TECHNICAL MEMORANDUM

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SUBJECT: Performance Evaluation - RTI Laboratories

Introduction

A study has been conducted as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network. The purpose of this study was to evaluate specific laboratory performance at the Research Triangle Institute (RTI). RTI is the prime contractor responsible for the analysis of air samples collected by the $PM_{2.5}$ Speciation Trends Network.

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

- Gravimetric Mass Analysis - ten loaded Teflon® filters previously tared at RTI
- Ion Chromatography (IC) Analysis - two loaded Nylon® filters, three anion spike solutions, and three cation spike solutions.
- TOT Carbon Analysis - three loaded Quartz filters and three spike solutions.

Detailed instructions for analyzing and reporting the PE samples were provided to RTI. The analytical facilities at NAREL are similar to those at RTI. Each PE sample, or a replicate of the PE sample, was also analyzed at NAREL. This report will discuss the analytical results reported by RTI 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. RTI routinely provides clean pre-weighed air filters to the various field sites within the network. 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 RTI where the gravimetric analysis is completed.

RTI 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.

RTI 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 Transmittance (TOT) technique is used at RTI 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 TOT technique requires heating 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), elemental carbon (EC), and carbonate carbon (CC) all of which may be added together to calculate the total carbon (TC).

Gravimetric Analysis

For this study, ten new filters were pre-weighed at RTI in the usual manner but were not shipped directly to a field site. These ten filters were shipped to NAREL in Montgomery, AL. All ten filters were immediately placed into the weighing chamber at NAREL for equilibration and determination of a NAREL tare weight. After the NAREL tare weights were determined, seven of the ten filters were loaded with $PM_{2.5}$ captured from the outside air near NAREL. A Met One SASS air sampler was used to load seven of the filters, and the remaining three filters were utilized as blanks. Following sample collection, filters were returned to the weighing chamber at NAREL to equilibrate and to determine the loaded mass. Finally, the ten filters were shipped back to RTI for their routine determination of the final filter weights.

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 one laboratory chamber blank.

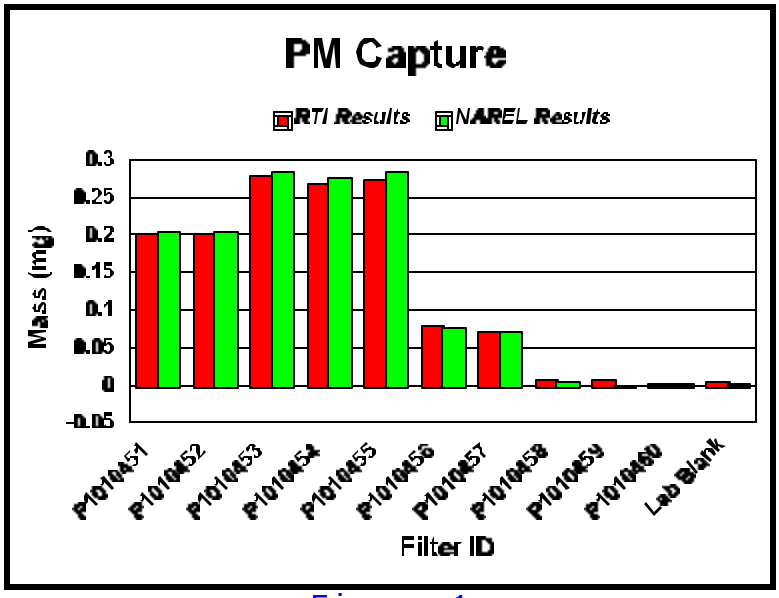

Figure 1

Figure 2 presents the inter-laboratory differences. Inter-laboratory differences were calculated by subtracting the $PM_{2.5}$ capture value determined at RTI 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.

