TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS

FROM: Eric Boswell / NAREL

AUTHOR: Steve Taylor / NAREL

DATE: September 19, 2013

SUBJECT: Gravimetric Inter-Laboratory Comparison Study

Introduction

The EPA's National Analytical 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 selected 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 2013 have been submitted by the participating test laboratories. Four EPA laboratories routinely participate in this study. EPA's Region 4 laboratory located in Athens, GA provides pre- and post-weighing of filters for the $PM_{2.5}$ Performance Evaluation Program (PEP). The Region 2 laboratory located in Edison, NJ provides quality assurance oversight of laboratories in Region 2 that weigh filters for the $PM_{2.5}$ program. The National Center for Radiation Field Operations (NCRFO) located in Las Vegas, NV provides pre- and post-weighing of Teflon® filters in support of the Tribal Air Monitoring Support (TAMS) $PM_{2.5}$ air monitoring program. The Office of Air Quality Planning and Standards (OAQPS) laboratory, located in Research Triangle Park (RTP), NC, performs special studies and serves as a backup weighing facility for the $PM_{2.5}$ PEP. Two additional laboratories participating in this study were the Puerto Rico Environmental Quality Board (PREQB) and the New Jersey Department of Environmental Protection (NJDEP) laboratories that provide gravimetric analyses for their agency's air monitoring program. This was the NJDEP laboratory's first gravimetric comparison study with NAREL. NAREL supplied the performance test (PT) samples and served as the reference laboratory for the study.

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 Super 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 PT studies administered by NAREL.

Experimental

Six sample sets consisting of ten new MTL Teflon® filters and two metallic weights were assembled for the 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 equilibrated in NAREL's weighing chamber. Pre-mass measurements were performed before the samples were 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. Each test lab completed its pre-mass measurements and returned the samples to NAREL. The returned samples were then equilibrated and weighed a second time to determine NAREL's pre-mass of record. Results of this weighing session were compared to NAREL's first weighing session to determine if any significant changes in mass occurred while the samples were out of NAREL's custody. As an additional QA check, a third weighing session was also performed on a different day to verify NAREL's pre-mass results.

Four sampling events using 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 remaining three filters from each set served as blanks. The loading schedule for the filters is shown in table 1. Table 1 shows that each lab received replicate samples of each loaded event except for the single filter loaded on July 30.

Table 1. Sampling Schedule for Loaded Gravimetric Filters

Filter _ID	Serial Number	Sample Start	Event Duration	Receiving Lab
T13-14905	T3599874	7/25/2013	30 hr	Region 2
T13-14906	T3599875	7/25/2013	30 hr	Region 2
T13-14907	T3599876	7/26/2013	48 hr	Region 2
T13-14908	T3599877	7/26/2013	48 hr	Region 2
T13-14909	T3599878	7/29/2013	24 hr	Region 2
T13-14910	T3599879	7/29/2013	24 hr	Region 2
T13-14911	T3599880	7/30/2013	20 hr	Region 2
T13-14915	T3599884	7/25/2013	30 hr	Region 4
T13-14916	T3599885	7/25/2013	30 hr	Region 4
T13-14917	T3599886	7/26/2013	48 hr	Region 4
T13-14918	T3599887	7/26/2013	48 hr	Region 4
T13-14919	T3599889	7/29/2013	24 hr	Region 4
T13-14920	T3599890	7/29/2013	24 hr	Region 4
T13-14921	T3599891	7/30/2013	20 hr	Region 4
T13-14925	T3599895	7/25/2013	30 hr	NCRFO

