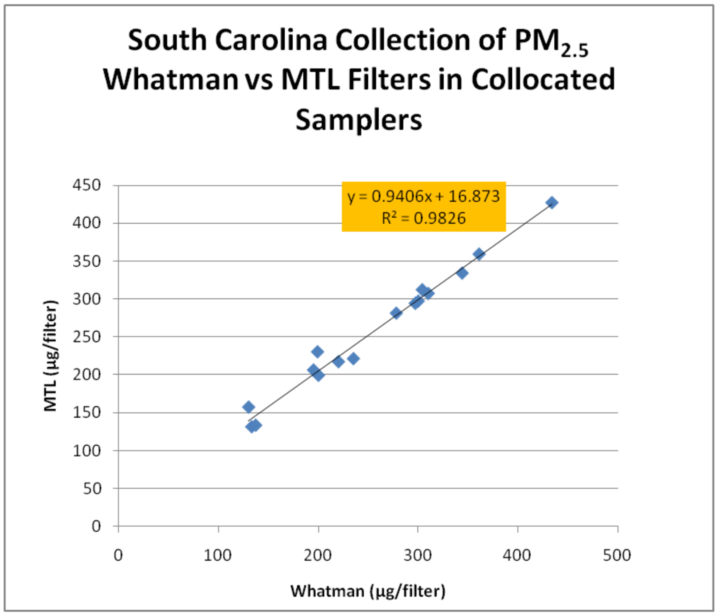


Figure 3. is scatter plot of the data based on comparing µg/filter in each data pair. Note the slope is nearly 1 to 1 and the intercept if divided by 24 m^3 would suggest a bias of about 0.7µg/m^3.

South Carolina reported two instances where their legacy R & P 2025 Partisol Samplers experienced jams in the shuttle mechanism when using cassettes containing MTL filters. Once was when a blue polycarbonate cassette was used and the other instance was when a white, delrin cassette was used. These pairings were not included in the results.

Figure 3. Scatter Plot of South Carolina MTL vs. Whatman Filter based PM $_{2.5}$ measurements

Florida

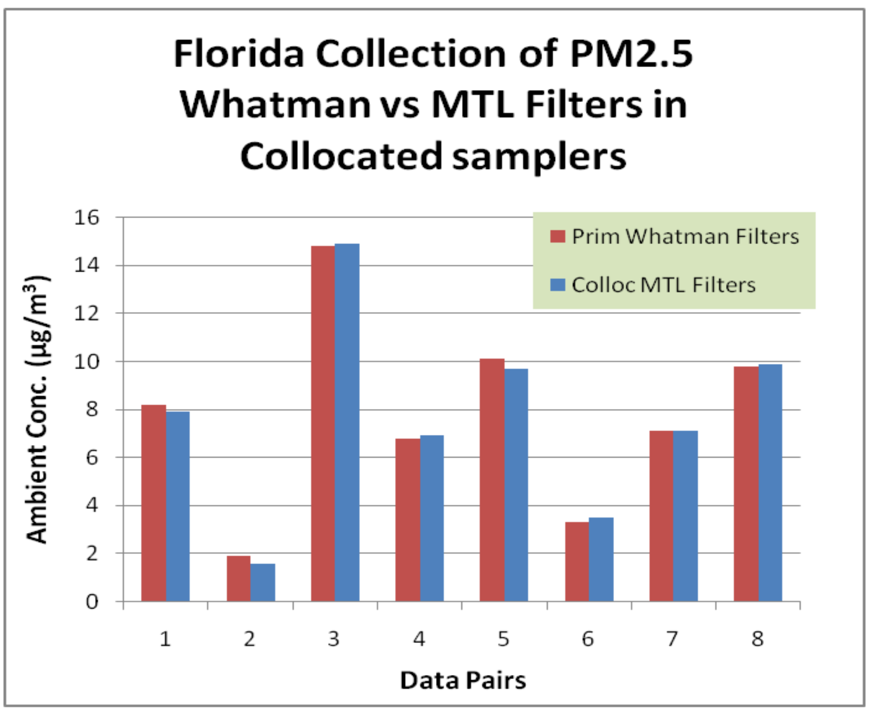


Figure 4 illustrates data submitted by Florida for 8 collocated sampling events. The average difference in concentration measured on the paired filters was 0.06 µg/m^3, and the standard deviation was 0.23 µg/m^3. On the scatter plot of µg/ filter in Figure 5, the slope is unity and the intercept would suggest a bias of -0.10 µg/m^3.

Figure 4. Florida $PM_{2.5}$ collected on Whatman and MTL Filters in Collocated Thermo 2025 Partisol Samplers.

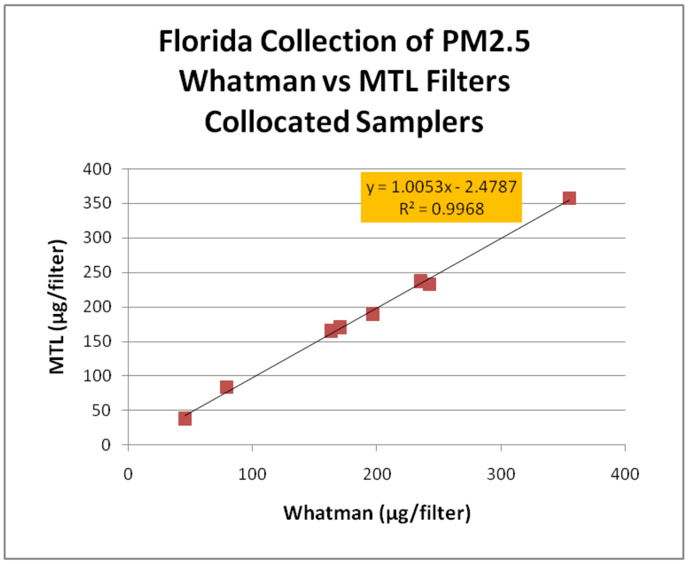


Figure 5. Scatter Plot of Florida MTL vs. Whatman Filter based $PM_{2.5}$ measurements

