TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS

FROM: Eric Boswell / NAREL

AUTHOR: Steve Taylor / NAREL

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SUBJECT: Gravimetric Inter-Laboratory Comparison Study

Introduction

The EPA's National Air and Radiation Environmental Laboratory (NAREL) conducts semi-annual gravimetric inter-laboratory comparison studies as part of its quality assurance support of EPA's Office of Air Quality Planning and Standards (OAQPS). The purpose of the gravimetric studies is to evaluate EPA and State laboratories that weigh Teflon® filters used for the determination of $PM_{2.5}$ collected with Federal Reference Method (FRM) ambient air samplers. Results for the second study of 2011 have been submitted by participating laboratories. The EPA participants were the Region 4 laboratory in Athens, GA; and the Office of Air Quality Planning and Standards (OAQPS) laboratory in Research Triangle Park (RTP), NC. Also participating in this study was the Puerto Rico Environmental Quality Board (PREQB) laboratory. NAREL coordinated this study by supplying performance test (PT) samples and served as the reference laboratory.

Mass determination of $PM_{2.5}$ is performed using a microbalance to weigh the Teflon® collection filter before and after the sampling event. The amount of particulate matter ($PM_{2.5}$) captured onto the surface of the filter can be calculated by a simple subtraction of the filter tare mass or Pre-mass from the sampled filter mass or Post-mass. In order to accurately measure particulate mass at microgram levels, the microbalance must be located in a clean, dust free environmental chamber with precise temperature and humidity control. Elimination of static from samples is also very important for accurate mass measurements.

Filters used in the study were 47 mm Teflon® filters manufactured by Measurement Technology Laboratory (MTL). 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 47 mm Polytetrafluoroethylene (PTFE) filters. Historically, Whatman has supplied 47 mm Teflon® filters to the networks. The MTL filters use the same filter membrane material as Whatman; however, the support ring is made from polyfluoroalkoxy (PFA) which is over twice as dense as the polymethylpentene (PMP) support ring used by Whatman. As a result, the nominal filter mass of the MTL filter is 377-410 mg compared to the Whatman nominal mass of 146-150 mg. NAREL has replaced its 200 mg high side quality control check weight with a 500 mg weight in order to accommodate the larger mass range. Another noticeable difference between MTL and Whatman filters is the serial number location. MTL filters have the serial number printed on both sides of the membrane instead of on the filter support ring.

Samples for this study were created at NAREL using Met One SASS air samplers to collect various amounts of $PM_{2.5}$ onto Teflon® filters. In addition to the loaded filter samples, blank filters and metallic weights were included as controls and to provide information concerning balance stability and calibration. This study compares captured mass determined by NAREL to captured mass determined by each of the participating laboratories.

Acceptance criteria for this type of comparison have not been established. There are PEP criteria established for laboratory and field blanks, and metallic standards. According to the PEP criteria, laboratory and field blanks should not vary by more than 0.015 mg and 0.030 mg respectively between Pre- and Post-measurements. Metallic standards should not vary by more than 0.003 mg. As an alternative to the PEP criteria, this study uses criteria based on actual mass data compiled from gravimetric PE studies administered by NAREL.

Experimental

Three sample sets consisting of ten new MTL Teflon® filters and two metallic weights were assembled for each of the participating test laboratories. Each filter was carefully inspected using a light table to check for pinholes and fibers. The metallic weights were commercially available 100 and 500 milligram stainless steel weights that were slightly altered by clipping a small corner section from each weight. The samples were placed into individual labeled Petri-slides and shipped by overnight mail to each test laboratory with instructions to Pre-weigh each sample following their standard operating procedures for the determination of $PM_{2.5}$ mass. Sample sets were then returned and NAREL's tare mass measurements were determined.

Three co-located Met One Super SASS air samplers were used to load seven filters from each sample set with $PM_{2.5}$ mass. The loading schedule for the filters is shown in table 1.

