TECHNICAL MEMORANDUM

TO: Jim Homolya / OAQPS

FROM: Eric Boswell / NAREL

COPY: Mike Poore / CARB

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DATE: March 25, 2004

SUBJECT: Performance Evaluation - CARB Laboratories

Introduction

A study has been conducted as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network (STN). The purpose of this study was to evaluate specific laboratory performance at the California Air Resources Board (CARB) facilities located in Sacramento. CARB has elected to implement STN protocols at their own laboratory facilities so that many of the $PM_{2.5}$ speciation samples collected within the state can be analyzed locally. Most states use laboratories at the Research Triangle Institute (RTI) which operates under a federal contract to analyze STN samples.

Performance Evaluation (PE) samples were prepared at the National Air and Radiation Environmental Laboratory (NAREL) and submitted to CARB for analysis. The PE samples consisted of the following components.

- Gravimetric Mass Analysis - two metallic weights and ten Teflon® filters previously tared at CARB.
- Ion Chromatography (IC) Analysis - six Nylon® filters, three anion spike solutions, and three cation spike solutions.
- TOT Carbon Analysis - six quartz filters and three spike solutions.
- XRF Elemental Analysis - five well characterized Teflon® filters

Results from the elemental analysis using x-ray fluorescence (XRF) will not be included in this report. CARB is currently in the process of purchasing a new XRF system to replace their old instrument which has been removed from service. Several weeks will probably be required to implement the new system. CARB's laboratory manager has decided to accumulate a backlog of XRF samples until the new system is brought on-line. The five PE filters submitted for XRF analysis have been stored along with the routine samples going into the backlog. EPA has decided to release this report now without the XRF results. A separate report will be written later to include the XRF results.

Detailed instructions for analyzing and reporting the PE samples were provided by NAREL. The analytical facilities at NAREL are similar to those at CARB. Each PE sample, or a replicate of the PE sample, was also analyzed at NAREL. This report will discuss the analytical results reported by CARB and will compare each result to an expected value.

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. CARB routinely provides clean pre-weighed air filters to the various field sites within the state. At the field site, an approved sampling device must be used to sample the air and deposit the very fine $PM_{2.5}$ onto the collection filter. The filter is then returned to CARB where the gravimetric analysis is completed.

CARB also provides clean Nylon® filters to the various field sites. The Nylon® filter is used to capture $PM_{2.5}$ for subsequent IC analysis. After the loaded filter is returned to the laboratory, the IC analysis typically proceeds by first extracting the filter using an appropriate solvent. The extract must be analyzed using an IC instrument that is optimized to determine the ions of interest. Target anions and target cations must be analyzed on separate IC instruments.

CARB routinely provides clean quartz filters to the various field sites. The quartz filter is used to capture $PM_{2.5}$ for subsequent carbon analysis. A thermal/optical technique is used at CARB to determine the carbon present on the quartz filter. A carefully measured portion of the quartz filter is placed into a special oven equipped to shine a laser through the sample. The oven is programmed to heat the quartz filter material to release captured $PM_{2.5}$. Carbon components released from the filter are swept through the oven by a controlled purge gas. The carbon released from the filter is catalytically converted to methane and measured by a flame ionization detector (FID) positioned at the end of the sample train. A thermogram produced by the analysis contains signals from the FID and from the laser. Interpretation of the thermogram provides results for organic carbon (OC) and elemental carbon (EC) the sum of which is reported as the total carbon (TC). The instrument at CARB is slightly different from the instrument at NAREL, and those differences shall be discussed later in the carbon analysis section of this report

Gravimetric Analysis

NAREL provided ten new Teflon® filters and two metallic weights for this study. Metallic weights were included in this study to provide a material which is not as susceptible to problems with electrical static as the true filter material. The filters and the weights were shipped to CARB with a request to determine tare mass using local standard procedures. After tare mass had been determined at CARB, the filters and metallic weights were shipped to NAREL in Montgomery, AL. The filters and the weights were immediately placed into the weighing chamber at NAREL for equilibration and determination of a NAREL tare mass. After the NAREL tare mass was determined, the filters were loaded with $PM_{2.5}$ captured from the outside air near NAREL. Met One air samplers were used to load seven of the filters, and the remaining three filters were utilized as blanks. Following sample collection, all filters and weights were returned to the weighing chamber at NAREL to equilibrate and to determine the loaded mass. Finally, the ten filters and two metallic weights were shipped back to CARB for their routine gravimetric determination of $PM_{2.5}$ capture.

Gravimetric Results

The results of this study are summarized in Figure 1. The critical information needed by the program is the mass of $PM_{2.5}$ deposited onto the surface of a collection filter, and therefore, $PM_{2.5}$ capture is plotted in Figure 1 for the seven loaded filters, three travel blanks, and two metallic weights.

Figure 2 presents the inter-laboratory differences. Inter-laboratory differences were calculated by subtracting the $PM_{2.5}$ capture value determined at CARB from the capture value determined at NAREL. Notice that a negative bar on the Figure 2 graph represents a smaller $PM_{2.5}$ capture value determined at NAREL.

The raw data reported from both laboratories have been tabulated for easy viewing. At the end of this report, Table 1 includes the results of ten shared filters and two metallic weights. Table 1 contains the tare weight, the final weight, and the calculated $PM_{2.5}$ capture. Table 1 also contains the calculated inter-laboratory difference for measuring the $PM_{2.5}$ capture which is graphed in Figure 2.

Figure 1

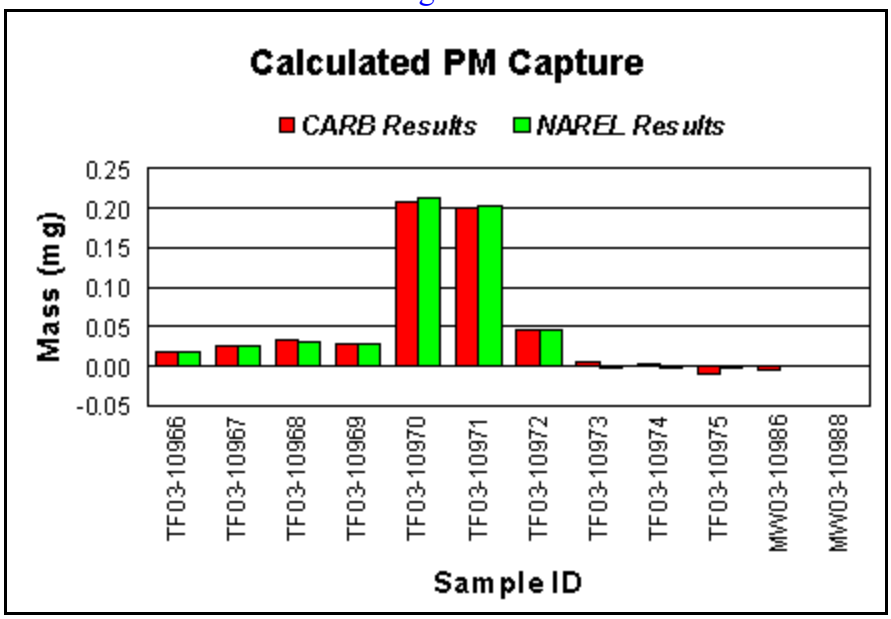
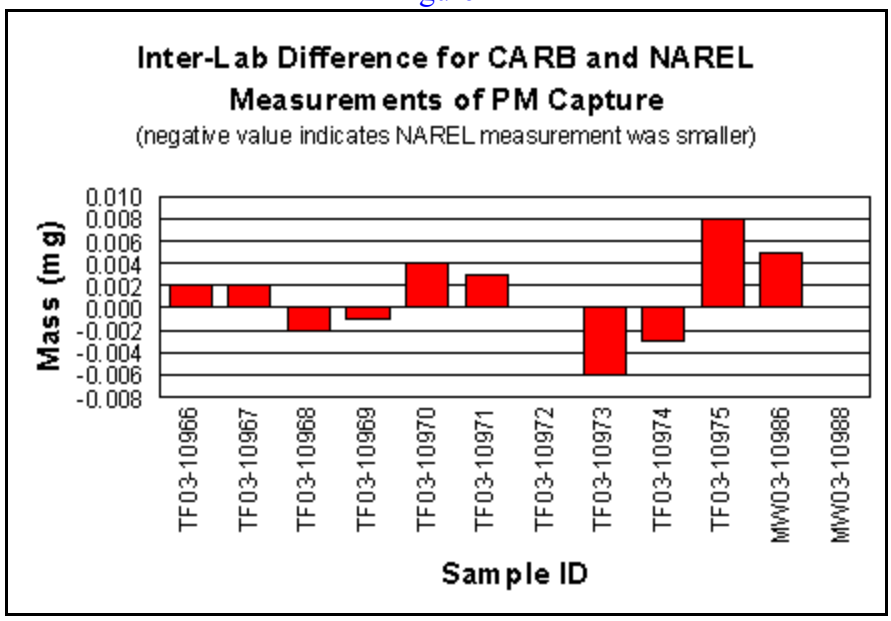


