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

January 1 through December 31, 2006

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

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Prepared by
RTI
P.O. Box 12194
3040 Cornwallis Road
Research Triangle Park, NC 27709

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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 135 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, 2006, 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 not audited by EPA personnel during 2006. However, RTI received performance audit samples as part of a multi-lab study conducted by EPA's Montgomery lab.

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. In 2005, a problem was noted with a manufacturer's lot of Teflon filters. In response, the Standard Operating Procedure (SOP) for gravimetric analysis was updated to increase the frequency of re-weighing in the laboratory in order to quickly recognize and correct future filter debris problems. Data quality for gravimetric mass results was generally found to be satisfactory during 2006.

Minimal problems with laboratory operations and filter media were reported by the Ion and OC/EC laboratories during 2006. Interlaboratory performance comparison results were satisfactory.

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. Interlaboratory performance comparison results performed by EPA's NAREL were satisfactory.

Operations in the Sampling Handling and Archiving Laboratory (SHAL) proceeded normally during 2006. A small number of samples were missed due to late return of coolers from the field sites. Shipping containers ("coolers") were changed during 2006 to a lighter type of container, thus reducing shipping expenses. No significant effect on shipping temperature was noted after the change in containers. 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 2006 (Sections 4.0 and 5.0). However, the calculation for uncertainties reported by XRF (trace elements) was reevaluated during 2006, and all the XRF data in AQS beginning with July 2003 was reloaded with revised uncertainty values. 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. RTI attempts to answer such questions promptly, and works with the agencies to determine the most appropriate data flags for particular situations.

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 for most chemical species.

Quality Issues

No Corrective Action Requests (CARs) were issued during 2006. However, 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
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, in consultation with recognized experts has identified correct and consistent methods for calculation for uncertainty.	Uncertainties were recalculated and reloaded into AQS for data beginning July 2003.
none	All	Investigate sampler-dependent background levels	RTI is examining historical data for evidence of systematic contamination with different sampler types (ongoing).	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 189-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 135 other sites from State and local agencies that are 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, 2006. 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, 2006. 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 (> 95%) is demonstrated overall. Some individual sites may have lower completeness; typically due to site maintenance or shipping problems.

- Spatial coverage - Selection of sites for STN is outside of RTI's control. The STN sites are generally selected to evaluate population-based health effects and tend to be in populated areas. Because of this, the STN has relatively little coverage of rural sites 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. The appropriate OC correction factor may differ among the four different STN sampler types.

- Intermittent media contamination issues - Equipment and media contamination issues arise from time to time, and may cause the occasional outliers reported by the monitoring agencies, in which the STN mass differs from the mass reported by a nearby FRM sampler. RTI makes an effort to flag data, retroactively if necessary, to invalidate or mark as suspicious any events reported by the monitoring agencies.

- 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. This work by RTI has resulted in a "whitepaper" that was delivered to EPA during 2006.[1]
    - Realism of total uncertainty estimates based on statistics from sites with side-by-side collocation of samplers -- Collocation results in the 2005 report and extended in the present 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]

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[1] Gutknecht, W. F., J. B. Flanagan, and A. McWilliams, “Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties.” RTI/0208858/TO2/04D, August 4, 2006.

[2] Flanagan, James B., R.K.M. Jayanty, E. Edward Rickman, Jr., and Max R. Peterson, "PM2.5 Speciation Trends Network: Evaluation of Whole-system Uncertainties Using Data from Sites with Collocated Samplers," *Journal of the Air and Waste Management Association*, 2006, 56, 492-499.

2.2 Summary of Data Completeness

Data completeness network-wide exceeded 95% for 2006. 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 2006. 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 sampler 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.

No formal corrective action requests (CARs) were opened during 2006. Two formal corrective action requests (CARs) were addressed during 2005, both of which were resolved and did not lead to further issues during 2006. See the 2005 report for further details.

- CAR 008 – 4/17/05 - Whatman Teflon Filter – Manufacturer’s Debris Problem.
- CAR 009 – 3/17/05 - Shipping error for 12/11/04 Paducah and Perkinstown coolers, and related data corrections.

2.3.1 Gravimetric Mass

No significant quality issues were identified in the Gravimetric Laboratory in 2006. However, the laboratory continued to monitor mass balance data and to perform enhanced inspection of the Teflon filters purchased for use in the program as a result of the problem identified in 2005 and documented under CAR 008. This inspection is performed in RTI’s Optical Microscopy Laboratory on randomly selected filters. A technician examines filters under enhanced lighting using a stereomicroscope at magnifications of 10x to 45x. No pervasive problem with extraneous contaminating debris was identified in 2006 in either this enhanced inspection or in routine visual inspection in the chamber.

2.3.2 Elemental Analysis

See section 3.4.1.1 for a description of quality issues and maintenance from Chester Labnet, which performs some of the elemental analysis by XRF for the STN contract.

In July 2006, RTI XRF 3 was approved by the EPA to analyze samples for the PM2.5 Speciation Program. Also, during 2006, XRF 1 required a new computer, vacuum pump, and instrument communication hardware, which did not necessitate instrument re-calibration. XRF 2 required a new high voltage power supply, pump, tray motor. The ThermoNoran XRF software was upgraded to be the same as XRF 1, and therefore this instrument required calibration. XRF 3 did not have any issues during 2006.

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

2.3.3 Ion Analysis

There were no corrective actions taken during this reporting period.

2.3.4 OC/EC Analysis

During a review of all 2006 quality control samples (instrument blanks, calibration samples, and duplicate and replicate analyses), it was discovered that the daily calibration check run on the T analyzer on October 29, 2006, had a calculated flame ionization detector (FID) response factor that was 89.42% of the average FID response factor for the last full 3-point calibration run on October 24, 2006. The acceptance range for the calculated FID response factor for the daily calibration check is 90% to 110% of the average FID response factor for the 3-point calibration. The 19 quartz filters analyzed on the T analyzer on October 29, 2006, were reanalyzed on February 9, 2007, and the results were reported to RTI’s SPIMS and the QA Officer for evaluation and possible future action. The repeat analysis data were the same, within the uncertainties of the measurements, as the data previously reported; therefore, revision to the existing data in AQS was not necessary.

2.3.5 Sample Handling and Archiving Laboratory (SHAL)

There were no major quality issues in the SHAL laboratory during 2006. No Corrective Actions were undertaken. However, a major change in SHAL procedures that may have impacted data, was a change in shipping containers used to transport filters to the field sites and back to RTI. In an effort to reduce the weight of the shipping containers, at the request of EPA, the packaging was changed from a rigid plastic cooler to an insulated fiberboard box. Preliminary indications are that the new packaging material did not change the receipt temperature distribution relative to the previous packaging material. See Section 3.5 for more discussion.

2.3.6 Data Processing

There were no corrective actions taken during this reporting period. However, uncertainties for trace elements by XRF were recalculated and reloaded to AQS. The rationale for recomputing the uncertainty estimates is contained in a whitepaper prepared by RTI during 2006.[1]

2.4 Other Quality Issues

Aside from the specific issues discussed above, 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:

- **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, however we understand that cyclones on the MetOne samplers are being replaced, for reasons related to this issue.

3.0 Laboratory Quality Control Summaries

3.1 Gravimetric Laboratory

The Gravimetric Laboratory's two weigh chambers were used to tare 21,042 Teflon filters between January 1 and December 31, 2006. During the same time period, the laboratory performed final ("post-sampling") weighings of 20,074 Teflon filters. 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 a contingency buffer factored into the number of filters tared each week to ensure an adequate number of tared filters for sampling and extra filters for use in-house blanks contamination monitoring. Filter weighing totals given in this report are those recorded by the laboratory's database application.

3.1.1 Quality Issues and Corrective Actions

No significant quality issues were identified in the Gravimetric Laboratory in 2006. However, the laboratory continued to monitor mass balance data and to perform enhanced inspection of the Teflon filters purchased for use in the program. This inspection is performed in RTI's Optical Microscopy Laboratory on randomly selected filters. A technician examines filters under enhanced lighting using a stereomicroscope at magnifications of 10x to 45x. No pervasive problem with extraneous contaminating debris was identified in 2006 in either this enhanced inspection or in routine visual inspection in the chamber.

3.1.2 Description of QC Checks Applied

Internal QC checks applied in the Gravimetric 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 Gravimetric 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 at purchase. Verified by the laboratory in conjunction with 2006 internal balance audit performed by RTI Quality Systems Program. Verification at North Carolina Department of Agriculture and Consumer Services (NCDA&CS) Standards Laboratory scheduled for 2007.]	<u>Chamber 1</u> 100-mg S/N 14056 11/20/06 Verification: 99.994 mg ± 0.00067 Laboratory Tolerance Interval: 99.991-99.997 mg	Average = 99.992 mg Std Dev = 0.0037 for 2292 weighings	Laboratory average falls within tolerance interval.
		200-mg S/N 14059 11/20/06 Verification: 199.995 mg ± 0.00045 Laboratory Tolerance Interval: 199.992-199.998 mg	Average = 199.990 mg Std Dev = 0.0067 for 2267 weighings	Laboratory average falls within tolerance interval.
		<u>Chamber 2</u> 100-mg S/N RTI01 11/20/06 Verification: 99.990 mg ± 0.00063 Laboratory Tolerance Interval: 99.987-99.993 mg	Average = 99.990 mg Std Dev = 0.0008 for 2205 weighings	Laboratory average falls within tolerance interval.
		100-mg S/N 58092 11/20/06 Verification: 100.000 mg ± 0.00050 Laboratory Tolerance Interval: 99.997-100.003 mg	Average = 100.001 mg Std Dev = 0.0010 for 1680 weighings	Laboratory average falls within tolerance interval.
		200-mg S/N 18659 11/20/06 Verification: 199.980 mg ± 0.00053 Laboratory Tolerance Interval: 199.977-199.983 mg	Mean = 199.980 mg Std Dev = 0.0011 for 2199 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
Working standard reference weights (cont'd)	Verified value ± 3 µg	200-mg S/N 58099 11/20/06 Verification: 200.002 mg ± 0.00047 Laboratory Tolerance Interval: 199.999-200.005 mg	Mean = 200.003 mg Std Dev = 0.0017 for 1681 weighings	Laboratory average falls within tolerance interval.
Balance Calibrations	Auto (internal) calibration daily	Daily	N/A	
	External calibration annually or as needed	All balances inspected and externally calibrated by Mettler Toledo on August 17, 2006, using NIST-traceable weight	N/A	Next inspection and external calibration scheduled for August 2007
RH/T Data Logger Calibrations	Annually	Purchased new data loggers with initial calibration by Dickson Calibration Services August 2006.	N/A	Next calibration or recertification scheduled for August 2007.
Laboratory (Filter) Blanks	Initial weight ± 15 µg	2574 total replicate weighings of 378 individual laboratory blanks	Average difference between final and initial weight = 3 µg Std Dev = 4.9 Min wt change = 0 µg Max wt change = 27 µg	27 total replicate weighings of 3 individual laboratory blank filters (1% of the replicate weighings; 0.8% of the individual laboratory blanks) exceeded the 15 µg criterion. Outliers were split between upper and lower outliers, indicating that RTI's steps to address negative outliers due to filter contamination issues in 2005 by increasing vigilance in filter inspection was successful.

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Replicates	Initial weight ± 15 µg	22,342 individual filters were weighed as pre-sampling (tared) replicates	Average = 0.5 µg	113 replicate weighings (0.5% of the weighings) exceeded the 15 µg criterion on the first pass. Outliers were reweighed in order to confirm a mass value with two weights within 5 µg of each other. These third weighings brought the number of individual outlier filters down to 11 filters (0.05% of the filters weighed).
		10,286 individual filters were weighed as post-sampling replicates	Average = 1.0 µg	189 replicate weighings (1.8% of the weighings) exceeded the 15 µg criterion on the first pass. Outliers were reweighed in order to confirm value with two weights within 5 µg of each other. . These third weighings brought the number of individual outlier filters down to 4 filters (0.045% of the filters weighed.)

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Lot Blanks (Lot Stability Filters) [All lot stability tests performed on 12 filters – 2 filters randomly selected from each of 6 randomly selected boxes]	24-hour weight change < ± 5 µg	Whatman Lot 5318001	24 hours = -25µg 48 hours = +1 µg 72 hours = -1 µg 96 hours = +1 µg	High 24-hour weight loss may be due to loss of extraneous debris from new filters with handling. Subsequent weight losses fall within required range.
		Whatman Lot 5124003	24 hours = -8 µg 48 hours = -1µg 72 hours = -2 µg 96 hours = +1 µg	Weight changes fall within required range.
		Whatman Lot 6102010 – (Rec'd lot four times and ran a lot stability test each time)	24 hours = -1 µg 48 hours = 0 µg 72 hours = 1 µg 96 hours = -1 µg	Weight changes fall within required range.
			24 hours = -2 µg 48 hours = +2 µg 72 hours = -2 µg 96 hours = +1 µg	Weight changes fall within required range.
			24 hours = -2 µg 48 hours = +1 µg 72 hours = +1 µg 96 hours = 0 µg	Weight changes fall within required range.
			24 hours = 0 µg 48 hours = 0 µg 72 hours = +1 µg 96 hours = -1 µg	Weight changes fall within required range.
		Whatman Lot 6177004 – (Rec'd lot three times and ran a lot stability test each time)	24 hours = -2 µg 48 hours = 0 µg 72 hours = +1 µg 96 hours = -1 µg	Weight changes fall within required range.
			24 hours = 0 µg 48 hours = -1 µg 72 hours = 0 µg 96 hours = 0 µg	Weight changes fall within required range.
			24 hours = -3 µg 48 hours = 0 µg 72 hours = -1 µg 96 hours = -1 µg	Weight changes fall within required range.
		Whatman Lot 6236013	24 hours = +1 µg 48 hours = -2 µg 72 hours = +1 µg 96 hours = +1 µg	Weight changes fall within required range.

Table 3-1. (Continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Balance Audits	Annually	Audits of all balances performed by RTI Quality Systems Program personnel on November 9, 2006, using Class S-1 NIST-traceable weights	N/A	Audit 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. A small number of outliers were noted. Laboratory blank outliers did not show a tendency to fall either below the lower warning limit or above the upper warning limit, indicating that there is no systematic issue of debris on Teflon. In the case of outlier replicates, Gravimetric Laboratory analysts reweighed outliers to validate weights. The balance test weights used in the laboratory are working standards and may fall out of tolerance due to wear (scratches or nicks during handling) or environmental contamination. The laboratory's primary standards are maintained by RTI's Quality Systems personnel and are used to audit the microbalances and verify the working mass standards annually.

3.1.4 Assessment of Between-instrument Comparability

In 2006, the Gravimetric Laboratory compiled inter-instrument (intra-laboratory) data to assess both instrumental and human factors of analytical comparability. Replicate averages for eight analysts since 2004 fell within a 2 µg range, much less than the calculated laboratory MDL of 7.2 µg per filter. Replicate averages for four microbalances fell within a 0.5 µg range. The slightly higher inter-analyst variation indicates that the human component contributes more to laboratory uncertainty than do the microbalances. There is slightly more variability in post-sampling replicate weighings than in pre-sampling replicate weighings, suggesting that sample composition affects laboratory uncertainty in the mass measurement. Random variability from collocated samplers is significantly larger than the laboratory replicate variability, indicating that field operations contribute the majority of the PM2.5 mass measurement uncertainty.

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 for the Gravimetric Laboratory.