Note on Figure 4 that the second data pair indicates the ambient concentration fell below 3 µg/m^3. The regulations in 40 CFR part 58 Appendix A dictate that this data cannot be included in the bias statistic. It is interesting to observe that the absolute difference in the concentrations of pair #2 was 0.3 µg/m^3, which is still within 2 standard deviations of the mean difference for all the collocated 2025 Partisol data pairs reported for this study. The relative percent difference for this data pair is 15.8%. Recall pair #13 in the South Carolina data that exhibited a relative percent difference of 15% could not be deleted from the statistical analysis because both were above 3 µg/m^3. Notwithstanding the regulations, the bias (average of percent relative differences) was calculated without and then with data pair #2. The resulting bias without data pair #2 was 0. 23%, and the upper and lower confidence limits, shown below, were split.

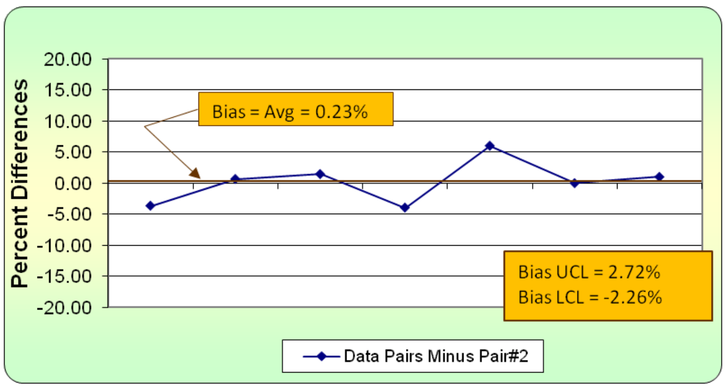


Figure 6. DASC tool analysis of Florida's Whatman vs. MLT Collocated $PM_{2.5}$ Data minus Pair #2

Including pair # 2 turned the bias negative (-1.7%) and dropped the lower confidence limit to -6.11%. Even though the effect was noticeable, this data falls within the acceptance criteria specified in 40 CFR Part 58 Appendix A.

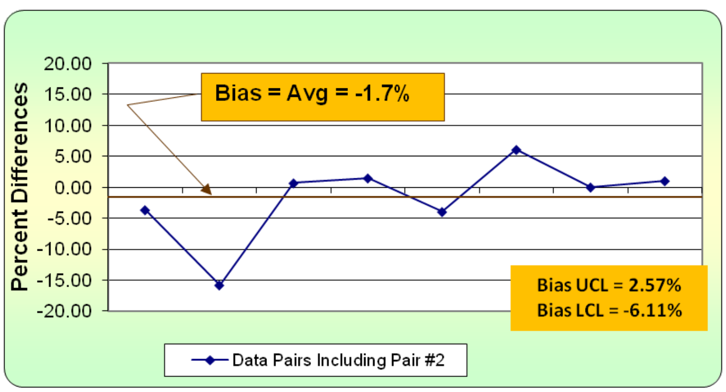
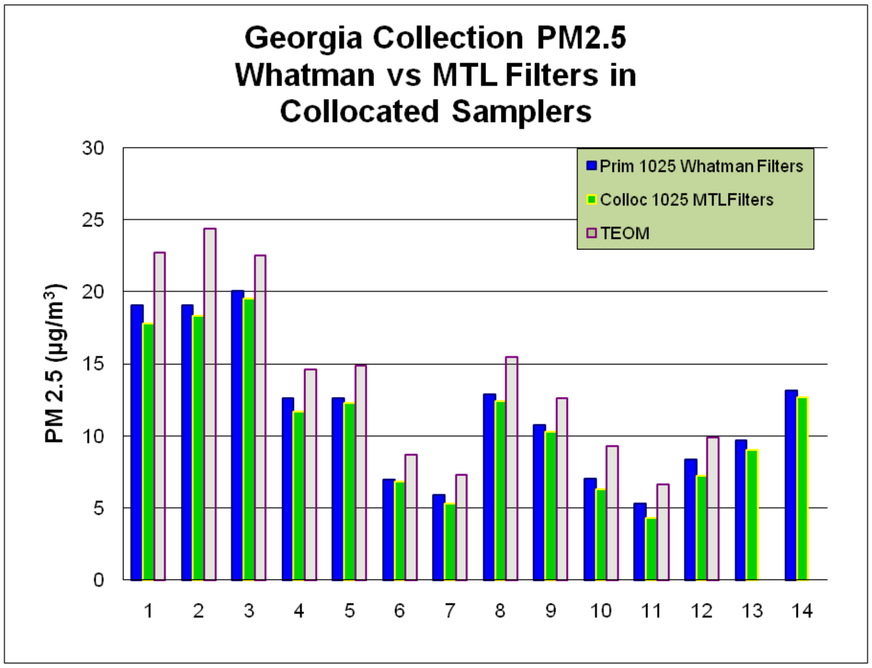


Figure 7. DASC tool analysis of Florida's Whatman vs. MLT Collocated $PM_{2.5}$ Data including Pair #2

