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Annual Data Summary Report for the Chemical Speciation of PM2.5 Filter Samples Project

January 1 through December 31, 2005

Prepared for:
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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EXECUTIVE SUMMARY

Introduction

The U.S. Environmental Protection Agency (EPA) established a PM2.5 Chemical Speciation Trends Network (STN) in 1999. The STN included a core set of 54 trends analysis sites and some 160 other sites. RTI is assisting in the PM2.5 STN by shipping ready-to-use filter packs and denuders to all the field sites and by conducting gravimetric and chemical analyses of several types of filters used in the samplers. RTI staff performed an extensive array of quality assurance/quality control (QA/QC) activities to ensure that the data provided to EPA and the States are of the highest quality. The laboratory QA activities in terms of accuracy, precision, data completion, and any corrective actions taken on the chemical speciation of samples from the STN sites from January 1 to December 31, 2005, are described in this report.

Data Quality

Analytical completeness exceeded 95%, and laboratory accuracy and precision were under control as demonstrated by routine QC samples, laboratory audits, and instrument intercomparison. The Research Triangle Institute (RTI) laboratories were audited by EPA personnel during July 2005, and also received performance audit samples. Except for one gravimetric value (which may have been affected by the manufacturer's debris) all results were within acceptable limits, as shown in Appendices D and E.

Laboratory Performance

Section 3.0 of this report provides the details of accuracy, precision, and other measures of laboratory performance. The laboratories consistently met their QC goals of routine analyses, which are detailed in Sections 3.1 (Gravimetry Laboratory), 3.2 (Ion Analysis), 3.3 (Organic and Elemental Carbon [OC/EC]), and 3.4 (X-ray Fluorescence).

Problems with the weighing chamber environmental controls in the Gravimetry Laboratory (Section 3.1) were dealt with aggressively so that a minimum of data had to be flagged as outside holding time or environmental criteria. The other issue affecting the gravimetric data was a filter debris problem originating with a particular manufacturer's lot. RTI arranged for the exchange of 5,000 filters from this lot. The Standard Operating Procedure (SOP) for gravimetric analysis has been updated to increase the frequency of re-weighing in the laboratory in order to quickly recognize and correct future instances (Section 2.3). Systems and performance audit results (Section 3.1.6) for gravimetric mass were found to be satisfactory.

Minimal problems with laboratory operations and filter media were reported by the Ion and OC/EC laboratories during 2005. Systems and performance audit results for these laboratories were satisfactory (Sections 3.2.6 and 3.3.6).

The X-ray fluorescence (XRF) laboratories operated by RTI and subcontractor Chester LabNet (CLN) generally met the prescribed QC criteria for analysis (Sections 3.4.1 and 3.4.2). Both laboratories had equipment downtime, which affected sample analysis logistics, but this had no effect on data quality. The RTI and CLN laboratories participate in an intercomparison (round-robin) program described in Section 3.4.2.4. Systems and performance audit results (Section 3.4.6) were satisfactory.

Operations in the Sampling Handling and Archiving Laboratory (SHAL) proceeded normally during 2005, with a few rare problems such as switching the paperwork for coolers shipped to two different sites (Section 3.5.1). A small number of samples were missed due to late return of coolers from the field sites. Systems and performance audit results (Section 3.5.6) were satisfactory. No significant quality issues were reported by the denuder refurbishment laboratory (Section 3.6).

No significant quality issues were reported by the data processing and data validation functions during 2005 (Sections 4.0 and 5.0). Data continues to be reviewed and posted to a secure website on a monthly basis for review. Finalized data are posted to the EPA AQS database approximately 60 days after initial posting (Section 4.0). A number of data users contacted SHAL, data processing, and quality assurance (QA) personnel with questions about specific data items, or to request explanations about apparent discrepancies.

Estimation of MDLs and Uncertainties

Method Detection Limits (MDLs) for all laboratory methods are provided in Appendix A. Uncertainties are estimated based on laboratory QC data, augmented by a 5% concentration-proportional term to account for field handling and sample volume uncertainties. Results from collocated samplers (Section 5.3) indicate that this uncertainty model is reasonable.

Quality Issues

Aside from the specific issues discussed in the two Corrective Action Requests (CARs) issued during 2005 (Section 2.1), there are some ongoing issues that have not been assigned CARs because there was no specific action that RTI could take, or because they required input and cooperation from others outside RTI. These issues are summarized in the following table.

CAR Number	Lab	Description	Response	Effect on Data
9	Grav.	Whatman Teflon Filter - Debris problem. Loose debris causes net filter weights to be occasionally too low.	5,000 filters were returned to manufacturer and replaced; mass balance outlier flag applied; SOPs for data screening and replicate analysis were updated.	Increased incidence of mass balance outliers (AQS '5' code). Data users should be aware of isolated outliers in gravimetric mass data during 2005.
10	SHAL	Shipping error for 12/11/04 Paducah and Perkinstown coolers	Corrected data in database. Increased supervision and training of SHAL workers.	None.
none	SHAL	Late-arriving coolers	DOPO and others are notified whenever coolers are received late from the field.	Data are flagged as missing.
none	XRF	Harmonize XRF uncertainty calculations	RTI is consulting with recognized experts to identify the correct and consistent methods for calculation for uncertainty.	More accurate uncertainty values in the future could assist modelers and other data users achieve more accurate results.
none	All	Investigate sampler-dependent background levels	RTI is examining historical data for evidence of systematic contamination with different sampler types (in progress).	Potential to inform users of increased incidence of certain types of outliers.

1.0 Introduction

1.1 Program Overview

In 1997, the U.S. Environmental Protection Agency (EPA) promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter. The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations (µg/ $meter^3$ of air) of particles with aerodynamic diameters less than 10 micrometers (the PM10 standard) and less than 2.5 micrometers (the PM2.5 standard). Currently, a 1500-site mass measurements network and a 214-site chemical speciation monitoring network have been established.

The ambient air data from the first network, which measures solely the mass of particulate matter, will be used principally for NAAQS comparison purposes in identifying areas that meet or do not meet the NAAQS criteria and in supporting designation of an area as attainment or non-attainment.

The smaller chemical Speciation Trends Network (STN) included a core set of 54 trends analysis sites and some 160 other sites from State and local agencies supported by RTI. This data summary report covers the quality assurance (QA) aspects of the collection and chemical speciation of samples from these sites from January 1 through December 31, 2005. Chemical speciation data will be used to support development of emission mitigation approaches to reduce ambient PM2.5 concentration levels. Such needs include emission inventory establishment, air quality model evaluations, and source attribution analysis. Other uses of the data sets will be regional haze assessments, estimating personal exposure to PM2.5 and its components, and evaluating potential linkages to health effects.

RTI is supporting the PM2.5 STN by shipping ready-to-use filter packs and denuders to the field sites and by conducting gravimetric and chemical analyses of the several types of filters used in the samplers. The details of the QA activities being performed are described in the RTI QA Project Plan (QAPP) for this project. The QAPP focuses on the QA activities associated with RTI’s role in performing these analyses, as well as in validating and reporting the data, and should be considered a companion document to this annual QA report.

1.2 Project/Task Description

The STN laboratory contract involves four broad areas:

1. Supplying each site or state with sample collection media (loaded filter packs, denuders, and absorbent cartridges) and field data documentation forms. RTI ships the collection media to monitoring agencies on a schedule specified by the Delivery Order Project Officer (DOPO).

2. Receiving the samples from the field sites and analyzing the sample media for mass and for an array of chemical constituents including elements (by EDXRF), soluble anions and cations (by ion chromatography), and carbonaceous species (using the Sunset thermal degradation/laser transmittance system). Analysis of semi-volatile organic compounds and examination of particles by electron or optical microscopy have been performed on a very limited basis.

3. Assembling validated sets of data from the analyses, preparing data reports for EPA management and the states, and entering data into the Air Quality System (AQS) data bank 60 days after initial data reports are first submitted to the DOPO and the states.

4. Establishing and applying a comprehensive quality assurance/quality control (QA/QC) system. RTI's Quality Management Plan, QAPP, and associated Standard Operating Procedures (SOPs) provide the documentation for RTI's quality system.

1.3 Major Laboratory Operational Areas

This report addresses the operation of the Sample Handling and Archiving Laboratory (SHAL) and QA/QC for the four major analytical areas active during the time period of January 1 through December 31, 2005. These analytical areas are the: (1) gravimetric determination of particulate mass on Teflon® filters; (2) determination of 48 elements on Teflon® filters using X-ray fluorescence spectrometry; (3) determination of nitrate, sulfate, sodium, ammonium and potassium on nylon or Teflon filters using ion chromatography; and (4) determination of organic carbon, elemental carbon, total carbon, and five other peaks (PK1C, PK2C, PK3C, PK4C, and PyrolC) on quartz filters using thermal optical transmittance. Also addressed is denuder refurbishment, data processing, and QA and data validation.

2.0 Quality Issues and Corrective Actions

2.1 Data Quality

RTI staff perform an extensive array of QA/QC activities to ensure that the data provided to EPA and the States are of the highest quality. Further, RTI makes every effort to provide data that can serve as the basis for making important decisions.

Data quality for the STN has several dimensions, but the primary goal should be usefulness to data users and understanding of the data set's characteristics. There are several metrics that are typically considered in assessing the quality of the STN dataset:

- Accuracy - All analyses standardized to reference values that are traceable to NIST.

- Precision - Measured both as laboratory and whole-system through regular QC replicates and results from samplers collocated at the same site.

- Completeness - Excellent completeness is demonstrated overall, but individual sites may have lower completeness. In addition, the STN has very poor rural site coverage in the western U.S., where IMPROVE sites predominate.

- Comparability - Intercomparison studies recently conducted by EPA have shown good agreement with programs such as the FRM network and IMPROVE results for most of the major chemical species. Other dimensions of comparability include comparability between the four different sampler types currently in use in the STN program: MetOne SASS, Andersen RAAS, URG MASS, and the R&P 2300. In addition, the data are often intercompared with data gathered by three additional sampler types: IMPROVE, PM2.5 FRM, and R&P 2025 (used in Texas). All these samplers operate at a variety of different flow rates, use different modes of flow control, and utilize different particle sizing technologies.

- Representativeness - Primary site selection and field sampling operations are out of RTI's control.

- Sensitivity/Detection - The ability to quantify major species such as gravimetric mass, organic carbon, sulfate, nitrate, ammonium, iron, etc. is adequate.

However, many of the trace elements are routinely below limits of detection. Data users should carefully screen out species that are present in such low levels that their inclusion would only add noise to their analysis. Method Detection Limits (MDLs) are provided in Appendix A.

In addition to these data quality assessment criteria, there are other issues that affect data usability. The following quality-related issues and other characteristics of the data set should be taken into account in an overall assessment of the dataset:

- Lack of blank correction - The main concern is the artifact in organic carbon (OC) measurement. The IMPROVE network includes blank correction for OC in its reported data. This is a fundamental difference between the data reported by STN and IMPROVE. Since STN uses four different sampler types, the appropriate OC correction factors should be made readily available to data users.

- Intermittent media contamination issues - Equipment and media contamination issues arise from time to time. RTI makes an effort to flag data, retroactively if necessary, to invalidate or mark as suspicious any affected data items.

- Improvement of uncertainty estimates:
  - -- Comparability between STN and other networks - RTI is working with U.C. Davis and other experts in XRF to define an acceptable method for determining XRF uncertainty.
  - -- Realism of total uncertainty estimates based on statistics from sites with side-by-side collocation of samplers. Collocation results provided elsewhere in this report indicate that uncertainties reported to AQS for several major species may be overestimated by a factor of 2x or 3x. These include sulfate, nitrate, and elemental carbon. Average uncertainties currently being reported for the majority of other species appear to be in reasonable agreement with uncertainties calculated from the collocation results.

2.2 Summary of Data Completeness

Data completeness network-wide exceeded 95% for 2005. Both trends and non-trends sites exceeded 95% completeness. Completeness is defined as the number of valid measurement values divided by the potential number of values. Data records with AQS validity status codes ("suspicious" data) are included in the completeness figure, but data records with an AQS null value code are counted as missing data.

Appendix B includes more details of the sampling events and completeness for the Reporting Batches delivered in 2005. Table B.1 shows the total number of sampling events included in each Reporting Batch. Table B.2 provides the total number of records delivered by type. Table B.3 shows the percentage of routine exposure records for each delivery batch group that were valid (i.e., not invalidated with an AIRS Null Value Code) relative to the number of records for scheduled events for that batch for all trends sites. Table B.4 shows the percentage of routine exposure records for each delivery batch group that were valid (i.e., not invalidated with an AIRS Null Value Code) relative to the number of records for scheduled events for that batch for all non-TRENDS sites. Blank cells indicate that no analyses were scheduled for a site during a particular delivery batch interval. Percentages less than 80 are usually the result of a sample being out of service or one or more exposures being missed because of problems at the site or problems with the shipping.

2.3 Corrective Actions

To ensure ongoing quality work, RTI reacts quickly and decisively to any unacceptable changes in data quality. These reactions are usually in the form of corrective actions. Most of these corrective actions have been in response to very short-term problems such that very few results were impacted negatively. What follows is a description of the major corrective actions taken to ensure the best possible PM2.5 data for the EPA and States.

Two formal corrective action requests (CARs) were opened and addressed during 2005.

- CAR 008 - 3/17/05 - Whatman Teflon Filter – Manufacturer's Debris Problem. In late 2004, the number of filters with a negative net weight seemed to be increasing. A retrospective analysis of the blank data revealed that the rate of filters with net weight changes of -30 micrograms/filter or more increased during the spring of 2004, with significant acceleration in early 2005. Corrective actions were successfully taken, and the frequency of negative net mass outliers has been held to a minimum. Specific actions taken in response to this problem included replacement of approximately 6000 filters from the affected lot, and increased frequency of replicate weighing in the laboratory. See Section 3.0 of this report for further discussion.

- CAR 009 - Shipping error for 12/11/04 Paducah and Perkinstown coolers, and related data corrections. Sample coolers for Perkinstown and Paducah were mixed up and sent to the wrong sites. The site operators noted the error and wrote in the correct site names on the respective forms. RTI attempted to fix the problem by interchanging the Chain of Custody (COC) numbers in the database, but some of the field data was not changed properly the first time. After the data had been reported to AQS, RTI received notification through EPA of a data error from one of the monitoring organizations. As a result, RTI examined the original data sheets and compared tem against the reported data and identified the additional changes that needed to be made.

2.3.1 Gravimetric Mass

There were several instances of facilities problems in the gravimetry laboratory during 2005. Problems included fan motors and humidification system components. These were met by actions from RTI's HVAC department and by equipment suppliers. Filter samples were generally not affected, but validity status codes may have been assigned in isolated cases when holding times, temperature, or relative humidity exceeded 2.12 guidelines. Chamber humidity and temperature sensors were calibrated by the chamber vendor in June 2005 as part of a comprehensive system calibration and preventive maintenance check. This service was obtained to address any existing facilities issues and prevent unplanned shutdown in the future. It should be noted that weighings were not performed when chambers were not working properly.

2.3.2 Elemental Analysis

No significant corrective actions have been taken; however, RTI XRF 1 was upgraded from analog to a digital system in October 2004 and has not been used to analyze PM2.5 filters due to instrumental problems.

2.3.3 Ion Analysis

There were no corrective actions taken during this reporting period.

2.3.4 OC/EC Analysis

No significant corrective actions have been taken.

2.3.5 Sample Handling and Archiving Laboratory (SHAL)

Problem: Coolers arriving late at the RTI SHAL laboratory delay the processing and analysis of filters and may even cause a missed sampling event if RTI cannot repack new filters into the modules and ship them to the site in time for the next sampling event. Late arriving coolers are typically due to late returns by the site or delays in transit by the carrier. A summary and graphic of late arriving coolers for the time frame of July 1 to December 31, 2004 is presented below.

Corrective Action: Late arriving coolers are usually caused by delays in the field or by Federal Express. When a shipment is late arriving at RTI, it may not be possible for RTI to ship a set of filter modules as scheduled. When this happens, RTI will notify the EPA DOPO and any missed sampling events are flagged as “scheduled but not collected” (AF).

2.3.6 Data Processing

There were no corrective actions taken during this reporting period.

2.4 Other Quality Issues

Aside from the specific issues discussed in the CARs, there are some ongoing issues that have not been assigned CARs because there was no specific action that RTI could take, or because they required input and cooperation from others outside RTI:

- **Uncertainty harmonization for XRF instruments.** RTI has written a series of reports, presentations, and whitepapers regarding the problem of achieving harmony between the uncertainties reported by the various EDXRF instruments in use by

STN and other PM-fine networks in the U.S., including IMPROVE. Dr. Bill Gutknecht, the RTI laboratory supervisor, has been in contact with experts at U.C. Davis and Alion, Inc. to determine how certain correction factors and the associated uncertainties were estimated historically. A specific recommendation for calculating uncertainties for XRF measurements with PM-fine samples will be forthcoming in early 2006. Lessons learned in this investigation may also be applicable to speciated analysis of PM-coarse.

- **Sampler-dependent background levels for certain elements.** It has been observed since the beginning of the network that certain samplers have a higher incidence of outliers for particular species. These appear to be a function of the materials used in manufacturing the sampler downtubes, denuders, modules and other sampling components. As the analytical laboratory, RTI has no authority to make changes in the sampler technology that was chosen for the network.

3.0 Laboratory Quality Control Summaries

3.1 Gravimetric Laboratory

The Gravimetry Laboratory's two weigh chambers were used to tare 24,676 Teflon filters between January 1 and December 31, 2005. During the same time period, the laboratory performed final ("post-sampling") weighings of 22,374 Teflon filters. This number includes filters weighed for the Hurricane Katrina surveillance monitoring effort. The difference between the number of tared filters and the number of final ("post-sampling") filters is partly due to the inherent lag time between initial and final weighing sessions. Determination of PM2.5 mass is based on two separate weighings performed several weeks apart. The total also reflects an increase in the number of filters weighed in the last three months of the year resulting from the laboratory's support to air monitoring conducted in EPA Regions 4 and 6 after Hurricanes Katrina and Rita hit the Gulf Coast. Filter weighing totals given in this report are those recorded by the laboratory's database application.

3.1.1 Quality Issues and Corrective Actions

In March 2005, the Gravimetry Laboratory noted extraneous contaminating debris on Teflon filters purchased for the program. This extraneous debris was considered the likely cause of negative mass blanks resulting from the loss of debris from the filters between tare weighing and final weighing. In most cases, the extraneous debris was very small and matched the filter and support ring in color and texture, making it difficult to see with the naked eye in normal chamber lighting. In response to this issue, the laboratory took several actions. First, RTI replaced all the filters from this lot and received replacement filters from a different lot. Thereafter, the number of filters selected for lot stability tests was increased from six filters (two filters from each of six randomly selected boxes of filters) to 12 filters (two filters from each of six randomly selected boxes of filters) in order to get an even more representative sampling of the filter stock received from the manufacturer. Additional visual inspection of filters was also performed. The frequency of replicate QC weighings was increased from an across-the-board 10% to 100% of tared (pre-sampled) filters and at least 33% of sampled filters.

3.1.2 Description of QC Checks Applied

Internal QC checks applied in the Gravimetry Laboratory are described in Table 3-1, along with results achieved during this reporting period.

Table 3-1. Summary of QC Checks Applied and Results Achieved in the Gravimetry Laboratory

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Working standard reference weights (mass reference standards)	Verified value ± 3 µg [Standard reference weights initially calibrated by Troemner and verified by North Carolina Department of Agriculture and Consumer Services (NCDA&CS) Standards Laboratory]	Chamber 1 100-mg S/N 12936 6/22/04 Class 1 Calibration: 99.95525 mg ± 0.00082 Laboratory Tolerance Interval: 99.951-99.959 mg	Average = 99.956 mg Std Dev = 0.0021 for 2844 weighings	Laboratory average falls within tolerance interval.
		200-mg S/N 12935 6/22/04 Class 1 Calibration: 199.99054 mg ± 0.00079 Laboratory Tolerance Interval: 199.987-199.994 mg	Average = 199.992 mg Std Dev = 0.0024 for 2843 weighings	Laboratory average falls within tolerance interval.
		Chamber 2 100-mg S/N 58096 8/25/04 Class 1 Calibration: 100.00798 mg ± 0.00082 Laboratory Tolerance Interval: 100.004-100.012 mg	Average = 100.006 mg Std Dev = 0.0017 for 664 weighings	Laboratory average falls within tolerance interval.
		100-mg S/N RTI01 6/22/04 Class 1 Calibration: 99.99279 mg ± 0.00082 Laboratory Tolerance Interval: 99.989-99.997 mg	Average = 99.991 mg Std Dev = 0.0010 for 600 weighings	Laboratory average falls within tolerance interval.
		100-mg S/N 58097 8/25/04 Class 1 Calibration: 100.00254 mg ± 0.00082 Laboratory Tolerance Interval: 99.999-100.006 mg	Average = 100.001 mg Std Dev = 0.0025 for 2491 weighings	Laboratory average falls within tolerance interval.
		200-mg S/N 58098 8/25/04 Class 1 Calibration: 200.00972 mg ± 0.00079 Laboratory Tolerance Interval: 200.006-200.014 mg	Mean = 200.010 mg Std Dev = 0.0036 for 670 weighings	Laboratory average falls within tolerance interval.

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
		200-mg S/N 18659 6/22/04 Class 1 Calibration: 199.97943 mg ± 0.00079 Laboratory Tolerance Interval: 199.976-199.983 mg 200-mg S/N 58099 8/25/04 Class 1 Calibration: 200.00628 mg ± 0.00079 Laboratory Tolerance Interval: 200.002-200.010 mg	Mean = 199.978 mg Std Dev = 0.0009 for 602 weighings Mean = 200.002 mg Std Dev = 0.0021 for 2489 weighings	Laboratory average falls within tolerance interval. Laboratory average falls within tolerance interval.
Balance Calibrations	Auto (internal) calibration daily External calibration annually or as needed	Daily Balance C - S/N 1118252777 (Chamber 1) and Balances D – S/N 1125430571 (replaced Balance A, which was removed from service on June 30, 2005), and B – S/N 1118311244 inspected and externally calibrated by Mettler Toledo on August 22, 2005, using NIST-traceable weight	N/A N/A	 Next inspection and external calibration scheduled for August 2006
RH/T Data Logger Calibrations	Annually	Chamber 1 Data Logger S/N 01042219 and Chamber 2 Data Logger S/N 00102174 currently in service calibrated by Dickson Calibration Services February 23, 2005, using NIST-traceable standards	N/A	Chamber 1 Data Logger S/N 03082408 and Chamber 2 Data Logger S/N 03082406 to be calibrated by Dickson Calibration Services February 2006

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Laboratory (Filter) Blanks	Initial weight ± 15 µg	2650 total replicate weighings of 349 individual laboratory blanks	Average difference between final and initial weight = 4 µg Std Dev = 0.0048 Min wt change = 0 µg Max wt change = 38 µg	71 total replicate weighings of 15 individual laboratory blanks (2.7% of the replicate weighings; 4.3% of the individual laboratory blanks) exceeded the 15 µg criterion. Only three replicate weighings of two individual laboratory blanks exhibited excess weight changes in the positive direction. Over 95% of the replicate laboratory blank weighing failures were in the negative direction, indicating probable contamination on the filters when tared that fell off or was removed before later reweighings.
Replicates	Initial weight ± 15 µg	20,329 Pre-sampled (Tared) Replicates 8413 Post-sampled Replicates	Average = 6 µg Average = 4 µg	Outliers were reweighed in order to confirm value with two weights within 5 µg of each other. Outliers were reweighed in order to confirm value with two weights within 5 µg of each other.

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Lot Blanks (Lot Stability Filters)	24-hour weight change < ± 5 µg	Whatman Lot 4279001 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -4 µg 48 hours = 0 µg 72 hours = 1 µg 96 hours = 2 µg	Fall well within required range
		Whatman Lot 4341004 - 6 filters weighed (2 randomly selected from each of 3 randomly selected boxes)	24 hours = -4 µg 48 hours = -2 µg 72 hours = 0 µg 96 hours = 0 µg	
		Whatman Lot 5103003 Test 1 (Rec'd this lot twice and ran a lot stability test each time) - 12 filters weighed (2 randomly selected from each of 6 randomly selected boxes)	24 hours = -2 µg 48 hours = 0 µg 72 hours = 1 µg 96 hours = 0 µg	
		Whatman Lot 5103003 Test 2 (Rec'd this lot twice and ran a lot stability test each time) - 12 filters weighed (2 randomly selected from each of 6 randomly selected boxes)	24 hours = -2 µg 48 hours = 1 µg 72 hours = -1 µg 96 hours = 0 µg	
		Whatman Lot 5103001 - 12 filters weighed (2 randomly selected from each of 6 randomly selected boxes)	24 hours = -2 µg 48 hours = -1 µg 72 hours = 1 µg 96 hours = -1 µg	
		Whatman Lot 5318001 - 12 filters weighed (2 randomly selected from each of 6 randomly selected boxes)	24 hours = 0 µg 48 hours = -1 µg 72 hours = 1 µg 96 hours = -1 µg	

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Balance Audits <u>Chamber 1</u> Balance C - S/N 118252777 <u>Chamber 2</u> Balance D – S/N 1125430571 (replaced Balance A, which was removed from service on June 30, 2005), and Balance B – S/N 1118311244	Annually	Performed by RTI Quality Systems Program personnel on November 29, 2005, using Class S-1 NIST-traceable weights	N/A	Included environmental evaluation, level test, scale-clarity test, zero-adjustment test, off-center (corner load) test, precision test, and accuracy test; all balances performed satisfactorily.

3.1.3 Summary of QC Results

Internal QC values generated by the laboratory usually met the criteria shown in Table 3-1. However, some outliers were noted. Laboratory blank outliers tended to fall below the lower warning limit, indicating that the issue of debris on Teflon filters is one that must be monitored. In the case of outlier replicates, Gravimetry Laboratory analysts reweighed outliers to validate weights.

3.1.4 Assessment of Between-instrument Comparability

Beginning in 2006, the Gravimetry Laboratory will introduce an inter-instrument (intra-laboratory) round-robin program to assess both instrumental and human factors of analytical comparability. A designated filter or filters will be weighed daily by all available staff on all balances. The compilation of this data will allow for an assessment of inter-instrument comparability that has not previously been evaluated in the laboratory. Results will be assessed for evidence of bias between balances and between analysts.

3.1.5 Determination of Uncertainties and Method Detection Limits

The Laboratory's MDL calculations are based on replicate weighings of a large number of filters from filter lot acceptance batches. Because of determination of gravimetric mass requires two separate weighings, each of which contributes to the total uncertainty, MDLs reported to AQS are shown in Appendix A. All balances use the same MDLs. Multiplicative factor of 1.414 is included to account for the fact that each filter must be weighed twice to generate the final net mass.

3.1.6 Audits, Performance Evaluations, Training, and Accreditations

Table 3-2 contains information regarding audits, performance evaluations (PEs), training, and accreditations.

Table 3-2. Description of Audits, PEs, Training, and Accreditations

Type of Evaluation	Date	Administered By	Significant Findings/Comments
Internal Audit	January 13, 2005	RTI FRM Project QA Officer	No significant deficiency findings were reported by the FRM QAO. Comment: For the first time, the internal audit included an inspection of the chambers with the aid of an ultraviolet light (black light) to highlight dust and debris in the weighing area. Some material was visible, especially behind computers and under racks, with the black light that might not be visible with normal chamber lighting. The auditor recommended that staff periodically use a black light to direct their cleaning efforts.
External	July 12, 2005	EPA/NAREL and OAQPS Audit Team	Two Teflon® filters were removed from the SHAL inventory during the audit so that NAREL could experimentally re-measure the tare mass already determined at RTI's Gravimetry Laboratory. Agreement between NAREL and RTI was excellent (within 1 µg) for one filter, but NAREL's tare mass was 30 µg smaller for the other filter described in Section 3.1.1 Comment: It is possible that a small piece of extraneous contaminating debris was attached to the filter for measurements taken at RTI, and somehow the debris was lost from the filter before measurements were made at RTI.
Accreditation		Louisiana Environmental Laboratory Accreditation Program (LELAP)	RTI is accredited for the determination of fine particulates in ambient air by the Federal Reference Method (FRM) for PM2.5.

3.2 Ions Analysis Laboratory

The Ion Analysis Laboratory used four ion chromatographs to extract and analyze 20,013 cation analyses (sodium, potassium and ammonium); 21,321 nitrate analyses; and 20,072 sulfate analyses performed on the STN program during the period January 1 through December 31, 2005.

3.2.1 Quality Issues and Corrective Actions

There were no quality issues or corrective actions during the reporting period.

3.2.2 Description of QC Checks Applied

Ion chromatographic analyses were performed by personnel from RTI's Environmental Chemistry Department (ECD). Four of our six ion chromatographic systems available were used for performance of the measurements. These are described in Table 3-3. The use of these four systems was determined by the workload.

Table 3-3. Description of Ion Chromatographic Systems Used for Analysis of PM2.5 Filter Samples

System No.	Dionex IC Model	Ions Measured
3	Model 500 (S3A)	SO_4, NO_3
4	DX-600 (D6A)	SO_4, NO_3
5	Model 500 (D5C)	Na, NH_4, K
6	DX-600 (D6C)	Na, NH_4, K

QA/QC checks for ion analyses are summarized in Table 3-4. For ion analyses, a daily multipoint calibration (7 points for cations; 8 points for anions) is performed over the range 0.05 to 25.0 ppm for each ion (Na^+, NH_4^+, and K^+ for cation analyses; NO_3^- and SO_4^{2-} for anion analyses) followed by QA/QC samples including (1) an RTI-prepared QC sample containing concentrations of each ion in the mid- to high-range of the calibration standard concentrations, (2) an RTI-prepared QC sample containing concentrations of each ion at the lower end of the calibration standard concentrations, and (3) a commercially-prepared, NIST-traceable QA sample containing known concentrations of each ion.

Table 3-4. Ion Analysis of PM2.5 – QA/QC Checks

QA/QC Check	Frequency	Requirements
Calibration Regression Parameters	Daily	r ≥ 0.999
Initial QA/QC Checks:		
- RTI-prepared QC sample at mid to high range concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
- RTI-prepared QC sample at lower end concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
- Commercially prepared, NIST traceable QA sample	Daily, immediately after calibration	Measured concentrations within 10% of known values
Periodic QA/QC Checks:		
- Replicate sample†	Every 20 samples	RPD = 5% at 100x MDL* RPD = 10% at 10x MDL* RPD = 100% at MDL*
- QA/QC sample	Every 20 samples	Measured concentrations within 10% of known values
- Matrix spiked sample extract	Every 20 samples	Recoveries within 90 to 100% of target values
- Duplicates‡	At least one per day	No limit set. This data gathered for comparability studies.
- Reagent Blanks	One reagent blank per reagent used (DI H2O and/or eluent) sample set extracted	No limit set. This data gathered for comparability studies.

* MDL = Minimum Detectable Limit RPD = Relative% Difference

†Replicates indicate a specific sample is run twice on the same instrument.

‡Duplicates indicate a specific sample is run on two different instruments.

The regression parameters (a,b,c and correlation coefficient, r) for the standard curve for each ion are compared with those obtained in the past. Typically, a correlation coefficient of 0.999 or better is obtained for each curve. If the correlation coefficient is <0.999, the analyst carefully examines the individual chromatograms for the calibration standards and reruns any standard that is judged to be out of line with respect to the other standards or to values (peak area and/or height) obtained in the past for the same standard. Possible causes for an invalid standard run include instrumental problems such as incomplete sampling by the autosampler. If necessary, a complete recalibration is performed.

When all individual calibrations have been judged acceptable, the results for the QA/QC samples are carefully examined. If the observed value for any ion being measured differs by more than 10% from the known value, the problem is identified and corrected. Any field samples are then analyzed.

During an analysis run, a replicate sample, a QA/QC sample, and a spiked sample are analyzed at the rate of at least one every 20 field samples. Precision objectives for replicate analyses are ±5% for concentrations that equal or exceed 100 times the minimum detectable limit (MDL), ±10% for concentrations at 10 times the MDL, and ±100% for concentrations at the MDL. MDLs for each instrument and analyte are listed in Table 3-5. The observed value for any ion being measured must be within 10% of the known value for the QA/QC samples given in Table 3-6, and ion recoveries for the spiked samples must be within 90 to 110% of the target value. If these acceptance criteria are not met for any QA/QC or spiked sample, the problem is identified and corrected. All field samples analyzed since the last acceptable check sample are then reanalyzed.

Table 3-5. MDL* for Each Instrument and Analyte

Instrument	Nitrate	Sulfate	Sodium	Ammonium	Potassium
S3A	0.066	0.074	na	na	na
D6A	0.070	0.100	na	na	na
D5C	na	na	0.290	0.160	0.134
D6C	na	na	0.290	0.160	0.134

* In µg/filter

Table 3-6. Definitions and Specifications for QA/QC Samples

Ion	Sample ID	Description/Specification
Anions	QA-CPI_LOW	0.6 ppm nitrate, 1.2 ppm sulfate
	QA-CPI_MED-HI	3.0 ppm nitrate, 6.0 ppm sulfate
	RTI-QC-HIGH	6.0 ppm nitrate, 12.0 ppm sulfate
	RTI-QC-LOW	0.6 ppm nitrate, 1.2 ppm sulfate
	RTI-QC-MED	1.5 ppm nitrate, 3.0 ppm sulfate
Cations	GFS 0.4 PPM QA	0.4 ppm each sodium, ammonium, and potassium
	GFS 4.0 PPM QA	4.0 ppm each sodium, ammonium, and potassium
	RTI 2.0 PPM QC Reg Std	2.0 ppm each sodium, ammonium, and potassium
	RTI 5.0 PPM QC	5.0 ppm each sodium, ammonium, and potassium

3.2.3 Summary of QC Results

QC checks performed included:

- Percent recovery for QC samples (standards prepared by RTI)
- Percent recovery for QA samples (commercial standards)
- Relative percent difference (RPD) for replicates
- Spike recovery
- Reagent blank (elution solution and DI water)

Table 3-7 shows recoveries for all five analytes (nitrate, sulfate, sodium, ammonium, and potassium) with low, medium, and high QC (prepared by RTI) samples and with low and medium-high QA samples (commercially prepared and NIST-traceable) for all of the instruments used for analysis.

Table 3-7. Average Percent Recovery for QA and QC Samples

Analyte	Sample ID	n	Conc. µg/mL	Avg% Rec *	SD	Min	Max
Nitrate	QA-CPI_LOW	490	0.6	98.6%	1.0%	0.564	0.610
	QA-CPI_MED-HI	404	3.0	101.1%	2.8%	2.683	3.145
	RTI-QC-HIGH	403	6.0	101.8%	0.9%	5.836	6.265
	RTI-QC-LOW	762	0.6	98.8%	1.3%	0.555	0.643
	RTI-QC-MED	963	1.5	99.0%	1.1%	1.403	1.531
Sulfate	QA-CPI_LOW	490	1.2	98.7%	1.0%	1.111	1.224
	QA-CPI_MED-HI	404	6.0	101.6%	2.7%	5.483	6.321
	RTI-QC-HIGH	403	12.0	102.2%	0.9%	11.708	12.905
	RTI-QC-LOW	762	1.2	99.7%	1.3%	1.109	1.280
	RTI-QC-MED	963	3.0	100.8%	1.0%	2.882	3.134
Sodium	GFS 0.4 PPM QA	607	0.4	103.1%	3.1%	0.386	0.518
	GFS 4.0 PPM QA	757	4.0	100.3%	1.1%	3.735	4.165
	RTI 2.0 PPM QC Reg Std	552	2.0	100.9%	1.0%	1.957	2.125
	RTI 5.0 PPM QC	463	5.0	100.7%	0.9%	4.894	5.182
Ammonium	GFS 0.4 PPM QA	807	0.4	102.3%	2.4%	0.378	0.441
	GFS 4.0 PPM QA	757	4.0	100.6%	1.2%	3.721	4.196
	RTI 2.0 PPM QC Reg Std	552	2.0	100.6%	1.2%	1.941	2.116
	RTI 5.0 PPM QC	463	5.0	100.8%	1.0%	4.853	5.240
Potassium	GFS 0.4 PPM QA	605	0.4	101.2%	1.4%	0.390	0.428
	GFS 4.0 PPM QA	757	4.0	99.7%	1.0%	3.728	4.104
	RTI 2.0 PPM QC Reg Std	551	2.0	100.9%	1.0%	1.950	2.099
	RTI 5.0 PPM QC	462	5.0	100.5%	1.1%	4.751	5.188

* Acceptance criteria for average percent recovery is ±10%.

Average recoveries for the QC samples ranged from 98.8% to 102.2% for the year. Average recoveries for the QA samples ranged from 98.6% to 103.1% for the year.

Table 3-8 shows percent recovery for all analyte spikes for the year. Average recoveries for the spikes ranged from 100.6% to 102.3%.

Table 3-9 presents filter blank (N BLANK) and reagent blank values for all analytes over the 12 month period. The blank data indicate that the filters supplied to the Sample Handling and Archiving Laboratory (SHAL) were of acceptable cleanliness and that the extraction tubes and the extraction procedure were not introducing contamination.

Table 3-8. Average Percent Recovery for Spikes

Analyte	Avg Recovery *	StDev	Count	Min	Max
Nitrate	100.6%	1.8%	904	88.3%	108.1%
Sulfate	100.7%	1.6%	904	90.2%	106.6%
Sodium	102.3%	2.4%	823	94.2%	113.4%
Ammonium	101.3%	2.9%	823	86.9%	114.5%
Potassium	101.3%	2.5%	823	93.9%	114.7%

*Acceptance criteria for average% recovery is ±10%.

Table 3-9. Filter Blank and Reagent Blank Values (ppm) for all Analytes

Analyte	Type	n	Avg	StDev	Min	Max
Nitrate	N QC *	135	0.009	0.012	0.000	0.040
	REAG **	620	0.001	0.005	0.000	0.025
Sulfate	N QC	135	0.002	0.005	0.000	0.018
	REAG	620	0.003	0.008	0.000	0.040
Sodium	N QC	151	-0.002	0.006	-0.017	0.011
	REAG	439	-0.001	0.004	-0.034	0.015
Ammonium	N QC	151	0.000	0.000	0.000	0.000
	REAG	439	0.000	0.000	0.000	0.009
Potassium	N QC	151	0.000	0.000	0.000	0.000
	REAG	439	0.000	0.001	0.000	0.015

* N QC is a blank filter extract analyzed to test the acceptability of the cleaned nylon filter batches. One nylon filter is tested from each bottle used for filter cleaning. If the ion loading for any ion is >1 ug, the filters from that bottle are rejected.

** REAG is a 25-ml aliquot of either deionized water or anion eluent that has been pipetted into an extraction tube and carried through the same extraction procedure as the filters are.

3.2.4 Assessment of Between-instrument Comparability

Anion duplicates were analyzed on instruments D6A and S3A. Cation duplicates were analyzed on instruments D5C and D6C. A comparison of the ranges reported between the two instruments indicates very close results.

Cation duplicates were analyzed on instruments D5C and D6C. A comparison of the ranges reported between the two instruments indicates very close results.

Table 3-10 compares QA and QC samples run on separate instruments on the same day. Each day, both Anion instruments ran at least two QC and three QA samples. Similarly, Cation instruments ran at least two QC and two QA samples on each instrument each day. This table shows that the difference between the two instruments using the same QA or QC sample are very small. The calculated average difference and standard deviation indicate a high level of between-instrument comparability.

Table 3-10. Between-Instrument Comparability

Analyte	QA/QC Type	Conc., µg/mL	n	Average * Difference	Standard Deviation of Diff.	Minimum Diff.	Maximum Diff.
Nitrate	QA-CPI_LOW	0.6	235	0.000	0.004	-0.015	0.012
	QA-CPI_MED-HI	3.0	158	-0.004	0.023	-0.104	0.061
	RTI-QC-HIGH	6.0	158	-0.005	0.041	-0.232	0.128
	RTI-QC-LOW	0.6	584	0.000	0.006	-0.024	0.035
	RTI-QC-MED	1.5	928	0.000	0.012	-0.070	0.060
Sulfate	QA-CPI_LOW	1.2	235	0.003	0.012	-0.078	0.038
	QA-CPI_MED-HI	6.0	158	-0.022	0.052	-0.220	0.170
	RTI-QC-HIGH	12.0	158	-0.023	0.139	-0.514	0.883
	RTI-QC-LOW	1.2	584	0.001	0.018	-0.098	0.071
	RTI-QC-MED	3.0	928	0.000	0.029	-0.149	0.135
Sodium	GFS 0.4 PPM QA	0.4	701	0.008	0.019	-0.079	0.113
	GFS 4.0 PPM QA	4.0	573	-0.002	0.032	-0.116	0.147
	RTI 2.0 PPM QC	2.0	306	0.010	0.021	-0.065	0.159
	RTI 5.0 PPM QC	5.0	218	0.007	0.045	-0.156	0.129
Ammonium	GFS 0.4 PPM QA	0.4	701	0.009	0.014	-0.025	0.038
	GFS 4.0 PPM QA	4.0	573	0.001	0.043	-0.102	0.178
	RTI 2.0 PPM QC	2.0	306	0.022	0.021	-0.066	0.086
	RTI 5.0 PPM QC	5.0	218	0.010	0.065	-0.209	0.283
Potassium	GFS 0.4 PPM QA	0.4	701	0.003	0.007	-0.015	0.027
	GFS 4.0 PPM QA	4.0	573	0.013	0.032	-0.145	0.119
	RTI 2.0 PPM QC	2.0	306	0.005	0.016	-0.050	0.061
	RTI 5.0 PPM QC	5.0	218	0.030	0.048	-0.218	0.168

* Differences are calculated as Concentration of D6A – Concentration of S3A for Anions and Concentration of D5C – Concentration of D6C for Cations.

3.2.5 Determination of Uncertainties and MDLs

Detection limits are determined by analyzing the lowest calibration standard 7 times and the detection limit, in µg/mL (or ppm), is calculated as 3 times the standard deviation of the 7 measurements. This detection limit is multiplied by 25 mL to determine the detection limits in µg/filter, which is the extraction volume for each filter. These calculations are performed for each instrument so that the detection limits are reported by instrument. Since most samples are not analyzed in replicate, analytical uncertainties must be estimated based on historical data and scientific judgment. A simple formula of the form $U = a \cdot C + b$ is used where U is the uncertainty and C is the concentration. The coefficients a and b vary by instrument and by analyte. The b coefficient is essentially MDL/3. The value for a is assumed to be 0.05 (5%). MDLs for the STN Program are summarized in Appendix A.

3.2.6 Audits, PEs, Training, and Accreditations

No deficiencies were found in an audit of the ion analysis laboratory performed by the U.S. Environmental Protection Agency (EPA) audit team from the National Air and Radiation Environmental Laboratory (NAREL) on July 12, 2005 (Appendix E). PE samples analyzed as a part of the audit were in good agreement with the NAREL expected values. All staff in the ion analysis laboratory have been fully trained in the extraction and analysis procedures used in the PM2.5 project. No additional training was needed this year.

3.3 Organic Carbon/Elemental Carbon Laboratory

The RTI OC/EC Laboratory analyzed 19,617 quartz filter samples by the STN method during the period January 1 through December 31, 2005, and reported the results of those analyses to the main STN database. Four Sunset Laboratory Carbon Aerosol Analyzers (designated by the letters R, S, T, and F) were used for STN analyses. The F analyzer was switched to other OC/EC analysis projects on March 11, 2005; while the remaining three analyzers were used for STN throughout 2005.

3.3.1 Quality Issues and Corrective Actions

No issues that affected the quality of reported data arose during the reporting period.

3.3.2 Description of QC Checks Applied

QC checks, acceptance criteria, and responses for the OC/EC Laboratory are summarized in Table 3-11.

Table 3-12 contains a list of all data flags assigned to carbon analysis data and the number of filter analysis results assigned each flag in the OC/EC Laboratory during the reporting period. Only flags assigned in OC/EC Laboratory data reports to RTI's Speciation Program Information Management System (SPIMS) are included in the table. The SHAL or the QA Officer may have assigned additional flags to the quartz filter samples based on field data or additional data validation checks.

Table 3-11. OC/EC Laboratory QC Checks, Acceptance Criteria, and Corrective Actions

QC Element	Frequency	Acceptance Criteria	Response When Outside Criteria
Method Detection Limit	After oven replacement or annually, whichever comes first	MDL $\leq$ 0.5 µg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples.
Calibration Peak Area	Every analysis	Within 95% to 105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter.
Instrument Blank	Daily and after about 30 samples	(1) Blank $\leq$0.3 µg/cm^2, and (2) calibration peak area 90% to 110% of average for the weekly three-point calibration.	Determine if the problem is with the filter or the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem, and run an acceptable instrument blank before analyzing samples.
Three-Point Calibration	Weekly	(1) Correlation Coefficient (R^2) $\geq$0.998 [with force-fit through 0,0], (2) 93% to 107% recovery for all three standards, and (3) FID response factor is 90% to 110% of the average response factor for all three standards.	Determine the cause of the nonlinearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed.
Calibration Check	Daily	(1) 93% to 107% recovery, (2) calibration peak area 90% to 110% of average for the weekly three-point calibration, and (3) FID response factor is 90% to 110% of average response factor for last three-point calibration.	Initiate corrective action, if necessary, to solve the problem before analyzing samples.
Duplicate Analyses	10% of all samples	(1) TC Values greater than 10 µg C/cm^2-- Less than 10% RPD, (2) TC Values 5 - 10 µg C/cm^2-- Less than 15% RPD, (3) TC Values less than 5 µg C/cm^2-- Within $\pm$0.75 µg C/cm^2.	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

Table 3-12. OC/EC Laboratory-Assigned Data Flags

Flag	Description	Number of Filters
LFA	Filter inspection flag - filter wet (Punch was dried in analyzer for 20 min, then analyzed as usual.)	1
LFU	Filter inspection flag - non-uniformity (Duplicate analysis failed applicable duplicate criterion.)	37
LFW	Filter inspection flag - sampled on wrong side of filter	1
LLI	ANALYSIS INVALID - Other (Filter was broken, and none of the pieces were large enough to get a punch for a valid analysis.)	1
	Total Number of Analyses Flagged by Analysts	40
	Total Number of OC/EC Analyses Reported	19,934
	Percent of OC/EC Analyses Flagged by Analysts	0.201%

3.3.3 Summary of QC Results

3.3.3.1 Instrument Blanks

Table 3-13 contains the number of instrument blanks run during the reporting period and the average, minimum, and maximum measured blank values for each of the four carbon aerosol analyzers used in the program. For all reported data, the last instrument blank run before reported samples were analyzed met the blank criterion for TC.

Table 3-13. OC/EC Instrument Blank Statistics

Blank Statistic	OC/EC Analyzer			
	Retrofit(R)	Second (S)	Third (T)	Fourth (F)
Number of Instrument Blanks	392	416	380	74
Mean Response (µg C/cm^2)	0.018	0.031	0.024	0.029
Standard Deviation	0.017	0.028	0.025	0.028
Minimum Response (µg C/cm^2)	0.000	0.000	0.000	-0.014
Maximum Response (µg C/cm^2)	0.159	0.227	0.140	0.200

3.3.3.2 Calibrations

Table 3-14 provides summary statistics for full 3-point calibrations by analyzer. In addition to number of 3-point calibrations run, the table includes average, minimum, and maximum values for slope and linearity (expressed as correlation coefficient, R^2) for the calibrations and for the three percentages used as QC checks on analysis results for each individual calibration standard. The three percentages separately calculated for the low-, mid-, and high-level calibration standards include:

1. FID response to the internal standard (expressed as a percentage of the average FID response to the internal standard for the 3-point calibration),

2. Recovery (mass of carbon measured expressed as a percentage of the mass of carbon in the spiked volume of standard used), and

3. FID response factor (expressed as a percentage of the average FID response factor for the 3-point calibration).

Table 3-15 provides summary statistics for daily calibration checks by analyzer. The table gives the number of calibration checks run on each analyzer and the average, minimum, and maximum values of the three percentages used as QC checks to determine if a calibration check is acceptable. The three percentages used to evaluate the validity of each calibration check analysis include:

1. Internal standard area (as a percentage of the average internal standard area for the last 3-point calibration),

2. Recovery (mass of carbon measured expressed as a percentage of the mass of carbon in the spiked volume of standard used), and

3. FID response factor (as a percentage of the average response factor for the last 3-point calibration).

A calibration check is acceptable only if it meets all three criteria.

3.3.3.3 Duplicate Analyses

Table 3-16 gives summary statistics for all duplicate STN OC/EC analyses run on all analyzers during the reporting period. A duplicate analysis was run on the same analyzer on about every tenth filter. A total of 2,306 duplicate STN analyses were run under the laboratory support contract in 2005. OC/EC analysis results for 37 of those duplicates failed the applicable duplicate criterion and were flagged as coming from a filter with a non-uniform deposit.

Table 3-14. OC/EC Three-Point Calibration Statistics

Variable/Statistic			OC/EC Analyzer R	S	T	F
Number of Full Calibrations Passing All Criteria			50	52	48	10
Number of Full Calibrations Failing Any Criterion			0	0	0	0
Slope (counts/µgC), forced through origin (0,0)		Average	8,584	5,027	5,898	10,171
		Minimum	8,033	4,756	4,866	9,798
		Maximum	9,037	5,395	6,565	10,474
Correlation Coefficient (R^2) (Criterion: ≥0.998)		Average	0.9997	0.9997	0.9998	0.9995
		Minimum	0.9987	0.9989	0.9987	0.9982
		Maximum	1.0000	1.0000	1.0000	1.0000
FID Response to Internal Standard as a percent of Average Internal Standard FID Response for 3-Point Cal (Criterion: 90% to 110%)	Low Cal	Average	100.08%	100.26%	100.13%	100.19%
		Minimum	99.34%	99.07%	98.86%	98.54%
		Maximum	101.59%	102.51%	101.91%	102.06%
	Mid Cal	Average	99.92%	99.96%	99.96%	100.52%
		Minimum	99.10%	98.06%	98.20%	98.42%
		Maximum	100.37%	102.12%	101.28%	102.24%
	High Cal	Average	100.00%	99.79%	99.91%	99.29%
		Minimum	99.28%	97.43%	98.55%	96.91%
		Maximum	101.29%	101.80%	101.09%	100.49%
Recovery: Mass of Carbon Measured as a percent of Mass of Carbon Spiked (Criterion: 93% to 107%)	Low Cal	Average	101.59%	101.43%	101.18%	102.52%
		Minimum	96.40%	95.45%	96.79%	97.93%
		Maximum	104.87%	104.78%	105.00%	104.81%
	Mid Cal	Average	99.82%	99.81%	99.61%	99.12%
		Minimum	96.03%	97.01%	97.40%	97.29%
		Maximum	101.64%	102.55%	102.31%	100.84%
	High Cal	Average	98.45%	98.75%	99.19%	98.37%
		Minimum	96.40%	95.47%	96.00%	96.75%
		Maximum	101.98%	102.39%	101.79%	102.14%
	All 3 Cals	Average	99.95%	100.00%	99.99%	100.00%
		Minimum	97.74%	99.99%	99.60%	99.98%
		Maximum	100.02%	100.01%	100.02%	100.02%
FID Response Factor as a percent of Average FID Response Factor for 3-Point Cal (Criterion: 90% to 110%)	Low Cal	Average	101.72%	101.69%	101.32%	102.71%
		Minimum	96.18%	95.60%	96.90%	96.68%
		Maximum	104.74%	106.89%	106.95%	105.43%
	Mid Cal	Average	101.34%	101.25%	100.49%	102.03%
		Minimum	96.34%	97.67%	94.84%	98.09%
		Maximum	105.03%	104.75%	102.71%	105.94%
	High Cal	Average	98.49%	98.55%	99.11%	97.67%
		Minimum	96.16%	95.72%	96.30%	95.88%
		Maximum	102.12%	102.37%	102.95%	102.64%

Table 3-15. OC/EC Daily Calibration Check Statistics

Variable/Statistic		R	S	T	F
Number of Cal Checks Passing All Criteria		238	248	224	46
Number of Cal Checks Failing Any Criterion		0	0	0	0
Internal Standard (IS) Area as a percent of Average IS Area for 3-Point Cal (Criterion: 90% to 110%)	Average	99.98%	99.61%	99.75%	100.51%
	Minimum	91.89%	91.06%	91.20%	90.00%
	Maximum	105.30%	106.30%	106.74%	105.95%
Recovery: Mass of Carbon Measured as a percent of Mass of Carbon Spiked (Criterion: 95% to 105%)	Average	100.74%	100.47%	100.81%	100.77%
	Minimum	95.11%	95.26%	95.00%	95.14%
	Maximum	104.92%	104.98%	104.99%	104.90%
FID Response Factor as a percent of Average Response Factor for 3-Point Cal (Criterion: 90% to 110%)	Average	100.73%	100.07%	100.56%	101.26%
	Minimum	92.46%	91.10%	90.09%	93.63%
	Maximum	107.89%	107.30%	109.71%	108.29%

Table 3-16. Duplicate OC/EC Analysis Statistics

Variable/Statistic		Analyzer			
		R	**S**	**T**	**F**
Total Number of Duplicate Analyses		756	776	704	124
Number of Analyses Flagged as Failing Duplicate Criteria		10	13	12	2
Percentage of Duplicate Analyses Failing Duplicate Criteria		1.32%	1.68%	1.70%	1.61%
OC Sample/Dup Plot	Slope	0.993	1.003	1.000	0.965
	Intercept	0.036	0.002	0.023	0.074
	R^2	0.997	0.997	0.997	0.996
EC Sample/Dup Plot	Slope	1.019	0.998	0.995	0.992
	Intercept	-0.007	0.006	0.005	0.006
	R^2	0.993	0.992	0.993	0.995
TC Sample/Dup Plot	Slope	0.997	1.005	0.998	0.971
	Intercept	0.027	-0.001	0.031	0.075
	R^2	0.998	0.997	0.998	0.997
Pk1C Sample/Dup Plot	Slope	0.993	0.973	0.993	0.954
	Intercept	0.009	0.024	0.007	0.035
	R^2	0.997	0.993	0.996	0.996
Pk2C Sample/Dup Plot	Slope	0.998	0.992	0.992	0.962
	Intercept	0.006	0.012	0.017	0.025
	R^2	0.990	0.987	0.989	0.984
Pk3C Sample/Dup Plot	Slope	1.006	0.985	0.992	0.940
	Intercept	0.003	0.010	0.012	0.024
	R^2	0.991	0.989	0.992	0.976
Pk4C Sample/Dup Plot	Slope	1.009	0.993	1.000	0.966
	Intercept	-0.002	0.005	0.008	0.010
	R^2	0.995	0.993	0.993	0.989
PyrolC Sample/Dup Plot	Slope	0.921	1.068	0.931	1.061
	Intercept	-0.001	0.001	0.000	-0.001
	R^2	0.948	0.953	0.961	0.987

3.3.4 Assessment of Between-Instrument Comparability

While duplicate analysis results (two punches from the same filter run on the same analyzer) agree fairly well, replicate analysis results (two or more punches from the same filter run on different analyzers) for the OC Peaks do not always agree as well, especially for Pk3 C, Pk4 C and Pyrol C. The level of oxygen contamination present in the analyzer ovens during the non-oxidizing heat ramps seems to be the primary cause of the differences in OC Peak measurements between analyzers.[1] Whether the oxygen comes from diffusion through seals inside the analyzer or from some type of carry-over from the preceding analysis is not known.

Trace amounts of contaminating oxygen cause some of the carbon in thermally unstable organic species to be evolved rather than forming char during the non-oxidizing heating ramps. This early evolution of organic carbon reduces the amount of organic char formed and shifts the OC/EC split time to an earlier time in the analysis. However, the presence of oxygen does not significantly change the OC:EC mass ratio. The bad news is that the presence of oxygen shifts the evolution of OC from the later OC Peaks (especially Pyrol C) to the earlier OC Peaks.

To assess between-analyzer comparability of OC, EC, TC, and the individual OC Peaks, RTI's OC/EC Laboratory analyzed 127 filters by the STN/TOT method on three Sunset Laboratory Carbon Aerosol Analyzers over a two-year period. The results of those analyses were used to estimate uncertainties (presented below) that take into account samples collected during all seasons of the year and analyzed on different analyzers during all of the stages of oxygen contamination as analyzer ovens age and are replaced.[2] An F-Test analysis of the peak data indicated that the three analyzers did not give equivalent results for all analytes, but the agreement was within the same general uncertainty as the long-standing Sunset Lab-determined uncertainties for OC, EC, and TC.

RTI is continuing to run replicate analyses across all OC/EC analyzers used for the program and continuing to run duplicate analyses on the same analyzer for about 10% of samples. Replicate analysis data will be used to refine uncertainty estimates, and duplicate analysis data will continue to alert sampling personnel and data users of possible filter deposit non-uniformity issues.

3.3.5 Determination of Uncertainties and MDLs

Table 3-17 gives estimated uncertainties for OC, EC, TC, and OC Peaks measured on multiple analyzers in RTI's OC/EC Laboratory. STN/TOT OC/EC analysis results for 127 filters analyzed on three Sunset Laboratory Carbon Aerosol Analyzers over a two-year period were used to determine the estimated absolute and relative uncertainties for all reported carbon fractions.

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[1]The helium supply line for each RTI OC/EC analyzer is fitted with two oxygen traps: a high-capacity trap followed by an indicating trap. Only ultra-high purity (UHP) helium is used for OC/EC analysis. All OC/EC analyzers, regardless of manufacturer or model, have this problem.

[2]Because of the large number of samples analyzed, each STN analyzer in RTI's OC/EC Laboratory requires two to four oven replacements each year.

Table 3-17. Estimated Uncertainties for OC/EC Carbon Fractions

Fraction	"Best Fit" Uncertainty (µgC/cm²)
OC	±(0.20 + 0.05*OC)
EC	±(0.20 + 0.05*EC)
TC	±(0.30 + 0.05*TC)
Pk1 C	±(0.20 + 0.05*Pk1 C)
Pk2 C	±(0.20 + 0.05*Pk2 C)
Pk3 C	±(0.30 + 0.05*Pk3 C)
Pk4 C	±(0.30 + 0.10*Pk4 C)
Pyrol C	±(0.20 + 1.40*Pyrol C)

The estimate for each carbon fraction was obtained by determining the standard deviation(s) of the three measurements from different analyzers for each of the 127 filters in the study. A plot of average measured loading with 1-sigma error bars for each filter (y-axis) vs. averaged measured loading (x-axis) was generated for each carbon fraction. Straight trend lines of the form y = ±(b + mx), where b is absolute uncertainty, m is relative uncertainty, and x is measured loading, were then generated for points above and below the ends of the 1s error bars with values for b and m that gave trend lines that bracketed the 1s error bars for all filters except a few (1 to 3) that appeared to be outliers.[3]

From the table, it is obvious that Pyrol C has by far the largest relative uncertainty. Pyrol C is a measure of the pyrolyzed organic carbon remaining on the filter punch after oxygen is added at the end of the four non-oxidizing heating ramps. If the sample contains little pyrolyzable organic carbon, the trace amounts of contaminating oxygen may prevent the formation of any Pyrol C. If the sample contains sufficient pyrolyzable OC to exceed the reaction capacity of the trace amounts of contaminating oxygen, then at least some Pyrol C will be measured. Because the trace amounts of contaminating oxygen differ slightly between analyzers, the distribution of OC among the OC Peaks differs more between analyzers than it does within duplicates run on the same analyzer. Because PyrolC is formed primarily during the evolution of Pk3 C and Pk4 C, these last-evolved OC Peaks typically have the largest between-analyzer variability and, therefore, larger measurement uncertainties.

[3]Peterson, M.R., and M.H. Richards. 2006. *Estimation of Uncertainties for Organic Carbon Peaks Data in Thermal-Optical-Transmittance Analysis of PM2.5 by the Speciation Trends Network Method.* To be presented at the A&WMA Symposium on Air Quality Measurement Methods and Technology, May 9-11, 2006, Durham, NC.

Table 3-18 gives target MDLs for all reported carbon fractions. MDL values for the five OC Peaks (Pk1-Pk4 and Pyrol C) were taken from the absolute uncertainties in Table 3-18. This same approach was used to determine reasonable target MDLs for OC, EC, and TC, all of which have proven to be attainable when an analyzer is functioning properly and all operating conditions are under control.

Table 3-18. Target MDLs for OC/EC Carbon Fractions

Fraction	Target MDL ($\mu gC/cm^2$)
OC	0.20
EC	0.20
TC	0.30
Pk1 C	0.20
Pk2 C	0.20
Pk3 C	0.30
Pk4 C	0.30
Pyrol C	0.20

3.3.6 Audits, PEs, Training, and Accreditations

3.3.6.1 Audits

Finding: RTI's OC/EC Laboratory was audited by EPA/NAREL's Jewell Smiley on July 17, 2005. The Technical Memorandum describing the audit and findings contained the following quote at the end of OC/EC Laboratory write-up:

> The general impressions of the OC/EC laboratory developed during this audit were very positive. Only one concern was noted. Some of the routine duplicate determinations should be scheduled to collect between-instrument precision data.[4]

Response: RTI's OC/EC Laboratory has conducted evaluations of both within- and between-analyzer variability since it added a second OC/EC analyzer in the first year of the STN laboratory support program. In September 2005, RTI began analyzing replicate punches from randomly chosen filters on all STN/TOT analyzers on a regular basis.

[4]Smiley, Jewell, et al. 2005. Technical Memorandum--RTI Laboratory Audit on July 12, 2005. Memorandum dated November 5, 2005. Available on-line at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/rti0705.pdf.

Under the first Chemical Speciation of PM2.5 Laboratory Support contract, only OC, EC, and TC were reported, and Sunset Laboratory Inc. had already determined between-analyzer uncertainties for those three fractions. The validity of Sunset Laboratory's uncertainties for OC, EC, and TC have been confirmed in all RTI replicate analysis studies, including the current large study reported in Section 3.3.5. Sufficient data has now been collected to allow estimation of uncertainties for OC Peaks measurements that include between-analyzer uncertainty, which is substantially larger than within-analyzer uncertainty for the reasons cited in Section 3.3.5 above.

Discussion: Two punches from the same filter analyzed on the same analyzer (which we refer to as a duplicate analysis) can be used to evaluate the uniformity of the filter deposit. Frequent non-uniformity flags can alert field sampling personnel and data users to potential problems with a specific sampler. Two or more punches from the same filter analyzed on different analyzers (which we refer to as replicate analyses) can be used to evaluate between-analyzer variability. This data can be used to estimate uncertainties for measured carbon fractions across analyzers. In other words, duplicates and replicates serve two different purposes, both of which are very important.

To best meet the two purposes described in the preceding paragraph, RTI's OC/EC Laboratory has added regular analysis of replicates (same filter, different analyzers) to its list of QC samples without decreasing the number of duplicate analyses (same filter, same analyzer) already being performed.