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

Type of Evaluation	Date	Administered By	Significant Findings/Comments
Internal Audit	February 23, 2006	RTI FRM and STN Project QA Officers	No significant deficiency findings were reported by the QAOs. The auditors loaned a black light to the laboratory for periodic use in the chamber to direct staff cleaning efforts.
Proficiency Evaluation (PE)	May 2006	EPA National Air and Radiation Environmental Laboratory (NAREL)	EPA NAREL conducted an experimental inter-comparison of speciation laboratories. Analyses were performed on real-world samples collected in Montgomery, AL. Results of the PE study are pending and have not yet been publicly released. RTI's Gravimetric Laboratory performance in the study was good.
External Audit	August 22, 2006	Louisiana Department of Environmental Quality (LDEQ) Environmental Laboratory Accreditation Program (LELAP) Audit Team	This audit was performed for the continuation of RTI's LELAP accreditation in support of RTI's FRM contract with LDEQ. No significant deficiency findings were reported. Minor findings issued by the audit team were, in general, specific to the State's accreditation requirements. One finding issued by LDEQ noted that, "The quality system documents do not include procedures and requirements for additional training in order to keep personnel current with new procedures, changes in existing procedures, and/or equipment changes." Although the Gravimetric Laboratory has had no major procedural or equipment changes that would necessitate extensive re-training of existing staff, periodic "refresher training" or QA reminders would be helpful in maintaining laboratory data quality. The Laboratory Supervisor is developing a plan for refresher training.
External Audit/Readiness Review	August 29, 2006	New York State Department of Environmental Conservation (NYSDEC) Audit Team	This site visit was a readiness review to evaluate RTI's laboratories for continuation of FRM program support and air toxics trace metals analysis. No deficiency findings were reported by the assessors.
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 22,411 cation analyses (sodium, potassium, and ammonium); 23,555 anion analyses (nitrate and sulfate) analyses performed on the STN program during the period January 1 through December 31, 2006.

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 are performed by personnel from RTI's Environmental Industrial Chemistry Department (EICD). Four of our six ion chromatographic systems 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 $\geq$ 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 percent 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 percent for concentrations that equal or exceed 100 times the minimum detectable limit (MDL), ±10 percent for concentrations at 10 times the MDL, and ±100 percent for concentrations at the MDL. MDL's for each instrument and analyte are listed in **Table 3-5**. The observed value for any ion being measured must be within 10 percent of the known value for the QA/QC samples, and ion recoveries for the spiked samples must be within 90 to 110 percent 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	Cnt	Conc. μg/mL	Avg % Rec *	SD	Min	Max
Nitrate	QA-CPI_LOW	410	0.6	99.1%	1.1%	0.566	0.615
	QA-CPI_MED-HI	323	3.0	102.0%	0.9%	2.990	3.193
	RTI-QC-HIGH	346	6.0	102.4%	1.2%	5.844	6.350
	RTI-QC-LOW	633	0.6	98.8%	1.4%	0.536	0.626
	RTI-QC-MED	814	1.5	99.2%	2.4%	0.589	1.571
Sulfate	QA-CPI_LOW	410	1.2	99.3%	1.1%	1.126	1.229
	QA-CPI_MED-HI	323	6.0	102.5%	1.2%	5.796	6.382
	RTI-QC-HIGH	346	12.0	102.6%	1.3%	11.676	12.690
	RTI-QC-LOW	633	1.2	99.7%	1.1%	1.075	1.259
	RTI-QC-MED	814	3.0	100.9%	2.4%	1.133	3.191
Sodium	GFS 0.4 PPM QA	658	0.4	102.9%	2.5%	0.385	0.456
	GFS 4.0 PPM QA	641	4.0	100.7%	1.0%	3.822	4.177
	RTI 2.0 PPM QC Reg Std	461	2.0	100.8%	1.2%	1.930	2.103
	RTI 5.0 PPM QC	393	5.0	101.1%	1.0%	4.829	5.211
Ammonium	GFS 0.4 PPM QA	658	0.4	100.6%	2.9%	0.326	0.430
	GFS 4.0 PPM QA	641	4.0	101.1%	1.3%	3.679	4.225
	RTI 2.0 PPM QC Reg Std	461	2.0	100.3%	1.5%	1.820	2.080
	RTI 5.0 PPM QC	393	5.0	101.6%	1.7%	4.560	5.371
Potassium	GFS 0.4 PPM QA	658	0.4	100.5%	2.0%	0.341	0.427
	GFS 4.0 PPM QA	641	4.0	99.4%	1.2%	3.807	4.142
	RTI 2.0 PPM QC Reg Std	461	2.0	100.9%	1.0%	1.956	2.074
	RTI 5.0 PPM QC	393	5.0	100.8%	1.1%	4.849	5.220

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

Average recoveries for the QC samples ranged from 98.8% to 102.6% for the year. Average recoveries for the QA samples ranged from 99.1% to 102.9% for the year.

Table 3-8 shows percent recovery for all analyte spikes for the year. Average recoveries for the spikes ranged from 100.4% to 101.4%.

Table 3-8. Average Percent Recovery for Spikes

Analyte	Avg Recovery *	StDev	Count	Min	Max
Nitrate	100.4%	1.6%	762	94.9%	110.1%
Sulfate	100.6%	1.3%	762	95.7%	105.0%
Sodium	101.4%	2.3%	729	94.9%	119.6%
Ammonium	101.1%	2.2%	729	91.1%	114.6%
Potassium	100.9%	2.3%	729	94.4%	118.1%

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

Table 3-9 presents filter blank (N BLANK) and reagent blank values for all analytes over the 12 month period.

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

Analyte	Type	Count	Avg	StDev	Min	Max
Nitrate	N QC	35	0.007	0.011	0.000	0.029
	REAG	712	0.000	0.003	0.000	0.019
Sulfate	N QC	35	0.004	0.007	0.000	0.026
	REAG	712	0.002	0.007	0.000	0.037
Sodium	N QC	37	-0.001	0.009	-0.020	0.028
	REAG	490	0.000	0.004	-0.023	0.036
Ammonium	N QC	37	0.000	0.000	0.000	0.000
	REAG	490	0.000	0.001	0.000	0.014
Potassium	N QC	37	0.000	0.000	0.000	0.000
	REAG	490	0.000	0.000	0.000	0.000

* 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.

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 2 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 2 QC and 3 QA samples. Similarly, Cation instruments ran at least 2 QC and 2 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	Cnt	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	159	-0.014	0.126	-1.563	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	159	-0.041	0.251	-3.124	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	484	0.004	0.031	-0.156	0.129
Ammonium	GFS 0.4 PPM QA	0.4	701	0.009	0.012	-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	484	0.003	0.049	-0.209	0.283
Potassium	GFS 0.4 PPM QA	0.4	701	0.003	0.007	-0.016	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	484	0.012	0.042	-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 25mL 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 experimental inter-comparison of speciation laboratories conducted by the U.S. Environmental Protection Agency (EPA) audit team from the National Air and Radiation Environmental Laboratory (NAREL) in May 2006, (a copy of the NAREL report is located at the AMTIC web site:

http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/Multilab-Speciation-PE-2006.pdf

PE samples analyzed as a part of the audit were in good agreement with the NAREL expected values. No technical systems audit was performed by EPA during 2006. 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 17,267 quartz filter samples by the STN method during the period January 1, 2006, through December 31, 2006, and reported the results of those analyses to RTI's Speciation Program Information Management System (SPIMS). Four Sunset Laboratory Carbon Aerosol Analyzers (designated by the letters R, S, T, and F) were used for STN analyses. The F analyzer, which had been used for other OC/EC analysis projects since March 11, 2005, was returned to the STN program on October 17, 2006; while the remaining three analyzers were used for STN throughout 2006.

3.3.1 Quality Issues and Corrective Actions

During a review of all 2006 quality control samples (instrument blanks, calibration samples, and duplicate and replicate analyses), it was discovered that the daily calibration check run on the T analyzer on October 29, 2006, had a calculated flame ionization detector (FID) response factor that was 89.42% of the average FID response factor for the last full 3-point calibration run on October 24, 2006. The acceptance range for the calculated FID response factor for the daily calibration check is 90% to 110% of the average FID response factor for the

3-point calibration. The 19 quartz filters analyzed on the T analyzer on October 29, 2006, were reanalyzed on February 9, 2007, and the results were reported to RTI's SPIMS and the QA Officer for evaluation and possible action. The repeat analysis data were the same, within the uncertainties of the measurements, as the data previously reported; therefore, revision to the existing data in AQS was not necessary.

3.3.2 Description of QC Checks Applied

Quality control (QC) checks, acceptance criteria, and corrective actions 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 SPIMS are included in the table. The Sample Handling and Archiving Laboratory (SHAL) or the QA Officer may have assigned additional flags to the quartz filter samples based on field data or additional data validation checks.

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.

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 3-11. 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.)	47
Total Number of Analyses Flagged by OC/EC Analysts		48
Total Number of OC/EC Analyses Reported		17,267
Percent of OC/EC Analyses Flagged by Analysts		0.278%

Table 3-13. OC/EC Instrument Blank Statistics

Blank Statistic	OC/EC Analyzer			
	Retrofit	Second	Third	Fourth
Number of Instrument Blanks	337	328	339	51
Mean Response (µg C/cm^2)	0.013	0.036	0.024	0.016
Standard Deviation	0.012	0.043	0.027	0.028
Minimum Response (µg C/cm^2)	0.000	0.000	0.001	-0.075
Maximum Response (µg C/cm^2)	0.111	0.287	0.262	0.106

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).

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			52	50	52	10
Number of Full Calibrations Failing Any Criterion			0	0	0	0
Slope (counts/μgC), forced through origin (0,0)		Average	8,789	5,433	6,471	10,207
		Minimum	8,056	4,917	6,099	9,783
		Maximum	9,299	5,867	6,784	10,766
Correlation Coefficient (R^2) (Criterion: ≥0.998)		Average	0.9996	0.9997	0.9997	0.9997
		Minimum	0.9983	0.9982	0.9980	0.9991
		Maximum	1.0000	1.0000	1.0000	0.9999
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	100.04%	99.89%	100.00%	100.51%
		Minimum	99.09%	97.56%	97.35%	99.60%
		Maximum	101.23%	102.17%	103.01%	102.48%
	Mid Cal	Average	100.01%	100.06%	100.02%	100.20%
		Minimum	98.65%	98.58%	98.21%	98.83%
		Maximum	100.91%	102.07%	101.60%	101.43%
	High Cal	Average	99.94%	100.04%	99.98%	99.29%
		Minimum	98.59%	97.84%	97.55%	96.60%
		Maximum	101.35%	101.68%	101.05%	100.23%
Recovery: Mass of Carbon Measured as a Percent of Mass of Carbon Spiked (Criterion: 93% to 107%)	Low Cal	Average	102.01%	102.38%	102.18%	101.60%
		Minimum	98.27%	98.15%	97.63%	98.78%
		Maximum	105.00%	104.96%	104.95%	103.05%
	Mid Cal	Average	99.79%	99.05%	99.50%	99.61%
		Minimum	96.39%	96.05%	97.20%	98.19%
		Maximum	101.71%	102.13%	102.43%	101.41%
	High Cal	Average	98.19%	98.57%	98.46%	98.78%
		Minimum	96.15%	96.07%	96.30%	97.51%
		Maximum	102.91%	102.96%	103.69%	100.18%
	All 3 Cals	Average	100.00%	100.00%	100.05%	100.00%
		Minimum	99.98%	99.99%	99.97%	99.99%
		Maximum	100.02%	100.01%	102.46%	100.02%
FID Response Factor as a Percent of Average FID Response Factor for 3-Point Cal (Criterion: 90% to 110%)	Low Cal	Average	102.06%	102.27%	102.13%	102.12%
		Minimum	98.42%	97.89%	96.15%	98.49%
		Maximum	105.35%	105.94%	105.16%	104.71%
	Mid Cal	Average	101.72%	100.52%	101.12%	101.78%
		Minimum	95.60%	93.90%	96.33%	98.51%
		Maximum	105.80%	105.50%	106.20%	103.90%
	High Cal	Average	98.14%	98.62%	98.39%	98.07%
		Minimum	95.89%	95.94%	95.98%	95.79%
		Maximum	102.44%	102.24%	103.03%	99.68%

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

Variable/Statistic		R	S	T	F
Number of Cal Checks Passing All Criteria		207	203	208	38
Number of Cal Checks Failing Any Criterion		0	0	1[†]	0
Internal Standard (IS) Area as a Percent of Average IS Area for 3-Point Cal (Criterion: 90% to 110%)	Average	99.97%	99.11%	100.29%	100.44%
	Minimum	92.83%	90.90%	90.66%	95.01%
	Maximum	104.00%	106.29%	106.30%	105.38%
Recovery: Mass of Carbon Measured as a Percent of Mass of Carbon Spiked (Criterion: 95% to 105%)	Average	100.44%	100.13%	100.11%	100.54%
	Minimum	95.15%	95.12%	95.04%	95.32%
	Maximum	104.78%	104.99%	104.94%	104.90%
FID Response Factor as a Percent of Average Response Factor for 3-Point Cal (Criterion: 90% to 110%)	Average	100.39%	99.23%	100.48%	100.95%
	Minimum	90.40%	91.69%	89.42%[†]	93.04%
	Maximum	107.05%	106.71%	107.05%	107.16%

[†] See Corrective Action in Section 3.3.1.

A calibration check is acceptable only if it meets all three criteria. One calibration check on one analyzer failed the FID response factor criterion on October 29, 2006, and the failure was not detected until a later review of all quality control data. The corrective action is described in detail in Section 3.3.1.

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 10th filter. A total of 2,101 duplicate STN analyses were run under the laboratory support contract in 2006. OC/EC analysis results for 47 of those duplicates failed the applicable duplicate criterion and were flagged as coming from a filter with a non-uniform deposit.

Table 3-16. Duplicate OC/EC Analysis Statistics

Variable/Statistic		Analyzer			
		R	**S**	**T**	**F**
Total Number of Duplicate Analyses		660	661	683	97
Number of Analyses Flagged as Failing Duplicate Criteria		14	15	17	1
Percentage of Duplicate Analyses Failing Duplicate Criteria		2.12%	2.27%	2.49%	1.03%
OC Sample/Dup Plot	Slope	1.005	0.968	0.980	1.004
	Intercept	0.018	0.105	0.038	0.003
	R^2	0.983	0.984	0.984	0.997
EC Sample/Dup Plot	Slope	0.995	0.988	0.983	0.985
	Intercept	0.006	0.012	0.006	0.019
	R^2	0.989	0.990	0.989	0.979
TC Sample/Dup Plot	Slope	1.003	0.973	0.985	1.010
	Intercept	0.025	0.109	0.029	-0.009
	R^2	0.985	0.988	0.987	0.998
Pk1C Sample/Dup Plot	Slope	1.000	0.960	1.002	0.967
	Intercept	0.003	0.027	0.003	0.008
	R^2	0.993	0.989	0.994	0.992
Pk2C Sample/Dup Plot	Slope	0.985	0.939	0.913	1.024
	Intercept	0.027	0.066	0.069	-0.004
	R^2	0.944	0.949	0.952	0.990
Pk3C Sample/Dup Plot	Slope	0.997	0.952	0.939	1.010
	Intercept	0.016	0.037	0.036	-0.004
	R^2	0.945	0.975	0.958	0.993
Pk4C Sample/Dup Plot	Slope	1.000	0.991	1.005	1.003
	Intercept	0.005	0.008	-0.007	0.008
	R^2	0.991	0.988	0.989	0.983
PyrolC Sample/Dup Plot	Slope	0.930	0.005†	0.016†	1.082
	Intercept	0.000	0.002†	0.001†	-0.002
	R^2	0.893	0.042†	0.144†	0.998

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. It appears that the presence of oxygen does not significantly change the OC:EC mass ratio. However, 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 2-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.[3]

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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 2-4 oven replacements each year.

[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*. Presented at the A&WMA Symposium on Air Quality Measurement Methods and Technology, May 9-11, 2006, Durham, NC.

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 organic carbon to exceed the reaction capacity of the trace amounts of contaminating oxygen, then at least some PyrolC 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.