Figure 2



IC Analysis

For this study, Nylon® filters and IC spike solutions were carefully prepared at NAREL and shipped to CARB for analysis. Met One samplers were used to load several Nylon® filters with $PM_{2.5}$ captured from the Montgomery air. Six filters were submitted to CARB for analysis, and replicates of each filter were retained at NAREL for in-house analysis. Six IC spike solutions were also prepared at NAREL. Each solution was designed for dilution by a factor of ten using reagent water available at the receiving laboratory. After dilution to full volume, each spike solution was utilized as the solvent to extract a clean blank filter also provided by the receiving laboratory. The filter extracts were analyzed using appropriate IC instrumentation available at the receiving laboratory. The results reported for each sample were based upon the concentration of analyte present in the final extract.

Two of the six filters submitted to CARB were actually Nylon® filter blanks. Four of the filters were replicates loaded with two separate 144-hour sampling events: one event started on November 20th and the second event started on December 1st. Samples were collected over long periods to insure that all analytes were present in the samples at detectable levels. No information was given to CARB regarding the history of these Nylon® filters. Three of the six IC spike solutions were prepared for analysis of the anions, and three solutions were prepared for the analysis of cations. These solutions were designed to offer a mid-level concentration, a low-level concentration, and a blank for each analyte. Replicates of all samples were analyzed at NAREL following the same instructions provided to CARB.

IC Results

Results for the mid-level IC spikes are presented as a bar graph in Figure 3. For each analyte, the mid-level concentration of the fully diluted spike solution was between 1 and 4 µg/mL. Figure 3 presents the expected result, the CARB result, and the NAREL result for each analyte.

Figure 3

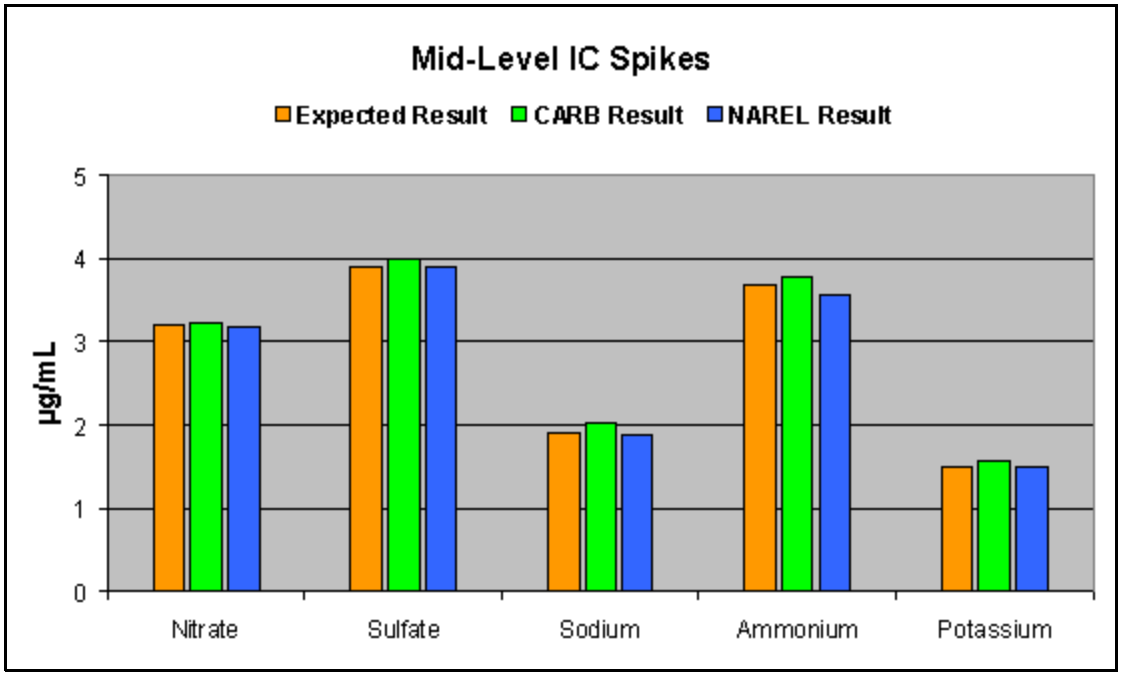
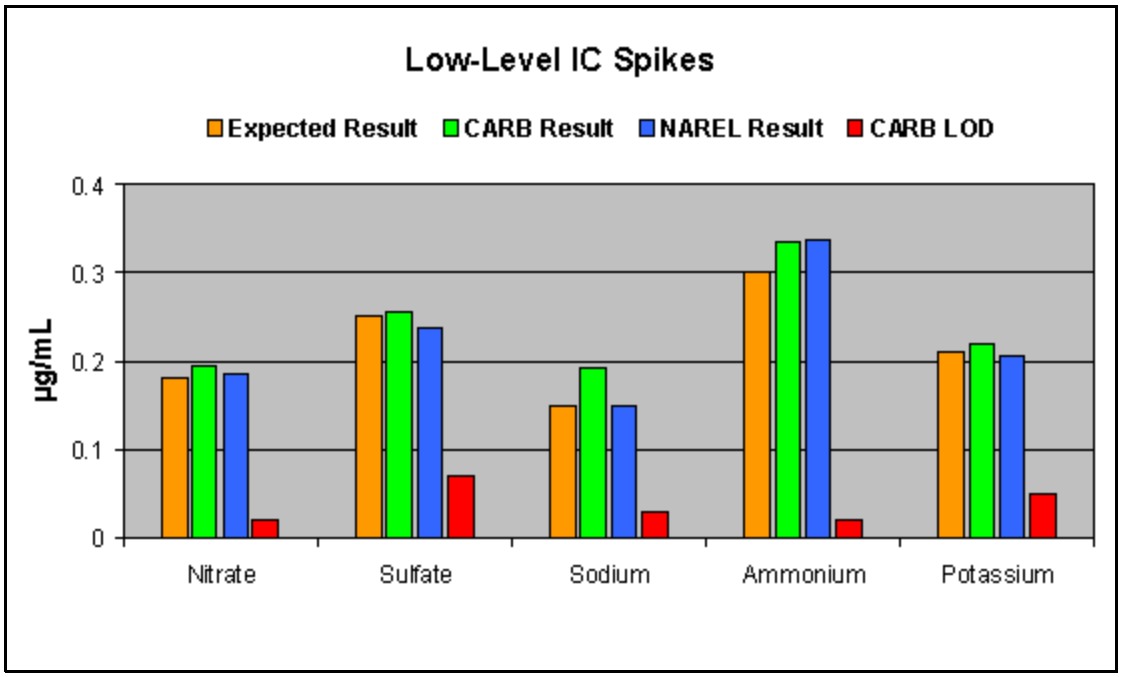


