TECHNICAL MEMORANDUM

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DATE: December 1, 2005

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. This was the final gravimetric performance study scheduled for 2005. 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 Research Triangle Institute (RTI) 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 RTI Laboratory facility serves as EPA's primary contractor providing laboratory services to support the $PM_{2.5}$ Speciation air monitoring network. RTI participated in this study because of additional contract work being performed as part of the Hurricane Katrina clean-up effort. 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 of $PM_{2.5}$ typically proceeds by weighing the Teflon7 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 $PM_{2.5}$ onto Teflon7 filters that were previously tared by all laboratories. Blank filter samples were included as controls to provide information about filter contamination and stability of mass loading. Metallic weights were also included as samples 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-sampling. Metallic standards should not vary by more than 0.003 mg. Previous NAREL gravimetric studies have used the PEP criteria as a guideline to measure laboratory performance. 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, each of the four participating laboratories was provided a set of samples consisting of ten new Teflon7 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. The sample sets were then returned to NAREL and placed into the weighing chamber for equilibration and determination of NAREL=s 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.

Teflon7 filters were loaded with $PM_{2.5}$ mass using two co-located Met One Super SASS air samplers. Each sampler has four flow controlled channels available to load 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. Event one sampled for 48 hours to create eight replicates. The next two events collected air for 24 and 20 hours respectively. The fourth event, using one sampler, collected air for sixteen hours to produce four replicate samples. Sampling events are summarized in Table 7. 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 Aofficial@ loaded mass.

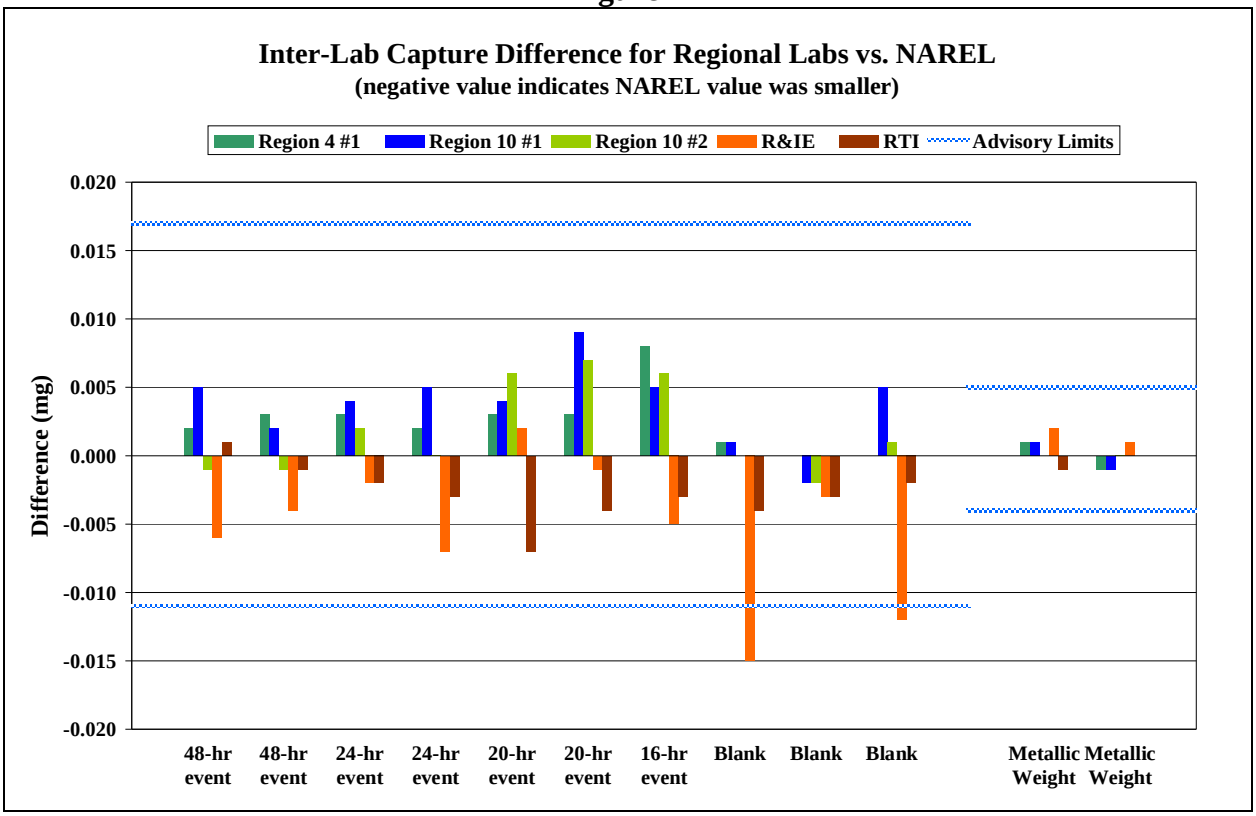
Immediately after a final Aofficial@ loaded mass was determined at NAREL, each sample set was placed into a cooler with frozen ice packs, a Dickson temperature logger, and a letter of instructions. The coolers were shipped to the participating laboratories by overnight Federal Express.

