TECHNICAL MEMORANDUM

TO: Dennis Mikel / OAQPS

FROM: Eric Boswell / NAREL

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DATE: June 5, 2007

SUBJECT: Gravimetric Inter-Laboratory Comparison Study

Introduction

The National Air and Radiation Environmental Laboratory (NAREL) has completed another gravimetric comparison study to evaluate laboratories that weigh Teflon® filters used in $PM_{2.5}$ air monitoring programs. EPA participants of this study included the Region 4 laboratory in Athens, GA; the Region 2 laboratory in Edison, NJ; the Radiation and Indoor Environments Laboratory (R&IE) in Las Vegas, NV; and the Office of Air Quality Planning and Standards (OAQPS) laboratory in Research Triangle Park (RTP), NC. The Region 4 laboratory provides pre- and post-weighing of filters for the $PM_{2.5}$ Performance Evaluation Program (PEP). The R&IE Laboratory provides pre- and post-weighing of Teflon® filters in support of the Tribal Air Monitoring Support (TAMS) $PM_{2.5}$ air monitoring program. Region 2 provides quality assurance oversight of laboratories in the region that weigh filters for the $PM_{2.5}$ program. The OAQPS laboratory was recently brought back into service and will serve as a backup weighing facility for the $PM_{2.5}$ PEP. A fourth laboratory included in this study is the Maryland Department of Health and Mental Hygiene (DHMH) Laboratory Division. The DHMH laboratory provides the Maryland Department of the Environment (MDE) analytical services that include weighing of Teflon® filters used to collect $PM_{2.5}$. NAREL coordinated this study by supplying performance evaluation (PE) samples and served as the reference laboratory.

Mass determination of $PM_{2.5}$ typically proceeds by weighing 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 tare or pre-mass from the loaded filter 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.

All laboratories participating in this study are equipped with microbalances capable of mass measurements of one microgram sensitivity. NAREL, Region 4, R&IE, OAQPS, and DHMH laboratories perform mass measurements inside environmentally controlled weighing rooms in order to maintain a constant temperature and humidity and to control dust contamination. The Region 2 laboratory utilizes a glove box that has been modified with temperature and humidity controls as well as HEPA filtered air to maintain constant environmental conditions. Samples are conditioned and weighed inside the modified glove box.

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 also 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. 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

To begin this study, five sample sets consisting of ten new Teflon® filters and two metallic weights were assembled. Each filter was carefully inspected using a light table to check for pinholes and fibers. The metallic weights were commercially available 100 and 200 milligram stainless steel weights that were slightly altered by clipping a small corner section from each weight. The filters and metallic weights were placed into individual labeled Petri slides. Sample sets were shipped to each laboratory with instructions to equilibrate and tare the samples following their standard operating procedures for the determination of $PM_{2.5}$ mass. The sample sets were then returned to NAREL and placed into the weighing chamber. Each filter was again inspected for pinholes and visible contamination. After allowing sufficient time for equilibration, the filters were weighed to determine NAREL's pre-mass. A second weigh session was also performed by a different analyst to verify the pre-mass results. After the NAREL pre-masses were established for all samples, seven of the ten filters from each of the sets were loaded with $PM_{2.5}$ collected from the ambient air at NAREL. The remaining three filters from each set were utilized as blanks.

Three co-located Met One SASS air samplers located on the NAREL roof are used to load Teflon® filters with $PM_{2.5}$ mass. One SASS and two Super SASS samplers have a total of eleven flow controlled channels available to create replicate samples. Loading ten filters at once, two from each sample set, gives each laboratory a duplicate pair of filters for each sampling event. Unfortunately, during the first sampling event, which was intended to create replicate samples with 69 hours of sampling time, one of the Super SASS samplers malfunctioned after a few hours of operation. The sampler malfunction resulted in four filters having only a few hours of capture for the first event. At the end of event one, the four filters removed from the failed sampler were mounted on the remaining Super SASS to add a total of 57 hours of sampling time. This resulted in a larger capture than the longer 69 hour event. Using the two remaining samplers, five more sampling events were needed to load the remaining filters. Sampling events are summarized in Table 8.

Following each collection event, samples were returned to NAREL's weighing chamber for equilibration and post-mass determination. A post-mass was also determined for the remaining blank filters and metallic weights. Weigh sessions by different analysts performed on different days were performed to verify mass stability of the samples. The last weigh session before shipping the samples to the sites became NAREL's mass of record.