Utah

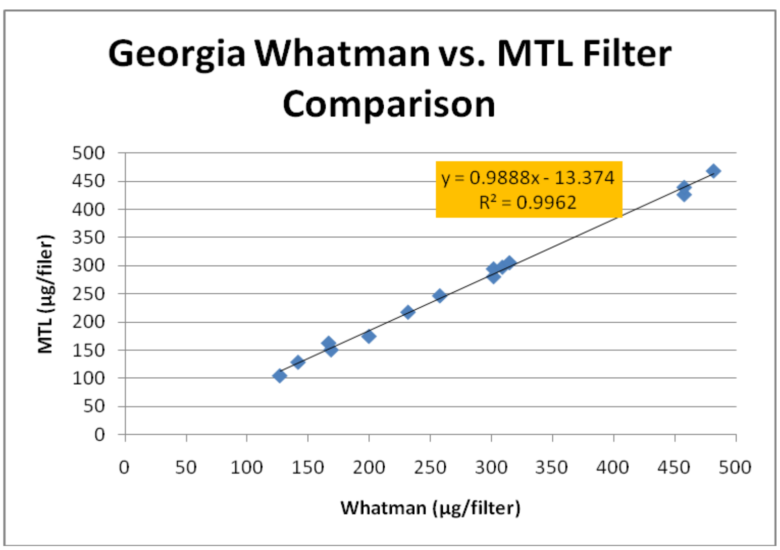
The Utah Division of Air Quality did not report any specific data. They did report that their test results were satisfactory and there were no mechanical issues associated with using the MTL filters in their Thermo 2025 Partisol samplers.

Georgia



The testing in Georgia yielded a bonus data set. Georgia was also running a Tapered Element Oscillating Microbalance (TEOM) at the South DeKalb site in Atlanta, GA. TEOMs have been designated by EPA as a Federal Equivalent Method for the measurement of $PM_{2.5}$ It is clearly seen that the TEOM consistently produced higher ambient measurements than the filter based measurements, although the data tracks with the filter- based data pretty well. This is a bias that has

Figure 8. Georgia $PM_{2.5}$ collected on Whatman and MTL Filters in Collocated Thermo 2025 Partisol Samplers and 24-hour values calculated from TEOM readings.



been recognized at other monitoring sites around the country. Given that the Whatman and MTL filter-base measurements are so close, a comparison with of the MTL filter base results with the TEOM results is beyond the scope and objectives of this study.

The average difference in measured concentrations between data pairs was very small, -0.7 $\mu g/m^3$. The standard deviation in the differences was 0.3 $\mu g/m^3$.

Figure 9. Scatter Plot of Georgia DNR MTL vs. Whatman Filter based $PM_{2.5}$ measurements

The scatter plot, in terms of µg/filter, also shows the close relationship between measurements on Whatman and MTL filters. The slope is 0.99 and the intercept is -13.4 which translates into an estimated bias of -0.6 $\mu g/m^3$.

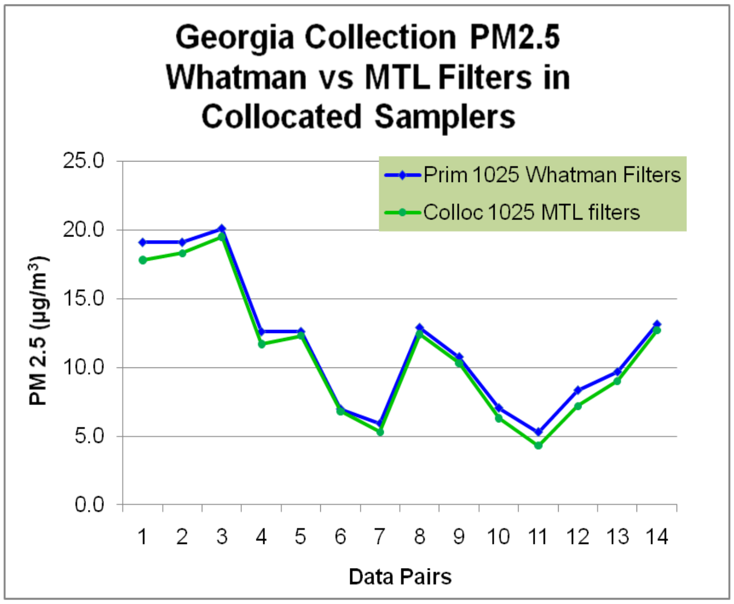


Figure 10. Georgia $PM_{2.5}$ collected on Whatman and MTL Filters in Collocated Thermo 2025 Partisol Samplers

The negative mean difference hints at one subtle but noticeable trend which can be seen more clearly on the line graph in Figure 10. The DASC tool analysis also supports the conclusion that there was a small negative bias reflected in the MTL filters analyses.

The bias, shown below in figure 11, was -6.9% and the (95%) upper and lower confidence limits were negative. It should be noted that the largest relative percent difference in measurements was seen in pair #11, which was the day with the lowest ambient concentration; but closer values would not reverse the overall trend of the data. Given the results from South Carolina, Florida, and EPA's test at the Region 4 Athens Laboratory, it is suspected that the negative bias in this case could be a consequence of having two separate labs involved in the gravimetric analyses.

