TECHNICAL MEMORANDUM

TO: Michael Papp / OAQPS

FROM: Eric Boswell / NAREL

COPY: Dennis Crumper / OAQPS
Nealson Watkins / OAQPS
Robert Mosley / R&IE-LV
Greg Noah / Region 4
Christopher Hall/Region 10

AUTHOR: Steve Taylor / NAREL

DATE: September 8, 2004

SUBJECT: Gravimetric Inter-Laboratory Comparison Study

Introduction

A gravimetric study has been conducted at the National Air and Radiation Environmental Laboratory (NAREL) to compare the performance of EPA weighing laboratories that perform $PM_{2.5}$ mass measurements. Participants of this study included the Region 4 Laboratory in Athens, GA, the Region 10 contract laboratory (Manchester Laboratory) in Washington, 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 and Region 10 laboratories provide pre-weighing and post-weighing of filters for the $PM_{2.5}$ Performance Evaluation Program (PEP). The R&IE Laboratory provides the $PM_{2.5}$ gravimetric analysis for the Tribal Air Monitoring Support (TAMS) program. The OAQPS Gravimetric Laboratory is a new facility that is in the process of becoming fully operational. NAREL coordinated this study by supplying Performance Evaluation (PE) samples and served as the reference laboratory. All laboratories participating in this study are equipped with environmentally controlled weighing chambers and microbalances capable of mass measurements of one microgram sensitivity.

Mass determination 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 weight from the loaded filter weight. 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.

Samples for this study were created at NAREL using Met One SASS air samplers to collect various amounts of $PM_{2.5}$ particulate matter onto Teflon® filters that were previously tared by all laboratories. Blank filters as well as metallic weights were also included as samples to provide additional information of each laboratory's performance. 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 has 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-sampling. Metallic standards should not vary by more than 0.003 mg. Although these criteria do not specifically apply to the mass comparisons determined in this study, they can be used as a general guideline to measure performance.

Experimental

To begin this study, each of the four participating laboratories was provided a set of samples consisting of ten new Teflon® filters and two metallic weights. Filters and weights were held in individual labeled petrislides. 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. 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. Laboratories were allowed one week to determine the initial weights before returning the samples to NAREL. The returned filters and metallic weights were immediately placed into the weighing chamber at NAREL for equilibration and determination of a NAREL tare mass. After the NAREL tare 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.

Teflon® filters were loaded with $PM_{2.5}$ mass using two Met One Super SASS air samplers. Each sampler has four flow controlled channels available for loading up to eight replicate samples. To insure that mass loads were similar for each lab, filters were loaded in replicate using four different sampling events. For the first event, two filters from each of the sample sets simultaneously collected air for twenty hours using four channels on each Super SASS. A second event ran for a total of seven hours, creating eight more replicates, two for each lab. A third event collected 45-hour replicates on eight filters. The fourth event, using one sampler, collected air for twenty-four hours to produce four replicate samples. Sampling events are summarized in Table 8. Following sample collection, filters were returned to the weighing chamber at NAREL to equilibrate and to determine the loaded mass as well as a final mass for the remaining blank filters and the metallic weights. Several weigh sessions during the week following sample collection were conducted to insure the mass stability of the filters. The last weigh session before shipping the filters to the sites became NAREL's "official" loaded mass.

Immediately after a final "official" loaded mass was determined at NAREL, each sample set was placed into a cooler with frozen ice packs, a Dickson temperature logger, 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, with ice packs and temperature loggers. Samples were placed in the NAREL weighing chamber and each sample's petrislide was opened slightly in order to equilibrate the filters. Data from the temperature loggers were also downloaded.

Gravimetric Results

A summary of all Inter-Laboratory capture differences is presented in Table 1. Figure 1 graphically presents the Inter-Laboratory differences for all samples. The dashed lines shown in Figure 1 indicate the program's ±0.015 mg laboratory blank criteria and the ±0.003 mg metallic weight criteria. These criteria do not apply to Inter-Laboratory capture differences and are included in Figure 1 for comparison purposes only. The Region 4 Laboratory delivered results from two analysts and both sets of data are included. Inter-Laboratory differences were calculated by subtracting the $PM_{2.5}$ capture value determined at each laboratory from the capture value determined at NAREL. NAREL's capture value was calculated using the "official" loaded mass determined immediately before the samples were shipped to the regional laboratories. Notice that a negative bar on the Figure 1 graph represents a smaller $PM_{2.5}$ capture value determined at NAREL. As seen in Figure 1, the majority of sample results compared very well with NAREL results.