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

Fraction	"Best Fit" Uncertainty ($\mu gC/cm^2$)
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)

Table 3-18 gives target MDL’s for all reported carbon fractions. MDL values for the five OC Peaks were taken from the absolute uncertainties in Table OCEC7. This same approach was used to determine reasonable target MDL’s 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 (μgC/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 System Audits

RTI's chemical speciation laboratories were not audited in 2006.

3.3.6.2 Performance Evaluations

RTI's OC/EC Laboratory was one of four laboratories participating in the May 2006 EPA/NAREL interlaboratory comparison study. As in previous years, RTI's data compared very favorably with EPA/NAREL's data.

3.3.6.3 Training

One new analyst was hired and trained during the reporting period. He has a BS in chemistry and biology. 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 November 2006.

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 five XRF instruments (3-RTI and 2-Chester) to analyze a total of 17,753 filters for 48 elements during the period January 1 through December 31, 2006.

3.4.1 Chester LabNet X-Ray Fluorescence

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:

- 4/20/06 - replaced detector and recalibrated; Cd recovery on QS standard jumped from a mean of 95% to 105%. Ca recovery of NIST SRM 1832 was on the order of 110 %. This is consistent with XRF-772 observations, as well as outside laboratory recoveries (Oregon DEQ, DRI)
- 11/6/06 – changed count-rate to 12 microseconds and performed energy calibration

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

- 1/17/06 – replaced ADC board and performed energy calibration
- 8/15/06 – increased voltage for condition 4 and recalibrated
- 11/11/06 – decommissioned XRF-771 until sample volume requires its use

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 2.06 and 4.54% for the 770 and between 1.87 and 6.17% for the 771. The Cd slope for 770 resulted in a jump from an approximate average percent recovery of 95% to an average of 105% after replacing the detector as described in 3.4.1.1.

Table 3-20A. Summary of Chester XRF 770 Laboratory QC Precision Data 1/1/2006 through 12/31/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	180	91.4	110.0	103.2	2.77	2.69	-3.44
Ti	180	92.4	107.9	99.4	2.31	2.32	.500
Fe	180	95.0	105.1	99.6	2.05	2.06	.500
Cd	180	90.7	112.2	99.7	4.53	4.54	9.87
Se	180	91.2	109.2	100.3	2.66	2.65	1.22
Pb	180	91.0	111.9	99.8	2.80	2.81	1.16

Table 3-20B. Summary of Chester XRF 771 Laboratory QC Precision Data 1/1/2006 through 12/31/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	278	87.5	104.3	96.5	2.24	2.32	.0015
Ti	278	91.4	108.5	99.7	3.12	3.13	.0251
Fe	278	95.2	105.2	110.7	1.89	1.87	.0155
Cd	277	85.0	121.3	103.7	6.39	6.17	.0600
Se	278	83.5	111.5	94.7	5.02	5.30	.0304
Pb	278	83.5	110.8	94.9	4.79	5.04	.0241

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 89.9 and 112.9% for the 770 and between 91.6 and 111.4% for the 771. The high Ca slope for instrument 770 can be explained as follows. After the detector was replaced in April, the resulting recalibration showed that SRM1832 Ca values laid at least 10% above the smoothly varying curve derived from atomic number (Z) versus log sensitivity. Analysis of NIST Partlicle Standard SRM2783 yielded a Ca recovery of 95%, which seemed to validate the Ca calibration factor derived from the calibration curve. 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 -- 1/1/2006 through 12/31/2006

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	89.9	107.0	99.5	3.86	3.88	-3.73
Si	90.4	109.4	99.3	3.75	3.78	-.620
Si	92.6	111.5	100.4	3.37	3.36	4.20
S	92.9	106.4	99.0	2.73	2.76	.650
K	91.9	104.8	99.6	3.43	3.44	-2.62
Ca	94.8	112.9	105.2	5.56	5.29	13.44
Ti	92.8	104.2	99.0	2.42	2.44	-.640
V	91.3	105.8	98.6	4.07	4.13	1.18
Mn	95.2	107.1	100.3	3.06	3.05	5.49
Fe	96.6	104.8	100.7	1.87	1.86	.720
Cu	92.1	106.6	100.0	3.35	3.36	-4.97
Zn	90.7	105.9	100.4	2.61	2.60	.210
Pb	95.8	108.5	102.6	2.52	2.46	-.690

Table 3-21B. Recovery Determined from Analysis of NIST SRMs 1832, 1833 and 2708 for Chester XRF 771 -- 1/1/2006 through 12/31/2006

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	91.6	107.1	98.2	4.78	4.87	18.9
Si	96.6	107.1	99.2	2.08	2.09	-1.08
Si	93.8	104.0	96.9	2.05	2.11	-1.99
S	92.8	111.4	99.6	3.88	3.9	-1.28
K	92.7	109.7	100.7	3.79	3.77	2.42
Ca	98.6	108.7	101.8	2.36	2.31	3.69
Ti	92.7	101.6	96.1	1.76	1.83	-1.89
V	94.8	102.9	98.0	1.77	1.81	-1.39
Mn	94.7	104.1	97.6	1.99	2.04	1.82
Fe	98	104.2	100.4	1.33	1.32	1.63
Cu	99.4	107.5	103.9	1.67	1.60	2.58
Zn	97.2	104.3	100.2	1.49	1.49	1.98
Pb	98.3	110.7	104.0	3.56	3.43	6.45

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 0.9977 to 0.9998, and the correlation coefficients for the 771 range from 0.9942 to 0.9995, 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	84	.9996	0.13	Si	51	.9988	-1.95
S	84	.9993	-0.11	S	66	.9981	-5.68
K	84	.9977	-0.13	K	48	.9942	-6.63
Ca	83	.9993	-0.37	Ca	37	.9974	-4.97
Fe	84	.9995	-0.79	Fe	66	.9995	0.27
Zn	60	.9998	-0.81	Zn	55	.9950	-0.16

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.

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 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, except in July 2006, RTI XRF 3 was approved by the EPA to analyze samples for the PM2.5 Speciation Program. Also, during 2006, XRF 1 required a new computer, vacuum pump, and instrument communication hardware, which did not necessitate instrument re-calibration. XRF 2 required a new high voltage power supply, pump, tray motor. The ThermoNoran XRF software was upgraded to be the same as XRF 1, and therefore this instrument required calibration. XRF 3 did not have any issues during 2006.

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 3-23.**

Table 3-23. 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. Comparison of the element's replicate values gives the measure of reproducibility or precision. The data used to monitor precision are presented in **Tables 3-24 through 3-29**. The percent coefficient of variation (%CV) for the average of all data for each of the six elements ranged between 0.18 and 0.61% for XRF 1, between 0.19 and 0.93% for XRF 2, and between 0.016 and 0.051% for XRF 3. Note that for XRF 3 titanium was moved to another condition on 10/5/06 and thus the change in the Micromatter QC values for XRF 3.

Table 3-24. Summary of RTI XRF 1 Laboratory QC Precision Data, µg/cm^2 1/1/2006 through 4/1/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	290	4.32	4.56	4.50	0.02	0.52	-0.4
Ti	290	5.66	5.78	5.74	0.02	0.29	0.2
Fe	290	6.46	6.56	6.51	0.01	0.22	-0.2
Cd	290	5.58	5.73	5.64	0.02	0.42	0.3
Se	290	3.98	4.07	4.02	0.02	0.39	-0.1
Pb	290	9.99	10.1	10.0	0.02	0.21	0.2

Table 3-25. Summary of RTI XRF 1 Laboratory QC Precision Data, µg/cm^2 7/13/2006 through 12/31/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	436	5.18	5.24	5.24	0.02	0.39	-0.3
Ti	436	5.30	5.46	5.41	0.02	0.29	0.1
Fe	436	6.37	6.47	6.41	0.01	0.18	0.0
Cd	436	5.46	5.59	5.51	0.02	0.32	-0.2
Se	436	3.94	4.21	4.01	0.02	0.61	-0.5
Pb	436	10.1	10.2	10.1	0.03	0.30	-0.1

Table 3-26. Summary of RTI XRF 2 Laboratory QC Precision Data, µg/cm^2 1/1/2006 through 9/5/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	821	5.17	5.24	5.20	0.01	0.20	-0.1
Ti	821	6.70	6.80	6.75	0.02	0.32	-0.1
Fe	821	6.49	7.06	7.01	0.04	0.51	-0.2
Cd	821	5.62	6.08	6.02	0.03	0.54	-0.3
Se	821	4.03	4.26	4.21	0.02	0.44	-0.6
Pb	821	11.1	11.9	11.3	0.11	0.93	0.6

Table 3-27. Summary of RTI XRF 2 Laboratory QC Precision Data, µg/cm^2 12/7/2006 through 12/31/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	43	5.18	5.23	5.20	0.01	0.19	-0.2
Ti	43	6.71	6.79	6.75	0.02	0.27	0.2
Fe	43	6.98	7.03	7.00	0.01	0.20	0.2
Cd	43	5.96	6.06	6.01	0.02	0.34	-0.3
Se	43	3.97	4.05	4.00	0.02	0.47	0.3
Pb	43	9.31	9.38	9.34	0.02	0.19	-0.1

Table 3-28. Summary of RTI XRF 3 Laboratory QC Precision Data, µg/cm^2 7/10/2006 through 10/4/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	248	9.60	9.69	9.65	0.02	0.19	-0.01
Ti	248	9.52	9.70	9.64	0.02	0.24	0.1
Fe	248	10.4	10.5	10.4	0.03	0.25	-0.2
Cd	248	5.58	5.70	5.65	0.02	0.39	-0.1
Se	248	3.97	4.05	4.01	0.02	0.45	-0.1
Pb	248	10.5	10.7	10.6	0.03	0.30	-0.03

Table 3-29. Summary of RTI XRF 3 Laboratory QC Precision Data, µg/cm^2 10/5/2006 through 12/31/2006

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	250	9.60	9.68	9.64	0.02	0.16	-0.1
Ti	250	8.96	9.06	9.01	0.01	0.16	-0.1
Fe	250	10.3	10.5	10.4	0.03	0.29	-0.2
Cd	250	5.58	5.72	5.64	0.02	0.37	-0.1
Se	250	3.95	4.04	4.00	0.02	0.51	-0.4
Pb	250	10.5	10.7	10.6	0.03	0.31	0.1

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 3-30 through 3-32** 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 95 and 105% for XRF 1 and XRF 2, and between 94 and 105% for XRF 3. 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. Also, XRF 3 was approved into the Speciation Program July 2006. The slope percent per year calculation for XRF 3 is calculated using the approval date from the EPA for the Speciation Program (July 10, 2006).

Table 3-30. Recovery Determined from Analysis of NIST SRMs 1832 and 2783 for RTI XRF 1 -- 1/1/2006 through 12/31/2006

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	95.1	98.6	96.5	0.16	1.11	-1.3
Si*	95.4	98.5	97.5	0.29	0.85	0.2
Si**	96.3	102	98.3	0.08	1.45	-0.6
Co	96.4	101	98.6	0.01	1.12	-1.0
K	99.2	104	102	0.01	1.27	-2.8
Ca	95.0	97.9	97.4	0.15	0.78	0.2
Ti	97.3	103	101	0.002	1.64	-1.2
V	95.2	103	97.2	0.11	2.30	3.7
Mn	97.3	105	101	0.09	1.96	1.1
Fe	99.7	104	101	0.04	1.33	-5.2
Cu	95.4	104	97.6	0.06	2.47	3.9
Zn	95.1	105	100	0.004	2.37	5.4
Pb	97.5	105	102	0.001	2.24	-0.4

* - SRM 1832
** - SRM 2783

Table 3-31. Recovery Determined from Analysis of NIST SRMs 1832 and 2783 for RTI XRF 2 -- 1/1/2006 through 12/31/2006

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	99.3	102	101	0.10	0.65	0.3
Si*	98.1	100	99.3	0.13	0.37	0.1
Si**	95.2	101	97.9	0.12	2.06	-1.2
Co	97.1	100	99.3	0.01	0.67	0.1
K	95.3	102	98.2	0.01	1.97	0.0
Ca	94.7	96.2	95.4	0.06	0.32	0.6
Ti	94.6	103	98.1	0.004	2.65	-1.6
V	102	104	103	0.02	0.46	0.4
Mn	98.0	99.2	98.7	0.02	0.35	0.5
Fe	100	105	103	0.04	1.57	-1.1
Cu	94.7	98.0	96.5	0.02	0.66	0.4
Zn	98.3	105	102	0.004	2.05	3.2
Pb	94.6	104	101	0.001	2.55	2.3

* - SRM 1832
** - SRM 2783

Table 3-32. Recovery Determined from Analysis of NIST SRMs 1832 and 2783 for RTI XRF 3 -- 7/1/2006 through 12/31/2006

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	97.2	99.1	98.3	0.07	0.45	-0.1
Si*	99.2	100	99.6	0.07	0.20	0.0
Si**	95.9	100	98.3	0.09	1.60	3.0
Co	99.0	102	101	0.01	0.65	-0.6
K	94.5	99.1	96.2	0.01	1.36	2.0
Ca	101	101	101	0.03	0.15	-0.3
Ti	96.6	104	101	0.003	2.21	0.8
V	96.9	98.9	98.3	0.02	0.49	-0.2
Mn	102	104	103	0.02	0.46	-0.6
Fe	103	105	104	0.03	0.92	1.6
Cu	95.2	97.0	96.3	0.01	0.43	-0.3
Zn	98.3	105	102	0.004	2.16	-2.2
Pb	94.6	104	101	0.001	2.94	0.5

* - SRM 1832
** - SRM 2783

Replicates were analyzed at a frequency of 5% of the number of filters analyzed in the RTI XRF Laboratory. Six elements were selected for comparison through regression analysis. **Table 3-33** shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients for XRF 1 range from 0.9979 to 0.9999, the correlation coefficients for XRF 2 range from 0.9992 to 1.0000, and the correlation coefficients for XRF 3 range from 0.9998 to 1.0000 indicating acceptable replication with all three instruments. Also, for the six elements, the average RPD on XRF 1 was less than 2%, the average RPD for the six elements on XRF 2 was less than 3%, and the average RPD for the six elements on XRF 3 was less than 1%.

Table 3-33. Replicates for XRF 1, XRF 2, and XRF 3

XRF 1				XRF 2			
Element	**n**	**Correlation Coefficient**	**Average RPD, %**	**Element**	**n**	**Correlation Coefficient**	**Average RPD,%**
Si	313	0.9980	0.53	Si	335	0.9994	-2.62
S	313	0.9999	-1.36	S	335	0.9999	0.27
K	313	0.9999	-0.21	K	335	0.9998	-0.38
Ca	313	0.9997	0.48	Ca	335	0.9995	0.23
Fe	313	0.9999	-1.28	Fe	335	1.0000	0.38
Zn	313	0.9979	0.18	Zn	335	0.9992	-0.63

XRF 3			
Element	**n**	**Correlation Coefficient**	**Average RPD,%**
Si	269	1.0000	0.35
S	269	1.0000	0.96
K	269	0.9999	-0.97
Ca	269	1.0000	0.34
Fe	269	1.0000	-0.87
Zn	269	0.9998	0.48

3.4.2.4 Assessment of Between-Instrument Comparability

Overview of Round-Robin Samples Run During 2006

In addition to passing internal QC samples as described in the sections above, the RTI and Chester Laboratories participated 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 3-34** summarizes the number of round robin filters analyzed during 2006.

Table 3-34. Numbers of Round Robin Filter Analyses Performed During 2006

Laboratory	Instrument	Filters
Chester Labnet	Kevex 770	36
Chester Labnet	Kevex 771	32
RTI	XRF 1	27
RTI	XRF 2	27
RTI	XRF 3	36
Total filters common to all instruments:		27

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 11 elements that were found in sufficient quantity on a majority of the filters. A total of 27 round robin filters were analyzed by all the STN instruments during 2006. Many additional filters were analyzed by one or more of the instruments, but only 27 had been analyzed by all five instruments exclusively during 2006. The statistics to follow in this section are restricted to latter filters.