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.

Gravimetric Results

Figure 1 presents the inter-laboratory capture differences for all samples with advisory limits. Inter-laboratory differences were calculated by subtracting the $PM_{2.5}$ capture value determined at each laboratory from the capture value determined at NAREL. The advisory limits were derived from all of the PE studies administered by NAREL during the past year. The 3-sigma limits are calculated from the inter-laboratory capture differences between NAREL and the participating laboratories. Region 10 laboratories delivered results from two analysts and both sets of data are included. NAREL=s capture value was calculated using the Aofficial@ 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

Figure 1



A summary of all inter-laboratory capture differences is presented in Table 1.

Table 1. Capture Difference Summary (mg) *

	Region 4	Region 10 #1	Region 10 #2	R&IE	RTI
48 Hour Event	0.002	0.005	-0.001	-0.006	0.001
48 Hour Event	0.003	0.002	-0.001	-0.004	-0.001
24 Hour Event	0.003	0.004	0.002	-0.002	-0.002
24 Hour Event	0.002	0.005	0.000	-0.007	-0.003
20 Hour Event	0.003	0.004	0.006	0.002	-0.007
20 Hour Event	0.003	0.009	0.007	-0.001	-0.004
16 Hour Event	0.008	0.005	0.006	-0.005	-0.003
Blank	0.001	0.001	0.000	-0.015	-0.004
Blank	0.000	-0.002	-0.002	-0.003	-0.003
Blank	0.000	0.005	0.001	-0.012	-0.002
Metallic Weight	0.001	0.001	0.000	0.002	-0.001
Metallic Weight	-0.001	-0.001	0.000	0.001	0.000

* Capture difference = NAREL capture - Region capture
A negative difference indicates a smaller capture for NAREL

Metallic weights were included in this study because they are more stable than a Teflon7 filter, especially a loaded Teflon7 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 Amass capture@ for the metallic weights. Ideally, the Amass capture@ for the metallic weight samples would be zero. A large difference between an initial and final mass could indicate a balance stability problem.

The temperature criteria for equilibration of Teflon7 filters is 20-23 ^{o}C, controlled to ? 2 ^{o}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 $PM_{2.5}$ mass capture for each of the four sampling events as well as the mass capture for the blank filters and metallic samples is presented graphically in figures 2 - 7 at the end of this report.

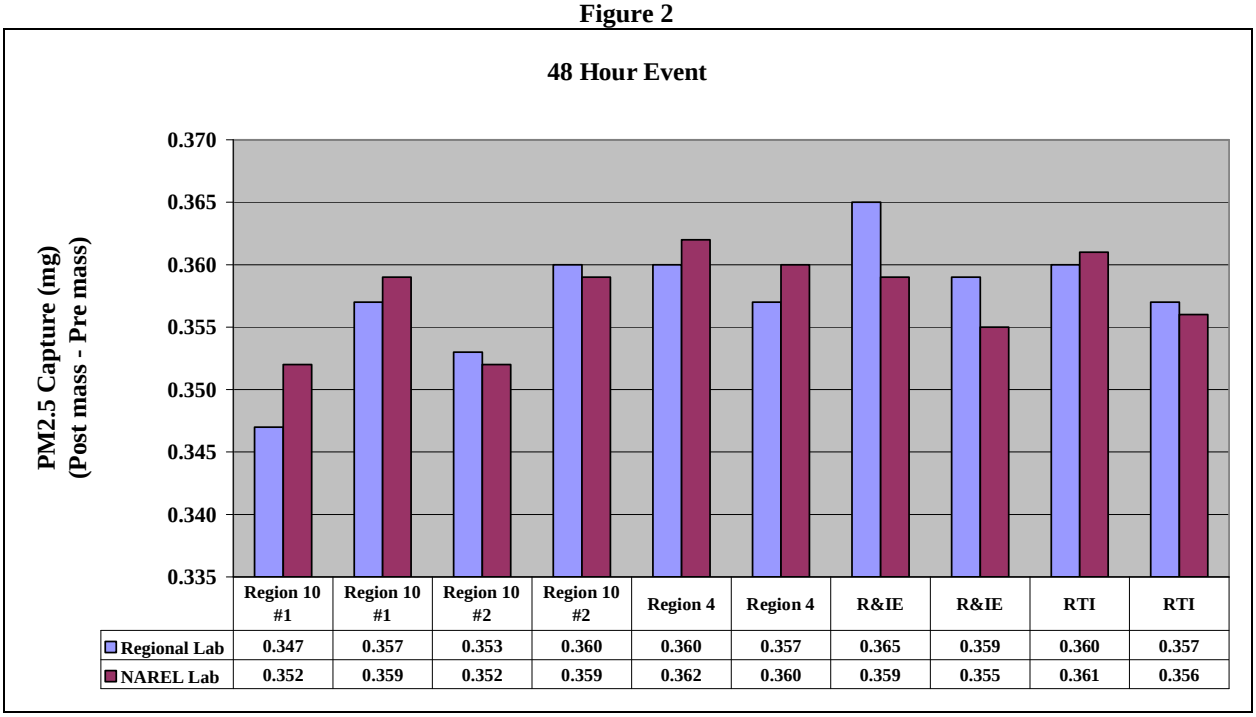
The raw data reported from all laboratories have been tabulated in Tables 2 - 6 at the end of this report. The tables include the results of all filters and the modified metallic standards weighed at each laboratory. The tables contain the filter tare mass, the final loaded mass, and the calculated $PM_{2.5}$ 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 7.