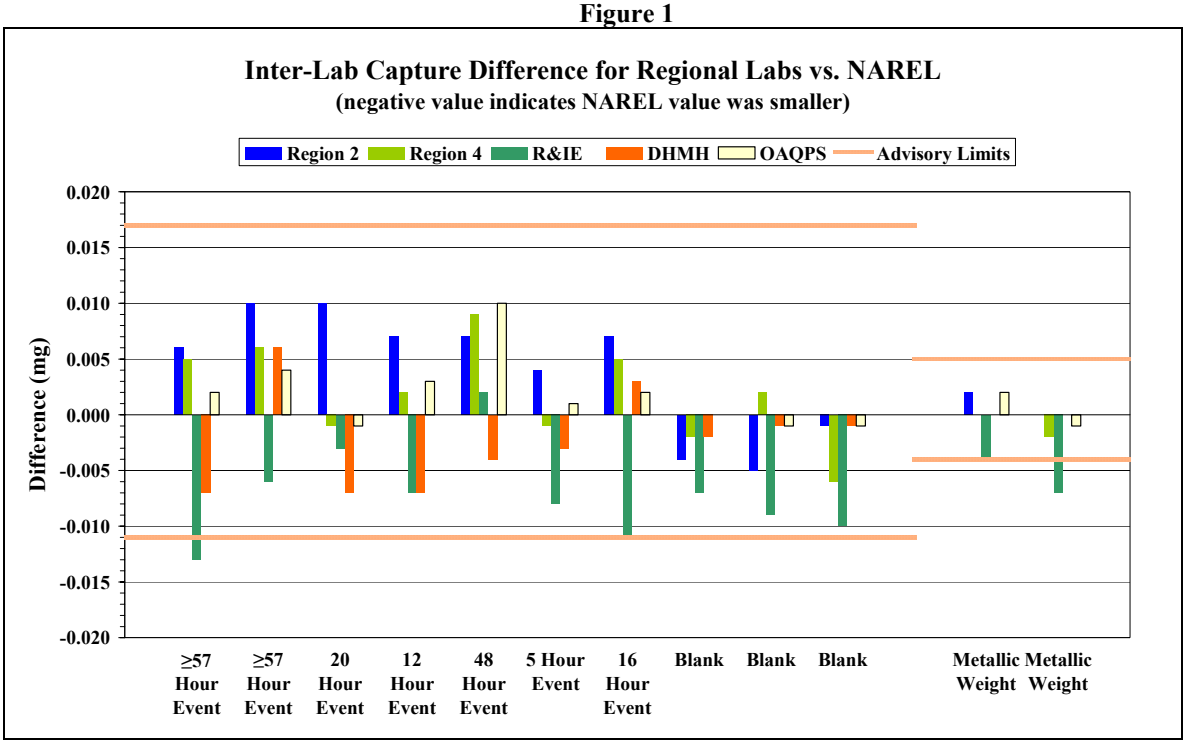
After the loaded mass was determined at NAREL, each sample set was placed into a cooler with frozen ice packs and a letter of instructions. The coolers were shipped to the participating laboratories by overnight Federal Express.

Instructions provided with the samples allowed laboratories two weeks from the time of receipt to equilibrate and obtain final mass measurements. All samples were then returned to NAREL and given a final inspection.

Gravimetric Results

Figure 1 presents the inter-laboratory capture differences for all samples. As stated earlier, the capture is calculated by subtracting the pre-mass from the post-mass. Inter-laboratory differences were calculated by subtracting the capture value reported by the test laboratory from the capture value determined at NAREL. The advisory limits shown in Figure 1 are 3-sigma limits derived from previous gravimetric PE studies administered by NAREL. Notice that a negative bar on the Figure 1 graph represents a smaller $PM_{2.5}$ capture value determined at NAREL and that the absence of a bar indicates perfect agreement with NAREL.

Figure 1



Metallic weights were included in this study because they are more stable than a Teflon® filter, especially a loaded Teflon® filter. 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 Tables 3 - 7 at the end of this report. The tables include the results of all filters and the modified metallic standards weighed at each laboratory. The tables contain the filter pre-mass, the final post-mass, and the calculated

$PM_{2.5}$ capture for each filter. The tables also contain the calculated inter-laboratory difference for measuring the $PM_{2.5}$ capture illustrated in Figure 1.

Conclusions

This study evaluated laboratories that perform gravimetric measurements of 47 mm Teflon® filter samples used to collect $PM_{2.5}$. Samples for this study were created at NAREL by loading Teflon® filters with $PM_{2.5}$ collected from the ambient air. 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 for each sample. Performance was evaluated by comparing mass capture results produced by NAREL to results produced by each participating laboratory. This method eliminates slight differences in balance calibration and environmental conditions among different laboratories since both pre- and post-weights are determined at each location using the same balance. Results of this study demonstrated overall good agreement with NAREL for the majority of measurements. Only one loaded filter sample, illustrated in Figure 1, fell slightly outside the lower three sigma advisory limit.