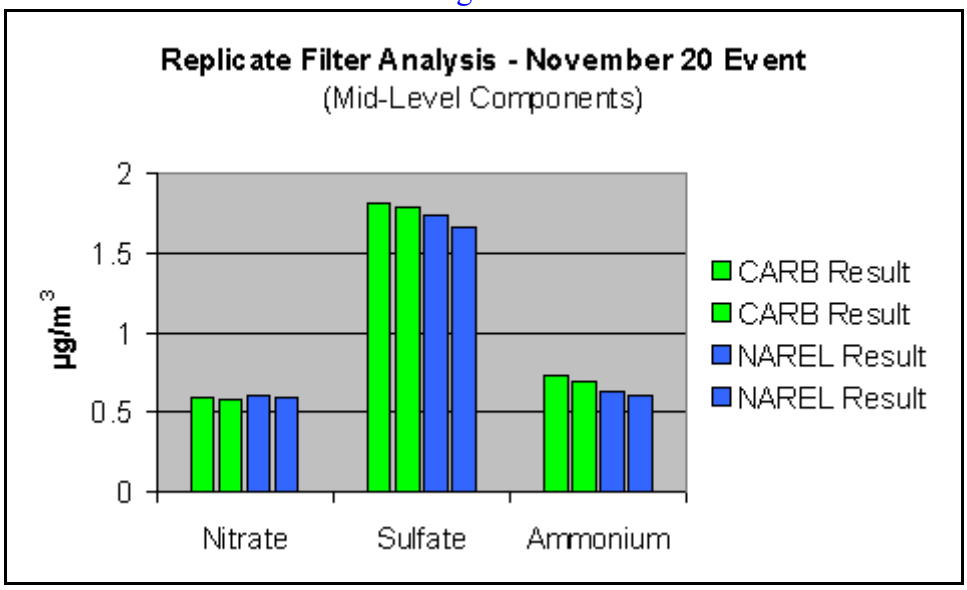
Figure 4



Results for the low-level spikes are presented as a bar graph in Figure 4. For each analyte, the low-level concentration of the fully diluted spike solution was between 0.15 and 0.35 µg/mL. Since the concentrations presented in Figure 4 are low, an extra bar was added to this graph showing the Limit of Detection (LOD) reported by CARB. The results from the IC spike solutions are summarized in Table 2 at the end of this report.

Results for four replicate filters are presented in Figure 5 and Figure 6. These filters were loaded with a 144-hour sampling event which began on November 20. Only two of these four Nylon® filter replicates were submitted to CARB for analysis, and the remaining two replicates were extracted and analyzed at NAREL. Nitrate, sulfate, and ammonium were the most abundant analytes captured from the Montgomery air during this sampling event, and these ions are plotted in Figure 5.

Figure 5



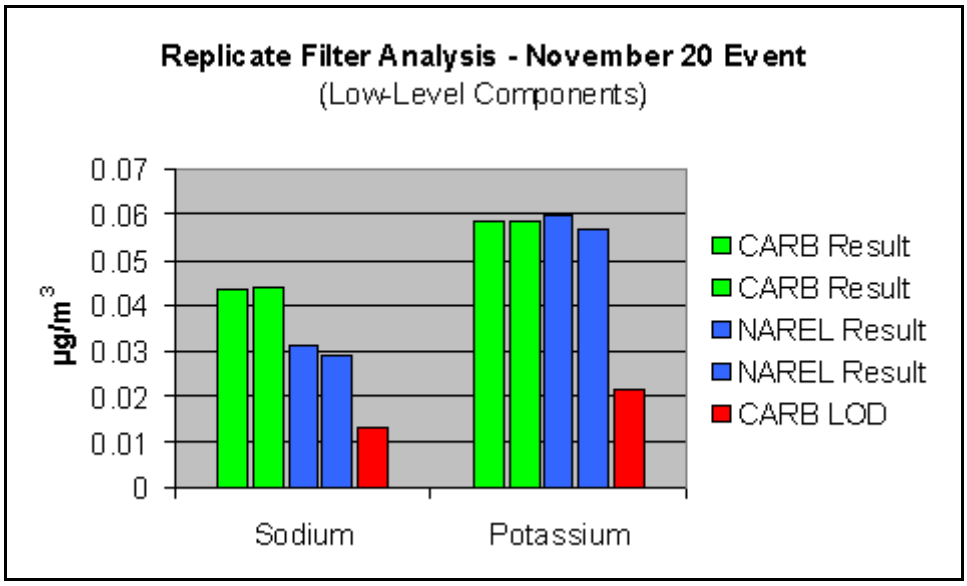
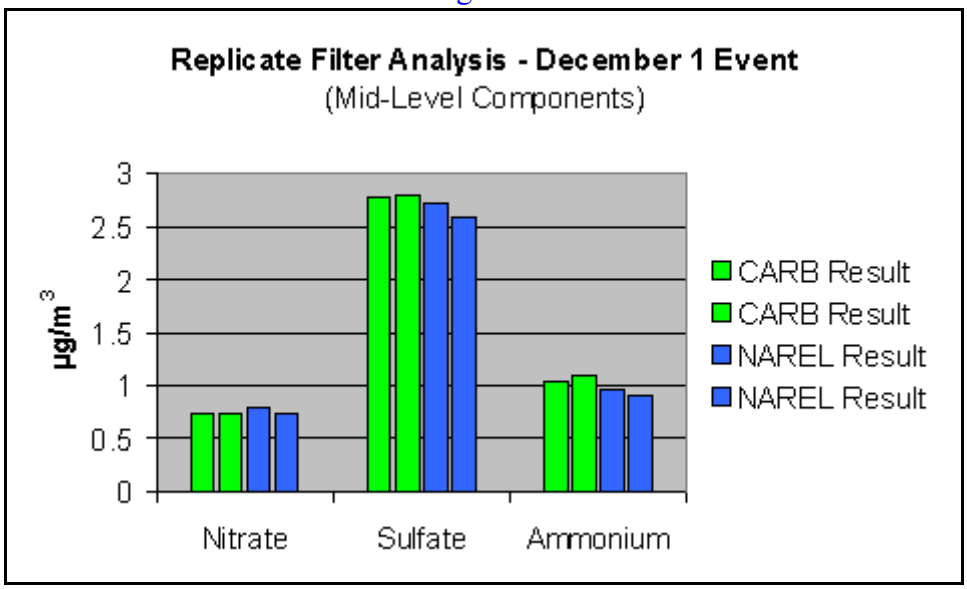


Figure 6

Sodium and potassium were present in the PM capture at lower concentrations, and these two ions are plotted in Figure 6. Since the concentrations presented in Figure 6 are relatively low, an extra bar was added to this graph showing CARB's LOD expressed as mass per cubic meter of air sampled.