Until 2004, replicate studies had consisted of periodic analysis of replicates of small numbers of filters (usually about 20) on all available analyzers over a period of a few days. These studies provided snapshots of how well analysis results agreed or disagreed across analyzers at a given time, but they were not thought to be adequate to provide estimates of uncertainties, especially for the OC Peaks, over the life of the speciation program because of changes in the distribution of OC among the OC Peaks that occur as analyzer ovens age. In 2004, 47 filters were analyzed on all RTI STN/TOT analyzers over a 1-month period. Results of that study were presented at a conference in April 2004.[5]

Currently, RTI is running replicate analyses of about four to eight filters per week on all STN analyzers used in the program. Replicate analysis data for 127 filters analyzed in 2004 and 2005 have already been evaluated to determine reasonable uncertainties and MDLs for the OC Peaks and to confirm that the uncertainties and MDLs used since the beginning of the program for OC, EC, and TC are still acceptable. Estimated uncertainties and MDLs based on the combined data are presented in the tables in Section 3.3.5 above. Future replicate analysis data will be added to this large data set to determine if uncertainties and MDLs change significantly over time.

[5]Peterson, M.R., M.H. Richards, J.L. Pritt, and C.M. Haas. 2004. *Reproducibility of Organic Carbon Peaks Data in Thermal-Optical-Transmittance Analysis of PM2.5 by the Speciation Trends Network Method*. Presented at the A&WMA Symposium on Air Quality Measurement Methods and Technology, Research Triangle Park, NC, April 2004.

3.3.6.2 Performance Evaluations

RTI's OC/EC Laboratory was one of four laboratories participating in the February 2005 EPA/NAREL interlaboratory comparison study. RTI's STN/TOT data, including the OC Peaks data, compared very favorably with EPA/NAREL's STN/TOT data, as shown in Appendix D.

3.3.6.3 Training

One new analyst was hired and trained during the reporting period. He has a BS in chemistry-biochemistry from a local university and came to RTI with previous chromatography and other laboratory experience. He went through intensive training in the operation of RTI's OC/EC analyzers and easily passed the analyst validation test given at the end of the training. He has been the second-shift analyst since July 2005.

3.3.6.4 Accreditations

There are no accreditation programs for OC/EC analysis.

3.4 X-ray Fluorescence Laboratories

The two X-ray fluorescence (XRF) laboratories, RTI and Chester LabNet, used two XRF instruments each to analyze a total of 19,317 filters for 48 elements during the period January 1 through December 31, 2005.

3.4.1 Chester LabNet X-Ray Fluorescence Laboratory

Chester LabNet was the original XRF contractor laboratory used for the STN program. During the period covered by this report, Chester operated two Kevex XRF instruments designated 770 and 771.

3.4.1.1 Quality Issues and Instrument Repair and Maintenance

The following repairs and maintenance were performed for XRF-770:

- 1/29/05 - replaced X-ray tube and power supply and recalibrated
- 2/8/05 - realigned X-ray tube and recalibrated
- 3/23/05 - recalibrated due to increase in excitation energy in condition 0
- 6/29/05 - replaced X-ray tube and recalibrated
- 7/19/05 - recalibrated due to decrease in excitation energy in condition 0

The following repairs and maintenance were performed for XRF-771:

- 9/12/05 - recalibrated due to decrease in excitation energy in condition 1
- 10/21/05 - replaced X-ray tube and recalibrated

3.4.1.2 Description of QC Checks Applied

QC activities for the analysis of elements by EDXRF for the RTI XRF laboratory, their frequency of application and control limits, comments and corrective actions are shown in Table 3-19.

Table 3-19. QC Procedures Performed in Support of XRF Elemental Analysis

QC Check	QC Frequency	Control Limits	Comments/Corrective Action
Calibration	As needed	± 5%	Calibration
Calibration verification[1]	Once per week	± 2 sigma	Recalibrate
Instrument precision[2]	Per 10 to 15 samples	± 10%	Re-analyze
Excitation condition check	Per 10 to 15 samples	± 10%	Re-analyze
Sample replicate precision	Per 10 samples	RPD < 2x uncertainty	Re-analyze if necessary

1 - Using NIST SRMs
2 – Micromatter QC

3.4.1.3 Summary of QC Results

Precision

Precision was monitored by the reproducibility of the multi-element Micromatter QC sample. The QC sample has six selected elements and is analyzed with each tray of samples. The comparison of the element's values gives the measure of reproducibility or precision. The data used to monitor precision are presented in Tables 3-20A and 3-20B, for the 770 and 771 instruments, respectively. The percent coefficient of variation (%CV) for the average of all data for each of the six elements ranged between 1.82 and 4.64% for the 770 and between 2.04 and 3.05% for the 771. The Ti and Cd outliers shown for minimum values in the XRF 771 table were experienced prior to the analysis of samples. The QS standard results post-analysis were well within acceptance range, as were the "averaged" values between pre and post analytical values.

Table 3-20A. Summary of Chester XRF 770 Laboratory QC Precision Data 1/1/2005 through 10/4/2005

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	240	91.1	110.6	101.9	3.03	2.97	0.77
Ti	240	93.9	103.5	99.2	1.86	1.88	-0.37
Fe	240	94.5	103.5	99.3	1.81	1.82	0.18
Cd	240	91.0	107.3	100.0	3.79	3.80	-6.6
Se	240	90.3	107.8	98.7	4.58	4.64	-9.49
Pb	240	90.4	106.9	99.2	4.37	4.40	-8.2

Table 3-20B. Summary of Chester XRF 771 Laboratory QC Precision Data 1/1/2005 through 10/4/2005

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	434	91.2	105.9	97.1	2.38	2.45	-0.80
Ti	434	85.6	106.0	96.1	2.79	2.90	2.56
Fe	434	90.4	103.2	96.8	1.97	2.04	0.55
Cd	434	89.8	107.7	98.0	3.11	3.05	-0.29
Se	434	91.0	108.2	99.2	2.82	2.84	1.42
Pb	434	91.4	108.5	99.3	2.54	2.56	1.10

Accuracy

Accuracy determinations are performed with three NIST thin film SRMs, four vapor deposited Micromatter standards, and one NIST particle size standard. Recovery is calculated by dividing the measured result by the expected value. Tables 3-21A and 3-21B show recovery for 12 elements spanning the atomic mass range of the 48 elements normally measured. The min and max recovery values for all the elements ranged between 90.2 and 110.3% for the 770 and between 88.0 and 112.6% for the 771. Averages over the reporting period were within the recovery goal of twice the standard deviation for both instruments; however individual measurements were sometimes outside this criterion. Corrective actions were taken whenever a recovery was outside specifications as follows:

- If one of the elements in Tables 3-21A and 3-21B fell outside of the 2-sigma limit, a single re-analysis of the standard was performed in that excitation condition. If re-analysis resulted in failure, then recalibration of that excitation condition was necessary.

- If recalibration demonstrated that the log of the inverse of the new calibration factor (log sensitivity) –vs- atomic number (Z) for the “failed element” did not conform to a smoothly varying curve defined by the log of the sensitivity factors –vs- atomic numbers for the remaining elements, then the calibration factor was “forced” to fit the curve, with the resulting calibration factor yielding “less than optimum” recovery values.

Table 3-21A. Recovery Determined from Analysis of NIST SRMs 1832, 1833, and 2708 for Chester XRF 770 -- 1/1/2005 through 12/31/2005

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	90.2	106.1	98.6	4.25	4.31	3.57
Si	96.8	108.1	103.3	3.07	2.97	1.13
Si	93.3	104.5	99.9	2.70	2.71	3.14
S	92.2	103.4	97.2	3.13	3.22	1.17
K	94.0	106.7	100.4	2.85	2.84	3.29
Ca	95.1	106.8	100.2	2.82	2.82	2.30
Ti	94.6	110.3	100.8	3.80	3.77	1.68
V	93.6	103.6	98.7	2.38	2.41	1.86
Mn	91.9	110.4	100.2	4.81	4.80	-7.45
Fe	96.5	105.6	101.0	2.55	2.53	-1.64
Cu	93.7	109.3	102.3	3.90	3.81	0.99
Zn	94.1	106.0	100.1	3.21	3.20	0.99
Pb	100.0	108.0	103.8	1.65	1.59	-0.91

Table 3-21B. Recovery Determined from Analysis of NIST SRMs 1832, 1833 and 2708 for Chester XRF 771 -- 1/1/2005 through 12/31/2005

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	88.0	101.8	97.2	3.90	4.01	7.67
Si	93.5	104.0	99.2	2.73	2.76	6.17
Si	91.6	101.6	95.4	2.51	2.65	8.10
S	93.9	106.1	99.2	2.70	2.73	-1.90
K	89.2	109.0	100.8	4.61	4.57	2.11
Ca	95.4	112.6	106.2	5.14	4.84	12.1
Ti	88.8	102.5	96.1	3.77	3.92	9.67
V	94.1	106.9	101.2	3.48	3.44	4.38
Mn	95.6	105.7	101.2	2.26	2.24	-1.86
Fe	92.9	102.2	98.6	2.58	2.62	3.61
Cu	93.9	105.8	99.4	2.36	2.37	0.29
Zn	97.5	107.2	101.7	2.42	2.38	0.88
Pb	93.6	107.0	100.8	2.81	2.79	4.34

Reproducibility

Replicate analysis of field samples are used to assess reproducibility of the analytical system. Replicates were analyzed at a frequency of 5% of the filters analyzed. Six elements were selected for comparison through regression analysis. Table 3-22 shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients for the 770 range from 0.9987 to 0.9997, and the correlation coefficients for the 771 range from 0.9992 to 0.9999, indicating acceptable replication on both instruments.

Table 3-22. Replicate Data for Chester XRF 770 and 771

Kevex 770				Kevex 771			
Element	**n**	**Correlation Coefficient**	**Average RPD**	**Element**	**n**	**Correlation Coefficient**	**Average RPD**
Si	173	.9990	1.44	Si	141	.9953	-3.41
S	173	.9992	0.08	S	141	.9987	-3.15
K	173	.9987	-0.14	K	141	.9948	-3.34
Ca	173	.9996	-0.14	Ca	141	.9991	-2.71
Fe	173	.9997	-0.05	Fe	141	.9990	-0.51
Zn	173	.9996	-0.42	Zn	141	.9982	-0.91

There are times when the distribution of a certain species across the filter is not uniform, and will not produce tight precision. This is important information for those who intend to use the data. It is Chester's position that re-analysis of particle deposits on filters received from the field represents the degree of confidence the client may expect more accurately than precision calculated from the uniformly distributed deposits from the Micromatter QC standard.

Failure of individual replicate analysis results to fall with 2x uncertainty can fall into several categories:

- The wrong sample can be re-analyzed, which is easily deduced and easily corrected by re-analyzing the correct sample.

- If one element in a sample lies outside the 2-sigma range, especially a volatile species such as Cl which can be an order of magnitude lower on subsequent analysis due to the low pressure atmosphere in the analysis chamber, no action is taken. However, if several elements in one excitation condition lie outside action levels, while other species in different excitation conditions demonstrate good precision, then the spectra for the excitation condition in question are examined for anomalies, and re-analysis of that excitation condition is performed.

3.4.1.4 Assessment of Between-instrument Comparability

For XRF, inter-instrument comparability is assessed by a round-robin filter exchange program coordinated by the RTI XRF laboratory. See Section 3.4.2.4 for comparative performance of both laboratories.

In addition, Chester has 125 samples which were analyzed by both XRF 770 and XRF 772, which will be used to gain EPA approval for use of the 772 on the STN program. Since the inception of the PM2.5 Speciation project, Chester has performed numerous comparisons between instruments via replicate analysis of a number of clients, but much of this data is proprietary and cannot be shared in this report.

3.4.1.5 Uncertainties and MDLs

The methods for determining uncertainties and MDLs are described in SOPs XR-002.02 and XR-006.01. MDLs were determined for the 770 and 771 instruments on 12/26/05, and are shown in Table 3-23. MDLs used during 2005 across analyzers are shown in Appendix A.

3.4.1.6 Audits, PEs, Training, and Accreditations

Chester LabNet has not received any audit visits from EPA on the STN program since the beginning of the speciation project, and would welcome any PE samples or other oversight, which the EPA might deem appropriate. No new laboratory personnel were trained during 2005, but plans for 2006 include the training of two additional analysts.

Another Chester client provides quarterly PE samples in the form of Micromatter vapor deposited standards for elements: Cr, Cu, Zn, Ga, As, Se, Cd, Te, and Pb. However, these PE samples were analyzed using instrument XRF 772, which is not currently approved for use on the STN program. These results will be provided to EPA in the revised instrument acceptance report, to be provided during the first quarter of 2006.

3.4.2 RTI International XRF Laboratory

3.4.2.1 Quality Issues and Instrument Maintenance and Repairs

No changes were made in the analytical procedures used by the RTI XRF Laboratory. However, during 2005 XRF 1 was serviced requiring a new tube and detector, which required instrument re-calibration. XRF 2 was serviced requiring a new tube, which required instrument calibration verification. Also, in October 2005 the Micromatter QC for XRF 1 was replaced with a new Micromatter QC sample. The new sample includes the same elements as the old QC sample.

3.4.2.2 Description of QC Checks Applied

QC activities for the analysis of elements by EDXRF for the RTI XRF Laboratory, their frequency of application and control limits, comments and corrective actions are shown in Table 3-24.

Table 3-23. Three-sigma MDLs[a] for Chester 770 and 771 Instruments

	770	771
Na	0.381	2.124
Mg	0.174	0.624
Al	0.099	0.240
Si	0.081	0.126
P	0.054	0.090
S	0.039	0.072
Cl	0.108	0.147
K	0.039	0.069
Ca	0.045	0.048
Sc	0.030	0.033
Ti	0.036	0.030
V	0.018	0.021
Cr	0.018	0.021
Mn	0.027	0.024
Fe	0.033	0.021
Co	0.018	0.015
Ni	0.018	0.015
Cu	0.018	0.018
Zn	0.018	0.015
Ga	0.045	0.051
Ge	0.030	0.030
As	0.027	0.027
Se	0.024	0.024
Br	0.021	0.021
Rb	0.024	0.021
Sr	0.030	0.027
Y	0.036	0.033

	770	771
Zr	0.045	0.039
Nb	0.054	0.051
Mo	0.063	0.066
Rh	0.123	0.084
Pd	0.126	0.081
Ag	0.129	0.090
Cd	0.129	0.099
In	0.141	0.111
Sn	0.159	0.129
Sb	0.180	0.153
Te	0.204	0.189
I	0.261	0.243
Cs	0.443	0.400
Ba	0.573	0.531
La	0.677	0.705
Ce	0.838	0.970
Sm	0.096	0.063
Eu	0.108	0.060
Tb	0.096	0.063
Hf	0.081	0.111
Ta	0.078	0.180
W	0.078	0.120
Ir	0.075	0.075
Au	0.078	0.069
Hg	0.072	0.045
Pb	0.060	0.060

Notes:
a - MDLs were converted to a 3-sigma basis from the 1-sigma MDLs reported by Chester.

Table 3-24. QC Procedures Performed in RTI XRF Elemental Analysis Laboratory

QC Check	QC Frequency	Control Limits	Comments/Corrective Action
Calibration	as needed	-----	-----
Calibration verification[1]	weekly	90-110% recovery	check calibration
Instrument precision[2]	analyzed with each tray of samples (10 tray autosampler)	within 5% CV	check calibration and reanalysis of tray
Energy calibration	daily	-----	-----
Sample replicate precision	5%	+/- 50 RPD	reanalysis

1 - Using NIST SRMs
2 – Micromatter QC

3.4.2.3 Summary of QC Results

Precision was monitored by the reproducibility of the measurements of the multi-element Micromatter QC sample. The QC sample has six selected elements and is analyzed with each tray of samples. The comparison of the element's values gives the measure of reproducibility or precision. The data used to monitor precision are presented in 3-25A through 3-25C. The percent coefficient of variation (%CV) for the average of all data for each of the six elements ranged between 0.22 and 4.51% for XRF 1 and between 0.22 and 3.24% for XRF 2. Note that XRF 1 Micromatter QC was replaced with a new Micromatter QC in October 2005 and the slope percent per year calculation is calculated by the days each Micromatter QC was in use on XRF 1.

Table 3-25A. Summary of RTI XRF 1 Laboratory QC Precision Data, ug/cm^2 1/1/2005 through 10/4/2005

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	777	9.00	9.76	9.26	0.04	0.42	0.3
Ti	777	8.14	8.27	8.22	0.02	0.22	0.2
Fe	777	10.1	10.3	10.2	0.04	0.37	-0.3
Cd	777	5.66	5.81	5.74	0.03	0.44	-0.1
Se	777	4.00	4.11	4.06	0.02	0.59	-1.3
Pb	777	11.2	11.6	11.4	0.06	0.53	-0.8

Table 3-25B. Summary of RTI XRF 1 Laboratory QC Precision Data, ug/cm^2 10/5/2005 through 12/31/2005

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	135	4.40	4.54	4.47	0.04	0.84	0.8
Ti	135	5.70	6.30	6.06	0.27	4.51	-4.8
Fe	135	6.50	6.74	6.64	0.09	1.43	-1.5
Cd	135	5.41	5.68	5.52	0.09	1.58	1.6
Se	135	3.99	4.06	4.02	0.02	0.39	0.0
Pb	135	9.70	10.1	9.84	0.15	1.57	1.7

Table 3-25C. Summary of RTI XRF 2 Laboratory QC Precision Data, ug/cm^2 1/1/2005 through 12/31/2005

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	1203	5.19	5.39	5.30	0.06	1.10	-0.2
Ti	1203	6.70	7.30	7.06	0.23	3.24	-0.6
Fe	1203	6.95	7.09	7.03	0.02	0.25	0.0
Cd	1203	5.94	6.11	6.03	0.03	0.41	0.0
Se	1203	4.19	4.39	4.25	0.02	0.56	-0.1
Pb	1203	8.98	9.13	9.03	0.02	0.22	0.0

n = number of observations
Min = minimum value observed
Max = maximum value observed
Std Dev = standard deviation
%CV = percent coefficient variation ((Std Dev/Average)*100)

Recovery or system accuracy was determined by the analysis of a series of NIST Standard Reference Materials (SRM) filters. Recovery is calculated by comparisons of measured and expected values. Tables 3-26A and 3-26B show recovery for 12 elements spanning the atomic mass range of the 48 elements normally measured. The recovery values for all the elements ranged between 90 and 108% for XRF 1 and between 91 and 110% for XRF 2. Note that in August 2004, NIST SRM 1833 developed a tear in the filter and was replaced with NIST SRM 2783. Even though SRM 2783 has additional analytes that were not included in SRM 1833, in being consistent with reporting, only the analytes included in SRM 1833 were reported.

Table 3-26A. Recovery Determined from Analysis of NIST SRMs 1832 and 2783 for RTI XRF 1 -- 1/1/2005 through 12/31/2005

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	90.8	94.3	92.7	0.90	0.97	-0.4
Si*	89.6	90.7	90.1	0.25	0.33	-0.3
Si**	93.6	100.0	96.8	2.37	2.44	-6.8 (-1.8 and 0.3)[a]
Co	97.7	99.5	98.1	0.45	0.46	0.4
K	94.1	100.5	97.7	1.79	1.83	-4.9
Ca	96.7	97.3	97.0	0.15	0.15	-0.2
Ti	96.0	104.5	101.3	2.20	2.18	-4.9
V	103.4	104.5	103.9	0.27	0.26	0.1
Mn	97.4	98.5	97.8	0.23	0.23	-0.2
Fe	95.0	99.3	97.0	1.64	1.69	-4.7
Cu	96.5	97.5	97.1	0.25	0.26	0.2
Zn	100.9	108.5	103.9	1.92	1.85	-0.3
Pb	89.6	108.8	97.8	4.36	4.43	-2.8

* - SRM 1832
** - SRM 2783
a – Even though the recoveries were within the control limits of 90-110%, the two values represent the slope before a slight shift in the recoveries and after the shift, which took place in 2005. The shift in recovery is evident on both XRF systems, which could indicate a possible degradation of silicon in the SRM sample.

Table 3-26B. Recovery Determined from Analysis of NIST SRMs 1832 and 2783 for RTI XRF 2 -- 1/1/2005 through 12/31/2005

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	94.6	96.5	95.4	0.39	0.41	0.2
Si*	90.5	91.7	91.0	0.23	0.25	0.3
Si**	92.9	98.7	95.1	2.23	2.35	-6.4 (-1.5 and 2.5)[a]
Co	98.1	101.3	100.0	0.61	0.61	0.4
K	91.3	97.0	94.1	1.49	1.58	0.8
Ca	97.9	99.5	99.0	0.45	0.46	1.1
Ti	92.6	106.0	99.3	2.62	2.63	-3.2
V	99.8	102.5	101.0	0.62	0.61	1.5
Mn	100.4	101.5	100.9	0.32	0.32	0.6
Fe	94.3	98.1	96.6	0.98	1.02	-1.7
Cu	96.7	98.2	97.6	0.34	0.34	0.6
Zn	97.8	105.8	102.2	1.95	1.91	3.9
Pb	95.9	110.1	100.9	3.17	3.13	-2.5

* - SRM 1832
** - SRM 2783
a – Even though the recoveries were within the control limits of 90-110%, the two values represent the slope before a slight shift in the recoveries and after the shift, which took place in 2005. The shift in recovery is evident on both XRF systems, which could indicate a possible degradation of silicon in the SRM sample.

Replicates were analyzed at a frequency of 5% of the filters analyzed in the RTI XRF Laboratory. Six elements were selected for comparison through regression analysis. Table 3-27 shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients for XRF 1 range from 0.9984 to 0.9999, and the correlation coefficients for XRF 2 range from 0.9992 to 0.9999, indicating acceptable replication on both instruments. Also, for the six elements the average RPD on XRF 1 was less than seven and the average RPD for the six elements on XRF 2 was less than four.

Table 3-27. Replicates

XRF 1				XRF 2			
Element	n	Correlation Coefficient	Average RPD	Element	n	Correlation Coefficient	Average RPD
Si	432	0.9984	6.49	Si	532	0.9999	2.90
S	432	0.9999	1.08	S	532	0.9999	1.27
K	432	0.9996	2.62	K	532	0.9992	2.56
Ca	432	0.9998	2.66	Ca	532	0.9998	3.32
Fe	432	0.9999	1.15	Fe	532	0.9998	1.92
Zn	432	0.9994	3.79	Zn	532	0.9993	3.73

3.4.2.4 Assessment of Between-Instrument Comparability

Overview of Round-Robin Samples Run During 2005

In addition to passing internal QC samples as described in the sections above, the RTI and Chester Laboratories participate in a "round-robin" filter program coordinated by the RTI XRF Laboratory. It should be emphasized that the round-robin program is only used to collect descriptive statistics about network performance; the results are not currently being used for QC purposes. The lag time between successive analyses and the potential for filter contamination and damage in transit make it impractical to use these filters for laboratory QC.

In the round-robin program, previously analyzed STN filters are recycled through all the instruments in the two laboratories. Table 3-28 summarizes the number of round robin filters analyzed during 2005.

Table 3-28. Counts of Round Robin Filter Analyses During 2005

Laboratory	Instrument	Filters
Chester Labnet	Kevex 770	32
Chester Labnet	Kevex 771	38
RTI	XRF 1	57
RTI	XRF 2	43
Total filters common to all instruments:		11

The majority of elements reported by XRF are present in quantities at or below the detection capabilities of the instruments; therefore, it was necessary to restrict the statistical analysis of the round robin results to 15 elements that were found in sufficient quantity on a majority of the filters. A total of 11 round robin filters were analyzed by all the STN instruments during 2005. Many additional filters were analyzed by one or more of the instruments, but only 11 had been analyzed by all four instruments exclusively during 2005. The statistics to follow in this section are restricted to filters that were analyzed by all four instruments during 2005.

Assessment of Bias and Precision

The primary purpose of the round robin program is to assess bias between instruments for the various elements. Inter-laboratory precision, a component of overall network error, can also be estimated based on these statistics.

One simple way to assess potential differences in performance of the different instruments is to perform linear regression in which the individual observations for each instrument are regressed against a reference value. Tables 3-29A and 3-29B show linear regression results when the data for the 11 filters are regressed vs. the median for the four instruments for each filter. The median value is used as the reference value, since the "true" value is unknown for these filters. Each instrument in the program reported zeros or low level detections in some of the elements (especially Ni, Cu, and Se), which can affect the calculation for slope or the correlation coefficient. The calculated uncertainty of these results for each instrument was not taken in account in doing the regression (i.e., no weighting factors were used).

Table 3-29A. Regression Results for 15 Elements - RTI XRF Instruments

Element	RTI #1				RTI #2			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	11	0.9985	0.9916	-0.158	11	0.9976	0.8703	0.004
S	11	0.9943	1.0067	0.128	11	0.9992	1.0166	0.037
K	11	0.9984	1.0145	-0.019	11	0.9982	1.0070	-0.038
Ca	11	0.9958	1.0940	-0.069	11	0.9996	1.0410	-0.020
Mn	11	0.9988	1.0245	0.003	11	0.9968	0.9675	-0.004
Fe	11	0.9996	1.1140	-0.004	11	0.9997	1.0310	-0.014
Ni	11	0.9927	1.1333	-0.000	11	0.9753	0.7671	-0.000
Cu	11	0.9136	1.1280	-0.017	11	0.9958	1.0750	0.001
Zn	11	0.9900	1.1030	0.007	11	0.9990	0.9902	0.003
Se	11	0.9914	0.7542	-0.003	11	0.9905	1.3210	-0.004
Pb	11	0.9970	1.1820	-0.008	11	0.9980	1.0340	-0.008

Note: Units for intercept are µg/filter; correlation coefficient and slope are dimensionless.

Table 3-29B. Regression Results for 15 Elements - Chester XRF Instruments

Element	Chester 770				Chester 771			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	11	0.9990	1.0500	0.047	11	0.9988	0.9940	0.217
S	11	0.9998	0.9905	0.003	11	0.9930	0.9474	0.031
K	11	0.9981	1.0765	-0.015	11	0.9972	0.9797	0.011
Ca	11	0.9974	0.9183	0.024	11	0.9998	0.9540	0.032
Mn	11	0.9995	1.1020	-0.013	11	0.9993	0.9639	0.010
Fe	11	0.9996	0.9671	0.004	11	0.9985	0.9900	-0.031
Ni	11	0.9767	0.9656	-0.001	11	0.9745	0.9727	0.006
Cu	11	0.9907	0.9831	0.005	11	0.9902	0.9924	-0.004
Zn	11	0.9952	1.0260	-0.011	11	0.9971	0.9724	-0.006
Se	11	0.9725	1.0107	0.002	11	0.9142	0.8440	0.012
Pb	11	0.9981	0.9814	-0.010	11	0.9976	0.9316	0.018

Note: Units for intercept are µg/filter; correlation coefficient and slope are dimensionless.

Comparison of Reported Uncertainties for Round-Robin Filters

The harmonization of uncertainty calculations for PM-fine networks in the U.S., including STN and IMPROVE, is currently a matter of discussion between RTI, EPA, and other experts in XRF analysis. RTI staff have prepared a number of reports and presentations on the subject over the past several years. The 2005 round robin data show that the uncertainty values reported by Chester's and RTI's instruments differ as expected based on our research into the different uncertainty calculation methodologies used by the respective instruments.

Our assessment of the algorithms used to calculate uncertainty has uncovered the following significant areas of difference affecting the comparability of Chester vs. RTI uncertainty values:

- Chester's software appears to overestimate the attenuation uncertainty for light elements (Na - Ca). This overestimate can be up to 12% of the total concentration. In the case of sulfur, this is an overestimate of a factor of 3x or 4x.

- RTI's ThermoNoran instrument does not include an attenuation correction at all. This will result in an underestimate of the uncertainty for the same group of light elements.

- RTI's ThermoNoran instrument does not include an estimated laboratory calibration error term. Chester's software includes a factor of 5% of concentration for this term.

Table 3-30 illustrates these characteristics for the 15 elements reported here. Note that these are laboratory uncertainties reported by the instruments. RTI adds an additional 5% of concentration to account for field handling and sample volume prior to reporting the uncertainties to AQS. Only the results for the 11 filters analyzed on all four instruments were used to make Table 3-30.

Table 3-30. Average Laboratory Uncertainties

Element	Chester 770	Chester 771	RTI #1	RTI #2
	Average Relative Uncertainty	Average Relative Uncertainty	Average Relative Uncertainty	Average Relative Uncertainty
Si	11.6%	11.8%	5.10%	2.00%
S	11.3%	11.3%	1.00%	1.20%
K	11.5%	11.8%	2.30%	3.30%
Ca	11.7%	11.7%	2.50%	3.40%
Mn	12.4%	10.8%	5.00%	7.30%
Fe	6.10%	6.20%	1.00%	1.40%
Ni	60.3%	32.4%	29.7%	40.7%
Cu	15.4%	18.7%	15.9%	11.7%
Zn	8.10%	7.00%	3.30%	4.10%
Se	44.8%	44.8%	57.5%	25.6%
Pb	18.8%	20.9%	9.80%	10.4%

3.4.2.5 Determination of Uncertainties and MDLs

MDLs are determined by obtaining data from the analysis of ten laboratory blanks. The MDLs are calculated as three times the average uncertainty for each element. The MDLs from XRF 1 and XRF 2 are presented in Table 3-31. Network-wide MDLs are summarized in Appendix A.

Uncertainties for each analytical result is automatically calculated by the ThermoNoran software, except for when the concentration value is zero, the software cannot calculate an uncertainty. To obtain an uncertainty value for when the concentration is zero, the following formula is used:

Uncertainty = slope * A * sqrt (3 * sqrt (B * t) + B * t) / t

Where:

t = livetime
A = scaling factor
B = background counts (cps) is incorporated during the importing of the data into the RTI XRF database.

3.4.2.6 Audits, PEs, Training, and Accreditations

In February 2005, RTI XRF laboratory received six 47mm Teflon filters from NAREL. These six samples were prepared by NAREL and were part of a PE study. During the onsite visit from NAREL in July 2005, results of the PE study showed good agreement among the participating labs as reported in the Multi-Lab Speciation PE Report by NAREL (Appendix D).

Results of the EPA systems audit conducted on 7/12/05 and reported 11/4/05 (Appendix E) included the following comments related to XRF analysis (page 12 of 13):

> ... the focus of the XRF audit was to discuss those samples that RTI had analyzed as part of a recent inter-laboratory comparison study sponsored by NAREL [see reference 2]. Results from this study showed aluminum to be the most controversial element reported. This study also showed that RTI generally reported uncertainties which were lower than those reported by the other participating labs. A few spectra were inspected and discussed during the audit. Two specific spectra were selected to be included in the final report for the study. Ultimately the final report included examples of the controversial spectra from all of the labs. The spectra from RTI contain a significant [diffusion peak] interference for aluminum and silicon which was not observed in the spectra from the other labs.
>
> Comment: This observation may not be a problem for RTI's analysis since there is no standard method for calculating XRF uncertainties. However, RTI may want to take a closer look at the way uncertainties were calculated for aluminum and silicon during this study. EPA has recently initiated dialog with all of the speciation labs to learn more about the XRF analysis at each lab, and clearly there is diversity among the different labs. Any progress toward standardizing the XRF analysis is a positive step for the speciation program.

Table 3-31. MDL Values for XRF 1 and XRF 2

Element	XRF 1	XRF 2	Element	XRF 1	XRF 2
Na	1.29159	0.38759	**Sr**	0.02147	0.02373
Mg	0.15481	0.11639	**Y**	0.02147	0.02599
Al	0.34917	0.1356	**Zr**	0.0226	0.03277
Si	0.17967	0.1017	**Nb**	0.03842	0.02825
P	0.0565	0.17176	**Mo**	0.03277	0.02938
S	0.10283	0.11978	**Ag**	0.08023	0.12656
Cl	0.21018	0.08588	**Cd**	0.08927	0.1356
K	0.05085	0.07458	**In**	0.15594	0.1582
Ca	0.05537	0.08249	**Sn**	0.20453	0.20114
Sc	0.10848	0.11978	**Sb**	0.27007	0.36273
Ti	0.04859	0.05424	**Cs**	0.27911	0.11074
V	0.0339	0.03955	**Ba**	0.10057	0.1017
Cr	0.02373	0.02486	**La**	0.08927	0.08814
Mn	0.01808	0.02034	**Ce**	0.08136	0.1017
Fe	0.01582	0.01695	**Sm**	0.05311	0.05311
Co	0.01356	0.01356	**Eu**	0.05424	0.04746
Ni	0.01356	0.01243	**Tb**	0.04407	0.04181
Cu	0.01808	0.01695	**Hf**	0.1921	0.06215
Zn	0.01921	0.01808	**Ta**	0.17515	0.03616
Ga	0.01921	0.01017	**W**	0.06102	0.02486
As	0.00904	0.00791	**Ir**	0.04972	0.02373
Se	0.0113	0.01356	**Au**	0.03955	0.01808
Br	0.00791	0.01469	**Hg**	0.05198	0.03277
Rb	0.01469	0.01695	**Pb**	0.03503	0.03164

RTI Response: RTI is currently investigating the calculation of uncertainties by the STN and IMPROVE Laboratories in an effort to bring the uncertainties reported for PM-fine measurement programs in the U.S. into agreement ("harmonization"). Ms. Joann Rice of EPA is being kept apprised of these efforts.

3.5 Sample Handling and Archiving Laboratory

3.5.1 Quality Issues and Corrective Actions

There were no major quality issues in the SHAL laboratory during 2005. One Corrective Action was undertaken to resolve a discrepancy in data reported to the AQS database. The discrepancy in the data was the result of the SHAL sending the incorrect cooler to two different field sampling locations. The site operators noted the problem on their respective Field Sampling Data Forms. Upon arrival back at the SHAL, the error was corrected and the analytical results for the filters were assigned to the correct sampling location, however, the field sampling parameters for the two samplers were not assigned to the correct locations. After the data for the two events was reported to AQS, RTI was notified by one of the sites that the field sampling information was not correct. RTI corrected the field sampling data for both locations and reposted the corrected data to AQS.

3.5.2 Description of QC Checks Applied

- The SHAL uses a customized database program written specifically for RTI's SHAL operation. This database has been refined over five years to incorporate many built-in QC checks. For example, RTI has assigned an inventory number to all filter modules in the network. The database will only accept allowable inventory numbers for filter modules. This avoids errors in data input for any filter module used for a sampling event. Another example is the unique number of the Teflon filters used by RTI. RTI purchases Teflon filters with a check sum digit in the numbering sequence. The database will only accept those filter numbers with the correct check sum. This prevents inadvertent entry of incorrect filter identification numbers.

- Bar-code readers are used to input identification numbers from modules, bins, containers and data forms to eliminate data transcription errors.

- A SHAL technician other than the one who prepared an outgoing shipment checks the package of outgoing filters. A checklist is used by the technician to verify that the package contents are correct before it is shipped from RTI. This check is performed on all outgoing shipments from the SHAL.

- Blank filters are taken from the SHAL refrigerator and sent unopened to the analytical laboratories for analysis. The results of the analysis of these QC filters are used to improve the overall quality of the program.

- The field site operators are provided contact information for the SHAL laboratory so they may communicate directly with personnel at RTI if any problems are discovered upon receipt of the filter modules. RTI personnel will attempt to resolve issues promptly. For example, a Field Data Form may be faxed from RTI to the site operator if necessary.

3.5.3 Summary of QC Results

During calendar year 2005, the SHAL shipped out and received back almost 20,000 coolers of filters. By employing the QC checks described in Section 3.5.2, the majority of the coolers shipped and received at RTI contained the correct filter modules and the required paperwork for completing the sampling event at the field site. The high number of correctly packaged shipments sent from RTI helped the field sampling locations meet their completion goals. (See Table B-3).

3.5.4 Summary of Scheduling Problems

Two shipping and receiving schedules are prepared for the STN. One schedule is for those sites sampling on the 1-in-3 day frequency and the other schedule is for those sites sampling on the 1-in-6 day frequency. The schedules indicate when each cooler will be sent from RTI, the scheduled sampling date for the filters, and the return ship date from the site back to RTI. The schedules are designed to allow RTI to send the sampling site clean filters allowing time for field site operators to set up and retrieve filters from the samplers. Late arriving shipments back to RTI may cause disruptions in the designated shipping schedule and could lead to missed sampling events. For instance, RTI may receive a shipment from the field sampling site, past the date that the filter modules were to be sent for a subsequent sampling event. When this happens, it may be impossible for RTI to send the filter modules to the sampling location for the next sampling event. This will mean a missed sampling event for that location. Late arriving shipments at RTI may be due to delays in transit or late return shipments from the site. Late shipments received at RTI during 2005 are summarized in Figures 3-1A and 3-1B.

Figure 3-1A. Late Coolers by Sites
(1/01/05 - 12/31/05)

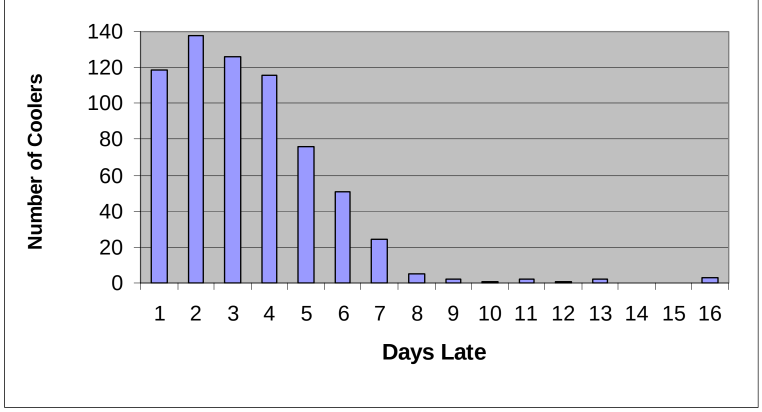
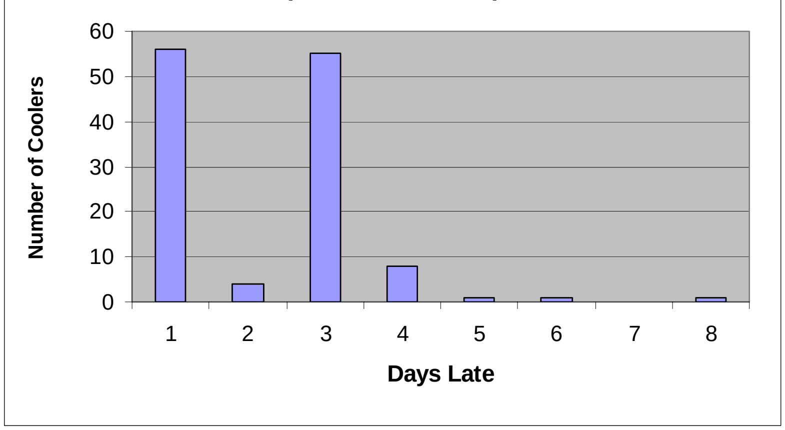


Figure 3-1B. Late Coolers by FedEx
(1/01/05 - 12/31/05)



Sites may also deviate from the sampling schedule and run filters on a date other than the scheduled date. Table 3-32 lists those sites with less than 95% of their filters run on the intended sampling date.

Table 3-32. Sites with Less than 95% of Filters Run on Intended Sampling Date

Airs Code	POC	Location	Events	On Date	Pct.
080010006	5	Commerce City, CO	102	81	79.4
080410011	5	RBD, CO	61	49	80.3
040137003	5	St Johns, AZ	47	39	83.0
471570047	5	Guthrie, TN	121	103	85.1
421010136	5	Elmwood, PA	61	54	88.5
330150014	5	Portsmouth, NH	121	114	94.2

3.5.4 Support Activities for Site Operators and Data Users

SHAL staff provided support to site operators and data users throughout 2005. A summary of email and phone communications with site operators and data users is presented in Table 3-33.

Table 3-33. Summary of SHAL Communications With Site Operators and Data Users

Description	Number of Communications
Site will send cooler late	130
Site needs schedule	26
Site did not receive cooler	43
Change of operator/site information	63
Sampler problems/questions	39
Field Blank/Trip Blank ran as routine sample	16
Request change of ship date from RTI	23
Site is stopping	27
QA	72
Data questions/reporting	173
Site did not send cooler	41
Other	134

3.5.5 Audits, PEs, Training, and Accreditations

- All new SHAL technicians must undergo a formal training process before they handle any filters. This process includes a Safety and Occupational Health Orientation, the viewing of a training video detailing the SHAL procedures, a review of the Standard Operating Procedure and instruction by senior staff in filter handling. A record of this training is kept on file.

- SHAL staff periodically review the Standard Operating Procedure and a record of this review is added to their training file.

- Since work in the SHAL involves lifting, during 2005 the North Carolina Department of Labor presented a course entitled "Lifting and Materials Movement and Preventing Slips in the Workplace" at RTI. All SHAL personnel attended this training.

- Throughout the year senior SHAL staff periodically observe the SHAL technicians processing the filter modules. A checklist of correct tasks has been prepared for each module type. The checklist is used during the observation of the technician. The SHAL supervisor keeps the completed checklists. Technicians are briefed following the review of any findings. A summary of the reviews for calendar year 2005 is shown in Table 3-34.

Table 3-34. Review of SHAL Technician Processing Filter Modules

Module Type	Number Observed	Findings	Findings Reviewed with Technician
MET ONE	28	6	6
Andersen	9	1	1
URG	2	0	0
R&P Spec	2	0	0

3.6 Denuder Refurbishment Laboratory

The Denuder Refurbishment Laboratory is located in RTI Building No. 3, Laboratory 220. The purpose of the laboratory is to clean and refurbish the coatings on acid-gas-removing denuders used in samplers of chemical speciation networks operated by EPA and various State and local agencies which utilize the RTI/EPA contract. The laboratory follows these protocols:

- Procedure for Coating Annular Denuders with Magnesium Oxide

- Standard Operating Procedure for Coating and Extracting Annular Denuders with Sodium Carbonate

- Procedures for Coating R & P Speciation Sampler "ChemComb" Denuders with Sodium Carbonate

- Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin.

3.6.1 Quality Issues and Corrective Actions

Ms. Constance Wall became the coordinator for the Denuder Refurbishment Laboratory. She reviewed the denuder refurbishment SOPs to ensure procedures were clearly stated and all processes were up to date. Minor revisions were made as required. Revisions mainly concerned glassware use and volumes of slurry; no revisions affected the quality of the actual denuder coating process.

The only significant problem encountered in the reporting period of operation has been the occasional receipt of broken or loose glass denuders. These were repaired by URG, Inc. and the costs were charged to the sampling site if breakage occurred there.

As personnel assignments or jobs changed, additional workers were trained in the techniques of denuder refurbishment. Hands-on training was conducted according to the several SOPs for denuder refurbishment. At present, there are four persons trained to refurbish denuders.

3.6.2 Operational Discussion

3.6.2.1 Numbers of Each Type of Denuder Serviced

Table 3-35 lists the type of denuders refurbished and the number of refurbishments completed in 2005.

Table 3-35. Denuder Refurbishments
January 1 through December 31, 2005

Denuder Type	Total Refurbished
R&P	1,554
MetOne	708
URG	24
Andersen	56

3.6.2.2 Scheduling of Replacements

Denuders for the Andersen and URG speciation samplers are being cleaned and then re-coated with magnesium oxide. They are replaced at the sites at three-month intervals.

MetOne speciation sampler aluminum honeycomb denuders are also coated with magnesium oxide. Because the MetOne denuders are part of the sampling module and six sets of modules are in circulation to each site, these denuders are refurbished at 18-month intervals. RTI is able to remove MgO from denuders using a dilute hydrochloric acid solution. As needed, RTI orders uncoated aluminum honeycomb denuder substrates from MetOne, cleans them with solvent and deionized water, and then coats them with magnesium oxide. The change-out occurs whenever the MetOne denuder assembly has been in use for 18 months.

R & P ChemComb™ glass honeycomb denuders are cleaned and coated with sodium carbonate/glycerol. R & P denuders are replaced after each 24-hour sampling use.

No XAD-4 resin coated denuders (for removal of organic vapors) were ordered by EPA/OAQPS during the reporting interval.

3.6.3 Description of QC Checks Applied and Results

QC checks for coating weight are now done only occasionally. Work in earlier years of the project(s) showed that coating weights on the same types of MgO-coated denuders were usually within 10% of one another and that the amount (number of moles) of MgO applied far exceeded the expected mass (number of moles) of acidic gases that would be drawn through the denuder during the cumulative sampling period. The sodium carbonate coated R&P denuders are difficult to examine since the coating is somewhat opaque and not pure white as is MgO and the mass applied is much smaller. We depend on ensuring that all the honeycomb annuli receive the sodium carbonate uniformly during the application process.

Thickness of coating has never been evaluated. This and the uniformity of coating applied are assessed through visual examination of the interior of the denuders by holding them up to a strong light and sighting down the annuli. Examination of the occasional broken Andersen or URG denuder has also shown that the MgO coating is complete and uniform.

4.0 Data Processing

4.1 Quality Issues and Corrective Actions

No significant quality issues or corrective actions arose during the period of this report.

4.2 Operational Summary

Routine data processing activities have remained largely unchanged since the beginning of the program. These include:

- Accepting data entered from field forms
- Accepting data from the laboratories
- Backing up and maintaining the data base
- Generating data monthly for validation and review
- Posting review data monthly to the Web site for external review
- Incorporating data change requested by the States
- Uploading finalized data to AQS
- Responding to user inquiries and data requests, including support to EPA and RTI personnel.

4.3 Operational Changes and Improvements

Operational changes and improvements made during the reporting period include:

- Made minor changes to automated QA/QC review spreadsheets to make them easier to review.

- Started posting additional QA/QC spreadsheets to external web site for EPA review. Current spreadsheets include:
  - Field and trip blank levels (including gravimetric mass, organic and elemental carbon; sulfate, nitrate, and ammonium by IC; and sodium, potassium, iron, nickel, and zinc by XRF).
  - Mass balance outliers (i.e., those where the ratio of analytes (other than gravimetric mass) differs from the measured gravimetric mass by more than the control limits).
  - Mass outliers
  - Sulfur to sulfate ratio outliers (i.e., those where the ratio of sulfur differs from the measured sulfate ion by more than the control limits).

4.4 Monthly Data Postings to Web Site

Each month, RTI posts data for samples received on or before the 15th of the previous month. Table 4-1 shows monthly totals for postings and Table 4-2 shows totals for events. Sample dates may overlap between different batches due to different shipping schedules for the 1-in-3 and 1-in-6 sampling schedules. In addition, the latest date may include samples received late (i.e., after the previous report's cutoff date). Note that the number of records reported per event varies with sampler type. Thus the number of records per event will vary depending on how many of each sampler type was operating during that period.

Table 4-1. Events Posted To Web Site

Report		Sample Date		Field Samples	Blanks		Total
Batch	Date	Earliest	Latest		Field	Trip	
60	1/13/2005	11/14/2004	12/14/2004	1,460	212	37	1,709
61	2/14/2005	12/17/2004	1/13/2005	1,274	79	206	1,559
62	3/11/2005	1/11/2005	2/12/2005	1,387	279	33	1,699
63	4/14/2005	12/11/2004	3/14/2005	1,312	211	48	1,571
64	5/12/2005	3/14/2005	4/13/2005	1,384	77	279	1,740
65	6/13/2005	4/16/2005	5/13/2005	1,387	2	57	1,446
66	7/15/2005	5/13/2005	6/12/2005	1,380	290	68	1,738
67	8/15/2005	6/14/2005	7/15/2005	1,479	72	107	1,658
68	9/13/2005	7/14/2005	8/11/2005	1,293	212	53	1,558
69	10/14/2005	8/14/2005	9/14/2005	1,464	216	36	1,716
70	11/14/2005	9/13/2005	10/15/2005	1,490	5	261	1,756
71	12/14/2005	10/14/2005	11/15/2005	1,385	282	29	1,696

Table 4-2. Records Posted To Web Site

Report		Sample Date		Field Samples	Blanks		Total
Batch	Date	Earliest	Latest		Field	Trip	
60	1/13/2005	11/14/2004	12/14/2004	166,980	24,312	4,269	195,561
61	2/14/2005	12/17/2004	1/13/2005	145,712	8,913	23,452	178,077
62	3/11/2005	1/11/2005	2/12/2005	158,716	31,881	3,764	194,361
63	4/14/2005	12/11/2004	3/14/2005	150,085	24,191	5,454	179,730
64	5/12/2005	3/14/2005	4/13/2005	157,989	8,681	31,975	198,645
65	6/13/2005	4/16/2005	5/13/2005	158,643	226	6,495	165,364
66	7/15/2005	5/13/2005	6/12/2005	157,946	33,162	7,660	198,768
67	8/15/2005	6/14/2005	7/15/2005	169,044	8,128	12,124	189,296
68	9/13/2005	7/14/2005	8/11/2005	148,011	24,362	6,037	178,410
69	10/14/2005	8/14/2005	9/14/2005	167,387	24,782	4,055	196,224
70	11/14/2005	9/13/2005	10/15/2005	170,683	548	29,967	201,198
71	12/14/2005	10/14/2005	11/15/2005	158,407	32,223	3,298	193,928

4.5 Postings to AQS

After data have been posted to the external website, sites have 45 days to review data and send corrections to RTI. RTI then is required to post data to AQS within 15 days. RTI met all processing deadlines for this reporting year. Table 4-3 contains totals of events posted to AQS. Table 4-4 contains totals of records posted to AQS. Note that blanks involve fewer records per event, as temperature and barometric pressure for field and trip blanks are not posted to AQS. Some data, such as results for the collocated shipping study were reported to the sites, but were not reported to AQS. In addition, the number of records posted per event varies with sampler type (with the URG posting volatile and total nitrate).

Table 4-3. Events Posted To AQS

Report Batch	Field Samples	Blanks		Total
		Field	Trip	
60	1,483	213	37	1,733
61	1,302	79	205	1,586
62	1,405	282	32	1,719
63	1,327	210	46	1,583
64	1,466	76	277	1,819
65	1,382	2	57	1,441
66	1,368	284	67	1,719
67	1,462	70	103	1,635
68	1,287	209	51	1,547
69	1,445	214	35	1,694
70	1,490	5	260	1,755

Table 4-4. Records Posted to AQS

Report Batch	Field Samples	Blanks		Total
		Field	Trip	
60	99,499	14,285	2,487	116,271
61	87,344	5,307	13,773	106,424
62	94,267	18,922	2,148	115,337
63	89,037	14,086	3,090	106,213
64	98,374	5,106	18,587	122,067
65	92,714	134	3,831	96,679
66	91,764	19,054	4,507	115,325
67	98,092	4,702	6,917	109,711
68	86,335	14,017	3,429	103,781
69	96,953	14,356	2,355	113,664
70	99,968	339	17,446	117,753

4.6 Data User Support Activities

RTI had continuing data user support throughout the year. Most responses may be categorized into four categories; data change requests, requests for old data, support requests for the Speciation Data Validation and Analysis Tool (SDVAT), and requests from data users.

4.6.1 Data Change Requests

Sites are asked to review their data and submit any changes to RTI within 45 days. RTI then processes these changes before posting the data to AQS. Sites report changes via e-mail. Many sites do not report unless they have changes, while others send a report back indicating there are no changes to be made. Table 4-5 shows a count of the number of change requests per batch. Note that many requests represent multiple sites (often an entire state).

Table 4-5. Change Requests Per Report Batch

Batch	**60**	**61**	**62**	**63**	**64**	**65**	**66**	**67**	**68**	**69**	**70**
Requests	8	14	10	10	14	9	11	6	6	5	7

4.6.2 Requests for Old Data

RTI keeps draft data reports on its internal site for approximately 60 days. This provides enough time for sites to review their data and request changes (changes are required to be sent to RTI within 45 days of posting on the internal site). RTI makes any requested changes before posting to AQS and then removes the draft (unmodified) data from the web site. Although we recommend that all data be retrieved from AQS, as these official data incorporate any and all changes made by the sites, a few sites have found the data review format supplied by RTI to be more convenient. Such requests are often made with respect to the use of the SDVAT program (described below). Requests for old data are less frequent than in earlier years. This is likely due to AQS enhancements that allow all speciation parameters to be retrieved in a single request.

4.6.3 SDVAT Support

RTI was previously contracted by EPA to produce a software program (SDVAT) to help Speciation sites to review and approve their data. Although EPA funding for SDVAT support ended in 2002, RTI has continued to provide limited support to current STN sites. Most of these questions are from new operators who need help importing site data into the SDVAT. Introduction of new analytes (for carbon analyses) under the new contract has caused problems with the now discontinued SDVAT program (as it was not designed to handle them). RTI has produced a short note that explains a workaround for the problem, which it sends out on request.

RTI has had requests on use of the SDVAT to review data in AQS. Unfortunately, because the SDVAT was developed during the transition from the legacy AQS to the reengineered AQS, adding AQS import capabilities was not feasible. Now that the record format and procedures are available, this could be added to a future version of the SDVAT, if funding were available.

4.6.4 Data User Communications

In general, RTI's STN activity is limited to sample analysis and module preparation. Because of this, we have limited involvement with STN data users. However, the data processing staff do field a few requests each year from data users. A short summary, by topic, is below:

- <u>Data Availability at end of calendar year</u> - Several calls were from state or regional personnel inquiring on data availability after the end of the calendar year. We explained the process and deadlines under the current process and provided estimates of when data would be available (typically in the April 15th monthly report). The delay reflects reporting (up to 45 days), site review (45 days), and RTI posting (15 days). Thus a sample run on December 31 would be received by RTI in early January (before January 15th) and reported on by RTI on or before February 15th. The site would have until April 1st to review their data and RTI would have until April 15th to post data to AQS.

- <u>Data Uncertainty</u>.
  - Several state and regional contacted us about data uncertainties and how they were calculated. Most were referred to our uncertainty calculations write-up.
  - A few users also asked about backfilling uncertainty data under the old contract. We indicated that the procedures are under development.

5.0 Quality Assurance and Data Validation

5.1 QA Activities

5.1.1 QAPP Updates

RTI's QAPP for STN was updated twice during 2005 and is posted on EPA's public web site, AMTIC. Changes to the QAPP during 2005 were as follows:

- September 27, 2005
  - EPA QA Lab Director changed to E.Boswell
  - Teflon filter catalog number changed
- July 11, 2005
  - Staffing changes at EPA and RTI
  - Numerous minor edits
  - Number of sites amended
  - Correspondence files to be stored as hardcopy and electronic
  - AIRS changed to AQS throughout
  - Denuder preparation procedure corrections
  - Gravimetric analysis QC sample frequency - increase in duplicate filter weighing in response to problems with Whatman filter lot.
  - Gravimetric Laboratory disaster recovery plan updated
  - Clarification of MDL calculations
  - Update number of balances from 2 to 3

5.1.2 SOP Updates

The following SOPs were updated during 2005:

Type	Title	Date Revised	Comment
SOP	Gravimetric Analysis	7/8/2005	Increased frequency of QC reweighings
SOP	Database Operations	7/11/2005	Maintenance updates
SOP	Disaster Recovery Plan--RTI CONFIDENTIAL	7/6/2005	Updated recovery plan for infrastructure changes at RTI
SOP	Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters	7/7/2005	New e-procurement procedures; enhanced Teflon filter inspection requirement in response to filter debris problem.
SOP	Sample Handling and Archiving Laboratory (SHAL)	7/11/2005	Maintenance updates; revised procedures for filter module assembly and disassembly
SOP	Assign Field Sample Flags for the Chemical Speciation Trends Network	7/7/2005	Major update incorporating more details of process
SOP	Document Control and Storage	7/6/2005	Maintenance updates

5.1.3 Internal Surveillance Activities

Internal surveillance activities during July included walkthroughs of all the laboratories to verify compliance with the SOPs prior to the EPA systems audit in July, 2005. An internal audit of the Gravimetry Laboratory was performed in January, 2005. Other inspections and investigations were prompted by issues such as the Whatman filter debris problem in the Gravimetry Laboratory. In addition, the QA Manager and Program Manager meet with laboratory supervisors on a monthly basis to discuss outstanding problems.

SHAL supervisors routinely inspect assembly of R&P model 2300 modules, which have proven to be problematic in the past. Inspection of these modules ensures that filters are fixed securely in the support rings so that bypass leaks do not occur. SHAL technicians also crosscheck each other's coolers before they are shipped to the sites.

5.1.4 Data User Support Activities

The QA Manager responded to a number of questions and requests for data during 2005. These originated from both network participants (state agency personnel and EPA) as well as data users who were not affiliated with the STN program.

- Requests for blank levels and other background data - RTI has received several requests for information such as network-wide average blank levels. When this information is readily available from monthly reports, etc., we try to provide this information. More extensive requests for data are referred to EPA staff.

- Artifacts, outliers, and poor comparison with FRM results - Reports from the state agencies regarding poor intercomparison with FRM results result in immediate investigation by the QA and technical staff. These reports are extremely important in identifying potential problems in the laboratory. However, they can also point to sampler-related issues such as leaks or sensor malfunctions.

- Data Uncertainties - Several states and regions contacted us about data uncertainties and how they were calculated. Most were referred to the uncertainty calculations write-up that was developed in 2003, when uncertainties were added to the deliverable data.

- Method Detection Limits (MDLs) - Periodic requests are received for the list of MDLs for the analyzers used by the STN program. Both MDLs and uncertainties are now included in data records uploaded to AQS. Data records prior to July 2003 lack this information, and the users are given a table of historical MDLs that was developed under RTI's previous contract.

5.2 Data Validation and Review

5.2.1 Review of Monthly Data Reports to STN Web Site

Each month, RTI reviews data completed during the previous month. The reviews include the following activities:

- Verification of data attribution to the correct site, POC, and date
- Visual review of report formats
- Investigation and corrective actions when discrepancies are found
- Automated range checks (barometric pressure, temperature)
- Level 1 checks (reconstructed mass balance, anion/cation balance, and sulfur/sulfate balance)

Tables 5-1 through 5-3 summarize the data flags attached to the data primarily through the data review process, although some of these were specified by either the field operator or one of the laboratories. Examining trends in flag percentages is a useful tool in diagnosing potential problems. For example, reporting batches 64, 65, and 71 have elevated numbers of QMB flags. These were the result of problems in the Gravimetry Laboratory which became the subject of corrective actions. Other trends in the data flags, such as the higher levels of DST flags (filter receipt temperature) in the summer, are out of the control of RTI.

5.2.2 Review of Monthly Data Packages to AQS

Approximately 60 days after initial posting on the RTI web site, the data are uploaded to the AQS database. Prior to uploading, the data processing staff prepares a QC summary report which is reviewed by the QA Manager. This summary and review includes the following main areas:

- Verification that changes requested by the state agencies have been implemented. This includes checking data flags that are different between original reporting (web site posting) and final AQS reporting.
- Verification that record counts match exactly the number of records previously reported on the RTI web site, with allowance for all records that were added and deleted during processing. Record changes include such things as elimination of duplicates, generation of aggregated nitrate values for MASS samplers, deletion of data for sites not reported to AQS (e.g., special studies).
- Scanning for unusual values such as start times other than midnight
- Scanning for formatting errors such as:
  - duplicate records
  - flags and other data in incorrect columns
  - previously delivered data (unless they are Modify records)
  - MDLs and uncertainties that do not agree between the original report and the AQS data file

Table 5-1. Summary of Validity Status Codes by Delivery Batch Number

AQS Validity Status Codes

Flag	Description	60	61	62	63	64	65	66	67	68	69	70	71
1	Critical Criteria Not Met						0.09%	0.04%					
2	Operational Criteria Not Met			0.02%					0.24%				
3	Possible field contamination					0.05%		0.06%					
4	Possible lab contamination		0.10%										
5	Outlier-cause unknown	3.87%	3.56%	2.45%	4.85%	6.68%	7.91%	5.87%	5.22%	3.70%	4.20%	4.97%	8.51%
A	High Winds	0.07%	0.06%	0.06%	0.06%			0.06%	0.06%	0.12%	0.06%	0.06%	0.25%
D	Sandblasting	0.05%		0.05%		0.10%		0.05%	0.06%	0.12%	0.27%		0.11%
E	Forest Fire					0.05%	0.07%	0.06%	0.47%	0.44%		0.06%	0.17%
F	Structural Fire	0.06%	0.19%						0.06%			0.07%	
H	Chemical Spills		0.08%			0.05%			0.06%				
I	Unusual Traffic Congestion											0.06%	
J	Construction/Demolition		0.16%	0.22%				0.11%	0.12%	0.37%	0.23%	0.50%	0.47%
K	Agricultural Tilling						0.07%		0.06%	0.06%		0.06%	
L	Highway Construction	0.06%					0.07%			0.06%	0.17%	0.06%	
M	Rerouting of Traffic										0.06%		
N	Sanding/salting of Streets		0.12%	0.46%	0.31%								
O	Infrequent Large Gatherings									0.06%			
P	Roofing Operations		0.16%	0.22%						0.06%	0.13%	0.17%	
Q	Prescribed Burning									0.06%			
R	Cleanup after Major Disaster		0.08%								0.06%		
U	Sahara Dust							0.17%		0.12%			
W	Flow Rate Average out of specs	0.11%				0.01%	0.04%	0.06%	0.11%	0.01%	0.06%	0.07%	
X	Filter Temperature Diff. out of spec	0.32%	0.19%	0.07%	0.13%	0.51%	0.47%	0.38%	0.80%	0.14%	0.13%	0.17%	0.23%
Y	Elapsed Sample Time out of specs		0.05%				0.13%						

Table 5-2. Summary of Null Value Codes by Delivery Batch Number

AQS Null Value Codes

Flag	Description	60	61	62	63	64	65	66	67	68	69	70	71
AB	Technician Unavailable	0.35%	0.12%	0.23%			0.34%	0.17%	0.29%	0.19%	0.06%	0.06%	0.06%
AC	Construction/Repairs in area										0.23%	0.11%	
AF	Sched. but not collected	0.31%	0.55%	0.55%	0.14%	0.32%	0.20%	0.28%	0.27%	0.38%	0.51%	0.22%	0.17%
AG	Sample Time out of Limits	0.58%	0.72%	0.69%	0.43%	0.51%	0.66%	0.87%	0.62%	0.66%	0.28%	0.91%	0.48%
AH	Samp. Flow Rate out of Limits	0.43%	0.64%	0.43%	0.56%	0.51%	0.56%	0.72%	0.41%	0.46%	0.60%	0.80%	0.43%
AI	Insuff. data (can't calculate)	0.05%	0.12%	0.06%		0.01%	0.13%	0.02%	0.07%	0.03%		0.06%	0.06%
AJ	Filter Damage	0.18%	0.13%	0.15%	0.04%	0.21%	0.03%	0.04%	0.27%	0.23%	0.04%	0.05%	0.19%
AK	Filter Leak									0.13%			
AL	Voided by Operator	0.07%	0.25%	0.12%	0.20%	0.29%	0.20%	0.06%	0.06%	0.06%	0.30%	0.17%	0.34%
AM	Miscellaneous void	0.34%	0.45%	0.16%	0.36%	0.41%	0.23%	0.09%	0.10%	0.16%	0.09%	0.15%	0.13%
AN	Machine Malfunction	1.50%	1.51%	0.94%	0.69%	1.06%	0.43%	0.53%	0.36%	1.02%	0.77%	0.99%	0.91%
AO	Bad Weather	0.07%	0.06%	0.07%			0.08%				0.63%	0.14%	0.19%
AQ	Collection Error	0.01%	0.14%	0.20%	0.17%	0.09%	0.20%	0.39%	0.08%	0.31%	0.09%	0.06%	0.35%
AR	Lab Error	0.21%	0.09%	0.22%	0.05%	0.21%	0.13%	0.13%	0.14%	0.35%	0.22%	0.06%	0.09%
AS	Poor QA Results	0.04%	0.06%						0.03%				
AU	Monitoring Waived			0.06%	0.37%	0.54%						0.06%	
AV	Power Failure	0.54%	0.57%	0.56%	0.34%	0.30%	0.60%	0.57%	0.80%	0.71%	0.43%	0.79%	0.48%
AW	Wildlife Damage						0.07%	0.03%	0.13%	0.17%			
BA	Maint. / Routine Repairs			0.16%	0.51%	0.12%	0.51%	0.18%	0.12%			0.22%	0.18%
BB	Unable to Reach Site	0.06%	0.18%	0.23%		0.05%	0.51%	0.11%		0.12%		0.17%	0.12%
BE	Building / Site Repair												0.06%
BI	Lost or Damaged in Transit	0.07%	0.00%			0.05%	0.01%						
BJ	Operator Error					0.05%							

Table 5-3. RTI-assigned Flags (not reported to AQS) by Delivery Batch Number

Flag	Description	60	61	62	63	64	65	66	67	68	69	70	71
ANB	Analysis not billable	0.21%	0.08%	0.13%	0.05%	0.29%	0.13%	0.15%	0.32%	0.37%	0.16%	0.10%	0.14%
APB	analysis partly billable	0.74%	0.66%	0.48%	0.51%	0.85%	0.54%	0.47%	0.25%	0.28%	0.34%	0.15%	0.56%
DFM	Filter missing	0.01%								0.03%		0.01%	
DMA	Module assembled in correctly									0.01%		0.02%	
DMC	Module condition invalid		0.01%										
DST	Receipt temperature >4C	33.10%	26.21%	14.79%	21.79%	51.83%	82.91%	88.89%	86.80%	97.55%	97.15%	87.07%	51.11%
FBS	Field or Trip Blank appears to be actual sample	0.06%								0.06%		0.07%	
FES	Field Environmental Substituted	0.01%	0.15%	0.10%	0.06%	0.04%	0.11%	0.05%	0.01%	0.14%	0.01%	0.15%	0.04%
FHT	Pickup holding time exceeded	5.45%	18.58%	12.60%	12.93%	5.26%	15.28%	18.04%	7.21%	10.67%	12.11%	12.94%	4.98%
FSL	Sample lost or damaged in shipment									0.06%			
LBD	Laboratory blank duplicate outside limits			0.00%		0.00%							
LFA	Filter inspection flags* - filter wet	0.01%	0.11%	0.01%	0.01%	0.06%		0.04%	0.01%	0.01%		0.02%	0.03%
LFH	Filter inspection flags* - Holes in filter												
LFL	Filter inspection flags* -Loose Material	0.01%								0.01%		0.03%	
LFO	Filter inspection flags* -Other									0.07%			
LFP	Filter inspection flags* -Pinholes												
LFT	Filter inspection flags* - Tear									0.03%	0.01%		0.01%
LHT	Lab holding times exceeded												
QAC	Anion/Cation ratio out of limits	0.08%	0.17%	0.11%	0.07%	0.11%	0.09%	0.13%	0.16%	0.08%	0.10%	0.13%	0.11%
QL1	Sulfur/Sulfate ratio out of limits	0.07%	0.07%	0.04%	0.04%	0.06%	0.07%	0.06%	0.09%	0.06%	0.05%	0.08%	0.07%
QMB	Mass balance ratio out of limits	3.78%	3.37%	2.31%	4.77%	6.55%	7.79%	5.73%	5.03%	3.52%	4.10%	4.83%	8.37%
SNB	Sample not billable	0.11%	0.24%	0.32%		0.10%	0.07%	0.05%		0.19%	0.17%		0.06%
SPB	Sample partly billable	2.85%	3.10%	3.03%	2.31%	2.51%	2.98%	2.43%	2.60%	2.77%	3.30%	3.72%	2.85%

5.3 Analysis of Collocated Data

The STN program operated six sites with collocated samplers during 2005. The data from these sites afforded an opportunity to calculate total precision and compare the values with the uncertainty values that are currently being reported to AQS. The AQS uncertainties are only estimates based on historical QC data and scientific judgment. Table 5-4 lists the collocated sites in STN.