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 3-35 and 3-36** show linear regression results when the data for the 27 filters are regressed vs. the median for the five instruments for

Table 3-35. Regression Results for 11 Elements - RTI XRF Instruments

Element	RTI #1				RTI #2			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	27	0.9988	1.0281	-0.1311	27	0.9993	0.9895	0.0344
S	27	0.9999	1.0035	0.0742	27	0.9998	1.0085	0.0076
K	27	0.9985	1.0036	0.0240	27	0.9984	1.0280	0.0006
Ca	27	0.9993	1.0422	-0.0156	27	0.9993	0.9945	-0.0186
Mn	27	0.9757	1.0312	-0.0207	27	0.9341	0.9159	-0.0197
Fe	27	0.9982	1.0812	-0.0018	27	0.9993	1.0083	0.0014
Ni	27	0.9949	1.0773	0.0071	27	0.9919	0.9150	-0.0047
Cu	27	0.9933	1.0179	-0.0004	27	0.9960	1.0340	-0.0106
Zn	27	0.9987	0.9833	0.0134	27	0.9992	0.9850	0.0011
Se	27	0.9630	0.9173	-0.0020	27	0.9196	0.9487	0.0066
Pb	27	0.9820	1.0460	0.0001	27	0.9723	1.1600	-0.0051

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

Element	RTI #3			
	n	Correlation Coefficient	Slope	Intercept
Si	27	0.9988	1.0106	-0.1308
S	27	0.9998	1.0079	0.1061
K	27	0.9984	0.9854	0.0044
Ca	27	0.9986	1.0326	-0.0459
Mn	27	0.9894	1.0050	0.0102
Fe	27	0.9978	1.0201	-0.0576
Ni	27	0.9869	0.9471	0.0057
Cu	27	0.9976	1.0452	0.0046
Zn	27	0.9981	1.0291	0.0125
Se	27	0.9403	1.0325	0.0018
Pb	27	0.9817	1.0559	-0.0125

Table 3-36. Regression Results for 11 Elements - Chester XRF Instruments

Element	Chester 770				Chester 771			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	27	0.9982	1.0075	0.1611	27	0.9982	0.9661	0.0951
S	27	0.9989	0.9029	0.3535	27	0.9960	0.9295	-0.5321
K	27	0.9980	0.9838	0.0164	27	0.9913	0.9836	-0.0688
Ca	27	0.9991	1.0083	0.0141	27	0.9989	0.9856	-0.0252
Mn	27	0.9869	0.9828	0.0051	27	0.9732	0.9476	0.0134
Fe	27	0.9973	0.9655	0.0089	27	0.9972	0.9112	0.1082
Ni	27	0.9885	0.9732	0.0022	27	0.9937	1.0127	-0.0032
Cu	27	0.9979	0.9653	0.0011	27	0.9985	0.9787	0.0044
Zn	27	0.9986	1.0174	-0.0190	27	0.9963	1.0566	-0.0307
Se	27	0.8563	0.8351	0.0017	27	0.6739	1.0128	0.0203
Pb	27	0.9503	0.9127	-0.0020	27	0.8129	0.6829	0.0517

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

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, Se, and Pb), 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).

Uncertainty Reporting

The effort to harmonize uncertainties within all the XRF analyzers used under the STN program was completed during 2006. Background discussion of the problem is found in the 2005 Data Summary Report.[2] Whitepapers written by RTI on this topic have been posted on the AMTIC web site: http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/xrfuncertov.pdf and http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/xrfdet.pdf.

This investigation showed that the uncertainty values reported by Chester's and RTI's instruments differed significantly, especially for some of the light elements. Analysis of the differences revealed the following principal issues which were corrected in the revised data:

- Chester's software overestimated the attenuation uncertainty for light elements (Na - Ca). This overestimate was up to 12% of the total concentration. In the case of sulfur, this is an overestimate of a factor of 3x or 4x in the uncertainty. Attenuation uncertainties for these elements were recalculated to be consistent with the revised RTI attenuation uncertainties (next bullet).

- 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. An attenuation correction factor was added to the RTI-ThermoNoran uncertainty factors to make them consistent with the corrected values from the Chester instruments (previous bullet).

- 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. A term of 5% for calibration error was included in the revised calculation for samples analyzed on the ThermoNoran instruments.

After approval of the revised approach by EPA, RTI proceeded to upload revised uncertainty values for all the XRF data posted to AQS after July 2003. Revision of this data was accomplished under another EPA Contract, 68-D-02-065. This revision of data ensures that the XRF uncertainty data generated by Chester and RTI are sufficiently comparable to be combined for applications such as source apportionment modeling.

3.4.2.5 Determination of Uncertainties and MDLs

MDLs are determined periodically by obtaining data from the analysis of ten laboratory blanks. The MDLs are calculated as three times the average counting uncertainty for each

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[2] 2005 Annual Data Summary Report. RTI/08858/004QAS, July 19, 2006.

element. This is equivalent to a "3-sigma" MDL – data users should be careful to know what multiple has been used in establishing the MDL when comparing values reported by different environmental laboratories, since other labs may use 1-sigma, 2-sigma, or 2.5-sigma. The calculated MDLs based on XRF uncertainty from XRF 1, XRF 2, and XRF 3 are presented in **Table 3-37**. Network-wide MDLs are summarized in Appendix A.

Table 3-37. MDL Values for XRF 1, XRF 2 and XRF 3, µg/filter

Element	XRF 1	XRF 2	XRF 3	Element	XRF 1	XRF 2	XRF 3
Na	0.70686	0.30942	0.38944	**Sr**	0.01762	0.12677	0.01737
Mg	0.16314	0.12288	0.10857	**Y**	0.02014	0.01746	0.02034
Al	0.44173	0.36274	0.26419	**Zr**	0.11938	0.11033	0.03154
Si	0.21961	0.18395	0.12511	**Nb**	0.02831	0.03372	0.03915
P	0.15882	0.14208	0.10826	**Mo**	0.03180	0.03203	0.04138
S	0.09972	0.09309	0.06779	**Ag**	0.08484	0.09665	0.11569
Cl	0.26123	0.07282	0.05078	**Cd**	0.07617	0.10498	0.12881
K	0.05587	0.11748	0.03549	**In**	0.12077	0.12667	0.18385
Ca	0.06434	0.07252	0.04302	**Sn**	0.19315	0.17164	0.24989
Sc	0.06299	0.06028	0.06149	**Sb**	0.28429	0.22947	0.29401
Ti	0.05191	0.04944	0.04940	**Cs**	0.13537	0.12365	0.17933
V	0.03579	0.03665	0.02511	**Ba**	0.09210	0.29516	0.08119
Cr	0.02276	0.02440	0.01729	**La**	0.09138	0.25768	0.06338
Mn	0.01717	0.01904	0.01475	**Ce**	0.08539	0.26451	0.05700
Fe	0.01589	0.01594	0.01060	**Sm**	0.05238	0.16512	0.04225
Co	0.01392	0.01221	0.00909	**Eu**	0.05186	0.05258	0.03958
Ni	0.01327	0.00986	0.00983	**Tb**	0.04588	0.10135	0.03269
Cu	0.01926	0.01275	0.01123	**Hf**	0.18893	0.05947	0.03342
Zn	0.01665	0.01365	0.01376	**Ta**	0.12726	0.05545	0.08631
Ga	0.01827	0.01281	0.02257	**W**	0.03539	0.04066	0.06258
As	0.00903	0.01336	0.01581	**Ir**	0.04371	0.04048	0.06934
Se	0.01172	0.01320	0.01702	**Au**	0.03200	0.03447	0.04146
Br	0.01049	0.01192	0.01537	**Hg**	0.05579	0.05725	0.07324
Rb	0.01261	0.01363	0.01415	**Pb**	0.02216	0.02420	0.04118

Counting uncertainties for each analytical result are automatically calculated by the ThermoNoran software, except when the concentration value is zero; the software cannot calculate an uncertainty. Total uncertainty is calculated using a combination of the counting uncertainty, attenuation uncertainty (if applicable), laboratory calibration uncertainty (5%) and field sampling and handling uncertainty (5%). The ThermoNoran software returns a zero counting uncertainty whenever the calculated mass for an element is calculated to be zero or negative. To obtain accounting 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 May 2006, RTI XRF laboratory received six 47mm Teflon filters from NAREL. These six samples were prepared by NAREL and were part of a PE study. No onsite audit was performed by NAREL during 2006; however, PE samples were received and analyzed. RTI results were in excellent agreement with EPA/NAREL's data.

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 2006. No Corrective Actions were undertaken. However, a major change in SHAL procedures that may have impacted data, was a change in shipping containers used to transport filters to the field sites and back to RTI. In an effort to reduce the weight of the shipping containers, at the request of EPA, the packaging was changed from a rigid plastic cooler to an insulated fiberboard box. This change was initiated near the beginning of calendar year 2006 and was fully implemented by April. A second change in packaging was also implemented. This change replaced the fiberboard box with a corrugated plastic box and was intended to increase the durability of the packaging. The plastic boxes were phased in during the second half of 2006. A photograph of the new packaging is shown in **Figure 3-1**.

Figure 3-1. Corrugated plastic box now used for shipping.

The change in packaging did not have a noticeable effect on the temperature of the incoming filters at RTI. A comparison of the received filter temperatures for the years 2000 through 2006 is shown in **Figure 3-2**. There is no noticeable difference in the data for 2006 using the new packaging as compared to earlier years and there should be no effect on the data.

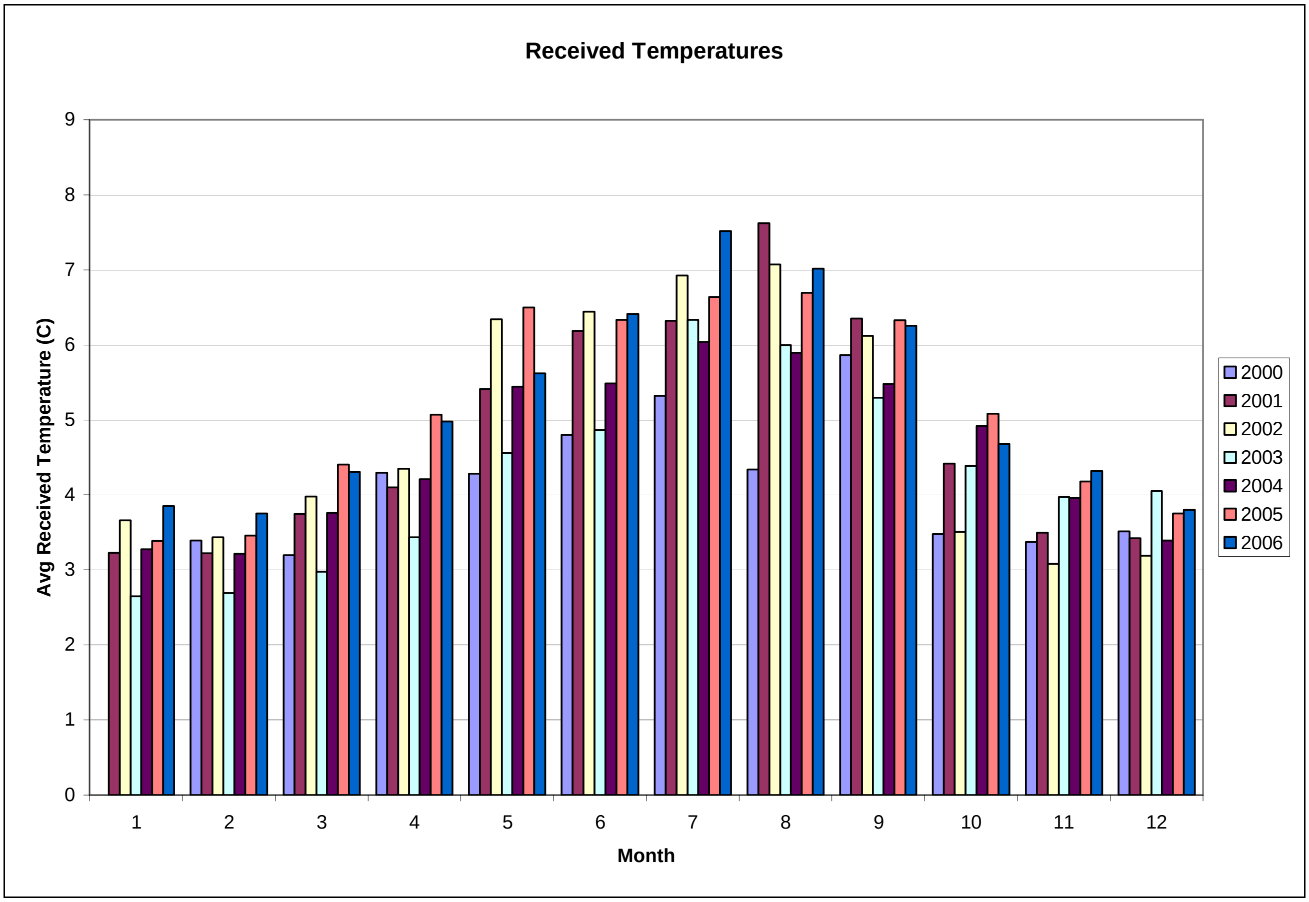


Figure 3-2. Comparison of the received filter temperatures for the years 2000 through 2006.

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 six 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, 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 2006, the SHAL shipped out and received back over 17,800 packages 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 2006 are summarized in **Figures 3-3A and 3-3B**. Sites may also deviate from the sampling schedule and run filters on a date other than the scheduled date. **Table 3-38** lists those sites with less than 95% of their filters run on the intended sampling date.