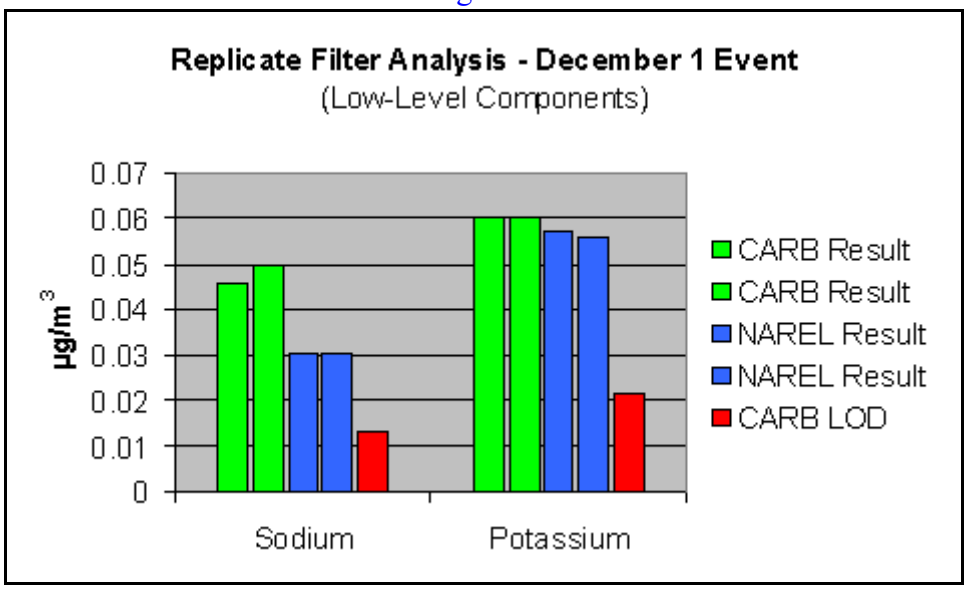
Results for four more replicate filters are presented in Figure 7 and Figure 8. These filters were loaded with another 144-hour sampling event which began on December 1. Once again, only two of these four Nylon® filter replicates were submitted to CARB for analysis, and the remaining two replicates were extracted and analyzed at NAREL. As observed in the previous event, the most abundant analytes were nitrate, sulfate, and ammonium which are plotted in Figure 7.

Figure 7



Sodium and potassium were present at low concentration during the December 1 event, and these two ions are plotted in Figure 8.

Figure 8



Results for all of the loaded Nylon® filters are presented in Table 3 and Table 4 at the end of this report. Two of the six Nylon® filters submitted to CARB for analysis were actually blank filters which were pre-cleaned at NAREL along with all the other Nylon® filters used in this study. The results for all blank Nylon® filters are presented in Table 5 at the end of this report.

Carbon Analysis

Earlier in the introduction of this report, it was stated that carbon analysis at CARB is slightly different from the carbon analysis at NAREL. The differences were described with great detail in a previous report [see reference 1]. Briefly stated here, the two labs operate different instrument hardware and also use different sample heating profiles during the analysis cycle. The carbon analyzer at NAREL was manufactured by Sunset Laboratories, and the carbon analyzer at CARB is a DRI Model 2001 manufactured by Atmoslytic Incorporated. NAREL's instrument is programmed to use the heating profile that RTI uses for all of the STN samples. CARB's instrument is currently programmed to use a custom heating profile that was implemented in the fall of 2002. The custom heating profile was adopted at that time to advance data comparability to a more desirable state.

For this study, quartz filters and TOT spike solutions were carefully prepared at NAREL and shipped to CARB for analysis. Met One samplers were used to load several quartz filters with $PM_{2.5}$ captured from the Montgomery air. Six filters were submitted to CARB for analysis, and replicates of each filter were retained at NAREL for in-house analysis. Two of the six filters submitted to CARB were actually quartz filter blanks, two filters were replicates of a 288-hour sampling event which began on October 29, and two filters were replicates of a 216-hour sampling event which began on November 10. No information was given to CARB regarding the history of the quartz filters. A routine analysis of each filter was requested.

Three TOT spike solutions were also prepared at NAREL. One solution was blank water, one solution provided a mid-level concentration of sucrose, and one solution contained a mid-level concentration of potassium hydrogen phthalate (KHP). No information was given to CARB regarding the composition of the spike solutions. The instructions for spiking and analyzing each solution are repeated here.

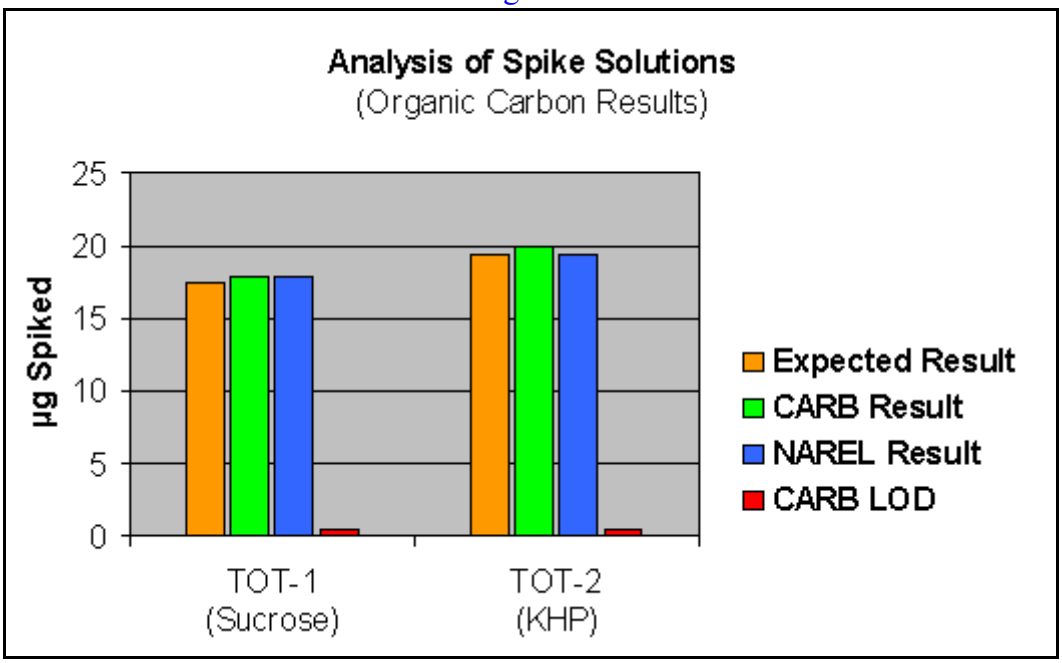
> *Pre-clean a standard-size punch from a blank quartz filter using the TOT instrument oven program. After the punch has cooled carefully spike 10.0 µL of the PE solution onto the clean quartz punch. Allow the solvent to evaporate from the punch, and then analyze the punch. This procedure should be similar to the daily and weekly calibration checks using a known concentration of sucrose.*

Raw data in the form of thermograms were provided to NAREL. The final results were reported as mass of carbon per square centimeter of filter material (µg/cm^2). All of CARB's analyses were performed using a punch size of 0.512 cm^2. This was smaller than the 1.5-cm^2 punch size used at NAREL. To facilitate the inter-laboratory comparisons, all of the results from aqueous spikes were converted to mass of carbon spiked, and results from the loaded filters were converted to mass of carbon per cubic meter of air sampled.