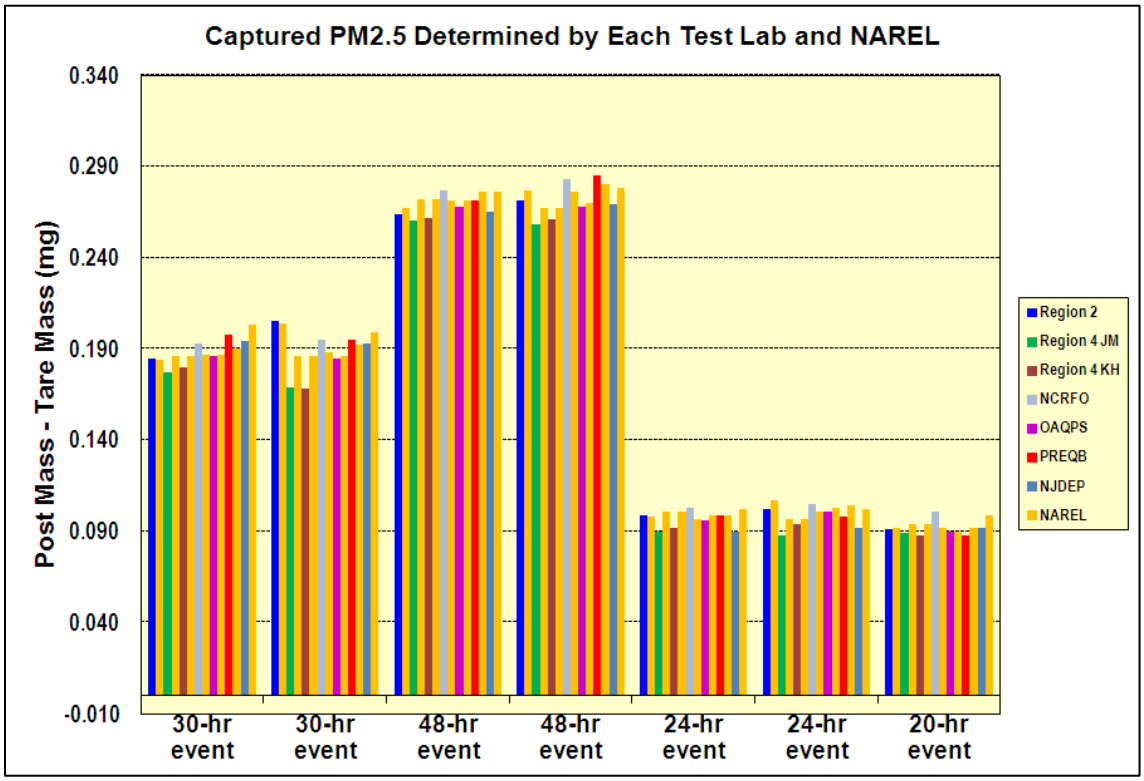
Filter _ID	Serial Number	Sample Start	Event Duration	Receiving Lab
T13-14926	T3599896	7/25/2013	30 hr	NCRFO
T13-14927	T3599897	7/26/2013	48 hr	NCRFO
T13-14928	T3599898	7/26/2013	48 hr	NCRFO
T13-14929	T3599899	7/29/2013	24 hr	NCRFO
T13-14930	T3599901	7/29/2013	24 hr	NCRFO
T13-14931	T3599902	7/30/2013	20 hr	NCRFO
T13-14935	T3599906	7/25/2013	30 hr	OAQPS
T13-14936	T3599907	7/25/2013	30 hr	OAQPS
T13-14937	T3599908	7/26/2013	48 hr	OAQPS
T13-14938	T3599909	7/26/2013	48 hr	OAQPS
T13-14939	T3599910	7/29/2013	24 hr	OAQPS
T13-14940	T3599911	7/29/2013	24 hr	OAQPS
T13-14941	T3599912	7/30/2013	20 hr	OAQPS
T13-14945	T3599916	7/25/2013	30 hr	PREQB
T13-14946	T3599917	7/25/2013	30 hr	PREQB
T13-14947	T3599918	7/26/2013	48 hr	PREQB
T13-14948	T3599919	7/26/2013	48 hr	PREQB
T13-14949	T3599920	7/29/2013	24 hr	PREQB
T13-14950	T3599921	7/29/2013	24 hr	PREQB
T13-14951	T3599922	7/30/2013	20 hr	PREQB
T13-14955	T3599926	7/25/2013	30 hr	NJDEP
T13-14956	T3599927	7/25/2013	30 hr	NJDEP
T13-14957	T3599928	7/26/2013	48 hr	NJDEP
T13-14958	T3599929	7/26/2013	48 hr	NJDEP
T13-14959	T3599930	7/29/2013	24 hr	NJDEP
T13-14960	T3599931	7/29/2013	24 hr	NJDEP
T13-14961	T3599932	7/30/2013	20 hr	NJDEP

Following each collection event, samples were returned to NAREL's weighing chamber for equilibration. After allowing several days for filter stabilization and equilibration, the first post-mass measurements were determined for the loaded filters as well as the blank filters and metallic weights. A second post-mass measurement of all samples was performed after several more days to verify stability of the samples. The last weighing session before shipping the samples to the test labs became NAREL's post-mass of record. The filters and metallic weights were packed into small coolers with ice substitute and shipped back to the test labs for post-weighing.