Figure 3-3A. Late Coolers Due to Delays at Sites (1/01/06 - 12/31/06)

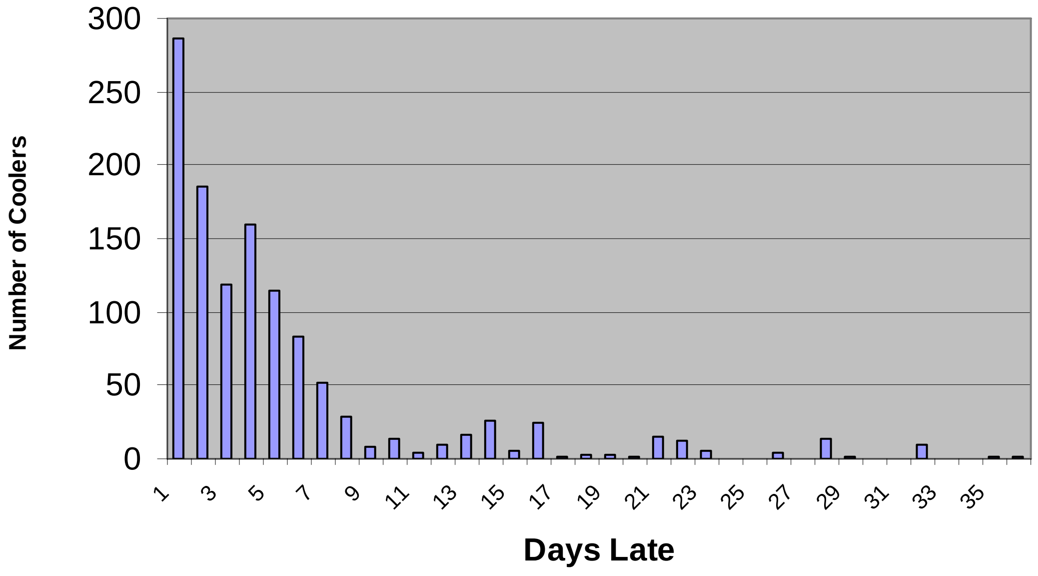


Figure 3-3B. Late Coolers Due to Delays in Shipping (1/01/06 - 12/31/06)

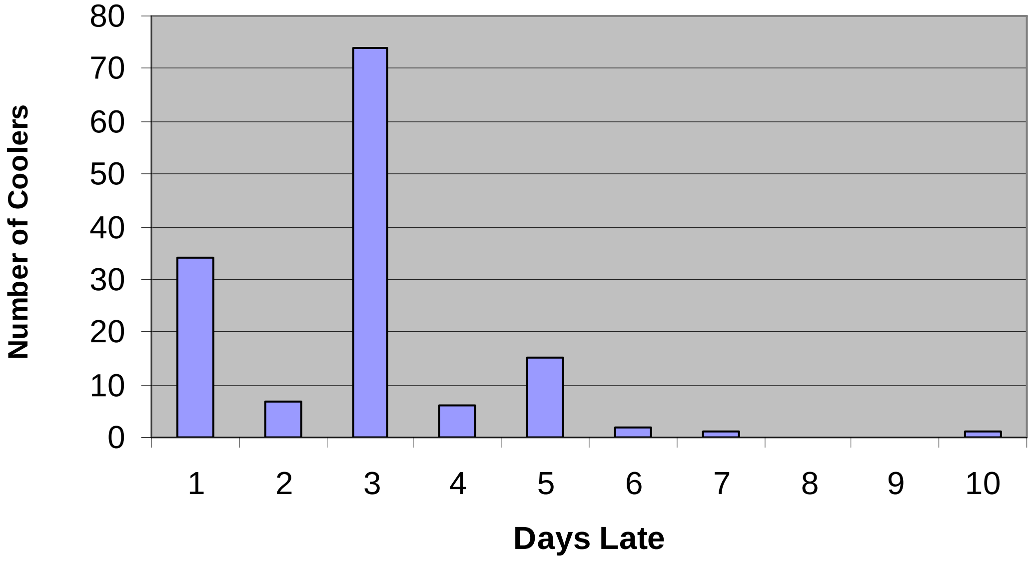


Table 3-38. Sites with Less than 95% of Filters Run on Intended Sampling Date

Airs Code	POC	Location	Events	On Date	Pct.
080410011	5	RBD	61	44	72
080010006	5	Commerce City	101	76	75
471570047	5	Guthrie	56	47	84
040137003	5	St Johns	57	49	86
471570024	5	Alabama (TN)	60	52	87
261630001	5	Allen Park	120	107	89
040130019	5	West Phoenix	10	9	90
060371103	5	North Los Angeles	61	56	92
130890002	5	South DeKalb	13	12	92
220150008	5	Shreveport Airport	47	44	94
360050083	6	NY Botanical Garden	16	15	94

3.5.5 Support Activities for Site Operators and Data Users

SHAL staff provided support to site operators and data users throughout 2006. A summary of email and phone communications with site operators and data users is presented in Table 3-39.

Table 3-39. Summary of SHAL Communications With Site Operators and Data Users

Description	Number of Communications
Site will send cooler late	190
Site needs schedule	26
Site did not receive cooler	45
Change of operator/site information	49
Sampler problems/questions	26
Field Blank/Trip Blank ran as routine sample	0
Request change of ship date from RTI	42
Site is stopping	20
Miscellaneous QA Issues	104
Data questions/reporting	150
Site did not send cooler	7
Other	248

3.5.6 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.

- 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 2006 is shown in **Table 3-40**.

Table 3-40. Review of SHAL Technician Processing Filter Modules

Module Type	Number Observed	Findings	Findings Reviewed with Technician
MET ONE	64	2	2
Andersen	1	0	0
URG	1	0	0
R&P Spec	11	1	1

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, Local and Tribal agencies which utilize the RTI/EPA contract. The laboratory follows these protocols which are kept on file in the laboratory:

- 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 continues to coordinate the Denuder Refurbishment Laboratory. She reviews the denuder refurbishment SOPs to ensure procedures are clearly stated and all processes are 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 Andersen-style and URG-style denuders. These were repaired by URG, Inc. and the costs were charged to the sampling site if breakage occurred there. Otherwise, the denuder laboratory account covered the cost of repairs.

Personnel have been cross-trained to be able to process denuders. 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 3-42 lists the type of denuders refurbished and the number of refurbishments completed in 2005.

Table 3-41. Denuder Refurbishments
January 1 through December 31, 2006

Denuder Type	Total Refurbished
R&P	1,138
MetOne	601
URG	23
Andersen	44

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 no longer done. 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. Now the newly-coated denuder surfaces are examined by holding the denuder up to a light and sighting along the interior to determine the coating is thoroughly applied and the annuli are not blocked.

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 interior of the occasional broken Andersen or URG denuder has also shown that the MgO coating is complete and uniformly applied.

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:

- Revised calculation of XRF (trace element) uncertainties to provide better agreement between different laboratories and instruments.
- Reposted AQS records for any XRF events that had their uncertainties modified by the revised calculation.
- A new parameter code (88502) was used for PM 2.5 gravimetric mass in the STN program. EPA made this change to make it easier for users to separate FRM and equivalent sampler measurements (using code 88101) from other samplers, such as the STN samplers.

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 Batch		Sample Date		Field Samples	Blanks		Total
Batch	**Date**	**Earliest**	**Latest**		**Field**	**Trip**	
72	1/13/2006	11/15/2005	12/15/2005	1308	74	81	1463
73	2/13/2006	12/15/2005	1/11/2006	1091	6	142	1239
74	3/14/2006	1/11/2006	2/16/2006	1523	273	81	1879
75	4/13/2006	2/16/2006	3/18/2006	1259	203	25	1487
76	5/12/2006	3/12/2006	4/14/2006	1171	72	224	1467
77	6/13/2006	4/11/2006	5/11/2006	1307	94	54	1455
78	7/11/2006	5/9/2006	6/14/2006	1351	162	38	1551
79	8/10/2006	6/15/2006	7/13/2006	1162	181	134	1477
80	9/13/2006	7/10/2006	8/16/2006	1264	68	33	1365
81	10/11/2006	8/13/2006	9/14/2006	1262	186	78	1526
82	11/14/2006	5/18/2006	10/17/2006	1139	68	216	1423
83	12/13/2006	10/13/2006	11/14/2006	1262	181	59	1502

Table 4-2. Records Posted To Web Site

Report		Sample Date		Field Samples	Blanks		Total
Batch	**Date**	**Earliest**	**Latest**		**Field**	**Trip**	
72	1/13/2006	11/15/2005	12/15/2005	149516	8348	9396	167260
73	2/13/2006	12/15/2005	1/11/2006	124328	687	16261	141276
74	3/14/2006	1/11/2006	2/16/2006	172768	30948	9303	213245
75	4/13/2006	2/16/2006	3/18/2006	142936	23089	2872	168897
76	5/12/2006	3/12/2006	4/14/2006	133064	8145	25515	166724
77	6/13/2006	4/11/2006	5/11/2006	148377	10630	6245	165252
78	7/11/2006	5/9/2006	6/14/2006	153324	18425	4341	176090
79	8/10/2006	6/15/2006	7/13/2006	132048	20614	15259	167921
80	9/13/2006	7/10/2006	8/16/2006	143312	7655	3834	154801
81	10/11/2006	8/13/2006	9/14/2006	142918	21116	9004	173038
82	11/14/2006	5/18/2006	10/17/2006	128964	7655	24675	161294
83	12/13/2006	10/13/2006	11/14/2006	142649	20571	6926	170146
84	1/11/2007	11/13/2006	12/13/2006	122686	7855	6103	136644

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

Batch	Field Samples	Blanks		Total
		Field	Trip	
71	1369	280	29	1,678
72	1327	73	80	1,480
73	1104	6	139	1,249
74	1553	272	81	1,906
75	1260	199	25	1,484
76	1180	72	221	1,473
77	1315	94	53	1,462
78	1371	163	38	1,572
79	1186	182	134	1,502
80	1292	68	33	1,393
81	1289	186	78	1,553
82	1148	68	217	1,433

Table 4-4. Records Posted to AQS

Batch	Field Samples	Blanks		Total
		Field	Trip	
71	91,934	18,790	1,949	112,673
72	89,041	4,905	5,378	99,324
73	74,074	404	9,345	83,823
74	104,191	18,252	5,441	127,884
75	83,283	13,146	1,654	98,083
76	79,166	4,834	14,823	98,823
77	88,205	6,308	3,557	98,070
78	91,957	10,931	2,550	105,438
79	79,534	12,202	8,994	100,730
80	86,662	4,564	2,215	93,441
81	86,457	12,474	5,236	104,167
82	77,000	4,564	14,555	96,119

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	72	73	74	75	76	77	78	79	80	81	82
Requests	9	8	12	8	8	6	10	7	10	10	6

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. EPA provided additional funding in 2006 to update the SDVAT to improve import of expanded data under the new contract. Although EPA no longer provides funding for SDVAT user support, RTI continues to provide limited support to current STN sites.

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:

- Data Availability at end of calendar year - 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.

- Site Changes - Several sites indicated that they had stopped, started, or relocated samplers during the last year. The PR site was found to have supplied the wrong AQS Site code and its data needed to be moved to the correct site.

- Data Questions - A number of sites had questions about individual data values. These were evaluated and the data flagged as appropriate. In at least one case, problems included systematic disagreement with FRM samplers on site. This was determined to be due to a poorly functioning flow controller.

- Speciation Data Validation and Analysis Tool (SDVAT) Questions - A number of sites requested copies of the SDVAT for use in reviewing their site's data. Several sites had problems importing data into the SDVAT. These were largely due to changes in the reports that were required with the new sampling contract. A new version of the SDVAT is now available and should eliminate most of the import problems previously experienced.

5.0 Quality Assurance and Data Validation

5.1 QA Activities

5.1.1 QAPP Updates

RTI's QAPP for STN was not updated during 2006.

5.1.2 SOP Updates

RTI’s SOPs were not updated during 2006.

5.1.3 Internal Surveillance Activities

Internal surveillance activities during 2006 included walkthroughs of all the laboratories to verify compliance with the SOPs. An internal audit of the Gravimetry Laboratory was performed in January, 2006. 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 2006. These originated from both network participants (state agency personnel and EPA) as well as data users who were not affiliated with the STN program.

A significant issue for several agencies was with perceived artifacts, outliers, based on poor comparison with their FRM results. Reports of this nature resulted 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. No systematic laboratory problems were found in researching these issues.

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 batch 72 has 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	72	73	74	75	76	77	78	79	80	81	82	83
2	Operational Criteria Not Met												
3	Possible field contamination						0.07%						
5	Outlier-cause unknown	10.26%	9.99%	3.91%	2.21%	4.61%	7.60%	9.09%	6.69%	7.87%	8.27%	5.44%	6.95%
A	High Winds	0.26%		0.67%	0.13%	0.21%					0.06%		0.15%
D	Sandblasting				0.06%	0.13%			0.06%		0.06%		
E	Forest Fire			0.21%	0.07%	0.13%	0.07%			0.07%	0.53%	0.28%	
F	Structural Fire	0.07%	0.07%			0.07%	0.14%				0.08%		
H	Chemical Spills												
I	Unusual Traffic Congestion						0.07%						
J	Construction/Demolition	0.33%	0.23%	0.31%	0.26%			0.13%		0.07%	0.64%	0.76%	0.75%
K	Agricultural Tilling	0.13%			0.33%	0.20%							0.13%
L	Highway Construction						0.06%			0.21%		0.14%	0.13%
M	Rerouting of Traffic												0.17%
N	Sanding/salting of Streets	0.17%	0.29%	0.10%	0.15%								0.07%
O	Infrequent Large Gatherings						0.07%			0.14%		0.07%	
P	Roofing Operations		0.17%	0.05%							0.06%		
Q	Prescribed Burning					0.07%				0.07%			
R	Cleanup after Major Disaster												
U	Sahara Dust												
W	Flow Rate Average out of specs	0.07%	0.05%	0.15%	0.38%	0.03%				0.14%			0.26%
X	Filter Temperature Diff. out of spec	0.31%	0.43%	0.41%	0.63%	0.33%	0.58%	0.13%	0.07%	0.37%	0.06%	0.14%	0.80%
Y	Elapsed Sample Time out of specs				0.13%		0.07%						

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

Flag	Description	72	73	74	75	76	77	78	79	80	81	82	83
2	Operational Criteria Not Met												
3	Possible field contamination						0.07%						
5	Outlier-cause unknown	10.26%	9.99%	3.91%	2.21%	4.61%	7.60%	9.09%	6.69%	7.87%	8.27%	5.44%	6.95%
A	High Winds	0.26%		0.67%	0.13%	0.21%					0.06%		0.15%
D	Sandblasting				0.06%	0.13%			0.06%		0.06%		
E	Forest Fire			0.21%	0.07%	0.13%	0.07%			0.07%	0.53%	0.28%	
F	Structural Fire	0.07%	0.07%			0.07%	0.14%				0.08%		
H	Chemical Spills												
I	Unusual Traffic Congestion						0.07%						
J	Construction/Demolition	0.33%	0.23%	0.31%	0.26%			0.13%		0.07%	0.64%	0.76%	0.75%
K	Agricultural Tilling	0.13%			0.33%	0.20%							0.13%
L	Highway Construction						0.06%			0.21%		0.14%	0.13%
M	Rerouting of Traffic												0.17%
N	Sanding/salting of Streets	0.17%	0.29%	0.10%	0.15%								0.07%
O	Infrequent Large Gatherings						0.07%			0.14%		0.07%	
P	Roofing Operations		0.17%	0.05%							0.06%		
Q	Prescribed Burning					0.07%				0.07%			
R	Cleanup after Major Disaster												
U	Sahara Dust												
W	Flow Rate Average out of specs	0.07%	0.05%	0.15%	0.38%	0.03%				0.14%			0.26%
X	Filter Temperature Diff. out of spec	0.31%	0.43%	0.41%	0.63%	0.33%	0.58%	0.13%	0.07%	0.37%	0.06%	0.14%	0.80%
Y	Elapsed Sample Time out of specs				0.13%		0.07%						

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

Flag	Description	72	73	74	75	76	77	78	79	80	81	82	83
ANB	Analysis not billable	0.55%	0.18%	0.21%	0.24%	0.17%	0.36%	0.07%	0.10%	0.02%	0.22%	0.20%	0.10%
APB	analysis partly billable	0.86%	0.73%	0.48%	0.20%	0.37%	0.23%	0.50%	0.40%	0.38%	0.54%	0.28%	0.34%
DFM	Filter missing	0.01%			0.01%			0.03%			0.01%	0.05%	0.01%
DMA	Module assembled in correctly												
DSI	Module condition invalid								0.07%		0.06%		
DST	Receipt temperature >4C	26.59%	23.15%	20.73%	27.29%	45.78%	54.80%	72.44%	73.06%	87.49%	82.11%	58.30%	29.83%
FBS	Field or Trip Blank appears to be actual sample			0.15%							0.06%		
FCE	Field Environmental Substituted	2.05%	1.58%	1.55%	1.61%	1.32%	2.64%	2.61%	2.19%	2.70%	2.04%	1.60%	1.51%
FES	Pickup holding time exceeded	0.15%	0.02%	0.04%	0.07%	0.06%	0.06%	0.21%	0.13%	0.21%	0.08%	0.06%	0.06%
FHT	Sample lost or damaged in shipment	20.54%	22.88%	12.25%	5.88%	13.06%	14.03%	5.70%	13.73%	14.98%	18.95%	5.95%	12.31%
FIC	Exposure Session Canceled or modules returned unexposed				0.07%								
FSL	Sample Lost						0.06%						
LBD	Laboratory blank duplicate outside limits											0.00%	
LFA	Filter inspection flags* - filter wet	0.03%	0.02%	0.05%	0.05%			0.04%	0.03%	0.02%	0.03%	0.05%	0.05%
LFH	Filter inspection flags* - Holes in filter									0.00%			0.00%
LFL	Filter inspection flags* -Loose Material					0.00%					0.04%		0.07%
LFO	Filter inspection flags* -Other					0.00%				0.04%			
LFP	Filter inspection flags* -Pinholes					0.04%							
LFT	Filter inspection flags* - Tear					0.00%	0.04%		0.01%				
LFU	Filter inspection flags* -Non-uniformity										0.00%		
LHT	Lab holding times exceeded	0.03%							0.00%	0.03%			
LLI	ANALYSIS INVALID - Other	0.00%											
QAC	Anion/Cation ratio out of limits	0.11%	0.11%	0.16%	0.13%	0.07%	0.07%	0.09%	0.16%	0.13%	0.27%	0.15%	0.10%
QL1	Sulfur/Sulfate ratio out of limits	0.06%	0.07%	0.07%	0.03%	0.05%	0.06%	0.05%	0.04%	0.04%	0.05%	0.03%	0.05%
QMB	Mass balance ratio out of limits	10.14%	9.87%	3.72%	2.06%	4.51%	7.48%	8.99%	6.53%	7.73%	7.99%	5.28%	6.84%
SNB	Sample not billable	0.07%	0.08%	0.17%	0.07%	0.12%	0.19%	0.06%	0.33%	0.21%	0.06%	0.40%	0.40%
SPB	Sample partly billable	4.01%	2.78%	2.11%	3.02%	3.16%	2.84%	3.29%	3.89%	4.13%	4.19%	3.42%	3.99%

5.3 Analysis of Collocated Data

The STN program operated six sites with collocated samplers during 2006. 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.