Table 1 Sampling Schedule for Gravimetric PT Filters

Filter ID	Serial Number	Sample Start	Hours Sampled	Receiving Lab
T11-14115	T1550504	10/20/2011	24	Region 4
T11-14116	T1550505	10/20/2011	24	Region 4
T11-14117	T1550506	10/20/2011	24	Region 4
T11-14118	T1550507	10/20/2011	24	Region 4
T11-14135	T1550524	10/20/2011	24	OAQPS
T11-14136	T1550525	10/20/2011	24	OAQPS
T11-14137	T1550526	10/20/2011	24	OAQPS
T11-14138	T1550527	10/20/2011	24	OAQPS
T11-14145	T1550534	10/20/2011	24	PREQB
T11-14146	T1550535	10/20/2011	24	PREQB
T11-14147	T1550536	10/20/2011	24	PREQB
T11-14148	T1550537	10/20/2011	24	PREQB
T11-14119	T1550508	10/21/2011	40	Region 4
T11-14120	T1550509	10/21/2011	40	Region 4
T11-14121	T1550510	10/21/2011	40	Region 4
T11-14139	T1550528	10/21/2011	40	OAQPS
T11-14140	T1550529	10/21/2011	40	OAQPS
T11-14141	T1550530	10/21/2011	40	OAQPS
T11-14149	T1550538	10/21/2011	40	PREQB
T11-14150	T1550539	10/21/2011	40	PREQB
T11-14151	T1550540	10/21/2011	40	PREQB

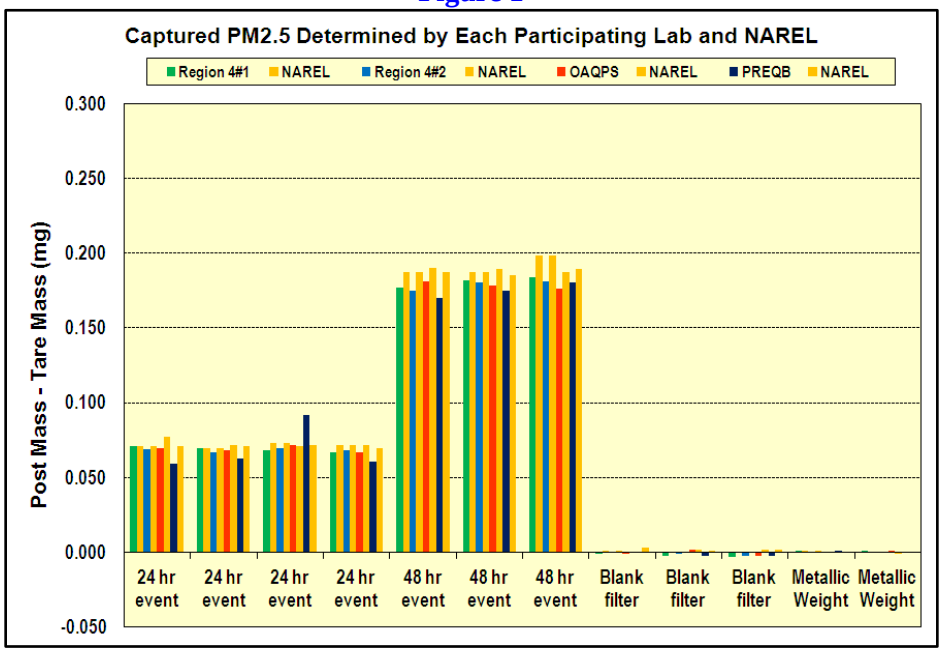
Table 1 shows that 21 filters were loaded using two sampling events. Twelve filters sampled in the 24-hour event created four replicates for each lab while the 40-hour event created three replicates for each lab.

Following each collection event, samples were returned to NAREL's weighing chamber for equilibration. After all samples were equilibrated, Post-mass measurements were determined for all loaded filters as well as the blank filters and metallic weights. The filters and metallic weights were packed into small coolers with ice substitute and shipped back to the test labs for their final weighing.