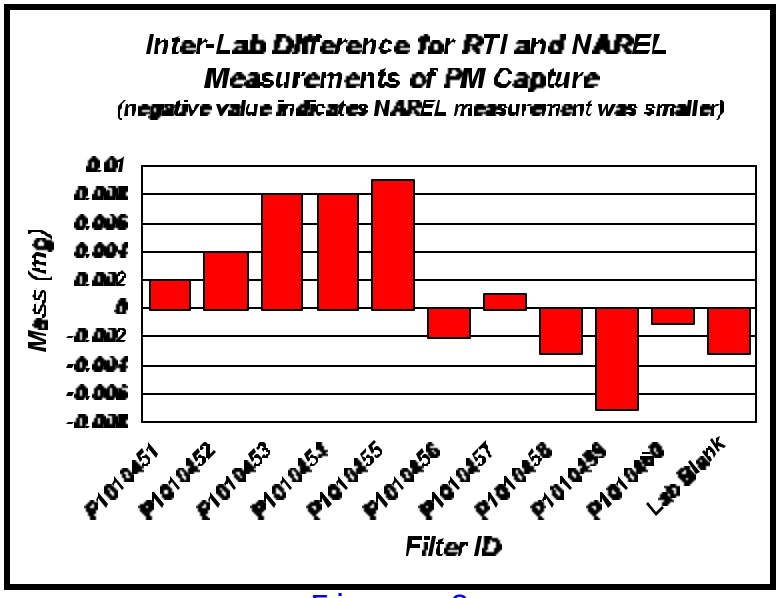

Figure 2

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 one independent chamber blank weighed at each laboratory. Table 1 contains the filter tare weight, the final loaded weight, and the calculated $PM_{2.5}$ capture for each filter. Table 1 also contains the calculated inter-laboratory difference for measuring the $PM_{2.5}$ capture which is graphed in Figure 2.

IC Analysis

For this study, Nylon® filters and IC spike solutions were carefully prepared at NAREL and shipped to RTI for analysis. A Met One SASS sampler was used to load several Nylon® filters with $PM_{2.5}$ captured from the Montgomery air. Two filters were submitted to RTI for analysis, and the 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.

One of the filters submitted to RTI was actually a Nylon® filter blank, and the other was loaded with a 72-hour $PM_{2.5}$ capture. No information was given to RTI 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 RTI.

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 1.5 and 3.5 :g/mL. Figure 3 presents the expected result, the RTI result, and the NAREL result for each analyte.

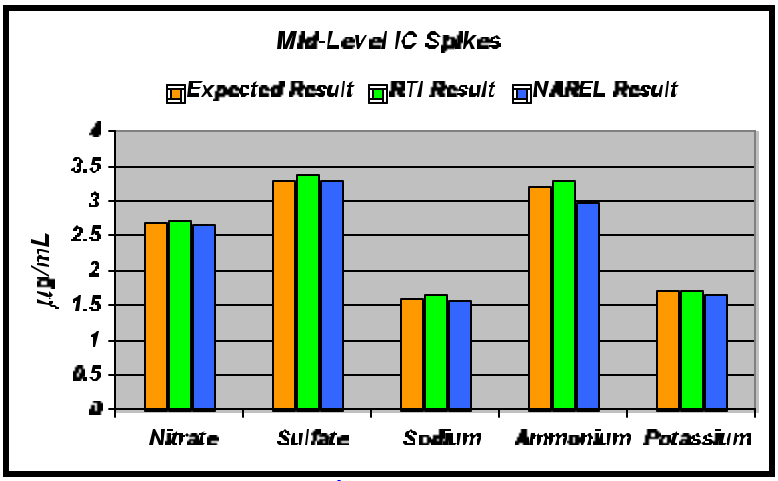

Figure 3

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 0.1 and 0.2 :g/mL. Since the concentrations presented in Figure 4 are low, an extra bar was added to this graph showing the Method Detection Limit (MDL) reported by RTI. The results from the IC spike solutions are summarized in Table 2 at the end of this report.