Table 5-4. Collocated sites in the STN

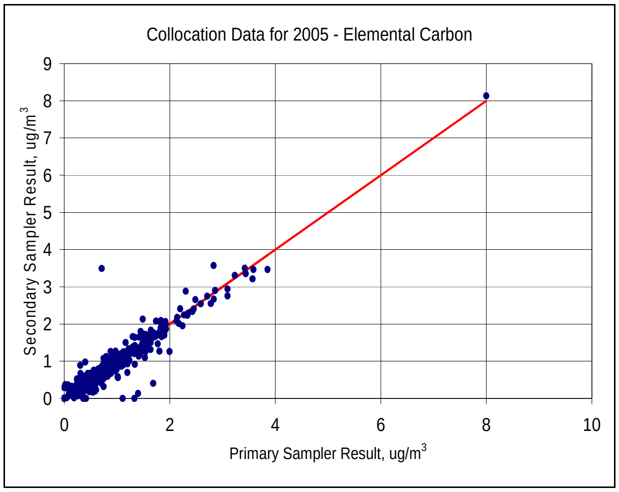
Location Name	State	AQS Code	Sampler Type
Bakersfield-California Ave	California	60290014	MetOne SASS
Deer Park	Texas	482011039	URG MASS
G.T. Craig	Ohio	390350060	MetOne SASS
New Brunswick	New Jersey	340230006	MetOne SASS
Riverside-Rubidoux	California	60658001	MetOne SASS
Roxbury (Boston)	Massachusetts	250250042	MetOne SASS

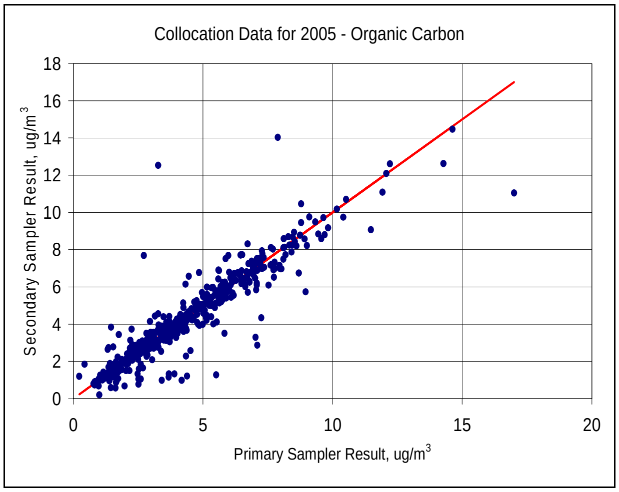
As indicated in the table, five of the sites use MetOne SASS samplers, and one uses a URG MASS sampler. None of the collocated sites used either the Andersen RAAS sampler or the R&P speciation sampler during 2005.

In general, the collocation data shows good or excellent agreement for the major analytes. The figures that follow (Figure 5-1) show examples of the comparisons for mass, sulfate, nitrate, sulfur, organic carbon, and elemental carbon. (This is not intended as an exhaustive list of elements -- these are presented as examples only.) The oblique line on each chart indicates perfect agreement (slope=1.000).

5.3.1 Precision

Tables 5-5 through 5-8 show the results of collocated sampling and provides a comparison with the uncertainties reported to AQS. The first column indicates the name of the chemical analyte. Columns 2-5 show the average and standard deviation of the analytical results. Note that the standard deviations reflect environmental variability of the concentration and are not determined by the laboratory uncertainties. The column titled "Average Relative Diff." is the average of the unsigned differences between the two samplers, which is calculated using the following formula:





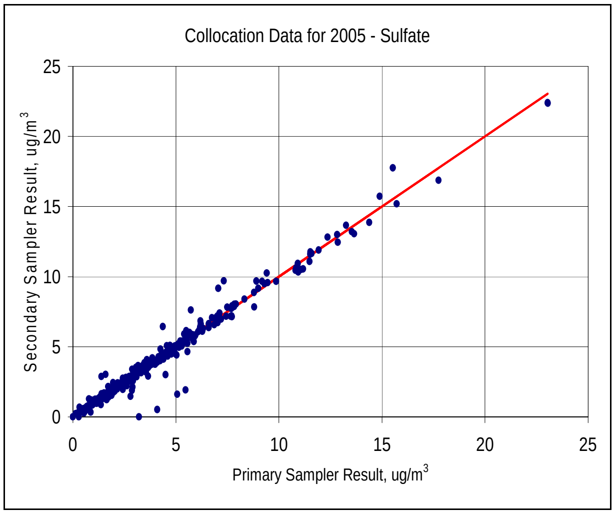
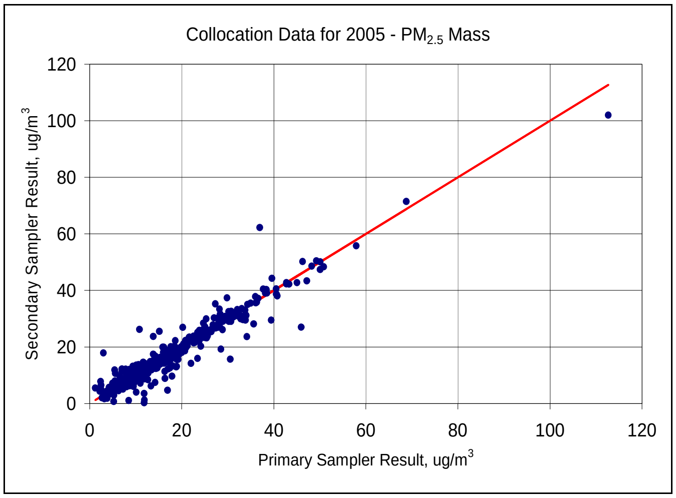
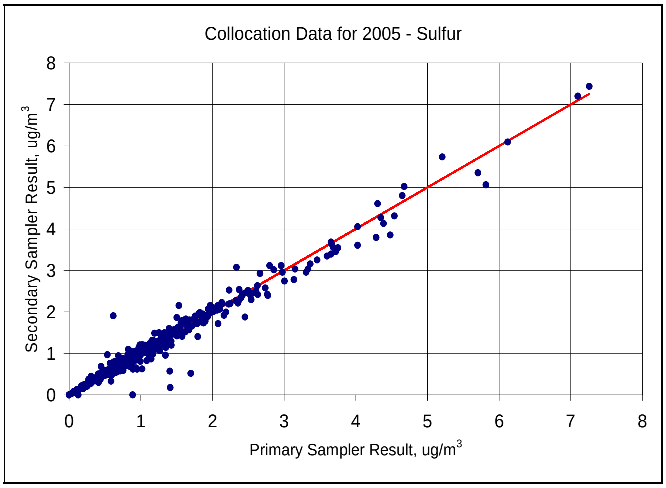


Figure 5-1. Examples of the comparisons for mass, sulfate, nitrate, sulfur, organic carbon, and elemental carbon.





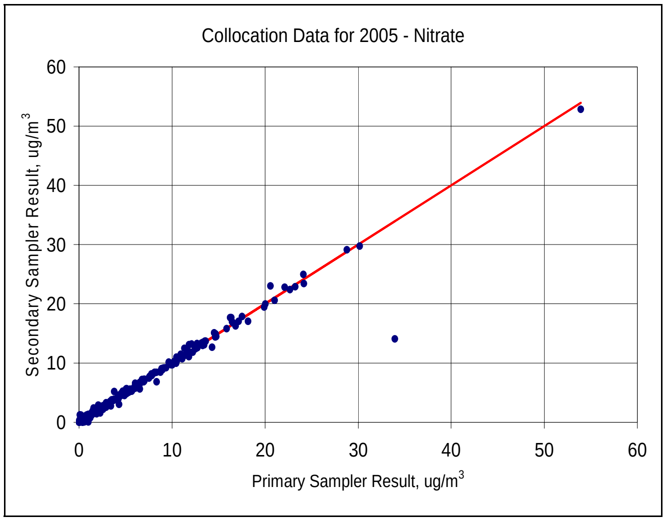


Figure 5-1. (Continued)

Table 5-5. Trace Elements by XRF

	Sampler 1		Sampler 2					
Analyte	**Average μg/m³**	**Standard Dev.[1] μg/m³**	**Average μg/m³**	**Standard Dev.[1] μg/m³**	**Average Relative Diff.[2] μg/m³**	**Average AQS Uncert.[3] μg/m³**	**Ratio[4] AQS/Col percent**	**Counts[5]**
Aluminum	0.084	0.099	0.081	0.116	31.4%	17.5%	55.6%	125
Arsenic	0.003	0.002	0.003	0.002	23.2%	21.6%	93.0%	136
Barium	0.023	0.026	0.024	0.019	26.6%	21.2%	79.7%	61
Bromine	0.005	0.003	0.005	0.002	18.3%	18.0%	98.6%	381
Calcium	0.083	0.131	0.079	0.080	17.8%	9.5%	53.2%	470
Cerium	0.026	0.024	0.028	0.025	23.9%	18.2%	76.2%	92
Chlorine	0.117	0.258	0.112	0.246	27.8%	14.5%	52.2%	190
Chromium	0.008	0.013	0.006	0.006	42.2%	22.3%	52.8%	123
Copper	0.011	0.018	0.009	0.008	26.8%	15.1%	56.4%	386
Europium	0.013	0.011	0.014	0.015	37.7%	22.9%	60.7%	30
Iron	0.157	0.167	0.157	0.169	14.4%	5.9%	40.9%	479
Lanthanum	0.019	0.020	0.020	0.022	25.6%	22.3%	87.4%	77
Lead	0.010	0.008	0.010	0.008	22.9%	24.3%	106.1%	177
Magnesium	0.038	0.021	0.040	0.031	26.8%	17.0%	63.6%	35
Manganese	0.007	0.007	0.007	0.007	23.2%	20.5%	88.5%	266
Mercury	0.005	0.002	0.005	0.002	27.3%	25.2%	92.4%	52
Nickel	0.004	0.004	0.004	0.003	27.3%	22.0%	80.4%	243
Potassium	0.095	0.119	0.094	0.122	10.6%	9.2%	86.7%	475
Samarium	0.012	0.010	0.011	0.010	27.6%	24.0%	87.0%	41
Selenium	0.003	0.002	0.003	0.002	19.2%	28.9%	150.6%	91
Silicon	0.166	0.198	0.159	0.166	24.6%	11.5%	46.6%	338
Sodium	0.165	0.156	0.173	0.159	20.4%	18.4%	90.4%	191
Strontium	0.004	0.004	0.004	0.003	20.4%	30.5%	149.3%	56
Sulfur	1.196	1.054	1.186	1.036	6.3%	6.7%	105.1%	477
Terbium	0.019	0.015	0.020	0.017	23.6%	31.0%	131.0%	94
Titanium	0.012	0.010	0.012	0.009	24.5%	19.7%	80.2%	235
Vanadium	0.006	0.004	0.006	0.003	20.6%	22.1%	107.4%	219
Zinc	0.023	0.034	0.023	0.034	14.8%	11.0%	73.9%	450
Zirconium	0.005	0.002	0.005	0.001	15.1%	34.0%	**225.7%**	12

NOTES:

1 The standard deviations are a function of the natural variability of the environmental levels, and are not indicative of the analytical precision.

2 Calculated as the average of the absolute value of the relative difference between the two samplers' values, divided by the square root of 2.

3 Average value of the relative uncertainties as reported to AQS.

4 AQS/ARD is the ratio of reported uncertainties divided by the uncertainty determined by average relative difference of the collocated samples. Values greater than 200% are shown in bold and discussed in the text.

5 Counts are the number of individual observations included in the statistics. Only observations where both concentration values were above twice the uncertainty are included in the statistics.

Table 5-6. Anions and Cations by IC

	Sampler 1		Sampler 2					
Analyte	**Average µg/m³**	**Standard Dev. [1] µg/m³**	**Average µg/m³**	**Standard Dev.[1] µg/m³**	**Average Relative Diff.[2] µg/m³**	**Average AQS Uncert.[3] µg/m³**	**Ratio[4] AQS/ARD percent**	**Counts[5]**
Sulfate	3.617	3.116	3.601	3.130	4.4%	9.8%	220.7%	482
Nitrate	4.434	5.968	4.380	5.800	4.7%	10.7%	228.9%	402
Ammonium	2.291	2.206	2.270	2.179	5.4%	7.1%	130.0%	483
Potassium	0.114	0.136	0.115	0.142	9.1%	7.6%	83.3%	258
Sodium	0.245	0.200	0.237	0.164	14.4%	24.3%	168.2%	263

NOTES:
1. The standard deviations are a function of the natural variability of the environmental levels, and are not indicative of the analytical precision.
2. Calculated as the average of the absolute value of the relative difference between the two samplers' values, divided by the square root of 2. (ARD.)
3. Average value of the relative uncertainties as reported to AQS.
4. AQS/ARD is the ratio of reported uncertainties divided by the uncertainty determined by average relative difference of the collocated samples. Values greater than 200% are shown in bold and discussed in the text.
5. Counts are the number of individual observations included in the statistics. Only observations where both concentration values were above twice the uncertainty are included in the statistics.

Table 5-7. Organic and Elemental Carbon

	Sampler 1		Sampler 2					
Analyte	**Average µg/m³**	**Standard Dev. [1] µg/m³**	**Average µg/m³**	**Standard Dev.[1] µg/m³**	**Average Relative Diff.[2] µg/m³**	**Average AQS Uncert.[3] µg/m³**	**Ratio[4] AQS/ARD percent**	**Counts[5]**
Elemental carbon	1.098	0.751	1.097	0.765	8.8%	29.2%	331.6%	335
Organic carbon	4.501	2.370	4.425	2.388	9.7%	12.3%	127.3%	499

NOTES:
1. The standard deviations are a function of the natural variability of the environmental levels, and are not indicative of the analytical precision.
2. Calculated as the average of the absolute value of the relative difference between the two samplers' values, divided by the square root of 2. (ARD.)
3. Average value of the relative uncertainties as reported to AQS.
4. AQS/ARD is the ratio of reported uncertainties divided by the uncertainty determined by average relative difference of the collocated samples. Values greater than 200% are shown in bold and discussed in the text.
5. Counts are the number of individual observations included in the statistics. Only observations where both concentration values were above twice the uncertainty are included in the statistics.

Table 5-8. Particulate Matter (Gravimetry)

	Sampler 1		Sampler 2					
Analyte	**Average µg/m³**	**Standard Dev. [1] µg/m³**	**Average µg/m³**	**Standard Dev.[1] µg/m³**	**Average Relative Diff.[2] µg/m³**	**Average AQS Uncert.[3] µg/m³**	**Ratio[4] AQS/ARD percent**	**Counts[5]**
PM2.5 mass	16.8674	11.3557	16.7068	11.2434	9.5%	5.8%	60.3%	476

NOTES:
1 The standard deviations are a function of the natural variability of the environmental levels, and are not indicative of the analytical precision.
2 Calculated as the average of the absolute value of the relative difference between the two samplers' values, divided by the square root of 2. (ARD.)
3 Average value of the relative uncertainties as reported to AQS.
4 AQS/ARD is the ratio of reported uncertainties divided by the uncertainty determined by average relative difference of the collocated samples. Values greater than 200% are shown in bold and discussed in the text.
5 Counts are the number of individual observations included in the statistics. Only observations where both concentration values were above twice the uncertainty are included in the statistics.

$$ARD = \frac{1}{\sqrt{2}} \sum \frac{|C_1 - C_2|}{(C_1 + C_2)/2}$$

Where:

- C_1 and C_2 are the concentrations from the primary and collocated samplers, respectively
- The factor of $1/\sqrt{2}$ is used to convert the difference to a single-sampler basis
- The summation is over all valid concentration values where the concentration (C1 or C2) is greater than twice the uncertainty reported to AQS

The column titled "Average AQS Uncert." is simply the grand average of all the relative uncertainties associated with the C_1 and C_2 values, and is calculated as follows:

$$AvAQS = \sum_i \sum_j U_{ij} / C_{ij}$$

Where

- U_{ij} and C_{ij} refer to the uncertainty and concentration for the i^{th} exposure with the j^{th} sampler (j=1 or 2).
- The criteria for inclusion in the average (index i) is the same as in the previous equation

The next column provides the ratio of AvAQS to ARD defined above. This is essentially the average under- or over-estimate of the uncertainty for each chemical species reported during 2005. Finally, the last column provides the number of sampling events included in the averages defined above. Only events where both concentrations were greater than twice their respective uncertainties were included.

Ratios greater than 200% or less than 50% indicate situations in which the uncertainties reported to AQS were different from the uncertainty estimated from collocation data by a factor of 2 or more. The following species disagreed by a factor of 2 or more; ratios are shown in parentheses:

- Silicon (46%) - underestimation of the uncertainty to AQS may be related to an XRF attenuation correction that is too small. Uncertainties for the XRF instruments are currently under investigation by RTI and EPA.

- Zirconium (226%) - only 12 events were included in the calculations, so this may be a statistical fluke.

- Sulfate (221%), nitrate (229%), and elemental carbon (332%) –RTI will investigate whether the MDLs used to calculate uncertainty for AQS are too large. If this is the case, the calculations will be revised.

The ratio for particulate mass (Table 5-8) is somewhat lower than expected (60%), though within a factor of 2. There was a problem with debris on the Whatman filters (described elsewhere in this report) that may have resulted in the actual uncertainty being greater than the estimated uncertainty provided to AQS

5.3.2 Bias

Biases between the primary and secondary samplers is small for all of the major analytes when data from all sites are combined. The overall averages for the primary and secondary samplers were compared using Student's t test, and only one element, copper, was found to have a significant difference between the two averages ($t = -3.77$).

5.4 Analysis of Trip and Field Blanks

In the STN program, field blanks are run at a frequency of 10% or more, while trip blanks are run at approximately 3%. Historical data has shown little difference between the two types of blanks, perhaps because the field SOPs for running them are very similar, the only difference being that the Field Blanks are mounted on the sampler for a few minutes, while the Trip Blanks are kept closed. Date from these blanks allow evaluation of contamination, which may come from a number of different sources. In addition, the Trip and Field Blank data can sometimes provide clues to problems in the analytical laboratories or with filters received from the manufacturers. Table 5-9 shows the distributions (percentiles) for trip and field blanks during 2005.

Table 5-9. Concentration Percentiles for Combined Trip and Field Blanks Reported During 2005

Anions and Cations by Ion Chromatography

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Nitrate (SASS/nylon)	0.0000	0.0000	0.0000	0.0254	0.0494	0.0775	0.1076
Nitrate (MASS/nylon)	0.0000	0.0109	0.0173	0.0236	0.0317	0.0474	0.0584
Nitrate (MASS/Teflon)	0.0000	0.0109	0.0161	0.0241	0.0377	0.0634	0.1197
Sulfate	0.0000	0.0000	0.0000	0.0000	0.0377	0.0637	0.1053
Ammonium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Potassium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium	0.0000	0.0000	0.0000	0.0000	0.0062	0.0343	0.0782

PM2.5 Mass by Gravimetry

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Particulate matter 2.5u	-0.5208	- 0.1042	0.1250	0.5208	1.0417	1.6667	2.1875

Organic and Elemental Carbon (OC/EC)

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Elemental carbon	0.0000	0.0000	0.0000	0.0004	0.0065	0.0372	0.0840
Organic carbon	0.3920	0.5096	0.6871	0.9396	1.1864	1.4473	1.7590
Pk1_OC	0.0858	0.1180	0.1706	0.2398	0.3281	0.4255	0.4728
Pk2_OC	0.1366	0.1753	0.2517	0.3759	0.5124	0.6616	0.7936
Pk3_OC	0.0698	0.0959	0.1352	0.1888	0.2727	0.4003	0.5451
Pk4_OC	0.0080	0.0167	0.0336	0.0600	0.0999	0.1671	0.2536
PyrolC	0.0000	0.0000	0.0000	0.0000	0.0037	0.0188	0.0321

Trace Elements by XRF

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Aluminum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0041	0.0080
Antimony	0.0000	0.0000	0.0000	0.0000	0.0014	0.0045	0.0076
Arsenic	0.0000	0.0000	0.0000	0.0000	0.0002	0.0007	0.0011
Barium	0.0000	0.0000	0.0000	0.0000	0.0006	0.0085	0.0201
Bromine	0.0000	0.0000	0.0000	0.0000	0.0003	0.0008	0.0012
Cadmium	0.0000	0.0000	0.0000	0.0000	0.0005	0.0021	0.0045
Calcium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0013	0.0026
Cerium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0031	0.0224
Cesium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0027	0.0096

Table 5-9. (Continued)

Trace Elements by XRF (continued)

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Chlorine	0.0000	0.0000	0.0000	0.0000	0.0001	0.0007	0.0012
Chromium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0011	0.0015
Cobalt	0.0000	0.0000	0.0000	0.0000	0.0002	0.0006	0.0008
Copper	0.0000	0.0000	0.0000	0.0000	0.0003	0.0009	0.0014
Europium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0005	0.0009
Gallium	0.0000	0.0000	0.0000	0.0001	0.0005	0.0010	0.0016
Gold	0.0000	0.0000	0.0000	0.0000	0.0004	0.0015	0.0034
Hafnium	0.0000	0.0000	0.0000	0.0000	0.0003	0.0008	0.0015
Indium	0.0000	0.0000	0.0000	0.0000	0.0006	0.0025	0.0055
Iridium	0.0000	0.0000	0.0000	0.0000	0.0003	0.0010	0.0019
Iron	0.0000	0.0000	0.0000	0.0002	0.0011	0.0032	0.0070
Lanthanum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0055	0.0194
Lead	0.0000	0.0000	0.0000	0.0000	0.0004	0.0013	0.0025
Magnesium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0028	0.0090
Manganese	0.0000	0.0000	0.0000	0.0000	0.0002	0.0008	0.0012
Mercury	0.0000	0.0000	0.0000	0.0000	0.0002	0.0011	0.0027
Molybdenum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0019
Nickel	0.0000	0.0000	0.0000	0.0000	0.0003	0.0008	0.0011
Niobium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0008	0.0019
Phosphorus	0.0000	0.0000	0.0000	0.0000	0.0003	0.0012	0.0021
Potassium	0.0000	0.0000	0.0000	0.0000	0.0005	0.0013	0.0021
Rubidium	0.0000	0.0000	0.0000	0.0000	0.0003	0.0008	0.0011
Samarium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0006	0.0012
Scandium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007	0.0013
Selenium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0009	0.0013
Silicon	0.0000	0.0000	0.0000	0.0000	0.0006	0.0025	0.0142
Silver	0.0000	0.0000	0.0000	0.0000	0.0007	0.0025	0.0053
Sodium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0079	0.0301
Strontium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0010	0.0013
Sulfur	0.0000	0.0000	0.0000	0.0001	0.0014	0.0022	0.0044
Tantalum	0.0000	0.0000	0.0000	0.0000	0.0003	0.0014	0.0041
Terbium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0009	0.0012
Tin	0.0000	0.0000	0.0000	0.0000	0.0012	0.0044	0.0084
Titanium	0.0000	0.0000	0.0000	0.0001	0.0005	0.0013	0.0016
Vanadium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0009	0.0013
Wolfram	0.0000	0.0000	0.0000	0.0001	0.0005	0.0023	0.0049
Yttrium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0011	0.0015
Zinc	0.0000	0.0000	0.0000	0.0000	0.0002	0.0007	0.0011
Zirconium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0008	0.0017

Notes: All units are micrograms per cubic meter.

Trip and Field Blanks During 2005 -- For XRF analysis, some of the largest values (95 percentile) belong to sodium, silicon, and iron. Several additional elements such as cerium, lanthanum, etc. also have large 95th percentile values, but these are unlikely to be present, and probably represent XRF instrument artifacts. Sodium may be high because it is a light element which means that accurate determination by XRF is problematic. One of the samplers, the R&P speciation sampler, uses sodium carbonate in the denuder for the nylon filter channel, which could potentially cause sodium contamination. RTI is currently running tests to gather more information on this potential problem. Iron is also a potential contaminant in some of the sampler types that use metal modules or inlet hardware. Potential contamination by sodium and iron will be discussed in the next section.

5.4.1 Outliers by Sampler Type

Table 5-10 shows 95th percentile values for EC, iron, and sodium ion for the four different sampler types that were in use during 2005. These three analytes showed outliers that are probably related to materials used in the construction of the samplers' inlets or filter modules. These are shown in bold in the Table.

- Elemental carbon for the R&P 2300 (RPSPEC) sampler is higher than for other samplers. This phenomenon has been reported previously, and is suspected to be the result of the use of silicone stopcock grease in the size-selective impactor that is built into the sampling modules. Little can be done to alleviate this problem without a significant redesign of the R&P 2300 size-selective inlets. Data users should be aware of this problem and screen their EC data for unusually high values. RTI cannot screen for high EC values in the routine (exposed) filter data because natural variability is large enough to mask most of the EC outliers.

- Iron outliers for the MetOne SASS sampler which occur occasionally may be due to stainless steel module. Although the iron outliers are easy to detect in the blank data, it would be very difficult to screen for this artifact in the routine filter data because natural variability is large enough to mask most of the outliers.

- Sodium ion levels for the R&P 2300 sampler are significantly higher than other types, possibly because of sodium carbonate denuder. Other samplers use magnesium oxide denuders.

5.4.2 Trends and Offsets in Blank Data

Other than the isolated outliers identified in the previous section, no significant trends or offsets have been observed in the trip and field data for any of the STN analytes.

Table 5-10. Outliers by Sampler Type for Selected Analytes

Analyte	Sampler	N	MEAN	MEDIAN	95th Pct.	Notes
EC	MASS	226	0.0043	0.0001	0.0245	
EC	RAAS	348	0.0125	0.0003	0.0564	
EC	**RPSPEC**	**217**	**0.0424**	**0.0008**	**0.3250**	1
EC	SASS	2641	0.0147	0.0005	0.0840	
Iron	MASS	225	0.0004	0.0001	0.0017	
Iron	RAAS	347	0.0006	0.0000	0.0021	
Iron	RPSPEC	218	0.0006	0.0001	0.0031	
Iron	**SASS**	**2640**	**0.0026**	**0.0003**	**0.0091**	2
Sodium Ion	MASS	225	0.0047	0.0023	0.0143	
Sodium Ion	RAAS	348	0.0086	0.0000	0.0333	
Sodium Ion	**RPSPEC**	**217**	**0.1413**	**0.0267**	**0.6440**	3
Sodium Ion	SASS	2641	0.0137	0.0000	0.0634	

Notes:

1 EC for RPSPEC sampler is higher than other samplers

2 Iron for the SASS module is higher than others possibly due to stainless steel module and low flow ratio

3 Sodium ion for the RPSPEC sampler is significantly higher than other types, possibly because of NaCO3 denuder.

6.0 External Audits

6.1 Performance Evaluation Audit Results

The RTI Laboratories participated in two performance audits sponsored by EPA (Appendices C and D.) These were as follows:

Author/Organization	Report Title, Date	Description	Conclusions/Findings
Jewell Smiley - EPA/NAREL (Appendix D)	Experimental Inter-comparison of Speciation Laboratories, September 19, 2005	Intercomparison of four laboratories currently providing PM2.5 speciation results for gravimetric mass, IC, OC/EC, and XRF.	RTI results were acceptable. Issue of lack of comparability of XRF uncertainty estimates was noted.
Steve Taylor EPA/NAREL (Appendix C)	Gravimetric Inter-Laboratory Comparison Study, November 23, 2005	Intercomparison of five different laboratories.	RTI results satisfactory.

6.2 System Audit Results

On July 12, 2005, a laboratory audit was conducted by National Air and Radiation Environmental Laboratory (NAREL) personnel. The audit report was received on November 4, 2005. The US EPA audit team included Eric Boswell and Jewell Smiley, with Dennis Crumpler and Joann Rice from the Office of Air Quality Planning and Standards (OAQPS). Solomon Ricks and Jeff Lance were also present during the audit as EPA observers. The audit included interviews and observations in the following areas:

- Gravimetric Laboratory
- Organic Carbon/Elemental Carbon (OC/EC) Laboratory
- X-ray Fluorescence (XRF) Laboratory
- Ion Chromatography (IC) Laboratory
- Sample Handling and Archiving Laboratory (SHAL)
- Program Management
- Quality Assurance
- Data Management

There were three major findings in the audit report (Appendix E), which are summarized in Table 6-1, along with RTI comments.

Table 6-1. Systems Audit Findings and Responses

No.	Audit Comment	RTI Response
1	Two Teflon® filters were removed from the SHAL inventory during the audit so that NAREL could experimentally re-measure the tare mass already determined at RTI's gravimetric lab. ... NAREL's tare mass was an alarming 30 micrograms smaller for one of the filters. Comment: This finding may be an indication of serious problems like the bad filter lot that was discovered several weeks before this audit. According to the corrective action report, the bad filter lot produced negative trip and field blanks. The questionable filter would have produced this effect if it had been utilized as a trip or field blank. RTI should continue to monitor the situation and explore potential reasons for the large variability in blank filters.	RTI recognized that there was a problem with a certain filter lot from Whatman, which was replaced at RTI's request. New filter reweighing procedures have been implemented which require 33+% replicate initial (tare) weighings, and 100% reweighings of exposed filters (postweighing).
2	All of the routine OC/EC duplicates are analyzed using the same instrument that performed the original analysis. This practice was acceptable in the past when the daily sucrose spikes were able to provide evidence of acceptable between-instrument performance. Now that OC subfractions are reported, there is no daily QC that provides the necessary assurance of acceptable between-instrument precision. Recommendation. RTI should schedule some of the routine OC/EC duplicates for analysis using a different instrument. For example, half of the scheduled duplicates could be analyzed using the same instrument, and the remaining duplicates could be analyzed using one of the available instruments that did not perform the original analysis.	The RTI OC/EC laboratory has implemented daily between-instrument precision checks.

Table 6-1. (Continued)

No.	Audit Comment	RTI Response
3	As stated earlier, the focus of the XRF audit was to discuss those samples that RTI had analyzed as part of a recent inter-laboratory comparison study sponsored by NAREL ... Results from this study showed aluminum to be the most controversial element reported. This study also showed that RTI generally reported uncertainties which were lower than those reported by the other participating labs. A few spectra were inspected and discussed during the audit. Two specific spectra were selected to be included in the final report for the study. Ultimately the final report included examples of the controversial spectra from all of the labs. The spectra from RTI contain a significant [diffusion peak] interference for aluminum and silicon which was not observed in the spectra from the other labs. Comment: This observation may not be a problem for RTI's analysis since there is no standard method for calculating XRF uncertainties. However, RTI may want to take a closer look at the way uncertainties were calculated for aluminum and silicon during this study. EPA has recently initiated dialog with all of the speciation labs to learn more about the XRF analysis at each lab, and clearly there is diversity among the different labs. Any progress toward standardizing the XRF analysis is a positive step for the speciation program.	RTI is currently researching the question of XRF uncertainties for fine particle analysis. We have discovered that of the several major laboratories currently conducting such analyses (including Chester Labnet, Cooper Environmental Services, the University of California at Davis, the Desert Research Institute, and RTI) there is no uniform consensus on how uncertainties are to be calculated and what components of uncertainty are included. Dr. Bill Gutknecht, director of the RTI laboratory group, is preparing an analysis report that will make recommendations for XRF uncertainty reporting.

6.3 Synoptic Summary of 2005 Speciation Trends and IMPROVE Network Audits

During 2005, EPA performed field audits at 16 sites (19 total samplers). Appendix F provides results of these audits. *Note that this is preliminary data. As of March 1, 2006, the final audit report has not been received from EPA.*

7.0 List of References

7.1 List of Current STN Documents

Type	Title	Date Revised	Author
SOP	Gravimetric Analysis	7/8/2005	Greene
SOP	Cleaning Nylon Filters Used for Collection of PM2.5 Material	8/14/2003	Hardison, E.
SOP	XRF Analysis of PM2.5 Deposits on Teflon Filters	8/14/2003	McWilliams
SOP	R&P Speciation Sampler Chemcomb Denuders with Sodium Carbonate	8/14/2003	Eaton
SOP	Coating and Extracting Annular Denuders with Sodium Carbonate	8/14/2003	Eaton
SOP	Coating Annular Denuders with XAD-4 Resin	8/14/2003	Eaton
SOP	Coating Aluminum Honeycomb Denuders with MgO	8/14/2003	Eaton
SOP	Sample Preparation and Analysis of PM20 and PM2.5 Samples by SEM	8/14/2003	Crankshaw
SOP	Coating Annular Denuders with MgO	8/15/2003	Eaton
SOP	Database Operations	7/11/2005	Rickman
SOP	Disaster Recovery Plan--RTI CONFIDENTIAL	7/6/2005	Rickman
SOP	Anion Analysis	8/14/2003	Hardison, E.
SOP	Cation Analysis	8/14/2003	Hardison, E.
SOP	Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters	7/7/2005	Hardison, E.
SOP	Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer	8/14/2003	Peterson
SOP	Sample Handling and Archiving Laboratory (SHAL)	7/11/2005	O'Rourke
SOP	Long-Term Archiving of PM2.5 Filters and Extracts	7/5/2002	Haas, C.
SOP	Assign Field Sample Flags for the Chemical Speciation Trends Network	7/7/2005	Wall, C.
SOP	Document Control and Storage	7/6/2005	Haas, D.
SOP	Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples	6/1/2000	DRI
SOP	Analysis of SVOC by GC/MS	7/1/2003	DRI
SOP	Analysis of Elements in Air Particulates by XRF (Kevex 770)	7/3/2003	Chester
SOP	Kevex XRF Spectrometer Calibration	7/3/2003	Chester
SOP	Kevex XRF Spectrometer Data Generation, Interpretation and Reporting Chester Labnet Proprietary Method	10/17/2002	Chester
SOP	Analysis of Elements in Air Particulates by XRF (Kevex 771)	8/6/2003	Chester
SOP	Sample Receipt and Log In	11/18/2002	Chester
QAPP	QAPP for PM2.5 of Chemical Speciation Samples	9/11/2005	RTI
Data	Semi-Annual Data Summary Report	5/12/2005	RTI
Data	Annual Data Summary Report	2/28/2006	RTI

7.2 Special Reports Issued During the Reporting Period

Type	Title	Date Revised	Author	Document No.
Data	Semi-Annual Data Summary Report	5/12/2005	RTI	RTI/08858/03QAS
Data	Annual Data Summary Report	2/28/2006	RTI	RTI/08858/04QAS
Report	Teflon Filter Manufacturing Defects March - April 2005	7/8/2005	RTI	RTI/08858/12/03S
Report	Tests of Acceptance of XRF Instrument #3 Operated by RTI	11/1/05	RTI	RTI/0208858/02/02D

List of Appendices

Appendix A

Method Detection Limits

Maximum Detection Limits by Analysis and Analyte

Analysis	Analyte	Mass (μg)	Concentration (ug/m^3) by Sampler Type			
			MASS	RASS	R and P	SASS
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.16	0.0072	0.017	0.012	0.019
Cations - PM2.5 (NH4, Na, K)	Potassium	0.13	0.006	0.014	0.0097	0.016
Cations - PM2.5 (NH4, Na, K)	Sodium	0.29	0.013	0.031	0.021	0.034
Mass - PM2.5	Particulate matter 2.5u	7.2	0.32	0.33	0.31	0.83
Nitrate - PM2.5	Nitrate	0.084		0.0089	0.0061	0.0098
Nitrate - PM2.5 (MASS/nylon)	Nitrate	0.084	0.0038			
Nitrate - PM2.5 (MASS/Teflon)	Nitrate	0.084	0.0038			
Organic and elemental carbon	Elemental carbon	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	Organic carbon	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	Pk1_OC	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	Pk2_OC	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	Pk3_OC	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	Pk4_OC	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	PyrolC	2.4	0.10	0.24	0.17	0.27
Organic and elemental carbon	Total carbon	2.4	0.10	0.24	0.17	0.27
Sulfate - PM2.5	Sulfate	0.12	0.0054	0.013	0.0087	0.014
Trace elements	Aluminum	0.22	0.0099	0.0098	0.0094	0.025
Trace elements	Antimony	0.38	0.017	0.017	0.016	0.042
Trace elements	Arsenic	0.037	0.00065	0.0016	0.0016	0.0041
Trace elements	Barium	0.85	0.0046	0.039	0.037	0.097
Trace elements	Bromine	0.031	0.00057	0.0014	0.0013	0.0034
Trace elements	Cadmium	0.17	0.0073	0.0076	0.0071	0.019
Trace elements	Calcium	0.073	0.0032	0.0033	0.0031	0.0082
Trace elements	Cerium	1.2	0.0041	0.056	0.054	0.14
Trace elements	Cesium	0.53	0.0048	0.024	0.023	0.061
Trace elements	Chlorine	0.13	0.0035	0.0058	0.0057	0.015
Trace elements	Chromium	0.025	0.0011	0.0011	0.0011	0.0028
Trace elements	Cobalt	0.02	0.00061	0.00091	0.00087	0.0023
Trace elements	Copper	0.024	0.0011	0.0011	0.0011	0.0028
Trace elements	Europium	0.16	0.0021	0.0074	0.007	0.018
Trace elements	Gallium	0.071	0.0012	0.0031	0.003	0.0079
Trace elements	Gold	0.13	0.0017	0.0056	0.0054	0.014
Trace elements	Hafnium	0.38	0.012	0.017	0.016	0.043
Trace elements	Indium	0.16	0.0067	0.0074	0.0071	0.019
Trace elements	Iridium	0.17	0.0018	0.0073	0.0071	0.019
Trace elements	Iron	0.028	0.00092	0.0013	0.0012	0.0032
Trace elements	Lanthanum	1	0.0038	0.046	0.044	0.11
Trace elements	Lead	0.085	0.0012	0.0038	0.0037	0.0096
Trace elements	Magnesium	0.43	0.0079	0.019	0.018	0.048
Trace elements	Manganese	0.033	0.00081	0.0015	0.0014	0.0038
Trace elements	Mercury	0.065	0.0015	0.0029	0.0028	0.0073
Trace elements	Molybdenum	0.085	0.0037	0.0037	0.0036	0.0095

Maximum Detection Limits by Analysis and Analyte

Analysis	Analyte	Mass (µg)	Concentration (ug/m^3) by Sampler Type			
			MASS	RASS	R and P	SASS
Trace elements	Nickel	0.018	0.00074	0.00082	0.00078	0.002
Trace elements	Niobium	0.067	0.0015	0.003	0.0029	0.0075
Trace elements	Phosphorus	0.15	0.0068	0.0071	0.0066	0.017
Trace elements	Potassium	0.11	0.0048	0.0048	0.0046	0.012
Trace elements	Rubidium	0.031	0.00084	0.0014	0.0014	0.0036
Trace elements	Samarium	0.089	0.0021	0.004	0.0039	0.01
Trace elements	Scandium	0.12	0.0055	0.0055	0.0052	0.014
Trace elements	Selenium	0.033	0.0011	0.0014	0.0014	0.0037
Trace elements	Silicon	0.18	0.008	0.008	0.0077	0.021
Trace elements	Silver	0.15	0.0055	0.0069	0.0066	0.017
Trace elements	Sodium	1.6	0.024	0.07	0.068	0.18
Trace elements	Strontium	0.036	0.001	0.0016	0.0016	0.0041
Trace elements	Sulfur	0.2	0.0042	0.009	0.0087	0.023
Trace elements	Tantalum	0.28	0.0033	0.013	0.012	0.032
Trace elements	Terbium	0.11	0.0019	0.0049	0.0047	0.012
Trace elements	Tin	0.26	0.0087	0.012	0.011	0.029
Trace elements	Titanium	0.051	0.0022	0.0023	0.0022	0.0057
Trace elements	Vanadium	0.037	0.0016	0.0017	0.0016	0.0041
Trace elements	Wolfram	0.21	0.0027	0.0092	0.0089	0.023
Trace elements	Yttrium	0.044	0.00096	0.002	0.0019	0.005
Trace elements	Zinc	0.025	0.0011	0.0011	0.0011	0.0029
Trace elements	Zirconium	0.054	0.0014	0.0024	0.0023	0.006

1. Individual laboratory instruments used for analysis may have differing MDL values. The maximum values are shown to permit comparison of detection limits among differing species.
2. Concentration detection limits vary among sampler types due to differing sample volumes.

Appendix B

Data Completeness Summary

Table B-1 Total Number of Sampling Events Included in each Reporting Batch

Sampling Events by Report Batch

Report Batch	Samples	Blanks		Total
		Field	Trip	
60	1,460	212	37	1,709
61	1,274	79	206	1,559
62	1,387	279	33	1,699
63	1,312	211	48	1,571
64	1,384	77	279	1,740
65	1,387	2	57	1,446
66	1,380	290	68	1,738
67	1,479	72	107	1,658
68	1,293	212	53	1,558
69	1,464	216	36	1,716
70	1,490	5	261	1,756
71	1,385	282	29	1,696
72	1,342	74	81	1,497
Total	18,037	2,011	1,295	21,343

Table B-2 Total Number of Records Delivered by Type

Records Posted by Report Batch

Report Batch	Samples	Blanks		Total
		Field	Trip	
60	166,980	24,312	4,269	195,561
61	145,712	8,913	23,452	178,077
62	158,716	31,881	3,764	194,361
63	150,085	24,191	5,454	179,730
64	157,989	8,681	31,975	198,645
65	158,643	226	6,495	165,364
66	157,946	33,162	7,660	198,768
67	169,044	8,128	12,124	189,296
68	148,011	24,362	6,037	178,410
69	167,387	24,782	4,055	196,224
70	170,683	548	29,967	201,198
71	158,407	32,223	3,298	193,928
72	153,303	8,348	9,396	171,047
Total	2,062,906	229,757	147,946	2,440,609

Table B-3. Percentage of Routine Exposure Records – STN Sites

Monthly Percent Data Completeness by Site – STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
20th St. Fire Station	120861016	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	63.6	100.0	84.3	100.0
Allen Park	261630001	5	SASS	100.0	90.0	100.0	100.0	100.0	100.0	100.0	100.0	90.0	90.0
Bakersfield-California Ave	060290014	5	SASS	88.9	90.0	0.0	71.4	70.0	88.9	93.4	75.0	100.0	88.9
Bakersfield-California Ave (Collocated)	060290014	6	SASS	88.9	90.0	0.0	37.5					100.0	79.0
Beacon Hill	530330080	6	MASS	99.3	99.6	99.7	92.6	80.0	100.0	100.0	88.9	100.0	100.0
Blair Street	295100085	6	SASS	100.0	100.0	100.0	93.4	100.0	100.0	100.0	99.2	93.1	90.0
Burlington	500070012	5	SASS	75.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Capitol	220330009	5	MASS	0.0	100.0	88.8	97.7	88.8	76.3	91.8	100.0	88.9	79.9
Chamizal	481410044	5	MASS	90.0	100.0	80.1	34.8	55.1	45.1	100.0	100.0	100.0	90.0
Chicopee	250130008	5	SASS	72.7	100.0	99.2	93.4	90.0	100.0	99.9	99.3	99.7	100.0
Com ED	170310076	5	MASS	86.5	88.9	100.0	100.0	100.0	100.0	92.1	100.0	100.0	99.8
Commerce City	080010006	5	SASS	100.0	100.0	100.0	91.0	85.7	100.0	92.7	100.0	100.0	100.0
CPW	450190049	5	SASS	100.0	92.7	100.0	100.0	100.0	100.0	100.0	100.0	81.8	99.9
Criscuolo Park	090090027	5	SASS	85.7	99.7	60.1	25.7	77.8	77.8	72.7	66.7	100.0	88.9
Deer Park	482011039	6	MASS	100.0	100.0	83.2	99.1	100.0	90.9	98.1	100.0	100.0	88.9
Deer Park (Collocated)	482011039	7	MASS	42.1	25.1	69.0	83.7	100.0				100.0	88.9
Dover	100010003	5	SASS	80.0	100.0	100.0	100.0	100.0	100.0	85.4	100.0	80.0	100.0
El Cajon	060730003	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Elizabeth Lab	340390004	5	SASS	84.2	99.3	75.0	100.0	99.6	99.1	99.3	99.6	100.0	86.2
Fairbanks State Bldg	020900010	6	SASS				100.0	100.0	100.0	100.0	99.8		83.3
Fargo NW	380171004	5	SASS	100.0	100.0	99.8	93.4	100.0	99.7	93.4	83.7	100.0	100.0
Fresno - First Street	060190008	5	SASS	85.2	86.2	99.2	84.3	100.0	100.0	100.0	90.7	100.0	100.0
G.T. Craig	390350060	5	SASS	100.0	99.8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
G.T. Craig - Collocated	390350060	6	SASS	83.3	88.9	87.5	100.0	89.6	100.0	100.0	61.0	100.0	100.0
Garinger High School	371190041	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	98.4	100.0	100.0	100.0
Guaynabo	720610005	5	SASS	100.0	100.0	100.0	100.0	90.0	100.0	90.4	85.9	90.9	90.0
Gulfport	280470008	5	SASS	100.0	100.0	88.6	98.0	99.8	100.0	99.9	100.0	44.4	
Guthrie	471570047	5	RAAS	100.0	100.0	98.8	100.0	100.0	100.0	100.0	99.2	60.5	99.3

Monthly Percent Data Completeness by Site – STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch 61	62	63	64	65	66	67	68	69	70
Hawthorne	490353006	5	SASS	90.0	99.9	100.0	90.0	99.0	90.0	100.0	100.0	100.0	100.0
Henrico Co.	510870014	5	SASS	100.0	88.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hinton	481130069	5	MASS	100.0	99.8	100.0	100.0	100.0	87.5	100.0	100.0	100.0	100.0
JFK Center	202090021	5	SASS	100.0	100.0	100.0	100.0	81.7	87.5	100.0	85.7	100.0	87.5
Lawrenceville	420030008	6	SASS	100.0	100.0	87.5	92.7	87.5	100.0	100.0	100.0	90.0	100.0
Lindon	490494001	5	SASS	100.0	100.0	100.0	100.0	100.0	98.5	100.0	100.0	100.0	100.0
McMillan Reservoir	110010043	5	RAAS	57.1	88.9	100.0	100.0	98.7	100.0	100.0	85.7	100.0	75.0
Missoula County Health Dept.	300630031	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	88.9	100.0	82.7
MLK	100032004	5	SASS	80.0	100.0	100.0	100.0	100.0	99.4	100.0	100.0	100.0	100.0
Nampa NNC	160270004	5	SASS	100.0	100.0	100.0	100.0	100.0	99.7	100.0	100.0	100.0	90.0
New Brunswick	340230006	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
New Brunswick (Collocated)	340230006	6	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	40.0	100.0	100.0
North Birmingham	010730023	5	SASS	100.0	100.0	100.0	100.0	100.0	99.9	100.0	100.0	90.8	100.0
NY Botanical Gardens	360050083	6	SASS	90.0	99.9	99.8	99.9	99.9	100.0	100.0	100.0	100.0	100.0
Peoria Site 1127	401431127	5	SASS	88.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	75.0
PHILA - AMS Laboratory	421010004	7	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	90.0
Philips	270530963	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	99.1	100.0	100.0	90.0
Phoenix Supersite	040139997	7	SASS	90.0	100.0	100.0	100.0	100.0	100.0	90.9	100.0	93.4	99.9
Portland N. Roselawn	410510246	6	SASS	100.0	99.3	88.9	100.0	100.0	99.7	100.0	100.0	100.0	100.0
Portsmouth	330150014	5	RAAS	100.0	99.0	100.0	90.0	100.0	97.9	90.9	88.9	100.0	100.0
Reno	320310016	5	SASS	88.9	100.0	100.0	100.0	100.0	99.9	100.0	100.0	100.0	100.0
Riverside-Rubidoux	060658001	5	SASS	100.0	90.0	100.0	90.9	100.0	100.0	100.0	87.5	99.8	99.8
Riverside-Rubidoux (Collocated)	060658001	6	SASS	100.0	82.7	100.0							
Roxbury (Boston)	250250042	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Roxbury (Boston) - collocated	250250042	6	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sacramento - Del Paso Manor	060670006	5	SASS	100.0	100.0	98.8	100.0	100.0	100.0	100.0	100.0	100.0	100.0
San Jose - Jackson Street	060850005	5	SASS	100.0	88.9	100.0	100.0	87.5	100.0	100.0	100.0	100.0	100.0
SER-DNR Headquarters	550790026	5	SASS	100.0	80.0	100.0	100.0	99.9	100.0	100.0	88.9	100.0	100.0
Simi Valley	061112002	5	SASS	80.0	100.0	100.0	40.0	40.0	100.0	100.0	80.0	100.0	65.9
South DeKalb	130890002	5	RAAS	100.0	90.0	100.0	100.0	100.0	100.0	100.0	87.7	100.0	100.0
Springfield Pumping Station	170310057	5	RAAS	100.0	80.0	100.0	100.0	100.0	99.4	98.5	100.0	98.5	96.3

Monthly Percent Data Completeness by Site – STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
Sydney	120573002	5	SASS	100.0	100.0	99.8	100.0	100.0	100.0	100.0	98.0	99.0	99.3
Urban League	440070022	5	RAAS	97.9	66.7	100.0	100.0	87.5	100.0	90.0	100.0	90.0	100.0
Washington Park	180970078	5	SASS	100.0	100.0	100.0	100.0	86.2	100.0	100.0	100.0	100.0	100.0
Woolworth St	310550019	5	SASS	96.4	96.0	96.8	86.2	97.0	84.9	96.9	97.0	97.0	84.9
WV - Guthrie Agricultural Center	540390011	5	SASS	100.0	100.0	100.0	90.9	100.0	100.0	100.0	100.0	100.0	100.0

Table B-4. Percentage of Routine Exposure Records – Non-STN Sites

Monthly Percent Data Completeness by Site – Non-STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
5 Points	391530023	5	SASS	100.0	78.5	100.0	100.0	18.5	80.0	100.0	100.0	100.0	50.0
AL - Phenix City	011130001	5	SASS				50.0	100.0	100.0	100.0	81.8	100.0	100.0
Alton	171192009	5	R & P 2300	0.0									
Alton	171192009	5	SASS	96.3	80.0	80.0	100.0	100.0	100.0	100.0	80.0	80.0	100.0
APCD (Barret)	211110048	5	SASS	100.0	99.7	100.0	60.0	100.0	100.0	99.7	100.0	100.0	100.0
Arendtsville	420010001	5	SASS	100.0	100.0	100.0	100.0	100.0	60.0	100.0	100.0	100.0	99.8
Army Reserve Center	191130037	5	R & P 2300	97.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Arnold	290990012	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	99.9	76.5	98.5	98.5
Ashland Health Department	210190017	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.9	100.0	100.0
Athens	130590001	5	RAAS	75.8	80.0	100.0	70.7	70.7	100.0	80.0	81.8	100.0	100.0
Augusta	132450091	5	RAAS	100.0	100.0	100.0	100.0	100.0	100.0	80.0	80.0	95.8	100.0
Bates House (USC)	450790019	5	SASS	100.0	100.0	100.0	100.0	100.0	80.0	99.7	97.9	40.0	83.3
Bismarck Residential	380150003	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bonne Terre	291860005	5	R & P 2300	100.0	70.0	87.5	90.9	70.0	100.0	100.0	80.8	90.9	82.7
Bountiful	490110004	5	SASS	100.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	80.0	83.3
Bowling Green-Kereiakes Park	212270007	5	SASS	100.0	100.0	100.0	100.0	80.0	100.0	97.9	100.0	100.0	100.0
Bristol	515200006	5	SASS	100.0	81.8	100.0	100.0	100.0	100.0	100.0	80.0	100.0	100.0
Buffalo	360290005	6	R & P 2300	100.0	100.0	100.0	97.9	97.9	100.0	96.4	100.0	100.0	100.0
Buncombe County Board of Education	370210034	5	SASS	80.0	100.0	100.0	100.0	100.0	80.0	60.0	100.0	100.0	100.0
Camden	340070003	5	SASS	100.0	100.0	100.0	99.2	100.0	100.0	99.9	100.0	100.0	99.6
Canal St. Post Office	360610062	5	SASS	100.0	90.0	99.2	99.1	99.9	100.0	84.3	79.6	100.0	89.7
Canton Fire Station	391510017	5	SASS	0.0	0.0	100.0	100.0	100.0	96.4	100.0	77.9	100.0	100.0
Canton Health Dept.	391510020	5	SASS	100.0									
Cape Romain	450190046	5	SASS	100.0	90.0	100.0	100.0	77.8	90.0	81.8	100.0	100.0	100.0
Chester	340273001	5	SASS	100.0	88.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	75.0
Chester (PA)	420450002	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	80.0	100.0

Monthly Percent Data Completeness by Site – Non-STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
Chesterfield	450250001	5	SASS	98.5	100.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	82.1
Chickasaw	010970003	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	77.9	100.0	80.0	100.0
Children's Park	040191028	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	80.0	100.0
Chiwaukee Prairie Site	550590019	5	SASS	100.0	100.0	100.0	85.4	100.0	100.0	100.0	100.0	77.9	100.0
Clio	010050002	5	SASS	80.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Columbus	132150011	5	RAAS	100.0	100.0	79.7	41.8	100.0	100.0	100.0	100.0	100.0	100.0
Courthouse Annex-Libby	300530018	5	SASS	80.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Covington - University College	211170007	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	80.0	100.0
Crossett	050030005	5	SASS	100.0	80.0	100.0	60.0	100.0	0.0				
Crown Z	530630016	5	RAAS	100.0	100.0	60.0	80.0	100.0	100.0	100.0	85.4	100.0	100.0
Dearborn	261630033	5	SASS	100.0	80.0	100.0	100.0	81.8	79.4	80.0	100.0	100.0	100.0
Decatur	011030011	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.9	80.0	100.0
Del Norte	350010023	5	R & P 2300	100.0	100.0	85.4	100.0	100.0	100.0	80.0	100.0	100.0	100.0
Douglas	130690002	5	RAAS	100.0	100.0	97.9	85.4	100.0	100.0	100.0	100.0	100.0	100.0
Duwamish	530330057	6	RAAS	100.0	85.4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Elkhart Pierre Moran	180390003	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	85.4	100.0	100.0	100.0
Ellis County WMA	400450890	5	SASS	100.0	100.0	99.7	100.0	80.0	60.0	80.0	100.0	100.0	100.0
Ellyson	120330004	6	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	84.8
Elmwood	421010136	5	SASS	77.0	99.7	60.0	80.0	100.0	100.0	100.0	80.0	100.0	100.0
Erie	420490003	5	SASS	54.3	100.0	100.0	100.0	81.8	85.4	100.0	100.0	100.0	100.0
Essex - Met One	240053001	5	SASS	100.0	100.0	100.0	100.0	87.5	100.0	90.0	100.0	100.0	100.0
Evansville - Mill Road	181630012	5	SASS	80.0	80.0	80.0	100.0	100.0	100.0	100.0	41.5	100.0	83.3
Florence	421255001	5	SASS	80.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	80.0	100.0
Fort Wayne CAAP	180030004	5	SASS	100.0									
Freemansburg	420950025	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Gary Iitri	180890022	5	SASS	100.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	100.0	66.7
General Hospital	390870010	5	SASS	100.0	100.0	99.7	100.0	80.0	100.0	100.0	9.0	85.4	83.3
Grand Junction - Powell Building	080770017	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Grand Rapids	260810020	5	SASS	99.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0	80.0	83.3
Greensburg	421290008	5	SASS	100.0	99.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Monthly Percent Data Completeness by Site – Non-STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch 61	62	63	64	65	66	67	68	69	70
Grenada	280430001	5	SASS	0.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	100.0	80.0
Hammond Purdue	180892004	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Harrisburg	420430401	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	68.2
Hattie Avenue	370670022	5	SASS	100.0	99.7	100.0	100.0	80.0	100.0	100.0	100.0	100.0	100.0
Hattiesburg	280350004	5	SASS	100.0	100.0	100.0	100.0	99.7	99.7	99.7	99.1	60.0	99.3
Haynes Pt.	110010042	6	RAAS	100.0	100.0	98.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hazard - Perry County Horse Park	211930003	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.9	100.0	100.0
Head Start	390990014	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hendersonville	471650007	5	SASS	80.0	100.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	83.3
Hickory	370350004	5	SASS	100.0	100.0	100.0	80.0	100.0	100.0	80.0	100.0	100.0	100.0
Holland	260050003	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Houghton Lake	261130001	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	80.0	80.0	100.0	100.0
HU-Beltsville	240330030	5	RAAS	100.0	100.0	80.0	100.0	80.0	80.0	100.0	100.0	100.0	100.0
Huntsville Old Airport	010890014	5	SASS	100.0	100.0	100.0	100.0	80.0	100.0	100.0	81.8	100.0	100.0
IL - Decatur	171150013	5	SASS	83.3	97.9	96.4	100.0	100.0	80.0	100.0	100.0	100.0	100.0
IS 52	360050110	5	R & P 2300	100.0	99.3	100.0	99.1	98.2	100.0	89.8	87.7	98.9	99.9
Jackson Hinds Co.	280490018	5	SASS	100.0	100.0	99.7	80.0	100.0	100.0	100.0	100.0	40.0	100.0
Jasper Post Office	180372001	5	SASS	50.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Jefferson Elementary (10th and Vine)	191630015	5	R & P 2300	100.0	90.0	100.0	90.9	100.0	92.7	100.0	88.9	45.5	30.0
Kalamazoo	260770008	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Kelo	460990006	5	SASS	99.7	98.5	95.5	95.5	95.5	95.5	95.5	97.6	100.0	100.0
Kingsport	471631007	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	83.3
Lake Forest Park	530330024	6	RAAS	100.0	100.0	100.0	100.0	100.0	99.7	80.0	100.0	100.0	100.0
Lancaster	420710007	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Laurel	280670002	5	SASS	100.0	80.0	100.0	85.4	100.0	100.0	100.0	100.0	60.0	100.0
Lawrence County	470990002	5	SASS	100.0	100.0	83.3	80.0	100.0	80.0	80.0	100.0	100.0	100.0
Lenoir Community College	371070004	5	SASS	25.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Lexington Health Department	210670012	5	SASS	100.0	97.9	100.0	100.0	100.0	77.0	100.0	80.0	100.0	100.0
Lexington (NC)	370570002	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Liberty	290470005	5	R & P 2300	100.0	90.0	100.0	100.0	100.0	100.0	84.3	77.8	100.0	100.0

Monthly Percent Data Completeness by Site – Non-STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
Liberty (PA)	420030064	6	SASS	100.0	80.0	100.0	100.0	100.0	100.0	100.0	100.0	80.0	100.0
Lockeland School	470370023	5	RAAS	100.0	100.0	100.0	100.0	61.8	20.0	100.0	100.0	100.0	100.0
London-Laurel County	211250004	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Lorain	390933002	5	SASS	100.0									
Lorain County - OH	390930016	5	SASS	100.0	95.5	95.5	98.8	100.0	80.0	100.0	80.0	80.0	97.0
Luna Pier	261150005	5	SASS	100.0	99.1	80.0	100.0	100.0	80.0	99.4	80.0	100.0	97.0
Luray Airport	511390004	5	SASS	100.0	99.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Macon	130210007	5	RAAS	100.0	100.0	100.0	100.0	100.0	99.7	100.0	100.0	100.0	100.0
Manchester	330110020	5	RAAS	80.0	100.0	80.0	100.0	60.0	100.0	100.0	100.0	100.0	100.0
Manitowoc, Woodland Dunes site	550710007	5	SASS	100.0	100.0								
Maple Canyon	390490081	6	SASS	100.0	99.7	100.0	100.0	100.0	100.0	96.4	100.0	100.0	25.0
Mayville Hubbard Township site	550270007	5	SASS	100.0	100.0	100.0	99.3	100.0	100.0	90.0	99.2	100.0	100.0
Mendenhall	370810013	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	85.4	100.0	100.0
Middletown	390171004	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Millbrook	371830014	5	SASS	100.0	100.0	100.0	100.0	100.0	75.0			100.0	100.0
Mille Lacs	270953051	5	SASS	77.8	100.0	88.9	100.0	76.3	70.9	99.9	100.0		
MN - Rochester	271095008	5	SASS	100.0	100.0	100.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0
MOMS	011011002	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	80.0	100.0
Moundsville Armory	540511002	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Naperville	170434002	5	SASS	100.0	100.0	79.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0
New Garden	420290100	5	SASS	65.4	100.0	100.0	100.0	100.0	99.7	40.0	80.0	80.0	100.0
NLR Parr	051190007	5	SASS	100.0	40.0	98.8	81.8	70.7	99.7	100.0	80.0	100.0	66.7
North Los Angeles	060371103	5	SASS	95.8	100.0	80.0	100.0	100.0	97.9	100.0	100.0	100.0	100.0
Northbrook	170314201	5	SASS	100.0	100.0	80.0	85.4	100.0	100.0	85.4	100.0	100.0	100.0
OCUSA Campus	401091037	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Olive Street	530330048	6	RAAS	100.0	100.0	100.0	100.0	100.0	100.0	80.0	85.4	100.0	100.0
Owensboro - KY Wesleyan College	210590014	5	SASS	100.0									
Owensboro Primary	210590005	5	SASS	50.0	94.3	100.0	80.0	99.4	100.0	100.0	100.0	100.0	100.0
Paducah Middle School	211451004	5	SASS	100.0	100.0	78.5	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Monthly Percent Data Completeness by Site – Non-STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
Pearl City	150032004	5	SASS	100.0	80.0	40.0	80.0	100.0	100.0	80.0	100.0	100.0	99.5
PerkinstownCASNET	551198001	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Perry County	420990301	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Pinnacle State Park	361010003	5	R & P 2300	80.0	100.0	88.9	81.8	100.0	88.8	80.9	99.8	100.0	99.3
Platteville	081230008	5	SASS	100.0	100.0	100.0	80.0	100.0	99.7	80.0	100.0	100.0	100.0
Pleasant Green (Central MO)	290530001	5	R & P 2300	80.0	60.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	83.3
Providence	010731009	5	SASS	100.0	98.5	100.0	100.0	100.0	100.0	97.9	100.0	80.0	100.0
Public Health Building	191530030	5	R & P 2300	100.0	100.0	80.0	100.0	80.0	80.0	100.0	80.0	100.0	100.0
Queens College	360810124	6	R & P 2300	90.9	65.4	83.7	93.4	97.0	100.0	89.4	98.7	81.8	99.9
RBD	080410011	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.7	100.0
Roanoke	517700014	5	SASS	100.0									
Rochester Primary	360551007	5	R & P 2300	91.0	80.0	100.0	80.9	97.6	79.0	81.8	88.9	100.0	99.9
Rockwell	371590021	5	SASS		80.0	100.0	100.0	100.0	100.0	100.0	97.9	100.0	100.0
Rome	131150005	5	RAAS	100.0	80.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Rossville	132950002	5	RAAS				69.8	100.0	100.0	100.0	100.0	100.0	100.0
Sault Ste Marie	260330901	5	SASS	100.0	89.9	100.0	100.0	100.0	100.0	99.8	100.0	81.8	100.0
Savannah	130510017	5	RAAS										
Scranton	420692006	5	SASS	60.0	80.0	100.0	77.9	80.0	100.0	100.0	100.0	65.4	100.0
Searcy	051450001	5	SASS	100.0	100.0	100.0	60.0	100.0	0.0				
Senior Center	040137020	5	SASS		100.0	100.0	100.0	100.0	99.7	100.0	100.0	100.0	100.0
Shenandoah High School	180650003	5	SASS	100.0	100.0	100.0	80.0	100.0	100.0	100.0	85.4	97.9	83.3
Shreveport Airport	220150008	5	MASS	100.0	100.0	100.0	97.9	82.1	5.1	100.0	82.1	73.0	100.0
Skyview	121030026	5	SASS	98.5	98.0	100.0	100.0	87.5	100.0	100.0	100.0	100.0	100.0
South Bend CAAP	181411008	5	SASS	100.0									
South Charleston Library	540391005	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Southwick Community Center	211110043	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	83.3
Spring Hill Elementary School	470931020	5	RAAS	100.0	100.0	100.0	97.9	100.0	100.0	100.0	100.0	100.0	83.3
St Johns	040137003	5	SASS		100.0	100.0	100.0	81.5	80.0	81.7	100.0	100.0	100.0
St Theo	390350038	6	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	72.6
St. Paul Harding	271230871	5	SASS	80.0	100.0	100.0	100.0						

Monthly Percent Data Completeness by Site – Non-STN Sites

Location	AQS Site	POC	Sampler Type	Report Batch									
				61	62	63	64	65	66	67	68	69	70
State College	420270100	5	SASS	100.0	100.0	77.9	100.0	100.0	60.0	100.0	100.0	100.0	83.3
Steubenville	390810017	5	SASS	100.0	95.5		80.0	100.0	80.0	100.0	20.0	0.0	0.0
Sunrise Acres	320030561	5	SASS	85.4	100.0	100.0	100.0	100.0	99.7	100.0	100.0	100.0	100.0
Taft	390610040	5	SASS	100.0	100.0	100.0	100.0	80.0	100.0	100.0	100.0	100.0	100.0
Tallahassee Community College	120730012	5	SASS	100.0	100.0	100.0	100.0	80.0	100.0	100.0	100.0	60.0	100.0
Taylors Fire Station	450450009	5	SASS	100.0	100.0	100.0	100.0	100.0	99.7	100.0	100.0	100.0	100.0
Toledo Airport	390950026	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	85.4	83.9	100.0
TRNP - NU	380530002	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
UTC	470654002	5	SASS	100.0	80.0	100.0	100.0	100.0	89.6	100.0	100.0	100.0	83.3
VEI - Phoenix	040139998	5	SASS	100.0	96.4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	87.8
Waukesha, Cleveland Ave. Site	551330027	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	97.9	100.0	100.0	100.0
West Phoenix	040130019	5	SASS	100.0	100.0	100.0	99.1	100.0	100.0	80.0	80.0	100.0	100.0
Whiteface	360310003	5	R & P 2300	55.6	60.0	99.5	99.6	99.0	99.9	93.4	98.8	99.9	90.0
Wichita Dept. of Environmental Health	201730010	5	R & P 2300	60.0	100.0	60.0	100.0	84.5	81.8	80.0	80.0	100.0	100.0
Wilbur Wright Middle School	391130031	5	SASS			75.0	80.0	100.0	100.0	100.0	100.0	100.0	100.0
William Owen Elem. School	370510009	5	SASS	100.0									
Wylam	010732003	5	SASS	100.0	80.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
York	421330008	5	SASS	99.1	100.0	100.0	100.0	100.0	80.0	99.1	100.0	100.0	82.8
Ypsilanti	261610008	5	SASS	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Appendix C

Gravimetric Inter-Laboratory Comparison Study

TECHNICAL MEMORANDUM

TO:	Michael Papp / OAQPS
FROM:	Eric Boswell / NAREL
COPY:	Dennis Crumper / OAQPS Dr. R.K.M. Jayanty / RTI Robert Mosley / R&IE-LV Greg Noah / Region 4 Christopher Hall/Region 10
AUTHOR:	Steve Taylor
DATE:	November 23, 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.