Carbon Results

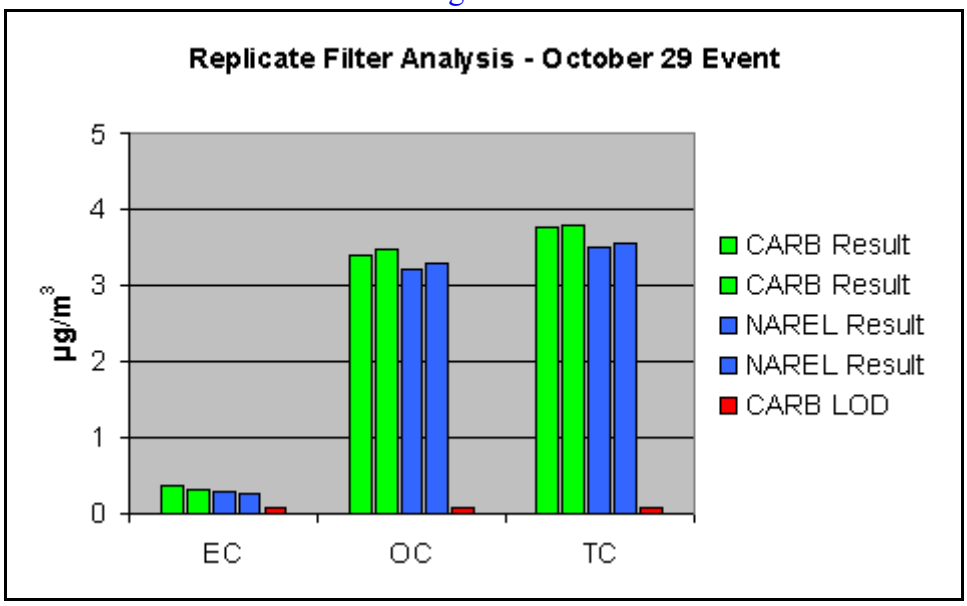
Results for the blind TOT spike solutions are presented as a bar graph in Figure 9. TOT-1 was a mid-level sucrose spike, TOT-2 was a mid-level KHP spike, and TOT-3 (not shown in the graph) was blank water. Figure 9 presents the expected result, the CARB result, the NAREL result, and the Limit of Detection (LOD) reported by CARB for the organic carbon analysis. All results reported for the three TOT spike solutions are presented in Table 6 at the end of this report.

Figure 9



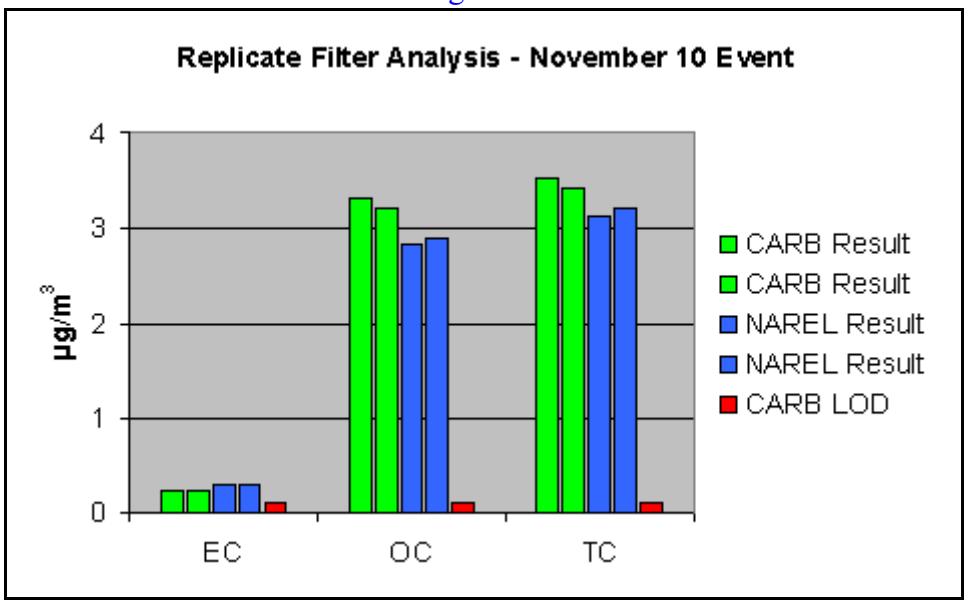
Results from four replicate filters are presented in Figure 10. These filters were loaded with a 288-hour sampling event which began on October 29. Only two of these four quartz filter replicates were submitted to CARB for analysis, and the remaining two replicates were analyzed at NAREL.

Figure 10



Results from four more replicate filters are presented in Figure 11. These filters were loaded with a 216-hour sampling event which began on November 10. Again only two of these replicates were submitted to CARB for analysis, and the remaining two replicates were analyzed at NAREL. Both sampling events were much longer than the normal 24-hour collection period because it was important to capture a sufficient amount of EC that would exceed the CARB LOD.

Figure 11



CARB does not report the organic carbon fractions and pyrolytic carbon [OC1, OC2, OC3, OC4, and PyrolC]. It would not be appropriate to compare these fractions to results produced at NAREL since CARB uses a custom heating profile during the sample analysis cycle. All results for the loaded quartz filters are presented in Table 7 and Table 8 at the end of this report. Two blank quartz filters were submitted to CARB for analysis, and the results for blanks are presented in Table 9 at the end of this report.

One thermogram from CARB and one thermogram from NAREL are shown in Figure 12 and Figure 13 respectively. These two thermograms were produced by analyzing replicate filters that were loaded during the October 29 sampling event. Even though the thermograms may look different, the calculated results from both labs show good agreement. In Figure 12 it is interesting to note that the OC/EC split point was assigned at approximately 900 seconds into the run, and this split point is not supported by the laser signals. The instrument software at CARB will not assign a split point before the helium/oxygen valve opens at approximately 900 seconds. The OC/EC split point in Figure 13 was assigned at approximately 400 seconds into the run, and for this analysis, the assignment was supported by the laser signal.