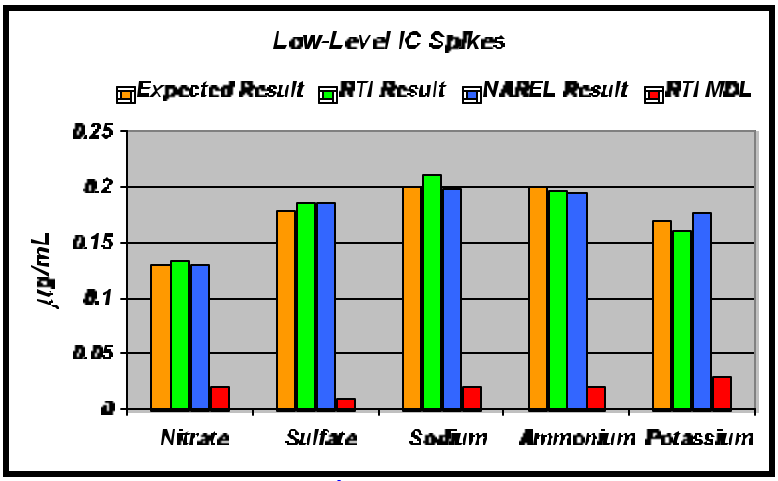

Figure 4

Results for five replicate 72-hour air samples are presented in Figure 5 and Figure 6. Only one of these five Nylon® filter replicates was submitted to RTI for analysis, and the remaining four replicates were extracted and analyzed at NAREL. Replicate filters were extracted and analyzed on separate days to incorporate a realistic variance in the NAREL results. 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. Nitrate, sodium, and potassium were present in the capture at lower concentrations, and these three ions are plotted in Figure 6. Since the concentrations presented in Figure 6 are relatively low, an extra bar was added to this

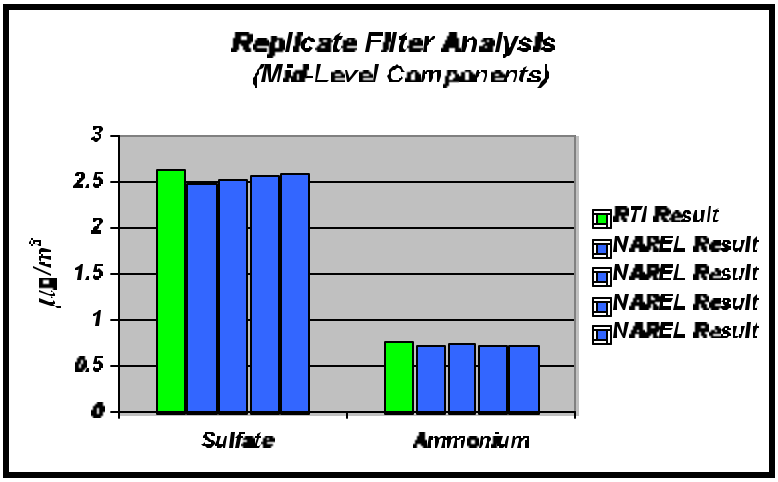

Figure 5

graph showing RTI's MDL expressed as mass per cubic meter of air sampled. All results from the loaded Nylon® filters are presented in Table 3 at the end of this report.

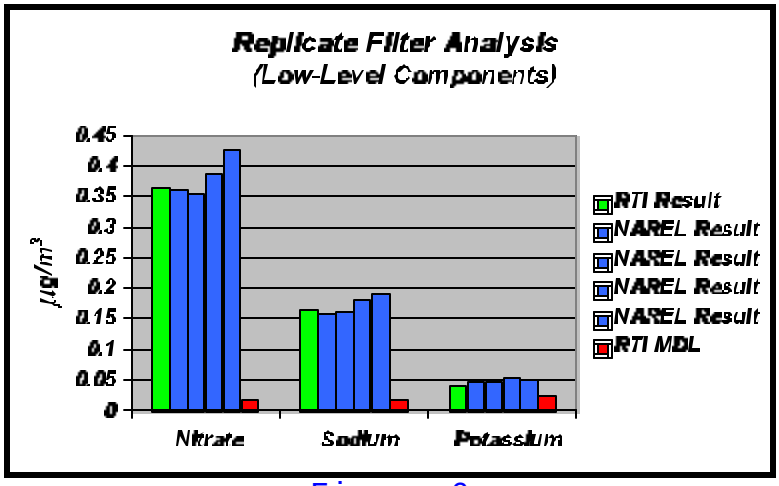

Figure 6

A second Nylon® filter (N01-10153) was submitted to RTI for analysis, and this filter was actually a blank filter pre-cleaned at NAREL along with all the other Nylon® filters used in this study. Three blank filters from this clean batch were analyzed at NAREL on separate days. The results from analysis of all blank Nylon® filters are presented in Table 4 at the end of this report.