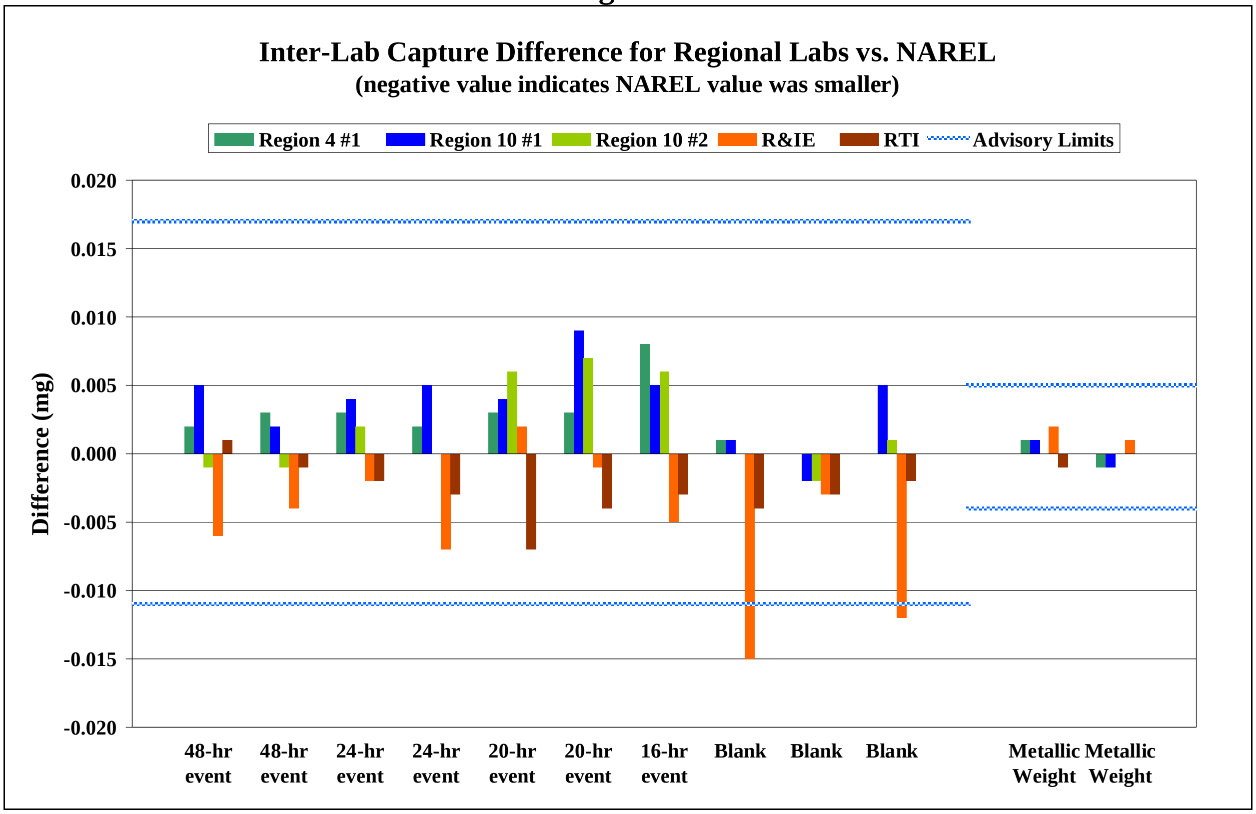
Immediately after a final Aofficial@ loaded mass was determined at NAREL, each sample set was placed into a cooler with frozen ice packs, a Dickson temperature logger, and a letter of instructions. The coolers were shipped to the participating laboratories by overnight Federal Express.

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.

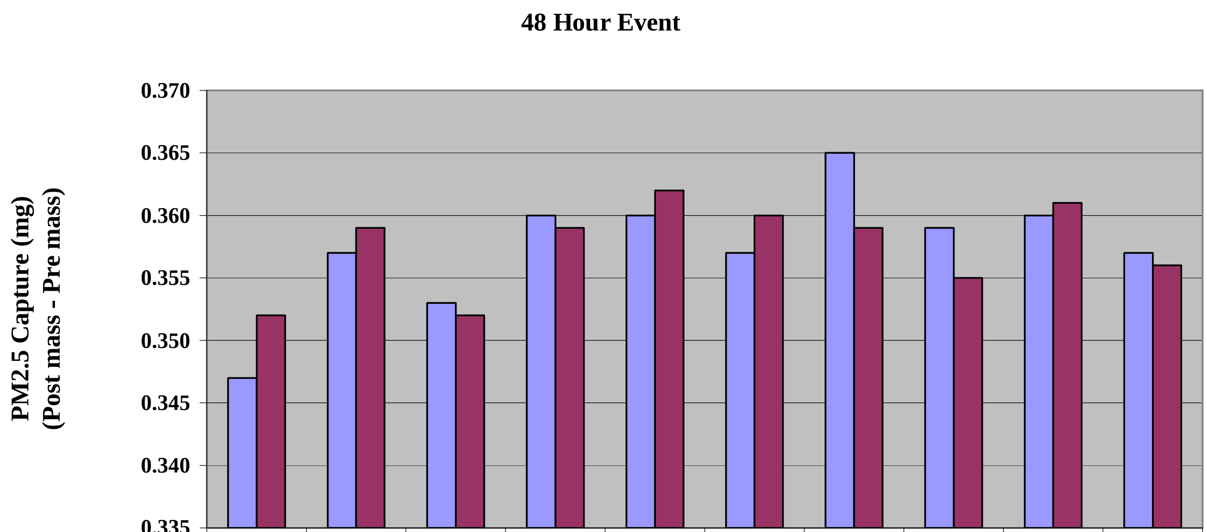
The raw data reported from all laboratories have been tabulated in Tables 2 - 6 at the end of this report. The tables include the results of all filters and the modified metallic standards weighed at each laboratory. The tables contain the filter tare mass, the final loaded mass, and the calculated $PM_{2.5}$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

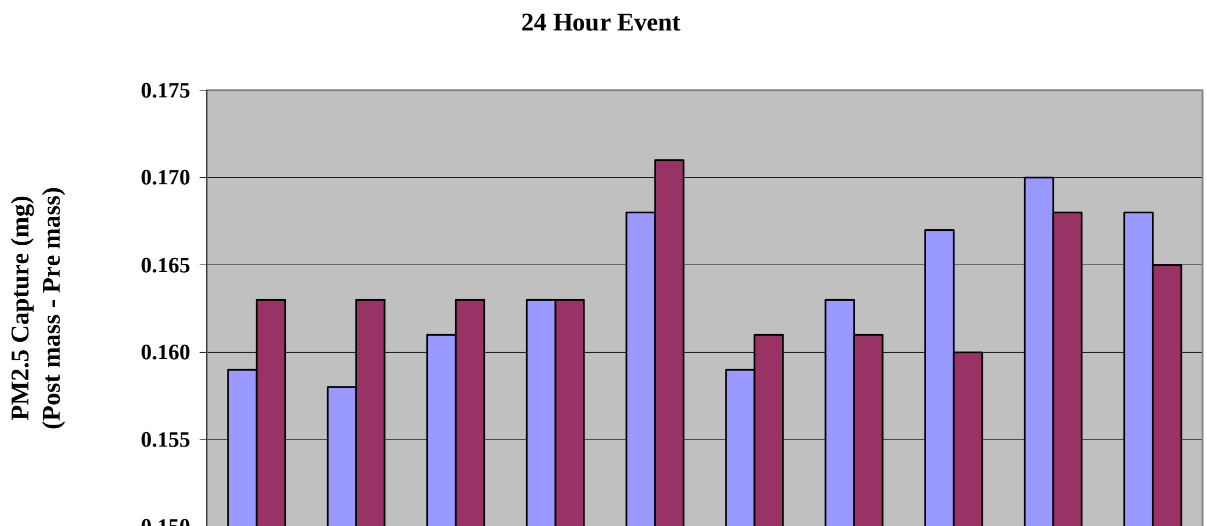
Errors were discovered in the Region 4 laboratory's reported results. Specifically, a sample ID mix-up of the two metallic samples resulted in incorrect results reported for those samples. Also, one metallic sample result appeared to have a transcription error that indicated a three milligram change 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



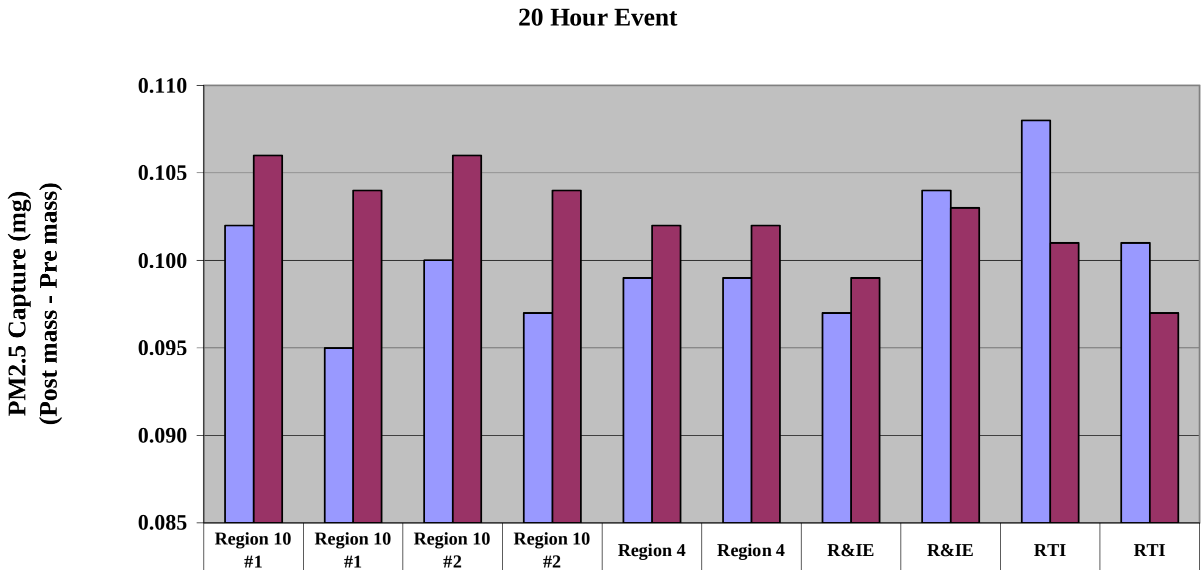
	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	0.347	0.357	0.353	0.360	0.360	0.357	0.365	0.359	0.360	0.357
NAREL Lab	0.352	0.359	0.352	0.359	0.362	0.360	0.359	0.355	0.361	0.356

Figure 3



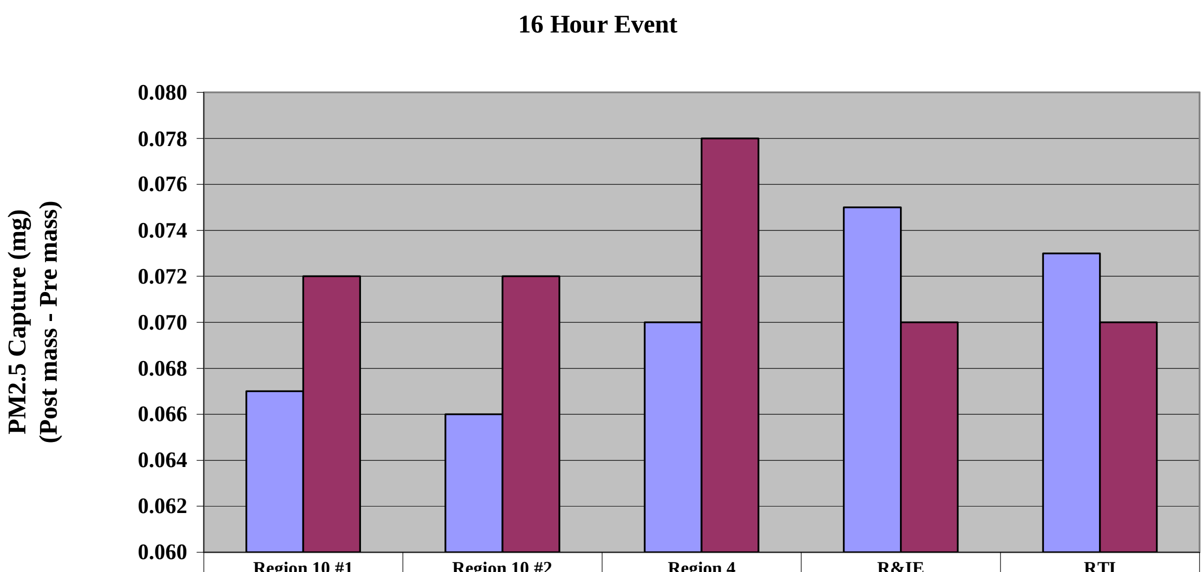
	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	0.159	0.158	0.161	0.163	0.168	0.159	0.163	0.167	0.170	0.168
NAREL Lab	0.163	0.163	0.163	0.163	0.171	0.161	0.161	0.160	0.168	0.165

Figure 4



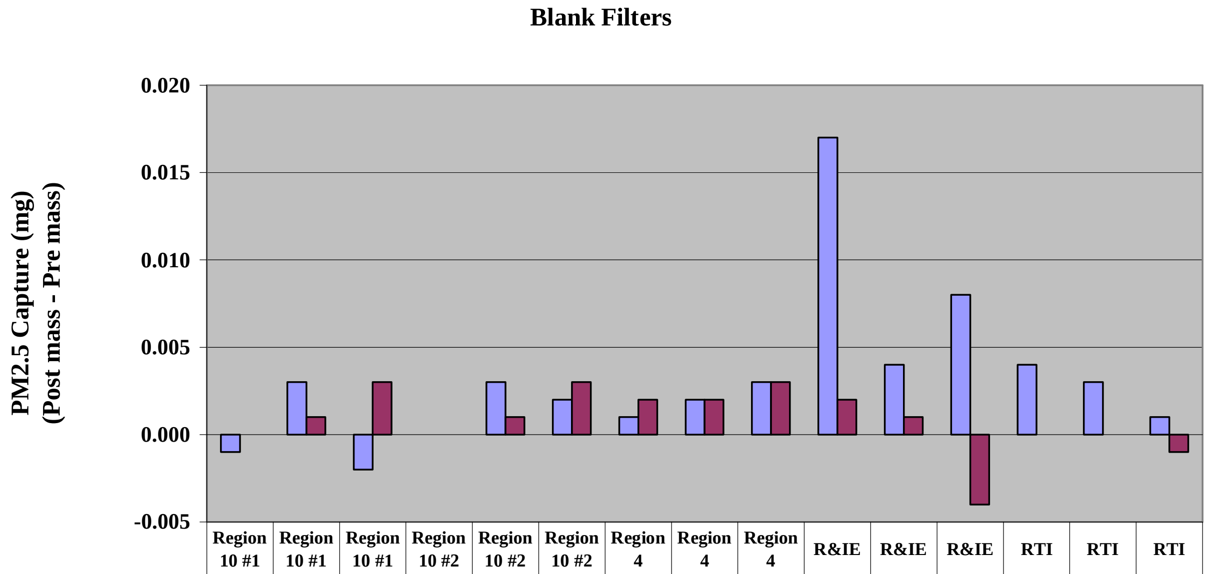
	Region 10 #1	Region 10 #1	Region 10 #2	Region 10 #2	Region 4	Region 4	R&IE	R&IE	RTI	RTI
Regional Lab	0.102	0.095	0.100	0.097	0.099	0.099	0.097	0.104	0.108	0.101
NAREL Lab	0.106	0.104	0.106	0.104	0.102	0.102	0.099	0.103	0.101	0.097

Figure 5



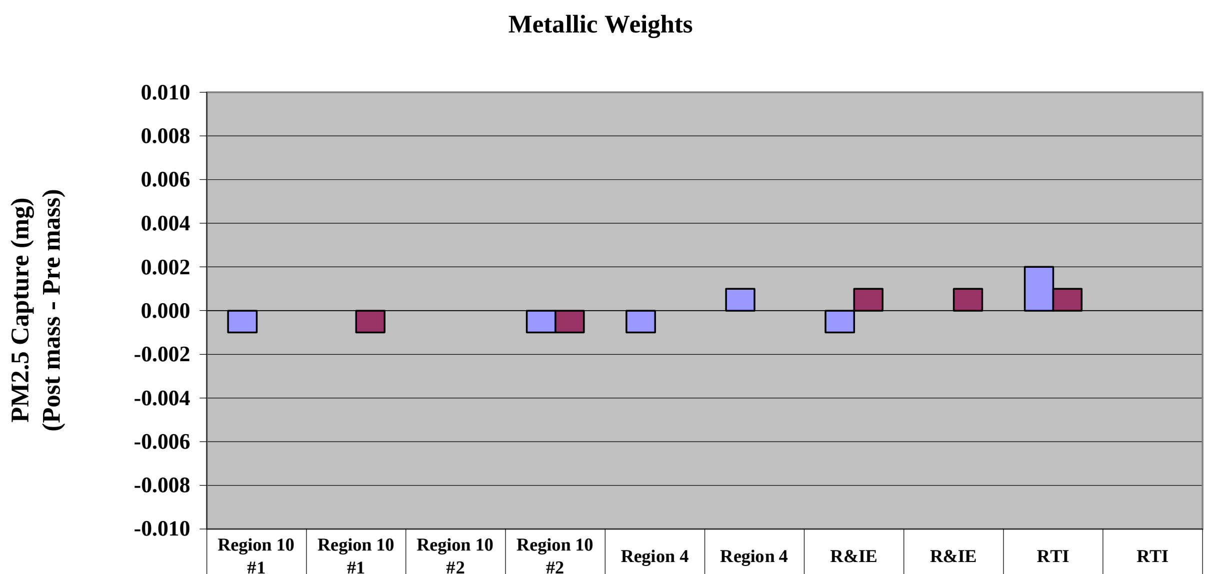
	Region 10 #1	Region 10 #2	Region 4	R&IE	RTI
Regional Lab	0.067	0.066	0.070	0.075	0.073
NAREL Lab	0.072	0.072	0.078	0.070	0.070

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 Region 4 (mg)	Tare Mass NAREL (mg)	Final Mass Region 4 (mg)	Final Mass NAREL (mg)	Captured PM2.5 Region 4 (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (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 Region 10 #1 (mg)	Tare Mass NAREL (mg)	Final Mass Region 10 #1 (mg)	Final Mass NAREL (mg)	Captured PM2.5 Region 10 #1 (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (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 Region 10 #2 (mg)	Tare Mass NAREL (mg)	Final Mass Region 10 #2 (mg)	Final Mass NAREL (mg)	Captured PM2.5 Region 10 #2 (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (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 R&IE (mg)	Tare Mass NAREL (mg)	Final Mass R&IE (mg)	Final Mass NAREL (mg)	Captured PM2.5 R&IE (mg)	Captured PM2.5 NAREL (mg)	Inter-Lab Difference* of Captured PM2.5 (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

	Tare Mass		Final Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5
Sample ID	**RTI (mg)**	**NAREL (mg)**	**RTI (mg)**	**NAREL (mg)**	**RTI (mg)**	**NAREL (mg)**	**(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

Appendix D

Experimental Inter-Comparison of Speciation Laboratories

TECHNICAL MEMORANDUM

TO:	Dennis Crumpler / OAQPS
FROM:	Eric Boswell / NAREL
COPY:	Mike Poore / CARB Dr. Richard Tropp / DRI RaeAnn Haynes / ODEQ Dr. R.K.M. Jayanty / RTI
AUTHOR:	Jewell Smiley / NAREL
DATE:	September 19, 2005
SUBJECT:	Experimental Inter-comparison of Speciation Laboratories

Introduction

This study was conducted as part of the EPA's quality assurance oversight for the $PM_{2.5}$ chemical speciation air monitoring networks that include the Speciation Trends Network (STN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. The purpose of this study was to evaluate specific laboratory performance at those laboratories that routinely analyze $PM_{2.5}$ chemical speciation samples.

This study required each participating laboratory to analyze a set of blind Performance Evaluation (PE) filter samples. The PE samples were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. NAREL was able to create replicate filter samples for this study by using co-located Met One speciation samplers. The co-located samplers were programmed to collect $PM_{2.5}$ from the Montgomery air and simultaneously load several filters during each collection event. A sufficient number of replicates were prepared so that each laboratory could receive the following set of PE samples.

- Gravimetric Mass Analysis - ten Teflon® filter samples and two metallic weights
- Ion Chromatography (IC) Analysis - six Nylon® filter samples or six Teflon® filter samples
- Carbon by Thermal Optical Analysis (TOA) - six quartz filter samples
- Elemental analysis by X-Ray Fluorescence (XRF) - six Teflon® filter samples

Detailed instructions for analyzing and reporting the PE samples were provided by NAREL. This report will compare and discuss the analytical results received from all of the laboratories. Some of the laboratories received a full set of PE samples, and some received a partial set due to limitations that will be explained later in the appropriate section of this report. Table 1 identifies all of the laboratories along with their level of participation.

Table 1. List of Participating Laboratories

Laboratory	Location	Analyses Reported
California Air Resources Board (CARB)	Sacramento, CA	Gravimetric mass IC analysis, Nylon® filters TOA carbon, modified STN method
Desert Research Institute (DRI)	Reno, NV	Gravimetric mass IC analysis, Teflon® filters IC analysis, Nylon® filters TOA carbon, STN method TOA carbon, IMPROVE method TOA carbon, IMPROVE-a method Elements by XRF
Oregon Dept. of Environmental Quality (ODEQ)	Portland, OR	Gravimetric mass IC analysis, Nylon® filters Elements by XRF
Research Triangle Institute (RTI)	Research Triangle Park, NC	Gravimetric mass IC analysis, Nylon® filters TOA carbon, STN method TOA carbon, IMPROVE method Elements by XRF
EPA's National Exposure Research Laboratory (NERL)	Research Triangle Park, NC	Elements by XRF
EPA's National Air and Radiation Environmental Laboratory (NAREL)	Montgomery, AL	Gravimetric mass IC analysis, Nylon® filters IC analysis, Teflon® filters TOA carbon, STN method TOA carbon, IMPROVE method TOA carbon, IMPROVE-a method

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 mass from the loaded filter mass. Each speciation laboratory routinely provides clean PRE-weighed air filters to the supported field sites. At the field site, an approved sampling device must be used to deposit the $PM_{2.5}$ onto the collection filter. The loaded filter is returned to the originating laboratory where the gravimetric analysis is completed by POST-weighing the filter. After the gravimetric measurements are complete, the Teflon® filter is examined further using XRF to determine the elemental composition of the filter deposit. Usually XRF is the final analysis of the Teflon® filter after which the filter is placed into an archive for storage, but in some cases the filter is subjected to one more [final] analysis to determine the ions present in the filter deposit.

If the Teflon® filter is examined for ions, it must be extracted, and the extract is subsequently analyzed using Ion Chromatography.

Most of the speciation laboratories provide clean Nylon® filters to the field sites. It is usually the Nylon® filter that 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.

The laboratories also provide clean quartz filters to the supported field sites. The quartz filter is used to capture $PM_{2.5}$ for subsequent carbon analysis. A thermal/optical analysis (TOA) is performed at the laboratory 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 at the sample. The TOA 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 the organic carbon (OC) and the elemental carbon (EC) the sum of which represents the total carbon (TC) present in the sample. Several slightly different TOA methods were used to analyze samples during this study. A more detailed description of each TOA method will be provided later in this report.

Gravimetric Analysis

Ten new filters and two metallic transfer weights were supplied by NAREL to each laboratory for this study. These samples were placed into individual petri slides and shipped by overnight mail to the receiving lab with instructions to PRE-weigh each filter and metallic weight using the local standard procedures. After tare measurements were completed at the receiving lab, the filters and metallic weights were returned to Montgomery and immediately placed into the weighing chamber at NAREL for equilibration and determination of a stable tare mass. Shortly after NAREL's tare measurements were complete, some of the filters were loaded with $PM_{2.5}$ captured from the Montgomery air. Co-located Met One SuperSASS air samplers were used to load seven of the filters in each sample set according to the sampling schedule presented in Table 2.

Table 2. Sampling Schedule for Gravimetric PE Filters

Filter ID	Serial Number	Sample Start	Event Duration	Receiving Lab
T05-11285	T2017288	20-Jan-05	24-hour	CARB
T05-11286	T2017289	20-Jan-05	24-hour	CARB
T05-11287	T2017290	21-Jan-05	48-hour	CARB
T05-11288	T2017291	21-Jan-05	48-hour	CARB
T05-11289	T2017292	23-Jan-05	12-hour	CARB
T05-11290	T2017293	23-Jan-05	12-hour	CARB
T05-11291	T2017310	24-Jan-05	24-hour	CARB

Table 2. Sampling Schedule for Gravimetric PE Filters

Filter ID	Serial Number	Sample Start	Event Duration	Receiving Lab
T05-11295	T2017314	20-Jan-05	24-hour	DRI
T05-11296	T2017315	20-Jan-05	24-hour	DRI
T05-11297	T2017316	21-Jan-05	48-hour	DRI
T05-11298	T2017317	21-Jan-05	48-hour	DRI
T05-11299	T2017318	23-Jan-05	12-hour	DRI
T05-11300	T2017319	23-Jan-05	12-hour	DRI
T05-11301	T2017320	24-Jan-05	24-hour	DRI
T05-11305	T2017324	20-Jan-05	24-hour	ODEQ
T05-11306	T2017325	20-Jan-05	24-hour	ODEQ
T05-11307	T2017326	21-Jan-05	48-hour	ODEQ
T05-11308	T2017327	21-Jan-05	48-hour	ODEQ
T05-11309	T2017328	23-Jan-05	12-hour	ODEQ
T05-11310	T2017329	23-Jan-05	12-hour	ODEQ
T05-11311	T2017330	24-Jan-05	24-hour	ODEQ
T05-11315	T2017334	20-Jan-05	24-hour	RTI
T05-11316	T2017335	20-Jan-05	24-hour	RTI
T05-11317	T2017358	21-Jan-05	48-hour	RTI
T05-11318	T2017337	21-Jan-05	48-hour	RTI
T05-11319	T2017338	23-Jan-05	12-hour	RTI
T05-11320	T2017339	23-Jan-05	12-hour	RTI
T05-11321	T2017354	24-Jan-05	24-hour	RTI

Table 2 shows twenty-eight filters that were loaded during four separate collection events. A sufficient number of replicates were prepared during each event such that each lab could be provided with an almost identical set of loaded filters. For example, eight replicates were created during a 24-hour collection event that started on January 20, and two of these replicates were submitted to each lab for analysis. Likewise, eight replicates were created during a 48-hour collection event that started on January 21, and two of these replicates were submitted to each lab for analysis. Table 2 does not list all of the filters that were PRE-weighed at the participating labs. Three of the ten filters that were PRE-weighed at each lab were not scheduled for loading because they were used as filter blanks for this study.

Following sample collection, the filters and the metallic weights were returned to the weighing chamber at NAREL and POST-weighed multiple times over the course of several days to demonstrate a stable final mass. Finally, the filters and metallic weights were placed into small Igloo® coolers with ice substitute and shipped back to the participating labs for POST-weighing. It is worth mentioning that the metallic weights were included in this study because they are usually less susceptible to weighing errors due to factors such as electrical static and volatility of filter constituents.

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 1

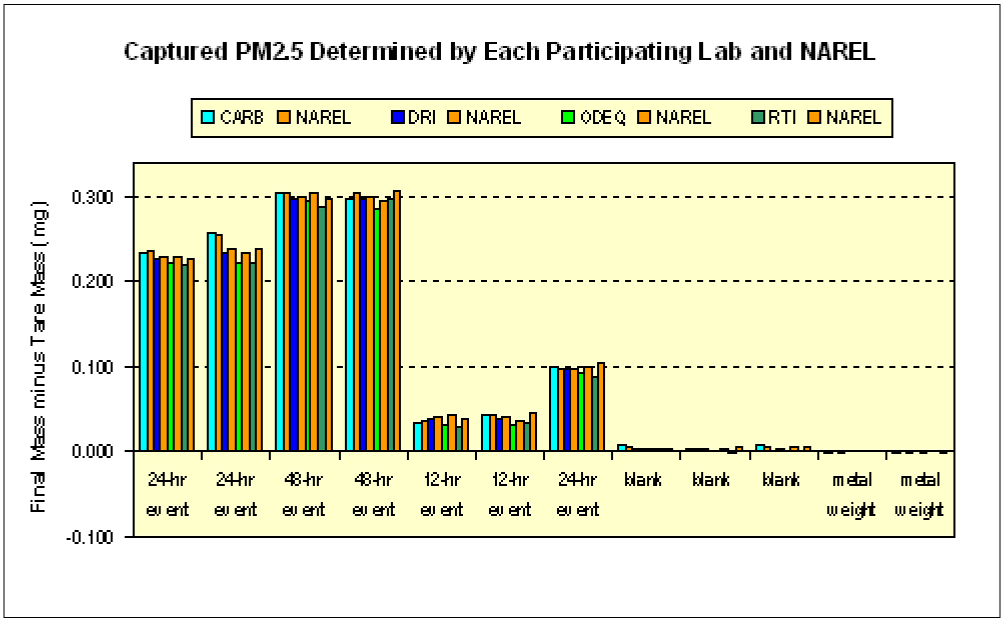
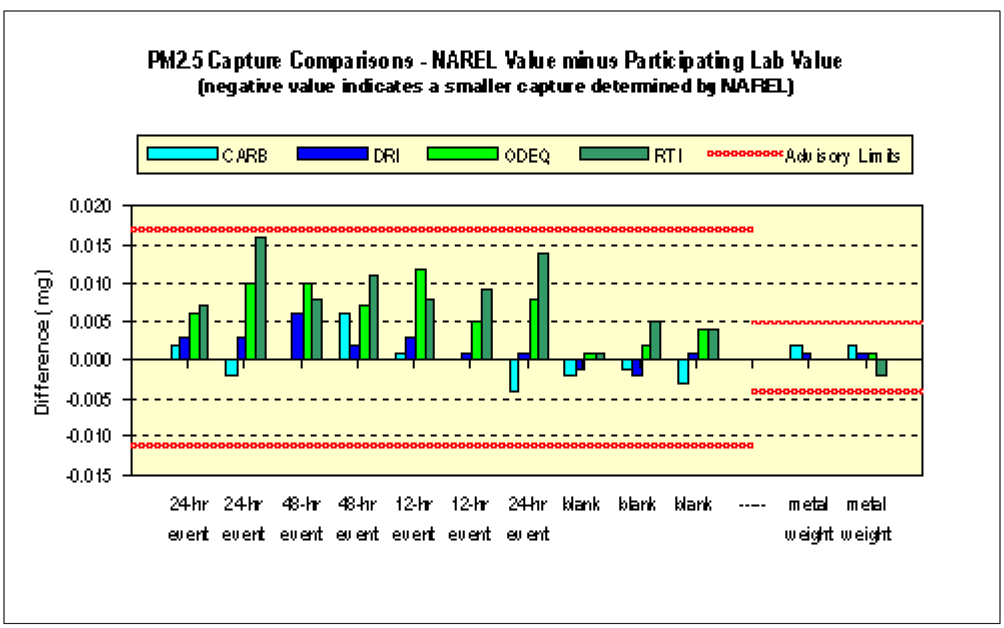


Figure 2 presents the inter-laboratory differences along with advisory limits. Inter-laboratory differences were calculated by subtracting the $PM_{2.5}$ capture value determined at each speciation lab from the capture value determined at NAREL. Notice that a negative bar on the Figure 2 graph represents a smaller $PM_{2.5}$ capture value determined at NAREL. The 3-sigma advisory limits were derived from all of the gravimetric PE studies administered by NAREL during the past year.

Figure 2



The raw data reported from all laboratories have been tabulated for easy viewing. At the end of this report, Table 9 contains the tare weight, the final loaded weight, and the calculated $PM_{2.5}$ capture for each sample. Table 9 also contains the calculated inter-laboratory difference for measuring the $PM_{2.5}$ capture which is graphed in Figure 2. RTI reported measurements made by several different analysts, and all of the results are included in Table 9. However, only the results from analyst #1 are presented in Figure 1 and Figure 2. Only one set of measurements from each lab were selected for graphical presentation because usually only one set of measurements are available for a routine sample.

All of the participating labs have an SOP for measuring the gravimetric mass of $PM_{2.5}$ filter samples. Most of the SOP's are currently available on the web for easy viewing (see reference 1 through 5).

IC Analysis

This study included the analysis of selected ions using three slightly different IC methods. Five labs analyzed a set of Nylon® filters using the STN method, two labs analyzed a set of Teflon® filters using the STN method, and finally two labs analyzed a set of Nylon® filters using the IMPROVE method. NAREL provided each lab with a set of six filters for each method tested. Each sample set contained two blank filters and four filters that were loaded with $PM_{2.5}$ collected from the Montgomery air. Co-located Met One SuperSASS air samplers were used to load filters and create replicates in each sample set according to the sampling schedule presented in Table 3.

Table 3. Sampling Schedule for Ion Chromatography PE Filters

Filter ID	Filter Medium	Sample Start	Event Duration	Receiving Lab	Method
N04-11197	Nylon®	24-Nov-04	116-hour	CARB	STN
N04-11198	Nylon®	24-Nov-04	116-hour	CARB	STN
N04-11208	Nylon®	29-Nov-04	159-hour	CARB	STN
N04-11209	Nylon®	29-Nov-04	159-hour	CARB	STN
N04-11199	Nylon®	24-Nov-04	116-hour	DRI	STN
N04-11200	Nylon®	24-Nov-04	116-hour	DRI	STN
N04-11210	Nylon®	29-Nov-04	159-hour	DRI	STN
N04-11211	Nylon®	29-Nov-04	159-hour	DRI	STN
N04-11201	Nylon®	24-Nov-04	116-hour	ODEQ	STN
N04-11202	Nylon®	24-Nov-04	116-hour	ODEQ	STN
N04-11212	Nylon®	29-Nov-04	159-hour	ODEQ	STN
N04-11213	Nylon®	29-Nov-04	159-hour	ODEQ	STN
N04-11203	Nylon®	24-Nov-04	116-hour	RTI	STN
N04-11204	Nylon®	24-Nov-04	116-hour	RTI	STN
N04-11214	Nylon®	29-Nov-04	159-hour	RTI	STN
N04-11215	Nylon®	29-Nov-04	159-hour	RTI	STN
N04-11205	Nylon®	24-Nov-04	116-hour	NAREL	STN
N04-11206	Nylon®	24-Nov-04	116-hour	NAREL	STN
N04-11216	Nylon®	29-Nov-04	159-hour	NAREL	STN
N04-11217	Nylon®	29-Nov-04	159-hour	NAREL	STN
T05-11333	Teflon®	03-Jan-05	144-hour	DRI	STN
T05-11334	Teflon®	03-Jan-05	144-hour	DRI	STN
T05-11337	Teflon®	04-Jan-05	216-hour	DRI	STN
T05-11338	Teflon®	04-Jan-05	216-hour	DRI	STN

Table 3. Sampling Schedule for Ion Chromatography PE Filters

Filter ID	Filter Medium	Sample Start	Event Duration	Receiving Lab	Method
T05-11335	Teflon®	03-Jan-05	144-hour	NAREL	STN
T05-11336	Teflon®	03-Jan-05	144-hour	NAREL	STN
T05-11339	Teflon®	04-Jan-05	216-hour	NAREL	STN
T05-11340	Teflon®	04-Jan-05	216-hour	NAREL	STN
N04-11229	Nylon®	07-Dec-04	161-hour	RTI	IMPROVE
N04-11230	Nylon®	07-Dec-04	161-hour	RTI	IMPROVE
N04-11233	Nylon®	08-Dec-04	130-hour	RTI	IMPROVE
N04-11234	Nylon®	08-Dec-04	130-hour	RTI	IMPROVE
N04-11231	Nylon®	07-Dec-04	161-hour	NAREL	IMPROVE
N04-11232	Nylon®	07-Dec-04	161-hour	NAREL	IMPROVE
N04-11235	Nylon®	08-Dec-04	130-hour	NAREL	IMPROVE
N04-11236	Nylon®	08-Dec-04	130-hour	NAREL	IMPROVE

Table 3 shows thirty-six filters that were loaded during six separate collection events. A sufficient number of replicates were prepared during each event such that each participating lab was provided with an almost identical set of loaded filters. For example, ten replicates were created during a 116-hour collection event that started on November 24, and two of these replicates were submitted to each lab for analysis. Likewise, ten replicates were created during a 159-hour collection event that started on November 29, and two of these replicates were submitted to each lab for analysis. The collection times used for this study were significantly longer than the normal 24-hours to boost the amount of $PM_{2.5}$ collected and raise the level of most analytes to above the detection threshold. Table 3 does not list the filter blanks that were provided to each participating lab.

A filter set was provided to each participating lab with instructions to use local standard procedures, as closely as possible, for the extraction and the IC analysis. No information was given to the participating labs about the history of the individual filters. The results were reported for each sample based upon the amount of analyte present on the filter (µg/filter).

All of the participating labs have an SOP for analyzing $PM_{2.5}$ filter samples by IC. Most of the SOP's are currently available on the web for easy viewing (see reference 6 through 13).

IC Results

Results from the analysis of Nylon® filters using the STN method are presented as a bar graph in Figure 3 and Figure 4. Ten replicates from the November 24 event are shown on the left side of the graphs, and ten replicates from the November 29 event are shown on the right side of the graphs. Nitrate, sulfate, and ammonium were the most abundant analytes captured from the Montgomery air, and these mid-level ions are plotted together in Figure 3. Sodium and potassium were present in the air at relatively low levels, and these ions are plotted in Figure 4. Since the low-level components are presented in Figure 4, an extra bar was added to this graph that represents the lowest calibration standard analyzed at NAREL. The lowest calibration standard is a good estimate of the practical quantitation limit for the analysis. Each cluster of ten bars in the graph is labeled with the ion reported, but the individual samples within each cluster are not identified. It is important to understand that the ten replicate samples within each cluster were consistently arranged, from left to right, in the same order.

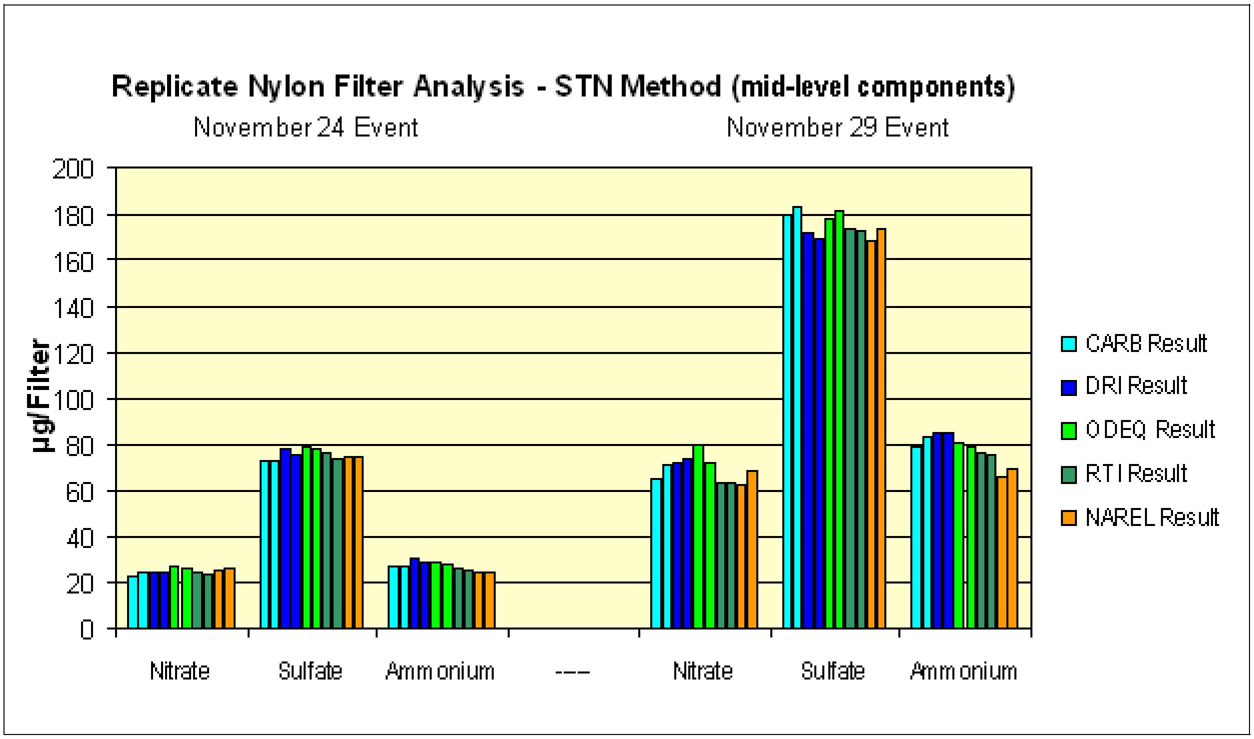


Figure 3

Good precision can be seen in Figure 3 and Figure 4. The inter-laboratory precision is almost as good as the precision within each lab.

Figure 4

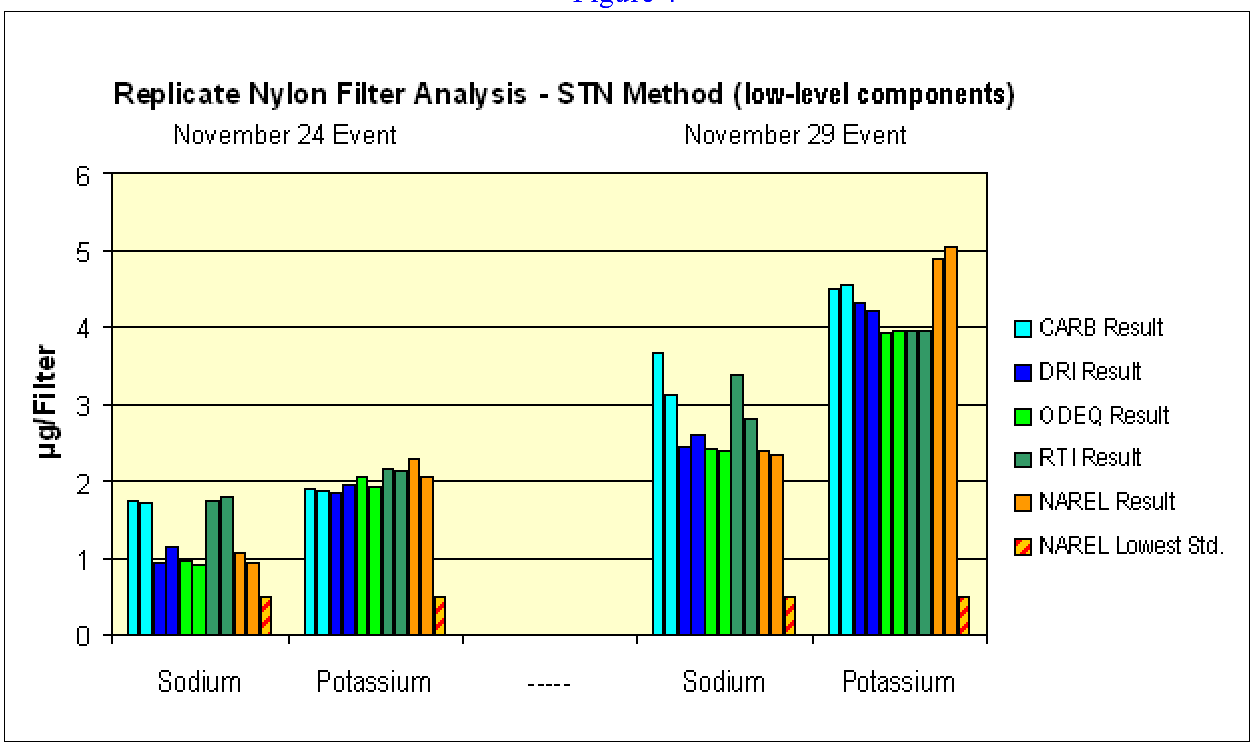


Figure 5 and Figure 6 show the results from replicate Teflon® filter samples that were created on January 3 and January 4. Half of the replicates were submitted to DRI for analysis using the STN method, and half were retained at NAREL for analysis using the same method. Teflon® filter samples are routinely analyzed at DRI as part of their work for the Texas Commission on Environmental Quality (TCEQ). The mid-level and the low-level components are presented again as separate graphs in Figure 5 and Figure 6 respectively. It is worth noting that nitrate was not a mid-level component on the Teflon® filters even though it probably was a mid-level component in the Montgomery air. Excellent precision is observed in Figure 5 for ammonium, especially considering the non-linear response curve that ammonium offers at the IC instrument. A small consistent (eleven percent) inter-laboratory bias is observed for sulfate in Figure 5. Good precision is observed for the low-level components shown in Figure 6.

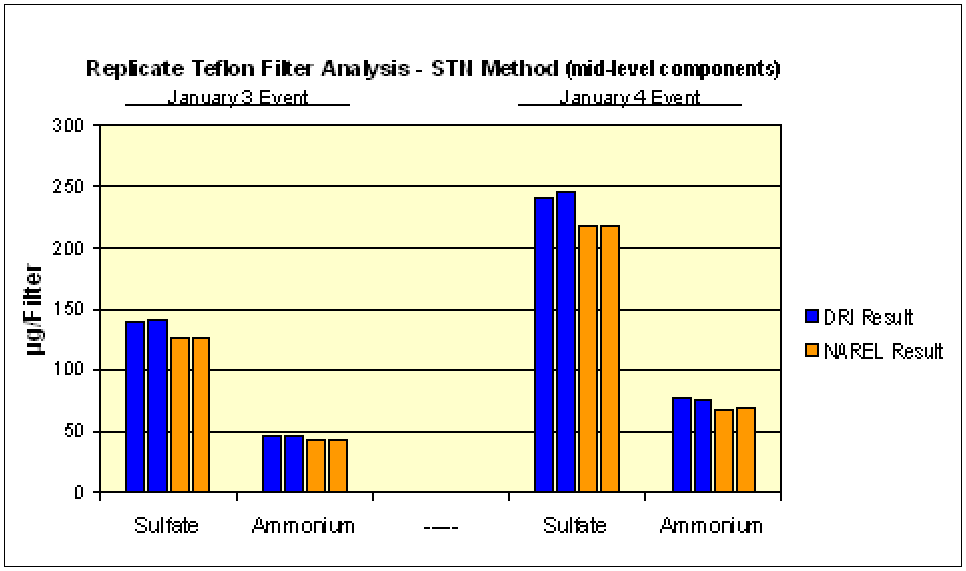


Figure 5

Figure 6

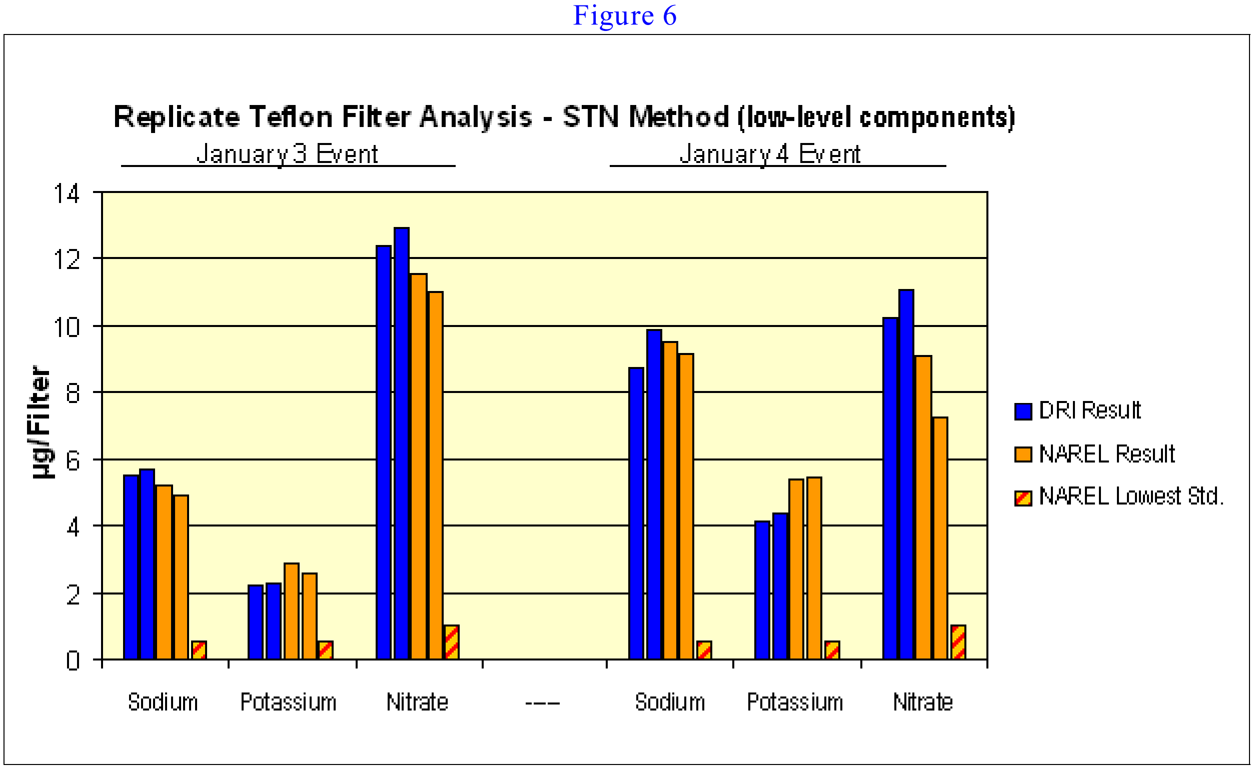
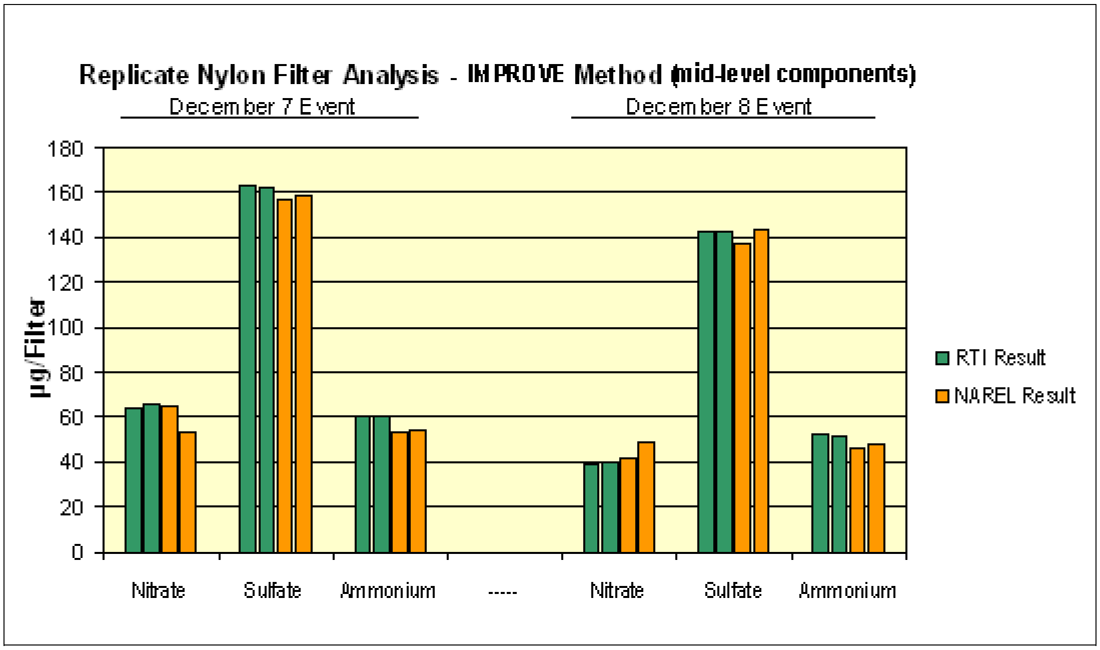
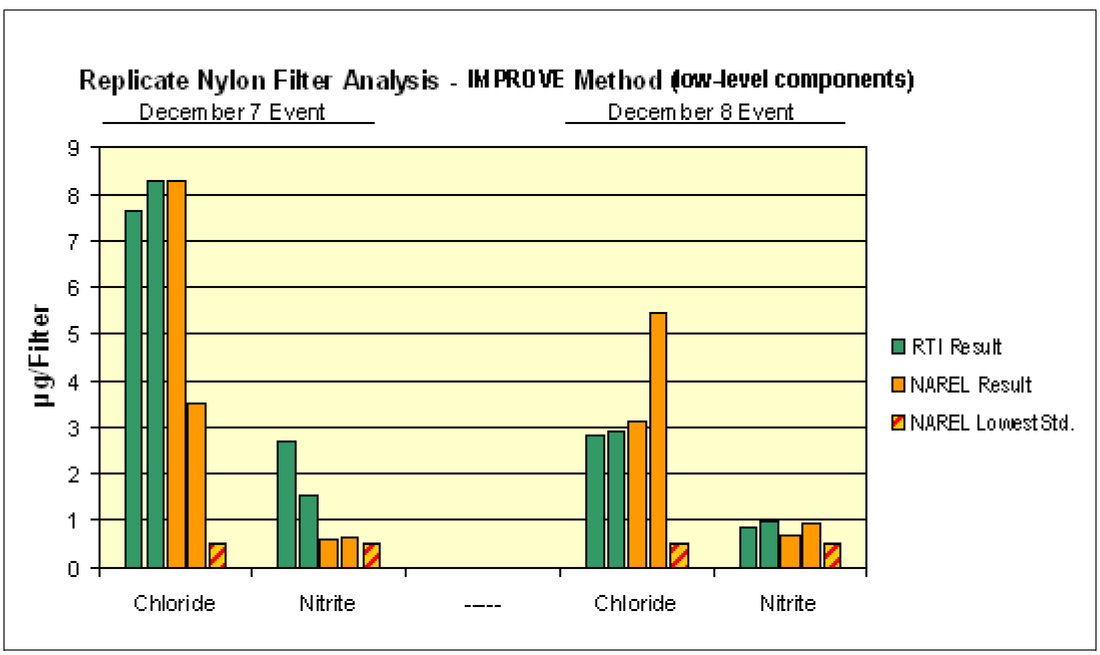


Figure 7



Nylon® filters are routinely analyzed at RTI using the IMPROVE method which is slightly different from the STN method with respect to the extraction procedure and the list of reported ions. Figure 7 shows good precision for all of the mid-level ions, but there is a problem in Figure 8 with the low-level components. Poor precision was reported by NAREL for the chloride analysis. After discovery of the problem, the filter extracts were re-analyzed with similar results. NAREL has not been able to explain the poor precision for chloride observed in Figure 8, but possible reasons include poor filter replication and accidental contamination of the filter extract. The variability observed for nitrite may be due to contamination which is frequently observed in blanks. Blanks were provided to all of the labs for this study even though the blank results are not presented in graphical format. The numerical results for all of the blanks and for all of the loaded filters are available in Table 10 at the end of this report.