Conclusions

Good agreement between NAREL and each participating laboratory was observed for the majority of mass measurements. Two blank filter results, illustrated in Figure 1, fell outside the lower three sigma advisory limit. Data for these samples (T05-11469 and T05-11477 listed in Table 5) indicate good between laboratory agreement for the initial tare measurements, however the post mass measurements reported by R&IE show a relatively large gain in mass for T05-11469 (0.017 mg) compared to NAREL's post measurement (0.002 mg). The R&IE captured mass for sample T05-11477 was also somewhat high for a blank filter (0.008 mg). The NAREL post measurement for T05-11477 showed a net loss of -0.004 mg.

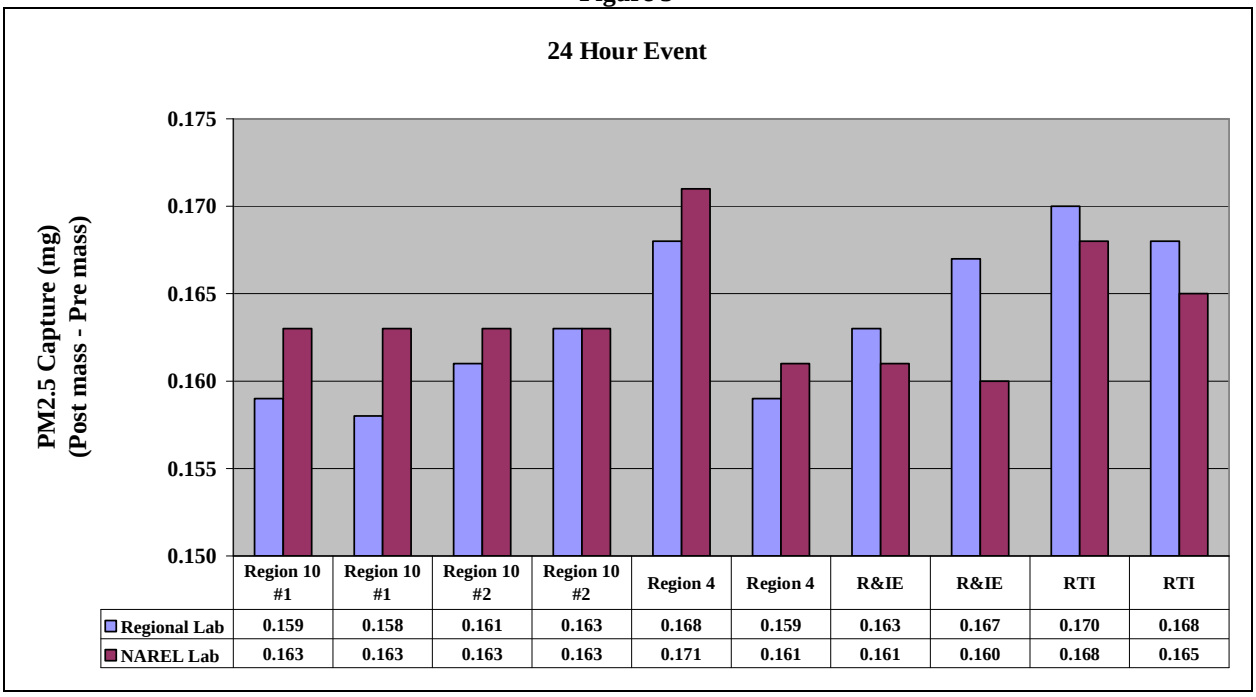
Errors were discovered in the Region 4 laboratory's reported results. Specifically, a sample ID mix-up of the two metallic samples resulted in incorrect results reported for those samples. Also, one metallic sample result appeared to have a transcription error that indicated a three milligram change between the pre and post mass measurements. A telephone conversation with the Region 4 analyst revealed that mass results for the PE samples were not automatically recorded from the balance into a database in the same way as normal samples. The PE sample results were hand written onto a data sheet which was then manually transferred into a spreadsheet. Examination of the original raw data sheet, faxed to NAREL, showed the correct result for the transcription error, however, the sample ID mix-up occurred in the original raw data. In this case, the mistake was obvious and could easily be corrected. Once corrections were made to the data, the Region 4 laboratory results compared well with NAREL's measurements. The figures and tables in this report display the corrected results for Region 4.