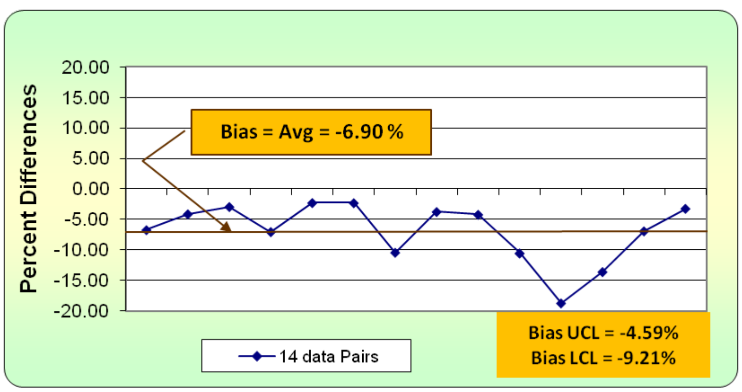


Figure 11. DASC tool analysis of Georgia's Whatman vs. MLT Collocated $PM_{2.5}$ Data

EPA's ORIA/NAREL provided the MTL filters and analyses, and the Georgia DNR tared and reweighed the Whatman filters. EPA plans to run a subsequent test in which ORIA/NAREL will supply and analyze both Whatman filters and MTL filters to the monitoring site at South Dekalb/ Atlanta, where they will be exposed in identical manner to the filters in this study. ORIA/NAREL will also conduct the post exposure reweighing. If the subsequent results are similar to those reported here then the conclusion would be that the bias is associated with slight differences in performance between the primary and the collocated sampler. Values that reflect no bias or that reverses the sign in the average would support the hypothesis that the bias introduced in the first assessment was a product of two different laboratories conducting the gravimetric analyses.

EPA Region 4 Ecosystems Support Division Laboratory in Athens, GA

The results of the bias test at EPA Region 4, are shown below in Figure 12. There were 33 random pairings from the 11 sampling events utilizing 6 BGI PQ200A FRM samplers. The field test also included 9 field blanks and 3 trip blanks. In 2 sampling events one of the samplers (not the same one in both) failed to complete the required minimum 23 hour run time. These two pairings were not valid for the purpose of determining any bias; therefore 31 valid random pairs were generated by the field test. The bias shown in Figure 13 as calculated from the EPA DASC

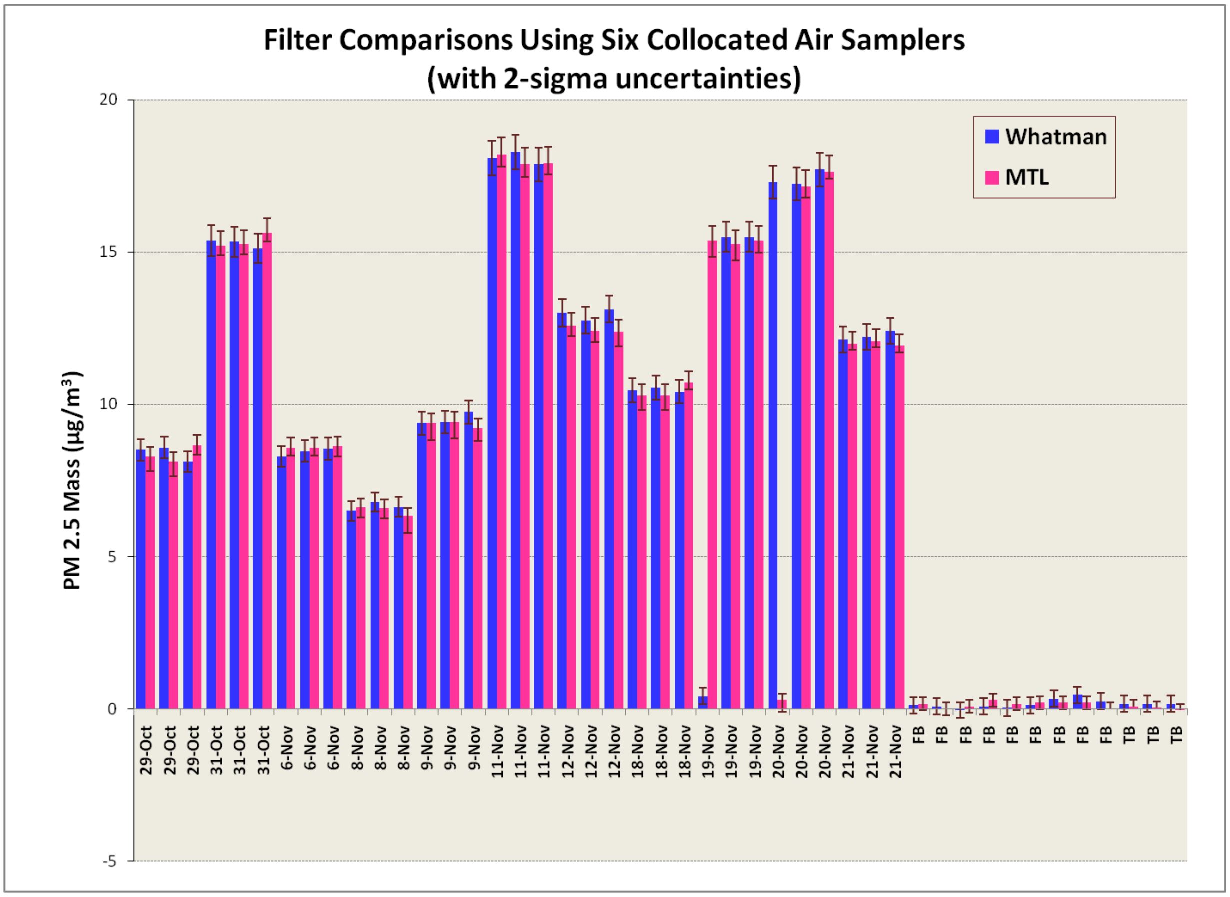


Figure 12. Bias test results from 6 BGI PQ200A $PM_{2.5}$ samplers using 3 Whatman filters and 3 MTL filters during each of 11 collocated sampling events