Gravimetric Results

Figures 1 and 2 summarize the results of this study. The $PM_{2.5}$ mass capture for the seven loaded filters, the three travel blanks, and two metallic weights are plotted in figure 1. Region 4 delivered results from two analysts and both data sets are included.

Figure 1



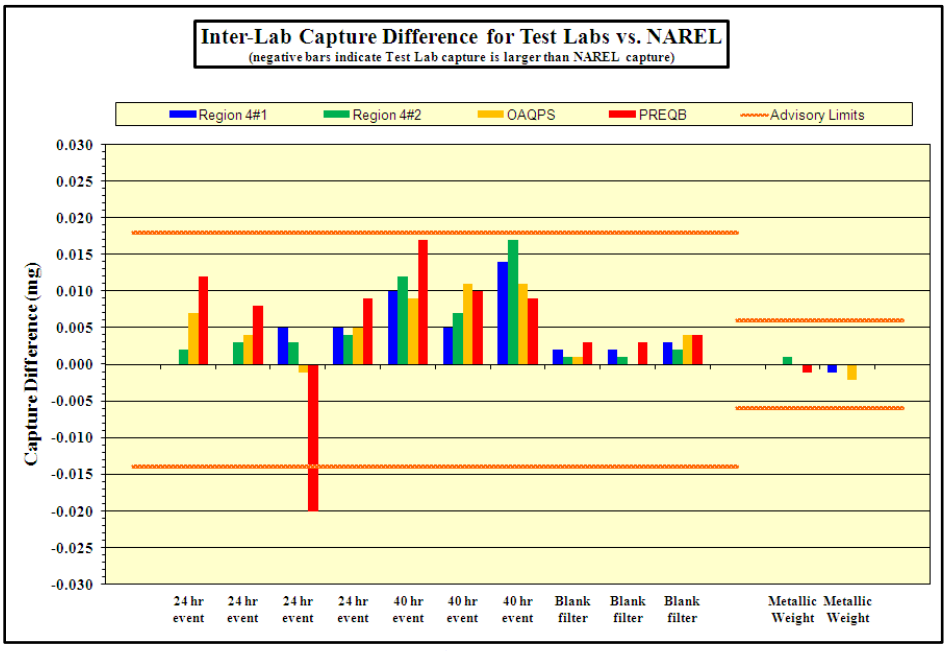


Figure 2

Figure 2 presents the inter-laboratory differences with advisory limits. Inter-laboratory differences were calculated by subtracting the $PM_{2.5}$ capture value determined at each test lab from the capture value determined at NAREL. Absence of a bar indicates a zero difference for that comparison. The 3-sigma advisory limits were derived from all of the gravimetric PT studies administered by NAREL during the past several years.

Figure 2 shows all comparisons are within the 3-sigma limits except for one outlier. Notice a majority of positive bars in figure 2, indicating a larger capture value determined by NAREL. Previous studies at NAREL have shown that it is not unusual for loaded filters to slowly lose mass over time due to loss of semivolatile organic components. Larger mass captures tend to lose more than lightly loaded filters. Table 2 lists the elapsed number of days between the sample loading dates and Post-mass measurements. For this study, the NAREL Post-mass measurements of the 40-hour samples were performed only two days after the end of the sampling event. The first test lab to weigh the loaded filters occurred eight days after the sampling event. Figure 1 shows that NAREL's capture was consistently higher than the test labs for the 40-hour event. Figure 1 also shows that the test labs had better agreement among themselves than with NAREL, suggesting that a longer stabilization period at NAREL could reduce the inter-laboratory capture differences between NAREL and the test labs. NAREL typically allows several days of filter stabilization. However, for this study, scheduling conflicts prevented this.