Figure 12

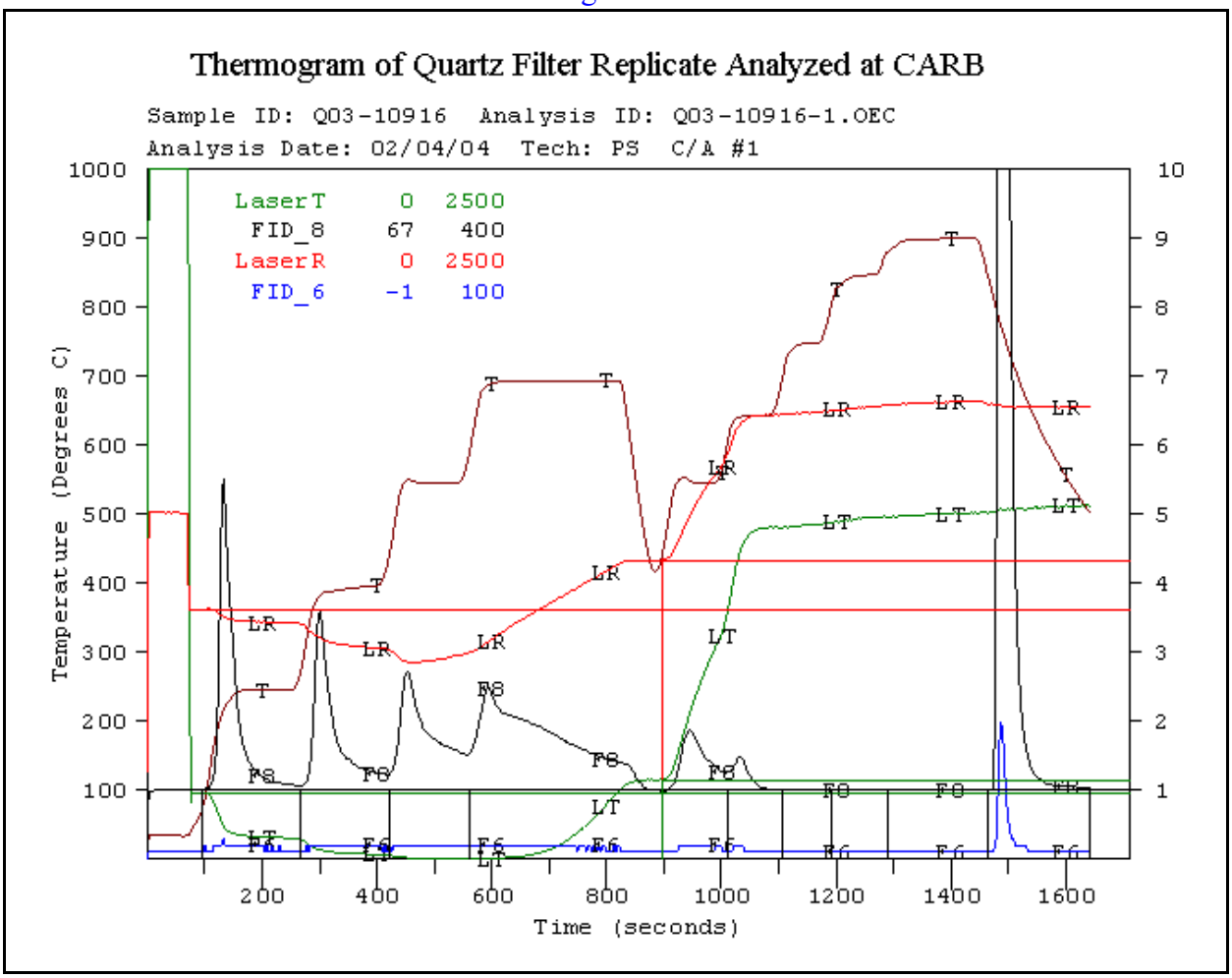
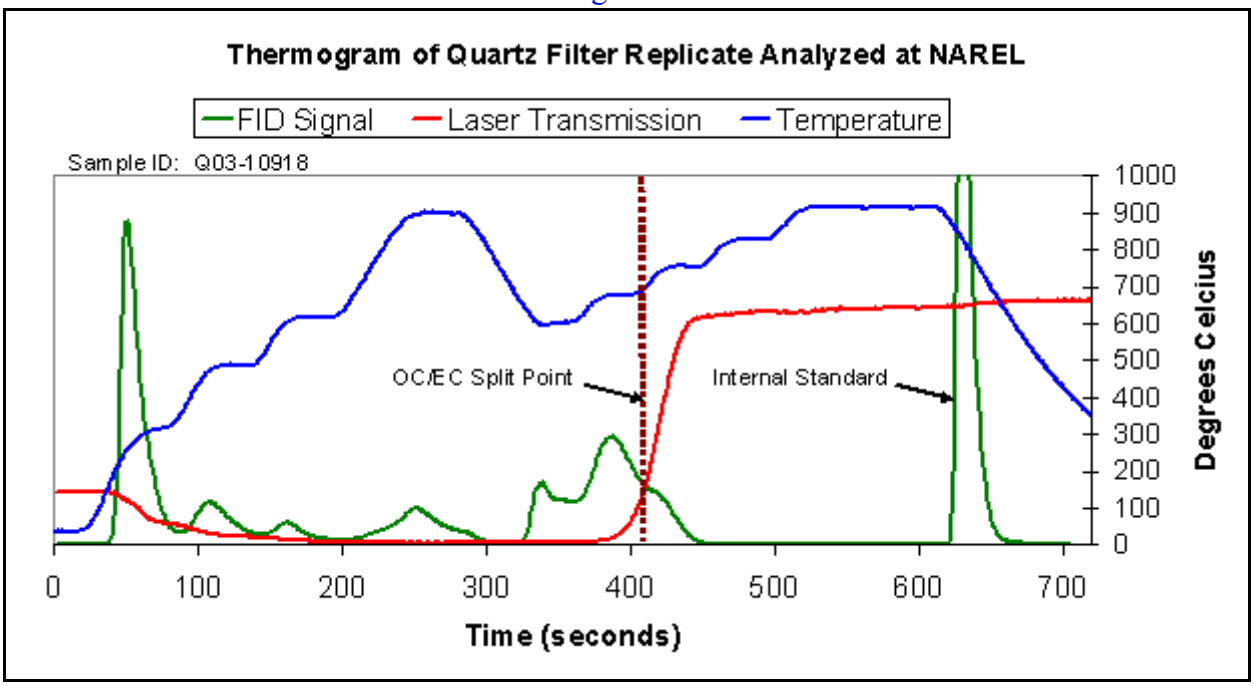


Figure 13



Conclusions

Good agreement was observed for all mass measurements performed at CARB and at NAREL. Good performance was observed for the metallic weights which provided a wide range of mass measurements. All three field blanks showed $PM_{2.5}$ capture well below the 0.030-mg failure threshold. The largest inter-laboratory difference for captured $PM_{2.5}$ was 0.008 mg which is below a reasonable warning limit of 0.015 mg and significantly below a reasonable failure limit of 0.030 mg. This study indicates good performance by the gravimetric laboratory at CARB.

Excellent recoveries (96-106%) were obtained at CARB and at NAREL for the mid-level IC spikes. Good recoveries (95-128%) were also observed for the low-level spikes. Sample spike solutions identified as A-3 and C-3 were actually blank water. These blanks provided a mechanism to measure laboratory contamination from a variety of sources such as (1) the reagent water used to dilute every sample, (2) the "clean" filter extracted by the test solution which is normally provided to the field for $PM_{2.5}$ capture, and (3) containers used to hold and transfer the sample during the extraction and analysis process. No significant contamination was reported for either blank, even though a very low level of sodium [0.005 µg/mL] was reported by NAREL for the cation blank [C-3], and a low level of nitrate [0.023 µg/mL] was reported by CARB for the anion blank [A-3].