Figure 8



Carbon Analysis

This study included the Thermal-Optical Analysis (TOA) of quartz fiber filters to determine the amount of carbon present in captured $PM_{2.5}$. NAREL provided each participating laboratory with a set of six 47-mm filters. Each sample set contained two blank filters and four filters that were loaded with $PM_{2.5}$ collected from the Montgomery air. Co-located Met One SuperSASS air samplers were used to load filters and create replicates in each sample set according to the sampling schedule presented in Table 4.

Table 4. Sampling Schedule for TOA Carbon PE Filters

Filter ID	Filter Medium	Sample Start	Event Duration	Receiving Lab	TOA Method(s)
Q04-11175	quartz	27-Apr-04	287-hr	CARB	STN (modified)
Q04-11176	quartz	27-Apr-04	287-hr	CARB	STN (modified)
Q04-11186	quartz	16-Nov-04	192-hr	CARB	STN (modified)
Q04-11187	quartz	16-Nov-04	192-hr	CARB	STN (modified)
Q04-11177	quartz	27-Apr-04	287-hr	DRI	STN, IMPROVE, and IMPROVEa
Q04-11178	quartz	27-Apr-04	287-hr	DRI	STN, IMPROVE, and IMPROVEa
Q04-11188	quartz	16-Nov-04	192-hr	DRI	STN, IMPROVE, and IMPROVEa
Q04-11189	quartz	16-Nov-04	192-hr	DRI	STN, IMPROVE, and IMPROVEa
Q04-11181	quartz	27-Apr-04	287-hr	RTI	STN and IMPROVE
Q04-11182	quartz	27-Apr-04	287-hr	RTI	STN and IMPROVE
Q04-11192	quartz	16-Nov-04	192-hr	RTI	STN and IMPROVE
Q04-11193	quartz	16-Nov-04	192-hr	RTI	STN and IMPROVE
Q04-11183	quartz	27-Apr-04	287-hr	NAREL	STN, IMPROVE, and IMPROVEa
Q04-11184	quartz	27-Apr-04	287-hr	NAREL	STN, IMPROVE, and IMPROVEa
Q04-11194	quartz	16-Nov-04	192-hr	NAREL	STN, IMPROVE, and IMPROVEa
Q04-11195	quartz	16-Nov-04	192-hr	NAREL	STN, IMPROVE, and IMPROVEa

Table 4 shows sixteen filters that were loaded during two separate collection events. A sufficient number of replicates were prepared during each event such that each participating lab was provided with an almost identical set of loaded filters. Eight replicates were created during the 287-hour springtime event that started on April 27, and two of these replicates were submitted to each lab for analysis. Likewise, eight replicates were created during the 192-hour autumn event that started on November 16, and two of these replicates were submitted to each lab for analysis. The collection times used for this study were significantly longer than the normal 24-hours to boost the amount of elemental carbon deposited on the filter. Table 4 does not list the two filter blanks that were provided to each participating lab.

A filter set was provided to each lab with instructions to use local standard procedures, as closely as possible, for the analysis. No information was given to the participating labs about the history of the individual filters. ODEQ did not participate in this part of the study because their quartz filters are shipped to RTI for analysis. The DRI and RTI labs are set up to analyze a large volume of samples and routinely operate several TOA instruments. Both DRI and RTI were able to analyze each filter several times using more than one instrument and using more than one TOA method. The results were reported for each sample based upon the amount of carbon per square centimeter of the filter deposit($\mu g\ C/cm^2$). Raw data were also supplied to NAREL so that some of the thermograms are included in this report.

This study has provided an excellent opportunity to see replicate filter samples analyzed by a variety of TOA methods. Therefore it is appropriate to ask, "what distinguishes one TOA method from another?" To answer this question we must first identify the critical elements of a TOA method. At least four different TOA methods have been identified in this report based upon the temperature protocol used during the analysis. The following table provides a brief description of each temperature protocol.

Table 5. Comparison of the Temperature Protocols for Four TOA Methods

STN Method TOT Analysis	CARB Method (modified STN) TOT Analysis	IMPROVE Method TOR Analysis	IMPROVE-a Method TOR Analysis	Carrier Gas	Carbon Fraction*
heater off (90s)	heater off (90s)	heater off (90s)	heater off (90s)	He Purge	-----
310°C (60s)	250°C (180s)	120°C (150-580s)	140°C (150-580s)	He	OC1
480°C (60s)	400°C (150s)	250°C (150-580s)	279°C (150-580s)	He	OC2
615°C (60s)	550°C (150s)	450°C (150-580s)	480°C (150-580s)	He	OC3
900°C (90s)	700°C (270s)	550°C (150-580s)	580°C (150-580s)	He	OC4
heater off (40s)	heater off (60s)	-----	-----	He	
600°C (35s)	550°C (100s)	550°C (150-580s)	580°C (150-580s)	He/O_2	EC1
675°C (45s)	650°C (100s)	700°C (150-580s)	740°C (150-580s)	He/O_2	EC2
750°C (45s)	750°C (100s)	800°C (150-580s)	840°C (150-580s)	He/O_2	EC3
825°C (45s)	850°C (100s)	-----	-----	He/O_2	
920°C (120s)	900°C (170s)	-----	-----	He/O_2	
heater off (110s)	heater off (200s)	heater off (150s)	heater off (200s)	He/O_2+IS	

**** The carbon fractions are not consistently defined among the different methods. See text for explanation.***

Beyond the thermal protocols listed in Table 5, each TOA method is further defined by the way optical measurements are made and utilized to calculate carbon fractions. For example, the optical measurements are used to distinguish the elemental carbon (EC) from the organic carbon (OC) present in the sample. In fact as we shall see, all of the carbon fractions have a functional definition that depends upon the method of analysis.

All of the instruments used for this study are equipped with a small tubular quartz oven and a laser/diode system. The sample analysis begins by placing a carefully measured [punched] segment of the filter sample into the oven directly in the path of the laser. A purge gas removes air from the oven and surrounds the sample with a stream of pure helium before the heating and data acquisition begin. Light from the laser will interact with the sample during the analysis. Some of the light will transmit through the sample, and some light will reflect from the surface of the sample. A diode detector can be positioned to measure the light transmitted through the sample, and this configuration is needed for a TOT (thermal optical transmittance) analysis. A diode can also be positioned to measure the reflected light, and this configuration is needed for a TOR (thermal optical reflectance) analysis. As the sample segment is heated and the pure helium phase of the analysis proceeds, some of the carbon may char to form a darker pyrolized carbon (PyrolC). All of the methods in this study use either TOT or TOR to evaluate the PyrolC. Four different instrument configurations were used for this study. The older

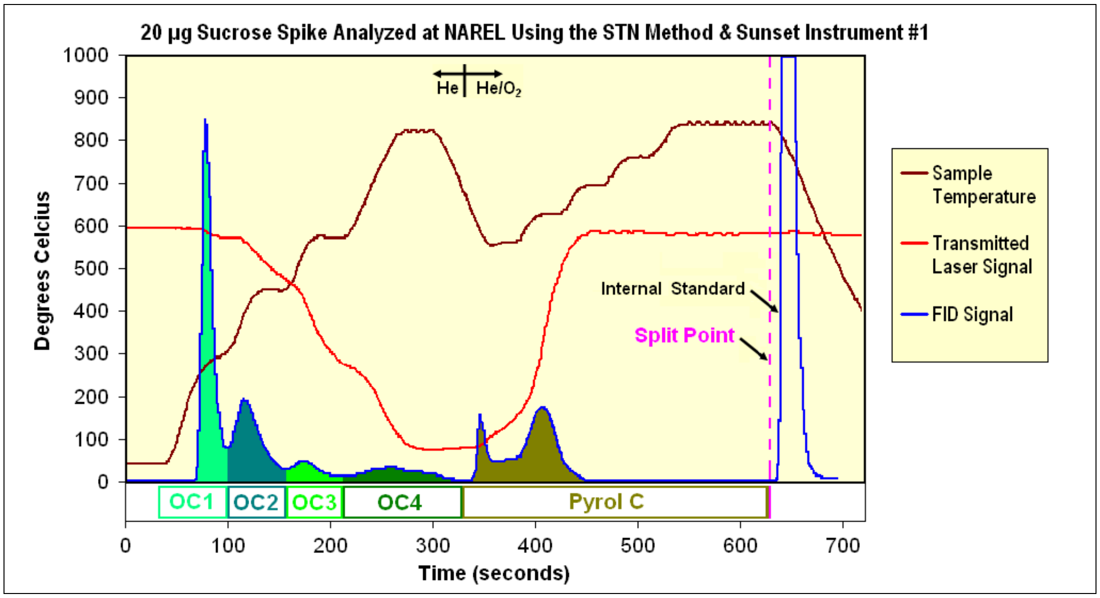
Sunset [single mode] instruments are equipped with only one diode detector and are configured for the TOT analysis. The older DRI/OGC instruments are also equipped with only one diode detector and are configured for the TOR analysis. The DRI Model 2001 instruments and the Sunset Dual Mode instruments are newer designs capable of measuring the transmitted and the reflected light simultaneously. These newer instruments provide more optical information and give the user a choice of the TOT or the TOR analysis. Table 6 shows specifically how the different instruments were used for analyzing the samples in this study.

Table 6. Summary of Report Packages for the TOA Analyses

Temperature Protocol	Optical Analysis	Instrument Model	Specific Instrument Reporting	Parameters Reported	Report Package Count
Modified STN	TOT	DRI Model 2001	CARB Instr. #1	OC, EC, TC	1
STN	TOT	DRI Model 2001	DRI Instr. #7	OC, EC, TC, OCsub, ECsub	2
			DRI Instr. #9	OC, EC, TC, OCsub, ECsub	3
		Sunset	RTI Instr. R	OC, EC, TC, OCsub	4
			RTI Instr. S	OC, EC, TC, OCsub	5
			RTI Instr. T	OC, EC, TC, OCsub	6
			NAREL Instr. #1	OC, EC, TC, OCsub	7
		Sunset (Dual Mode)	RTI Instr. F	OC, EC, TC, OCsub	8
IMPROVE	TOR	DRI/OGC	DRI Instr. #4	OC, EC, TC, OCsub, ECsub	9
			DRI Instr. #5	OC, EC, TC, OCsub, ECsub	10
		Sunset (Dual Mode)	RTI Instr. F	OC, EC, TC, OCsub, ECsub	11
			NAREL Instr. #2	OC, EC, TC, OCsub, ECsub	12
IMPROVE-a	TOR	DRI Model 2001	DRI Instr. #7	OC, EC, TC, OCsub, ECsub	13
			DRI Instr. #9	OC, EC, TC, OCsub, ECsub	14
		Sunset (Dual Mode)	NAREL Instr. #2	OC, EC, TC, OCsub, ECsub	15

All of the instruments in this study operate by heating a punched segment of the sample in the presence of a controlled carrier gas. Any carbonaceous material released from the quartz filter segment is swept through a series of zones that rapidly convert the released carbon to methane which is measured by a Flame Ionization Detector (FID) positioned at the end of the sample train. During the first [non-oxidizing] stage of the analysis, the carrier gas is pure helium. Oxygen is added to the carrier during the second stage of the analysis which is designed to remove any remaining carbonaceous material from the quartz residue. Most of the OC is released during the first stage of the analysis, but the EC and any PyrolC that may have formed are more difficult to oxidize, and they are expected to release during the second stage of the analysis. A known mass of methane is injected through the oven at the end of the analysis to serve as an Internal Standard (IS). Signals from the FID and from the laser may be plotted along a time axis to construct a thermogram. An example of a thermogram is shown in Figure 9. This is a thermogram of a sucrose spike which was analyzed at NAREL as a routine calibration check sample. The sucrose spike contains no EC but has a strong tendency to char and form PyrolC.

Figure 9



After the raw data acquisition is complete, the thermogram is evaluated to determine the amount of OC and the amount of EC that were present in the original sample. All of the participating labs report the Total Carbon (TC) as the sum of the OC and the EC fractions: TC = OC + EC. Other carbon fractions may be calculated such as the OC subfractions: OC = OC1 + OC2 + OC3 + OC4 + PyrolC. Figure 9 shows an example of OC subfractions that were calculated by a Sunset instrument. EC subfractions may be calculated as well. For example, three EC subfractions are calculated for IMPROVE samples: EC = EC1 + EC2 + EC3. Unfortunately the rules [and consequently the software programs] used to determine these carbon fractions are not the same for all of the instruments. For example, we will see later that some of the instruments reported a negative PyrolC, but other instruments have adopted different rules that do not allow a negative PyrolC.

A "split point" must be established in each thermogram that separates the OC and the EC. The laser signal must be examined as part of determining the split point. If any of the original OC chars during the first stage of the analysis, the laser signal will decrease from its initial value, and will not recover until later in the run. The point at which the recovering laser signal reaches its initial value is usually the split point. Some samples do not form char, however, and the laser signal does not decrease and fall below its initial value. In this case, the split point is usually assigned when the oxygen valve opens for the second phase of the analysis to begin. All of the instruments follow these general rules, but there is a specific case that is controversial, and it occurs when the laser signal indicates an "early" split point. The split point is considered "early" if it is assigned during the first phase of the analysis before the oxygen valve opens. Most of the instruments were programmed to allow an early split point if the laser signal supports that assignment, but the DRI/OGC instruments did not allow early split points.

As we examine the results from all of the participating labs, it is important to understand the methods that were used, so that valid comparisons can be made. All of the results presented in this report have been identified with the instrument that performed the analysis as well as the thermal protocol and optical configuration that was used. All of the participating labs have an SOP for the TOA method(s) used at their laboratory. Most of the SOP's are currently available on the web for easy viewing (see reference 14 through 18).

Carbon Results

Results from the analysis of replicate quartz filters using the STN method are presented below as a bar graph. Notice that each bar in the graph is labeled with the instrument number, the lab, and the last three digits of the sample number. Figure 10 shows results from replicates that were created on April 27, and Figure 11 shows the results from replicates created on November 16. The bar segments show the OC and EC components of the total carbon but do not show the more detailed fractions. The results are presented again in Figure 12 and Figure 13 with more detail.

Figure 10

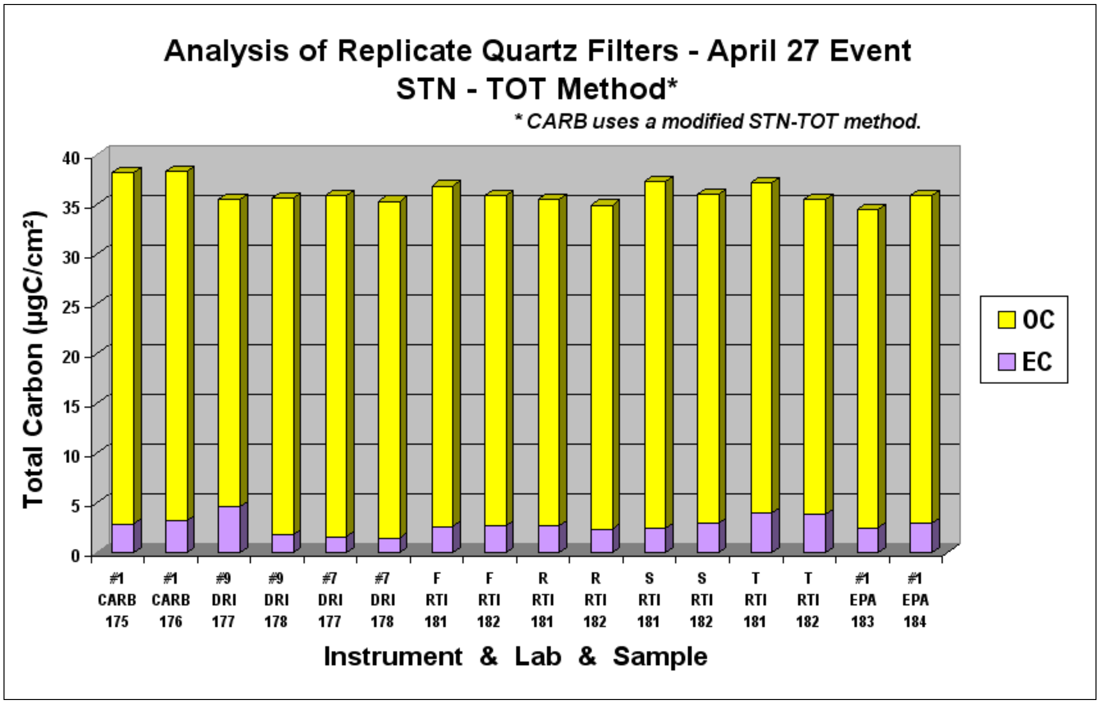
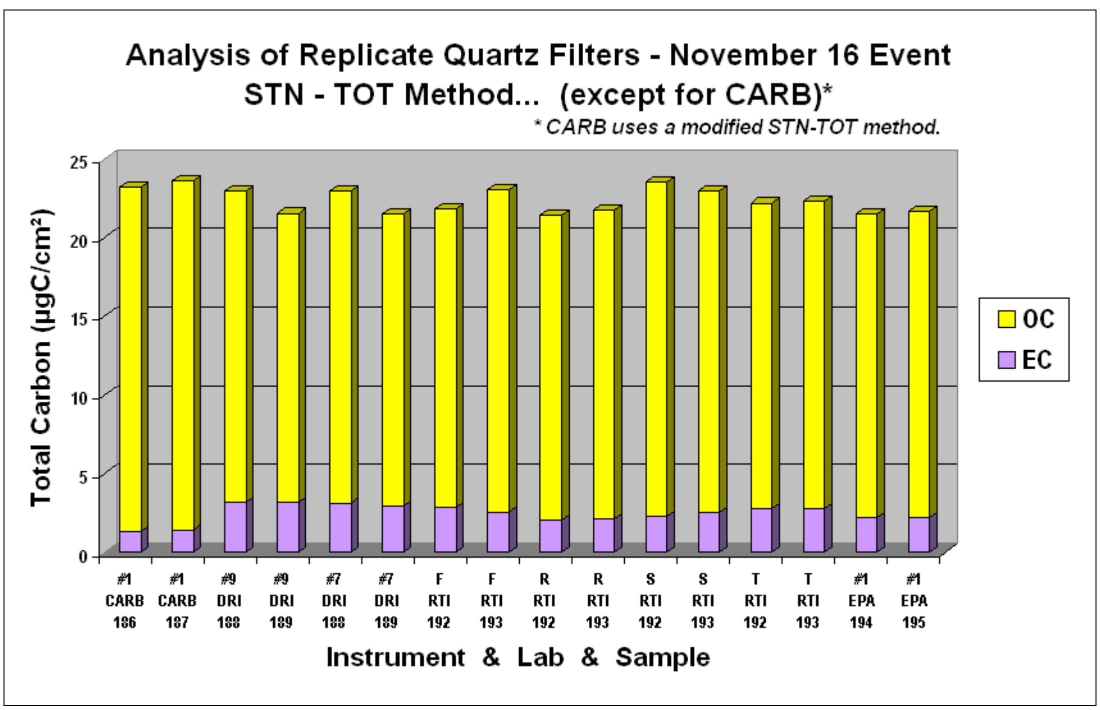


Figure 11



This time in Figure 12 and Figure 13, the OC subfractions are revealed. The subfractions from CARB are not presented since CARB does not use the STN temperature protocol. As shown previously in Figure 9, some of the subfractions are directly related to the temperature set points. PyrolC, on the other hand, is related to the split point. Notice that PyrolC was negative for some of the DRI results, and the reported OC4 result was "adjusted" to maintain proper size of the stacked bar whose height represents the TC. The adjustment was performed by adding the reported OC4 value and the [negative] PyrolC value. The adjustment was performed strictly for graphical purposes.

Figure 12

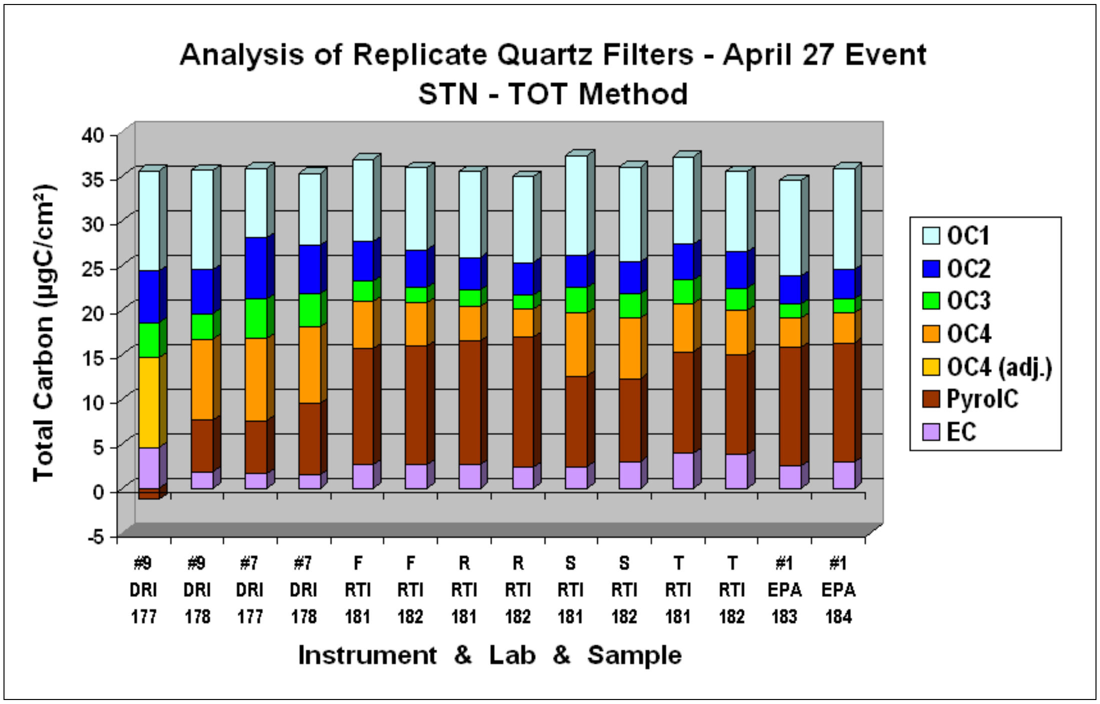
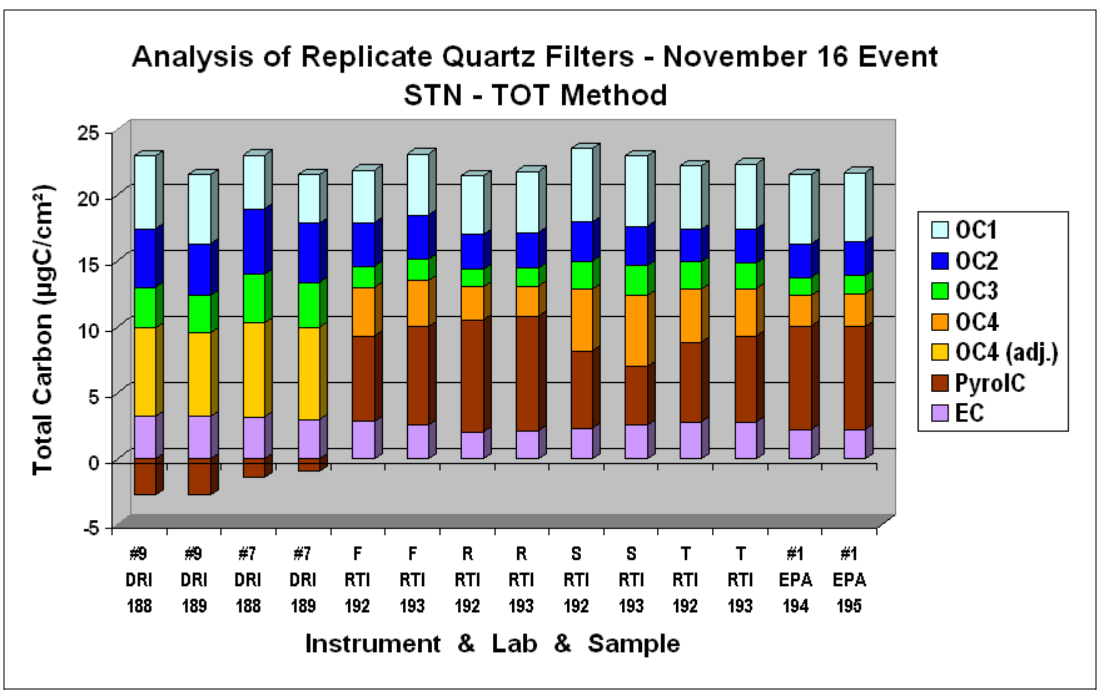


Figure 13



Some of the labs were able to analyze the PE samples using the IMPROVE and the IMPROVE-a methods. The results in Figure 14 and Figure 15 show the OC and EC components of the total carbon but do not show the more detailed fractions. It can be seen in these plots that the two methods agree quite well. The IMPROVE steering committee had just approved the new IMPROVE-a method earlier this year when these PE samples were analyzed. The new IMPROVE-a method was designed to maintain as much consistency as possible with years of old data produced by the DRI/OGC instrument using the IMPROVE method. The previous results for the STN method agree quite well for TC but show EC values that are significantly smaller than those shown here.

Figure 14

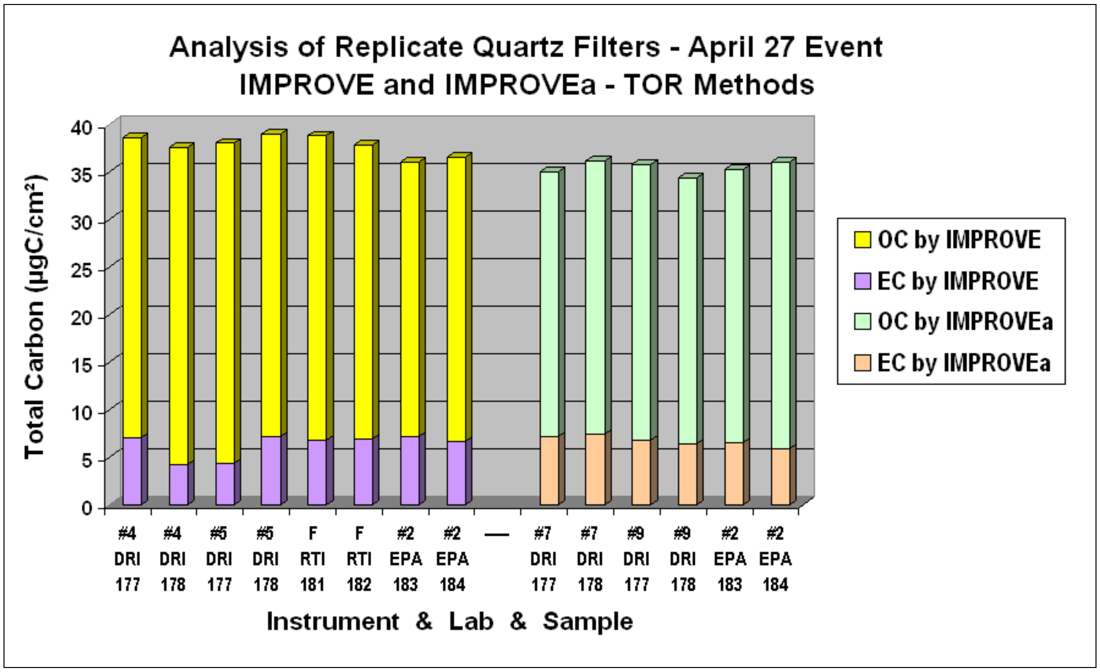


Figure 15

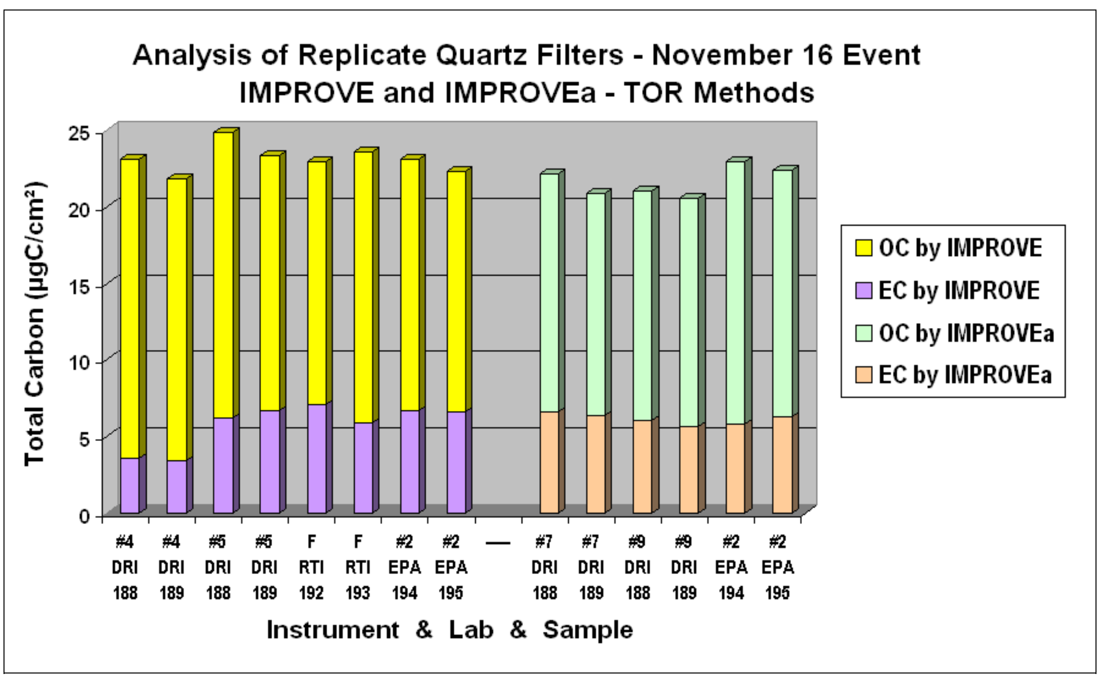


Figure 16 and Figure 17 show the IMPROVE and the IMPROVE-a results again with more detail. Good agreement can be seen for OC subfractions when the IMPROVE-a method was used. Worse precision can be seen among the instruments when the IMPROVE method was used. The DRI/OGC instruments #4 and #5 reported consistently low values for the IMPROVE PyrolC, and this may be related to air leaks during the first stage of the analysis. The two Sunset Dual Mode instruments (RTI F and EPA #2) reported consistently low values for the IMPROVE OC1 fraction. This may be explained by a difference in the accuracy of the temperature measurements inside the sample oven. The OC1 fraction is very sensitive to the 120°C set point specified by the IMPROVE method.

Figure 16

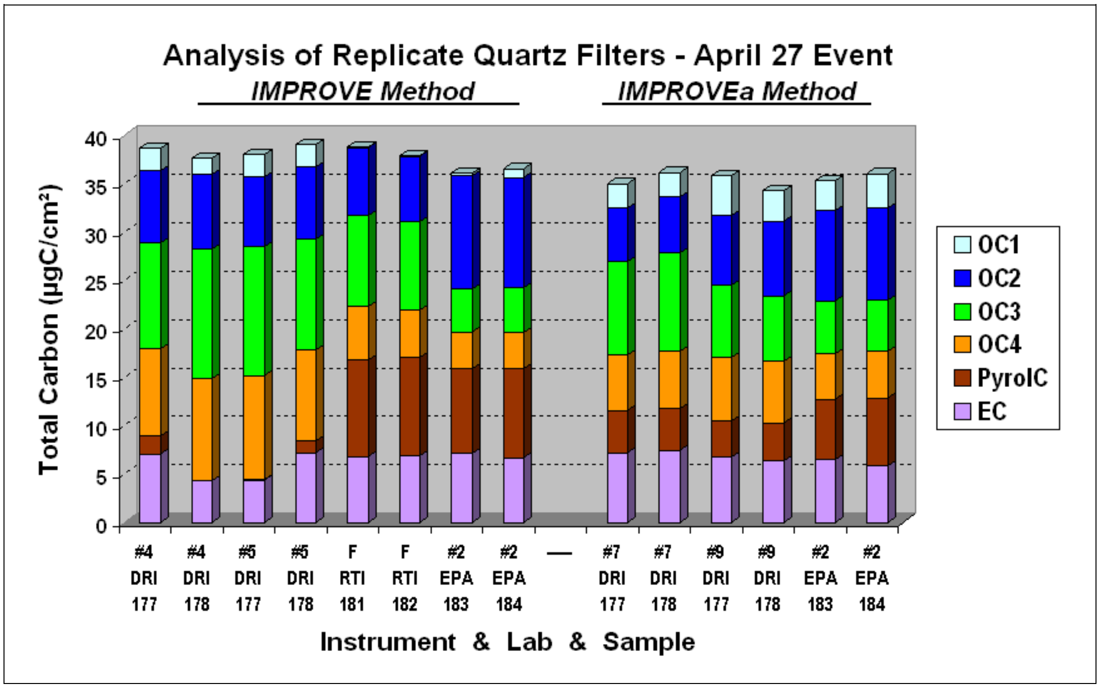
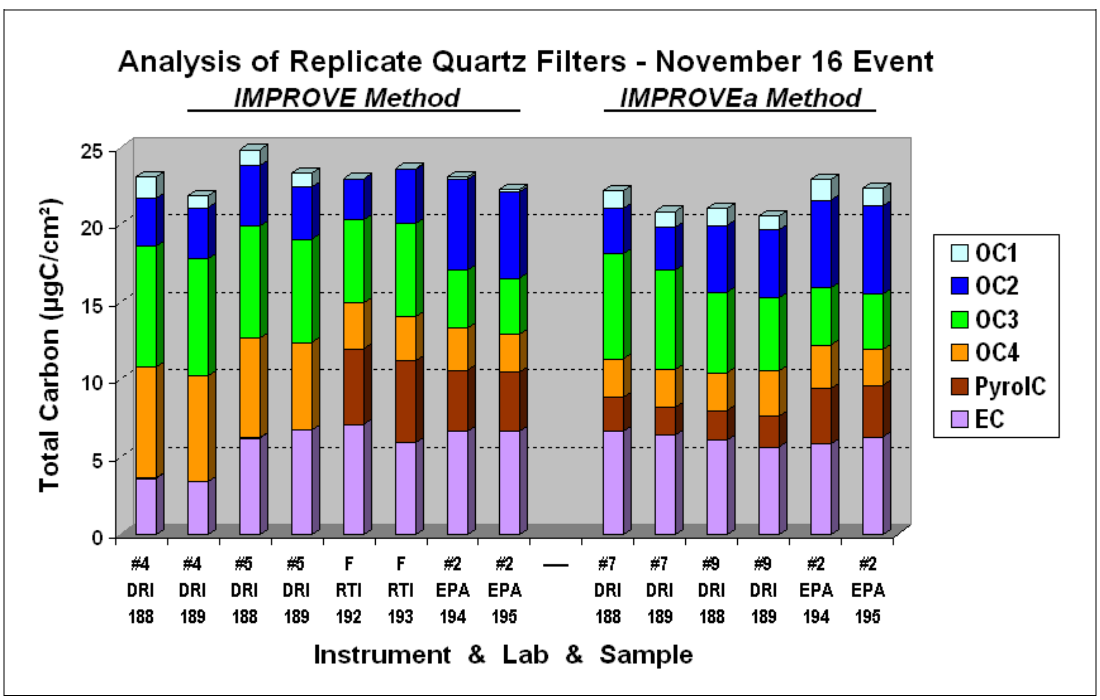


Figure 17



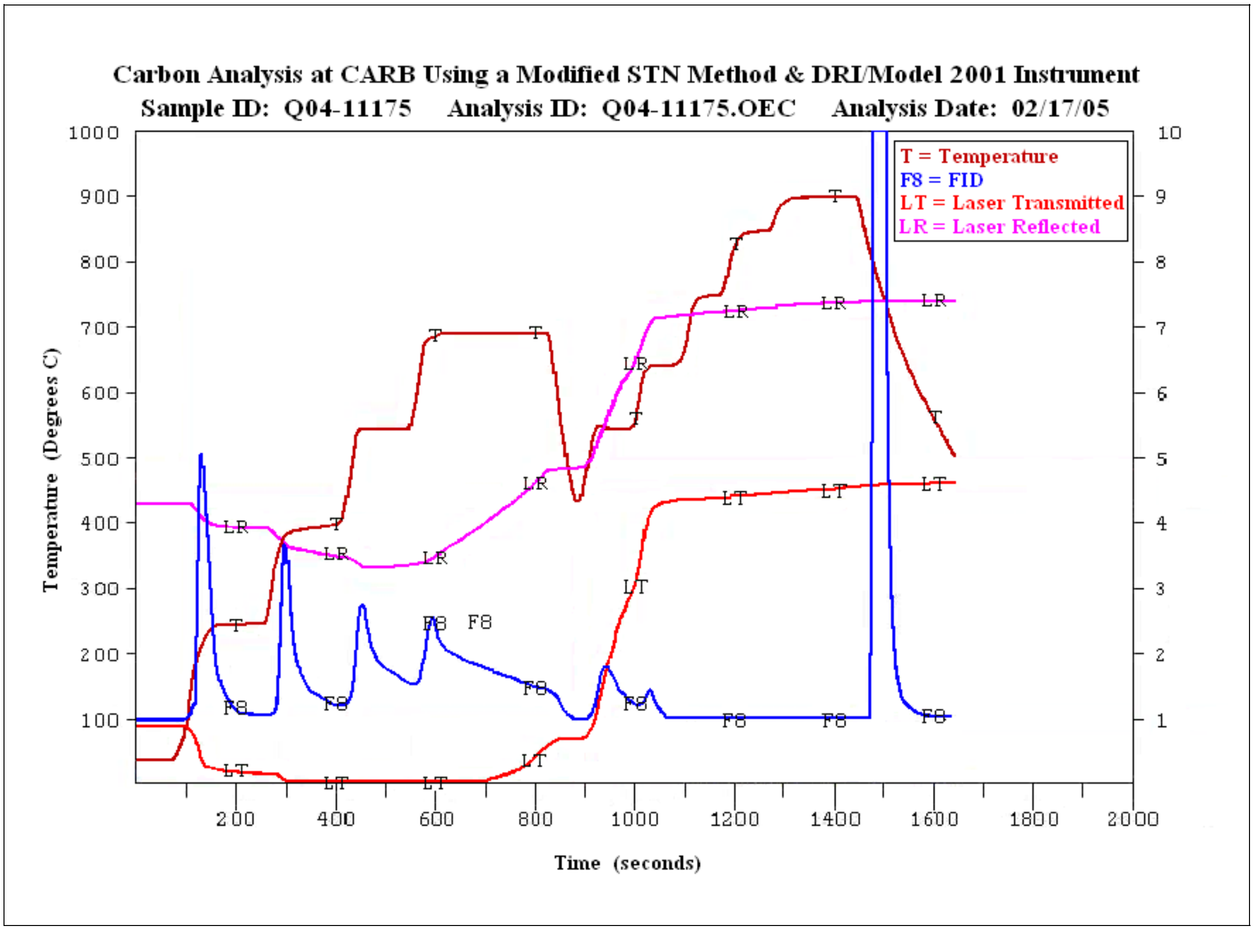
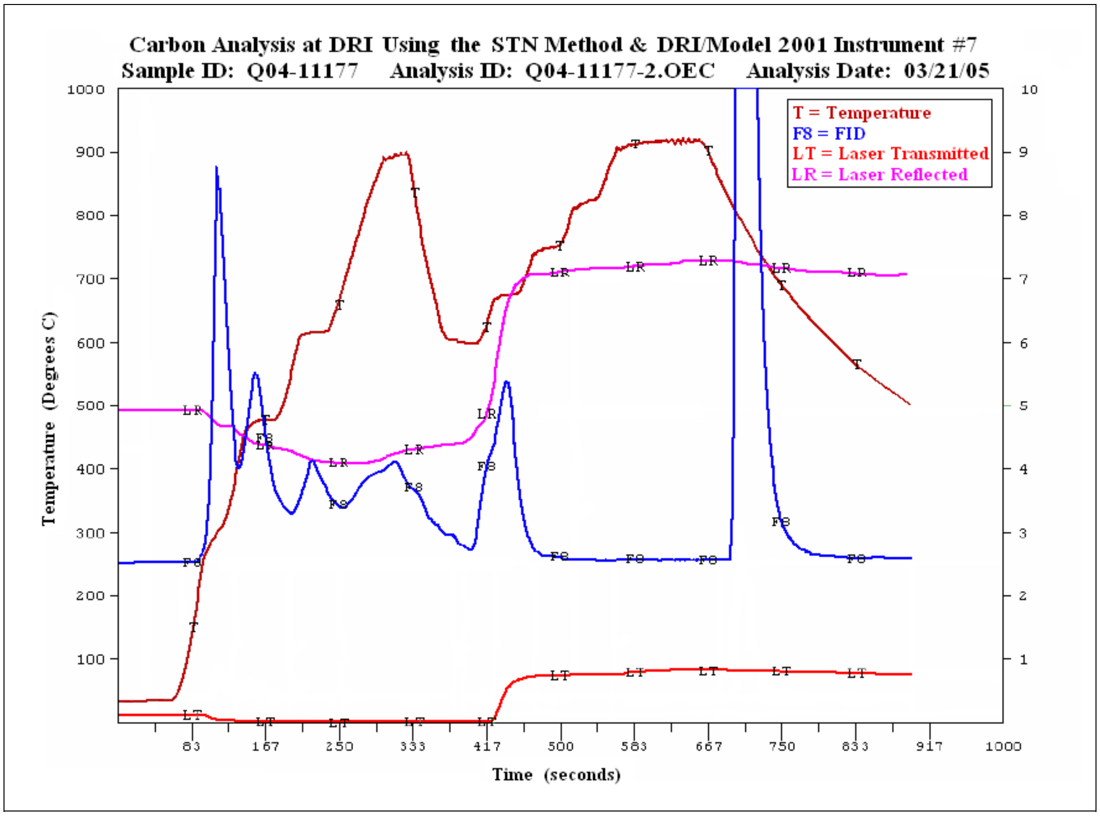


Figure 18

This report includes several thermograms from all of the instruments that were used for this study, and each thermogram was derived from the analysis of a replicate PE sample that was loaded during the collection event which started on April 27, 2004. Figure 18 shows the first thermogram submitted by CARB using their modified STN method and DRI/Model 2001 #1 instrument. CARB has adopted a modified temperature protocol because about three years ago they observed symptoms of an air leak during the first [non-oxidizing] stage of their analysis using the STN method. Experiments were performed to learn more about the problem (see reference 19). Their experiments included changes to the temperature protocol. During their experiments, CARB observed the leak symptoms to become less severe as the first stage maximum temperature was reduced from the STN method value of 900°C. The thermogram shows that CARB's method currently uses a 700°C maximum temperature for the first stage of the analysis. The laser signals in Figure 18 still show some sign of a possible leak. Both laser signals decrease normally from their initial values as char forms. Unfortunately, both signals increase significantly before the oxygen valve opens at approximately 850 seconds into the run. It could be argued that the sample itself contains oxidizing compounds that cause the char to oxidize prematurely. If this were the case, we should see the same symptoms in the thermograms that follow Figure 18.

Figures 19 through 22 show individual thermograms from various instruments using the STN method.

Figure 19



Figures 19 and 20 were produced at DRI using the STN method and DRI/Model 2001 instruments.

Figure 20

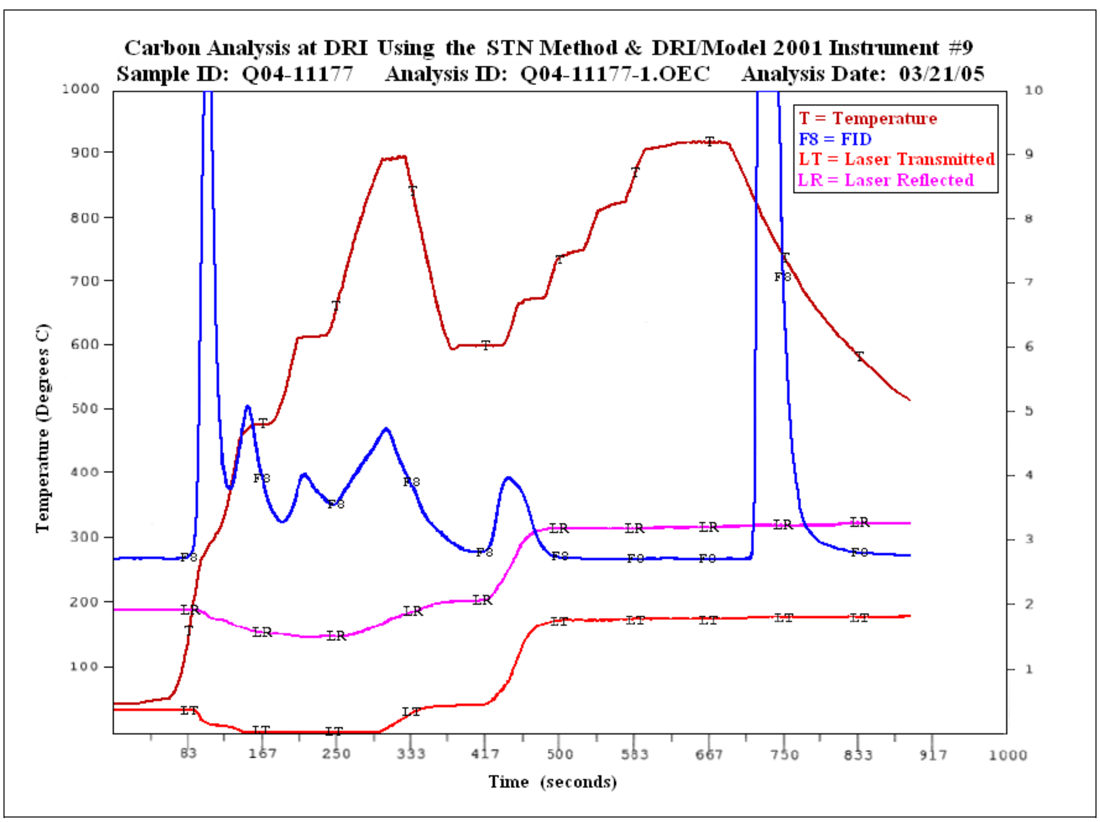


Figure 21

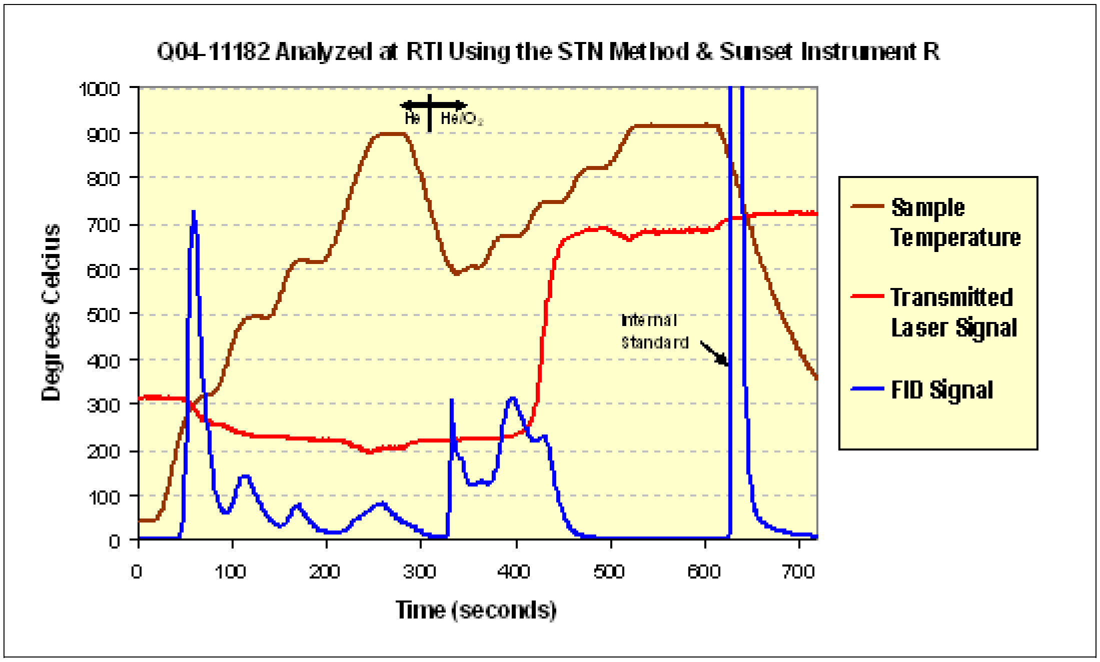


Figure 21 is a thermogram produced at RTI using the STN method and their Sunset instrument R. Figure 22 is a thermogram produced at NAREL using the STN method and their Sunset instrument #1. Both thermograms were produced by an older model Sunset [single mode] instrument, as indicated by a single laser signal, configured to perform the TOT analysis. It should be explained that all of the Sunset thermograms were produced at NAREL from the information inside the raw data files, and the laser signal(s) presented here were not processed using the Sunset software to correct for temperature dependence of the laser/diode system.

Figure 22

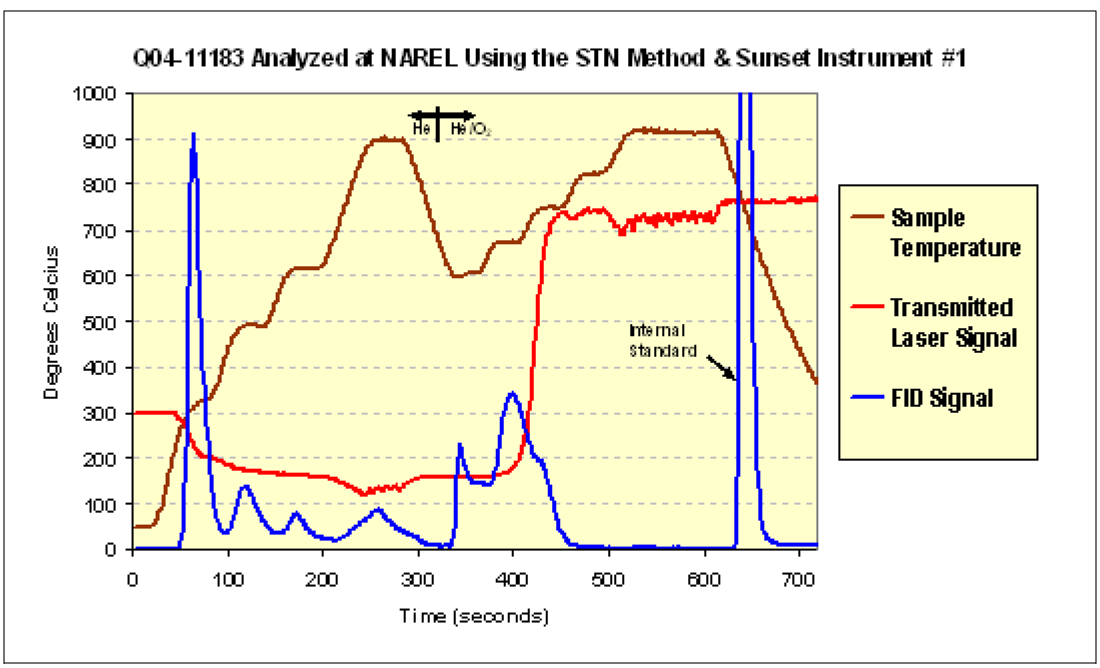


Figure 23

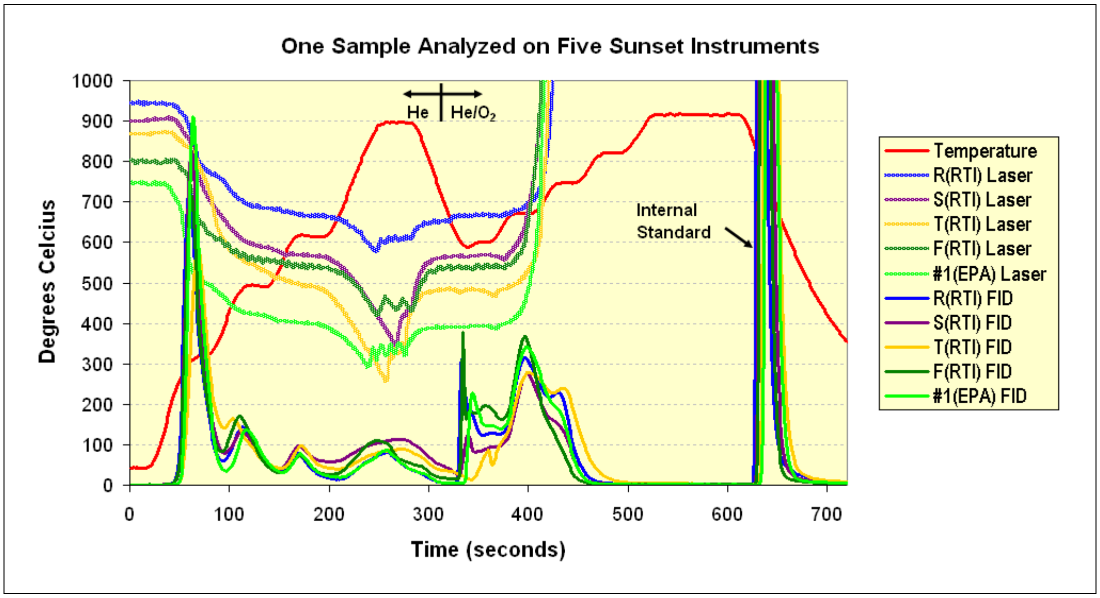


Figure 23 is a composite of five thermograms. Two of the analyses were presented earlier as individual thermograms in Figure 21 and Figure 22. The single temperature trace was taken from the first analysis using the "R" instrument. All of the laser signals have been amplified and allowed to go off-scale during the later part of the thermogram so that critical features of each laser trace may be seen more clearly.

Figure 24 is the first IMPROVE thermogram produced at DRI using the DRI/OGC instrument #4.

Figure 24

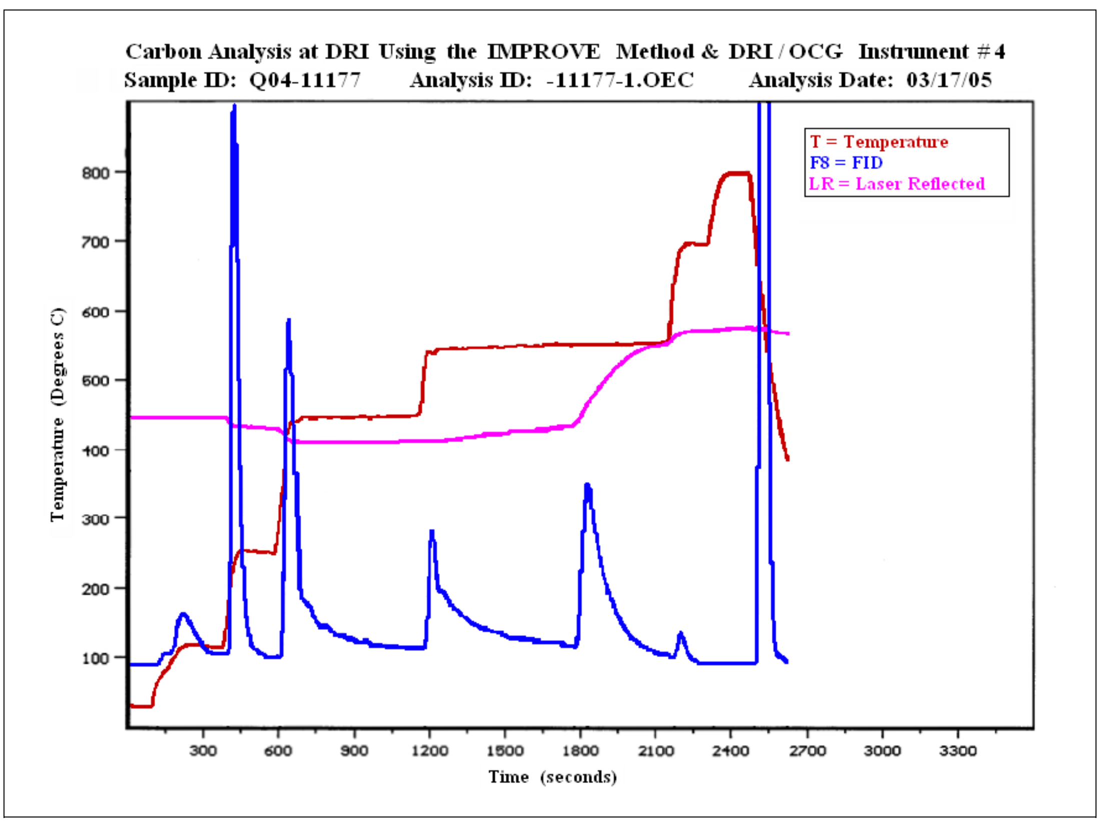


Figure 25

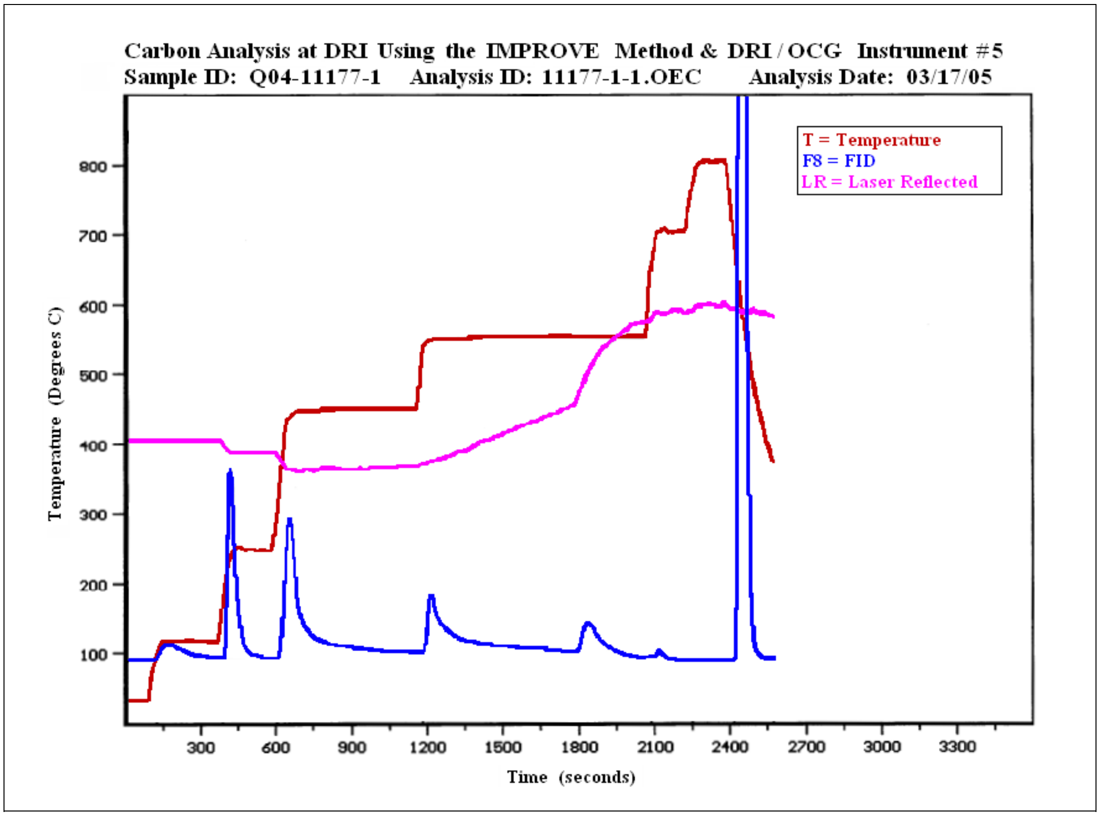


Figure 25 is another IMPROVE thermogram produced at DRI using their DRI/OGC instrument #5. This thermogram shows some evidence of an air leak during the first stage of analysis as indicated by the premature rise of the laser signal before the oxygen valve opens at approximately 1800 seconds. Much less premature rise of the laser signal can be observed in the other IMPROVE thermograms presented in Figures 24, 26, and 27.

Figure 26

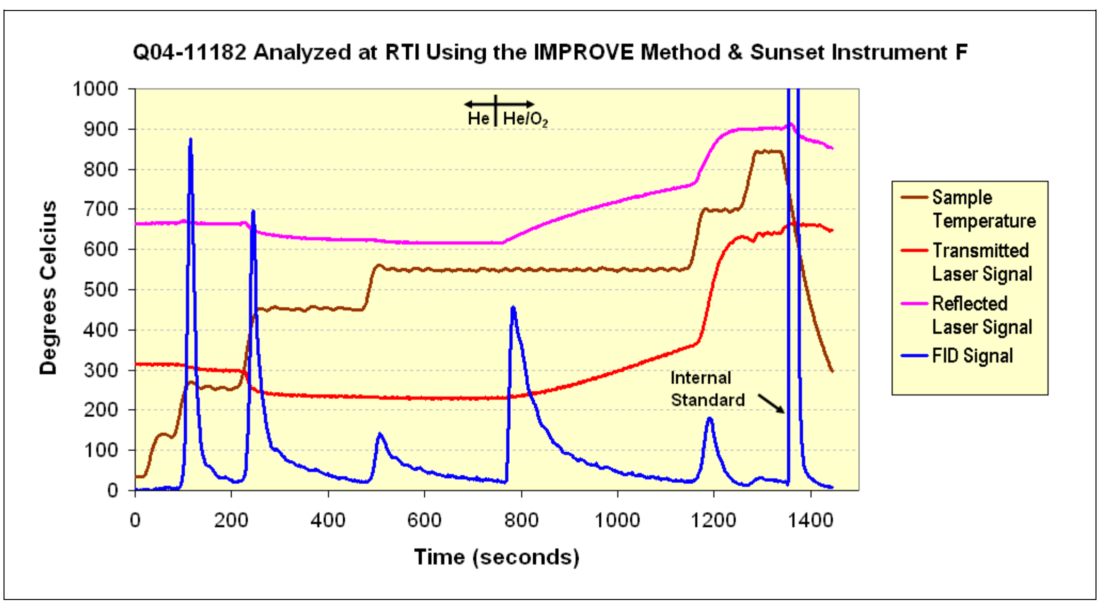


Figure 27

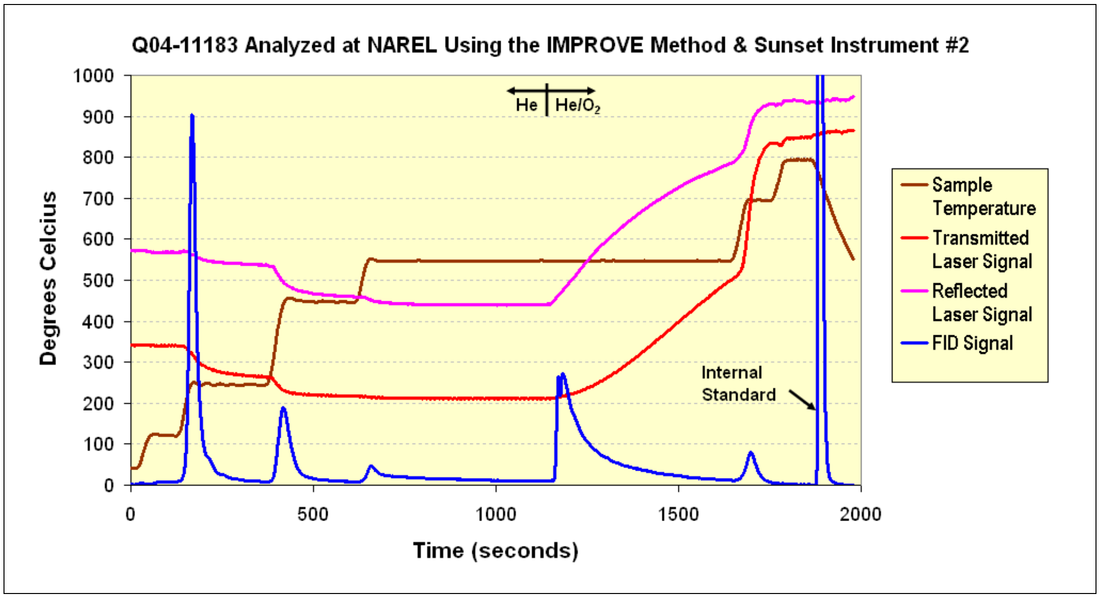


Figure 27 is the last of the IMPROVE thermograms, and Figure 28 is the first of three IMPROVE-a thermograms. Figure 28 was produced at DRI using their DRI/Model 2001 instrument #7. It is easy to interpret from this thermogram that the oxygen valve opened at approximately 1300 seconds and the split point was assigned shortly thereafter at approximately 1350 seconds. Notice that the transmitted laser signal usually supports a split point that is slightly later than the split point supported by the reflected laser signal. In this thermogram, the transmitted laser signals support a split point at approximately 1400 seconds.