Gravimetric Results

The mass capture results reported by the test labs and NAREL for loaded filters are shown in figure 1. Each bar shown in figure 1 represents the mass capture determined by a test lab followed by NAREL's determination for the same loaded filter. As stated earlier, the capture is calculated by subtracting the pre-mass from the post-mass.

Figure 1



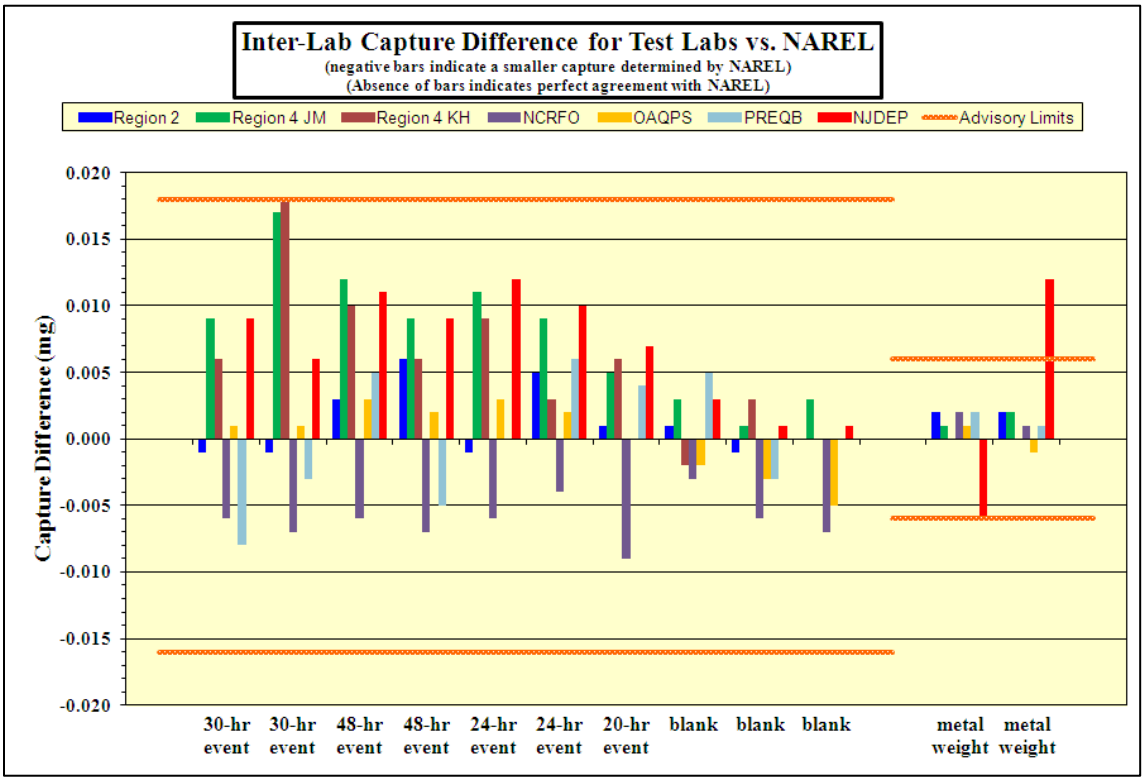


Figure 2

Figure 2 presents the inter-laboratory capture differences for all samples. 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 2 are 3-sigma limits derived from previous

gravimetric PT studies administered by NAREL. The absence of a bar indicates perfect agreement between NAREL and the test lab.