The most interesting results shown in figure 1 are for the metallic weights. The metallic weights initially sent to each laboratory were returned to each lab along with the filters for determination of a captured mass. Tables 1 and 2 compare two of the five participating laboratories' pre- and post-weight measurements of the metallic samples with NAREL's measurements.

Table 1. R&IE Metallic Weight Sample Results

	Pre-Mass		Pre-Mass	Post-Mass		Post-Mass
Sample ID	R&IE (mg)	NAREL (mg)	Difference (mg)	R&IE (mg)	NAREL (mg)	Difference (mg)
MW07-12043	192.420	192.420	0.000	192.424	192.420	-0.004
MW07-12044	97.545	97.546	0.001	97.552	97.546	-0.006

Table 2. Region 2 Metallic Weight Sample Results

	Pre-Mass		Pre-Mass	Post-Mass		Post-Mass
Sample ID	Region 2 (mg)	NAREL (mg)	Difference (mg)	Region 2 (mg)	NAREL (mg)	Difference (mg)
MW07-12041	181.328	181.334	0.006	181.329	181.335	0.006
MW07-12042	88.203	88.206	0.003	88.202	88.207	0.005

Table 1 shows that R&IE had very good agreement with NAREL for the pre-mass measurements. However, their post-mass measurements for the same samples showed a relatively large gain in mass for the metal weights. As a result, the calculated captured mass is at the warning limit for one metallic sample and exceeds the warning limit for the second metallic.

Table 2 shows a relatively large difference in mass measurements between Region 2 and NAREL for the metallic samples. In this case the bias is consistent for both the pre- and post-measurements. The consistent bias allows the calculated captured mass of the metallic weights to agree very well with NAREL's captured mass results.

As stated earlier, filter samples were examined carefully during each phase of the study. Inspection of the filters on their return from the pre-mass determinations revealed pin-holes in

four filters returned from the Region 2 lab and in one filter returned from the R&IE lab. The damage appears to have been caused by the forceps used to handle the filters. Normally, filters with pin-holes would not be used to collect air samples. For this study, the damaged filter from the R&IE lab was used as a blank sample while the Region 2 damaged filters were used as a blank and for events having only a few hours of collection time. The final inspection of filters returned at the end of the study found two more damaged filters from the Region 2 sample set and five additional damaged filters from R&IE. All filters from the remaining three laboratories were undamaged which indicates they were properly handled by the filter support ring. The last column in table 8 indicates which filters were damaged.

Table 3. Gravimetric Data Region 2

	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference* of	Sampling
Sample ID	Region 2 (mg)	NAREL (mg)	Region 2 (mg)	NAREL (mg)	Region 2 (mg)	NAREL (mg)	Captured PM2.5 (mg)	Duration Hours
T07-12059	144.410	144.419	144.769	144.784	0.359	0.365	0.006	57
T07-12060	144.433	144.442	144.818	144.837	0.385	0.395	0.010	57
T07-12061	144.767	144.775	144.900	144.918	0.133	0.143	0.010	20
T07-12062	143.794	143.798	143.858	143.869	0.064	0.071	0.007	12
T07-12063	145.033	145.041	145.426	145.441	0.393	0.400	0.007	48
T07-12064	144.615	144.626	144.634	144.649	0.019	0.023	0.004	5
T07-12065	143.178	143.186	143.235	143.250	0.057	0.064	0.007	16
T07-12066	143.097	143.109	143.103	143.111	0.006	0.002	-0.004	0
T07-12067	146.823	146.839	146.826	146.837	0.003	-0.002	-0.005	0
T07-12068	145.329	145.343	145.330	145.343	0.001	0.000	-0.001	0
MW07-12041	181.328	181.334	181.329	181.335	-0.001	0.001	0.002	
MW07-12042	88.203	88.206	88.202	88.207	0.001	0.001	0.000	