Figure 28

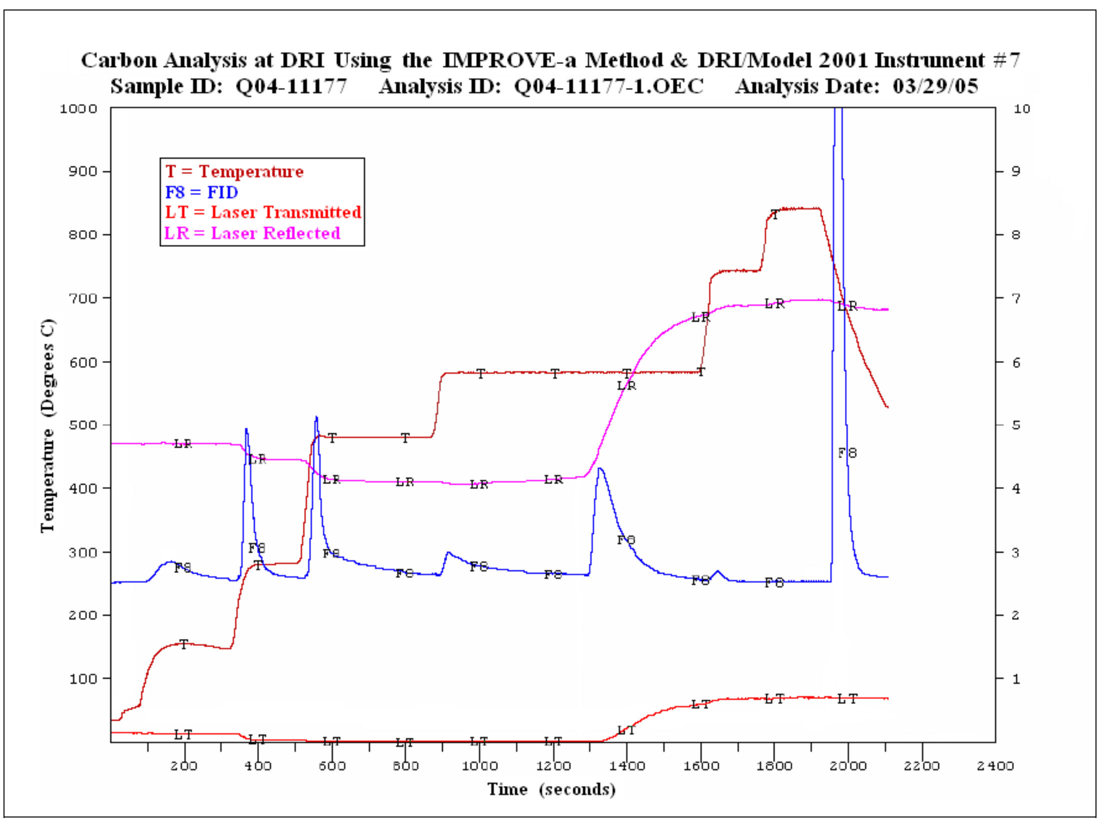


Figure 29

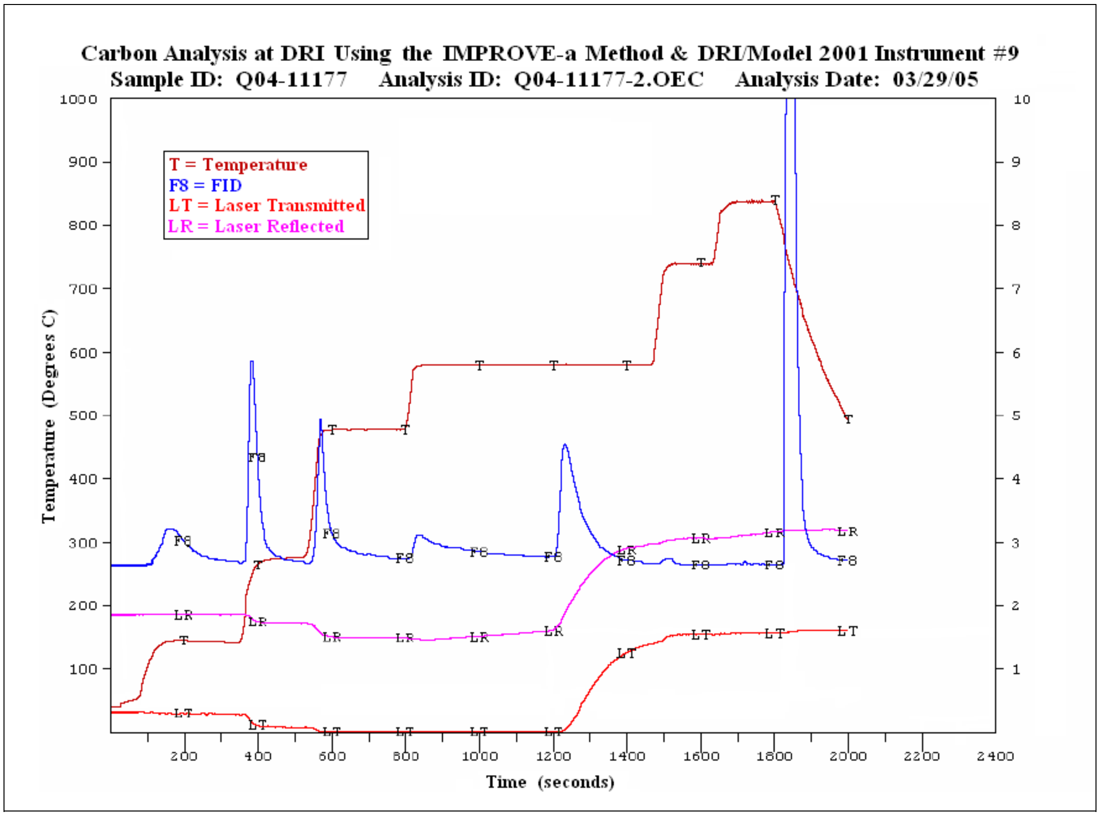
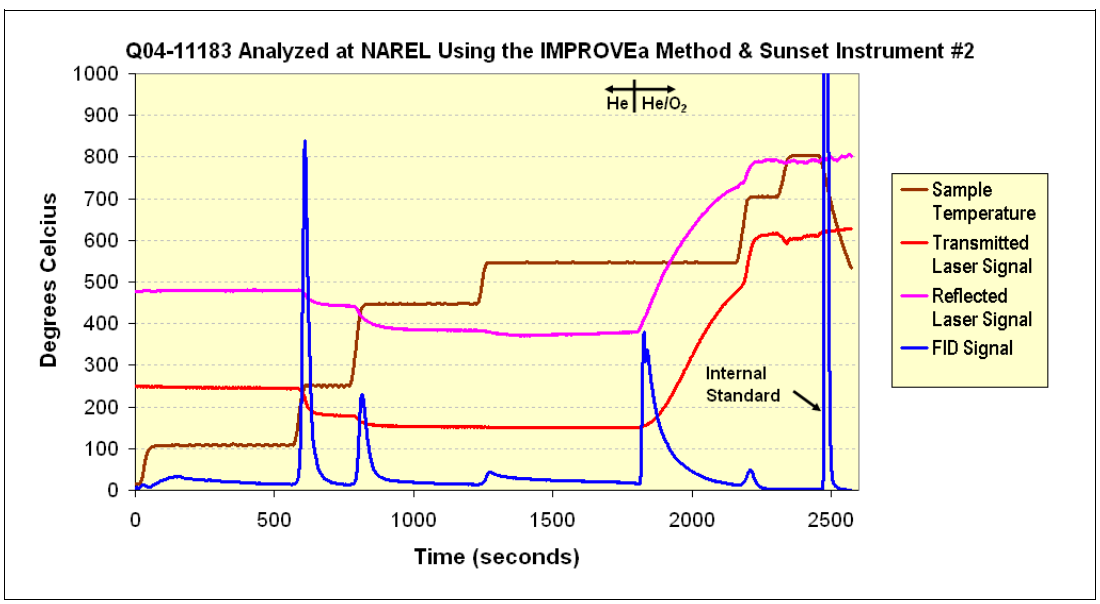


Figure 29 was produced at DRI using the IMPROVE-a method and the DRI/Model 2001 instrument #9. Figure 30 is the last thermogram presented in this report, and it was produced at NAREL using their Sunset (Dual Mode) instrument which was optimized to run the IMPROVE-a method. Thirteen thermograms have been presented, and each one represents the analysis of a stable residue that was loaded onto the filter during a single collection event. Results from all of the quartz filters are presented in Table 11 at the end of this report. This table includes the uncertainty of measurement when it was available. Table 11 also contains results from the blank filters that were part of each set of PE samples.

Figure 30



XRF Analysis

NAREL provided each participating laboratory with a set of six 47-mm filters for elemental analysis using energy dispersive XRF. Each sample set contained two blank filters and four filters that were loaded with $PM_{2.5}$ collected from the Montgomery air. Co-located Met One SuperSASS air samplers were used to load filters and create replicates in each sample set according to the sampling schedule presented in Table 7.

Table 7. Sampling Schedule for XRF PE Filters

Filter ID	Serial Number	Sample Start	Event Duration	Receiving Lab
T04-11257	T2017266	16-Dec-04	138-hr	DRI
T04-11258	T2017268	16-Dec-04	138-hr	DRI
T04-11267	T2017278	23-Dec-04	192-hr	DRI
T04-11268	T2017279	23-Dec-04	192-hr	DRI
T04-11259	T2017269	16-Dec-04	138-hr	ODEQ
T04-11260	T2017270	16-Dec-04	138-hr	ODEQ
T04-11269	T2017280	23-Dec-04	192-hr	ODEQ
T04-11270	T2017281	23-Dec-04	192-hr	ODEQ
T04-11261	T2017271	16-Dec-04	138-hr	RTI
T04-11262	T2017272	16-Dec-04	138-hr	RTI
T04-11271	T2017282	23-Dec-04	192-hr	RTI
T04-11272	T2017283	23-Dec-04	192-hr	RTI
T04-11263	T2017273	16-Dec-04	138-hr	EPA - NERL
T04-11264	T2017274	16-Dec-04	138-hr	EPA - NERL
T04-11273	T2017284	23-Dec-04	192-hr	EPA - NERL
T04-11274	T2017285	23-Dec-04	192-hr	EPA - NERL

Hidden replicate filters were present within each sample set. Table 7 shows that two of the loaded filters in each set were replicates of the same collection event. The results were reported to NAREL as mass of the element per square centimeter of deposit ($\mu g/cm^2$), and a one-sigma uncertainty was provided for each analytical result. Those results were multiplied by the total area of a filter deposit, 11.3 cm^2, to produce final results in units of micrograms of the element per filter (µg/filter).

A request was made for each lab to provide specific information that will help us better understand how the analytical results were produced. A questionnaire was prepared and distributed to each lab. The questionnaire was designed to document those instrument conditions that were used to produce the XRF spectra. The information provided by each lab may be viewed in Tables 13 through 17 at the end of this report.

A second request was made for each lab to provide two specific XRF spectra. As requested, each lab provided the primary spectrum from which aluminum was determined for two samples. One spectrum was created during the analysis of a replicate PE sample collected on December 16, 2004 (see Table 7). The second spectrum was created during the analysis of a PE filter blank. These spectra are included in this report to serve as an example of the raw data produced at each lab.

XRF Results

A large number of XRF results were reported for this study. Forty-eight elements are routinely reported for each sample, and twenty-four samples were reported.

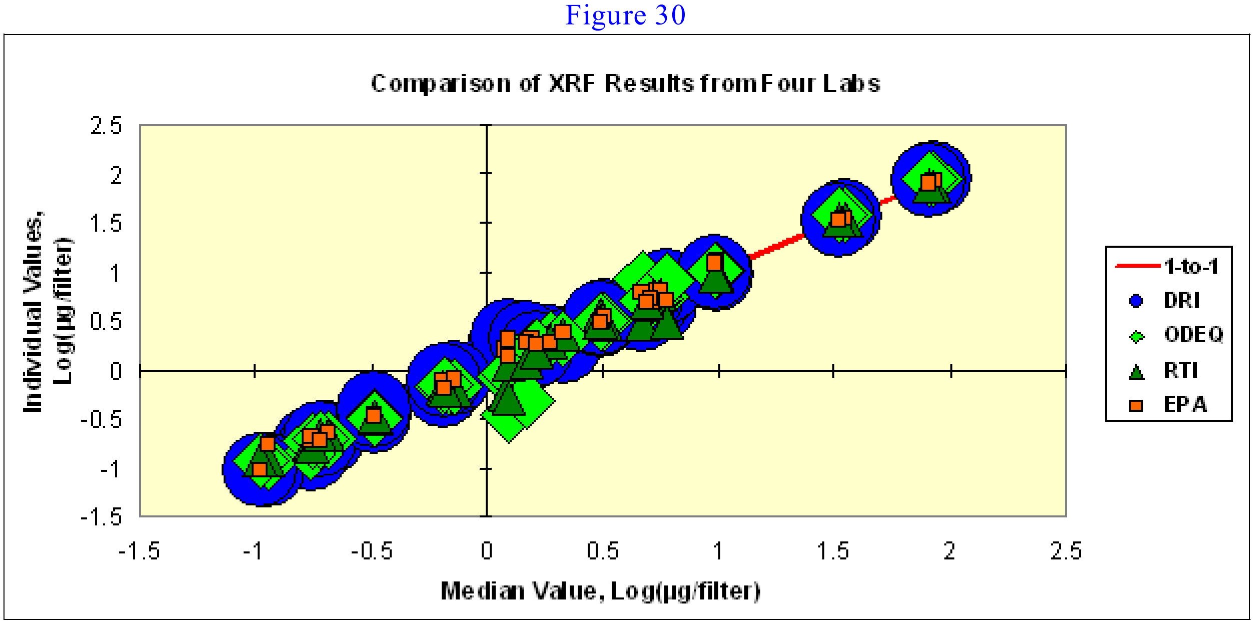
(48 elements/analysis) x (24 analyses) = 1152 results

CARB did not participate in this part of the study because the XRF lab was temporarily out of service due to the purchase of a new instrument. The results from all reporting laboratories are included in Table 12 at the end of this report. Table 12 also contains a median value calculated for some of the elements. A median value was calculated only when all of the reporting labs determined a concentration greater than three times the expressed uncertainty. Six of the heavy elements (Sm, Eu, Tb, Hf, Ta, and Ir) were not included in EPA's analysis, and therefore these EPA results are missing from the table of results.

All of the results have been compared to the median values by constructing a scatter plot shown in Figure 30. A log-log plot was constructed with the median values forming a straight line of unity slope. The corresponding results from all of the labs were superimposed on the median line. Most of the results were very near the median indicating good agreement among the participating labs. Even though Figure 30 gives a quick visual impression of many results that cover a wide range of concentrations, this scatter plot does not identify the element plotted nor the sample.

The more significant XRF results are presented again as stacked bar graphs in Figures 31 and 32. Each bar segment represents an individual value reported by one of the labs. Elements are identified along the horizontal axis, and the elements are arranged from left to right in order of decreasing concentration. The vertical axis of each bar graph is a linear scale, and each bar is normalized to the sum of results reported by all instruments identified in the legend. Each bar segment is color coded to identify the laboratory and labeled to show the reported concentration value. Again, the only results shown in the graphs are those that are significantly above the reported uncertainty. Those significant results can be identified in Table 12 by looking for a calculated median.

Figure 30



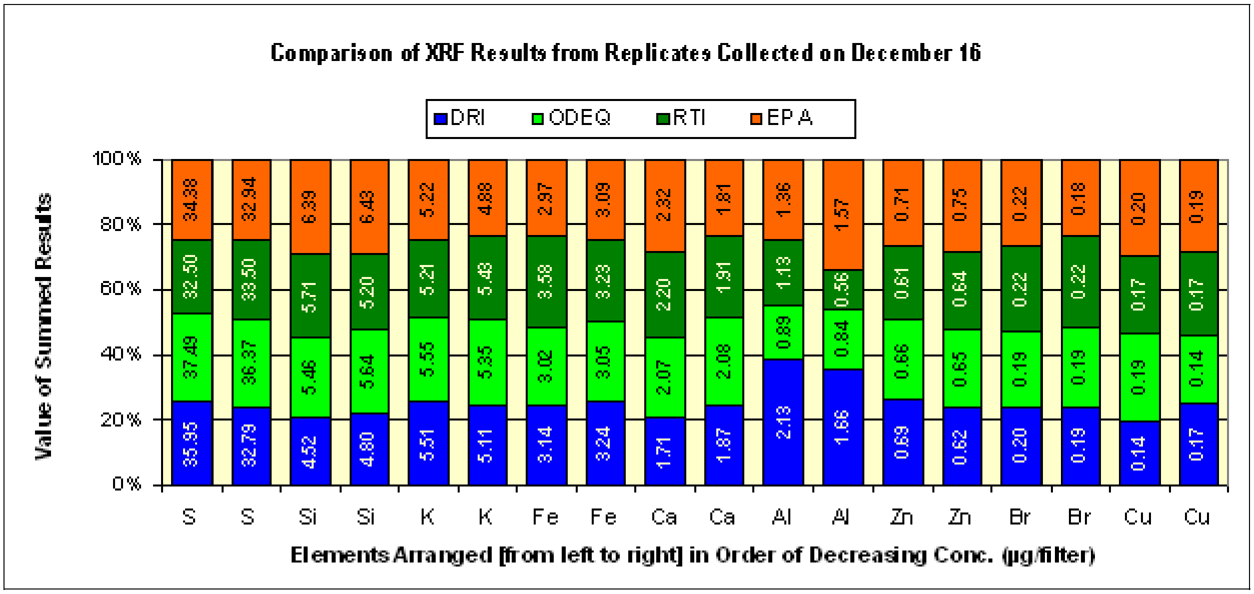


Figure 31

Figure 31 shows results from eight filter replicates created on December 16, 2004, and identified as samples T04-11257 through T04-11264 in Table 12. Two of these replicates were analyzed at each of the four participating laboratories. The most inconsistently reported element in Figure 31 was aluminum with values ranging from 0.56 to 2.13 µg/filter. It is worth noting that aluminum was a very small signal in the raw data spectra produced at all of the labs.

Figure 32 shows results from eight more filter replicates created on December 23, 2004, and identified as samples T04-11267 through T04-11274 in Table 12. The most inconsistent results observed in Figure 32 are for Al and Na, and both of these elements are observed as very small signals within the spectra produced at all of the labs.

Figure 32

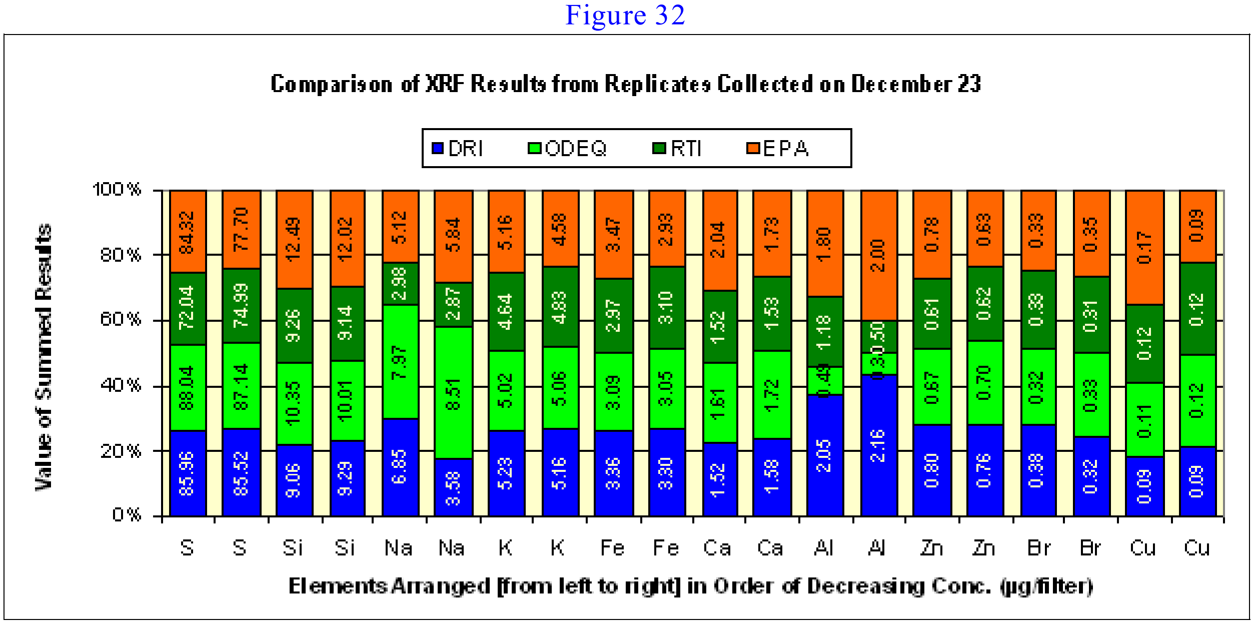
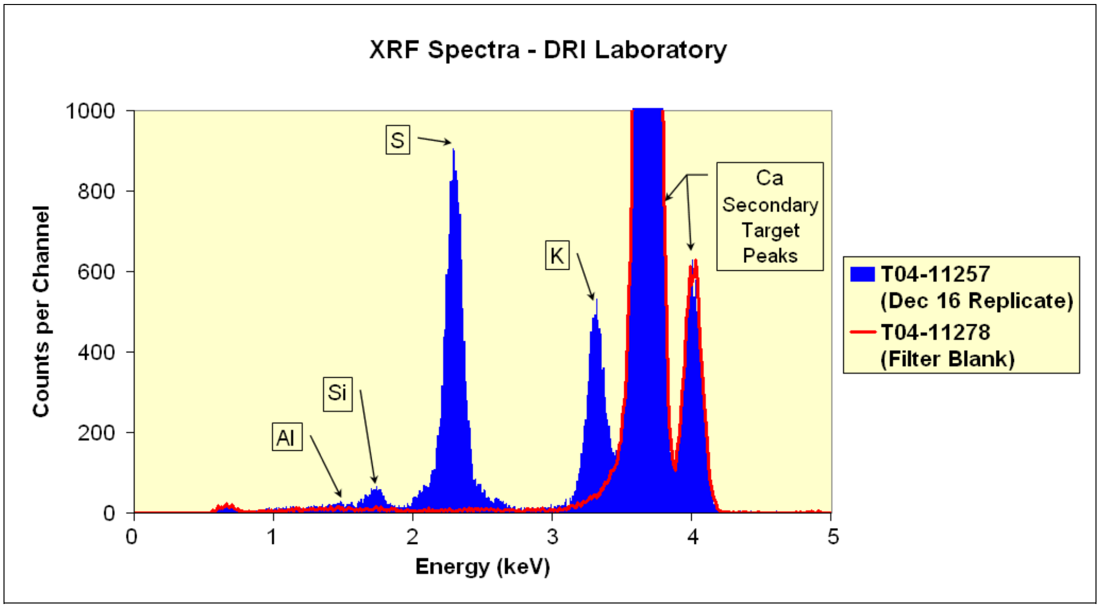


Figure 33



A few spectra have been included in this report to give us an example of the raw data produced at each lab. Figure 33 shows two superimposed spectra that were produced at DRI. The conditions that produced these spectra are listed in column #1 of Table 13 at the end of this report. Al, Si, S, and K were detected above background in sample T04-11257 based upon these spectra.

Figure 34 shows two superimposed spectra that were produced at ODEQ. The conditions that produced these spectra are listed in column #1 of Table 14 at the end of this report. Al, Si, S, and K were detected above background in sample T04-11259 based upon these spectra. It is especially interesting to look at the signal for Al in all of the sepctra, since all of the labs reported Al present [above background] in the December 16 replicates.

Figure 34

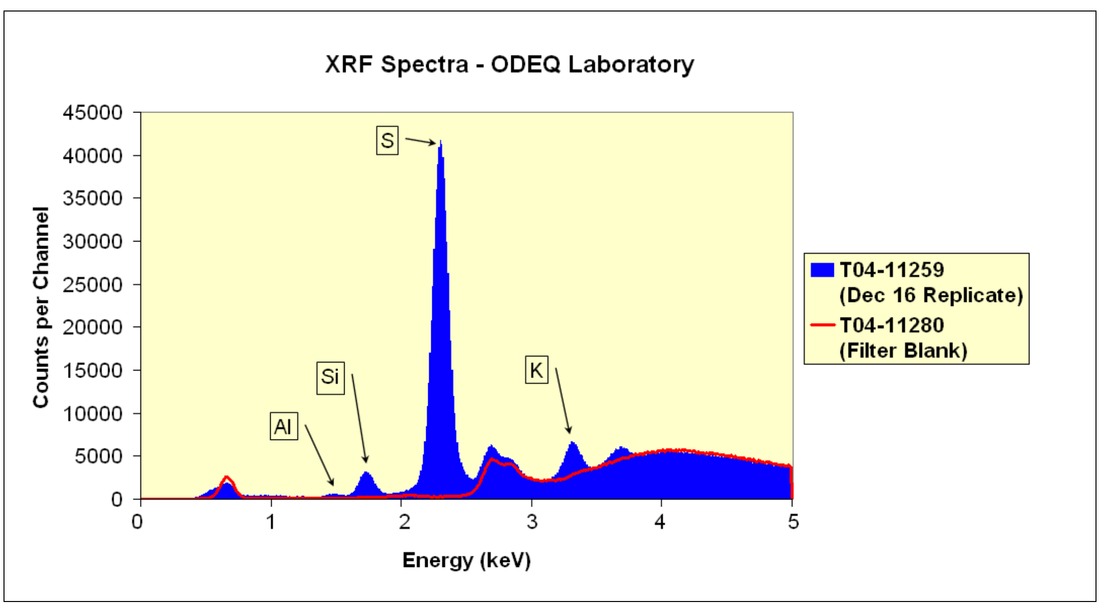


Figure 35

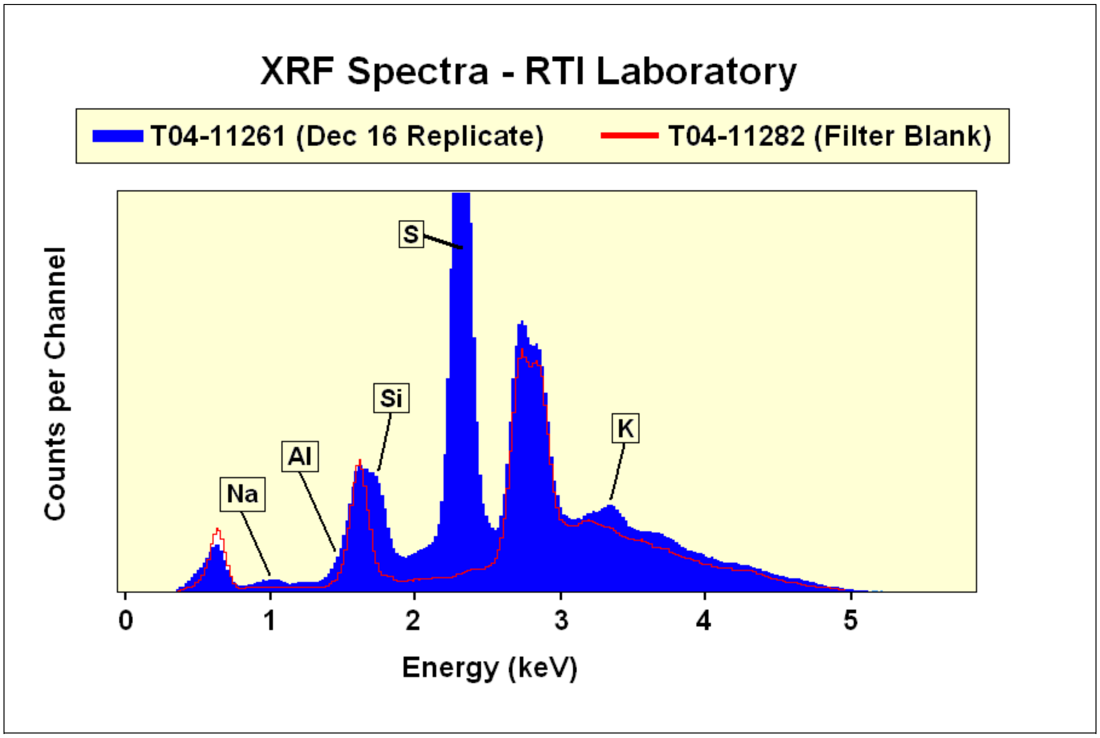
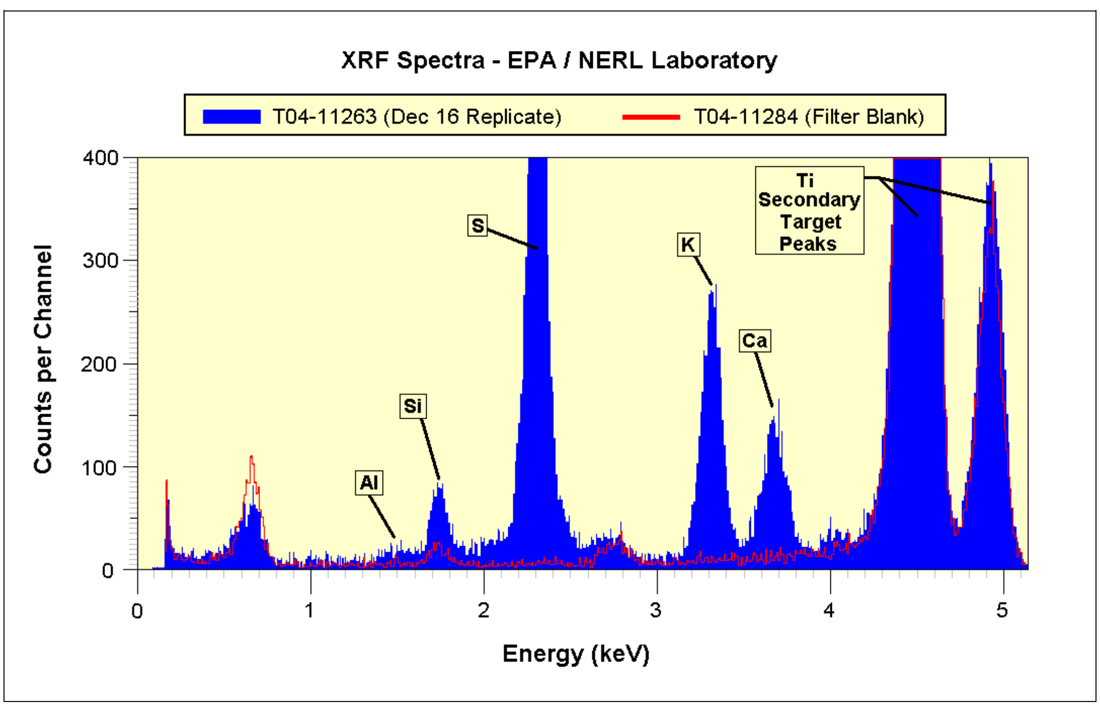


Figure 35 shows spectra that were produced at RTI using the conditions listed in column #1 of Table 16. Our last spectra shown in Figure 36 were produced at EPA's NERL facility using the conditions listed in column #5 of Table 17. We appreciate the effort that our participating labs made to provide us with the raw data presented here.

Figure 36



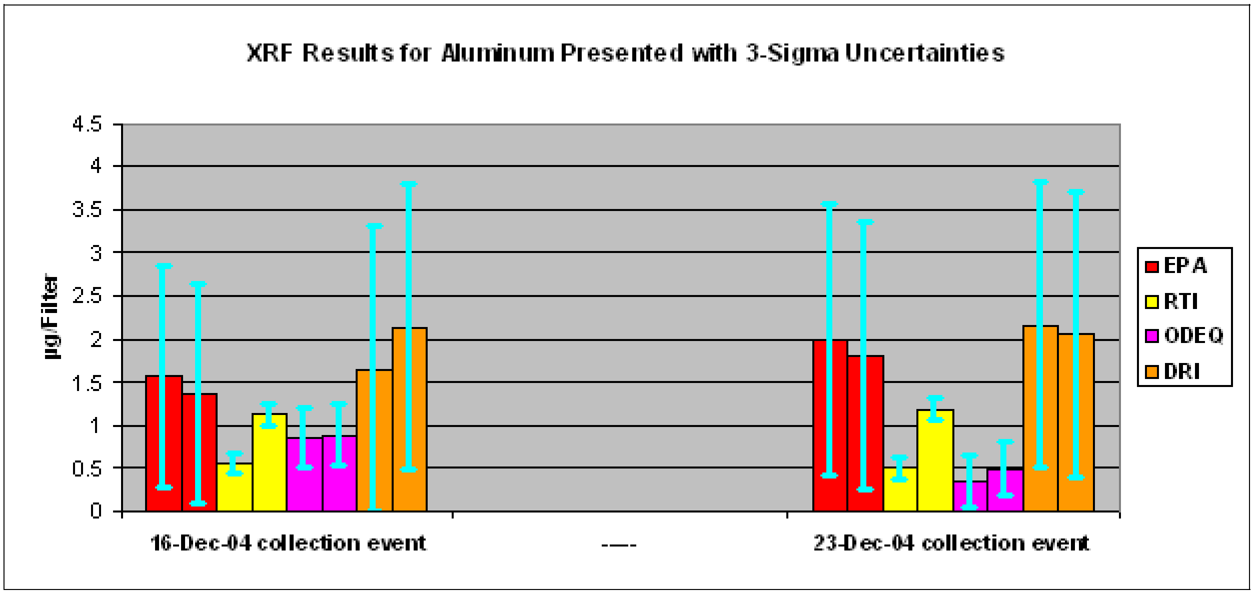


Figure 37

Figure 37 presents another view of the XRF results for aluminum which allows us to examine the uncertainty reported by each lab. Notice that the error bars represent a 3-sigma uncertainty which was used to select those results presented previously in Figures 30 through 32. Figure 37 shows results from eight filter replicates that were collected on December 16 and eight filter replicates that were collected on December 23. It is a worthy exercise to compare the spectra presented earlier with the uncertainties presented here. It is surprising that RTI consistently reported the smallest uncertainty for both collection events since RTI's spectra [in Figure 35] contain a significant interference very near aluminum.

Figure 38 presents a similar view of the XRF results for silicon. RTI reported substantially smaller uncertainties for silicon even though the spectrum shows silicon as a shoulder on the interference peak. All four of the labs actually determined silicon and aluminum from the spectra presented in this report.

Figure 38

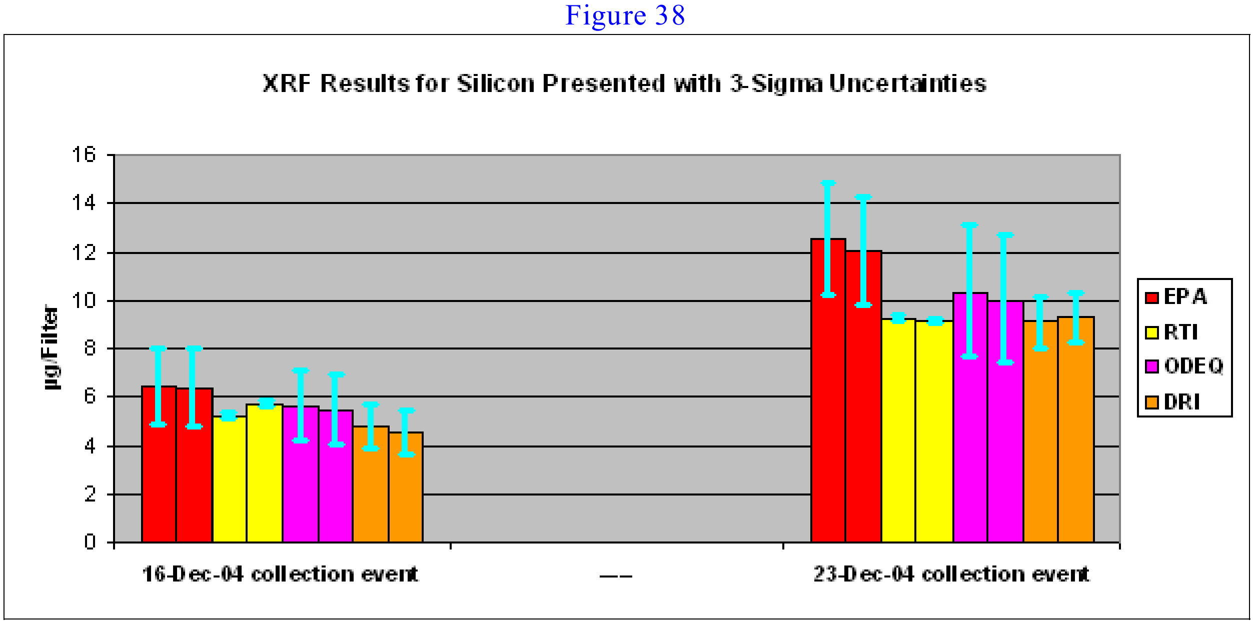


Table 8. Summary of XRF Results and Uncertainties (µg/filter)								
	EPA Results	**EPA Uncert.**	**RTI Results**	**RTI Uncert.**	**ODEQ Results**	**ODEQ Uncert.**	**DRI Results**	**DRI Uncert.**
Replicates from Dec 16								
Mean	1.475	0.141	1.169	0.034	1.164	0.261	1.272	0.194
Max	34.381	1.011	33.505	0.158	37.487	3.020	35.945	0.951
Min	-0.659	0.014	0.000	0.004	-1.153	0.008	0.000	0.006
Std. Dev.	5.266	0.208	4.823	0.035	5.399	0.591	5.025	0.253
Count	84	84	96	96	96	96	96	96
Replicates from Dec 23								
Mean	2.787	0.183	2.069	0.037	2.452	0.376	2.532	0.204
Max	84.316	2.287	74.987	0.237	88.042	7.077	85.959	0.993
Min	-0.064	0.015	0.000	0.004	-0.921	0.009	0.000	0.006
Std. Dev.	12.489	0.370	10.593	0.046	12.646	1.091	12.328	0.265
Count	84	84	96	96	96	96	96	96
Blank Filters								
Mean	0.062	0.076	0.001	0.023	-0.064	0.163	0.048	0.184
Max	1.037	0.554	0.023	0.131	0.042	2.258	1.401	0.942
Min	-0.462	0.014	0.000	0.002	-1.449	0.007	0.000	0.001
Std. Dev.	0.223	0.104	0.004	0.025	0.216	0.433	0.163	0.248
Count	84	84	96	96	96	96	96	96

Table 8 is a summary of the XRF results and the uncertainties grouped by sample type. For each sample type, two filters were analyzed at each lab. Each lab reported 96 results for each sample type, except for the EPA lab. We should remember that six of the heavy elements (Sm, Eu, Tb, Hf, Ta, and Ir) were not included in EPA's analysis, and this may skew the statistics to some extent. It is appropriate to compare these statistics as long as we fully appreciate the fact that there was no "true value" for any of the results with the possible exception of the blank filters. It is worth noting that for all three sample types, the mean uncertainty reported by RTI is considerably smaller than the mean uncertainty reported by the other labs. This may indicate a real difference in the way uncertainties are calculated at RTI, or it may indicate a real difference in the raw data itself. This report has presented only a small sample of the raw data.

Conclusions

This study was designed to evaluate the analytical performance of several $PM_{2.5}$ speciation labs. The approach was simple. Each lab analyzed an almost identical set of blind PE samples, and the results reported from all of the labs have been compared. The scope of this study included four analytical techniques, and multiple methods were reported for IC, TOA carbon, and XRF. At least one EPA lab was able to report results for most of the methods used during this study.

Four labs analyzed a set of PE samples for gravimetric mass, and all of the labs performed well. Results for all of the samples were inside the 3-sigma advisory limits established by NAREL.

Five different labs reported IC results for at least one set of PE samples, and only one problem was observed in the IC results. NAREL reported poor analytical precision for chloride that was present in two replicates. No other problems were observed in the IC results.

Four labs analyzed a set of quartz PE filters, and all of the labs, except CARB, analyzed each filter multiple times in order to report results from more than one instrument and also report results using more than one TOA method. Ultimately a total of fifteen data packages were used to report TOA results, and we should remember that each data package contained hidden replicates. Good precision was observed for all of the TC values reported, regardless of method and regardless of instrument. As expected, the precision was best for TC followed closely by OC. EC results for the STN method were lower than EC results reported for the IMPROVE and IMPROVE-a methods. The worst precision was observed for the DRI/OGC instruments running the IMPROVE method. There was some evidence in the raw data that a variable air leak may have contributed to the poor precision. Raw data from the CARB instrument also contained some evidence of an air leak. The thermograms included in this report help show critical information that is difficult to communicate with text.

None of the labs that reported XRF results used the same instrument. Therefore different hardware and different software were used to produce the results. XRF spectra were presented to illustrate the dramatic differences in raw data even though replicate samples were analyzed. Despite these facts, good agreement was observed for most of the elements that were significantly above the reported uncertainty. The largest disagreement in the XRF results was observed for aluminum and sodium. Both of these elements produce poor instrument response [compared to heavier elements], and larger uncertainties are expected for the lighter elements. This study has raised an important question about how uncertainties are calculated. There is no standard method for calculating the uncertainty. Each lab used a custom method to calculate the XRF uncertainty. It would be difficult to predict the outcome of using a single method at all labs since there were significant differences in the raw data.

Special effort has been made to collect information from the participating labs that help us better understand how the analytical results were produced. And that information has been included in this report. The author would like to take this opportunity to thank those individuals who answered questions, responded to the questionnaire, and provided the requested raw data. They have helped make this a better report!

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Table 9. Gravimetric Mass PE Results

Sample ID	Sample Description	Tare Mass Test Lab (mg)	Tare Mass NAREL (mg)	Final Mass Test Lab (mg)	Final Mass NAREL (mg)	Captured $PM_{2.5}$ Test Lab (mg)	Captured $PM_{2.5}$ NAREL (mg)	Inter-Lab Difference* of Captured $PM_{2.5}$ (mg)	Name of the Test Lab
T05-11285	24-hr collection event, 01/20/05	145.839	145.838	146.073	146.074	0.234	0.236	0.002	CARB
T05-11286	24-hr collection event, 01/20/05	145.389	145.389	145.646	145.644	0.257	0.255	-0.002	CARB
T05-11287	48-hr collection event, 01/21/05	143.933	143.935	144.237	144.239	0.304	0.304	0.000	CARB
T05-11288	48-hr collection event, 01/21/05	144.683	144.685	144.982	144.990	0.299	0.305	0.006	CARB
T05-11289	12-hr collection event, 01/23/05	145.799	145.797	145.834	145.833	0.035	0.036	0.001	CARB
T05-11290	12-hr collection event, 01/23/05	141.825	141.822	141.868	141.865	0.043	0.043	0.000	CARB
T05-11291	24-hr collection event, 01/24/05	142.169	142.169	142.269	142.265	0.100	0.096	-0.004	CARB
T05-11292	filter blank	141.304	141.302	141.310	141.306	0.006	0.004	-0.002	CARB
T05-11293	filter blank	141.055	141.054	141.058	141.056	0.003	0.002	-0.001	CARB
T05-11294	filter blank	142.774	142.773	142.781	142.777	0.007	0.004	-0.003	CARB
MW05-11325	metallic transfer weight	94.833	94.834	94.831	94.834	-0.002	0.000	0.002	DRI
MW05-11326	metallic transfer weight	190.521	190.521	190.520	190.522	-0.001	0.001	0.002	DRI
T05-11295	24-hr collection event, 01/20/05	143.964	143.952	144.191	144.182	0.227	0.230	0.003	DRI
T05-11296	24-hr collection event, 01/20/05	144.544	144.531	144.778	144.768	0.234	0.237	0.003	DRI
T05-11297	48-hr collection event, 01/21/05	143.429	143.415	143.724	143.716	0.295	0.301	0.006	DRI
T05-11298	48-hr collection event, 01/21/05	141.519	141.506	141.817	141.806	0.298	0.300	0.002	DRI
T05-11299	12-hr collection event, 01/23/05	140.397	140.383	140.435	140.424	0.038	0.041	0.003	DRI
T05-11300	12-hr collection event, 01/23/05	141.449	141.436	141.488	141.476	0.039	0.040	0.001	DRI
T05-11301	24-hr collection event, 01/24/05	142.167	142.155	142.263	142.252	0.096	0.097	0.001	DRI
T05-11302	filter blank	143.707	143.694	143.710	143.696	0.003	0.002	-0.001	DRI
T05-11303	filter blank	139.756	139.744	139.759	139.745	0.003	0.001	-0.002	DRI
T05-11304	filter blank	143.332	143.318	143.333	143.320	0.001	0.002	0.001	DRI
MW05-11327	metallic transfer weight	97.351	97.356	97.350	97.356	-0.001	0.000	0.001	DRI
MW05-11328	metallic transfer weight	196.224	196.235	196.223	196.235	-0.001	0.000	0.001	DRI

Table 9. Gravimetric Mass PE Results

Sample ID	Sample Description	Tare Mass		Final 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)		
T05-11305	24-hr collection event, 01/20/05	144.336	144.337	144.559	144.566	0.223	0.229	0.006	ODEQ
T05-11306	24-hr collection event, 01/20/05	142.974	142.972	143.197	143.205	0.223	0.233	0.010	ODEQ
T05-11307	48-hr collection event, 01/21/05	139.657	139.657	139.951	139.961	0.294	0.304	0.010	ODEQ
T05-11308	48-hr collection event, 01/21/05	141.301	141.301	141.587	141.594	0.286	0.293	0.007	ODEQ
T05-11309	12-hr collection event, 01/23/05	142.031	142.029	142.062	142.072	0.031	0.043	0.012	ODEQ
T05-11310	12-hr collection event, 01/23/05	141.468	141.468	141.500	141.505	0.032	0.037	0.005	ODEQ
T05-11311	24-hr collection event, 01/24/05	142.483	142.484	142.575	142.584	0.092	0.100	0.008	ODEQ
T05-11312	filter blank	141.487	141.487	141.489	141.490	0.002	0.003	0.001	ODEQ
T05-11313	filter blank	142.208	142.208	142.209	142.211	0.001	0.003	0.002	ODEQ
T05-11314	filter blank	140.697	140.698	140.698	140.703	0.001	0.005	0.004	ODEQ
MW05-11329	metallic transfer weight	93.775	93.776	93.775	93.776	0.000	0.000	0.000	ODEQ
MW05-11330	metallic transfer weight	188.879	188.880	188.878	188.880	-0.001	0.000	0.001	ODEQ
T05-11315	24-hr collection event, 01/20/05	139.752	139.751	139.972	139.978	0.220	0.227	0.007	RTI analyst 1
T05-11316	24-hr collection event, 01/20/05	139.527	139.527	139.749	139.765	0.222	0.238	0.016	RTI analyst 1
T05-11317	48-hr collection event, 01/21/05	142.196	142.196	142.483	142.491	0.287	0.295	0.008	RTI analyst 1
T05-11318	48-hr collection event, 01/21/05	142.533	142.531	142.829	142.838	0.296	0.307	0.011	RTI analyst 1
T05-11319	12-hr collection event, 01/23/05	141.306	141.306	141.336	141.344	0.030	0.038	0.008	RTI analyst 1
T05-11320	12-hr collection event, 01/23/05	140.549	140.549	140.584	140.593	0.035	0.044	0.009	RTI analyst 1
T05-11321	24-hr collection event, 01/24/05	140.300	140.297	140.389	140.400	0.089	0.103	0.014	RTI analyst 1
T05-11322	filter blank	141.646	141.648	141.648	141.651	0.002	0.003	0.001	RTI analyst 1
T05-11323	filter blank	145.693	145.692	145.692	145.696	-0.001	0.004	0.005	RTI analyst 1
T05-11324	filter blank	141.573	141.574	141.573	141.578	0.000	0.004	0.004	RTI analyst 1
MW05-11331	metallic transfer weight	97.545	97.546	97.545	97.546	0.000	0.000	0.000	RTI analyst 1
MW05-11332	metallic transfer weight	192.421	192.422	192.422	192.421	0.001	-0.001	-0.002	RTI analyst 1

Table 10. Ion Chromatography PE Results

Sample ID	Filter Medium	Sample Description	Lab	Method	Concentration (µg/filter)						
					Chloride	Nitrate	Nitrite	Sulfate	Ammonium	Potassium	Sodium
N04-11197	Nylon®	116-hr event, 11/24/04	CARB	STN	-----	22.484	-----	72.523	27.236	1.898	1.737
N04-11198	Nylon®	116-hr event, 11/24/04	CARB	STN	-----	24.106	-----	72.282	26.203	1.877	1.712
N04-11199	Nylon®	116-hr event, 11/24/04	DRI	STN	-----	24.039	-----	77.679	29.991	1.865	0.948
N04-11200	Nylon®	116-hr event, 11/24/04	DRI	STN	-----	23.931	-----	75.704	28.340	1.943	1.166
N04-11201	Nylon®	116-hr event, 11/24/04	ODEQ	STN	-----	26.700	-----	79.100	28.600	2.070	<3.6
N04-11202	Nylon®	116-hr event, 11/24/04	ODEQ	STN	-----	25.300	-----	77.600	27.600	1.920	<3.6
N04-11203	Nylon®	116-hr event, 11/24/04	RTI	STN	-----	24.496	-----	76.586	25.559	2.147	1.744
N04-11204	Nylon®	116-hr event, 11/24/04	RTI	STN	-----	23.129	-----	73.608	25.117	2.126	1.796
N04-11205	Nylon®	116-hr event, 11/24/04	NAREL	STN	-----	24.977	-----	74.782	23.975	2.289	1.061
N04-11206	Nylon®	116-hr event, 11/24/04	NAREL	STN	-----	25.489	-----	74.382	24.138	2.051	0.941
N04-11208	Nylon®	159-hr event, 11/29/04	CARB	STN	-----	64.668	-----	179.290	79.350	4.506	3.679
N04-11209	Nylon®	159-hr event, 11/29/04	CARB	STN	-----	71.148	-----	182.763	83.395	4.547	3.130
N04-11210	Nylon®	159-hr event, 11/29/04	DRI	STN	-----	71.388	-----	172.308	84.330	4.320	2.445
N04-11211	Nylon®	159-hr event, 11/29/04	DRI	STN	-----	73.851	-----	169.050	84.293	4.205	2.610
N04-11212	Nylon®	159-hr event, 11/29/04	ODEQ	STN	-----	79.700	-----	178.000	80.700	3.940	<3.6
N04-11213	Nylon®	159-hr event, 11/29/04	ODEQ	STN	-----	71.400	-----	181.000	78.300	3.970	<3.6
N04-11214	Nylon®	159-hr event, 11/29/04	RTI	STN	-----	63.602	-----	173.368	75.905	3.960	3.397
N04-11215	Nylon®	159-hr event, 11/29/04	RTI	STN	-----	63.719	-----	172.912	75.583	3.967	2.798
N04-11216	Nylon®	159-hr event, 11/29/04	NAREL	STN	-----	62.957	-----	168.679	65.752	4.888	2.411
N04-11217	Nylon®	159-hr event, 11/29/04	NAREL	STN	-----	68.779	-----	173.945	69.657	5.044	2.330
N04-11219	Nylon®	filter blank	CARB	STN	-----	BMDL*	-----	BMDL*	BMDL*	BMDL*	BMDL*
N04-11220	Nylon®	filter blank	CARB	STN	-----	3.323	-----	BMDL*	BMDL*	BMDL*	BMDL*
N04-11221	Nylon®	filter blank	DRI	STN	-----	0.000	-----	0.000	0.189	0.000	0.081
N04-11222	Nylon®	filter blank	DRI	STN	-----	0.000	-----	0.000	0.114	0.000	0.000
N04-11223	Nylon®	filter blank	ODEQ	STN	-----	<1.4	-----	<1.4	<0.72	<1.1	<3.6
N04-11224	Nylon®	filter blank	ODEQ	STN	-----	<1.4	-----	<1.4	<0.72	<1.1	<3.6
N04-11225	Nylon®	filter blank	RTI	STN	-----	1.537	-----	BMDL*	BMDL*	BMDL*	0.050
N04-11226	Nylon®	filter blank	RTI	STN	-----	0.878	-----	BMDL*	BMDL*	BMDL*	0.030

Table 10. Ion Chromatography PE Results

Sample ID	Filter Medium	Sample Description	Lab	Method	Concentration (µg/filter)						
					Chloride	Nitrate	Nitrite	Sulfate	Ammonium	Potassium	Sodium
N04-11227	Nylon®	filter blank	NAREL	STN	-----	BMDL*	-----	BMDL*	BMDL*	BMDL*	BMDL*
N04-11228	Nylon®	filter blank	NAREL	STN	-----	BMDL*	-----	BMDL*	BMDL*	BMDL*	BMDL*
N04-11229	Nylon®	161-hr event, 12/07/04	RTI	IMPROVE	7.641	63.645	2.698	163.338	60.791	-----	-----
N04-11230	Nylon®	161-hr event, 12/07/04	RTI	IMPROVE	8.273	65.815	1.533	161.422	60.242	-----	-----
N04-11231	Nylon®	161-hr event, 12/07/04	NAREL	IMPROVE	8.285	64.306	0.602	156.938	53.281	-----	-----
N04-11232	Nylon®	161-hr event, 12/07/04	NAREL	IMPROVE	3.506	53.172	0.633	158.214	53.945	-----	-----
N04-11233	Nylon®	161-hr event, 12/07/04	RTI	IMPROVE	2.836	39.038	0.855	142.790	51.997	-----	-----
N04-11234	Nylon®	161-hr event, 12/07/04	RTI	IMPROVE	2.926	39.349	0.976	141.670	50.925	-----	-----
N04-11235	Nylon®	161-hr event, 12/07/04	NAREL	IMPROVE	3.133	41.645	0.676	137.541	45.648	-----	-----
N04-11236	Nylon®	161-hr event, 12/07/04	NAREL	IMPROVE	5.474	48.054	0.948	143.390	47.280	-----	-----
N04-11237	Nylon®	filter blank	RTI	IMPROVE	0.083	BMDL*	0.716	BMDL*	BMDL*	-----	-----
N04-11238	Nylon®	filter blank	RTI	IMPROVE	0.062	BMDL*	1.048	BMDL*	BMDL*	-----	-----
N04-11239	Nylon®	filter blank	NAREL	IMPROVE	BMDL*	BMDL*	0.440	BMDL*	BMDL*	-----	-----
N04-11240	Nylon®	filter blank	NAREL	IMPROVE	BMDL*	BMDL*	BMDL*	BMDL*	BMDL*	-----	-----
T05-11333	Teflon®	144-hr event, 01/03/05	DRI	STN	-----	12.370	-----	139.584	46.423	2.202	5.493
T05-11334	Teflon®	144-hr event, 01/03/05	DRI	STN	-----	12.889	-----	141.185	46.128	2.289	5.657
T05-11335	Teflon®	144-hr event, 01/03/05	NAREL	STN	-----	11.555	-----	125.824	42.733	2.882	5.204
T05-11336	Teflon®	144-hr event, 01/03/05	NAREL	STN	-----	10.988	-----	126.785	43.562	2.546	4.885
T05-11337	Teflon®	216-hr event, 01/04/05	DRI	STN	-----	10.274	-----	241.056	75.974	4.119	8.731
T05-11338	Teflon®	216-hr event, 01/04/05	DRI	STN	-----	11.050	-----	245.164	75.126	4.385	9.891
T05-11339	Teflon®	216-hr event, 01/04/05	NAREL	STN	-----	9.125	-----	217.998	67.936	5.356	9.503
T05-11340	Teflon®	216-hr event, 01/04/05	NAREL	STN	-----	7.224	-----	217.855	69.121	5.431	9.136
T05-11341	Teflon®	filter blank	DRI	STN	-----	BMDL*	-----	BMDL*	BMDL*	BMDL*	BMDL*
T05-11342	Teflon®	filter blank	DRI	STN	-----	BMDL*	-----	BMDL*	BMDL*	BMDL*	BMDL*
T05-11343	Teflon®	filter blank	NAREL	STN	-----	BMDL*	-----	BMDL*	BMDL*	BMDL*	0.180
T05-11344	Teflon®	filter blank	NAREL	STN	-----	0.533	-----	BMDL*	BMDL*	BMDL*	0.204

BMDL = Below Method Detection Limit

Table 11. TOA Carbon PE Results

Sample ID	Sample Description	Lab	Instrument (see text)*	Method	Concentration (µg C/cm²)							
					EC	OC	TC	OC1	OC2	OC3	OC4	Pyrol C
Q04-11175	287-hr event, 04/27/04	CARB	#1	STN (mod.)	2.91	35.24	38.14	-----	-----	-----	-----	-----
Q04-11176	287-hr event, 04/27/04	CARB	#1	STN (mod.)	3.22	35.11	38.33	-----	-----	-----	-----	-----
Q04-11177	287-hr event, 04/27/04	DRI	#9	STN	4.6 ± 1.5	30.9 ± 3.7	35.5 ± 3.7	11.2 ± 4.8	5.8 ± 1.2	4.0 ± 0.9	11.2 ± 1.4	-1.2 ± 1.0
Q04-11177	287-hr event, 04/27/04	DRI	#7	STN	1.6 ± 0.5	34.2 ± 4.1	35.9 ± 3.7	7.8 ± 3.3	6.8 ± 1.4	4.5 ± 1.0	9.2 ± 1.1	5.9 ± 4.9
Q04-11178	287-hr event, 04/27/04	DRI	#9	STN	1.9 ± 0.6	33.8 ± 4.1	35.7 ± 3.7	11.2 ± 4.8	4.9 ± 1.0	2.8 ± 0.7	9.0 ± 1.1	5.8 ± 4.8
Q04-11178	287-hr event, 04/27/04	DRI	#7	STN	1.5 ± 0.5	33.8 ± 4.1	35.3 ± 3.7	8.1 ± 3.4	5.5 ± 1.2	3.7 ± 0.9	8.5 ± 1.0	8.0 ± 6.6
Q04-11181	287-hr event, 04/27/04	RTI	R	STN	2.7 ± 0.3	32.9 ± 1.8	35.5 ± 2.1	9.68	3.68	1.82	3.89	13.80
Q04-11181	287-hr event, 04/27/04	RTI	R	STN	2.6 ± 0.3	32.7 ± 1.8	35.3 ± 2.1	9.66	3.66	1.67	3.12	14.59
Q04-11181	287-hr event, 04/27/04	RTI	S	STN	2.5 ± 0.3	34.8 ± 1.9	37.3 ± 2.2	11.15	3.67	2.82	7.06	10.13
Q04-11181	287-hr event, 04/27/04	RTI	T	STN	3.9 ± 0.4	33.2 ± 1.9	37.1 ± 2.2	9.80	3.98	2.67	5.40	11.34
Q04-11181	287-hr event, 04/27/04	RTI	F	STN	2.6 ± 0.3	34.2 ± 1.9	36.9 ± 2.1	9.22	4.41	2.35	5.28	12.96
Q04-11182	287-hr event, 04/27/04	RTI	R	STN	2.4 ± 0.3	32.6 ± 1.8	34.9 ± 2.0	9.66	3.59	1.64	3.12	14.55
Q04-11182	287-hr event, 04/27/04	RTI	S	STN	3.0 ± 0.4	33.0 ± 1.8	36.0 ± 2.1	10.60	3.58	2.73	6.77	9.29
Q04-11182	287-hr event, 04/27/04	RTI	T	STN	3.8 ± 0.4	31.6 ± 1.8	35.5 ± 2.1	9.03	4.04	2.46	5.01	11.11
Q04-11182	287-hr event, 04/27/04	RTI	T	STN	3.9 ± 0.4	32.3 ± 1.8	36.2 ± 2.1	9.40	3.93	2.39	4.58	11.96
Q04-11182	287-hr event, 04/27/04	RTI	F	STN	2.7 ± 0.3	33.2 ± 1.9	35.9 ± 2.1	9.20	4.19	1.76	4.81	13.25
Q04-11183	287-hr event, 04/27/04	NAREL	#1	STN	2.5 ± 0.3	32.0 ± 1.8	34.4 ± 2.0	10.68	3.09	1.65	3.21	13.32
Q04-11184	287-hr event, 04/27/04	NAREL	#1	STN	3.0 ± 0.3	32.9 ± 1.8	35.9 ± 2.1	11.32	3.29	1.59	3.34	13.32
Q04-11186	192-hr event, 11/16/04	CARB	#1	STN (mod.)	1.32	21.89	23.21	-----	-----	-----	-----	-----
Q04-11187	192-hr event, 11/16/04	CARB	#1	STN (mod.)	1.44	22.15	23.59	-----	-----	-----	-----	-----
Q04-11188	192-hr event, 11/16/04	DRI	#9	STN	3.2 ± 1.0	19.7 ± 2.4	22.9 ± 2.4	5.5 ± 2.4	4.4 ± 0.9	3.1 ± 0.7	9.5 ± 1.2	-2.8 ± 2.3
Q04-11188	192-hr event, 11/16/04	DRI	#7	STN	3.1 ± 1.0	19.8 ± 2.4	23.0 ± 2.4	4.0 ± 1.7	5.0 ± 1.1	3.7 ± 0.9	8.6 ± 1.1	-1.4 ± 1.2
Q04-11189	192-hr event, 11/16/04	DRI	#9	STN	3.2 ± 1.0	18.3 ± 2.2	21.5 ± 2.3	5.3 ± 2.2	3.9 ± 0.8	2.8 ± 0.7	9.1 ± 1.1	-2.8 ± 2.3
Q04-11189	192-hr event, 11/16/04	DRI	#7	STN	3.0 ± 0.9	18.6 ± 2.2	21.5 ± 2.3	3.7 ± 1.6	4.5 ± 1.0	3.4 ± 0.8	8.0 ± 1.0	-1.0 ± 0.8
Q04-11192	192-hr event, 11/16/04	RTI	R	STN	2.0 ± 0.3	19.4 ± 1.2	21.4 ± 1.4	4.44	2.65	1.33	2.51	8.48
Q04-11192	192-hr event, 11/16/04	RTI	S	STN	2.3 ± 0.3	21.2 ± 1.3	23.5 ± 1.5	5.55	3.00	2.11	4.65	5.88