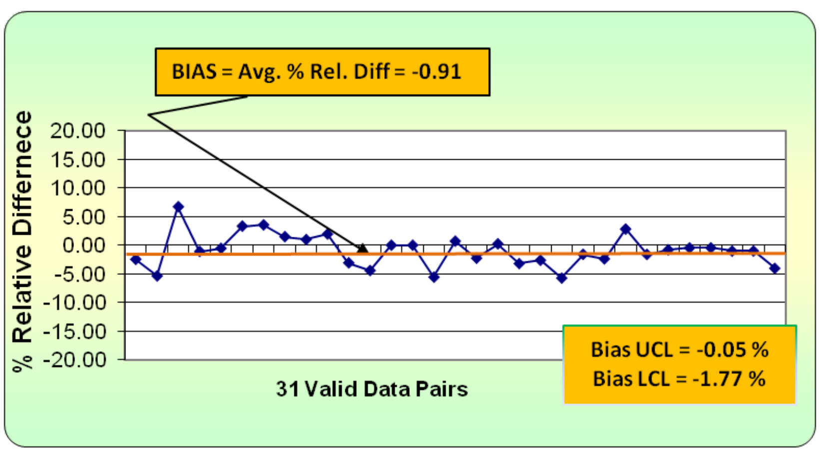


Figure 13. DASC tool analysis of PM2.5 Data collected on Collocated Samplers at EPA Region 4's SESD Lab in Athens, Georgia.

Tool was an unsurprising -0.91%. The upper and lower confidence limits were both negative which might suggest a very small negative bias; however, the value is well within the acceptance limits for bias specified in 40 CFR Part 58 Appendix A.

The use of three samplers for each filter during each sampling event and the collection of several field blanks and trip blanks facilitated the opportunity for NAREL to perform a 2-sigma uncertainty test on the randomly paired measurements of $PM_{2.5}$ mass on Whatman vs. MTL filters. As seen in Figure 12, a 2-sigma uncertainty is added to and subtracted from the measured mass gain of each filter so the whiskers are 4-sigma. This provides a 95% confidence that the real value lays The 1-sigma calculation is the square root of the sum of the squares of two uncertainties shown by the equation below. The first component is a simple standard deviation of all the blanks that were collected. In this analysis the range of values of field and trip blanks was so small that both sets of values were combined for the statistic. The second component in the equation is a type of precision metric calculated from each three values (or two values in the two cases of sampler malfunction). The relative deviation is the difference between each filter's mass gain and the average of the mass gains of all three (or 2) filters of the same type use for a sampling event. "One" standard deviation of all the relative deviations is determined for each type of filter for the entire sampling campaign. This standard deviation is multiplied by each filter's mass gain to derive the field measurement uncertainty for each mass gain value.

$$1\sigma_i = \surd[(Sd_{blk})^2 + (Sd_{rel.dev} \text{ x } M_i)^2] \text{ where}$$

Sd_{blk} = Standard deviation of the measured masses of the blanks,
$Sd_{rel.dev}$ = Standard deviation of the relative deviations of exposed (loaded) filters in %,
M_i = the mass/filter, of each sampling event, $\boldsymbol{i}$.

The average precision of both Whatman and MTL filter-based $PM_{2.5}$ measurements were the same (0.0% deviation) and the standard deviations around the means were an identical (1.4%). The average precision of the field and trip blanks was 0.0%, but the standard deviation of the precisions for both sets of filters differed substantially from the loaded filters, 82% for Whatman blanks and 89% for the MTL blanks. The relative deviations, and therefore the standard deviations, for precisions of each type of filter blanks were exaggerated due to the very small mass gain values (the largest value was 8.0 μg and the smallest was 0.0 μg). The impact of the blank uncertainty on the 1-sigma value is minimal because the mass gain on each blank was small and the standard deviation of the mass gains was correspondingly small.

If the 4-sigma brackets for a data pair overlap horizontally then uncertainty of the measurement makes the real value of each essentially indistinguishable from the other. Note that the whiskers on every valid pair overlap!

EPA ORD NERL XRF Evaluation of MTL Filters with and without Printed Serial Numbers

Project Objectives and Scope:

A complete report of the analysis that was conducted by EPA ORD NERL is located at http://www.epa.gov/ttn/amtic/quality.html [Information will eventually be migrated to a "Monitoring Filter QA/QC" Page]. The results of this analysis are summarized here.

The ORD NERL was supplied with 10 MTL filters with the filter ID marked on the filter itself, near the outer edge. NERL provided and analyzed 10 Whatman filters of the same model (product number) used historically by the PM2.5 FRM network. Filter ID numbers were marked on the support ring. NERL also analyzed 8 MTL filters with no ID markings. They verified that these MTL filters were the same product that MTL proposed to sell to EPA for the $PM_{2.5}$, PM-10, and low-volume Pb sampling networks with the exception that no serial numbers were printed on the filter membrane.

The objective was to determine if the MTL filter membrane contains any background levels elements that should be identified and quantified prior to using the MTL filters for collection and quantification of trace metals and Pb using XRF. The need to print the serial numbers on the filter membrane area sparked particular interest.

The ORD NERL utilized a Kevex™ energy dispersive x-ray spectrometer for these analyses. The Kevex™ was selected because its analytical capabilities and the requisite algorithms to convert the raw spectral data to concentrations are well understood. The Kevex™ also uses the largest diameter excitation beam of all commercial XRF instruments. It is still not clear that the beam is wide enough to impinge on the MTL serial numbers printed on the perimeter of the exposed membrane; however, it was concluded that the Kevex™ represents the highest probability of exposure.