Metallic weights were included in this study because they are less susceptible to weighing errors due to factors such as electrical static and volatility of filter constituents. This is indicated by the much tighter advisory limits for the weights. The same 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 used to calculate the mass capture and the inter-lab capture differences shown in figures 1 and 2 are presented 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. Table 3 allows laboratories a convenient way to compare each of its measurements with NAREL's corresponding measurement. Analysis of the data in table 3 can sometimes help in determining a cause for discrepancies in results between test labs and NAREL. For example, figure 2 shows that one metallic weight result from NJDEP fell outside the 3-sigma advisory limits. Table 2 contains data extracted from table 3 of the pre- and post-mass measurements for the metal weights and the measurement difference between NAREL and NJDEP. A conversation with the NJDEP gravimetric lab manager revealed that the metallic weights that NAREL used for the study were not compatible with the auto-handler routinely used to load filters onto their balance. The metal weights had to be manually weighed by the analyst, which was a deviation from normal procedures. Notice that the largest measurement differences between labs (0.011 mg and -0.012 mg) were in the pre-mass measurements. The post-mass measurements were in much better agreement possibly indicating an improvement in the analyst's technique for non-standard manual weighings.

Table 2. Metallic weight measurements for NJDEP and NAREL

Sample ID	Pre-Mass		Pre-Mass Difference	Post-Mass		Post-Mass Difference
	NJDEP (mg)	NAREL (mg)	(mg)	NJDEP (mg)	NAREL (mg)	(mg)
MW13-14975	496.635	496.646	0.011	496.642	496.647	0.005
MW13-14976	83.544	83.532	-0.012	83.532	83.532	0.000

Conclusions

This inter-laboratory gravimetric study evaluated six federal and state 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 Teflon® 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 consisting of ten Teflon® filters and two metallic weights in order to determine the mass capture. NAREL served as the reference lab by weighing all samples. NAREL's pre-mass of record for each sample was determined shortly after each test lab had performed its pre-mass measurements. NAREL's post-mass of record was determined shortly before the sample sets were shipped back to the test labs for their final post-mass measurements. Performance was evaluated by comparing mass capture results determined by NAREL to mass capture results determined by each test laboratory. The results of this study as illustrated in figure 2 indicate overall good inter-laboratory agreement between the test laboratories and NAREL.

Table 3. Gravimetric Mass PT Results

Sample ID	Sample Description	Tare Mass		Loaded 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)		
T13-14905	30-hr event	375.924	375.939	376.109	376.123	0.185	0.184	-0.001	Region 2
T13-14906	30-hr event	370.949	370.963	371.154	371.167	0.205	0.204	-0.001	Region 2
T13-14907	48-hr event	371.024	371.038	371.288	371.305	0.264	0.267	0.003	Region 2
T13-14908	48-hr event	372.160	372.174	372.431	372.451	0.271	0.277	0.006	Region 2
T13-14909	24-hr event	371.722	371.736	371.821	371.834	0.099	0.098	-0.001	Region 2
T13-14910	24-hr event	374.246	374.260	374.348	374.367	0.102	0.107	0.005	Region 2
T13-14911	20-hr event	378.520	378.535	378.611	378.627	0.091	0.092	0.001	Region 2
T13-14912	Blank	377.210	377.224	377.210	377.225	0.000	0.001	0.001	Region 2
T13-14913	Blank	360.449	360.466	360.451	360.467	0.002	0.001	-0.001	Region 2
T13-14914	Blank	364.649	364.664	364.651	364.666	0.002	0.002	0.000	Region 2
MW13-14965	metallic weight	474.030	474.035	474.030	474.037	0.000	0.002	0.002	Region 2
MW13-14966	metallic weight	94.828	94.831	94.826	94.831	-0.002	0.000	0.002	Region 2
T13-14915	30-hr event	364.672	364.667	364.849	364.853	0.177	0.186	0.009	Region 4 JM
T13-14916	30-hr event	363.931	363.915	364.100	364.101	0.169	0.186	0.017	Region 4 JM
T13-14917	48-hr event	365.455	365.449	365.715	365.721	0.260	0.272	0.012	Region 4 JM
T13-14918	48-hr event	362.434	362.430	362.692	362.697	0.258	0.267	0.009	Region 4 JM
T13-14919	24-hr event	365.980	365.976	366.070	366.077	0.090	0.101	0.011	Region 4 JM
T13-14920	24-hr event	366.807	366.800	366.895	366.897	0.088	0.097	0.009	Region 4 JM
T13-14921	20-hr event	366.215	366.212	366.304	366.306	0.089	0.094	0.005	Region 4 JM