Figure 2



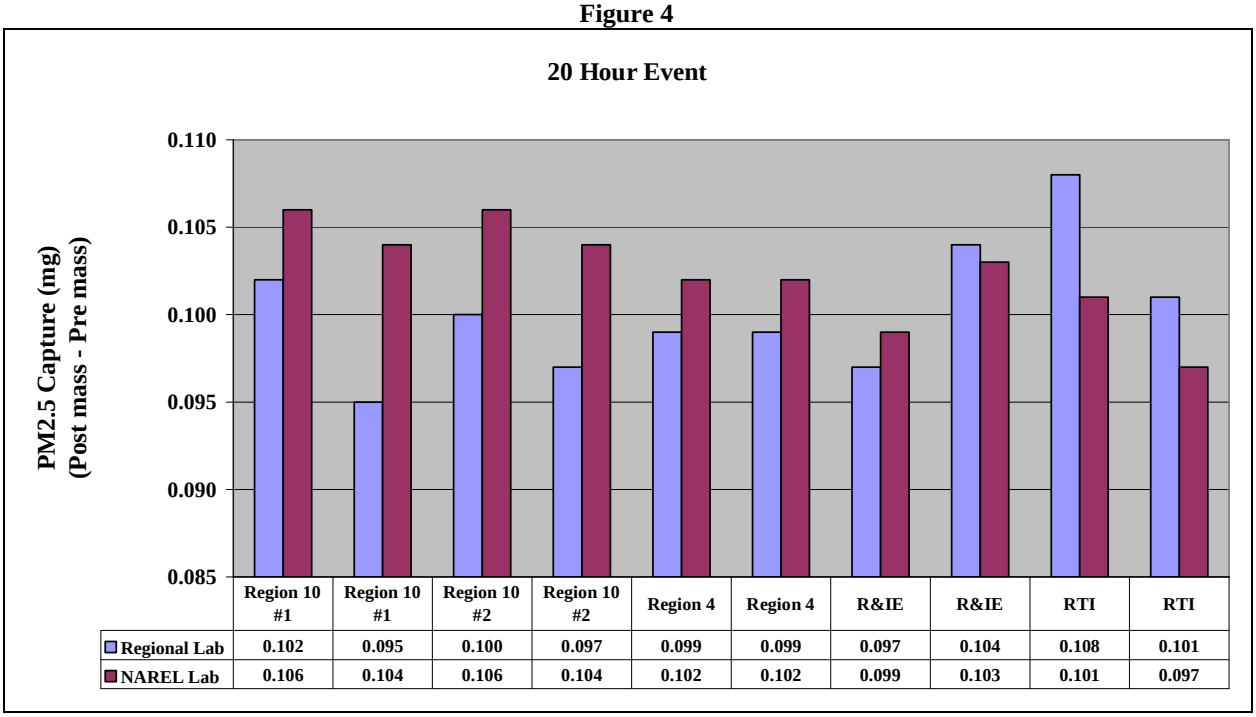
	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	0.347	0.357	0.353	0.360	0.360	0.357	0.365	0.359	0.360	0.357
NAREL Lab	0.352	0.359	0.352	0.359	0.362	0.360	0.359	0.355	0.361	0.356