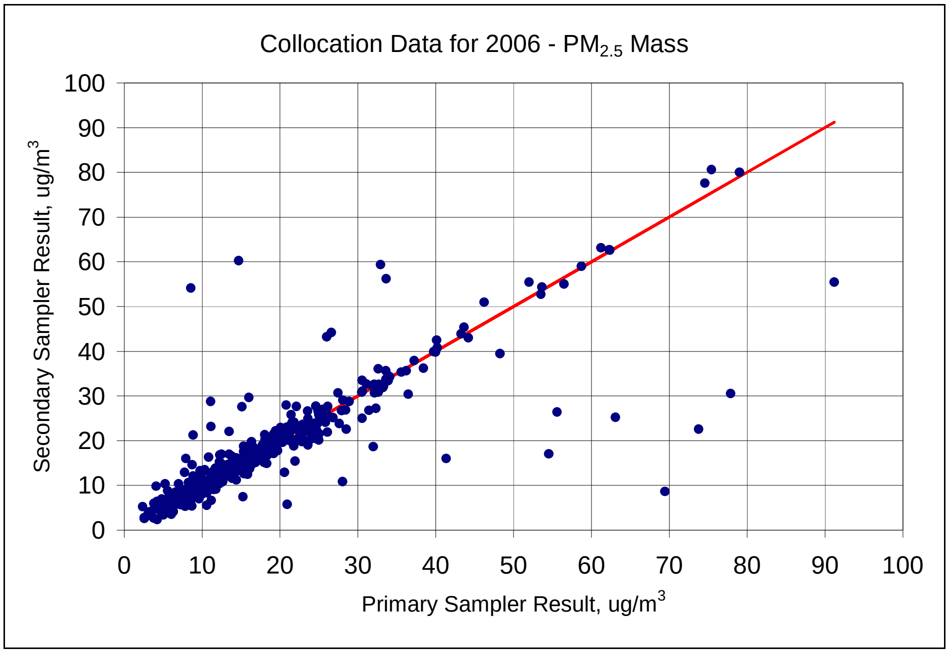
Table 5-4. Collocated sites in the STN

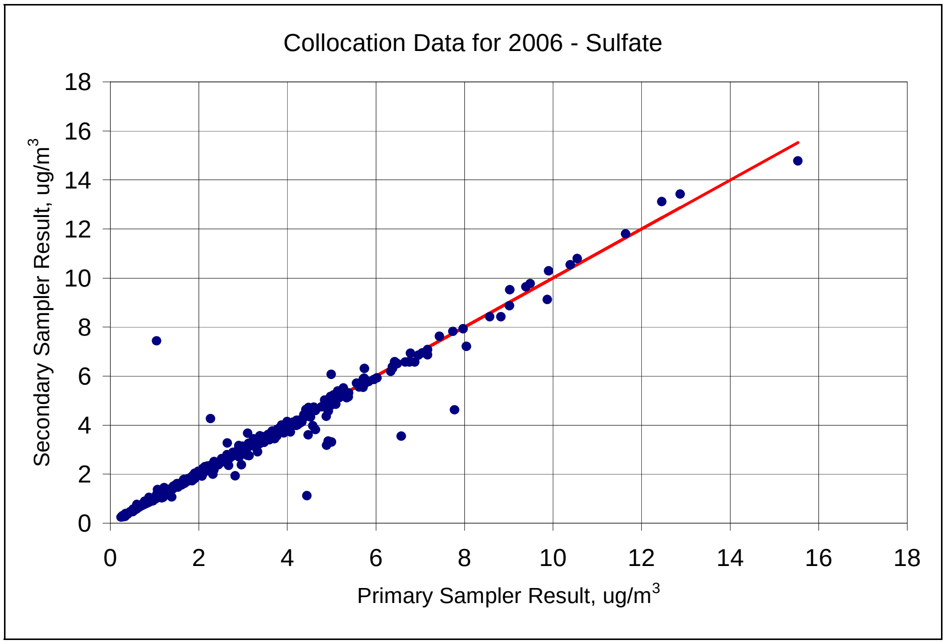
Location Name	State	AQS Code	Sampler Type
Bakersfield-California Ave	California	60290014	MetOne SASS
Deer Park	Texas	482011039	URG MASS
G.T. Craig	Ohio	390350060	MetOne SASS
New Brunswick	New Jersey	340230006	MetOne SASS
Riverside-Rubidoux	California	60658001	MetOne SASS
Roxbury (Boston)	Massachusetts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

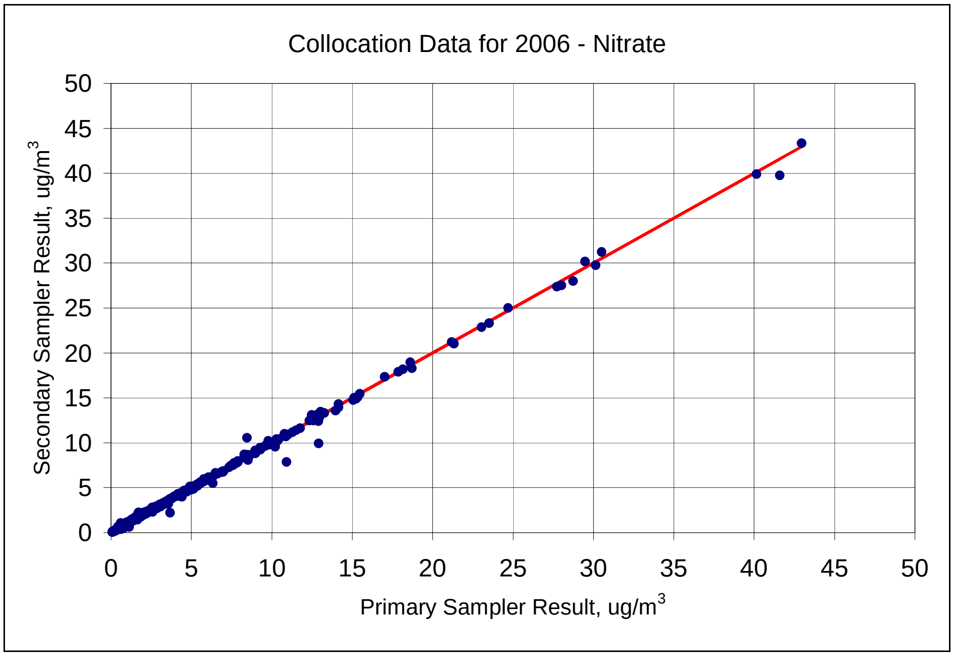
As indicated in the table, five of the sites use MetOne SASS samplers, and one uses a URG MASS sampler. None of the collocated sites used either the Andersen RAAS sampler or the R&P speciation sampler during 2006. For statistical analysis, the data presented in this section for the SASS and MASS samplers have generally been merged, since the amount of data for the MASS sampler is relatively small.

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).

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







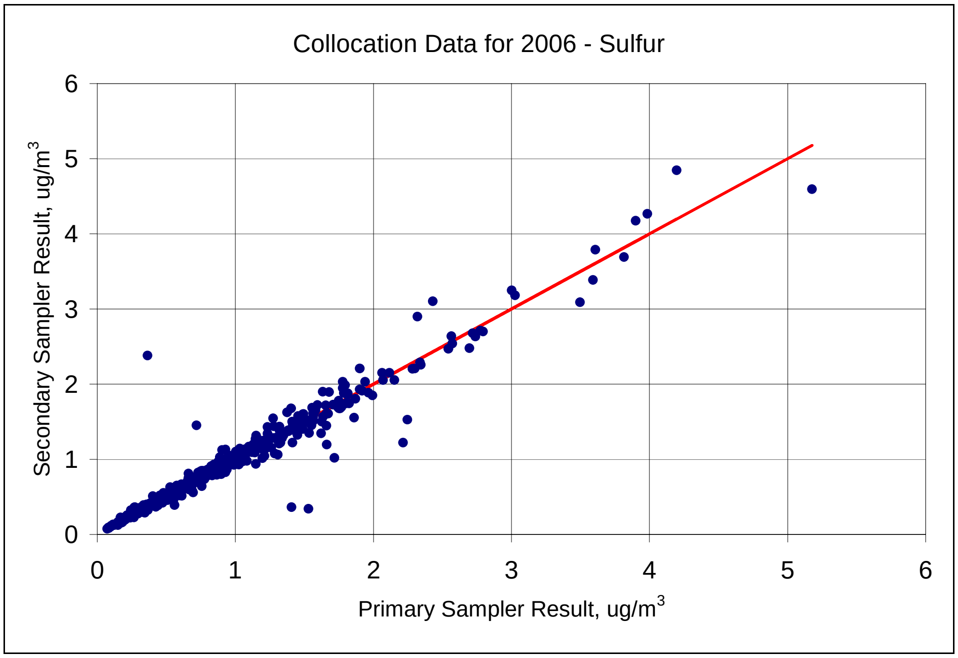
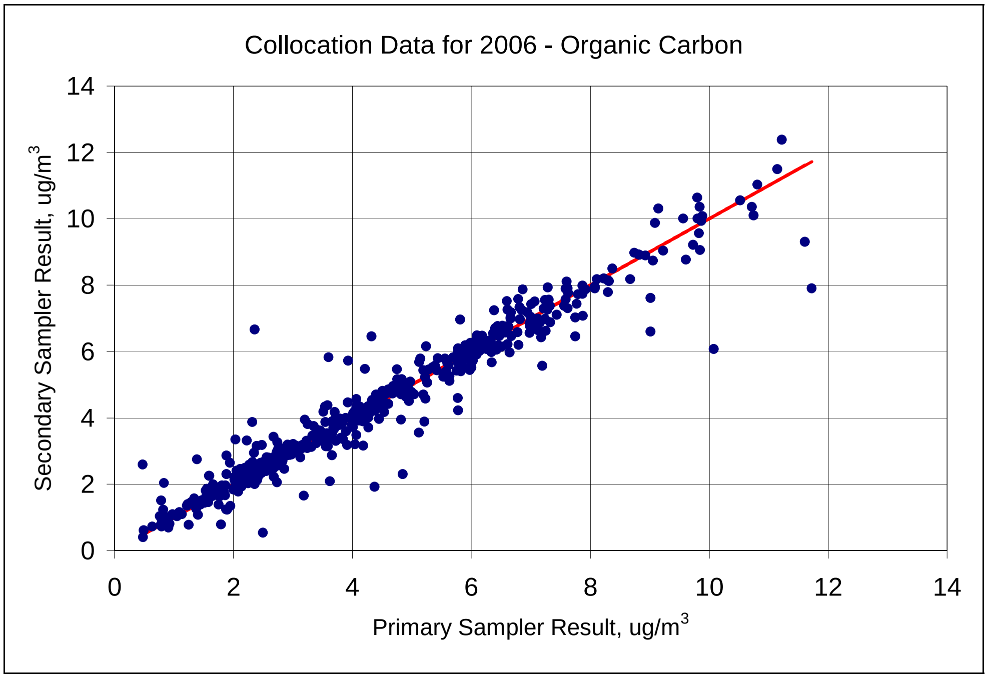


Figure 5-1. (Continued)



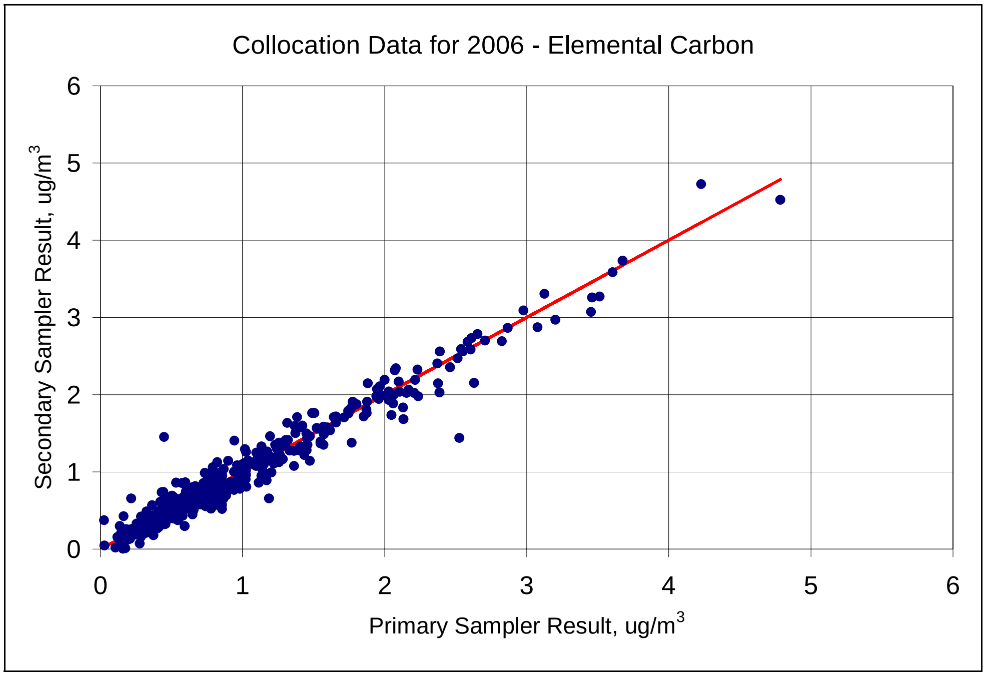


Figure 5-1. (Continued)

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. Column 2 shows the average value from the primary sampler. 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:

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

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

Table 5-5. Trace Elements by XRF

	Sampler 1		Sampler 2					
Analyte	**Average µg/m^3**	**Standard Dev.[1] µg/m^3**	**Average µg/m^3**	**Standard Dev.[1] µg/m^3**	**Average Relative Diff.[2] µg/m^3**	**Average AQS Uncert.[3] µg/m^3**	**Ratio[4] AQS/Col percent**	**Counts[5]**
Aluminum	0.110	0.164	0.106	0.150	24.9%	19.8%	79.6%	210
Arsenic	0.003	0.004	0.003	0.005	26.9%	23.4%	87.0%	111
Barium	0.041	0.072	0.045	0.080	37.8%	23.6%	62.6%	28
Bromine	0.005	0.003	0.005	0.003	20.0%	16.9%	84.5%	353
Calcium	0.091	0.109	0.091	0.095	17.2%	9.2%	53.7%	433
Chlorine	0.119	0.225	0.132	0.275	28.3%	13.9%	49.2%	179
Chromium	0.007	0.011	0.007	0.012	44.9%	24.3%	54.2%	102
Copper	0.011	0.013	0.009	0.007	24.6%	14.0%	56.7%	381
Europium	0.010	0.010	0.010	0.008	23.4%	21.4%	91.7%	35
Gallium	0.004	0.003	0.004	0.004	17.0%	29.8%	175.4%	13
Iron	0.166	0.186	0.167	0.166	13.7%	6.5%	47.2%	450
Lanthanum	0.027	0.036	0.031	0.038	27.8%	21.8%	78.3%	12
Lead	0.012	0.013	0.012	0.013	20.8%	23.6%	113.3%	162
Magnesium	0.046	0.050	0.049	0.054	29.0%	17.5%	60.1%	84
Manganese	0.006	0.005	0.006	0.005	22.1%	20.6%	93.4%	218
Mercury	0.006	0.004	0.005	0.003	21.8%	26.1%	119.9%	47
Nickel	0.003	0.003	0.003	0.003	28.6%	19.3%	67.6%	239
Potassium	0.100	0.190	0.092	0.089	8.9%	8.6%	96.8%	448
Selenium	0.003	0.003	0.003	0.004	24.0%	30.2%	126.1%	76
Silicon	0.197	0.320	0.192	0.275	16.0%	11.1%	69.5%	411
Sodium	0.214	0.186	0.222	0.204	18.1%	15.7%	86.6%	192
Strontium	0.004	0.007	0.004	0.008	20.4%	30.1%	147.5%	76
Sulfur	0.952	0.719	0.953	0.724	5.4%	6.7%	123.0%	450
Terbium	0.016	0.014	0.017	0.016	17.3%	33.2%	191.6%	18
Titanium	0.014	0.018	0.014	0.015	23.0%	19.1%	82.9%	175
Vanadium	0.008	0.005	0.008	0.006	20.7%	19.9%	95.7%	230
Zinc	0.023	0.040	0.023	0.039	13.4%	11.3%	84.6%	428
Zirconium	0.005	0.003	0.005	0.002	20.3%	32.1%	158.6%	24
Aluminum	0.110	0.164	0.106	0.150	24.9%	19.8%	79.6%	210

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.