Table 2

		Days Between Sampling and Post-Wt.	
Laboratory	**Date of Post_Wt.**	**24-hr Sample***	**40-hr Sample****
NAREL	10/26/11	5	2
OAQPS	11/01/11	11	8
Region 4 #1	11/09/11	19	16
Region 4 #2	11/10/11	20	17
PREQB	11/10/11	20	17

*** 24-hr Sample End Date - 10/21/11**

**** 40-hr Sample End Date - 10/24/11**

Metallic weights were included in this study because they are usually less susceptible to weighing errors due to factors such as electrical static and volatility of filter constituents. The metallic weights were weighed at each laboratory during the initial tare sessions as well as during the final loaded sessions. The difference in initial and final mass is the calculated "mass capture" for the metallic weights. Ideally, the "mass capture" for the metallic weight samples would be zero. A large difference between an initial and final mass could indicate a balance stability or calibration problem.

The raw data reported from all laboratories have been tabulated in table 3 at the end of this report. The table includes the results of all filters and the metallic standards weighed at each laboratory. The tables contain the filter Pre-mass, the Post-mass, and the calculated $PM_{2.5}$ capture for each sample.

Conclusions

This inter-laboratory study evaluated laboratories that perform gravimetric measurements of $PM_{2.5}$ collected on 47-mm Teflon® filters. The Teflon® filters used for this study were manufactured by Measurement Technology Laboratory (MTL). Samples for this study were created by loading filters with $PM_{2.5}$ collected from the ambient air using co-located Met One samplers. Blank filters and metallic weights were also included as samples. Each laboratory was allowed to Pre-weigh and Post-weigh a unique set of samples in order to determine the mass capture. NAREL served as the reference lab by weighing all samples. Performance was evaluated by comparing mass capture results produced by NAREL to results produced by each participating laboratory. The results of this study show overall good inter-laboratory agreement of all participating laboratories.

Table 3. Gravimetric Mass PT Results

Sample ID	Sample Description	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$ (mg)	Name of the Test Lab
		Test Lab (mg)	NAREL (mg)	Test Lab (mg)	NAREL (mg)	Test Lab (mg)	NAREL (mg)		
T11-14115	24-hour Event	373.795	373.790	373.866	373.861	0.071	0.071	0.000	Region 4 #1
T11-14116	24-hour Event	378.608	378.601	378.678	378.671	0.070	0.070	0.000	Region 4 #1
T11-14117	24-hour Event	385.409	385.401	385.477	385.474	0.068	0.073	0.005	Region 4 #1
T11-14118	24-hour Event	377.692	377.684	377.759	377.756	0.067	0.072	0.005	Region 4 #1
T11-14119	40-hour Event	372.595	372.588	372.772	372.775	0.177	0.187	0.010	Region 4 #1
T11-14120	40-hour Event	376.371	376.366	376.553	376.553	0.182	0.187	0.005	Region 4 #1
T11-14121	40-hour Event	382.025	382.018	382.209	382.216	0.184	0.198	0.014	Region 4 #1
T11-14122	Blank	377.827	377.819	377.826	377.820	-0.001	0.001	0.002	Region 4 #1
T11-14123	Blank	377.804	377.797	377.802	377.797	-0.002	0.000	0.002	Region 4 #1
T11-14124	Blank	380.719	380.711	380.716	380.711	-0.003	0.000	0.003	Region 4 #1
MW11-14155	Metal Weight	478.384	478.384	478.385	478.385	0.001	0.001	0.000	Region 4 #1
MW11-14156	Metal Weight	91.557	91.558	91.558	91.558	0.001	0.000	-0.001	Region 4 #1
T11-14115	24-hour Event	373.797	373.790	373.866	373.861	0.069	0.071	0.002	Region 4 #2
T11-14116	24-hour Event	378.608	378.601	378.675	378.671	0.067	0.070	0.003	Region 4 #2
T11-14117	24-hour Event	385.409	385.401	385.479	385.474	0.070	0.073	0.003	Region 4 #2
T11-14118	24-hour Event	377.692	377.684	377.760	377.756	0.068	0.072	0.004	Region 4 #2
T11-14119	40-hour Event	372.596	372.588	372.771	372.775	0.175	0.187	0.012	Region 4 #2