Figure 3



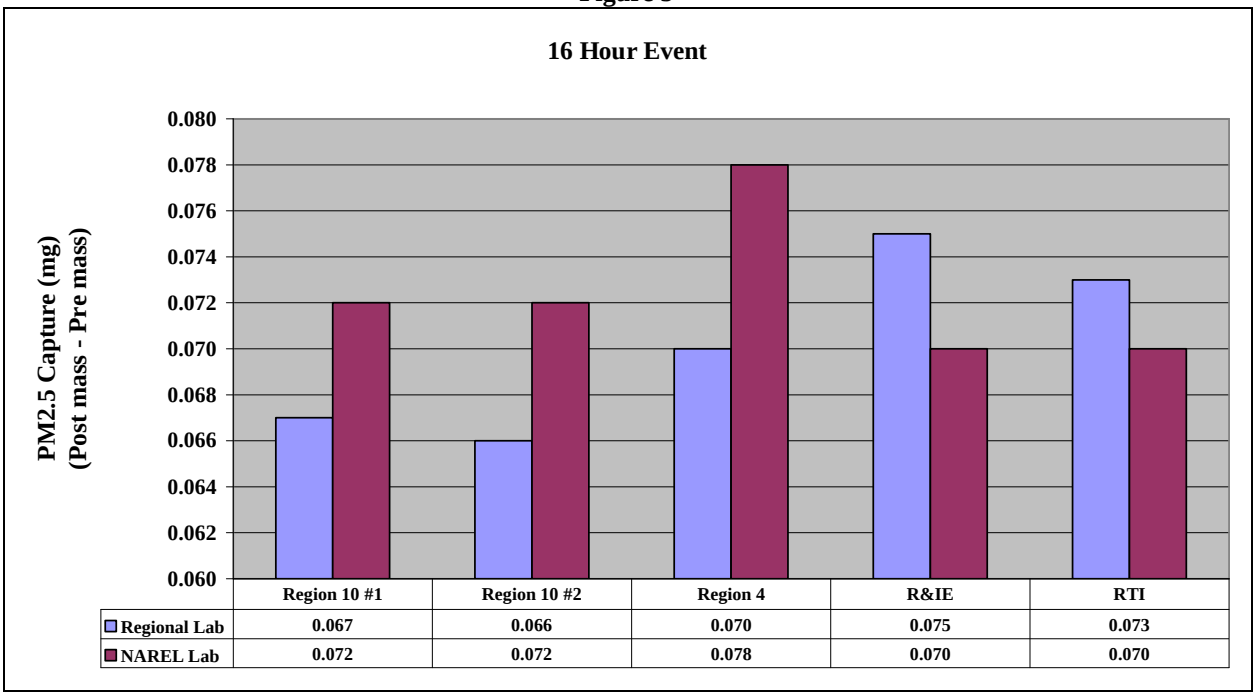
	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	0.159	0.158	0.161	0.163	0.168	0.159	0.163	0.167	0.170	0.168
NAREL Lab	0.163	0.163	0.163	0.163	0.171	0.161	0.161	0.160	0.168	0.165

Figure 4



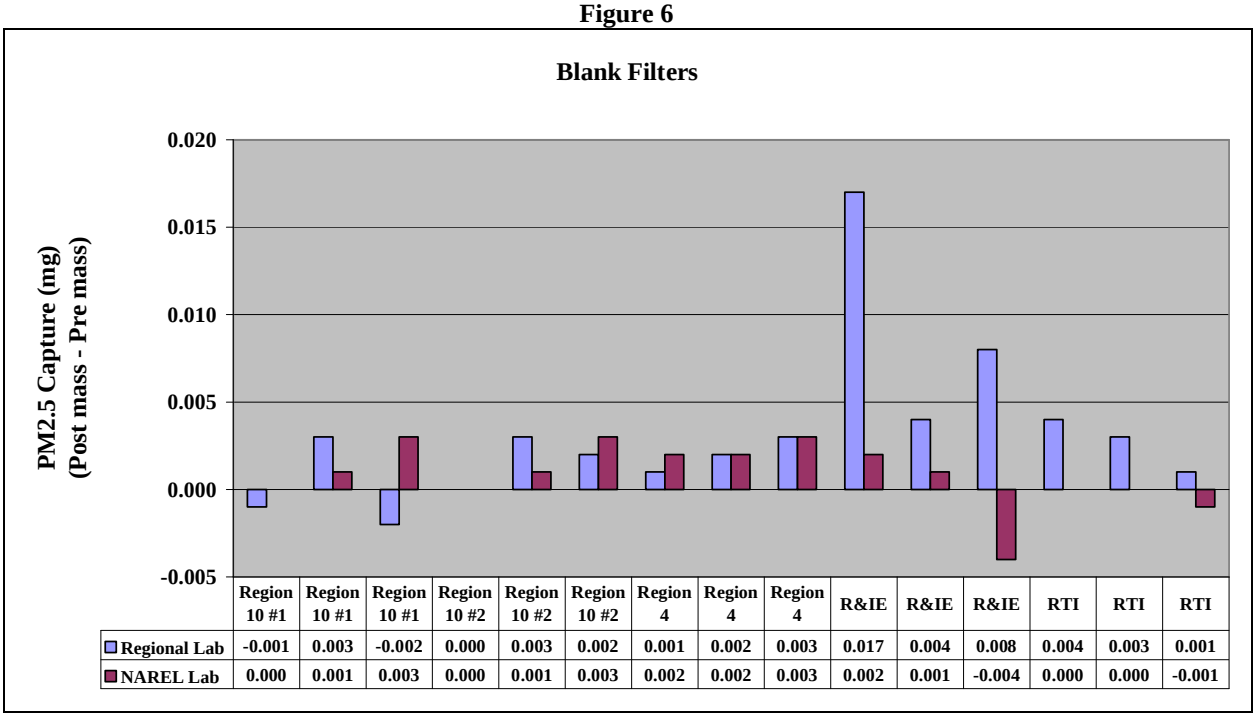
	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	0.102	0.095	0.100	0.097	0.099	0.099	0.097	0.104	0.108	0.101
NAREL Lab	0.106	0.104	0.106	0.104	0.102	0.102	0.099	0.103	0.101	0.097