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. Only samples with more than 11 acceptable values were included

Table 5-6. Anions and Cations by IC

	Sampler 1		Sampler 2					
Analyte	**Average ug/m3**	**Standard Dev. ug/m3[1]**	**Average ug/m3**	**Standard Dev. ug/m3[1]**	**Average Relative Diff.[2]**	**Average Rel. AQS Uncert.[3]**	**Ratio AQS/ARD percent[4]**	**Counts[5]**
Sulfate	2.882	2.202	2.858	2.185	3.2%	7.3%	224.8%	450
Nitrate (SASS)	4.624	6.380	4.599	6.328	3.5%	7.3%	207.2%	387
Nitrate (MASS/nylon)	0.394	0.289	0.390	0.266	20.3%	7.3%	36.2%	62
Nitrate (MASS/Teflon)	0.301	0.231	0.333	0.231	18.5%	7.5%	40.4%	62
Ammonium	2.147	2.276	2.122	2.239	4.8%	7.1%	147.6%	450
Potassium	0.118	0.251	0.118	0.255	9.7%	8.3%	84.8%	251
Sodium	0.263	0.214	0.278	0.242	13.8%	22.5%	162.8%	248

Table 5-7. Organic and Elemental Carbon

	Sampler 1		Sampler 2					
Analyte	**Average ug/m3**	**Standard Dev. ug/m3[1]**	**Average ug/m3**	**Standard Dev. ug/m3[1]**	**Average Relative Diff.[2]**	**Average Rel. AQS Uncert.[3]**	**Ratio AQS/ARD percent[4]**	**Counts[5]**
Elemental carbon	1.171	0.748	1.156	0.740	7.6%	29.3%	388.1%	326
Organic carbon	4.468	2.415	4.453	2.372	6.7%	12.5%	185.1%	464
Pk1_OC	1.429	0.744	1.425	0.708	10.9%	25.2%	232.4%	357
Pk2_OC	1.403	0.690	1.405	0.714	11.2%	24.4%	217.4%	452
Pk3_OC	1.103	0.474	1.107	0.464	9.3%	27.8%	297.7%	390
Pk4_OC	1.203	0.607	1.196	0.599	14.7%	27.3%	185.3%	300
Total carbon	5.397	3.012	5.379	2.980	6.2%	13.9%	225.6%	466

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.

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. Only samples with more than 11 acceptable values were included in the table.

Table 5-8. Particulate Matter (Gravimetry)

	Sampler 1		Sampler 2					
Analyte	**Average ug/m3**	**Standard Dev. ug/m3[1]**	**Average ug/m3**	**Standard Dev. ug/m3[1]**	**Average Relative Diff.[2]**	**Average Rel. AQS Uncert.[3]**	**Ratio AQS/ARD percent[4]**	**Counts[5]**
PM2.5 Mass	17.658	13.182	17.425	12.284	10.1%	5.6%	388.1%	326

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.

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. Only samples with more than 11 acceptable values were included in the table.

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 2006. 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:

- Uncertainties for iron and chlorine were underestimated by a factor of slightly more than 2 in the values posted to AQS compared with the estimates based on collocation. No other elements that met the screening criterion of more than 10 valid observations showed differences of greater than 2x between the average uncertainty posted to AQS and the average uncertainty estimated from the collocated samplers.

- Sulfate (224%) and nitrate (207%) - It appears that the laboratory and field components of uncertainty are both less than the assumed 5% each (for a total of 7%). RTI needs to consult with EPA about the best way to deal with this apparent overestimation, since changing the estimated uncertainty to agree with the findings from the collocated data analysis would create a discontinuity in the data set.

- Elemental carbon (388%) – This is consistent with last year's report, which also had a very high ratio for elemental carbon. A high ratio means that the uncertainty estimated from collocation data is less, on average, than the uncertainties loaded into AQS. As with the uncertainties for sulfate and nitrate, RTI needs to consult with EPA about the best way to deal with this apparent overestimation, since changing the estimated uncertainty to agree with the findings from the collocated data analysis would create a discontinuity in the data set.

- The ratio for particulate mass (Table 5-8) is somewhat lower than expected (56%), though within a factor of 2. This is consistent with last year's report, when a ratio of 60% was observed. This means that the actual uncertainty is somewhat greater than what is being loaded into AQS. This could be caused by a combination of field contamination and filter media problems such as those observed in 2005, when manufacturing debris was suspected of causing poor weighing precision.

5.3.2 Bias

Biases between the primary and secondary samplers are small for all of the major analytes, as shown in Tables 5-5 through 5-8 above.

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 is 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 2006.

Table 5-9. Concentration Percentiles for Combined Trip and Field Blanks Reported During 2006

Anions and Cations by Ion Chromatography

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Ammonium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0138
Potassium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium	0.0000	0.0000	0.0000	0.0000	0.0084	0.0292	0.0520
Nitrate (Teflon excluding MASS)	0.0000	0.0000	0.0000	0.0000	0.0430	0.0622	0.0809
Nitrate (MASS/nylon)	0.0000	0.0095	0.0170	0.0231	0.0316	0.0436	0.0559
Nitrate (MASS/Teflon)	0.0000	0.0132	0.0169	0.0216	0.0333	0.0515	0.0652
Sulfate	0.0000	0.0000	0.0000	0.0000	0.0358	0.0497	0.0663

PM2.5 Mass by Gravimetry

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Particulate matter 2.5u	-0.2083	0.0000	0.1250	0.5208	1.0417	1.6667	2.0833

Organic and Elemental Carbon (OC/EC)

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Elemental carbon	0.0000	0.0000	0.0000	0.0000	0.0018	0.0119	0.0350
Organic carbon	0.4246	0.5521	0.7510	0.9561	1.1648	1.3980	1.5593
Pk1_OC	0.1012	0.1346	0.1894	0.2592	0.3416	0.4092	0.4538
Pk2_OC	0.1462	0.1953	0.2819	0.3765	0.4749	0.5848	0.6724
Pk3_OC	0.0705	0.1034	0.1485	0.2126	0.2922	0.3901	0.4760
Pk4_OC	0.0089	0.0161	0.0306	0.0507	0.0831	0.1559	0.2177
PyrolC	0.0000	0.0000	0.0000	0.0003	0.0036	0.0129	0.0235
Total carbon	0.4275	0.5562	0.7583	0.9637	1.1718	1.4016	1.5659

Trace Elements by XRF

ANALYTE	Percentiles						
	5	10	25	50	75	90	95
Aluminum	0.0000	0.0000	0.0000	0.0000	0.0004	0.0053	0.0091
Antimony	0.0000	0.0000	0.0000	0.0000	0.0004	0.0032	0.0063
Arsenic	0.0000	0.0000	0.0000	0.0000	0.0001	0.0006	0.0010
Barium	0.0000	0.0000	0.0000	0.0000	0.0006	0.0079	0.0187
Bromine	0.0000	0.0000	0.0000	0.0000	0.0005	0.0014	0.0030
Cadmium	0.0000	0.0000	0.0000	0.0000	0.0003	0.0014	0.0033
Calcium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0013	0.0025
Cerium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0119
Cesium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0017	0.0086

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	0.0000	0.0004	0.0007
Chromium	0.0000	0.0000	0.0000	0.0000	0.0005	0.0012	0.0018
Cobalt	0.0000	0.0000	0.0000	0.0000	0.0003	0.0007	0.0010
Copper	0.0000	0.0000	0.0000	0.0000	0.0003	0.0009	0.0013
Europium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0007
Gallium	0.0000	0.0000	0.0000	0.0002	0.0007	0.0014	0.0027
Gold	0.0000	0.0000	0.0000	0.0000	0.0002	0.0011	0.0021
Hafnium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0007
Indium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0018	0.0042
Iridium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0008	0.0014
Iron	0.0000	0.0000	0.0000	0.0000	0.0006	0.0023	0.0064
Lanthanum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0035	0.0120
Lead	0.0000	0.0000	0.0000	0.0000	0.0004	0.0027	0.0059
Magnesium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0061	0.0149
Manganese	0.0000	0.0000	0.0000	0.0001	0.0005	0.0010	0.0013
Mercury	0.0000	0.0000	0.0000	0.0000	0.0002	0.0013	0.0032
Molybdenum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007	0.0029
Nickel	0.0000	0.0000	0.0000	0.0000	0.0003	0.0007	0.0010
Niobium	0.0000	0.0000	0.0000	0.0000	0.0001	0.0012	0.0032
Phosphorus	0.0000	0.0000	0.0000	0.0000	0.0004	0.0028	0.0045
Potassium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0011	0.0018
Rubidium	0.0000	0.0000	0.0000	0.0000	0.0005	0.0012	0.0020
Samarium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.0012
Scandium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.0013
Selenium	0.0000	0.0000	0.0000	0.0000	0.0005	0.0013	0.0029
Silicon	0.0000	0.0000	0.0000	0.0000	0.0008	0.0072	0.0145
Silver	0.0000	0.0000	0.0000	0.0000	0.0006	0.0025	0.0055
Sodium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0038	0.0179
Strontium	0.0000	0.0000	0.0000	0.0000	0.0005	0.0011	0.0015
Sulfur	0.0000	0.0000	0.0000	0.0000	0.0005	0.0015	0.0019
Tantalum	0.0000	0.0000	0.0000	0.0000	0.0002	0.0010	0.0029
Terbium	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0008
Tin	0.0000	0.0000	0.0000	0.0000	0.0005	0.0037	0.0073
Titanium	0.0000	0.0000	0.0000	0.0000	0.0002	0.0007	0.0013
Vanadium	0.0000	0.0000	0.0000	0.0000	0.0003	0.0009	0.0013
Wolfram	0.0000	0.0000	0.0000	0.0000	0.0003	0.0013	0.0032
Yttrium	0.0000	0.0000	0.0000	0.0000	0.0004	0.0012	0.0019
Zinc	0.0000	0.0000	0.0000	0.0001	0.0004	0.0010	0.0013
Zirconium	0.0000	0.0000	0.0000	0.0000	0.0003	0.0014	0.0032

Notes: All units are micrograms per cubic meter.

Trip and Field Blanks During 2006 -- 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. 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 materials used in construction of the sampling 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	136	0.0030	0.0000	0.0160	
EC	RAAS	217	0.0077	0.0000	0.0316	
EC	**RPSPEC**	**155**	**0.0201**	**0.0000**	**0.1547**	**1**
EC	SASS	2179	0.0073	0.0000	0.0363	
Iron	MASS	137	0.0003	0.0000	0.0010	
Iron	RAAS	217	0.0003	0.0000	0.0016	
Iron	RPSPEC	155	0.0009	0.0000	0.0019	
Iron	**SASS**	**2180**	**0.0021**	**0.0000**	**0.0080**	**2**
Sodium Ion	MASS	137	0.0049	0.0023	0.0154	
Sodium Ion	RAAS	217	0.0061	0.0000	0.0345	
Sodium Ion	**RPSPEC**	**154**	**0.0788**	**0.0295**	**0.3311**	**3**
Sodium Ion	SASS	2181	0.0125	0.0000	0.0421	

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 a performance audit sponsored by EPA. See the AMTIC web site:

http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/Multilab-Speciation-PE-2006.pdf.

Author/Organization	Report Title, Date	Description	Conclusions/Findings
Jewell Smiley - EPA/NAREL	Experimental Inter-comparison of Speciation Laboratories, March 5, 2007	Intercomparison of seven laboratories currently providing PM2.5 analyses for gravimetric mass, IC, OC/EC, and XRF.	RTI results were acceptable.

6.2 System Audit Results

There was no technical systems audit by EPA during 2006. Results from the 2005 audit were followed-up successfully as described in the 2005 report.