Sample ID	Sample Description	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$ (mg)	Name of the Test Lab
		Test Lab (mg)	NAREL (mg)	Test Lab (mg)	NAREL (mg)	Test Lab (mg)	NAREL (mg)		
T11-14120	40-hour Event	376.372	376.366	376.552	376.553	0.180	0.187	0.007	Region 4 #2
T11-14121	40-hour Event	382.027	382.018	382.208	382.216	0.181	0.198	0.017	Region 4 #2
T11-14122	Blank	377.828	377.819	377.828	377.820	0.000	0.001	0.001	Region 4 #2
T11-14123	Blank	377.804	377.797	377.803	377.797	-0.001	0.000	0.001	Region 4 #2
T11-14124	Blank	380.719	380.711	380.717	380.711	-0.002	0.000	0.002	Region 4 #2
MW11-14155	Metal Weight	478.385	478.384	478.385	478.385	0.000	0.001	0.001	Region 4 #2
MW11-14156	Metal Weight	91.557	91.558	91.557	91.558	0.000	0.000	0.000	Region 4 #2
T11-14135	24-hour Event	376.010	376.006	376.080	376.083	0.070	0.077	0.007	OAQPS
T11-14136	24-hour Event	379.865	379.862	379.933	379.934	0.068	0.072	0.004	OAQPS
T11-14137	24-hour Event	391.276	391.274	391.348	391.345	0.072	0.071	-0.001	OAQPS
T11-14138	24-hour Event	387.419	387.417	387.486	387.489	0.067	0.072	0.005	OAQPS
T11-14139	40-hour Event	385.274	385.273	385.455	385.463	0.181	0.190	0.009	OAQPS
T11-14140	40-hour Event	381.410	381.408	381.588	381.597	0.178	0.189	0.011	OAQPS
T11-14141	40-hour Event	385.492	385.487	385.668	385.674	0.176	0.187	0.011	OAQPS
T11-14142	Blank	387.815	387.813	387.814	387.813	-0.001	0.000	0.001	OAQPS
T11-14143	Blank	386.042	386.042	386.044	386.044	0.002	0.002	0.000	OAQPS
T11-14144	Blank	390.378	390.373	390.376	390.375	-0.002	0.002	0.004	OAQPS
MW11-14159	Metal Weight	487.044	487.045	487.044	487.045	0.000	0.000	0.000	OAQPS

Sample ID	Sample Description	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$ (mg)	Name of the Test Lab
		Test Lab (mg)	NAREL (mg)	Test Lab (mg)	NAREL (mg)	Test Lab (mg)	NAREL (mg)		
MW11-14160	Metal Weight	99.713	99.715	99.714	99.714	0.001	-0.001	-0.002	OAQPS
T11-14145	24-hour Event	386.113	386.103	386.172	386.174	0.059	0.071	0.012	PREQB
T11-14146	24-hour Event	386.495	386.489	386.558	386.560	0.063	0.071	0.008	PREQB
T11-14147	24-hour Event	386.262	386.252	386.354	386.324	0.092	0.072	-0.020	PREQB
T11-14148	24-hour Event	381.859	381.852	381.920	381.922	0.061	0.070	0.009	PREQB
T11-14149	40-hour Event	387.643	387.629	387.813	387.816	0.170	0.187	0.017	PREQB
T11-14150	40-hour Event	381.977	381.971	382.152	382.156	0.175	0.185	0.010	PREQB
T11-14151	40-hour Event	390.286	390.283	390.466	390.472	0.180	0.189	0.009	PREQB
T11-14152	Blank	389.108	389.105	389.108	389.108	0.000	0.003	0.003	PREQB
T11-14153	Blank	389.535	389.531	389.533	389.532	-0.002	0.001	0.003	PREQB
T11-14154	Blank	387.446	387.443	387.444	387.445	-0.002	0.002	0.004	PREQB
MW11-14161	Metal Weight	486.748	486.748	486.749	486.748	0.001	0.000	-0.001	PREQB
MW11-14162	Metal Weight	87.550	87.549	87.550	87.549	0.000	0.000	0.000	PREQB

**** Negative values indicate a smaller capture determined by NAREL.***