Carbon Analysis

For this study, quartz filters and TOT spike solutions were carefully prepared at NAREL and shipped to RTI for analysis. A Met One SASS sampler was used to load several quartz filters with $PM_{2.5}$ captured from the Montgomery air. Three filters were submitted to RTI for analysis, and the replicates of each filter were retained at NAREL for in-house analysis. Two of the three filters submitted to RTI were actually quartz filter blanks, and one filter was loaded with a 46-hour $PM_{2.5}$ capture. No information was given to RTI 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 low-level concentration of sucrose, and one solution contained a mid-level concentration of sucrose. No information was given to RTI regarding the composition of the TOT 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.*

The final results from RTI were reported as mass of carbon per square centimeter of filter material ($\mu g/cm^2$). Once received at NAREL, the results from the loaded filter 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 7. TOT-1 was a mid-level sucrose spike, TOT-3 was a low-level sucrose spike, and TOT-2 (not shown in the graph) was blank water. Figure 7 presents the expected result, the RTI result, the NAREL result, and the result uncertainty reported by RTI for the organic carbon analysis.

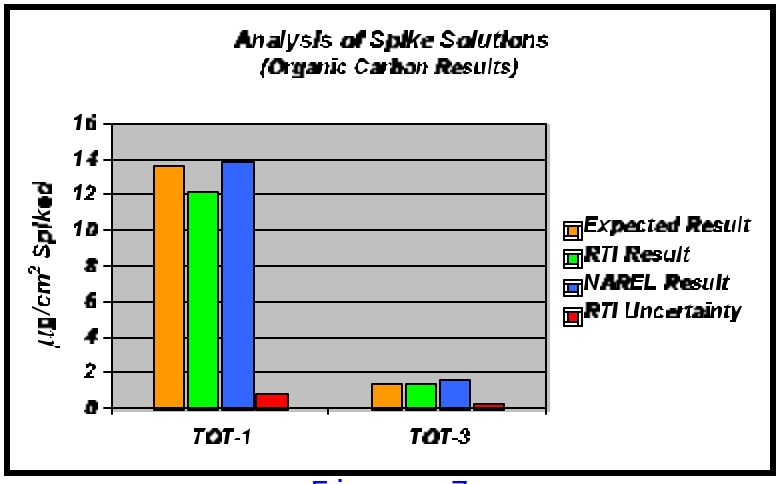

Figure 7

The EC, OC, and TC results for the loaded quartz filter replicates are presented in Figure 8. The graph presents results from one analysis performed at RTI and four analyses performed at NAREL. The uncertainty of measurement expressed by RTI has been converted to units of mass captured per cubic meter of air sampled. CC was not detected by either laboratory and therefore is not presented in the graph.

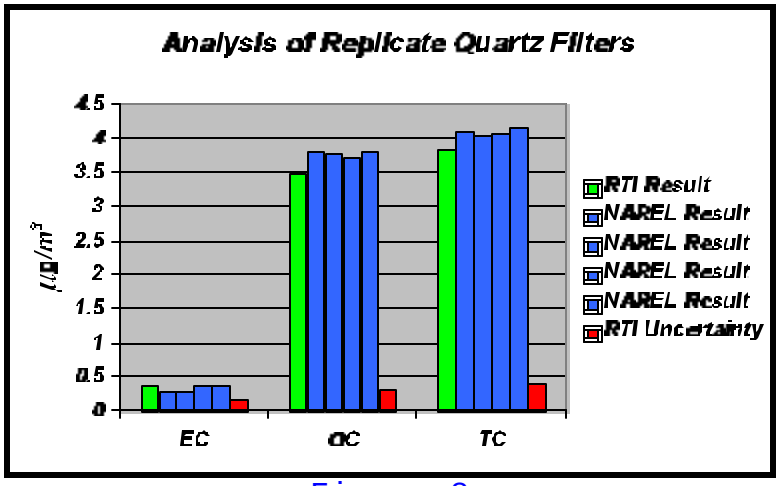

Figure 8

All results for the sucrose spike solutions are listed in Table 5 at the end of this report. All data for the loaded quartz filters and the blank quartz filters are also listed at the end of this report in Table 6 and Table 7 respectively.