Table 11. TOA Carbon PE Results

Sample ID	Sample Description	Lab	Instrument (see text)*	Method	Concentration (µg C/cm²)							
					EC	OC	TC	OC1	OC2	OC3	OC4	Pyrol C
Q04-11192	192-hr event, 11/16/04	RTI	T	STN	2.8 ± 0.3	19.4 ± 1.2	22.2 ± 1.4	4.79	2.50	2.05	4.02	6.02
Q04-11192	192-hr event, 11/16/04	RTI	F	STN	2.8 ± 0.3	19.0 ± 1.2	21.9 ± 1.4	3.99	3.29	1.59	3.68	6.46
Q04-11192	192-hr event, 11/16/04	RTI	F	STN	2.8 ± 0.3	19.0 ± 1.1	21.8 ± 1.4	4.03	3.25	1.55	3.72	6.43
Q04-11193	192-hr event, 11/16/04	RTI	R	STN	2.1 ± 0.3	19.7 ± 1.2	21.8 ± 1.4	4.62	2.73	1.33	2.30	8.68
Q04-11193	192-hr event, 11/16/04	RTI	S	STN	2.5 ± 0.3	20.4 ± 1.2	23.0 ± 1.4	5.37	2.94	2.25	5.39	4.47
Q04-11193	192-hr event, 11/16/04	RTI	S	STN	2.6 ± 0.3	19.8 ± 1.2	22.4 ± 1.4	5.24	2.79	2.36	6.01	3.39
Q04-11193	192-hr event, 11/16/04	RTI	T	STN	2.8 ± 0.3	19.5 ± 1.2	22.3 ± 1.4	4.91	2.57	1.96	3.58	6.52
Q04-11193	192-hr event, 11/16/04	RTI	F	STN	2.6 ± 0.3	20.5 ± 1.2	23.1 ± 1.5	4.62	3.34	1.63	3.46	7.46
Q04-11194	192-hr event, 11/16/04	NAREL	#1	STN	2.2 ± 0.3	19.3 ± 1.2	21.5 ± 1.4	5.21	2.57	1.38	2.31	7.85
Q04-11195	192-hr event, 11/16/04	NAREL	#1	STN	2.2 ± 0.3	19.4 ± 1.2	21.7 ± 1.4	5.19	2.58	1.41	2.50	7.75
Q04-11241	filter blank	CARB	#1	STN (mod.)	<0.8	<0.8	<0.8	-----	-----	-----	-----	-----
Q04-11242	filter blank	CARB	#1	STN (mod.)	<0.8	<0.8	<0.8	-----	-----	-----	-----	-----
Q04-11243	filter blank	DRI	#9	STN	0.0 ± 0.1	0.5 ± 0.3	0.5 ± 0.3	0.2 ± 0.1	0.3 ± 0.1	0.0 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11243	filter blank	DRI	#7	STN	0.0 ± 0.1	0.4 ± 0.3	0.4 ± 0.3	0.2 ± 0.1	0.2 ± 0.1	0.0 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11244	filter blank	DRI	#9	STN	0.0 ± 0.1	0.3 ± 0.3	0.3 ± 0.3	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11244	filter blank	DRI	#7	STN	0.0 ± 0.1	0.5 ± 0.3	0.5 ± 0.3	0.3 ± 0.1	0.2 ± 0.1	0.0 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11247	filter blank	RTI	R	STN	0.0 ± 0.2	0.1 ± 0.2	0.1 ± 0.3	0.06	0.04	0.01	0.00	0.00
Q04-11247	filter blank	RTI	R	STN	0.1 ± 0.2	0.4 ± 0.2	0.5 ± 0.3	0.06	0.20	0.12	0.07	0.00
Q04-11247	filter blank	RTI	S	STN	0.0 ± 0.2	0.2 ± 0.2	0.2 ± 0.3	0.03	0.12	0.04	0.00	0.00
Q04-11247	filter blank	RTI	T	STN	0.0 ± 0.2	0.1 ± 0.2	0.1 ± 0.3	0.02	0.05	0.05	0.00	0.00
Q04-11247	filter blank	RTI	F	STN	0.0 ± 0.2	0.3 ± 0.2	0.3 ± 0.3	0.06	0.10	0.04	0.04	0.02
Q04-11248	filter blank	RTI	R	STN	0.0 ± 0.2	0.2 ± 0.2	0.2 ± 0.3	0.05	0.08	0.03	0.01	0.00
Q04-11248	filter blank	RTI	S	STN	0.0 ± 0.2	0.3 ± 0.2	0.3 ± 0.3	0.03	0.15	0.05	0.05	0.01
Q04-11248	filter blank	RTI	T	STN	0.0 ± 0.2	0.2 ± 0.2	0.2 ± 0.3	0.03	0.04	0.05	0.03	0.00
Q04-11248	filter blank	RTI	T	STN	0.0 ± 0.2	0.1 ± 0.2	0.1 ± 0.3	0.02	0.04	0.05	0.01	0.00
Q04-11248	filter blank	RTI	F	STN	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.3	0.00	0.00	0.00	0.00	0.00

Table 11. TOA Carbon PE Results

Sample ID	Sample Description	Lab	Instrument (see text)*	Method	Concentration (µg C/cm²)							
					EC	OC	TC	OC1	OC2	OC3	OC4	Pyrol C
Q04-11249	filter blank	NAREL	#1	STN	0.0 ± 0.2	0.5 ± 0.2	0.5 ± 0.3	0.06	0.22	0.09	0.07	0.03
Q04-11250	filter blank	NAREL	#1	STN	0.0 ± 0.2	0.4 ± 0.2	0.4 ± 0.3	0.06	0.19	0.08	0.06	-0.02
Q04-11177	287-hr event, 04/27/04	DRI	#4	IMPROVE	7.1 ± 3.8	31.5 ± 2.1	38.6 ± 1.9	2.3 ± 0.4	7.5 ± 0.6	11.0 ± 2.8	9.0 ± 1.8	1.8 ± 2.2
Q04-11177	287-hr event, 04/27/04	DRI	#5	IMPROVE	4.4 ± 2.4	33.6 ± 2.2	37.9 ± 1.8	2.3 ± 0.4	7.2 ± 0.6	13.3 ± 3.4	10.8 ± 2.1	0.0 ± 0.1
Q04-11178	287-hr event, 04/27/04	DRI	#4	IMPROVE	4.3 ± 2.3	33.3 ± 2.2	37.6 ± 1.8	1.7 ± 0.3	7.7 ± 0.6	13.4 ± 3.4	10.5 ± 2.1	0.0 ± 0.1
Q04-11178	287-hr event, 04/27/04	DRI	#5	IMPROVE	7.2 ± 3.9	31.8 ± 2.1	39.0 ± 1.9	2.3 ± 0.4	7.5 ± 0.6	11.4 ± 2.9	9.4 ± 1.8	1.3 ± 1.5
Q04-11181	287-hr event, 04/27/04	RTI	F	IMPROVE	6.8 ± 0.5	31.9 ± 1.8	38.8 ± 2.2	0.05	7.00	9.42	5.48	9.97
Q04-11182	287-hr event, 04/27/04	RTI	F	IMPROVE	6.9 ± 0.5	31.0 ± 1.7	37.8 ± 2.2	0.06	6.69	9.19	4.83	10.18
Q04-11183	287-hr event, 04/27/04	NAREL	#2	IMPROVE	7.2 ± 0.6	28.9 ± 1.6	36.1 ± 2.1	0.24	11.69	4.45	3.77	8.73
Q04-11184	287-hr event, 04/27/04	NAREL	#2	IMPROVE	6.7 ± 0.5	29.8 ± 1.7	36.5 ± 2.1	0.88	11.39	4.65	3.69	9.21
Q04-11188	192-hr event, 11/16/04	DRI	#4	IMPROVE	3.6 ± 1.9	19.5 ± 1.3	23.0 ± 1.1	1.4 ± 0.3	3.1 ± 0.3	7.8 ± 2.0	7.2 ± 1.4	0.0 ± 0.1
Q04-11188	192-hr event, 11/16/04	DRI	#5	IMPROVE	6.2 ± 3.3	18.6 ± 1.2	24.8 ± 1.2	1.0 ± 0.2	3.9 ± 0.3	7.2 ± 1.8	6.5 ± 1.3	0.0 ± 0.1
Q04-11189	192-hr event, 11/16/04	DRI	#4	IMPROVE	3.4 ± 1.8	18.4 ± 1.2	21.9 ± 1.1	0.8 ± 0.1	3.3 ± 0.3	7.6 ± 1.9	6.8 ± 1.3	0.0 ± 0.1
Q04-11189	192-hr event, 11/16/04	DRI	#5	IMPROVE	6.7 ± 3.6	16.6 ± 1.1	23.3 ± 1.2	0.9 ± 0.2	3.4 ± 0.3	6.7 ± 1.7	5.7 ± 1.1	0.0 ± 0.1
Q04-11192	192-hr event, 11/16/04	RTI	F	IMPROVE	7.1 ± 0.6	15.9 ± 1.0	23.0 ± 1.4	0.01	2.61	5.40	2.97	4.87
Q04-11193	192-hr event, 11/16/04	RTI	F	IMPROVE	5.9 ± 0.5	17.7 ± 1.1	23.6 ± 1.5	0.05	3.50	6.02	2.80	5.34
Q04-11194	192-hr event, 11/16/04	NAREL	#2	IMPROVE	6.7 ± 0.5	16.4 ± 1.0	23.1 ± 1.5	0.19	5.85	3.71	2.74	3.93
Q04-11195	192-hr event, 11/16/04	NAREL	#2	IMPROVE	6.6 ± 0.5	15.7 ± 1.0	22.3 ± 1.4	0.17	5.58	3.62	2.44	3.83
Q04-11243	filter blank	DRI	#4	IMPROVE	0.0 ± 0.1	0.4 ± 0.4	0.4 ± 0.4	0.0 ± 0.0	0.0 ± 0.1	0.3 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11243	filter blank	DRI	#5	IMPROVE	0.0 ± 0.1	0.3 ± 0.3	0.3 ± 0.4	0.0 ± 0.0	0.0 ± 0.1	0.3 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11244	filter blank	DRI	#4	IMPROVE	0.0 ± 0.1	0.2 ± 0.3	0.2 ± 0.3	0.0 ± 0.0	0.0 ± 0.1	0.2 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11244	filter blank	DRI	#5	IMPROVE	0.0 ± 0.1	0.5 ± 0.4	0.5 ± 0.4	0.0 ± 0.0	0.0 ± 0.1	0.4 ± 0.2	0.1 ± 0.1	0.0 ± 0.1
Q04-11247	filter blank	RTI	F	IMPROVE	0.1 ± 0.2	0.5 ± 0.2	0.5 ± 0.3	0.03	0.06	0.18	0.12	0.07
Q04-11248	filter blank	RTI	F	IMPROVE	0.0 ± 0.2	0.2 ± 0.2	0.2 ± 0.3	0.00	0.00	0.07	0.07	0.07
Q04-11249	filter blank	NAREL	#2	IMPROVE	0.0 ± 0.2	0.3 ± 0.2	0.3 ± 0.3	0.04	0.06	0.20	0.02	0.01
Q04-11250	filter blank	NAREL	#2	IMPROVE	0.0 ± 0.2	0.4 ± 0.2	0.4 ± 0.3	0.04	0.06	0.19	0.06	0.08

Table 11. TOA Carbon PE Results

Sample ID	Sample Description	Lab	Instrument (see text)*	Method	Concentration (µg C/cm²)							
					EC	OC	TC	OC1	OC2	OC3	OC4	Pyrol C
Q04-11177	287-hr event, 04/27/04	DRI	#7	IMPROVE-a	7.2 ± 0.8	27.8 ± 1.0	35.0 ± 1.3	2.5 ± 0.3	5.6 ± 1.6	9.6 ± 4.0	5.7 ± 0.6	4.4 ± 0.6
Q04-11177	287-hr event, 04/27/04	DRI	#9	IMPROVE-a	6.8 ± 0.7	29.0 ± 1.1	35.8 ± 1.3	4.2 ± 0.5	7.2 ± 2.0	7.4 ± 3.1	6.6 ± 0.7	3.7 ± 0.5
Q04-11178	287-hr event, 04/27/04	DRI	#7	IMPROVE-a	7.5 ± 0.8	28.6 ± 1.0	36.1 ± 1.3	2.5 ± 0.3	5.8 ± 1.6	10.2 ± 4.2	6.0 ± 0.6	4.3 ± 0.5
Q04-11178	287-hr event, 04/27/04	DRI	#9	IMPROVE-a	6.4 ± 0.7	27.9 ± 1.0	34.3 ± 1.2	3.2 ± 0.4	7.7 ± 2.2	6.7 ± 2.8	6.3 ± 0.6	3.9 ± 0.5
Q04-11183	287-hr event, 04/27/04	NAREL	#2	IMPROVE-a	6.5 ± 0.5	28.7 ± 1.6	35.3 ± 2.1	3.07	9.33	5.43	4.72	6.19
Q04-11184	287-hr event, 04/27/04	NAREL	#2	IMPROVE-a	5.9 ± 0.5	30.1 ± 1.7	36.0 ± 2.1	3.49	9.50	5.30	4.82	7.02
Q04-11188	192-hr event, 11/16/04	DRI	#7	IMPROVE-a	6.6 ± 0.7	15.5 ± 0.6	22.2 ± 0.8	1.1 ± 0.1	3.0 ± 0.8	6.8 ± 2.8	2.5 ± 0.3	2.2 ± 0.3
Q04-11188	192-hr event, 11/16/04	DRI	#9	IMPROVE-a	6.1 ± 0.7	14.9 ± 0.6	21.0 ± 0.8	1.1 ± 0.1	4.3 ± 1.2	5.2 ± 2.2	2.4 ± 0.3	1.9 ± 0.2
Q04-11189	192-hr event, 11/16/04	DRI	#7	IMPROVE-a	6.4 ± 0.7	14.5 ± 0.6	20.8 ± 0.8	1.0 ± 0.1	2.8 ± 0.8	6.4 ± 2.7	2.5 ± 0.3	1.8 ± 0.2
Q04-11189	192-hr event, 11/16/04	DRI	#9	IMPROVE-a	5.6 ± 0.6	14.9 ± 0.6	20.6 ± 0.8	0.9 ± 0.1	4.4 ± 1.2	4.8 ± 2.0	2.9 ± 0.3	2.0 ± 0.3
Q04-11194	192-hr event, 11/16/04	NAREL	#2	IMPROVE-a	5.8 ± 0.5	17.1 ± 1.1	22.9 ± 1.5	1.36	5.63	3.71	2.83	3.56
Q04-11195	192-hr event, 11/16/04	NAREL	#2	IMPROVE-a	6.3 ± 0.5	16.1 ± 1.0	22.4 ± 1.4	1.17	5.66	3.58	2.33	3.33
Q04-11243	filter blank	DRI	#7	IMPROVE-a	0.0 ± 0.1	0.5 ± 0.5	0.5 ± 0.5	0.1 ± 0.0	0.1 ± 0.1	0.3 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11243	filter blank	DRI	#9	IMPROVE-a	0.0 ± 0.1	0.3 ± 0.4	0.3 ± 0.4	0.0 ± 0.0	0.1 ± 0.1	0.3 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11244	filter blank	DRI	#7	IMPROVE-a	0.0 ± 0.1	0.6 ± 0.6	0.6 ± 0.6	0.1 ± 0.0	0.1 ± 0.1	0.4 ± 0.3	0.1 ± 0.1	0.0 ± 0.1
Q04-11244	filter blank	DRI	#9	IMPROVE-a	0.0 ± 0.1	0.1 ± 0.3	0.1 ± 0.3	0.0 ± 0.0	0.0 ± 0.1	0.1 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
Q04-11249	filter blank	NAREL	#2	IMPROVE-a	-----	-----	-----	-----	-----	-----	-----	-----
Q04-11250	filter blank	NAREL	#2	IMPROVE-a	-----	-----	-----	-----	-----	-----	-----	-----

***** Instruments identified as CARB #1, DRI #7, and DRI #9 are DRI/Model 2001 instruments capable of the TOR and the TOT analysis. The DRI #4 and #5 instruments are older DRI/OGC instruments set up for the TOR analysis. RTI instruments identified as R, S, T, and the NAREL #1 instrument are early model Sunset instruments set up for the TOT analysis. The instruments identified as RTI F and NAREL #2 are newer Sunset Dual Mode instruments capable of the TOR and the TOT analysis.***

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Na	11	138-hr event	T04-11257	4.676 ± 0.859	T04-11259	2.536 ± 2.291	T04-11261	2.091 ± 0.124	T04-11263	4.609 ± 0.805	-----
Mg	12	138-hr event	T04-11257	0.599 ± 0.817	T04-11259	-0.022 ± 0.405	T04-11261	0.025 ± 0.043	T04-11263	1.514 ± 0.426	-----
Al	13	138-hr event	T04-11257	1.659 ± 0.550	T04-11259	0.839 ± 0.115	T04-11261	0.558 ± 0.041	T04-11263	1.570 ± 0.428	1.20
Si	14	138-hr event	T04-11257	4.800 ± 0.299	T04-11259	5.637 ± 0.495	T04-11261	5.196 ± 0.035	T04-11263	6.428 ± 0.534	5.42
P	15	138-hr event	T04-11257	1.370 ± 0.054	T04-11259	-0.209 ± 0.085	T04-11261	0.000 ± 0.130	T04-11263	0.492 ± 0.242	-----
S	16	138-hr event	T04-11257	35.945 ± 0.295	T04-11259	37.487 ± 3.020	T04-11261	32.499 ± 0.158	T04-11263	34.381 ± 1.011	35.16
Cl	17	138-hr event	T04-11257	0.411 ± 0.038	T04-11259	0.059 ± 0.270	T04-11261	0.622 ± 0.037	T04-11263	0.576 ± 0.091	-----
K	19	138-hr event	T04-11257	5.512 ± 0.006	T04-11259	5.546 ± 0.449	T04-11261	5.206 ± 0.044	T04-11263	5.219 ± 0.159	5.37
Ca	20	138-hr event	T04-11257	1.867 ± 0.047	T04-11259	2.082 ± 0.174	T04-11261	1.914 ± 0.029	T04-11263	1.808 ± 0.065	1.89
Sc	21	138-hr event	T04-11257	0.000 ± 0.028	T04-11259	0.002 ± 0.025	T04-11261	0.000 ± 0.041	T04-11263	0.016 ± 0.022	-----
Ti	22	138-hr event	T04-11257	0.072 ± 0.026	T04-11259	0.198 ± 0.049	T04-11261	0.000 ± 0.025	T04-11263	0.143 ± 0.045	-----
V	23	138-hr event	T04-11257	0.009 ± 0.009	T04-11259	0.029 ± 0.017	T04-11261	0.078 ± 0.012	T04-11263	0.013 ± 0.016	-----
Cr	24	138-hr event	T04-11257	0.005 ± 0.040	T04-11259	0.007 ± 0.008	T04-11261	0.000 ± 0.010	T04-11263	0.060 ± 0.015	-----
Mn	25	138-hr event	T04-11257	0.133 ± 0.114	T04-11259	0.090 ± 0.016	T04-11261	0.097 ± 0.008	T04-11263	0.132 ± 0.031	-----
Fe	26	138-hr event	T04-11257	3.239 ± 0.180	T04-11259	3.045 ± 0.246	T04-11261	3.225 ± 0.025	T04-11263	3.086 ± 0.107	3.16
Co	27	138-hr event	T04-11257	0.009 ± 0.019	T04-11259	-0.018 ± 0.019	T04-11261	0.000 ± 0.009	T04-11263	-0.054 ± 0.026	-----
Ni	28	138-hr event	T04-11257	0.000 ± 0.031	T04-11259	0.001 ± 0.008	T04-11261	0.096 ± 0.005	T04-11263	0.030 ± 0.018	-----
Cu	29	138-hr event	T04-11257	0.170 ± 0.024	T04-11259	0.141 ± 0.015	T04-11261	0.172 ± 0.006	T04-11263	0.193 ± 0.020	0.17
Zn	30	138-hr event	T04-11257	0.689 ± 0.034	T04-11259	0.663 ± 0.054	T04-11261	0.613 ± 0.009	T04-11263	0.708 ± 0.055	0.68
Ga	31	138-hr event	T04-11257	0.041 ± 0.097	T04-11259	-0.015 ± 0.054	T04-11261	0.003 ± 0.004	T04-11263	0.009 ± 0.028	-----
As	33	138-hr event	T04-11257	0.066 ± 0.026	T04-11259	0.079 ± 0.018	T04-11261	0.124 ± 0.006	T04-11263	0.065 ± 0.041	-----
Se	34	138-hr event	T04-11257	0.000 ± 0.023	T04-11259	0.048 ± 0.011	T04-11261	0.067 ± 0.006	T04-11263	0.119 ± 0.025	-----
Br	35	138-hr event	T04-11257	0.199 ± 0.026	T04-11259	0.188 ± 0.018	T04-11261	0.216 ± 0.007	T04-11263	0.220 ± 0.029	0.21
Rb	37	138-hr event	T04-11257	0.000 ± 0.024	T04-11259	-0.005 ± 0.009	T04-11261	0.007 ± 0.008	T04-11263	0.030 ± 0.024	-----
Sr	38	138-hr event	T04-11257	0.007 ± 0.057	T04-11259	0.007 ± 0.010	T04-11261	0.008 ± 0.009	T04-11263	0.021 ± 0.057	-----
Y	39	138-hr event	T04-11257	0.066 ± 0.037	T04-11259	-0.006 ± 0.011	T04-11261	0.014 ± 0.010	T04-11263	-0.010 ± 0.059	-----
Zr	40	138-hr event	T04-11257	0.104 ± 0.078	T04-11259	-0.002 ± 0.012	T04-11261	0.000 ± 0.011	T04-11263	0.079 ± 0.053	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Nb	41	138-hr event	T04-11257	0.000 ± 0.062	T04-11259	-0.009 ± 0.014	T04-11261	0.000 ± 0.009	T04-11263	-0.026 ± 0.055	-----
Mo	42	138-hr event	T04-11257	0.016 ± 0.081	T04-11259	0.005 ± 0.016	T04-11261	0.000 ± 0.010	T04-11263	0.003 ± 0.053	-----
Ag	47	138-hr event	T04-11257	0.032 ± 0.085	T04-11259	-0.005 ± 0.034	T04-11261	0.000 ± 0.039	T04-11263	0.101 ± 0.236	-----
Cd	48	138-hr event	T04-11257	0.000 ± 0.094	T04-11259	0.009 ± 0.035	T04-11261	0.000 ± 0.045	T04-11263	0.046 ± 0.135	-----
In	49	138-hr event	T04-11257	0.014 ± 0.092	T04-11259	-0.012 ± 0.036	T04-11261	0.114 ± 0.061	T04-11263	0.106 ± 0.245	-----
Sn	50	138-hr event	T04-11257	0.000 ± 0.108	T04-11259	0.040 ± 0.040	T04-11261	0.000 ± 0.062	T04-11263	0.047 ± 0.128	-----
Sb	51	138-hr event	T04-11257	0.226 ± 0.098	T04-11259	0.012 ± 0.044	T04-11261	0.701 ± 0.136	T04-11263	0.209 ± 0.095	-----
Cs	55	138-hr event	T04-11257	0.099 ± 0.225	T04-11259	-0.052 ± 0.073	T04-11261	0.000 ± 0.043	T04-11263	0.125 ± 0.054	-----
Ba	56	138-hr event	T04-11257	0.145 ± 0.243	T04-11259	0.008 ± 0.101	T04-11261	0.000 ± 0.055	T04-11263	0.207 ± 0.091	-----
La	57	138-hr event	T04-11257	0.000 ± 0.496	T04-11259	-0.075 ± 0.125	T04-11261	0.000 ± 0.038	T04-11263	0.318 ± 0.068	-----
Ce	58	138-hr event	T04-11257	0.203 ± 0.412	T04-11259	-0.049 ± 0.155	T04-11261	0.000 ± 0.043	T04-11263	0.043 ± 0.051	-----
Sm	62	138-hr event	T04-11257	0.000 ± 0.683	T04-11259	-0.223 ± 0.558	T04-11261	0.000 ± 0.021	T04-11263	not reported	-----
Eu	63	138-hr event	T04-11257	0.735 ± 0.871	T04-11259	-1.153 ± 0.843	T04-11261	0.000 ± 0.026	T04-11263	not reported	-----
Tb	65	138-hr event	T04-11257	0.052 ± 0.945	T04-11259	-1.086 ± 1.823	T04-11261	0.147 ± 0.062	T04-11263	not reported	-----
Hf	72	138-hr event	T04-11257	0.000 ± 0.229	T04-11259	-0.047 ± 0.204	T04-11261	0.049 ± 0.024	T04-11263	not reported	-----
Ta	73	138-hr event	T04-11257	0.000 ± 0.122	T04-11259	-0.100 ± 0.227	T04-11261	0.000 ± 0.018	T04-11263	not reported	-----
W	74	138-hr event	T04-11257	0.000 ± 0.292	T04-11259	-0.079 ± 0.058	T04-11261	0.000 ± 0.011	T04-11263	0.056 ± 0.078	-----
Ir	77	138-hr event	T04-11257	0.000 ± 0.105	T04-11259	-0.014 ± 0.034	T04-11261	0.000 ± 0.008	T04-11263	not reported	-----
Au	79	138-hr event	T04-11257	0.000 ± 0.111	T04-11259	-0.046 ± 0.026	T04-11261	0.023 ± 0.009	T04-11263	-0.091 ± 0.044	-----
Hg	80	138-hr event	T04-11257	0.000 ± 0.042	T04-11259	-0.011 ± 0.022	T04-11261	0.133 ± 0.011	T04-11263	-0.073 ± 0.042	-----
Pb	82	138-hr event	T04-11257	0.084 ± 0.081	T04-11259	0.199 ± 0.034	T04-11261	0.255 ± 0.020	T04-11263	0.352 ± 0.077	-----
Na	11	138-hr event	T04-11258	5.015 ± 0.866	T04-11260	3.153 ± 2.302	T04-11262	1.774 ± 0.124	T04-11264	4.488 ± 0.794	-----
Mg	12	138-hr event	T04-11258	0.260 ± 0.814	T04-11260	-0.095 ± 0.406	T04-11262	0.000 ± 0.057	T04-11264	2.330 ± 0.460	-----
Al	13	138-hr event	T04-11258	2.133 ± 0.553	T04-11260	0.890 ± 0.119	T04-11262	1.125 ± 0.042	T04-11264	1.361 ± 0.424	1.24
Si	14	138-hr event	T04-11258	4.518 ± 0.296	T04-11260	5.464 ± 0.480	T04-11262	5.708 ± 0.036	T04-11264	6.391 ± 0.536	5.59
P	15	138-hr event	T04-11258	1.268 ± 0.054	T04-11260	-0.213 ± 0.083	T04-11262	0.000 ± 0.132	T04-11264	0.015 ± 0.239	-----
S	16	138-hr event	T04-11258	32.793 ± 0.270	T04-11260	36.366 ± 2.930	T04-11262	33.505 ± 0.158	T04-11264	32.938 ± 0.977	33.22

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Cl	17	138-hr event	T04-11258	0.423 ± 0.038	T04-11260	0.092 ± 0.263	T04-11262	0.703 ± 0.038	T04-11264	0.659 ± 0.095	-----
K	19	138-hr event	T04-11258	5.105 ± 0.006	T04-11260	5.353 ± 0.433	T04-11262	5.429 ± 0.045	T04-11264	4.876 ± 0.153	5.23
Ca	20	138-hr event	T04-11258	1.709 ± 0.047	T04-11260	2.070 ± 0.173	T04-11262	2.204 ± 0.029	T04-11264	2.318 ± 0.075	2.14
Sc	21	138-hr event	T04-11258	0.000 ± 0.028	T04-11260	-0.054 ± 0.026	T04-11262	0.000 ± 0.040	T04-11264	-0.006 ± 0.024	-----
Ti	22	138-hr event	T04-11258	0.140 ± 0.026	T04-11260	0.098 ± 0.051	T04-11262	0.000 ± 0.025	T04-11264	0.236 ± 0.045	-----
V	23	138-hr event	T04-11258	0.000 ± 0.009	T04-11260	0.007 ± 0.018	T04-11262	0.086 ± 0.012	T04-11264	-0.004 ± 0.016	-----
Cr	24	138-hr event	T04-11258	0.005 ± 0.040	T04-11260	0.036 ± 0.009	T04-11262	0.000 ± 0.010	T04-11264	0.020 ± 0.014	-----
Mn	25	138-hr event	T04-11258	0.111 ± 0.114	T04-11260	0.084 ± 0.015	T04-11262	0.081 ± 0.008	T04-11264	0.175 ± 0.033	-----
Fe	26	138-hr event	T04-11258	3.137 ± 0.180	T04-11260	3.023 ± 0.244	T04-11262	3.578 ± 0.026	T04-11264	2.967 ± 0.105	3.08
Co	27	138-hr event	T04-11258	0.020 ± 0.019	T04-11260	-0.036 ± 0.019	T04-11262	0.000 ± 0.010	T04-11264	-0.047 ± 0.025	-----
Ni	28	138-hr event	T04-11258	0.023 ± 0.031	T04-11260	0.015 ± 0.009	T04-11262	1.597 ± 0.014	T04-11264	0.048 ± 0.019	-----
Cu	29	138-hr event	T04-11258	0.136 ± 0.024	T04-11260	0.185 ± 0.018	T04-11262	0.166 ± 0.007	T04-11264	0.204 ± 0.021	0.18
Zn	30	138-hr event	T04-11258	0.622 ± 0.034	T04-11260	0.654 ± 0.054	T04-11262	0.637 ± 0.009	T04-11264	0.746 ± 0.056	0.65
Ga	31	138-hr event	T04-11258	0.063 ± 0.097	T04-11260	-0.003 ± 0.054	T04-11262	0.006 ± 0.004	T04-11264	-0.032 ± 0.028	-----
As	33	138-hr event	T04-11258	0.000 ± 0.026	T04-11260	0.066 ± 0.019	T04-11262	0.124 ± 0.006	T04-11264	0.059 ± 0.038	-----
Se	34	138-hr event	T04-11258	0.000 ± 0.023	T04-11260	0.045 ± 0.011	T04-11262	0.068 ± 0.006	T04-11264	0.049 ± 0.022	-----
Br	35	138-hr event	T04-11258	0.188 ± 0.026	T04-11260	0.192 ± 0.018	T04-11262	0.217 ± 0.007	T04-11264	0.184 ± 0.031	0.19
Rb	37	138-hr event	T04-11258	0.000 ± 0.024	T04-11260	0.007 ± 0.010	T04-11262	0.003 ± 0.008	T04-11264	0.031 ± 0.024	-----
Sr	38	138-hr event	T04-11258	0.007 ± 0.057	T04-11260	0.021 ± 0.010	T04-11262	0.013 ± 0.009	T04-11264	-0.078 ± 0.053	-----
Y	39	138-hr event	T04-11258	0.020 ± 0.037	T04-11260	-0.001 ± 0.011	T04-11262	0.000 ± 0.007	T04-11264	-0.007 ± 0.060	-----
Zr	40	138-hr event	T04-11258	0.059 ± 0.077	T04-11260	0.002 ± 0.013	T04-11262	0.000 ± 0.011	T04-11264	0.050 ± 0.051	-----
Nb	41	138-hr event	T04-11258	0.099 ± 0.062	T04-11260	0.001 ± 0.015	T04-11262	0.000 ± 0.009	T04-11264	0.133 ± 0.067	-----
Mo	42	138-hr event	T04-11258	0.005 ± 0.081	T04-11260	0.004 ± 0.018	T04-11262	0.000 ± 0.009	T04-11264	0.177 ± 0.066	-----
Ag	47	138-hr event	T04-11258	0.032 ± 0.085	T04-11260	0.026 ± 0.035	T04-11262	0.000 ± 0.040	T04-11264	-0.659 ± 0.246	-----
Cd	48	138-hr event	T04-11258	0.181 ± 0.095	T04-11260	0.069 ± 0.037	T04-11262	0.066 ± 0.063	T04-11264	0.426 ± 0.147	-----
In	49	138-hr event	T04-11258	0.002 ± 0.092	T04-11260	-0.017 ± 0.038	T04-11262	0.158 ± 0.059	T04-11264	0.149 ± 0.244	-----
Sn	50	138-hr event	T04-11258	0.000 ± 0.108	T04-11260	0.075 ± 0.043	T04-11262	0.193 ± 0.081	T04-11264	-0.148 ± 0.124	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Sb	51	138-hr event	T04-11258	0.090 ± 0.097	T04-11260	0.021 ± 0.046	T04-11262	0.000 ± 0.104	T04-11264	0.224 ± 0.101	-----
Cs	55	138-hr event	T04-11258	0.000 ± 0.224	T04-11260	0.087 ± 0.080	T04-11262	0.000 ± 0.043	T04-11264	0.074 ± 0.054	-----
Ba	56	138-hr event	T04-11258	0.000 ± 0.240	T04-11260	0.095 ± 0.110	T04-11262	0.000 ± 0.055	T04-11264	0.044 ± 0.092	-----
La	57	138-hr event	T04-11258	0.000 ± 0.493	T04-11260	0.010 ± 0.138	T04-11262	0.000 ± 0.037	T04-11264	0.200 ± 0.066	-----
Ce	58	138-hr event	T04-11258	0.000 ± 0.410	T04-11260	-0.029 ± 0.170	T04-11262	0.000 ± 0.043	T04-11264	0.150 ± 0.051	-----
Sm	62	138-hr event	T04-11258	0.000 ± 0.693	T04-11260	-0.301 ± 0.609	T04-11262	0.000 ± 0.021	T04-11264	not reported	-----
Eu	63	138-hr event	T04-11258	0.000 ± 0.852	T04-11260	-1.004 ± 0.922	T04-11262	0.000 ± 0.027	T04-11264	not reported	-----
Tb	65	138-hr event	T04-11258	0.346 ± 0.951	T04-11260	-0.679 ± 2.000	T04-11262	0.090 ± 0.064	T04-11264	not reported	-----
Hf	72	138-hr event	T04-11258	0.154 ± 0.229	T04-11260	0.037 ± 0.204	T04-11262	0.049 ± 0.024	T04-11264	not reported	-----
Ta	73	138-hr event	T04-11258	0.000 ± 0.122	T04-11260	-0.056 ± 0.227	T04-11262	0.000 ± 0.024	T04-11264	not reported	-----
W	74	138-hr event	T04-11258	0.007 ± 0.293	T04-11260	0.011 ± 0.058	T04-11262	0.000 ± 0.013	T04-11264	-0.026 ± 0.078	-----
Ir	77	138-hr event	T04-11258	0.000 ± 0.104	T04-11260	0.016 ± 0.034	T04-11262	0.000 ± 0.008	T04-11264	not reported	-----
Au	79	138-hr event	T04-11258	0.000 ± 0.111	T04-11260	-0.007 ± 0.026	T04-11262	0.015 ± 0.009	T04-11264	0.013 ± 0.046	-----
Hg	80	138-hr event	T04-11258	0.034 ± 0.042	T04-11260	-0.002 ± 0.022	T04-11262	0.136 ± 0.012	T04-11264	0.054 ± 0.055	-----
Pb	82	138-hr event	T04-11258	0.185 ± 0.081	T04-11260	0.230 ± 0.036	T04-11262	0.255 ± 0.020	T04-11264	0.255 ± 0.073	-----
Na	11	192-hr event	T04-11267	3.580 ± 0.835	T04-11269	8.509 ± 2.450	T04-11271	2.870 ± 0.147	T04-11273	5.835 ± 0.918	4.71
Mg	12	192-hr event	T04-11267	0.339 ± 0.815	T04-11269	0.021 ± 0.416	T04-11271	0.071 ± 0.050	T04-11273	1.544 ± 0.450	-----
Al	13	192-hr event	T04-11267	2.156 ± 0.553	T04-11269	0.344 ± 0.100	T04-11271	0.497 ± 0.044	T04-11273	1.998 ± 0.522	1.25
Si	14	192-hr event	T04-11267	9.060 ± 0.350	T04-11269	10.352 ± 0.906	T04-11271	9.260 ± 0.042	T04-11273	12.486 ± 0.769	9.81
P	15	192-hr event	T04-11267	3.607 ± 0.062	T04-11269	-0.500 ± 0.189	T04-11271	0.000 ± 0.175	T04-11273	0.417 ± 0.339	-----
S	16	192-hr event	T04-11267	85.959 ± 0.693	T04-11269	88.042 ± 7.077	T04-11271	72.038 ± 0.226	T04-11273	84.316 ± 2.287	85.14
Cl	17	192-hr event	T04-11267	0.671 ± 0.040	T04-11269	-0.504 ± 0.628	T04-11271	0.977 ± 0.046	T04-11273	0.977 ± 0.112	-----
K	19	192-hr event	T04-11267	5.230 ± 0.006	T04-11269	5.021 ± 0.407	T04-11271	4.642 ± 0.043	T04-11273	5.159 ± 0.159	5.09
Ca	20	192-hr event	T04-11267	1.516 ± 0.046	T04-11269	1.610 ± 0.137	T04-11271	1.523 ± 0.028	T04-11273	2.039 ± 0.070	1.57
Sc	21	192-hr event	T04-11267	0.000 ± 0.028	T04-11269	-0.026 ± 0.023	T04-11271	0.000 ± 0.043	T04-11273	-0.032 ± 0.023	-----
Ti	22	192-hr event	T04-11267	0.174 ± 0.026	T04-11269	0.177 ± 0.055	T04-11271	0.000 ± 0.025	T04-11273	0.060 ± 0.044	-----
V	23	192-hr event	T04-11267	0.020 ± 0.009	T04-11269	0.035 ± 0.019	T04-11271	0.079 ± 0.014	T04-11273	0.047 ± 0.018	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Cr	24	192-hr event	T04-11267	0.005 ± 0.040	T04-11269	-0.005 ± 0.009	T04-11271	0.000 ± 0.011	T04-11273	0.059 ± 0.015	-----
Mn	25	192-hr event	T04-11267	0.088 ± 0.114	T04-11269	0.105 ± 0.016	T04-11271	0.103 ± 0.008	T04-11273	0.092 ± 0.031	-----
Fe	26	192-hr event	T04-11267	3.363 ± 0.180	T04-11269	3.091 ± 0.249	T04-11271	2.967 ± 0.024	T04-11273	3.475 ± 0.118	3.23
Co	27	192-hr event	T04-11267	0.000 ± 0.019	T04-11269	-0.041 ± 0.019	T04-11271	0.000 ± 0.009	T04-11273	-0.022 ± 0.028	-----
Ni	28	192-hr event	T04-11267	0.011 ± 0.031	T04-11269	0.030 ± 0.010	T04-11271	0.032 ± 0.004	T04-11273	0.483 ± 0.032	-----
Cu	29	192-hr event	T04-11267	0.090 ± 0.024	T04-11269	0.109 ± 0.013	T04-11271	0.119 ± 0.006	T04-11273	0.173 ± 0.020	0.11
Zn	30	192-hr event	T04-11267	0.802 ± 0.034	T04-11269	0.671 ± 0.055	T04-11271	0.611 ± 0.009	T04-11273	0.782 ± 0.058	0.73
Ga	31	192-hr event	T04-11267	0.233 ± 0.098	T04-11269	-0.014 ± 0.054	T04-11271	0.002 ± 0.004	T04-11273	-0.012 ± 0.029	-----
As	33	192-hr event	T04-11267	0.054 ± 0.026	T04-11269	0.082 ± 0.019	T04-11271	0.129 ± 0.006	T04-11273	0.065 ± 0.041	-----
Se	34	192-hr event	T04-11267	0.000 ± 0.023	T04-11269	0.111 ± 0.014	T04-11271	0.116 ± 0.006	T04-11273	0.208 ± 0.030	-----
Br	35	192-hr event	T04-11267	0.323 ± 0.026	T04-11269	0.331 ± 0.029	T04-11271	0.313 ± 0.007	T04-11273	0.345 ± 0.035	0.33
Rb	37	192-hr event	T04-11267	0.000 ± 0.024	T04-11269	0.003 ± 0.011	T04-11271	0.000 ± 0.006	T04-11273	-0.011 ± 0.024	-----
Sr	38	192-hr event	T04-11267	0.029 ± 0.057	T04-11269	0.007 ± 0.011	T04-11271	0.042 ± 0.010	T04-11273	0.143 ± 0.071	-----
Y	39	192-hr event	T04-11267	0.020 ± 0.037	T04-11269	-0.012 ± 0.012	T04-11271	0.024 ± 0.011	T04-11273	0.147 ± 0.069	-----
Zr	40	192-hr event	T04-11267	0.115 ± 0.078	T04-11269	-0.003 ± 0.014	T04-11271	0.000 ± 0.011	T04-11273	0.081 ± 0.054	-----
Nb	41	192-hr event	T04-11267	0.000 ± 0.062	T04-11269	0.014 ± 0.016	T04-11271	0.000 ± 0.010	T04-11273	-0.006 ± 0.053	-----
Mo	42	192-hr event	T04-11267	0.038 ± 0.082	T04-11269	0.008 ± 0.019	T04-11271	0.000 ± 0.010	T04-11273	0.218 ± 0.068	-----
Ag	47	192-hr event	T04-11267	0.000 ± 0.085	T04-11269	0.020 ± 0.037	T04-11271	0.077 ± 0.053	T04-11273	0.001 ± 0.242	-----
Cd	48	192-hr event	T04-11267	0.102 ± 0.094	T04-11269	-0.009 ± 0.038	T04-11271	0.000 ± 0.045	T04-11273	-0.064 ± 0.138	-----
In	49	192-hr event	T04-11267	0.000 ± 0.092	T04-11269	-0.028 ± 0.040	T04-11271	0.063 ± 0.063	T04-11273	0.286 ± 0.250	-----
Sn	50	192-hr event	T04-11267	0.000 ± 0.108	T04-11269	-0.012 ± 0.044	T04-11271	0.193 ± 0.087	T04-11273	-0.019 ± 0.128	-----
Sb	51	192-hr event	T04-11267	0.079 ± 0.097	T04-11269	-0.011 ± 0.049	T04-11271	0.000 ± 0.110	T04-11273	0.151 ± 0.099	-----
Cs	55	192-hr event	T04-11267	0.099 ± 0.225	T04-11269	-0.003 ± 0.085	T04-11271	0.000 ± 0.045	T04-11273	0.069 ± 0.055	-----
Ba	56	192-hr event	T04-11267	0.000 ± 0.242	T04-11269	-0.063 ± 0.118	T04-11271	0.000 ± 0.056	T04-11273	0.432 ± 0.095	-----
La	57	192-hr event	T04-11267	0.000 ± 0.495	T04-11269	-0.042 ± 0.148	T04-11271	0.000 ± 0.038	T04-11273	0.208 ± 0.068	-----
Ce	58	192-hr event	T04-11267	0.000 ± 0.410	T04-11269	-0.128 ± 0.183	T04-11271	0.000 ± 0.045	T04-11273	0.056 ± 0.053	-----
Sm	62	192-hr event	T04-11267	0.000 ± 0.689	T04-11269	-0.487 ± 0.653	T04-11271	0.000 ± 0.021	T04-11273	not reported	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Eu	63	192-hr event	T04-11267	0.226 ± 0.864	T04-11269	-0.921 ± 0.990	T04-11271	0.000 ± 0.027	T04-11273	not reported	-----
Tb	65	192-hr event	T04-11267	0.000 ± 0.932	T04-11269	1.155 ± 2.159	T04-11271	0.079 ± 0.060	T04-11273	not reported	-----
Hf	72	192-hr event	T04-11267	0.000 ± 0.229	T04-11269	0.146 ± 0.205	T04-11271	0.028 ± 0.024	T04-11273	not reported	-----
Ta	73	192-hr event	T04-11267	0.000 ± 0.122	T04-11269	-0.091 ± 0.227	T04-11271	0.000 ± 0.016	T04-11273	not reported	-----
W	74	192-hr event	T04-11267	0.041 ± 0.293	T04-11269	-0.026 ± 0.059	T04-11271	0.000 ± 0.011	T04-11273	0.080 ± 0.086	-----
Ir	77	192-hr event	T04-11267	0.000 ± 0.105	T04-11269	0.005 ± 0.034	T04-11271	0.000 ± 0.008	T04-11273	not reported	-----
Au	79	192-hr event	T04-11267	0.000 ± 0.111	T04-11269	-0.048 ± 0.027	T04-11271	0.035 ± 0.010	T04-11273	-0.054 ± 0.049	-----
Hg	80	192-hr event	T04-11267	0.068 ± 0.042	T04-11269	-0.002 ± 0.022	T04-11271	0.224 ± 0.012	T04-11273	-0.014 ± 0.053	-----
Pb	82	192-hr event	T04-11267	0.242 ± 0.081	T04-11269	0.207 ± 0.035	T04-11271	0.243 ± 0.020	T04-11273	0.292 ± 0.078	-----
Na	11	192-hr event	T04-11268	6.846 ± 0.906	T04-11270	7.969 ± 2.427	T04-11272	2.983 ± 0.147	T04-11274	5.115 ± 0.844	5.98
Mg	12	192-hr event	T04-11268	1.209 ± 0.825	T04-11270	0.268 ± 0.415	T04-11272	0.381 ± 0.050	T04-11274	0.355 ± 0.418	-----
Al	13	192-hr event	T04-11268	2.054 ± 0.551	T04-11270	0.490 ± 0.104	T04-11272	1.182 ± 0.043	T04-11274	1.800 ± 0.515	1.49
Si	14	192-hr event	T04-11268	9.286 ± 0.353	T04-11270	10.011 ± 0.876	T04-11272	9.137 ± 0.041	T04-11274	12.016 ± 0.743	9.65
P	15	192-hr event	T04-11268	3.437 ± 0.061	T04-11270	-0.587 ± 0.189	T04-11272	0.000 ± 0.178	T04-11274	1.023 ± 0.334	-----
S	16	192-hr event	T04-11268	85.518 ± 0.689	T04-11270	87.139 ± 7.004	T04-11272	74.987 ± 0.237	T04-11274	77.701 ± 2.121	81.61
Cl	17	192-hr event	T04-11268	0.423 ± 0.038	T04-11270	-0.368 ± 0.621	T04-11272	0.932 ± 0.046	T04-11274	0.599 ± 0.104	-----
K	19	192-hr event	T04-11268	5.162 ± 0.006	T04-11270	5.062 ± 0.410	T04-11272	4.833 ± 0.043	T04-11274	4.584 ± 0.149	4.95
Ca	20	192-hr event	T04-11268	1.584 ± 0.046	T04-11270	1.723 ± 0.145	T04-11272	1.533 ± 0.028	T04-11274	1.728 ± 0.064	1.65
Sc	21	192-hr event	T04-11268	0.000 ± 0.028	T04-11270	-0.030 ± 0.024	T04-11272	0.000 ± 0.043	T04-11274	-0.009 ± 0.023	-----
Ti	22	192-hr event	T04-11268	0.106 ± 0.026	T04-11270	0.191 ± 0.055	T04-11272	0.000 ± 0.025	T04-11274	0.121 ± 0.045	-----
V	23	192-hr event	T04-11268	0.000 ± 0.009	T04-11270	0.039 ± 0.019	T04-11272	0.043 ± 0.015	T04-11274	0.049 ± 0.017	-----
Cr	24	192-hr event	T04-11268	0.027 ± 0.040	T04-11270	0.000 ± 0.009	T04-11272	0.000 ± 0.010	T04-11274	0.052 ± 0.015	-----
Mn	25	192-hr event	T04-11268	0.066 ± 0.114	T04-11270	0.129 ± 0.018	T04-11272	0.086 ± 0.008	T04-11274	0.086 ± 0.030	-----
Fe	26	192-hr event	T04-11268	3.295 ± 0.180	T04-11270	3.046 ± 0.246	T04-11272	3.095 ± 0.024	T04-11274	2.926 ± 0.103	3.07
Co	27	192-hr event	T04-11268	0.000 ± 0.019	T04-11270	-0.031 ± 0.019	T04-11272	0.000 ± 0.009	T04-11274	-0.014 ± 0.026	-----
Ni	28	192-hr event	T04-11268	0.113 ± 0.031	T04-11270	0.038 ± 0.010	T04-11272	0.063 ± 0.005	T04-11274	0.027 ± 0.018	-----
Cu	29	192-hr event	T04-11268	0.090 ± 0.024	T04-11270	0.117 ± 0.014	T04-11272	0.118 ± 0.006	T04-11274	0.091 ± 0.018	0.10

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Zn	30	192-hr event	T04-11268	0.757 ± 0.034	T04-11270	0.695 ± 0.057	T04-11272	0.618 ± 0.009	T04-11274	0.627 ± 0.052	0.66
Ga	31	192-hr event	T04-11268	0.000 ± 0.097	T04-11270	-0.011 ± 0.054	T04-11272	0.012 ± 0.004	T04-11274	-0.035 ± 0.027	-----
As	33	192-hr event	T04-11268	0.043 ± 0.026	T04-11270	0.078 ± 0.019	T04-11272	0.110 ± 0.006	T04-11274	0.130 ± 0.039	-----
Se	34	192-hr event	T04-11268	0.023 ± 0.023	T04-11270	0.103 ± 0.013	T04-11272	0.122 ± 0.006	T04-11274	0.107 ± 0.025	-----
Br	35	192-hr event	T04-11268	0.380 ± 0.027	T04-11270	0.322 ± 0.028	T04-11272	0.325 ± 0.008	T04-11274	0.330 ± 0.035	0.33
Rb	37	192-hr event	T04-11268	0.000 ± 0.024	T04-11270	0.009 ± 0.010	T04-11272	0.000 ± 0.006	T04-11274	0.070 ± 0.025	-----
Sr	38	192-hr event	T04-11268	0.000 ± 0.057	T04-11270	0.016 ± 0.011	T04-11272	0.025 ± 0.010	T04-11274	0.000 ± 0.063	-----
Y	39	192-hr event	T04-11268	0.032 ± 0.037	T04-11270	-0.018 ± 0.012	T04-11272	0.001 ± 0.011	T04-11274	0.116 ± 0.065	-----
Zr	40	192-hr event	T04-11268	0.115 ± 0.078	T04-11270	-0.006 ± 0.014	T04-11272	0.052 ± 0.016	T04-11274	0.154 ± 0.061	-----
Nb	41	192-hr event	T04-11268	0.032 ± 0.062	T04-11270	0.019 ± 0.016	T04-11272	0.000 ± 0.010	T04-11274	0.088 ± 0.062	-----
Mo	42	192-hr event	T04-11268	0.000 ± 0.081	T04-11270	-0.002 ± 0.019	T04-11272	0.000 ± 0.010	T04-11274	0.090 ± 0.062	-----
Ag	47	192-hr event	T04-11268	0.000 ± 0.085	T04-11270	0.041 ± 0.036	T04-11272	0.000 ± 0.040	T04-11274	0.145 ± 0.253	-----
Cd	48	192-hr event	T04-11268	0.023 ± 0.094	T04-11270	0.062 ± 0.038	T04-11272	0.000 ± 0.047	T04-11274	0.108 ± 0.145	-----
In	49	192-hr event	T04-11268	0.000 ± 0.092	T04-11270	0.005 ± 0.040	T04-11272	0.000 ± 0.049	T04-11274	0.167 ± 0.242	-----
Sn	50	192-hr event	T04-11268	0.000 ± 0.108	T04-11270	0.033 ± 0.043	T04-11272	0.000 ± 0.062	T04-11274	0.169 ± 0.124	-----
Sb	51	192-hr event	T04-11268	0.045 ± 0.097	T04-11270	0.078 ± 0.049	T04-11272	0.045 ± 0.147	T04-11274	0.039 ± 0.093	-----
Cs	55	192-hr event	T04-11268	0.000 ± 0.224	T04-11270	-0.014 ± 0.084	T04-11272	0.000 ± 0.045	T04-11274	-0.026 ± 0.053	-----
Ba	56	192-hr event	T04-11268	1.071 ± 0.249	T04-11270	0.040 ± 0.116	T04-11272	0.000 ± 0.054	T04-11274	0.329 ± 0.092	-----
La	57	192-hr event	T04-11268	0.000 ± 0.496	T04-11270	0.021 ± 0.147	T04-11272	0.000 ± 0.038	T04-11274	0.259 ± 0.067	-----
Ce	58	192-hr event	T04-11268	0.147 ± 0.412	T04-11270	-0.063 ± 0.181	T04-11272	0.000 ± 0.044	T04-11274	0.010 ± 0.052	-----
Sm	62	192-hr event	T04-11268	0.312 ± 0.697	T04-11270	0.208 ± 0.643	T04-11272	0.000 ± 0.021	T04-11274	not reported	-----
Eu	63	192-hr event	T04-11268	0.068 ± 0.862	T04-11270	0.482 ± 0.976	T04-11272	0.000 ± 0.026	T04-11274	not reported	-----
Tb	65	192-hr event	T04-11268	1.962 ± 0.993	T04-11270	0.668 ± 2.131	T04-11272	0.064 ± 0.061	T04-11274	not reported	-----
Hf	72	192-hr event	T04-11268	0.000 ± 0.229	T04-11270	0.019 ± 0.204	T04-11272	0.053 ± 0.024	T04-11274	not reported	-----
Ta	73	192-hr event	T04-11268	0.115 ± 0.123	T04-11270	-0.041 ± 0.227	T04-11272	0.000 ± 0.017	T04-11274	not reported	-----
W	74	192-hr event	T04-11268	0.000 ± 0.290	T04-11270	0.017 ± 0.059	T04-11272	0.000 ± 0.011	T04-11274	0.047 ± 0.075	-----
Ir	77	192-hr event	T04-11268	0.000 ± 0.104	T04-11270	0.000 ± 0.035	T04-11272	0.000 ± 0.008	T04-11274	not reported	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Au	79	192-hr event	T04-11268	0.192 ± 0.111	T04-11270	-0.031 ± 0.027	T04-11272	0.034 ± 0.010	T04-11274	0.074 ± 0.047	-----
Hg	80	192-hr event	T04-11268	0.000 ± 0.042	T04-11270	0.017 ± 0.022	T04-11272	0.217 ± 0.011	T04-11274	0.122 ± 0.053	-----
Pb	82	192-hr event	T04-11268	0.174 ± 0.081	T04-11270	0.215 ± 0.035	T04-11272	0.205 ± 0.020	T04-11274	0.229 ± 0.071	-----
Na	11	blank filter	T04-11277	0.000 ± 0.753	T04-11279	-0.258 ± 2.258	T04-11281	0.000 ± 0.131	T04-11283	0.174 ± 0.554	-----
Mg	12	blank filter	T04-11277	0.181 ± 0.812	T04-11279	-0.030 ± 0.399	T04-11281	0.000 ± 0.038	T04-11283	0.949 ± 0.370	-----
Al	13	blank filter	T04-11277	0.000 ± 0.539	T04-11279	-0.034 ± 0.080	T04-11281	0.000 ± 0.049	T04-11283	-0.075 ± 0.239	-----
Si	14	blank filter	T04-11277	0.111 ± 0.249	T04-11279	-0.012 ± 0.048	T04-11281	0.000 ± 0.033	T04-11283	0.980 ± 0.280	-----
P	15	blank filter	T04-11277	0.000 ± 0.050	T04-11279	-0.023 ± 0.028	T04-11281	0.000 ± 0.058	T04-11283	-0.212 ± 0.098	-----
S	16	blank filter	T04-11277	0.079 ± 0.014	T04-11279	-0.040 ± 0.047	T04-11281	0.000 ± 0.036	T04-11283	0.116 ± 0.077	-----
Cl	17	blank filter	T04-11277	0.005 ± 0.037	T04-11279	-0.001 ± 0.028	T04-11281	0.000 ± 0.030	T04-11283	0.025 ± 0.053	-----
K	19	blank filter	T04-11277	0.156 ± 0.001	T04-11279	0.004 ± 0.017	T04-11281	0.000 ± 0.026	T04-11283	-0.037 ± 0.040	-----
Ca	20	blank filter	T04-11277	0.002 ± 0.043	T04-11279	-0.029 ± 0.014	T04-11281	0.000 ± 0.024	T04-11283	-0.027 ± 0.023	-----
Sc	21	blank filter	T04-11277	0.005 ± 0.028	T04-11279	-0.003 ± 0.014	T04-11281	0.000 ± 0.038	T04-11283	0.032 ± 0.017	-----
Ti	22	blank filter	T04-11277	0.000 ± 0.026	T04-11279	-0.002 ± 0.048	T04-11281	0.008 ± 0.016	T04-11283	-0.056 ± 0.036	-----
V	23	blank filter	T04-11277	0.000 ± 0.009	T04-11279	-0.007 ± 0.017	T04-11281	0.000 ± 0.012	T04-11283	-0.015 ± 0.014	-----
Cr	24	blank filter	T04-11277	0.000 ± 0.040	T04-11279	-0.005 ± 0.008	T04-11281	0.000 ± 0.008	T04-11283	0.040 ± 0.014	-----
Mn	25	blank filter	T04-11277	0.000 ± 0.113	T04-11279	0.008 ± 0.013	T04-11281	0.000 ± 0.006	T04-11283	0.106 ± 0.027	-----
Fe	26	blank filter	T04-11277	0.041 ± 0.170	T04-11279	-0.005 ± 0.011	T04-11281	0.000 ± 0.005	T04-11283	-0.008 ± 0.020	-----
Co	27	blank filter	T04-11277	0.009 ± 0.019	T04-11279	0.015 ± 0.008	T04-11281	0.000 ± 0.004	T04-11283	-0.075 ± 0.017	-----
Ni	28	blank filter	T04-11277	0.000 ± 0.031	T04-11279	-0.001 ± 0.008	T04-11281	0.006 ± 0.003	T04-11283	-0.025 ± 0.015	-----
Cu	29	blank filter	T04-11277	0.000 ± 0.024	T04-11279	0.008 ± 0.008	T04-11281	0.000 ± 0.005	T04-11283	0.011 ± 0.015	-----
Zn	30	blank filter	T04-11277	0.011 ± 0.032	T04-11279	-0.004 ± 0.007	T04-11281	0.000 ± 0.006	T04-11283	-0.110 ± 0.019	-----
Ga	31	blank filter	T04-11277	0.000 ± 0.098	T04-11279	-0.006 ± 0.054	T04-11281	0.000 ± 0.002	T04-11283	-0.002 ± 0.025	-----
As	33	blank filter	T04-11277	0.000 ± 0.026	T04-11279	0.000 ± 0.012	T04-11281	0.001 ± 0.003	T04-11283	-0.006 ± 0.030	-----
Se	34	blank filter	T04-11277	0.000 ± 0.023	T04-11279	-0.005 ± 0.009	T04-11281	0.000 ± 0.003	T04-11283	-0.019 ± 0.018	-----
Br	35	blank filter	T04-11277	0.007 ± 0.026	T04-11279	-0.001 ± 0.009	T04-11281	0.000 ± 0.004	T04-11283	-0.028 ± 0.020	-----
Rb	37	blank filter	T04-11277	0.000 ± 0.024	T04-11279	-0.002 ± 0.009	T04-11281	0.000 ± 0.005	T04-11283	0.032 ± 0.021	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Sr	38	blank filter	T04-11277	0.000 ± 0.057	T04-11279	0.000 ± 0.010	T04-11281	0.000 ± 0.006	T04-11283	0.080 ± 0.065	-----
Y	39	blank filter	T04-11277	0.009 ± 0.037	T04-11279	-0.011 ± 0.011	T04-11281	0.000 ± 0.007	T04-11283	-0.025 ± 0.054	-----
Zr	40	blank filter	T04-11277	0.000 ± 0.077	T04-11279	0.004 ± 0.013	T04-11281	0.000 ± 0.010	T04-11283	0.023 ± 0.044	-----
Nb	41	blank filter	T04-11277	0.043 ± 0.062	T04-11279	0.004 ± 0.015	T04-11281	0.000 ± 0.009	T04-11283	-0.028 ± 0.052	-----
Mo	42	blank filter	T04-11277	0.000 ± 0.081	T04-11279	-0.013 ± 0.017	T04-11281	0.000 ± 0.009	T04-11283	-0.023 ± 0.048	-----
Ag	47	blank filter	T04-11277	0.000 ± 0.085	T04-11279	0.005 ± 0.034	T04-11281	0.000 ± 0.039	T04-11283	-0.462 ± 0.155	-----
Cd	48	blank filter	T04-11277	0.000 ± 0.094	T04-11279	0.004 ± 0.036	T04-11281	0.000 ± 0.044	T04-11283	0.169 ± 0.085	-----
In	49	blank filter	T04-11277	0.000 ± 0.092	T04-11279	-0.001 ± 0.037	T04-11281	0.000 ± 0.045	T04-11283	0.143 ± 0.097	-----
Sn	50	blank filter	T04-11277	0.057 ± 0.108	T04-11279	-0.019 ± 0.040	T04-11281	0.000 ± 0.054	T04-11283	-0.018 ± 0.050	-----
Sb	51	blank filter	T04-11277	0.124 ± 0.098	T04-11279	-0.002 ± 0.045	T04-11281	0.000 ± 0.103	T04-11283	0.065 ± 0.049	-----
Cs	55	blank filter	T04-11277	0.000 ± 0.224	T04-11279	-0.041 ± 0.077	T04-11281	0.000 ± 0.035	T04-11283	0.012 ± 0.047	-----
Ba	56	blank filter	T04-11277	0.000 ± 0.240	T04-11279	-0.053 ± 0.106	T04-11281	0.000 ± 0.035	T04-11283	0.117 ± 0.080	-----
La	57	blank filter	T04-11277	0.000 ± 0.495	T04-11279	-0.114 ± 0.134	T04-11281	0.000 ± 0.028	T04-11283	0.107 ± 0.059	-----
Ce	58	blank filter	T04-11277	0.000 ± 0.411	T04-11279	-0.187 ± 0.166	T04-11281	0.000 ± 0.033	T04-11283	0.038 ± 0.045	-----
Sm	62	blank filter	T04-11277	0.000 ± 0.684	T04-11279	-0.093 ± 0.591	T04-11281	0.000 ± 0.017	T04-11283	not reported	-----
Eu	63	blank filter	T04-11277	1.401 ± 0.880	T04-11279	-0.760 ± 0.895	T04-11281	0.000 ± 0.015	T04-11283	not reported	-----
Tb	65	blank filter	T04-11277	0.007 ± 0.942	T04-11279	-1.449 ± 1.938	T04-11281	0.000 ± 0.014	T04-11283	not reported	-----
Hf	72	blank filter	T04-11277	0.000 ± 0.229	T04-11279	0.010 ± 0.204	T04-11281	0.000 ± 0.020	T04-11283	not reported	-----
Ta	73	blank filter	T04-11277	0.115 ± 0.123	T04-11279	-0.042 ± 0.226	T04-11281	0.000 ± 0.011	T04-11283	not reported	-----
W	74	blank filter	T04-11277	0.000 ± 0.292	T04-11279	-0.006 ± 0.052	T04-11281	0.011 ± 0.009	T04-11283	0.071 ± 0.070	-----
Ir	77	blank filter	T04-11277	0.000 ± 0.104	T04-11279	0.010 ± 0.033	T04-11281	0.000 ± 0.007	T04-11283	not reported	-----
Au	79	blank filter	T04-11277	0.068 ± 0.111	T04-11279	-0.004 ± 0.025	T04-11281	0.000 ± 0.005	T04-11283	-0.033 ± 0.040	-----
Hg	80	blank filter	T04-11277	0.023 ± 0.042	T04-11279	-0.009 ± 0.022	T04-11281	0.000 ± 0.009	T04-11283	-0.107 ± 0.040	-----
Pb	82	blank filter	T04-11277	0.000 ± 0.081	T04-11279	0.004 ± 0.028	T04-11281	0.012 ± 0.011	T04-11283	0.041 ± 0.061	-----
Na	11	blank filter	T04-11278	0.000 ± 0.759	T04-11280	-0.247 ± 2.258	T04-11282	0.000 ± 0.129	T04-11284	0.846 ± 0.546	-----
Mg	12	blank filter	T04-11278	0.418 ± 0.815	T04-11280	-0.170 ± 0.400	T04-11282	0.000 ± 0.041	T04-11284	-0.145 ± 0.360	-----
Al	13	blank filter	T04-11278	0.179 ± 0.542	T04-11280	-0.090 ± 0.081	T04-11282	0.000 ± 0.051	T04-11284	0.288 ± 0.243	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Si	14	blank filter	T04-11278	0.145 ± 0.250	T04-11280	-0.019 ± 0.048	T04-11282	0.000 ± 0.034	T04-11284	1.037 ± 0.274	-----
P	15	blank filter	T04-11278	0.000 ± 0.050	T04-11280	-0.011 ± 0.027	T04-11282	0.000 ± 0.057	T04-11284	-0.065 ± 0.104	-----
S	16	blank filter	T04-11278	0.000 ± 0.012	T04-11280	0.042 ± 0.045	T04-11282	0.000 ± 0.033	T04-11284	-0.021 ± 0.077	-----
Cl	17	blank filter	T04-11278	0.000 ± 0.037	T04-11280	0.039 ± 0.024	T04-11282	0.000 ± 0.028	T04-11284	-0.092 ± 0.046	-----
K	19	blank filter	T04-11278	0.066 ± 0.001	T04-11280	-0.002 ± 0.016	T04-11282	0.023 ± 0.018	T04-11284	0.062 ± 0.042	-----
Ca	20	blank filter	T04-11278	0.000 ± 0.043	T04-11280	0.004 ± 0.013	T04-11282	0.000 ± 0.024	T04-11284	-0.059 ± 0.023	-----
Sc	21	blank filter	T04-11278	0.005 ± 0.028	T04-11280	0.017 ± 0.014	T04-11282	0.000 ± 0.036	T04-11284	0.024 ± 0.017	-----
Ti	22	blank filter	T04-11278	0.000 ± 0.026	T04-11280	0.011 ± 0.046	T04-11282	0.021 ± 0.015	T04-11284	0.037 ± 0.037	-----
V	23	blank filter	T04-11278	0.000 ± 0.009	T04-11280	0.001 ± 0.016	T04-11282	0.000 ± 0.012	T04-11284	0.013 ± 0.014	-----
Cr	24	blank filter	T04-11278	0.000 ± 0.040	T04-11280	-0.001 ± 0.008	T04-11282	0.000 ± 0.007	T04-11284	0.044 ± 0.014	-----
Mn	25	blank filter	T04-11278	0.043 ± 0.114	T04-11280	-0.007 ± 0.012	T04-11282	0.000 ± 0.006	T04-11284	0.048 ± 0.025	-----
Fe	26	blank filter	T04-11278	0.063 ± 0.171	T04-11280	-0.006 ± 0.011	T04-11282	0.000 ± 0.005	T04-11284	-0.035 ± 0.018	-----
Co	27	blank filter	T04-11278	0.020 ± 0.019	T04-11280	0.006 ± 0.008	T04-11282	0.000 ± 0.004	T04-11284	-0.031 ± 0.018	-----
Ni	28	blank filter	T04-11278	0.000 ± 0.031	T04-11280	-0.006 ± 0.008	T04-11282	0.000 ± 0.004	T04-11284	0.009 ± 0.016	-----
Cu	29	blank filter	T04-11278	0.000 ± 0.024	T04-11280	-0.014 ± 0.008	T04-11282	0.008 ± 0.004	T04-11284	0.013 ± 0.015	-----
Zn	30	blank filter	T04-11278	0.000 ± 0.032	T04-11280	-0.002 ± 0.007	T04-11282	0.000 ± 0.006	T04-11284	-0.029 ± 0.023	-----
Ga	31	blank filter	T04-11278	0.131 ± 0.098	T04-11280	-0.008 ± 0.054	T04-11282	0.001 ± 0.003	T04-11284	0.013 ± 0.024	-----
As	33	blank filter	T04-11278	0.000 ± 0.026	T04-11280	0.002 ± 0.012	T04-11282	0.000 ± 0.002	T04-11284	-0.005 ± 0.028	-----
Se	34	blank filter	T04-11278	0.000 ± 0.023	T04-11280	-0.004 ± 0.009	T04-11282	0.000 ± 0.003	T04-11284	0.022 ± 0.019	-----
Br	35	blank filter	T04-11278	0.000 ± 0.026	T04-11280	-0.001 ± 0.009	T04-11282	0.000 ± 0.003	T04-11284	0.001 ± 0.019	-----
Rb	37	blank filter	T04-11278	0.020 ± 0.024	T04-11280	-0.002 ± 0.009	T04-11282	0.003 ± 0.007	T04-11284	0.024 ± 0.020	-----
Sr	38	blank filter	T04-11278	0.041 ± 0.057	T04-11280	0.001 ± 0.010	T04-11282	0.000 ± 0.006	T04-11284	0.028 ± 0.054	-----
Y	39	blank filter	T04-11278	0.000 ± 0.037	T04-11280	-0.003 ± 0.011	T04-11282	0.000 ± 0.006	T04-11284	0.018 ± 0.054	-----
Zr	40	blank filter	T04-11278	0.000 ± 0.077	T04-11280	-0.008 ± 0.012	T04-11282	0.000 ± 0.010	T04-11284	0.113 ± 0.050	-----
Nb	41	blank filter	T04-11278	0.000 ± 0.062	T04-11280	-0.011 ± 0.014	T04-11282	0.000 ± 0.008	T04-11284	0.158 ± 0.062	-----
Mo	42	blank filter	T04-11278	0.016 ± 0.081	T04-11280	0.017 ± 0.016	T04-11282	0.000 ± 0.009	T04-11284	0.188 ± 0.061	-----
Ag	47	blank filter	T04-11278	0.000 ± 0.085	T04-11280	0.001 ± 0.034	T04-11282	0.000 ± 0.034	T04-11284	-0.046 ± 0.175	-----