Quality Assurance/Quality Control

The ORD NERL complied with their standard QA/QC procedures for XRF analyses. At the beginning and end of a run of samples a set of quality control filters are analyzed to monitor the operational status of the spectrometer. The QC parameters that are reviewed are (1) peak areas (which monitors change in sensitivity); (2) background areaș (which monitors contamination or background changes); (3) CHAN or centroid (which monitors gain and baseline adjustment to insure that spectra are assigned the correct centroid); and (4) FWHM (which monitors degradation of the detector resolution). These parameters are measured for elements ranging from sodium to lead and include atmospheric argon. The target and tolerance values are based on the average and standard deviation of at least 10 analyses of the quality control filters. The allowable range includes the target value plus or minus three standard deviations. Any deviation from these established limits is automatically flagged at run-time for quick review. This process results in a total of 68 measurements to assure proper operating condition of the XRF spectrometer. These tolerances were applied to the QC standards for the blank filter analyses (XRFID 3205). Table 1 gives a summary of the QC failures for XRFID 3205. There were only two failures – one peak area, one blank peak area - not exceeding 5-sigma. (1-sigma is one standard deviation of all the data points included in the array.) This met the target of 5 or less deviations greater than 3-sigma for the Kevex spectrometer.

Table 4. Number and Type of QC Failures for Each Sample Run

		Beginning QC				End QC			
XRFID	Analysis Start Date	Bkgd Area	Peak Area	Centroid	FWHM	Bkgd Area	Peak Area	Centroid	FWHM
3205	9/30/10	0	1	0	0	1	0	0	0

To monitor the accuracy of the spectrometer, reference materials of known concentrations are analyzed and the beginning and end of each sample run. NIST certified reference standard, Standard Reference Material SRM1833-1425 and SRM 1832-1365, were analyzed at the beginning and end respectively of each analysis. The acceptance criterion for accuracy is that the XRF concentration ± 3 times the uncertainty must overlap the NIST certified concentration ± 1 times its reported uncertainty.

Table 5 shows the percent difference between the SRM element concentrations from each analysis and the NIST certified concentrations. XRF results not meeting the acceptance criterion are in bold font.

Table 5. Percent Difference Between the SRM Element Concentrations from Each Analysis and the NIST Certified Concentrations

	SRM 1833 - % Difference from NIST concentrations						SRM 1832 - % Difference from NIST concentrations							
XRFID	Si	K	Ti	Fe	Zn	Pb	Na	Al	Si	Ca	V	Mn	Co	Cu
3205	0.0	-8.1	-0.6	-3.8	-0.9	3.6	4.2	5.6	-2.3	0.4	7.4	4.6	4.8	**-10.3**

The reported Cu concentration for SRM 1832-1356 had been previously determined to be higher than the true value (R. Kellogg, personal communication). A concentration reported incorrectly high would lead to measured concentrations low compared to the reported value and possibly to failures in the acceptance criteria. For XRF ID's 2894 – 2903, XRF results for Cu did not meet the acceptance criterion for accuracy. Based on information previously reported, this result was expected and can be disregarded in the accuracy evaluation. All other elements in the newer SRM filters met the acceptance criterion for accuracy.

Results and Conclusions from XRF Analysis of Blank MTL Filters

The data tables presented in NERL's report include frequency of detection and average signal-to-noise. Average concentrations of all elements on all blank filter types were lower than the limit of quantification. All elements on all blank filter types had an average signal-to-noise of greater than 3.0, with most being below 1.0. Nearly all elements on all filters were detected at a frequency of 20% or less – most were always below detection. Since most values were below the limit of detection, meaningful graphs or charts could not be generated.

These results indicate that the "on-filter" markings do not have a significant influence on the XRF analytical results. However, the markings were located on the edge of the filter, so it could be that the markings simply were not impacted by the fluorescer radiation. Thus, it could not be determined from this experiment whether the markings have sufficiently low elemental composition to influence the XRF results or if the markings simply were not in the active XRF analysis area of the filter. A firm conclusion on the influence of serial numbers printed on the interior of the filter membrane area must be based on further analyses.

Additional analyses are planned involving ICPMS analysis of the ink and filters that have serial numbers printed on them. Additional XRF analyses are planned for filters that have bar-coded serial numbers printed on the interior area of the filter membrane.

Appendix 1

Data Submitted by Participating State and Federal Laboratories

South Carolina Collocated Whatman vs. MTL Filter $PM_{2.5}$ Results

						MTL			Whatman					
installdate	run date	day	cass color	cassID	filter#	BH DUP ug/m3	NetWgt mg/filter		BH Ref ug/m3	NetWgt mg/filter	filter #		DiffNetWgt µg/filter	Diff conc. (µg/m^3)
7-Oct	11-Oct	Mon	blue	62291	0559381	17.7	0.427		18.0	0.434	0559380		-7.000	-0.30
	14-Oct	Thur	blue	91128	1500186	14.9	0.359		15.0	0.361	0559416		-2.000	-0.10
	17-Oct	Sun	blue	74629	0559453	13.0	0.312		12.6	0.304	0559479		8.000	0.40
18-Oct	20-Oct	Wed	white	10484	1500187	22.7	0.547		void			magazine not installed		
	23-Oct	Sat	white	126	0559562	9.2	0.221		9.7	0.235	0559597		-14.000	-0.50
	26-Oct	Tue	white	84489	1500188	6.5	0.157		6.3	0.130	0559601		27.000	0.20
28-Oct	29-Oct	Fri	blue	78136	0559627	9.0	0.217		9.1	0.220	0559676		-3.000	-0.10
	1-Nov	Mon	white	2525	1500189	9980	void		12.6	0.303	0559679	filter exchange failure		
	4-Nov	Thur	white	125	0559715	5.4	0.131		5.5	0.133	0559713		-2.000	-0.10
	7-Nov	Sun	blue	21943	1500190	9980	void		7.6	0.183	0559767	filter exchange failure		
8-Nov	10-Nov	Wed	white	110	0559799	12.3	0.297		12.4	0.300	0559815		-3.000	-0.10
	13-Nov	Sat	blue	91105	1500191	12.2	0.294		12.3	0.297	0559819		-3.000	-0.10
15-Nov	16-Nov	Tue	white	15041	0559872	8.3	0.199		8.4	0.200	0559873		-1.000	-0.10
	19-Nov	Fri	blue	78131	1500192	13.9	0.334		14.3	0.344	0559934		-10.000	-0.40
	22-Nov	Mon	blue	51381	0559933	11.7	0.281		11.5	0.278	0559938		3.000	0.20
23-Nov	25-Nov	Thur	white	2506	1500193	9.5	0.230		8.2	0.199	0685002		31.000	1.30
	28-Nov	Sun	white	15040	0559986	8.5	0.206		8.1	0.195	0685007		11.000	0.40
29-Nov	1-Dec	Wed	blue	21475	1500194	5.5	0.133		5.7	0.137	0685039		-4.000	-0.20
	4-Dec	Sat	white	78143	0685048	12.7	0.307		12.9	0.310	0685145		-3.000	-0.20
												AVG	1.750	0.019
											Std Dev		12.222929	0.412642