Conclusions

Good agreement was observed for all mass measurements performed at RTI and at NAREL. All three field blanks showed $PM_{2.5}$ capture well below the 0.030-mg failure threshold. The independent chamber blank at both laboratories also showed $PM_{2.5}$ capture well below the program limit of 0.015 mg. The largest inter-laboratory difference for captured $PM_{2.5}$ was 0.009 mg which is smaller than 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 RTI.

Excellent recoveries (93-103%) were obtained at RTI and at NAREL for the mid-level IC spikes. Better than expected recoveries (95-106%) were observed for the low-level spikes. Sample spike solutions identified as A-2 and C-2 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 contamination was reported for the anion blank (A-2), but a very low level of sodium was reported for the cation blank (C-2). The sodium was reported at 0.019 : g/mL which is below the 0.02 : g/mL expressed MDL.

Replicate Nylon® filters from a 72-hour collection event were available for this study. The longer-than-normal collection period was necessary to provide a sample with all ions sufficiently above the detection threshold. The results reported by RTI show excellent 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. All RPD's were below 20 percent, and this was true even for those ions present in the sample at a low level! Blank Nylon® filters were also prepared for this study, and no significant filter contamination was reported by either laboratory. This study indicates good performance by the IC laboratory at RTI.

Good recoveries were obtained at RTI and at NAREL for the mid-level sucrose spike (90% and 102% respectively). Good recoveries (101%-119%) were also observed for the low-level sucrose spike. The sample spike solution identified as TOT-2 was actually blank water. This blank spike provided a mechanism to evaluate the measurement baseline at both laboratories. Both laboratories reported the blank spike below the calculated uncertainty of measurement.

Replicate quartz® filters from a 46-hour collection event were available for this study. The longer-than-normal collection period was necessary to provide a sample with OC and EC sufficiently above the detection threshold. The results reported by RTI show excellent agreement with the results produced at NAREL. A difference from the mean value was calculated for the EC, OC, and TC present in the sample, and this Relative Percent Difference (RPD) is included in Table 6. All RPD's were below 20 percent, and this was true even for the EC which was at a very low level in the sample! Blank quartz filters were also prepared for this study, and no significant filter contamination was reported by either laboratory. This study indicates good performance by the OC/EC laboratory at RTI.

Good performance was observed from all three of the RTI laboratories tested during this study.

Table 1. Gravimetric Data

Filter ID	Tare Mass RTI (mg)	Tare Mass NAREL (mg)	Final Mass RTI (mg)	Final Mass NAREL (mg)	Captured $PM_{2.5}$ RTI (mg)	Captured $PM_{2.5}$ NAREL (mg)	Inter-Lab Difference* of Captured $PM_{2.5}$ (mg)
P1010451	147.184	147.182	147.386	147.386	0.202	0.204	0.002
P1010452	147.533	147.533	147.734	147.738	0.201	0.205	0.004
P1010453	148.273	148.272	148.550	148.557	0.277	0.285	0.008
P1010454	148.057	148.059	148.324	148.334	0.267	0.275	0.008
P1010455	143.813	143.814	144.087	144.097	0.274	0.283	0.009
P1010456	142.341	142.341	142.419	142.417	0.078	0.076	-0.002
P1010457	143.183	143.186	143.254	143.258	0.071	0.072	0.001
P1010458	147.253	147.253	147.259	147.256	0.006	0.003	-0.003
P1010459	146.213	146.216	146.219	146.215	0.006	-0.001	-0.007
P1010460	147.767	147.763	147.769	147.764	0.002	0.001	-0.001
Lab Blank	146.085	140.508	146.089	140.509	0.004	0.001	-0.003