Replicate Nylon® filters from two sampling events were available for this study. The longer-than-normal collection periods were necessary to provide a sample with all ions sufficiently above the detection threshold. The results reported by CARB show good agreement with the results produced at NAREL. A difference from the mean value was calculated for each analyte, and this Relative Percent Difference (RPD) is included in Table 3 and Table 4. All RPD's were below 20 percent except for sodium. The highest RPD for sodium was 27 percent which is not bad since sodium was present at a low level... less than three times CARB's LOD. Blank Nylon® filters were also provided for this study. Nitrate was reported for one blank filter at 0.12 µg/mL which was six times

the reported LOD. No other significant filter contamination was reported by either laboratory. This study indicates good performance by the IC laboratory at CARB.

Good recoveries were obtained at CARB and at NAREL for the mid-level sucrose spike (102% and 102% respectively). Good recoveries (104% and 101% respectively) were also observed for the mid-level KHP spike, TOT-2. The spike solution identified as TOT-3 was actually blank water. This blank spike provided a mechanism to evaluate the measurement baseline at both laboratories. Neither laboratory reported contamination above CARB's LOD.

Replicate quartz filters from two sampling events were available for this study. The longer-than-normal collection periods were used again, this time to boost the amount of EC captured from the relatively clean Montgomery air. The OC and the EC results reported by CARB show good agreement with the results produced at NAREL. A difference from the mean value was calculated for each sample, and this Relative Percent Difference (RPD) is included in Table 7 and Table 8. All RPD's were below 20 percent even though some of the EC values were near the LOD! Blank quartz filters were also prepared for this study, and no significant contamination was reported by either laboratory.

Thermograms were examined during this study because raw data provides valuable information regarding the analysis. There is still a noticeable [unexplained] difference in the behavior of the laser signals when thermograms produced at NAREL are compared to thermograms produced at CARB even though replicate samples were analyzed at each laboratory. This evidence is not new. It was first noticed and described during a PE study with NAREL almost two years ago [see reference 2]. Steps were taken at that time to look for a possible instrument malfunction, but a malfunction was not discovered. As stated earlier in this report, changes were made to the heating profile for CARB's instrument, and the custom heating profile produces data that agrees better with NAREL's analysis.

Results from this PE study indicate overall good performance at CARB. Another report will be written to include results from the XRF samples once they are available.

References

1. EPA/NAREL. February 26, 2003. Technical Memorandum: CARB Laboratory Audit. U.S. Environmental Protection Agency. [currently available on the web] http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/carbrept.pdf

2. EPA/NAREL. September 12, 2002. Technical Memorandum: Performance Evaluation CARB Laboratory. U.S. Environmental Protection Agency. [currently available on the web] http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/carb2002.pdf

Table 1. Gravimetric Data

Sample ID	Tare Mass		Final Mass		Captured $PM_{2.5}$		Inter-Lab Difference* of Captured $PM_{2.5}$ (mg)
	CARB (mg)	NAREL (mg)	CARB (mg)	NAREL (mg)	CARB (mg)	NAREL (mg)	
TF03-10966	143.491	143.490	143.508	143.509	0.017	0.019	0.002
TF03-10967	144.087	144.090	144.112	144.117	0.025	0.027	0.002
TF03-10968	142.744	142.745	142.776	142.775	0.032	0.030	-0.002
TF03-10969	145.728	145.731	145.757	145.759	0.029	0.028	-0.001
TF03-10970	145.392	145.394	145.601	145.607	0.209	0.213	0.004
TF03-10971	142.139	142.140	142.340	142.344	0.201	0.204	0.003
TF03-10972	145.433	145.432	145.480	145.479	0.047	0.047	0.000
TF03-10973	143.462	143.466	143.467	143.465	0.005	-0.001	-0.006
TF03-10974	142.901	142.904	142.903	142.903	0.002	-0.001	-0.003
TF03-10975	144.801	144.796	144.792	144.795	-0.009	-0.001	0.008
MW03-10986	195.733	195.734	195.729	195.735	-0.004	0.001	0.005
MW03-10988	98.551	98.551	98.552	98.552	0.001	0.001	0.000

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

Table 2. IC Spike Solutions

Sample ID	Analyte	Expected Result (μg/mL)	CARB Result (μg/mL)	NAREL Result (μg/mL)	CARB Recovery	NAREL Recovery	CARB LOD* (μg/mL)
A-1	Nitrate	3.200	3.217	3.190	101%	100%	0.02
A-1	Sulfate	0.250	0.255	0.238	102%	95%	0.07
A-2	Nitrate	0.180	0.194	0.184	108%	102%	0.02
A-2	Sulfate	3.900	4.005	3.894	103%	100%	0.07
A-3	Nitrate	0.000	0.023	0.000	-----	-----	0.02
A-3	Sulfate	0.000	< LOD	0.000	-----	-----	0.07
C-1	Sodium	0.150	0.192	0.149	128%	99%	0.03
C-1	Ammonium	3.700	3.790	3.550	102%	96%	0.02
C-1	Potassium	1.500	1.557	1.494	104%	100%	0.05
C-2	Sodium	1.900	2.019	1.873	106%	99%	0.03
C-2	Ammonium	0.300	0.335	0.338	112%	113%	0.02
C-2	Potassium	0.210	0.220	0.206	105%	98%	0.05
C-3	Sodium	0.000	< LOD	0.005	-----	-----	0.03
C-3	Ammonium	0.000	< LOD	0.000	-----	-----	0.02
C-3	Potassium	0.000	< LOD	0.000	-----	-----	0.05

**** LOD = Limit of Detection***

Table 3. Nylon Filter Replicates - November 20 Event

Analyte	Sample ID	CARB Result (μg/mL)	NAREL Result (μg/mL)	Air Volume (m^3)	Air Conc. (μg/m^3)	CARB LOD* (μg/m^3)	Air Conc. RPD**
Nitrate	N03-10944	1.374	-----	58.073	0.592	0.009	0%
	N03-10945	1.354	-----	58.133	0.582	-----	-2%
	N03-10946	-----	1.405	58.125	0.604	-----	2%
	N03-10948	-----	1.378	58.129	0.593	-----	0%
Sulfate	N03-10944	4.197	-----	58.073	1.807	0.085	3%
	N03-10945	4.161	-----	58.133	1.790	-----	2%
	N03-10946	-----	4.041	58.125	1.738	-----	-1%
	N03-10948	-----	3.849	58.129	1.655	-----	-5%
Sodium	N03-10944	0.101	-----	58.073	0.043	0.036	18%
	N03-10945	0.102	-----	58.133	0.044	-----	19%
	N03-10946	-----	0.073	58.125	0.031	-----	-15%
	N03-10948	-----	0.067	58.129	0.029	-----	-22%
Ammonium	N03-10944	1.696	-----	58.073	0.730	0.024	10%
	N03-10945	1.611	-----	58.133	0.693	-----	4%
	N03-10946	-----	1.462	58.125	0.629	-----	-5%
	N03-10948	-----	1.397	58.129	0.601	-----	-9%
Potassium	N03-10944	0.136	-----	58.073	0.059	0.061	0%
	N03-10945	0.136	-----	58.133	0.059	-----	0%
	N03-10946	-----	0.139	58.125	0.060	-----	3%
	N03-10948	-----	0.132	58.129	0.057	-----	-3%