Florida DEP MTL "Test" Filter PM2.5 Lab Results

							Mass Conc. (ug/m3)						
Sample Date	Filter ID	Pre Weight Date	Pre Weight (mg)	Post Weight Date	Post Weight (mg)	Delta (ug)	MTL "Test" Filter (Co-located)	Regular FRM Filter (Primary)		CV	MTL (ug/filter)	Whatman (ug/filter)	Difference D (ug/filter)
09/23/10	P1500197	09/20/10	401.278	09/21/10	401.469	191	7.9	8.2	-0.3	1.021	189.6	196.8	-7.2
09/26/10	P1500198	09/20/10	402.916	09/21/10	402.955	39	1.6	1.9	-0.3	1.021	38.4	45.6	-7.2
10/02/10	P1500199	09/28/10	410.463	10/18/10	410.822	359	14.9	14.8	0.1	0.699	357.6	355.2	2.4
10/05/10	P1500200	09/28/10	411.219	10/18/10	411.385	166	6.9	6.8	0.1	0.699	165.6	163.2	2.4
10/23/10	P1500251	10/18/10	410.834	11/08/10	411.068	234	9.7	10.1	-0.4	1.451	232.8	242.4	-9.6
10/26/10	P1500252	10/18/10	406.103	11/08/10	406.187	84	3.5	3.3	0.2	1.129	84	79.2	4.8
10/29/10	P1500253	10/26/10	407.062	11/08/10	407.233	171	7.1	7.1	0	0.269	170.4	170.4	0
11/01/10	P1500254	10/26/10	403.295	11/08/10	403.533	238	9.9	9.8	0.1	0.699	237.6	235.2	2.4
11/02/10	P1500255	10/26/10	404.151	11/08/10	404.150	-1	Blank	NA					
								AVG Diff	-0.062			Avg Diff	-1.5
								Std Dev	0.233			Std Dev	5.58

Georgia DNR (S. Dekalb) Collocated Whatman vs. MTL filters, $PM_{2.5}$

											MTL Filters Tared and weighed by EPA ORIA/NAREL-Collocated 2025				Whatman filters Tared and weighed by GA DNR-From prim 2025 FRM Sampler						
Magazine Number	Filter Serial Number	Cassette Number	Tare Mass (mg)	Tare Mass Date	Lab Out Date	Sampling Date	Lab In Date	Sampling Mass (mg)		Post Sampling Date	PM Mass (mg/filter)	Air Volume (m3)	PM Mass Concentration (µg/m3)		PM Mass (mg/filter)	Air Volume (m3)	PM Mass Concentration (µg/m3)		Diff Mass MTL-What (mg/filter)	Diff Conc MTL-What (µg/m3)	RPD %
038	P1500226	21671	402.141	09/15/10	09/l6/10	09/2l/10	10/05/10	402.567		10/07/10	0.426	24.0	17.8		0.458	24.0	19.1		-0.032	-1.28	-6.7%
038	P1500227	21672	399.932	09/15/10	09/l6/10	09/22110	10/05/10	400.371	*	10/07/10	0.439	24.0	18.3		0.458	24.0	19.1		-0.019	-0.78	-4.1%
038	P1500228	21673	405797	09/15/10	09/l6/10	09/23/10	10/05/10	406.265		10/07/10	0.468	24.0	19.5		0.482	24.0	20.1		-0.014	-0.58	-2.9%
038	P1500229	21674	405.188	09/15/10	09/l6/10	09/24/10	10/05/10	405.468		10/07/10	0.280	24.0	11.7		0.302	24.0	12.6		-0.022	-0.88	-7.0%
038	Pl500230	21687	405.334	09/15/10	09/l6/10	09/25/10	10/05/10	405.628		10/07/10	0.294	24.0	12.3		0.302	24.0	12.6		-0.008	-0.28	-2.3%
038	P1500231	21775	403.671	09/15/10	09/l6/10	09/26/10	10/05/10	403.833		10/07/10	0.162	24.0	6.8		0.167	24.0	7.0		-0.005	-0.16	-2.3%
038	Pl500232	21777	400.908	09/15/10	09/l6/10	09/27/10	10/05/10	401.036		10/07/10	0.128	24.0	5.3		0.142	24.0	5.9		-0.014	-0.62	-10.4%
039	Pl500234	21779	406.105	09/15/10	09/l6/10	10/01/10	10/13/10	406.402		10/l4/10	0.297	24.0	12.4		0.309	24.0	12.9		-0.012	-0.48	-3.7%
039	Pl500235	21780	399.578	09/15/10	09/l6/10	10/02/10	10/13/10	399.824		10/l4/10	0.246	24.0	10.3		0.258	24.0	10.8		-0.012	-0.45	-4.2%
039	Pl500236	32235	392.599	09/15/10	09/l6/10	10/03/10	10/13/10	392.749		10/l4/10	0.150	24.0	6.3		0.169	24.0	7.0		-0.019	-0.74	-10.5%
039	Pl500237	32242	403.069	09/15/10	09/l6/10	10/04/10	10/13/10	403.173		10/l4/10	0.104	24.0	4.3		0.127	24.0	5.3		-0.023	-0.99	-18.7%
039	P1500238	32243	405.990	09/15/10	09/l6/10	10/05/10	10/13/10	406.164		10/l4/10	0.174	24.0	7.2		0.200	24.0	8.3		-0.026	-1.13	-13.6%
039	P1500239	32244	398.868	09/15/10	09/l6/10	10/06/10	10/13/10	399.085		10/l4/10	0.217	24.0	9.0		0.232	24.0	9.7		-0.015	-0.67	-6.9%
039	P1500240	32249	392.521	09/15/10	09/l6/10	10/07/10	10/13/10	392.826		10/l4/10	0.305	24.0	12.7		0.315	24.0	13.1		-0.010	-0.42	-3.2%
038	P1500233	21778	398.051	09/15/10	09/l6/10	*FE*	10/05/10	398.058		10/07/10	0.007	*FE*	0.3	**							
039	Pl500241	32254	394.999	09/15/10	09/l6/10	FE	10/13/10	395.001		10/l4/10	0.002	FE	0.1								
**This post sampling mass measurement may have been very slightly affected by an accident in the laboratory.*																	Avg		-0.017	-0.68	-6.9%
** the PM concentration calculatedfor thisfield blank was based upon an air volume of 24 cubic meters.*																	Std Dev		0.007	0.32	4.9%