**** Negative values indicate a larger capture determined by RTI.***

Table 2. IC Spike Solutions

Sample ID	Analyte	Expected Result (:g/mL)	RTI Result (:g/mL)	NAREL Result (:g/mL)	RTI Recovery	NAREL Recovery	RTI MDL (:g/mL)
A-1	Nitrate	2.700	2.719	2.669	101%	99%	0.02
A-1	Sulfate	0.180	0.185	0.186	103%	103%	0.01
A-2	Nitrate	0.000	0.000	0.000	-----	-----	0.02
A-2	Sulfate	0.000	0.000	0.000	-----	-----	0.01
A-3	Nitrate	0.130	0.134	0.131	103%	101%	0.02
A-3	Sulfate	3.300	3.379	3.303	102%	100%	0.01
C-1	Sodium	0.200	0.212	0.198	106%	99%	0.02
C-1	Ammonium	0.200	0.197	0.194	99%	97%	0.02
C-1	Potassium	1.700	1.705	1.668	100%	98%	0.03
C-2	Sodium	0.000	0.013	0.000	-----	-----	0.02
C-2	Ammonium	0.000	0.000	0.000	-----	-----	0.02
C-2	Potassium	0.000	0.000	0.000	-----	-----	0.03
C-3	Sodium	1.600	1.653	1.556	103%	97%	0.02
C-3	Ammonium	3.200	3.283	2.976	103%	93%	0.02
C-3	Potassium	0.170	0.161	0.176	95%	104%	0.03

Table 3. Loaded Nylon Filters

Analyte	Sample ID	RTI Result (:g/mL)	NAREL Result (:g/mL)	Air Volume (m^3)	Air Conc. (:g/m^3)	RTI MDL* (:g/m^3)	Air Conc. RPD**
Nitrate	N01-10147	0.424	-----	29.072	0.365	0.017	-4%
	N01-10148	-----	0.421	29.068	0.362	-----	-4%
	N01-10149	-----	0.413	29.040	0.356	-----	-6%
	N01-10150	-----	0.413	26.776	0.386	-----	2%
	N01-10151	-----	0.460	26.979	0.426	-----	12%
Sulfate	N01-10147	3.039	-----	29.072	2.613	0.009	3%
	N01-10148	-----	2.871	29.068	2.470	-----	-3%
	N01-10149	-----	2.916	29.040	2.511	-----	-1%
	N01-10150	-----	2.737	26.776	2.555	-----	0%
	N01-10151	-----	2.787	26.979	2.582	-----	1%
Sodium	N01-10147	0.192	-----	29.072	0.165	0.017	-4%
	N01-10148	-----	0.186	29.068	0.160	-----	-7%
	N01-10149	-----	0.186	29.040	0.160	-----	-7%
	N01-10150	-----	0.194	26.776	0.181	-----	6%
	N01-10151	-----	0.206	26.979	0.191	-----	11%
Ammonium	N01-10147	0.883	-----	29.072	0.759	0.017	5%
	N01-10148	-----	0.825	29.068	0.709	-----	-2%
	N01-10149	-----	0.850	29.040	0.732	-----	1%
	N01-10150	-----	0.769	26.776	0.718	-----	-1%
	N01-10151	-----	0.757	26.979	0.701	-----	-3%
Potassium	N01-10147	0.048	-----	29.072	0.041	0.026	-14%
	N01-10148	-----	0.054	29.068	0.047	-----	-3%
	N01-10149	-----	0.055	29.040	0.047	-----	-2%
	N01-10150	-----	0.059	26.776	0.055	-----	15%
	N01-10151	-----	0.055	29.979	0.051	-----	5%

* MDL = Method Detection Limit

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

Table 4. Blank Nylon Filters

Analyte	Sample ID	RTI Result (:g/mL)	NAREL Result (:g/mL)	RTI MDL* (:g/mL)
Nitrate	N01-10153	0.000	-----	0.02
	N01-10152	-----	0.000	-----
	N01-10154	-----	0.000	-----
	N01-10155	-----	0.000	-----
Sulfate	N01-10153	0.000	-----	0.01
	N01-10152	-----	0.000	-----
	N01-10154	-----	0.000	-----
	N01-10155	-----	0.000	-----
Sodium	N01-10153	0.001	-----	0.02
	N01-10152	-----	0.000	-----
	N01-10154	-----	0.000	-----
	N01-10155	-----	0.000	-----
Ammonium	N01-10153	0.000	-----	0.02
	N01-10152	-----	0.000	-----
	N01-10154	-----	0.000	-----
	N01-10155	-----	0.000	-----
Potassium	N01-10153	0.000	-----	0.03
	N01-10152	-----	0.000	-----
	N01-10154	-----	0.000	-----
	N01-10155	-----	0.000	-----