* Negative values indicate a larger capture determined by Region 2

Table 4. Gravimetric Data Region 4

Sample ID	Pre-Mass Region 4 (mg)	Pre-Mass NAREL (mg)	Post-Mass Region 4 (mg)	Post-Mass NAREL (mg)	Captured PM2.5 Region 4 (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
T07-12049	144.856	144.853	145.261	145.263	0.405	0.410	0.005	57
T07-12050	147.687	147.683	148.065	148.067	0.378	0.384	0.006	57
T07-12051	148.485	148.482	148.631	148.627	0.146	0.145	-0.001	20
T07-12052	149.381	149.377	149.449	149.447	0.068	0.070	0.002	12
T07-12053	145.844	145.839	146.235	146.239	0.391	0.400	0.009	48
T07-12054	145.145	145.145	145.168	145.167	0.023	0.022	-0.001	5
T07-12055	147.429	147.422	147.491	147.489	0.062	0.067	0.005	16
T07-12056	144.684	144.683	144.686	144.683	0.002	0.000	-0.002	0
T07-12057	144.906	144.901	144.905	144.902	-0.001	0.001	0.002	0
T07-12058	146.545	146.543	146.551	146.543	0.006	0.000	-0.006	0
MW07-12039	190.519	190.520	190.520	190.521	0.001	0.001	0.000	
MW07-12040	94.831	94.833	94.833	94.833	0.002	0.000	-0.002	

* Negative values indicate a larger capture determined by Region 4

Table 5. Gravimetric Data R&IE

Sample ID	Pre-Mass R&IE (mg)	Pre-Mass NAREL (mg)	Post-Mass R&IE (mg)	Post-Mass NAREL (mg)	Captured PM2.5 R&IE (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
T07-12069	145.095	145.091	145.447	145.430	0.352	0.339	-0.013	69
T07-12070	143.247	143.240	143.594	143.581	0.347	0.341	-0.006	69
T07-12071	145.032	145.025	145.178	145.168	0.146	0.143	-0.003	20
T07-12072	142.720	142.718	142.796	142.787	0.076	0.069	-0.007	12
T07-12073	141.889	141.881	142.282	142.276	0.393	0.395	0.002	48
T07-12074	140.830	140.825	140.858	140.845	0.028	0.020	-0.008	5
T07-12075	141.423	141.415	141.428	141.413	0.005	-0.002	-0.007	0
T07-12076	142.130	142.125	142.199	142.183	0.069	0.058	-0.011	16
T07-12077	141.008	141.002	141.019	141.004	0.011	0.002	-0.009	0
T07-12078	142.392	142.387	142.402	142.387	0.010	0.000	-0.010	0
MW07-12043	192.420	192.420	192.424	192.420	0.004	0.000	-0.004	
MW07-12044	97.545	97.546	97.552	97.546	0.007	0.000	-0.007	

* Negative values indicate a larger capture determined by R&IE

Table 6. Gravimetric Data DHMH

Sample ID	Pre-Mass DHMH (mg)	Pre-Mass NAREL (mg)	Post-Mass DHMH (mg)	Post-Mass NAREL (mg)	Captured PM2.5 DHMH (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
T07-12089	148.473	148.480	148.833	148.833	0.360	0.353	-0.007	69
T07-12090	145.784	145.785	146.142	146.149	0.358	0.364	0.006	69
T07-12091	148.163	148.168	148.321	148.319	0.158	0.151	-0.007	20
T07-12092	145.955	145.961	146.042	146.041	0.087	0.080	-0.007	12
T07-12093	139.315	139.322	139.712	139.715	0.397	0.393	-0.004	48
T07-12094	144.390	144.395	144.414	144.416	0.024	0.021	-0.003	5
T07-12095	143.190	143.194	143.247	143.254	0.057	0.060	0.003	16
T07-12096	143.604	143.608	143.608	143.610	0.004	0.002	-0.002	0
T07-12097	144.660	144.663	144.662	144.664	0.002	0.001	-0.001	0
T07-12098	142.754	142.757	142.755	142.757	0.001	0.000	-0.001	0
MW07-12047	186.997	186.995	186.997	186.995	0.000	0.000	0.000	
MW07-12048	90.603	90.603	90.603	90.603	0.000	0.000	0.000	