Figure 5



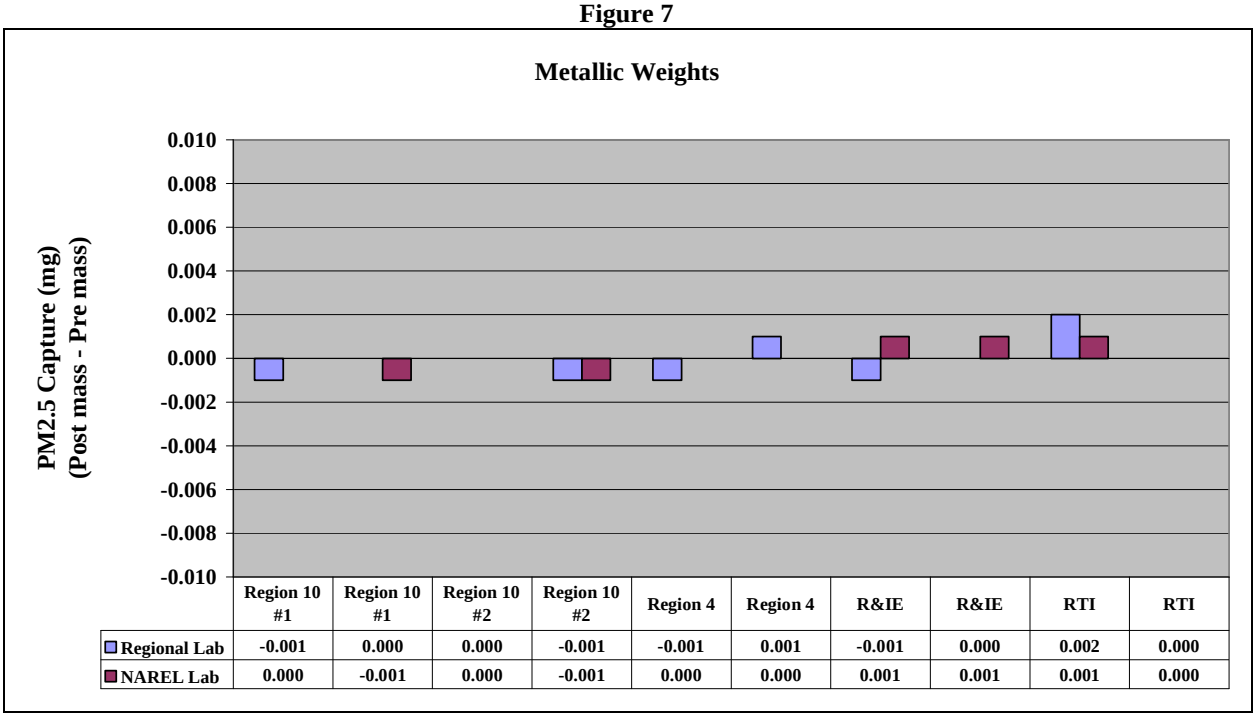
	Region 10 #1	Region 10 #2	Region 4	R&IE	RTI
Regional Lab	0.067	0.066	0.070	0.075	0.073
NAREL Lab	0.072	0.072	0.078	0.070	0.070

Figure 6



	Region 10 #1	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 10 #2	Region 4	Region 4	Region 4	R&IE	R&IE	R&IE	RTI	RTI	RTI
Regional Lab	-0.001	0.003	-0.002	0.000	0.003	0.002	0.001	0.002	0.003	0.017	0.004	0.008	0.004	0.003	0.001
NAREL Lab	0.000	0.001	0.003	0.000	0.001	0.003	0.002	0.002	0.003	0.002	0.001	-0.004	0.000	0.000	-0.001