Table 12. XRF PE Results

Element	Z	Sample Description	DRI Sample ID	DRI (µg/filter)	ODEQ Sample ID	ODEQ (µg/filter)	RTI Sample ID	RTI (µg/filter)	EPA-NERL Sample ID	EPA-NERL (µg/filter)	Median* (µg/filter)
Cd	48	blank filter	T04-11278	0.068 ± 0.094	T04-11280	-0.005 ± 0.035	T04-11282	0.000 ± 0.046	T04-11284	0.065 ± 0.096	-----
In	49	blank filter	T04-11278	0.000 ± 0.092	T04-11280	-0.011 ± 0.037	T04-11282	0.000 ± 0.045	T04-11284	0.011 ± 0.099	-----
Sn	50	blank filter	T04-11278	0.057 ± 0.108	T04-11280	0.013 ± 0.039	T04-11282	0.000 ± 0.056	T04-11284	0.138 ± 0.054	-----
Sb	51	blank filter	T04-11278	0.034 ± 0.097	T04-11280	-0.012 ± 0.044	T04-11282	0.000 ± 0.097	T04-11284	0.113 ± 0.048	-----
Cs	55	blank filter	T04-11278	0.077 ± 0.225	T04-11280	-0.021 ± 0.074	T04-11282	0.000 ± 0.032	T04-11284	0.039 ± 0.046	-----
Ba	56	blank filter	T04-11278	0.000 ± 0.241	T04-11280	-0.090 ± 0.101	T04-11282	0.000 ± 0.031	T04-11284	0.067 ± 0.078	-----
La	57	blank filter	T04-11278	0.000 ± 0.495	T04-11280	-0.054 ± 0.129	T04-11282	0.000 ± 0.025	T04-11284	0.143 ± 0.058	-----
Ce	58	blank filter	T04-11278	0.068 ± 0.412	T04-11280	-0.107 ± 0.159	T04-11282	0.000 ± 0.031	T04-11284	0.102 ± 0.045	-----
Sm	62	blank filter	T04-11278	0.000 ± 0.683	T04-11280	-0.578 ± 0.568	T04-11282	0.000 ± 0.016	T04-11284	not reported	-----
Eu	63	blank filter	T04-11278	0.622 ± 0.869	T04-11280	-1.191 ± 0.861	T04-11282	0.006 ± 0.012	T04-11284	not reported	-----
Tb	65	blank filter	T04-11278	0.000 ± 0.940	T04-11280	-0.333 ± 1.864	T04-11282	0.000 ± 0.014	T04-11284	not reported	-----
Hf	72	blank filter	T04-11278	0.000 ± 0.229	T04-11280	-0.025 ± 0.204	T04-11282	0.008 ± 0.016	T04-11284	not reported	-----
Ta	73	blank filter	T04-11278	0.000 ± 0.122	T04-11280	-0.020 ± 0.227	T04-11282	0.012 ± 0.015	T04-11284	not reported	-----
W	74	blank filter	T04-11278	0.000 ± 0.292	T04-11280	0.001 ± 0.053	T04-11282	0.000 ± 0.007	T04-11284	-0.082 ± 0.066	-----
Ir	77	blank filter	T04-11278	0.047 ± 0.105	T04-11280	0.007 ± 0.034	T04-11282	0.000 ± 0.006	T04-11284	not reported	-----
Au	79	blank filter	T04-11278	0.000 ± 0.111	T04-11280	0.001 ± 0.025	T04-11282	0.008 ± 0.006	T04-11284	0.192 ± 0.045	-----
Hg	80	blank filter	T04-11278	0.000 ± 0.042	T04-11280	0.001 ± 0.022	T04-11282	0.000 ± 0.008	T04-11284	-0.031 ± 0.040	-----
Pb	82	blank filter	T04-11278	0.050 ± 0.081	T04-11280	-0.008 ± 0.028	T04-11282	0.000 ± 0.007	T04-11284	0.059 ± 0.057	-----

***** *Median was calculated only when the result from all reporting labs was greater than three times the uncertainty.***

Table 13. XRF Analysis at the DRI Laboratory										
Instrument: PanAnalytical Epsilon 5 Software: E5 Version 1.0B										
	Instrument Conditions for Routine Sample Analysis									
Parameter	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
X-ray tube parameters: Tube voltage (kV)	25	40	40	75	100	100	100	100	100	100
Tube current (mA)	24	15	15	8	6	6	6	6	6	6
Tube anode material	Gd	Gd	Gd	Gd	Gd	Gd	Gd	Gd	Gd	Gd
Direct excitation of sample: Filter Material										
Filter thickness (mm)										
Secondary excitation of sample: Secondary Fluorescor	CaF_2	Ti	Fe	Ge	Zr	Mo	Ag	CsI	BaF_2	Al_2O_3
Filter material										
Filter thickness (mm)										
Acquisition time (seconds)	200	200	200	200	100	100	100	100	100	100
Energy range acquired (keV)	0-20	0-20	0-20	0-20	0-20	0-20	0-40	0-80	0-80	0-80
Number of [MCA] channels	2048	2048	2048	2048	2048	2048	4096	8192	8192	8192
Sample rotation (yes/no)	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Beam spot size, diameter (mm)	20	20	20	20	20	20	20	20	20	20
Atmosphere (vacuum, He, air)	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum
Elements Reported	Na Mg Al Si P S Cl K	Ca Sc	Ti V Cr	Mn Fe Co Ni Cu Zn	Ga As Se Br Rb Hf Ta W Ir Au Hg Tl Pb	Sr Y	Zr Nb Mo	Pd Ag Cd In	Sn Sb	Cs Ba La Ce Sm Eu Tb

Table 14. XRF Analysis at the ODEQ Laboratory										
Instrument: Kevex771 Software: WinXRF V2.41										
	Instrument Conditions for Routine Sample Analysis									
Parameter	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
X-ray tube parameters: Tube voltage (kV)	7.5	35	40	45	40	58				
Tube current (mA)	0.9	2.1	2.1	2.1	0.9	1.5				
Tube anode material	Rh	Rh	Rh	Rh	Rh	Rh				
Direct excitation of sample: Filter Material	Whatman 41	na	na	na	Rh	W				
Filter thickness (mm)	1 layer	na	na	na	0.1	0.1				
Secondary excitation of sample: Secondary Fluorescor	none	Ti	Fe	Ge	none	none				
Filter material	na	none	none	none	na	na				
Filter thickness (mm)	na	na	na	na	na	na				
Acquisition time (seconds)	400	400	400	400	400	400				
Energy range acquired (keV)	10	10	10	10	20	80				
Number of [MCA] channels	1024	1024	1024	1024	2048	4096				
Sample rotation (yes/no)	no	no	no	no	no	no				
Beam spot size, diameter (mm)	unknown	unknown	unknown	unknown	unknown	unknown				
Atmosphere (vacuum, He, air)	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum				
Elements Reported	Na Mg Al Si P	S Cl K Ca	Sc Ti V Cr	Mn Fe Co Ni Cu Zn	Ga As Se Br Rb Sr Y Zr Nb Mo Hf Ta W Ir Au Hg Pb	Ag Cd In Sn Sb Cs Ba La Ce Sm Eu Tb				

Table 15. XRF Analysis at the RTI Laboratory										
Instrument: ThermoNoran QuanX Software: Wintrace 3.0 Build 35										
Parameter	Instrument Conditions for Routine Sample Analysis									
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
X-ray tube parameters: Tube voltage (kV)	5	10	30	50	50					
Tube current (mA)	1.20	1.98	1.66	1.00	1.00					
Tube anode material	Rh	Rh	Rh	Rh	Rh					
Direct excitation of sample: Filter Material	no filter	Graphite	Pd Thin	Pd Thick	Cu Thin					
Filter thickness (**g/cm^2**)	na	0.06	0.03	0.15	0.338					
Secondary excitation of sample: Secondary Fluorescor	na	na	na	na	na					
Filter material	na	na	na	na	na					
Filter thickness (mm)	na	na	na	na	na					
Acquisition time (seconds)	300	300	250	200	200					
Energy range acquired (keV)	0-10	0-10	0-20	0-40	0-40					
Number of [MCA] channels	512	512	1024	2048	2048					
Sample rotation (yes/no)	no	no	no	no	no					
Beam spot size, diameter (mm)	9.5mm x 11mm Elipse	9.5mm x 11mm Elipse	9.5mm x 11mm Elipse	9.5mm x 11mm Elipse	9.5mm x 11mm Elipse					
Atmosphere (vacuum, He, air)	vacuum	vacuum	vacuum	vacuum	vacuum					
Elements Reported	Na Mg P	Al Si S K Ca Sc Cs	Cl Ti V Cr Mn Fe Co Ni Cu Zn La Ce Sm Eu Tb Hf	Ga As Se Br Rb Sr Y Zr Nb Mo Ta W Ir Au Hg Pb	Ag Cd In Sn Sb Ba					

Table 16. XRF Analysis at the RTI Laboratory										
Instrument: ThermoNoran QuanX EC Software: Wintrace 3.0 Build 31										
	Instrument Conditions for Routine Sample Analysis									
Parameter	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
X-ray tube parameters: Tube voltage (kV)	5	10	30	50	50					
Tube current (mA)	1.98	1.98	1.66	1.00	1.00					
Tube anode material	Rh	Rh	Rh	Rh	Rh					
Direct excitation of sample: Filter Material	no filter	Graphite	Pd Thin	Pd Med Thick	Cu Thin					
Filter thickness (**g/cm^2**)	na	0.06	0.03	0.09	0.338					
Secondary excitation of sample: Secondary Fluorescor	na	na	na	na	na					
Filter material	na	na	na	na	na					
Filter thickness (mm)	na	na	na	na	na					
Acquisition time (seconds)	300	300	300	300	300					
Energy range acquired (keV)	0-10	0-10	0-20	0-40	0-40					
Number of [MCA] channels	512	512	1024	2048	2048					
Sample rotation (yes/no)	no	no	no	no	no					
Beam spot size, diameter (mm)	10mm x 12mm Elipse	10mm x 12mm Elipse	10mm x 12mm Elipse	10mm x 12mm Elipse	10mm x 12mm Elipse					
Atmosphere (vacuum, He, air)	vacuum	vacuum	vacuum	vacuum	vacuum					
Elements Reported	Na Mg Al Si	P S Cl K Ca Sc	Ti V Cr Mn Fe Co Ni Cu Zn Cs Ba La Ce Sm Eu Tb Hf	Ga As Se Br Rb Sr Y Zr Nb Mo Ta W Ir Au Hg Pb	Ag Cd In Sn Sb					

Table 17. XRF Analysis at EPA's NERL Laboratory										
Instrument: Kevex771-EDX Software: LSQEPA v3-2004F (custom software)										
	Instrument Conditions for Routine Sample Analysis									
Parameter	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
X-ray tube parameters: Tube voltage (kV)	55	55	40	40	40	15				
Tube current (mA)	0.75	0.75	1.00	1.00	1.00	1.6				
Tube anode material	Rh	Rh	Rh	Rh	Rh	Rh				
Direct excitation of sample: Filter Material	none	none	none	none	none	none				
Filter thickness (mm)	none	none	none	none	none	none				
Secondary excitation of sample: Secondary Fluorescor	Zr	Ag	Ge	Fe	Ti	Al				
Filter material	none	none	none	none	none	none				
Filter thickness (mm)	none	none	none	none	none	none				
Acquisition time (seconds)	200	100	100	200	200	200				
Energy range acquired (keV)	20	20	10	10	10	10				
Number of [MCA] channels	1024	1024	1024	1024	1024	1024				
Sample rotation (yes/no)	no	no	no	no	no	no				
Beam spot size, diameter (mm)	~20	~20	~20	~20	~20	~20				
Atmosphere (vacuum, He, air)	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum				
Elements Reported	Cu Zn Ga Ge As Se Br Rb W Pt Au Hg Tl Pb	Rb Sr Y Zr Nb Mo	Cr Mn Fe Co Ni Cu	K Ca Sc Ti V CrCd In Sn Sb Te I Cs Ba La Ce	Al Si P S Cl K Ca Sc Rh Pd Ag Cd In Sn Sb	Na Mg				

Appendix E

Systems Audit Report

TECHNICAL MEMORANDUM

TO:	Dennis Crumpler / OAQPS
FROM:	Eric Boswell / NAREL
COPY:	Dr. R.K.M. Jayanty, RTI
AUTHOR:	Jewell Smiley / NAREL
DATE:	November 4, 2005
SUBJECT:	RTI Laboratory Audit

Introduction

On July 12, 2005, a laboratory audit was conducted at the Research Triangle Institute (RTI) as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network (STN). RTI is the prime contractor providing analytical services to support over two hundred field sites collecting speciation samples. The US EPA audit team included Eric Boswell and Jewell Smiley from the National Air and Radiation Environmental Laboratory (NAREL) with Dennis Crumpler and Joann Rice from the Office of Air Quality Planning and Standards (OAQPS). Solomon Ricks and Jeff Lance were also present during the audit as EPA observers. This audit was a routine annual inspection of the laboratory systems and operations required for acceptable contract performance.

Summary of Audit Proceedings

After a brief meeting with the RTI senior staff and supervisors, the audit team separated as necessary to complete specific assignments for the audit process. At least one member of the RTI staff was always available to escort and assist each auditor. The following specific areas on the RTI campus were visited and inspected.

✓ Gravimetric Laboratory - Ms. Lisa Greene

✓ Organic Carbon/Elemental Carbon (OC/EC) Laboratory - Dr. Max Peterson

✓ X-ray Fluorescence (XRF) Laboratory - Dr. William Gutknecht, Ms. Andrea McWilliams

✓ Ion Chromatography (IC) Laboratory - Dr. Eva Hardison

✓ Sample Handling and Archiving Laboratory (SHAL) - Mr. Jim O'Rourke

Besides the areas mentioned above, interviews were conducted with the following RTI staff.

✓ Dr. R.K.M. Jayanty - RTI Services Program Manager

✓ Dr. Jim Flanagan - Quality Assurance Manager

✓ Mr. Ed Rickman - Data Management Technical Supervisor

RTI has been analyzing samples from the $PM_{2.5}$ STN since the network began in February of 2000. Members of the audit team were familiar with RTI's current Quality Assurance Project Plan (QAPP) and pertinent SOPs. A report from the previous year's on-site audit was available for reference and followup [see reference 1]. Also available was a 119-page report prepared by RTI which summarized the quality control data and corrective actions during the period July 1 through December 31, 2004. RTI was one of several laboratories to participate in a Performance Evaluation (PE) study earlier in 2005 [see reference 2], and results from that PE study were discussed with RTI staff during the audit. Several experimental activities were also performed during the course of this audit which will be described later within the appropriate section of this report.

Gravimetric Laboratory

The gravimetric laboratory is equipped with two weighing chambers located in building 11. Ms. Lisa Greene is the supervisor of this lab, and she was interviewed by Jewell Smiley and Joann Rice with Solomon Ricks observing. The interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOPs.

- *Standard Operating Procedure for PM2.5 Gravimetric analysis* [see reference 3]
- *Standard Operating Procedures for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters* [see reference 4]

Both of the weighing chambers are configured to satisfy conditions of cleanliness, constant temperature, and constant humidity required by the program. Accurate control of climate inside the weighing chamber is important because balance calibration is very sensitive to temperature, and the equilibrated mass of an air filter sample is sensitive to humidity. Mass determination typically proceeds by weighing the Teflon® collection filter before and after the sampling event. The amount of Particulate Matter (PM) captured onto the surface of the filter can be calculated by a simple subtraction of the tare weight from the loaded filter weight.

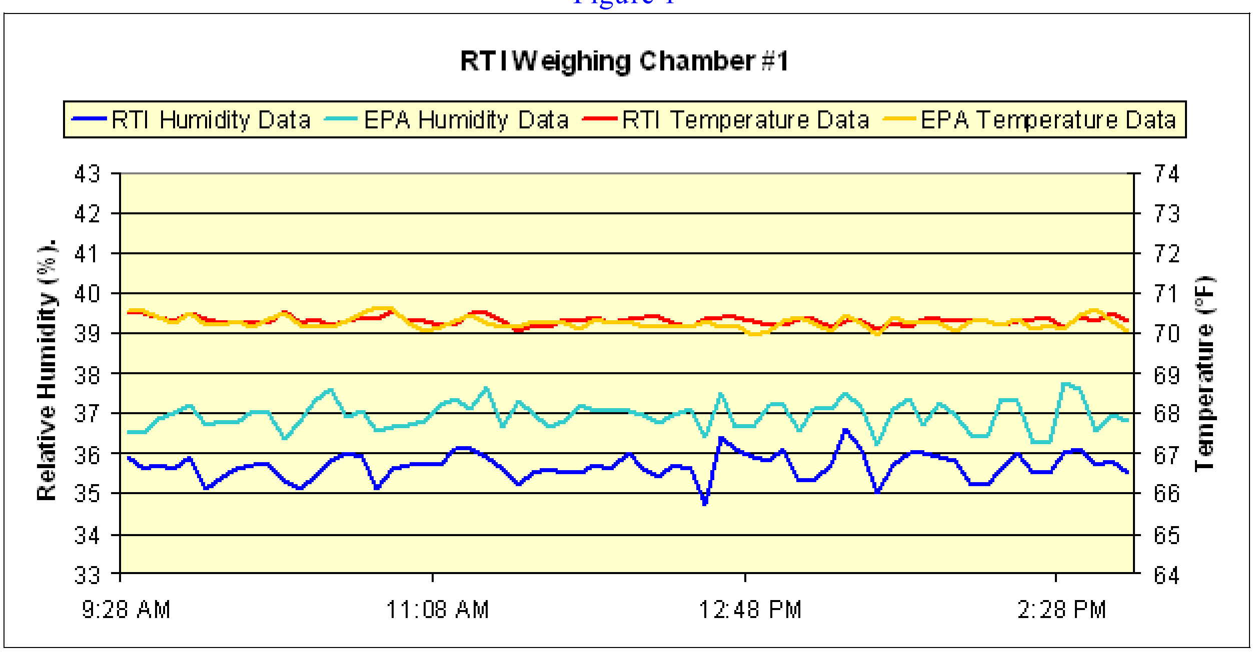
A few items were hand-carried to the audit from NAREL so that experimental measurements could be made during the audit. Two metallic weights and four Teflon® filter samples were presented to Lisa with a request to weigh each item at least twice during the day. It should be explained that two of the filter samples were loaded with $PM_{2.5}$ captured from the Montgomery air in January of 2005 and two filters were blank. Metallic weights were included in the sample set to represent a very stable reference material for measuring gravimetric mass. All of the test samples were placed into Chamber #1 and given approximately one hour to equilibrate before the first weighing session was performed. Mr. Maurice Gerald was the analyst selected to perform the work using microbalance "C" for all of the measurements. Results are presented in Table 1 along with mass values previously determined at NAREL. Maurice was able to weigh the test samples four times with about an hour separating each weigh session. Table 1 shows good inter-laboratory agreement for all three sample types.

Table 1. Gravimetric Mass Determinations

Sample ID	Sample Description	NAREL Value Determined on July 7 (mg)	All RTI Values Determined on July 12			
			~11 AM (mg)	~12 AM (mg)	~1 PM (mg)	~2:30 PM (mg)
MW05-11331	metallic wt.	97.546	97.545	97.545	97.545	97.545
MW05-11332	metallic wt.	192.422	192.421	192.421	192.421	192.420
T05-11317	loaded filter	142.486	142.482	142.482	142.482	142.483
T05-11318	loaded filter	142.826	142.823	142.823	142.824	142.824
T05-11322	blank filter	141.665	141.663	141.663	141.664	141.664
T05-11323	blank filter	145.708	145.705	145.705	145.705	145.705

Two Dickson data loggers were also carried to the audit from NAREL so that independent measurements of temperature and humidity could be recorded during the audit. One of the data loggers was placed into each weighing chamber immediately near RTI's device for measuring the temperature and humidity. Measurements were downloaded from all of the devices at the end of the day, and these data are presented in Figure 1 and Figure 2. Figure 1 shows good agreement between the temperature loggers placed into Chamber #1, but less agreement was observed for the humidity readings. The graph shows that humidity values measured by RTI's device were consistently lower by a small amount. The average relative humidity (RH) recorded by NAREL's device was 36.9 %, and the average RH recorded by RTI's device was 35.7 % during the same period. Both data loggers had an expected accuracy of ± 2 % RH. All of the measurement differences shown in Figure 1 are within the stated accuracy of each logging device.

Figure 1



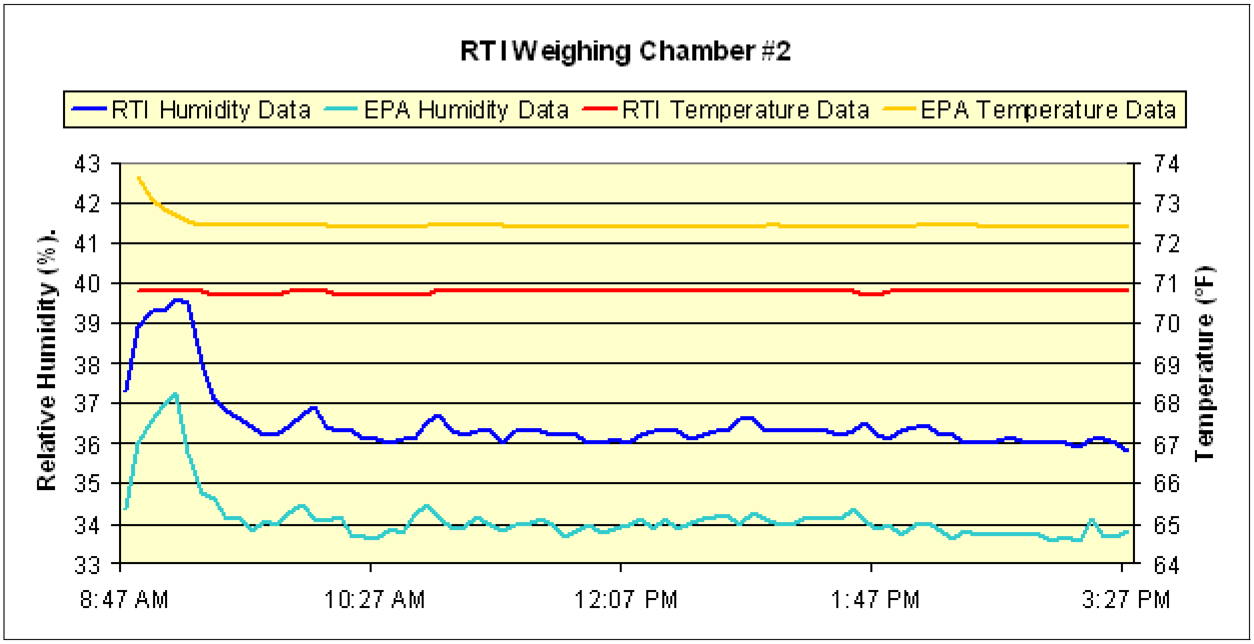


Figure 2

Figure 2 shows the humidity and temperature data collected inside chamber #2. Both loggers show a dramatic peak in RH at about 9 AM. This surge in humidity was probably due to four extra people entering the chamber during this period. Three auditors and the supervisor entered the chamber at approximately 8:45 AM, and remained inside the chamber for about twenty minutes. The graph for chamber #2 shows humidity values measured by RTI's device consistently above those recorded by NAREL's device. The average RH recorded by NAREL's logger was 34.1 %, and the average RH recorded by RTI's device was 36.5 % during the same period.

Figure 2 shows a noticeable difference in temperature values measured inside chamber #2. The average temperature recorded by RTI's logger was 70.8 °F, and the average temperature recorded by NAREL's logger was 72.5 °F. According to RTI's QAPP, their logger is expected to have an accuracy of ± 2 °C (± 3.6 °F). NAREL's logger is expected to have an accuracy of ± 0.5 °F, and it was certified to provide this level of accuracy about one month before RTI's audit. Although difference between loggers can be seen in Figure 2, none of the temperature and humidity discrepancies are greater that RTI's stated measurement uncertainties.

Figure 3 shows one more comparison. Both of NAREL's data loggers were removed from the weighing chamber at NAREL on July 11, one day before the audit at RTI. Before they were removed, both of the loggers were located immediately near the other inside NAREL's chamber. Figure 3 shows the temperature and humidity data that were recorded by both loggers from midnight to about 8 AM at which time they were removed from the chamber and placed inside a small Igloo® container for transporting to the audit. It is important to realize that NAREL's two loggers were not exactly identical, and the most significant difference can be seen in the humidity measurements. The logger that was used to make measurements in RTI's chamber #1 shows an average RH of 35.9 % while the logger used to make measurements in RTI's chamber #2 shows an average RH of 35.5 % for the same time period. If NAREL's data loggers had been switched during the audit so that each device was placed into the opposite chamber, then the RH comparisons would have shown better agreement [by about 0.4 %] for both of RTI's chambers.

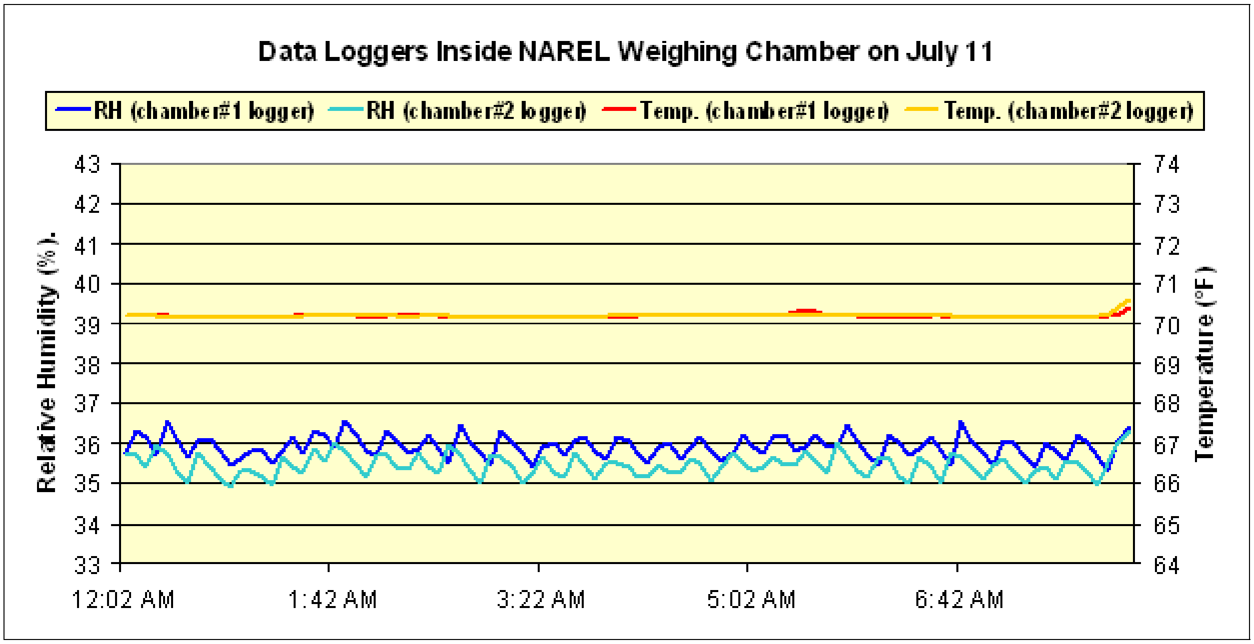


Figure 3

So how good is the temperature and humidity control at RTI? This audit has shown that both chambers were within RTI's stated control limits for temperature (68-73.4°F) and for RH (30-40%) regardless of which device was selected to provide the measurements.

Later during the audit, two Teflon® filters were removed from the SHAL inventory and traveled with the auditors back to NAREL. These two filters were placed into NAREL's weighing chamber for re-equilibration and weighing so that an independent tare mass could be determined for each filter. Those results are presented in Table 2, and excellent agreement was observed for one filter, but poor agreement was observed for the second filter.

Table 2

Teflon® Filter ID	Filter Description	RTI Tare Mass (mg)	NAREL Tare Mass (mg)	Difference (mg)
12227086	Inventory Filter 1	151.324	151.325	0.001
12227075	Inventory Filter 2	151.099	151.069	0.030

NAREL's tare mass for the second filter was thirty micrograms (30 µg) lighter than the tare mass determined at RTI. Effort was made to discover a reason for this discrepancy. The filter identification was verified by checking the bar code label as well as the serial number on the filter itself. Data transcription errors were unlikely since duplicate tare measurements had been made at RTI, and both measurements agreed within one microgram. Four measurements were made at NAREL over the course of eight days, and all of NAREL's measurements agreed within two micrograms. It is possible that a small piece of extraneous contaminating debris was attached to the filter for measurements taken at RTI, and somehow the debris was lost from the filter before measurements were made at NAREL. Other explanations are also possible.

Dialog was initiated between NAREL and RTI to further investigate this significant finding. The auditors learned that corrective actions had been taken by RTI earlier in the year to deal with a defective lot of Teflon® filters. RTI had observed abnormal gravimetric mass results for filters that were supplied to the field sites during March and April of 2005. The problem revealed itself in two ways: (1) a high frequency of negative results was observed in the gravimetric mass results for the trip and field blanks and (2) a high frequency of outliers was observed in the reconstructed mass balance results for loaded filters. Several filters were examined in RTI's optical microscopy laboratory at magnifications of 3.5x to 40x under enhanced lighting. According to RTI's corrective action report, "*crumbs of filter and/or support ring material were found along the support ring. This material flaked easily from the ring with normal handling.*" RTI's report also stated that *"The negative weights may have been caused by loose debris falling off the filters between the initial and final weighings"*. RTI's corrective actions included the return of 6000 unused filters to the manufacturer for replacement. RTI also increased their frequency of weighing filters in duplicate. For example, duplicate tare measurements were increased from 10 % to 100 % of the filters, and duplicate post-weighing was increased from 10 % to 30 % of the filters. It may be a coincidence that NAREL's audit finding is very similar to the blank problems described in this corrective action report.

No other deficiencies were observed as a result of this audit. The overall impression of the gravimetric lab was very positive. Earlier in the year RTI's gravimetric lab weighed several samples that were split with NAREL [see reference 2], and all of those results were within advisory limits.

Carbon Analysis Laboratory

Dr. Max Peterson is the technical supervisor of the carbon analysis laboratory located in building 3. Mr. Melville Richards and Mr. Eric Poitras were analysts working in the lab during the audit. Jewell Smiley and Joann Rice conducted this part of the audit. The interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOP [see reference 5].

- *Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical Transmittance Carbon Analyzer.*

New quartz filters must be thermally cleaned before they are delivered to the SHAL, mounted into the appropriate sampler module, and shipped to the field for sample collection. Upon return to the laboratory, each loaded filter must be analyzed using one of the four Sunset instruments set up to run a thermal/optical method specified for all STN samples. The STN method uses a specific heating protocol to thermally remove carbon from the quartz filter material while the optical transparency of the sample is monitored by shining a laser through the sample. The STN method of carbon analysis is described in the RTI's SOP [see reference 5]. RTI currently uses the STN method to report organic carbon (OC) and elemental carbon (EC) the sum of which represents the total carbon (TC). RTI also reports five OC subfractions: OC1, OC2, OC3, OC4, and PyrolC. RTI began reporting the OC subfractions in July of 2003 after a new contract was awarded.

Special attention was given to the OC subfractions during the last on-site audit because of concern that the STN thermal protocol might not provide sufficient data quality for the subfractions [see reference 1]. There was concern that the STN method might show poor precision for the subfractions over time and between instruments. Some of the earliest evidence came from sucrose spikes which are routinely analyzed at RTI as daily calibration checks. The sucrose spikes have shown good precision for the total carbon measurement over time and between instruments, but unfortunately, sucrose shows poor precision for some of the OC subfractions. It was suggested in RTI's last audit report that we need to learn more about the data quality of the OC subfractions. Specifically, we need to learn more about the between-instrument precision. The lab routinely schedules 10 % of the filter samples for a duplicate analysis, but all of the duplicates are analyzed using the same instrument that performed the original analysis. A recommendation was made within the last audit report to change the way duplicates are scheduled so that some of the duplicates are analyzed using a different instrument. Thus far RTI has not implemented this suggestion for the OC/EC lab. As a consequence, the sucrose spikes are the only routine quality control measure of the between-instrument precision.

RTI recently participated in a study that compared OC/EC results from four different labs [see reference 2], and results from this study were discussed during the audit. A sufficient number of $PM_{2.5}$ filter replicates were prepared at NAREL so that each participating lab received an almost identical set of samples, and each set of samples contained blind duplicates. RTI analyzed each filter sample using all four of the Sunset instruments. RTI's results from this study showed good precision for the blind duplicates and good precision among the instruments. RTI's results were virtually indistinguishable from NAREL's results, even when the OC subfractions were compared.

Later during the audit, two quartz® filters were removed from the SHAL inventory and traveled with the auditors back to NAREL. These filters were analyzed at NAREL to determine the amount of total carbon present on each filter. No significant contamination was observed on either filter.

The general impressions of the OC/EC laboratory developed during this audit were very positive. Only one concern was noted. Some of the routine duplicate determinations should be scheduled to collect between-instrument precision data.

X-Ray Fluorescence Analysis

The PM captured onto the surface of the Teflon® filter is not only weighed to determine its mass but is also analyzed to determine its elemental composition using the energy dispersive X-Ray Fluorescence (XRF) technique. The XRF analysis may not proceed before the gravimetric analysis has been completed. Historically RTI has used one of its remote subcontractor laboratories in Oregon to perform the XRF analysis, but since February of 2002, RTI has operated its own local XRF laboratory to provide a larger sample capacity. There are currently two local instruments at RTI and three remote instruments in Oregon that have been approved for analysis of STN samples.

Dr. Bill Gutknecht is responsible for the review of all XRF data, and Ms. Andrea McWilliams is the analyst responsible for operating both of local instruments. They were interviewed by Jewell Smiley and Joann Rice during this part of the audit. The interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOP [see reference 6].

- *Standard Operating Procedure for the X-Ray Fluorescence Analysis of PM2.5 Deposits on Teflon Filters.*

The focus of the XRF audit was to discuss those samples that RTI had analyzed as part of a recent inter-laboratory comparison study sponsored by NAREL [see reference 2]. A sufficient number of $PM_{2.5}$ filter replicates were prepared at NAREL so that each participating lab received an almost identical set of filter samples for XRF analysis. NAREL had received the analytical results from all of the participating labs, and had finished comparing the results reported from different labs. All of the labs reported an uncertainty along with every analytical result. Good agreement was observed among the participating labs for most of the elements that were significantly above the reported uncertainty. The most noticeable exception was aluminum. The auditors were anxious to examine some of RTI's raw data spectra, and of particular interest were the spectra from which aluminum results were derived. RTI's spectra that were used to determine the lighter elements contained a significant interference peak which Andrea described as a diffraction peak. The diffraction peak was not fully resolved from aluminum, nor was it fully resolved from silicon. One would expect an interference of this type to increase the uncertainty of aluminum and silicon results. Yet when RTI's uncertainties were compared to those reported from the other labs, RTI's uncertainties were actually smaller. This study has provided some evidence that RTI may be reporting some uncertainties that are too small. Andrea was asked to explain how the uncertainties were calculated at RTI, and she was not certain how some of the components of uncertainty were calculated by the XRF software.

Ion Chromatography (IC) Laboratory

The IC laboratory is located in building 6 where Dr. Eva Hardison is the technical supervisor, and Mr. David Hardison was the analyst on duty during the audit. Both of them were interviewed by Jewell Smiley and Joann Rice for compliance to good laboratory practices, the QAPP, and the following SOPs.

- *Standard Operating Procedures for PM2.5 Anion Analysis* [see reference 7]
- *Standard Operating Procedures for PM2.5 Cation Analysis* [see reference 8]
- *Standard Operating Procedures for Cleaning Nylon Filters Used for Collection of PM2.5 Material* [see reference 9]

The laboratory is equipped with multiple automated Dionex IC instruments and also has access to equipment for cleaning and extracting Nylon® filters. Four IC instruments were set up for anions and two for cations. At the instrument, multilevel calibration curves are established daily, and the calibration is checked by a second source standard. Duplicate injections have been used to evaluate precision, and post spikes have been used to evaluate accuracy. Control charts were available for recent spikes, duplicates, and laboratory blanks.

Later during the audit, two Nylon® filters were removed from the SHAL inventory and traveled with the auditors back to NAREL. These two filters were extracted and analyzed at NAREL to determine trace level ions that might be present on the filters. No ions were detected on either filter above NAREL's method detection limit.

The interviews and inspections made during this part of the audit were very satisfying, and no deficiencies associated with the IC laboratory were observed during this audit.

Sample Handling and Archiving Laboratory (SHAL)

The SHAL is currently located approximately three miles from RTI's main campus. Moving off-campus to this facility was necessary to handle the large number of samples produced by the speciation network. The network currently produces more than 5000 filter samples per month.

The SHAL is organized to be a central point for all laboratory operations. Every sample passes through the SHAL at least twice. Clean air filters are delivered to the SHAL from the analytical laboratories ready to be packaged and delivered to the field sites. Critical bookkeeping is required to insure sample integrity and to make sure that the proper equipment and information is sent to the field in a timely manner. Loaded filters returning from the field are received at the SHAL, removed from the sampler module, logged into the electronic database, and physically delivered back to the analytical laboratories where the final analysis is completed. After the final analysis is completed, each filter sample is maintained inside a refrigerated archive at RTI for up to 5.5 years, and the IC extracts are kept for six months.

The air filter is protected from the time it leaves the SHAL until it is returned from the field. Each air filter must be mounted into an appropriate sampler module to protect it from accidental contamination. Three different types of filters are required for all of the analytical fractions, and four different types of air samplers are currently operated in the field. Different samplers require different filter modules which are expensive and must be cleaned for reuse. It can be readily seen that the SHAL has a critical role for the overall operations. The correct filter must be mounted into the correct module and mailed to the correct field site on schedule. The SHAL maintains direct interaction with the field sites and with the analytical laboratories.

Eric Boswell, Jewell Smiley, Joann Rice, Dennis Crumpler, and Solomon Ricks visited the SHAL during the afternoon portion of the audit. All of the auditors were able to observe a staged demonstration of the filter assembly/disassembled process. This demonstration was planned in advance so that materials would be available. New filters which had been prepared at NAREL were used for the demonstration, and clean Met One SASS modules were supplied by RTI. SASS modules were selected for this demonstration because the majority of states use Met One air samplers at their sites. During the demonstration two Teflon® filters, two Nylon® filters, and two quartz filters were installed into six SASS modules using procedures routinely executed in the SHAL. The modules were immediately disassembled so that the filters could be recovered and placed back into their protective petri slides. Extra filters were brought from NAREL to serve as travel blanks which were not removed from their protective petri slides. All filters were carried back to NAREL for analysis.

Results from the module assembly/disassembly demonstration showed no measurable contamination transferred to the Nylon® filters and no contamination above 0.4 $\mu g/cm^2$ total carbon (4.7 µg/filter) was observed for the quartz filters. Results for the assembled Teflon® filters are shown in Table 3 along with the associated trip blanks and laboratory chamber blanks. No significant level of contamination was transferred to the Teflon® test filters during the demonstration.

Table 3

Teflon® Filter ID	Filter Description	Tare Mass (mg)	Loaded Mass (mg)	Filter Residue (mg)
T05-11430	Assembled Filter 1	145.396	145.394	-0.002
T05-11431	Assembled Filter 2	145.420	145.420	0.000
T05-11432	Trip Blank 1	144.909	144.907	-0.002
T05-11433	Trip Blank 2	145.904	145.904	0.000
T2112375	Lab Blank 1	144.008	144.008	0.000
T2112400	Lab Blank 2	144.511	144.509	-0.002
T2112425	Lab Blank 3	147.536	147.536	0.000

Other Staff Interviews

Dr. R.K.M. Jayanty, Dr. Jim Flanagan, and Mr. Ed Rickman were interviewed by Eric Boswell and Dennis Crumpler with Jeff Lantz observing. The following topics were discussed.

1. Facility and Equipment
    a. Facility, Equipment, and Support Services
    b. Security
    c. Health and Safety
    d. Waste Management
2. Organizational Structure and Management Policies
    a. Personnel
    b. Job Descriptions and Qualifications
    c. Training Program and Training Records
3. Quality Assurance
    a. Standard Operating Procedures
    b. Performance Evaluation Results and Corrective Action Responses
    c. Previous Audit Reports and Responses
    d. Quality Reports to Management
    e. Quality Control Records and Oversight
    f. Review Process for QAPP's
    g. Review Process for Client Data Packages

4. Procurement
    a. Materials and Equipment
    b. Services
5. Document Control
    a. Controlled Document Production
    b. Document Distribution and Tracking
    c. Revisions to Control Documents
    d. Retrieval and Disposal of Outdated Documents
6. Computer Management and Software Control
    a. Personnel and Training
    b. Facilities and Equipment
    c. Procedures
    d. Security
    e. Data Entry
    f. Records and Archives

Conclusions

Observations have been made by the audit team to determine RTI's compliance with good laboratory practices, the QAPP, and SOPs. This audit has produced the following findings, comments, and recommendations.

1. Two Teflon® filters were removed from the SHAL inventory during the audit so that NAREL could experimentally re-measure the tare mass already determined at RTI's gravimetric lab. As shown previously in Table 2, NAREL's tare mass was an alarming 30 micrograms smaller for one of the filters.

    Comment: This finding may be an indication of serious problems like the bad filter lot that was discovered several weeks before this audit. According to the corrective action report, the bad filter lot produced negative trip and field blanks. The questionable filter would have produced this effect if it had been utilized as a trip or field blank. RTI should continue to monitor the situation and explore potential reasons for the large variability in blank filters.

2. All of the routine OC/EC duplicates are analyzed using the same instrument that performed the original analysis. This practice was acceptable in the past when the daily sucrose spikes were able to provide evidence of acceptable between-instrument performance. Now that OC subfractions are reported, there is no daily QC that provides the necessary assurance of acceptable between-instrument precision.

Recommendation. RTI should schedule some of the routine OC/EC duplicates for analysis using a different instrument. For example, half of the scheduled duplicates could be analyzed using the same instrument, and the remaining duplicates could be analyzed using one of the available instruments that did not perform the original analysis.

3. As stated earlier, the focus of the XRF audit was to discuss those samples that RTI had analyzed as part of a recent inter-laboratory comparison study sponsored by NAREL [see reference 2]. Results from this study showed aluminum to be the most controversial element reported. This study also showed that RTI generally reported uncertainties which were lower than those reported by the other participating labs. A few spectra were inspected and discussed during the audit. Two specific spectra were selected to be included in the final report for the study. Ultimately the final report included examples of the controversial spectra from all of the labs. The spectra from RTI contain a significant [diffusion peak] interference for aluminum and silicon which was not observed in the spectra from the other labs.

   Comment: This observation may not be a problem for RTI's analysis since there is no standard method for calculating XRF uncertainties. However, RTI may want to take a closer look at the way uncertainties were calculated for aluminum and silicon during this study. EPA has recently initiated dialog with all of the speciation labs to learn more about the XRF analysis at each lab, and clearly there is diversity among the different labs. Any progress toward standardizing the XRF analysis is a positive step for the speciation program.

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Appendix F

Synoptic Summary of 2005 Speciation Trends and IMPROVE Network Audits

Draft July 17, 2006
Speciation Network information may be extracted for use in 2005 Data Summary Report

MEMORANDUM

SUBJECT: Synoptic Summary of 2005 Speciation Trends and IMPROVE Network Audits

FROM: Dennis Crumpler, EPA Quality Assurance Lead for Speciation and IMPROVE
Ambient Air Monitoring Group, AQAD (C304-06)

Jeff Lantz, Quality Assurance Lead for Monitoring Field Operations
Office of Radiation and Indoor Air, Las Vegas

TO: Addressees

The following is a digested version of the 2005 Audit Summaries of the Speciation Trends and IMPROVE networks. This version reflects further comments from UC Davis and auditors on the findings of the IMPROVE audits. The most significant change reflects the adverse findings criteria for temperature Attached is an Excel spreadsheet that compiles and summarizes the findings, from which this synopsis is drawn. We will post the audits on AMTIC for 30 days to allow the Programs to respond to the findings (look for 2005 Speciation/ IMPROVE Audit Reports). After 30 days, the audits will be posted for public viewing.

Speciation Trends and State Supplemental Sites

A total of 16 sites and 19 samplers were audited this past year by EPA-certified auditors. **Eleven out of 19 samplers passed all parameter and audit criteria.** Sites that exhibited sampler performance that fell outside of acceptance criteria for measurement quality objectives were as follows:

Significant findings:

At two sites, a total of seven channels exhibited leaks of 0.10 L/min or greater (site with four channels that initially failed corrected the problems on date of the audit):
One siting issue where samplers located < 1 meter apart and one site failed with a safety issue.

Minor findings or parameters that initially failed but were corrected by the operator on site:

- Two sites marginally failed a leak test and were corrected on date of audit.
- One barometric pressure > 10 mm from standard.
- Three clock times > 5 minutes from standard.
- Two sites with Tamb > 2 degrees from the standard.
- One site with Tfil > 2 degrees from the standard.
- Two sites with flow rates outside of 10 percent acceptance criteria, but these were corrected on site, re-audited, and passed.

Next steps:

It was noted that many of the sites were utilized for special studies underway for assessing network and programmatic questions. The goal for the future will be to audit more sites and a higher percentage of routine network sites. A newly initiated, mandatory parameter check report by network operators will be used to identify sites that are good candidates for audits. A program of certifying EPA and State/Local/Tribal auditors and audit procedures will also be initiated in order to incorporate more audit activities into the annual report. This will include a revised training class that reflects updated QAPP provisions, new audit report forms that will lead to fully electronic reporting and implementation of past and latest experiential knowledge. We will be implementing a new online auditor recertification course to save on time and travel expenses for auditors and trainers.

In a period where budgets are shrinking and under severe scrutiny, it is necessary that samplers operating outside of the acceptable parameter ranges will be corrected at the time of the audit. (Mechanical failure that must be corrected by factory service would be the exception.) This procedure will be mandatory and therefore ensure that the sampler is operating within design when the auditor departs.

IMPROVE and IMPROVE Protocol Sites

A total of 34 sites and 35 samplers were audited this past year by EPA-certified auditors. **Five sites out of the 35 passed all parameters and audit criteria.** Sampler performance that fell outside of acceptance criteria for IMPROVE measurement quality objectives were as follows:

Significant findings:

- Two clocks were >±60 minutes from reference standard.
- Two leaks where the **Vacuum** reading < 33mm Hg.
- Two sites where calibration plug was missing, thus creating zero flow through filter (**for 12 weeks**).
- Five flowrates with difference > ±10 percent of theoretical or the flow rate was questionable due to differences between calibration values and the expected design flow.

- Three sites with temperature reading > ±10 degrees Celsius from reference standard.
- Four flow rates calculated from the vacuum reading were > ±10 percent of flow measured by standard.
- One reference standard failed during audit of sampler flow rates.
- Three sites reported operator errors with respect to handling filter cassettes or reading the instrument temperature sensor.
- One had flies that were observed in one exposed filter cassette (fly eggs on the filter).
- One site was improperly positioned with respect to an adjacent shelter which caused water to drip onto one module box and then it infiltrated the sample train and sharp cut cyclone. (This has been corrected as of the writing of this memorandum.)

Minor Findings:

- Ten clocks were >±5 minutes from reference standard but less than 60 minutes from standard.
- Sixteen sites with a temperature reading > ±2 degrees Celsius from reference standard but less than 10 degrees.
- One equipment installation-Channel D down tube severely misaligned.

Next Steps:

Several important issues have been identified as action items for the coming year.

1. We have discovered that, in some cases, the calibration may be valid but that the flow rate calculated from the magnehelic and/or vacuum gauge readings may not coincide with the expected design flow rate.

- In most cases, a satisfactory correlation existed between the flow measured by the reference standard and the flow calculated from calibration factors and readings of the magnehelic and vacuum gauges; however,
- There are some situations where a site's reference standard flow rate reading did not correlate well with the expected design flow rate. The following example illustrates.

At the Bronx, NY, site the Module C reference flow rate was 26.0 L/m.
The flow rate based on the magnehelic and vacuum readings: 25.1 and 25.4 L/m.
Current audit test [(26.0-25.1)/26.0] x 100% = 3.4 %; which passes.
Expected design flow rate under the condition during that audit: ~ 22.8 L/m.
Suggested additional test: [(22.8-26.1)/22.8] x 100% = 14.5%

- We conclude that another test in the IMPROVE Audit should compare the reference standard flow rate to the design flow rate for that site and channel.

2. The procedure for implementing follow-up actions to parameters or conditions that do not meet acceptance criteria should be revised. It appeared that in several cases of sampler issues, the operator was capable and able to correct the issue. We believe that for many of the problems this will often be the case. A desirable outcome would be for the site to be functioning within all acceptance criteria prior to the conclusion of an audit. We would like to work with folks from IMPROVE to resolve, at the time of the audit, all the problems that are uncovered, so that follow-up audits, which are time consuming and expensive, may be avoided. IMPROVE has decided to include more training to encourage site operators to check and reset clocks as needed on every filter exchange date.

3. A communication tool will be implemented between IMPROVE and the EPA/State/Tribal Audit Team to provide initial audit feedback and preliminary findings. A website is being sought to host a warehouse of currently needed information. The warehouse would contain a list of currently certified auditors, the compendium of magnehelic and vacuum gauge coefficients, site operator names and contact information, and directions to the sites. From this website, certified auditors will be able to retrieve, independently of effort by IMPROVE or EPA, the information needed to audit each site. As the corps of auditors and the certification program solidifies, we will implement the construction of a contemplated audit schedule each year and post it on the website, but room will be made to make a few unscheduled site audits, if necessary, or the opportunity arises due to audits scheduled for speciation trends or (or evolving NCORE) monitoring sites. Not withstanding all auditors will be required to provide IMPROVE (both UC Davis and the Operator) with at least a 2-weeks notice of the audit date, contingent on the availability of the operator.

4. We have a goal to audit 40-45 IMPROVE and IMPROVE Protocol sites each year. We will realize this goal this year by certifying approximately 10 additional EPA and State/Local/Tribal auditors and recertifying the current corps of 11. The training program will be combined with the speciation trends network auditor training. The training class will be updated yearly to reflect the findings and experience of the auditor corps from the previous year's audits. We will also amend QAPP and SOPs, and revise audit report forms that will lead to fully electronic reporting to reflect the lessoned learned. We will develop and initiate (if time permits in 2006, but by the middle of 2007) a new online auditor recertification course to save on time and travel expenses for auditors and trainers.

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2005 Summary of Audits

Audits are "Pass (P)" or "Adverse finding (A)" based on audit criteria. "(A)P" means an initial adverse finding which passed after recalibration. "Parameter of concern" box identifies the specific issue for which the audit identified and adverse finding for the site or sampler, e.g., Safety, Siting Criteria (Site), Clock, Module # Leak Check (#A-Leak), Flow rate (Flow), Filter Temperature (Tfil); Calibration Plug Missing (Plug); Magnehelic reading (Mag); Vacuum reading (Vac). Reference Standard Failure (Ref). Operator Procedural Error (OpEr) RED denotes failure issue; BLUE denotes passed parameter(s) of interest. Parameter passes but value in question, e.g. flow set point [(P)?]. Equidment installation issue (Equip). Filter Contamination (Filt C)

Monitoring Site Location	General pass/ Adverse finding	Date	Parameters with Adverse findings	AQS Site ID No.	Monitoring Instrument	FLOW RATES												Comments and other findings
						Ch1 (A)	Ch2 (B)	Ch 3 (C)	Ch 4 (D)	5	6	7	8	9	10	11	12	
Atlanta	A	7/19/2005	Leak	130890002	Andersen 401 RAAS	P	P	P	P									Initial leak check failed channels 1-4;
Atlanta post Correction	A	7/19/2005	Leak	130890002	Andersen 401 RAAS	P	P	P	P									
Atlanta Follow-up Action	(A)P	7/26/2005	Leak	130890002		NA	NA	NA	NA									Hoses and HEPA replaced on 7/26 and reported by Mactech; Region has not verified
Bakersfield (Primary)	P	5/17/2005		060290014	Metone													
Bakersfield (collo.)	A	5/17/2005	Leak	060290014	Metone	P	P	P										Sampler displayed leak of 0.1 L/m, but criteria is 0.08 l/m and it was not clear if the sampler really failed
Bakersfield (collo.)	A		Tamb			P	P	P										Tamb off by 2.5°C
Beacon Hill,WA	P	3/28/2005	None	530330080	URG 400	P												All paramters for both samplers passed a this site
	P		None		URG 450	P												
Deer Park (Primary)	P	6/7/2005	None		URG 400	P												
	(A)P		Tfil		URG 450	P												Initial Tfil failure but passed after recalibration
Deer Park Colloc.	P	6/7/2005	None	482011039	URG 400	P												
	(A)P		BP	482011039	URG 450	P												Initial Barometric Pressure failed but passed after recalibration
Fresno, CA	P	5/20/2005	None	060190008	Metone SASS	P	P	P										
Phoenix	(A)P	5/24/2005	Clock	040139997	Metone SASS	P	P	P										Initially failed Clock check but passed after recalibration
Rubbidoux	(A)P	5/18/2005	Tamb, leak, flow	060658001	Metone SASS	P	P	P										Site passed but earlier audit (April 05) failed several paramters and routine operator was not there to correct issues
Amazon Park, Eugene, OR	A	6/23/2005	Siting	SLAM Site	Metone SASS	P	P	P										Sampler was located less than 1 meter from a High volume PM-10 sampler; should be between 2-4 meters
NW Nazarene College, I	P	9/20/2005	None	160270004	Metone SASS	P	P	P										
Tacoma, WA Unit A	P	3/31/2005	None	SPMS	Metone SASS	P	P	P										
Tacoma, WA Unit B	P	3/31/2005	None	SPMS	Metone SASS	P	P	P										
Commerce City - 7101 E	P	12/20/2005	None	080010006	Metone SASS	P	P	P										
New Brunswick, NJ	P	8/12/2005	Safety	034023006	Metone SASS	P	P	P										Platform for single sampler need repair or Replacement
New Brunswick, NJ	P	8/12/2005		034023007	Metone SASS	P	P	P										
Essex MD	P	11/29/2005	None	240053001	Metone SASS	P	P	P										
Hu-Beltsville, MD	A	11/19/2005	Clock	240330030	Andersen RAAS 401	P	P	P										Clock Failed with -6 min reading; no indication of reset; previous 05 audits indicated clock variability
Bismarck Residential	P	8/30/2005	None	380150003	Metone SASS	P	P	P										Sampler Passed all Parameters
National Park (TRNP - NU)	p	8/31/2005	Leak	380530002	Metone SASS	P	P	P										Sampler Failed the Leak test on all three channels and passed all other parameters.