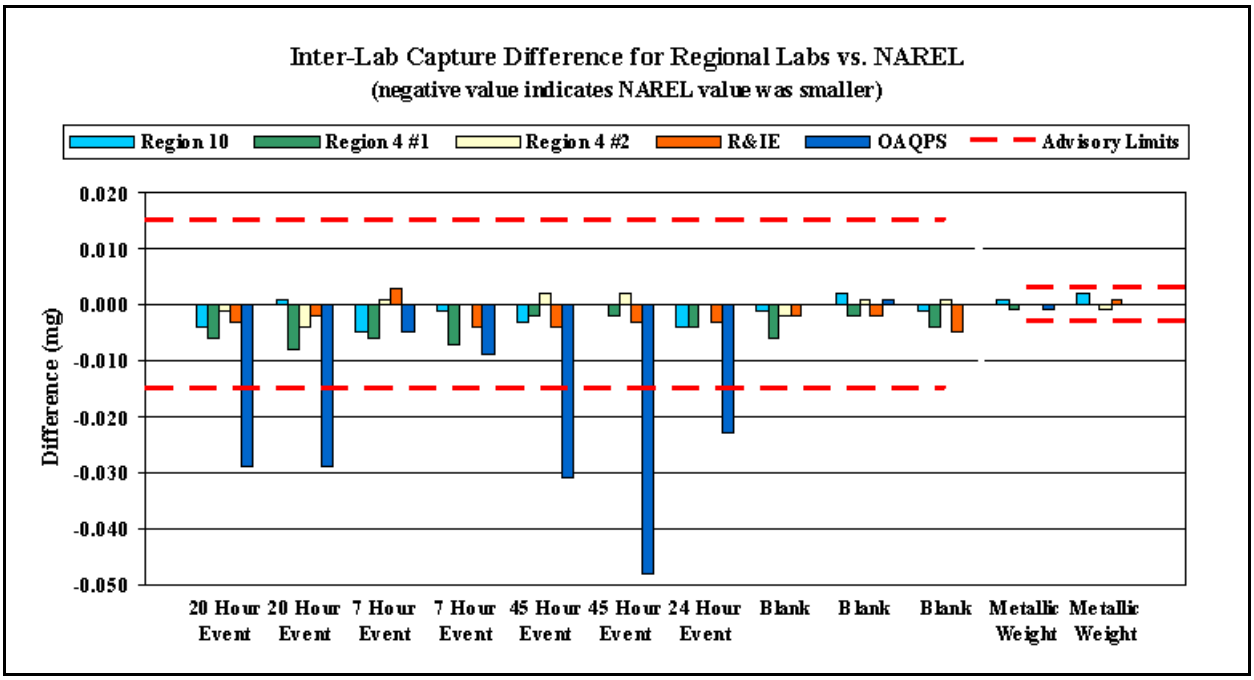

Figure 1

Five of the loaded samples analyzed by the OAQPS Laboratory exceeded the negative fifteen microgram advisory limit, indicating a significant mass gain over NAREL's "official" loaded mass determinations. Sample contamination is not a probable cause of the indicated mass gains since there is very good inter-laboratory agreement for the blank filters. Also, the metallic weight mass determinations were in agreement, suggesting good balance calibration. It was learned that a problem with the humidity control in the OAQPS gravimetric chamber allowed the humidity to reach approximately 55% relative humidity (RH) during equilibration and weighing of the samples. The $PM_{2.5}$ Program criteria for humidity specifies a range of 30 - 40 % RH controlled to ± 5% RH over 24 hours. Examination of data for these samples revealed that the filters with the largest captures also

had the largest mass gains. The correlation of filter loading to mass gain for these samples demonstrates the effects of elevated RH and the importance of maintaining chamber conditions within Program limits. All returned OAQPS samples were placed into NAREL's weighing chamber to equilibrate at 35% RH and were then reweighed. The data presented in Table 2 compares NAREL's loaded mass measurements before shipping and after the return of the OAQPS samples. The minor differences in the before and after measurements shown in Table 2 indicate that the mass increase due to the higher RH in the OAQPS Laboratory is reversible when the filters are re-equilibrated at 35% RH. The negative values indicate a slight loss of mass capture over the two week period between measurements.