Table 3. Gravimetric Mass PT Results

Sample ID	Sample Description	Tare Mass		Loaded 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)		
T13-14922	Blank	368.177	368.171	368.174	368.171	-0.003	0.000	0.003	Region 4 JM
T13-14923	Blank	372.575	372.571	372.574	372.571	-0.001	0.000	0.001	Region 4 JM
T13-14924	Blank	366.256	366.249	366.253	366.249	-0.003	0.000	0.003	Region 4 JM
MW13-14967	metallic weight	469.850	469.849	469.850	469.850	0.000	0.001	0.001	Region 4 JM
MW13-14968	metallic weight	99.714	99.713	99.713	99.714	-0.001	0.001	0.002	Region 4 JM
T13-14915	30-hr event	364.672	364.667	364.852	364.853	0.180	0.186	0.006	Region 4 KH
T13-14916	30-hr event	363.931	363.915	364.099	364.101	0.168	0.186	0.018	Region 4 KH
T13-14917	48-hr event	365.456	365.449	365.718	365.721	0.262	0.272	0.010	Region 4 KH
T13-14918	48-hr event	362.435	362.430	362.696	362.697	0.261	0.267	0.006	Region 4 KH
T13-14919	24-hr event	365.982	365.976	366.074	366.077	0.092	0.101	0.009	Region 4 KH
T13-14920	24-hr event	366.806	366.800	366.900	366.897	0.094	0.097	0.003	Region 4 KH
T13-14921	20-hr event	366.218	366.212	366.306	366.306	0.088	0.094	0.006	Region 4 KH
T13-14922	Blank	368.174	368.171	368.176	368.171	0.002	0.000	-0.002	Region 4 KH
T13-14923	Blank	372.576	372.571	372.573	372.571	-0.003	0.000	0.003	Region 4 KH
T13-14924	Blank	366.255	366.249	366.255	366.249	0.000	0.000	0.000	Region 4 KH
MW13-14967	metallic weight	469.847	469.849	469.848	469.850	0.001	0.001	0.000	Region 4 KH
MW13-14968	metallic weight	99.712	99.713	99.713	99.714	0.001	0.001	0.000	Region 4 KH
T13-14925	30-hr event	369.827	369.825	370.020	370.012	0.193	0.187	-0.006	NCRFO
T13-14926	30-hr event	367.416	367.413	367.611	367.601	0.195	0.188	-0.007	NCRFO

Table 3. Gravimetric Mass PT Results

Sample ID	Sample Description	Tare Mass		Loaded 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)		
T13-14927	48-hr event	366.478	366.473	366.755	366.744	0.277	0.271	-0.006	NCRFO
T13-14928	48-hr event	368.199	368.197	368.482	368.473	0.283	0.276	-0.007	NCRFO
T13-14929	24-hr event	368.794	368.792	368.897	368.889	0.103	0.097	-0.006	NCRFO
T13-14930	24-hr event	372.938	372.935	373.043	373.036	0.105	0.101	-0.004	NCRFO
T13-14931	20-hr event	366.747	366.745	366.848	366.837	0.101	0.092	-0.009	NCRFO
T13-14932	Blank	371.918	371.914	371.921	371.914	0.003	0.000	-0.003	NCRFO
T13-14933	Blank	368.511	368.510	368.517	368.510	0.006	0.000	-0.006	NCRFO
T13-14934	Blank	369.267	369.265	369.274	369.265	0.007	0.000	-0.007	NCRFO
MW13-14969	metallic weight	495.541	495.543	495.540	495.544	-0.001	0.001	0.002	NCRFO
MW13-14970	metallic weight	84.757	84.755	84.756	84.755	-0.001	0.000	0.001	NCRFO
T13-14935	30-hr event	369.428	369.421	369.614	369.608	0.186	0.187	0.001	OAQPS
T13-14936	30-hr event	369.342	369.335	369.527	369.521	0.185	0.186	0.001	OAQPS
T13-14937	48-hr event	369.091	369.084	369.359	369.355	0.268	0.271	0.003	OAQPS
T13-14938	48-hr event	373.659	373.652	373.927	373.922	0.268	0.270	0.002	OAQPS
T13-14939	24-hr event	368.686	368.679	368.782	368.778	0.096	0.099	0.003	OAQPS
T13-14940	24-hr event	373.751	373.742	373.852	373.845	0.101	0.103	0.002	OAQPS
T13-14941	20-hr event	368.467	368.461	368.557	368.551	0.090	0.090	0.000	OAQPS
T13-14942	Blank	365.498	365.495	365.500	365.495	0.002	0.000	-0.002	OAQPS
T13-14943	Blank	369.864	369.859	369.866	369.858	0.002	-0.001	-0.003	OAQPS