Whatman vs. MTL Filter BIAS: 6 BGI PQ200 Samplers, 11 Samping events, EPA Region 4 Athens, GA,								
Sampling Date	**Cassette Number**	**Whatman (µg/m^3)**	**Sampler ID**	**Whatman 2-sigma Uncert. (µg/m^3)**	**Cassette Number**	**MTL (µg/m^3)**	**Sampler ID**	**MTL 2-sigma Uncert. (µg/m^3)**
29-Oct	W593	8.500	629	0.353	M643	8.292	636	0.312
29-Oct	W595	8.583	637	0.354	M645	8.125	630	0.309
29-Oct	W597	8.125	633	0.346	M647	8.667	631	0.320
31-Oct	W600	15.375	629	0.495	M650	15.208	636	0.473
31-Oct	W601	15.333	637	0.494	M651	15.250	630	0.474
31-Oct	W603	15.125	633	0.489	M653	15.625	631	0.484
6-Nov	W604	8.292	629	0.349	M654	8.583	636	0.318
6-Nov	W605	8.458	637	0.352	M655	8.583	630	0.318
6-Nov	W606	8.542	633	0.353	M656	8.625	631	0.319
8-Nov	W607	6.500	636	0.320	M657	6.625	629	0.279
8-Nov	W608	6.792	630	0.324	M658	6.583	637	0.279
8-Nov	W609	6.625	631	0.322	M659	6.333	633	0.274
9-Nov	W610	9.375	636	0.369	M660	9.375	629	0.335
9-Nov	W613	9.417	630	0.369	M663	9.417	637	0.336
9-Nov	W615	9.750	631	0.376	M665	9.208	633	0.332
11-Nov	W618	18.083	629	0.558	M668	18.208	636	0.549
11-Nov	W619	18.292	637	0.563	M669	17.875	630	0.541
11-Nov	W620	17.875	633	0.553	M670	17.917	631	0.542
12-Nov	W621	13.000	636	0.442	M671	12.583	629	0.409
12-Nov	W623	12.750	637	0.437	M673	12.417	630	0.405
12-Nov	W624	13.125	631	0.445	M674	12.375	633	0.404
18-Nov	W625	10.458	629	0.390	M675	10.292	636	0.355
18-Nov	W626	10.542	630	0.391	M676	10.292	637	0.355
18-Nov	W627	10.417	633	0.389	M677	10.708	631	0.365
19-Nov	W628	0.417	629	0.267	M678	15.375	630	0.477
19-Nov	W629	15.500	637	0.498	M679	15.250	633	0.474
19-Nov	W630	15.500	636	0.498	M680	15.375	631	0.477
20-Nov	W631	17.292	636	0.540	M681	0.292	629	0.210
20-Nov	W633	17.250	630	0.539	M683	17.167	637	0.523
20-Nov	W634	17.708	631	0.550	M684	17.625	633	0.534
21-Nov	W635	12.125	636	0.424	M685	12.000	629	0.395
21-Nov	W637	12.208	630	0.425	M687	12.083	637	0.397
21-Nov	W639	12.417	631	0.430	M689	11.917	633	0.393
FB	W594	0.125	629	0.267	M644	0.167	636	0.210
FB	W596	0.083	637	0.267	M646	0.000	630	0.210
FB	W598	-0.042	633	0.267	M648	0.083	631	0.210
FB	W611	0.083	636	0.267	M661	0.292	629	0.210
FB	W614	0.042	630	0.267	M664	0.167	637	0.210
FB	W616	0.125	631	0.267	M666	0.208	633	0.210
FB	W636	0.333	636	0.267	M686	0.208	629	0.210
FB	W638	0.458	630	0.267	M688	0.208	637	0.210
FB	W640	0.250	631	0.267	M690	0.000	633	0.210
TB	W599	0.167	-----	0.267	M649	0.083	-----	0.210
TB	W617	0.167	-----	0.267	M667	0.042	-----	0.210
TB	W641	0.167	-----	0.267	M691	-0.042	-----	0.210