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 problem. PEP criteria for routine balance checks using metallic weights is ±0.003 mg. All results for the metallic weights were within criteria.

The temperature criteria for equilibration of Teflon® filters is 20-23 °C, controlled to ± 2 °C for 24 hours. Data recovered from the temperature loggers assigned to each set of samples indicated that all participating laboratories were within criteria.

The raw data reported from all laboratories have been tabulated for easy viewing in Tables 3 - 7 at the end of this report. The tables include the results of all shared filters and the modified metallic standards weighed at each laboratory. The tables contain the filter tare mass, the final loaded 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. A schedule of the sampling events used to load the filters is presented in Table 8.

Conclusions

Excellent inter-laboratory agreement was observed for all mass measurements performed by the three established laboratories, Region 4, Region 10, and R&IE. The greatest difference in calculated mass capture was only eight micrograms, which is much better than Program criteria for laboratory blanks (0.015 mg). The OAQPS Laboratory showed very good inter-laboratory agreement for the metallic weights and also for filters that were not loaded or lightly loaded. Elevated humidity inside their weighing chamber prevented comparable measurements for the more heavily loaded filters. OAQPS is aware of the humidity issue in their laboratory and is taking steps to improve control of their chamber's humidity.

Table 1. Capture Difference Summary (mg) *

	Region 10	Region 4 #1	Region 4 #2	R&IE	OAQPS
20 Hour Event	-0.004	-0.006	-0.001	-0.003	-0.029
20 Hour Event	0.001	-0.008	-0.004	-0.002	-0.029
7 Hour Event	-0.005	-0.006	0.001	0.003	-0.005
7 Hour Event	-0.001	-0.007	0.000	-0.004	-0.009
45 Hour Event	-0.003	-0.002	0.002	-0.004	-0.031
45 Hour Event	0.000	-0.002	0.002	-0.003	-0.048
24 Hour Event	-0.004	-0.004	0.000	-0.003	-0.023
Blank Filter	-0.001	-0.006	-0.002	-0.002	0.000
Blank Filter	0.002	-0.002	0.001	-0.002	0.001
Blank Filter	-0.001	-0.004	0.001	-0.005	0.000
Metallic Weight	0.001	-0.001	0.000	0.000	-0.001
Metallic Weight	0.002	0.000	-0.001	0.001	0.000
Max Difference	-0.005	-0.008	-0.004	-0.005	-0.048

* A negative difference indicates a smaller capture for NAREL

Table 2. Post Mass Results for OAQPS Samples

Sample ID	NAREL Initial 8/11/2004 Mass (mg)	NAREL Post 8/30/2004 Mass (mg)	Mass Change (mg)	Sample Load Time (Hrs)
T2112442	142.980	142.969	-0.011	20
T2112443	141.459	141.450	-0.009	20
T2112444	143.329	143.320	-0.009	7
T2112446	141.469	141.469	0.000	7
T2112447	143.171	143.162	-0.009	45
T2112448	142.969	142.961	-0.008	45
T2112449	143.054	143.050	-0.004	24
T2017251	141.890	141.891	0.001	0
T2017252	141.268	141.267	-0.001	0
T2017253	140.327	140.326	-0.001	0
MW04-11098	97.546	97.545	-0.001	Metallic
MW04-11099	192.422	192.421	-0.001	Metallic

* A negative difference indicates a mass loss

Table 3. Gravimetric Data Region 10

	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$
Filter ID	Region 10 (mg)	NAREL (mg)	Region 10 (mg)	NAREL (mg)	Region 10 (mg)	NAREL (mg)	(mg)
T2112432	141.329	141.334	141.598	141.599	0.269	0.265	-0.004
T2112433	141.609	141.610	141.906	141.908	0.297	0.298	0.001
T2112434	143.269	143.275	143.356	143.357	0.087	0.082	-0.005
T2112435	142.454	142.459	142.542	142.546	0.088	0.087	-0.001
T2112436	140.603	140.609	141.169	141.172	0.566	0.563	-0.003
T2112437	142.649	142.653	143.228	143.232	0.579	0.579	0.000
T2112438	141.634	141.640	141.839	141.841	0.205	0.201	-0.004
T2112439	144.737	144.740	144.740	144.742	0.003	0.002	-0.001
T2112440	141.170	141.170	141.171	141.173	0.001	0.003	0.002
T2112441	143.045	143.049	143.049	143.052	0.004	0.003	-0.001
MW04-11094	93.774	93.776	93.773	93.776	-0.001	0.000	0.001
MW04-11095	188.877	188.879	188.876	188.880	-0.001	0.001	0.002

* Negative values indicate a larger capture determined by Region 10.