Table 3. Gravimetric Mass PT Results

Sample ID	Sample Description	Tare Mass		Loaded 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)		
T13-14944	Blank	371.552	371.546	371.557	371.546	0.005	0.000	-0.005	OAQPS
MW13-14971	metallic weight	479.574	479.567	479.574	479.568	0.000	0.001	0.001	OAQPS
MW13-14972	metallic weight	96.353	96.351	96.354	96.351	0.001	0.000	-0.001	OAQPS
T13-14945	30-hr event	373.747	373.747	373.945	373.937	0.198	0.190	-0.008	PREQB
T13-14946	30-hr event	367.362	367.360	367.557	367.552	0.195	0.192	-0.003	PREQB
T13-14947	48-hr event	374.140	374.137	374.411	374.413	0.271	0.276	0.005	PREQB
T13-14948	48-hr event	372.372	372.375	372.657	372.655	0.285	0.280	-0.005	PREQB
T13-14949	24-hr event	366.650	366.651	366.749	366.750	0.099	0.099	0.000	PREQB
T13-14950	24-hr event	369.488	369.488	369.586	369.592	0.098	0.104	0.006	PREQB
T13-14951	20-hr event	369.872	369.872	369.960	369.964	0.088	0.092	0.004	PREQB
T13-14952	Blank	370.356	370.356	370.354	370.359	-0.002	0.003	0.005	PREQB
T13-14953	Blank	369.494	369.495	369.498	369.496	0.004	0.001	-0.003	PREQB
T13-14954	Blank	371.791	371.792	371.792	371.793	0.001	0.001	0.000	PREQB
MW13-14973	metallic weight	484.901	484.900	484.900	484.901	-0.001	0.001	0.002	PREQB
MW13-14974	metallic weight	87.548	87.548	87.547	87.548	-0.001	0.000	0.001	PREQB
T13-14955	30-hr event	378.147	378.143	378.341	378.346	0.194	0.203	0.009	NJDEP
T13-14956	30-hr event	378.061	378.056	378.254	378.255	0.193	0.199	0.006	NJDEP
T13-14957	48-hr event	371.748	371.744	372.013	372.020	0.265	0.276	0.011	NJDEP
T13-14958	48-hr event	371.379	371.377	371.648	371.655	0.269	0.278	0.009	NJDEP

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Sample ID	Sample Description	Tare Mass		Loaded 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)		
T13-14959	24-hr event	376.634	376.627	376.724	376.729	0.090	0.102	0.012	NJDEP
T13-14960	24-hr event	375.041	375.035	375.133	375.137	0.092	0.102	0.010	NJDEP
T13-14961	20-hr event	373.154	373.153	373.246	373.252	0.092	0.099	0.007	NJDEP
T13-14962	Blank	378.712	378.710	378.711	378.712	-0.001	0.002	0.003	NJDEP
T13-14963	Blank	377.558	377.556	377.559	377.558	0.001	0.002	0.001	NJDEP
T13-14964	Blank	375.441	375.438	375.442	375.440	0.001	0.002	0.001	NJDEP
MW13-14975	metallic weight	496.635	496.646	496.642	496.647	0.007	0.001	-0.006	NJDEP
MW13-14976	metallic weight	83.544	83.532	83.532	83.532	-0.012	0.000	0.012	NJDEP

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