Figure 7



	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	-0.001	0.000	0.000	-0.001	-0.001	0.001	-0.001	0.000	0.002	0.000
NAREL Lab	0.000	-0.001	0.000	-0.001	0.000	0.000	0.001	0.001	0.001	0.000

Table 2. Gravimetric Data Region 4

Sample ID	Tare Mass		Final Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5
	Region 4 (mg)	NAREL (mg)	Region 4 (mg)	NAREL (mg)	Region 4 (mg)	NAREL (mg)	(mg)
T05-11448	145.295	145.292	145.655	145.654	0.360	0.362	0.002
T05-11449	145.101	145.098	145.458	145.458	0.357	0.360	0.003
T05-11450	145.604	145.601	145.772	145.772	0.168	0.171	0.003
T05-11451	143.939	143.936	144.098	144.097	0.159	0.161	0.002
T05-11452	145.717	145.713	145.816	145.815	0.099	0.102	0.003
T05-11453	143.732	143.729	143.831	143.831	0.099	0.102	0.003
T05-11454	144.517	144.512	144.587	144.590	0.070	0.078	0.008
T05-11455	145.713	145.709	145.714	145.711	0.001	0.002	0.001
T05-11456	146.201	146.196	146.203	146.198	0.002	0.002	0.000
T05-11457	145.503	145.497	145.506	145.500	0.003	0.003	0.000
MW05-11488	191.060	191.061	191.059	191.061	-0.001	0.000	0.001
MW05-11489	96.351	96.353	96.352	96.353	0.001	0.000	-0.001

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

Table 3. Gravimetric Data Region 10 Analyst 1

Sample ID	Tare Mass		Final Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5
	Region 10 #1 (mg)	NAREL (mg)	Region 10 #1 (mg)	NAREL (mg)	Region 10 #1 (mg)	NAREL (mg)	(mg)
T05-11458	147.727	147.727	148.074	148.079	0.347	0.352	0.005
T05-11459	149.029	149.032	149.386	149.391	0.357	0.359	0.002
T05-11460	149.483	149.487	149.642	149.650	0.159	0.163	0.004
T05-11461	145.360	145.362	145.518	145.525	0.158	0.163	0.005
T05-11462	144.141	144.146	144.243	144.252	0.102	0.106	0.004
T05-11463	144.088	144.090	144.183	144.194	0.095	0.104	0.009
T05-11464	146.516	146.521	146.583	146.593	0.067	0.072	0.005
T05-11465	147.334	147.337	147.333	147.337	-0.001	0.000	0.001
T05-11466	146.276	146.282	146.279	146.283	0.003	0.001	-0.002
T05-11467	146.333	146.334	146.331	146.337	-0.002	0.003	0.005
MW05-11490	193.819	193.822	193.819	193.822	-0.001	0.000	0.001
MW05-11491	92.959	92.960	92.958	92.959	0.000	-0.001	-0.001

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

Table 4. Gravimetric Data Region 10 Analyst 2

Sample ID	Tare Mass		Final Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5
	Region 10 #2 (mg)	NAREL (mg)	Region 10 #2 (mg)	NAREL (mg)	Region 10 #2 (mg)	NAREL (mg)	(mg)
T05-11458	147.724	147.727	148.077	148.079	0.353	0.352	-0.001
T05-11459	149.028	149.032	149.388	149.391	0.360	0.359	-0.001
T05-11460	149.482	149.487	149.643	149.650	0.161	0.163	0.002
T05-11461	145.358	145.362	145.521	145.525	0.163	0.163	0.000
T05-11462	144.143	144.146	144.243	144.252	0.100	0.106	0.006
T05-11463	144.088	144.090	144.185	144.194	0.097	0.104	0.007
T05-11464	146.517	146.521	146.583	146.593	0.066	0.072	0.006
T05-11465	147.334	147.337	147.334	147.337	0.000	0.000	0.000
T05-11466	146.277	146.282	146.280	146.283	0.003	0.001	-0.002
T05-11467	146.333	146.334	146.335	146.337	0.002	0.003	0.001
MW05-11490	193.820	193.822	193.819	193.822	0.000	0.000	0.000
MW05-11491	92.958	92.960	92.958	92.959	-0.001	-0.001	0.000