Table 4. Gravimetric Data Region 4

	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$
Filter ID	Region 4 Analyst 1 (mg)	NAREL (mg)	Region 4 Analyst 1 (mg)	NAREL (mg)	Region 4 Analyst 1 (mg)	NAREL (mg)	(mg)
T2112416	144.303	144.303	144.589	144.583	0.286	0.280	-0.006
T2112422	145.354	145.356	145.637	145.631	0.283	0.275	-0.008
T2112423	144.739	144.738	144.834	144.827	0.095	0.089	-0.006
T2112424	144.597	144.596	144.688	144.680	0.091	0.084	-0.007
T2112426	143.432	143.428	144.008	144.002	0.576	0.574	-0.002
T2112427	140.426	140.422	141.001	140.995	0.575	0.573	-0.002
T2112428	144.743	144.742	144.946	144.941	0.203	0.199	-0.004
T2112429	145.146	145.146	145.151	145.145	0.005	-0.001	-0.006
T2112430	145.293	145.290	145.294	145.289	0.001	-0.001	-0.002
T2112431	142.656	142.653	142.662	142.655	0.006	0.002	-0.004
MW04-11092	94.831	94.834	94.832	94.834	0.001	0.000	-0.001
MW04-11093	190.521	190.521	190.521	190.521	0.000	0.000	0.000

* Negative values indicate a larger capture determined by Region 4.

Table 5. Gravimetric Data Region 4

	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$
Filter ID	Region 4 Analyst 2 (mg)	NAREL (mg)	Region 4 Analyst 2 (mg)	NAREL (mg)	Region 4 Analyst 2 (mg)	NAREL (mg)	(mg)
T2112416	144.303	144.303	144.584	144.583	0.281	0.280	-0.001
T2112422	145.355	145.356	145.634	145.631	0.279	0.275	-0.004
T2112423	144.739	144.738	144.827	144.827	0.088	0.089	0.001
T2112424	144.599	144.596	144.683	144.680	0.084	0.084	0.000
T2112426	143.432	143.428	144.004	144.002	0.572	0.574	0.002
T2112427	140.426	140.422	140.997	140.995	0.571	0.573	0.002
T2112428	144.743	144.742	144.942	144.941	0.199	0.199	0.000
T2112429	145.147	145.146	145.148	145.145	0.001	-0.001	-0.002
T2112430	145.293	145.290	145.291	145.289	-0.002	-0.001	0.001
T2112431	142.655	142.653	142.656	142.655	0.001	0.002	0.001
MW04-11092	94.832	94.834	94.832	94.834	0.000	0.000	0.000
MW04-11093	190.520	190.521	190.521	190.521	0.001	0.000	-0.001

* Negative values indicate a larger capture determined by Region 4.

Table 6. Gravimetric Data R&IE

	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$
Filter ID	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL (mg)	(mg)
T2017254	141.532	141.527	141.809	141.801	0.277	0.274	-0.003
T2017255	141.152	141.145	141.424	141.415	0.272	0.270	-0.002
T2017256	142.664	142.657	142.748	142.744	0.084	0.087	0.003
T2017257	139.287	139.280	139.374	139.363	0.087	0.083	-0.004
T2017258	142.757	142.750	143.333	143.322	0.576	0.572	-0.004
T2017259	144.640	144.635	145.205	145.197	0.565	0.562	-0.003
T2017260	142.764	142.757	142.963	142.953	0.199	0.196	-0.003
T2017261	138.306	138.299	138.309	138.300	0.003	0.001	-0.002
T2017262	140.424	140.417	140.427	140.418	0.003	0.001	-0.002
T2017263	140.632	140.625	140.635	140.623	0.003	-0.002	-0.005
MW04-11096	97.356	97.356	97.355	97.355	-0.001	-0.001	0.000
MW04-11097	196.234	196.235	196.233	196.235	-0.001	0.000	0.001