* Negative values indicate a larger capture determined by DHMH

Table 7. Gravimetric Data OAQPS

Sample ID	Pre-Mass OAQPS (mg)	Pre-Mass NAREL (mg)	Post-Mass OAQPS (mg)	Post-Mass NAREL (mg)	Captured PM2.5 OAQPS (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
T07-12079	144.574	144.576	144.917	144.921	0.343	0.345	0.002	69
T07-12080	143.528	143.528	143.870	143.874	0.342	0.346	0.004	69
T07-12081	140.492	140.496	140.686	140.689	0.194	0.193	-0.001	20
T07-12082	145.544	145.543	145.621	145.623	0.077	0.080	0.003	12
T07-12083	144.735	144.735	145.202	145.212	0.467	0.477	0.010	48
T07-12084	144.873	144.875	144.894	144.897	0.021	0.022	0.001	5
T07-12085	145.427	145.428	145.484	145.487	0.057	0.059	0.002	16
T07-12086	145.932	145.933	145.932	145.933	0.000	0.000	0.000	0
T07-12087	144.282	144.282	144.284	144.283	0.002	0.001	-0.001	0
T07-12088	147.037	147.039	147.038	147.039	0.001	0.000	-0.001	0
MW07-12045	193.821	193.820	193.820	193.821	-0.001	0.001	0.002	
MW07-12046	92.957	92.960	92.957	92.959	0.000	-0.001	-0.001	

* Negative values indicate a larger capture determined by OAQPS

Table 8. Sampling Schedule

Sample_ID	Filter_ID	Event	Event Start	Event Duration (hr)	Receiving Lab	Filter Condition
T07-12049	T7039794	1	4/12/2007	57	Region 4	OK
T07-12050	T7039795	1	4/12/2007	57	Region 4	OK
T07-12051	T7039796	2	4/18/2007	20	Region 4	OK
T07-12052	T7039797	3	4/19/2007	12	Region 4	OK
T07-12053	T7039798	4	4/20/2007	48	Region 4	OK
T07-12054	T7039799	5	4/23/2007	5	Region 4	OK
T07-12055	T7039800	6	4/23/2007	16	Region 4	OK
T07-12056	T7039801			0	Region 4	OK
T07-12057	T7039802			0	Region 4	OK
T07-12058	T7039803			0	Region 4	OK
T07-12059	T7039804	1	4/12/2007	57	Region 2	OK
T07-12060	T7039805	1	4/12/2007	57	Region 2	post-mass scratch
T07-12061	T7039806	2	4/18/2007	20	Region 2	OK
T07-12062	T7039807	3	4/19/2007	12	Region 2	pin hole
T07-12063	T7039808	4	4/20/2007	48	Region 2	OK
T07-12064	T7039809	5	4/23/2007	5	Region 2	pin hole
T07-12065	T7039810	6	4/23/2007	16	Region 2	OK
T07-12066	T7039811			0	Region 2	post-mass pin hole
T07-12067	T7039812			0	Region 2	pin hole
T07-12068	T7039813			0	Region 2	pin hole
T07-12069	T7039814	1	4/12/2007	69	R&IE	post-mass pin hole
T07-12070	T7039815	1	4/12/2007	69	R&IE	OK
T07-12071	T7039816	2	4/18/2007	20	R&IE	OK
T07-12072	T7039817	3	4/19/2007	12	R&IE	post-mass pin hole
T07-12073	T7039818	4	4/20/2007	48	R&IE	OK
T07-12074	T7039819	5	4/23/2007	5	R&IE	OK
T07-12075	T7039820	6	4/23/2007	0	R&IE	pin hole
T07-12076	T7039821			16	R&IE	post-mass pin hole
T07-12077	T7039822			0	R&IE	post-mass pin hole
T07-12078	T7039826			0	R&IE	post-mass pin hole
T07-12079	T7039827	1	4/12/2007	69	OAQPS	OK
T07-12080	T7039828	1	4/12/2007	69	OAQPS	OK
T07-12081	T7039829	2	4/18/2007	20	OAQPS	OK
T07-12082	T7039830	3	4/19/2007	12	OAQPS	OK
T07-12083	T7039831	4	4/20/2007	48	OAQPS	OK
T07-12084	T7039832	5	4/23/2007	5	OAQPS	OK
T07-12085	T7039833	6	4/23/2007	16	OAQPS	OK
T07-12086	T7039834			0	OAQPS	OK
T07-12087	T7039835			0	OAQPS	OK
T07-12088	T7039836			0	OAQPS	OK

T07-12089	T7039837	1	4/12/2007	69	DHMH	OK
T07-12090	T7039838	1	4/12/2007	69	DHMH	OK
T07-12091	T7039839	2	4/18/2007	20	DHMH	OK
T07-12092	T7039840	3	4/19/2007	12	DHMH	OK
T07-12093	T7039841	4	4/20/2007	48	DHMH	OK
T07-12094	T7039842	5	4/23/2007	5	DHMH	OK
T07-12095	T7039843	6	4/23/2007	16	DHMH	OK
T07-12096	T7039844			0	DHMH	OK
T07-12097	T7039845			0	DHMH	OK
T07-12098	T7039846			0	DHMH	OK