**** LOD = Limit of Detection***

***** RPD = Relative Percent Difference = (result - average result)/average result***

Table 4. Nylon Filter Replicates - December 1 Event

Analyte	Sample ID	CARB Result (μg/mL)	NAREL Result (μg/mL)	Air Volume (m^3)	Air Conc. (μg/m^3)	CARB LOD* (μg/m^3)	Air Conc. RPD**
Nitrate	N03-10952	1.729	-----	58.119	0.744	0.013	-1%
	N03-10953	1.723	-----	58.166	0.741	-----	-2%
	N03-10954	-----	1.833	58.197	0.788	-----	5%
	N03-10956	-----	1.727	58.189	0.742	-----	-2%
Sulfate	N03-10952	6.447	-----	58.119	2.773	0.045	2%
	N03-10953	6.478	-----	58.166	2.784	-----	3%
	N03-10954	-----	6.336	58.197	2.722	-----	0%
	N03-10956	-----	5.991	58.189	2.574	-----	-5%
Sodium	N03-10952	0.106	-----	58.119	0.046	0.019	16%
	N03-10953	0.116	-----	58.166	0.050	-----	27%
	N03-10954	-----	0.071	58.197	0.031	-----	-22%
	N03-10956	-----	0.071	58.189	0.031	-----	-22%
Ammonium	N03-10952	2.421	-----	58.119	1.041	0.013	4%
	N03-10953	2.563	-----	58.166	1.102	-----	10%
	N03-10954	-----	2.207	58.197	0.948	-----	-5%
	N03-10956	-----	2.093	58.189	0.899	-----	-10%
Potassium	N03-10952	0.140	-----	58.119	0.060	0.032	3%
	N03-10953	0.140	-----	58.166	0.060	-----	3%
	N03-10954	-----	0.133	58.197	0.057	-----	-2%
	N03-10956	-----	0.131	58.189	0.056	-----	-4%

**** LOD = Limit of Detection***

***** RPD = Relative Percent Difference = (result - average result)/average result***

Table 5. Blank Nylon Filters

Analyte	Sample ID	CARB Result (μg/mL)	NAREL Result (μg/mL)	CARB LOD* (μg/mL)
Nitrate	N03-10960	0.021	-----	0.02
	N03-10961	0.120	-----	0.02
	N03-10962	-----	0.000	-----
	N03-10963	-----	0.000	-----
Sulfate	N03-10960	<LOD	-----	0.07
	N03-10961	<LOD	-----	0.07
	N03-10962	-----	0.000	-----
	N03-10963	-----	0.000	-----
Sodium	N03-10960	<LOD	-----	0.03
	N03-10961	<LOD	-----	0.03
	N03-10962	-----	0.003	-----
	N03-10963	-----	0.000	-----
Ammonium	N03-10960	0.020	-----	0.02
	N03-10961	<LOD	-----	0.02
	N03-10962	-----	0.000	-----
	N03-10963	-----	0.000	-----
Potassium	N03-10960	<LOD	-----	0.05
	N03-10961	<LOD	-----	0.05
	N03-10962	-----	0.000	-----
	N03-10963	-----	0.000	-----

**** LOD = Limit of Detection***

Table 6. Carbon Spike Solutions

Sample ID	Analyte	Expected Result (μg spiked)	CARB Result (μg spiked)	NAREL Result (μg spiked)	CARB Recovery	NAREL Recovery	CARB LOD* (μg spiked)
TOT-1	EC	0.00	<LOD	0.00	-----	-----	0.4
TOT-1	OC	17.49	17.83	17.84	102%	102%	0.4
TOT-1	TC	17.49	17.83	17.84	102%	102%	0.4
TOT-2	EC	0.00	<LOD	0.00	-----	-----	0.4
TOT-2	OC	19.31	20.03	19.41	104%	101%	0.4
TOT-2	TC	19.31	20.03	19.41	104%	101%	0.4
TOT-3	EC	0.00	<LOD	0.00	-----	-----	0.4
TOT-3	OC	0.00	<LOD	0.30	-----	-----	0.4
TOT-3	TC	0.00	<LOD	0.30	-----	-----	0.4

**** LOD = Limit of Detection***

Table 7. Quartz Filter Replicates - October 29 Event

Analyte	Sample ID	CARB Result ($\mu g/cm^2$)	NAREL Result ($\mu g/cm^2$)	Air Volume (m^3)	Air Conc. ($\mu g/m^3$)	CARB LOD* ($\mu g/m^3$)	Air Conc. RPD**
EC	Q03-10916	3.61	-----	115.85	0.366	0.08	18%
	Q03-10917	3.22	-----	115.90	0.327	0.08	5%
	Q03-10918	-----	2.86	115.89	0.290	-----	-6%
	Q03-10919	-----	2.52	115.85	0.255	-----	-18%
OC	Q03-10916	33.49	-----	115.85	3.400	0.08	1%
	Q03-10917	34.35	-----	115.90	3.485	0.08	4%
	Q03-10918	-----	31.79	115.89	3.226	-----	-4%
	Q03-10919	-----	32.54	115.85	3.303	-----	-2%
TC	Q03-10916	37.10	-----	115.85	3.766	0.08	3%
	Q03-10917	37.57	-----	115.90	3.812	0.08	4%
	Q03-10918	-----	34.65	115.89	3.516	-----	-4%
	Q03-10919	-----	35.05	115.85	3.558	-----	-3%

**** LOD = Limit of Detection***

***** RPD = Relative Percent Difference = (result - average result)/average result***

Table 8. Quartz Filter Replicates - November 10 Event

Analyte	Sample ID	CARB Result ($\mu g/cm^2$)	NAREL Result ($\mu g/cm^2$)	Air Volume (m^3)	Air Conc. ($\mu g/m^3$)	CARB LOD* ($\mu g/m^3$)	Air Conc. RPD**
EC	Q03-10933	1.63	-----	86.83	0.221	0.11	-14%
	Q03-10934	1.64	-----	86.83	0.222	0.11	-14%
	Q03-10935	-----	2.14	86.83	0.290	-----	12%
	Q03-10936	-----	2.20	86.83	0.298	-----	16%
OC	Q03-10933	24.38	-----	86.83	3.302	0.11	8%
	Q03-10934	23.61	-----	86.83	3.198	0.11	5%
	Q03-10935	-----	20.94	86.83	2.837	-----	-7%
	Q03-10936	-----	21.42	86.83	2.902	-----	-5%
TC	Q03-10933	26.02	-----	86.83	3.524	0.11	6%
	Q03-10934	25.25	-----	86.83	3.420	0.11	3%
	Q03-10935	-----	23.08	86.83	3.127	-----	-6%
	Q03-10936	-----	23.63	86.83	3.200	-----	-4%

**** LOD = Limit of Detection***

***** RPD = Relative Percent Difference = (result - average result)/average result***

Table 9. Blank Quartz Filters

Analyte	Sample ID	CARB Result ($\mu g/cm^2$)	NAREL Result ($\mu g/cm^2$)	CARB LOD* ($\mu g/cm^2$)
EC	Q03-10927	<0.8	-----	0.80
	Q03-10928	-----	0.00	-----
OC	Q03-10927	<0.8	-----	0.80
	Q03-10928	-----	0.20	-----
TC	Q03-10927	<0.8	-----	0.80
	Q03-10928	-----	0.20	-----

**** LOD = Limit of Detection***