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

Table 7. Gravimetric Data OAQPS

	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$
Filter ID	OAQPS (mg)	NAREL (mg)	OAQPS (mg)	NAREL (mg)	OAQPS (mg)	NAREL (mg)	(mg)
T2112442	142.704	142.701	143.012	142.980	0.308	0.279	-0.029
T2112443	141.186	141.178	141.496	141.459	0.310	0.281	-0.029
T2112444	143.242	143.238	143.338	143.329	0.096	0.091	-0.005
T2112446	141.386	141.380	141.484	141.469	0.098	0.089	-0.009
T2112447	142.603	142.597	143.208	143.171	0.605	0.574	-0.031
T2112448	142.390	142.390	143.017	142.969	0.627	0.579	-0.048
T2112449	142.868	142.864	143.081	143.054	0.213	0.190	-0.023
T2017251	141.891	141.889	141.892	141.890	0.001	0.001	0.000
T2017252	141.268	141.265	141.270	141.268	0.002	0.003	0.001
T2017253	140.328	140.325	140.330	140.327	0.002	0.002	0.000
MW04-11098	97.545	97.545	97.547	97.546	0.002	0.001	-0.001
MW04-11099	192.421	192.421	192.422	192.422	0.001	0.001	0.000

* Negative values indicate a larger capture determined by OAQPS

Table 8. Filter Loading Schedule

Filter ID	Sample Start	Event Duration	Receiving Lab
T2112416	02-Aug-04	20 Hour Event	Region 4
T2112422	02-Aug-04	20 Hour Event	Region 4
T2112432	02-Aug-04	20 Hour Event	Region 10
T2112433	02-Aug-04	20 Hour Event	Region 10
T2112442	02-Aug-04	20 Hour Event	OAQPS Lab
T2112443	02-Aug-04	20 Hour Event	OAQPS Lab
T2017254	02-Aug-04	20 Hour Event	R&IE
T2017255	02-Aug-04	20 Hour Event	R&IE
T2112423	03-Aug-04	7 Hour Event	Region 4
T2112424	03-Aug-04	7 Hour Event	Region 4
T2112434	03-Aug-04	7 Hour Event	Region 10
T2112435	03-Aug-04	7 Hour Event	Region 10
T2112444	03-Aug-04	7 Hour Event	OAQPS Lab
T2112446	03-Aug-04	7 Hour Event	OAQPS Lab
T2017256	03-Aug-04	7 Hour Event	R&IE
T2017257	03-Aug-04	7 Hour Event	R&IE
T2112426	03-Aug-04	45 Hour Event	Region 4
T2112427	03-Aug-04	45 Hour Event	Region 4
T2112436	03-Aug-04	45 Hour Event	Region 10
T2112437	03-Aug-04	45 Hour Event	Region 10
T2112447	03-Aug-04	45 Hour Event	OAQPS Lab
T2112448	03-Aug-04	45 Hour Event	OAQPS Lab
T2017258	03-Aug-04	45 Hour Event	R&IE
T2017259	03-Aug-04	45 Hour Event	R&IE
T2112428	05-Aug-04	24 Hour Event	Region 4
T2112438	05-Aug-04	24 Hour Event	Region 10
T2112449	05-Aug-04	24 Hour Event	OAQPS Lab
T2017260	05-Aug-04	24 Hour Event	R&IE
T2112429	Blank	0 Hour Event	Region 4
T2112430	Blank	0 Hour Event	Region 4
T2112431	Blank	0 Hour Event	Region 4
T2112439	Blank	0 Hour Event	Region 10
T2112440	Blank	0 Hour Event	Region 10
T2112441	Blank	0 Hour Event	Region 10
T2017251	Blank	0 Hour Event	OAQPS Lab
T2017252	Blank	0 Hour Event	OAQPS Lab
T2017253	Blank	0 Hour Event	OAQPS Lab
T2017261	Blank	0 Hour Event	R&IE
T2017262	Blank	0 Hour Event	R&IE
T2017263	Blank	0 Hour Event	R&IE