* MDL = Method Detection Limit

Table 5. Carbon Spike Solutions

Sample ID	Analyte	Expected Result (:g/cm^2)	RTI Result (:g/cm^2)	NAREL Result (:g/cm^2)	RTI Recovery	NAREL Recovery	RTI Uncertainty (:g/cm^2)
TOT-1	CC	0.00	0.00	0.00	-----	-----	-----
TOT-1	EC	0.00	0.07	0.01	-----	-----	0.20
TOT-1	OC	13.61	12.21	13.88	90%	102%	0.81
TOT-1	TC	13.61	12.29	13.89	90%	102%	0.91
TOT-2	CC	0.00	0.00	0.00	-----	-----	-----
TOT-2	EC	0.00	0.02	0.00	-----	-----	0.20
TOT-2	OC	0.00	0.13	0.14	-----	-----	0.21
TOT-2	TC	0.00	0.14	0.15	-----	-----	0.31
TOT-3	CC	0.00	0.00	0.00	-----	-----	-----
TOT-3	EC	0.00	0.04	0.00	-----	-----	0.20
TOT-3	OC	1.36	1.37	1.61	101%	119%	0.27
TOT-3	TC	1.36	1.41	1.61	104%	119%	0.37

Table 6. Loaded Quartz Filters

Analyte	Sample ID	RTI Result (:g/cm^2)	NAREL Result (:g/cm^2)	Air Volume (m^3)	Air Conc. (:g/m^3)	RTI Uncertainty (:g/m^3)	Air Conc. RPD*
CC	Q01-10165	0.00	-----	18.573	0.00	-----	-----
	Q01-10166	-----	0.00	18.547	0.00	-----	-----
	Q01-10167	-----	0.00	18.556	0.00	-----	-----
	Q01-10168	-----	0.00	18.865	0.00	-----	-----
	Q01-10169	-----	0.00	18.843	0.00	-----	-----
EC	Q01-10165	0.58	-----	18.573	0.37	0.23	11%
	Q01-10166	-----	0.44	18.547	0.28	-----	-15%
	Q01-10167	-----	0.45	18.556	0.29	-----	-12%
	Q01-10168	-----	0.58	18.865	0.36	-----	9%
	Q01-10169	-----	0.57	18.843	0.35	-----	6%
OC	Q01-10165	5.49	-----	18.573	3.47	0.47	-6%
	Q01-10166	-----	6.01	18.547	3.81	-----	3%
	Q01-10167	-----	5.94	18.556	3.76	-----	1%
	Q01-10168	-----	5.93	18.865	3.70	-----	0%
	Q01-10169	-----	6.08	18.843	3.79	-----	2%
TC	Q01-10165	6.60	-----	18.573	3.84	0.60	-5%
	Q01-10166	-----	6.45	18.547	4.09	-----	1%
	Q01-10167	-----	6.39	18.556	4.05	-----	0%
	Q01-10168	-----	6.51	18.865	4.06	-----	1%
	Q01-10169	-----	6.64	18.843	4.15	-----	3%

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

Table 7. Blank Quartz Filters

Analyte	Sample ID	RTI Result (:g/cm^2)	NAREL Result (:g/cm^2)	RTI Uncertainty (:g/cm^2)
CC	Q01-10170	0.00	-----	-----
	Q01-10171	0.00	-----	-----
	Q01-10172	-----	0.00	-----
	Q01-10173	-----	0.00	-----
	Q01-10174	-----	0.00	-----
EC	Q01-10170	0.04	-----	0.20
	Q01-10171	0.03	-----	0.20
	Q01-10172	-----	0.04	-----
	Q01-10173	-----	0.17	-----
	Q01-10174	-----	0.06	-----
OC	Q01-10170	0.17	-----	0.21
	Q01-10171	0.14	-----	0.21
	Q01-10172	-----	0.18	-----
	Q01-10173	-----	0.61	-----
	Q01-10174	-----	0.24	-----
TC	Q01-10170	0.21	-----	0.31
	Q01-10171	0.17	-----	0.31
	Q01-10172	-----	0.22	-----
	Q01-10173	-----	0.78	-----
	Q01-10174	-----	0.30	-----