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

Table 5. Gravimetric Data R&IE

Sample ID	Tare Mass		Final Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5
	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL (mg)	(mg)
T05-11468	148.505	148.498	148.870	148.857	0.365	0.359	-0.006
T05-11470	146.850	146.845	147.209	147.200	0.359	0.355	-0.004
T05-11471	144.999	144.994	145.162	145.155	0.163	0.161	-0.002
T05-11472	144.930	144.927	145.097	145.087	0.167	0.160	-0.007
T05-11473	146.365	146.362	146.462	146.461	0.097	0.099	0.002
T05-11474	145.926	145.923	146.030	146.026	0.104	0.103	-0.001
T05-11475	145.574	145.569	145.649	145.639	0.075	0.070	-0.005
T05-11469	146.592	146.589	146.609	146.591	0.017	0.002	-0.015
T05-11476	145.384	145.382	145.388	145.383	0.004	0.001	-0.003
T05-11477	146.142	146.142	146.150	146.138	0.008	-0.004	-0.012
MW05-11492	186.993	186.995	186.992	186.996	-0.001	0.001	0.002
MW05-11493	90.601	90.603	90.601	90.604	0.000	0.001	0.001

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

Table 6. Gravimetric Data RTI

Sample ID	Tare Mass RTI (mg)	Tare Mass NAREL (mg)	Final Mass RTI (mg)	Final Mass NAREL (mg)	Captured PM2.5 RTI (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (mg)
T05-11478	146.062	146.063	146.422	146.424	0.360	0.361	0.001
T05-11479	146.532	146.535	146.889	146.891	0.357	0.356	-0.001
T05-11480	145.912	145.912	146.082	146.080	0.170	0.168	-0.002
T05-11481	144.168	144.168	144.336	144.333	0.168	0.165	-0.003
T05-11482	145.799	145.805	145.907	145.906	0.108	0.101	-0.007
T05-11483	145.921	145.924	146.022	146.021	0.101	0.097	-0.004
T05-11484	145.901	145.901	145.974	145.971	0.073	0.070	-0.003
T05-11485	148.313	148.315	148.317	148.315	0.004	0.000	-0.004
T05-11486	148.360	148.362	148.363	148.362	0.003	0.000	-0.003
T05-11487	147.228	147.229	147.229	147.228	0.001	-0.001	-0.002
MW05-11494	181.334	181.336	181.336	181.337	0.002	0.001	-0.001
MW05-11495	88.207	88.208	88.207	88.208	0.000	0.000	0.000

* Negative values indicate a larger capture determined by RTI

Table 7. Sampling Schedule

Lab ID	Filter ID	Sample Start	Event Duration (hours)	Receiving Lab
T05-11448	T2223306	9/29/2005	48	Region 4
T05-11449	T2223307	9/29/2005	48	Region 4
T05-11450	T2223308	10/3/2005	24	Region 4
T05-11451	T2223309	10/3/2005	24	Region 4
T05-11452	T2223310	10/4/2005	20	Region 4
T05-11453	T2223311	10/4/2005	20	Region 4
T05-11454	T2223312	10/5/2005	16	Region 4
T05-11455	T2223314		0	Region 4
T05-11456	T2223315		0	Region 4
T05-11457	T2223316		0	Region 4
T05-11458	T2223317	9/29/2005	48	Region 10
T05-11459	T2223318	9/29/2005	48	Region 10
T05-11460	T2223319	10/3/2005	24	Region 10
T05-11461	T2223320	10/3/2005	24	Region 10
T05-11462	T2223321	10/4/2005	20	Region 10
T05-11463	T2223323	10/4/2005	20	Region 10
T05-11464	T2223324	10/5/2005	16	Region 10
T05-11465	T2223327		0	Region 10
T05-11466	T2223328		0	Region 10
T05-11467	T2223329		0	Region 10
T05-11468	T2223330	9/29/2005	48	R&IE
T05-11470	T2223332	9/29/2005	48	R&IE
T05-11471	T2223333	10/3/2005	24	R&IE
T05-11472	T2223334	10/3/2005	24	R&IE
T05-11473	T2223335	10/4/2005	20	R&IE
T05-11474	T2223336	10/4/2005	20	R&IE
T05-11475	T2223337	10/5/2005	16	R&IE
T05-11476	T2223338		0	R&IE
T05-11477	T2223339		0	R&IE
T05-11469	T2223331		0	R&IE
T05-11478	T2223340	9/29/2005	48	RTI
T05-11479	T2223341	9/29/2005	48	RTI
T05-11480	T2223342	10/3/2005	24	RTI
T05-11481	T2223343	10/3/2005	24	RTI
T05-11482	T2223344	10/4/2005	20	RTI
T05-11483	T2223345	10/4/2005	20	RTI
T05-11484	T2223346	10/5/2005	16	RTI
T05-11485	T2223347		0	RTI
T05-11486	T2223348		0	RTI
T05-11487	T2223349		0	RTI