7.0 List of References

7.1 List of STN Documents

Type	Title	Date Revised	Author	Document No.
SOP	Gravimetric Analysis	7/8/2005	Greene	N/A
SOP	Cleaning Nylon Filters Used for Collection of PM2.5 Material	8/14/2003	Hardison, E.	N/A
SOP	XRF Analysis of PM2.5 Deposits on Teflon Filters	8/14/2003	McWilliams	N/A
SOP	R&P Speciation Sampler Chemcomb Denuders with Sodium Carbonate	8/14/2003	Eaton	N/A
SOP	Coating and Extracting Annular Denuders with Sodium Carbonate	8/14/2003	Eaton	N/A
SOP	Coating Annular Denuders with XAD-4 Resin	8/14/2003	Eaton	N/A
SOP	Coating Aluminum Honeycomb Denuders with MgO	8/14/2003	Eaton	N/A
SOP	Sample Preparation and Analysis of PM20 and PM2.5 Samples by SEM	8/14/2003	Crankshaw	N/A
SOP	Coating Annular Denuders with MgO	8/15/2003	Eaton	N/A
SOP	Database Operations	7/11/2005	Rickman	N/A
SOP	Disaster Recovery Plan--RTI CONFIDENTIAL	7/6/2005	Rickman	N/A
SOP	Anion Analysis	8/14/2003	Hardison, E.	N/A
SOP	Cation Analysis	8/14/2003	Hardison, E.	N/A
SOP	Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters	7/7/2005	Hardison, E.	N/A
SOP	Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer	8/14/2003	Peterson	N/A
SOP	Sample Handling and Archiving Laboratory (SHAL)	7/11/2005	O'Rourke	N/A
SOP	Long-Term Archiving of PM2.5 Filters and Extracts	7/5/2002	Haas, C.	N/A
SOP	Assign Field Sample Flags for the Chemical Speciation Trends Network	7/7/2005	Wall, C.	N/A
SOP	Document Control and Storage	7/6/2005	Haas, D.	N/A
SOP	Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples	6/1/2000	DRI	N/A
SOP	Analysis of SVOC by GC/MS	7/1/2003	DRI	N/A
SOP	Analysis of Elements in Air Particulates by XRF (Kevex 770)	7/3/2003	Chester	N/A
SOP	Kevex XRF Spectrometer Calibration	7/3/2003	Chester	N/A
SOP	Kevex XRF Spectrometer Data Generation, Interpretation and Reporting Chester Labnet Proprietary Method	10/17/2002	Chester	N/A

Type	Title	Date Revised	Author	Document No.
SOP	Analysis of Elements in Air Particulates by XRF (Kevex 771)	8/6/2003	Chester	N/A
SOP	Sample Receipt and Log In	11/18/2002	Chester	N/A
QAPP	QAPP for PM2.5 of Chemical Speciation Samples	9/11/2005	RTI	RTI/08858/12/01S
Data	Semi-Annual Data Summary Report	1/30/2004	RTI	RTI/8858/01QAS
Data	Semi-Annual Data Summary Report	7/31/2004	RTI	RTI/8858/02QAS
Data	Semi-Annual Data Summary Report	5/12/2005	RTI	RTI/8858/03QAS
Data	2005 Annual Data Summary Report	7/19/2006	RTI	RTI/8858/04QAS
Data	2006 Annual Data Summary Report	2/28/2007	RTI	RTI/8858/05QAS
Report	XRF Uncertainties	10/14/2004	RTI	RTI/08858/TO2/01D
Report	Review of Sodium Ion Contamination Issue for STN	1/19/2005	RTI	RTI/08858/12/02S
Report	Teflon Filter Manufacturing Defects March - April 2005	8/23/2005	RTI	RTI/08858/12/03S
Report	Test of Acceptance of XRF Instrument #772 Operated by Chester LabNet	12/20/2005	RTI	RTI/0208858/TO2/02D

7.2 Special Reports Issued During the Reporting Period

Type	Title	Date Revised	Author	Document No.
Data	2005 Annual Data Summary Report	7/19/06	RTI	RTI/08858/04QAS
Report	Tests of Acceptance of X-ray Fluorescence Instrument #3 Operated by RTI International	5/1/06	RTI	RTI/0208858/TO2/03D
Report	Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties	8/4/06	RTI	RTI/0208858/TO2/04D

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	0.24	0.01	0.026	0.017	0.027
Cations - PM2.5 (NH4, Na, K)	Potassium	0.23	0.0095	0.024	0.016	0.025
Cations - PM2.5 (NH4, Na, K)	Sodium	0.29	0.013	0.03	0.021	0.033
Mass - PM2.5	Particulate matter 2.5u	7.2	0.32	0.32	0.31	0.81
Nitrate - PM2.5	Nitrate	0.084		0.0084	0.0059	0.0088
Nitrate - PM2.5 (MASS/nylon)	Nitrate	0.084	0.0035			
Nitrate - PM2.5 (MASS/teflon	Nitrate	0.084	0.0035			
Organic and elemental carbon	Elemental carbon	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	Organic carbon	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	Pk1_OC	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	Pk2_OC	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	Pk3_OC	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	Pk4_OC	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	PyrolC	2.4	0.11	0.24	0.17	0.32
Organic and elemental carbon	Total carbon	2.4	0.11	0.24	0.17	0.32
Sulfate - PM2.5	Sulfate	0.12	0.005	0.012	0.0085	0.013
Trace elements	Aluminum	0.24	0.0056	0.01	0.01	0.025
Trace elements	Antimony	0.4	0.017	0.018	0.017	0.045
Trace elements	Arsenic	0.036	0.00069	0.0015	0.0015	0.0038
Trace elements	Barium	0.85	0.0046	0.036	0.036	0.092
Trace elements	Bromine	0.029	0.00074	0.0012	0.0012	0.0031
Trace elements	Cadmium	0.18	0.0078	0.0078	0.0077	0.02
Trace elements	Calcium	0.073	0.0032	0.0032	0.0031	0.0082
Trace elements	Cerium	1.2	0.0041	0.052	0.053	0.13
Trace elements	Cesium	0.53	0.014	0.022	0.023	0.057
Trace elements	Chlorine	0.15	0.0033	0.0064	0.0062	0.015
Trace elements	Chromium	0.025	0.0011	0.0011	0.0011	0.0028
Trace elements	Cobalt	0.02	0.00057	0.00085	0.00086	0.0022
Trace elements	Copper	0.024	0.00069	0.0011	0.001	0.0026
Trace elements	Europium	0.16	0.0021	0.0069	0.0069	0.018
Trace elements	Gallium	0.051	0.001	0.0022	0.0022	0.0053
Trace elements	Gold	0.078	0.0023	0.0034	0.0033	0.0083
Trace elements	Hafnium	0.38	0.0025	0.016	0.016	0.041
Trace elements	Indium	0.21	0.0092	0.0093	0.0091	0.024
Trace elements	Iridium	0.086	0.003	0.0036	0.0036	0.0092
Trace elements	Iron	0.032	0.00072	0.0014	0.0014	0.0034
Trace elements	Lanthanum	1	0.0036	0.042	0.043	0.11
Trace elements	Lead	0.079	0.002	0.0033	0.0034	0.0085
Trace elements	Magnesium	0.63	0.005	0.027	0.026	0.065
Trace elements	Manganese	0.033	0.00081	0.0014	0.0014	0.0036
Trace elements	Mercury	0.091	0.0039	0.004	0.0039	0.01
Trace elements	Molybdenum	0.087	0.0038	0.0038	0.0037	0.0097
Trace elements	Nickel	0.018	0.00051	0.00079	0.00077	0.0019

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	Niobium	0.06	0.002	0.0026	0.0026	0.0065
Trace elements	Phosphorus	0.15	0.0068	0.0069	0.0066	0.017
Trace elements	Potassium	0.11	0.0031	0.0047	0.0045	0.011
Trace elements	Rubidium	0.031	0.00084	0.0013	0.0013	0.0034
Trace elements	Samarium	0.096	0.0021	0.0042	0.0041	0.01
Trace elements	Scandium	0.36	0.016	0.016	0.015	0.04
Trace elements	Selenium	0.031	0.00082	0.0013	0.0013	0.0033
Trace elements	Silicon	0.18	0.0047	0.0078	0.0076	0.019
Trace elements	Silver	0.15	0.0061	0.0064	0.0064	0.016
Trace elements	Sodium	2.1	0.017	0.093	0.09	0.22
Trace elements	Strontium	0.036	0.001	0.0015	0.0015	0.0039
Trace elements	Sulfur	0.095	0.0042	0.0042	0.0041	0.011
Trace elements	Tantalum	0.28	0.0041	0.012	0.012	0.03
Trace elements	Terbium	0.11	0.0019	0.0046	0.0046	0.012
Trace elements	Tin	0.31	0.013	0.013	0.013	0.034
Trace elements	Titanium	0.051	0.0022	0.0023	0.0022	0.0058
Trace elements	Vanadium	0.037	0.0016	0.0016	0.0016	0.0042
Trace elements	Wolfram	0.2	0.0031	0.0084	0.0085	0.021
Trace elements	Yttrium	0.044	0.0012	0.0019	0.0019	0.0047
Trace elements	Zinc	0.034	0.0015	0.0015	0.0015	0.0038
Trace elements	Zirconium	0.052	0.0019	0.0022	0.0022	0.0056

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		Sample Date		Field Samples	Blanks		Total
Batch	Date	Earliest	Latest		Field	Trip	
72	1/13/2006	11/15/2005	12/15/2005	1308	74	81	1463
73	2/13/2006	12/15/2005	1/11/2006	1091	6	142	1239
74	3/14/2006	1/11/2006	2/16/2006	1523	273	81	1879
75	4/13/2006	2/16/2006	3/18/2006	1259	203	25	1487
76	5/12/2006	3/12/2006	4/14/2006	1171	72	224	1467
77	6/13/2006	4/11/2006	5/11/2006	1307	94	54	1455
78	7/11/2006	5/9/2006	6/14/2006	1351	162	38	1551
79	8/10/2006	6/15/2006	7/13/2006	1162	181	134	1477
80	9/13/2006	7/10/2006	8/16/2006	1264	68	33	1365
81	10/11/2006	8/13/2006	9/14/2006	1262	186	78	1526
82	11/14/2006	5/18/2006	10/17/2006	1139	68	216	1423
83	12/13/2006	10/13/2006	11/14/2006	1262	181	59	1502

Table B-2 Total Number of Records Delivered by Type

Records Posted by Report Batch

Report		Sample Date		Field Samples	Blanks		Total
Batch	Date	Earliest	Latest		Field	Trip	
72	1/13/2006	11/15/2005	12/15/2005	149516	8348	9396	167260
73	2/13/2006	12/15/2005	1/11/2006	124328	687	16261	141276
74	3/14/2006	1/11/2006	2/16/2006	172768	30948	9303	213245
75	4/13/2006	2/16/2006	3/18/2006	142936	23089	2872	168897
76	5/12/2006	3/12/2006	4/14/2006	133064	8145	25515	166724
77	6/13/2006	4/11/2006	5/11/2006	148377	10630	6245	165252
78	7/11/2006	5/9/2006	6/14/2006	153324	18425	4341	176090
79	8/10/2006	6/15/2006	7/13/2006	132048	20614	15259	167921
80	9/13/2006	7/10/2006	8/16/2006	143312	7655	3834	154801
81	10/11/2006	8/13/2006	9/14/2006	142918	21116	9004	173038
82	11/14/2006	5/18/2006	10/17/2006	128964	7655	24675	161294
83	12/13/2006	10/13/2006	11/14/2006	142649	20571	6926	170146
84	1/11/2007	11/13/2006	12/13/2006	122686	7855	6103	136644

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											
				71	**72**	**73**	**74**	**75**	**76**	**77**	**78**	**79**	**80**	**81**	**82**
20th St. Fire Station	120861016	5	SASS	70	100	88									
Alabama (TN)	471570024	5	SASS								100	99	100	89	100
Allen Park	261630001	5	SASS	100	99	89	100	89	75	81	100	90	91	89	100
Bakersfield-California Ave	060290014	5	SASS	90	60	89	100	100	100	75	90	100	100	100	100
Bakersfield-California Ave (Collocated)	060290014	6	SASS	90	60	89	100	100	100	86	100	100	100	100	100
Beacon Hill	530330080	6	MASS	100	100	100	93	100							
Beacon Hill - Met One	530330080	6	SASS											99	70
Blair Street	295100085	6	SASS	100	90	100	92	100	100	100	90	86	89	90	100
Burlington	500070012	5	SASS	100	79	100	100	78	91	100	100	100	91	100	100
Capitol	220330009	5	MASS	99	100	80	89	100	100	61	88	85	98	78	80
Chamizal	481410044	5	MASS	100	100	100	100	100	100	84	36	8	88	91	100
Chicopee	250130008	5	SASS	38	27			100	81	100	82	88	85	20	
Com ED	170310076	5	MASS	100	100	67									
Com Ed - Met One	170310076	5	SASS			100	92	100	91	100	100	99	90	99	88
Commerce City	080010006	5	SASS	100	100	100	91	100	81	99	100	100	100	100	100
CPW	450190049	5	SASS	100	89	100	97	91	93	87	100	99	96	98	89
Criscuolo Park	090090027	5	SASS	90	89	78	78	87	100	100	90	100	70	88	75
Deer Park	482011039	6	MASS	100	92	47	77	90	100	91	92	81	91	91	58
Deer Park (Collocated)	482011039	7	MASS	36	19	69	100	90	91	100	100	100	100	100	99
Dover	100010003	5	SASS	100	100	100	100	100	100	100	100	99	100	100	100
El Cajon	060730003	5	SASS	100	100	100	100	88	89	100	91	88	80	88	75
Elizabeth Lab	340390004	5	SASS	100	86	100	100	100	100	100	100	63	90	88	100
Fargo NW	380171004	5	SASS	100	90	100	100	100	100	100	100	100	100	100	100
Fresno - First Street	060190008	5	SASS	100	84	100	100	100	100	100	100	100	100	100	100
G.T. Craig	390350060	5	SASS	100	88	100	100	100	99	100	100	100	100	90	100
G.T. Craig - Collocated	390350060	6	SASS	100	100	71	89	100	89	88	60	75	80	67	100
Garinger High School	371190041	5	SASS	93	70	89	92	100	93	100	91	100	100	70	100
Guaynabo	720610001	5	SASS	96	52	96	80	21	0						
Gulfport	280470008	5	SASS				90	100	100	100	100	88	100	75	100

				Report Batch											
Guthrie	471570047	5	RAAS	100	100	100	100	100	93	50					
Hawthorne	490353006	5	SASS	100	100	89	95	99	100	100	100	100	100	100	100
Henrico Co.	510870014	5	SASS	100	100	100	89	100	100	100	100	100	100	100	100
Hinton	481130069	5	MASS	91	100	100	100	100	90	88	100	100	91	100	100
JFK Center	202090021	5	SASS	100	100	100	100	100	100	90	100	71	100	100	88
Lawrenceville	420030008	6	SASS	100	99	71	89	100	100	100	90	100	100	86	100
Lindon	490494001	5	SASS	100	100	100	100	100	99	100	100	80	100	88	100
McMillan Reservoir	110010043	5	RAAS	89	100	100	89	100	100	100	100	100	100	100	100
Missoula County Health Dept.	300630031	5	SASS	100	100	100	92	100	75	90	82	90	83	90	89
MLK	100032004	5	SASS	100	100	100	100	100	100	100	100	100	100	83	60
Nampa NNC	160270004	5	SASS	100	73	100	100	100	100	100	92	99			
New Brunswick	340230006	5	SASS	100	100	100	100	100	100	100	100	63	90	88	100
New Brunswick (Collocated)	340230006	6	SASS	100	100	100	100	100	100	100	100	60	80	100	100
North Birmingham	010730023	5	SASS	90	100	100	100	100	100	100	91	100	100	100	100
NY Botanical Gardens	360050083	6	SASS	100	99	100									
Peoria Site 1127	401431127	5	SASS	100	100	100	100	100	100	100	100	100	100	70	100
PHILA - AMS Laboratory	421010004	7	SASS	80	92	100	100	100	100	100	100	100	91	100	100
Philips	270530963	5	SASS	100	90	88	100	89	100	98	100	100	100	100	100
Phoenix Supersite	040139997	7	SASS	100	100	89	100	89	90	100	91	100	91	99	100
Portland N. Roselawn	410510246	6	SASS	100	93	100	100	100	100	100	100	100	100	100	92
Portsmouth	330150014	5	RAAS	90	100	100	100	89	100	100	100	78	100	100	100
Reno	320310016	5	SASS	100	90	100	100	100	100	93	100	100	100	100	100
Riverside-Rubidoux	060658001	5	SASS	100	100	100	100	100	100	100	83	90	100	90	100
Riverside-Rubidoux (Collocated)	060658001	6	SASS					100	100	100	83	90	100	90	100
Roxbury (Boston)	250250042	5	SASS	100	100	100	98	100	100	100	83	100	82	100	100
Roxbury (Boston) - collocated	250250042	6	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Sacramento - Del Paso Manor	060670006	5	SASS	100	90	100	100	100	100	100	100	100	100	100	100
San Jose - Jackson Street	060850005	5	SASS	100	86	100	100	100	100	100	100	78	80	100	100
SER-DNR Headquarters	550790026	5	SASS	90	83	100	67	89	90	93	73	100	100	100	100
Simi Valley	061112002	5	SASS	100	100	100	100	100	100	100	80	100	100	83	100
South DeKalb	130890002	5	RAAS	100	100	100									
South DeKalb - Met One	130890002	5	SASS			100	100	92	100	100	100	100	91	100	100
Springfield Pumping Station	170310057	5	RAAS	80	100	100									
Springfield Pumping Station - Met One	170310057	5	SASS			100	100	100	100	83	80	80	60	100	100

				Report Batch											
St. Lukes Meridian (IMS)	160010010	5	SASS									80	100	100	100
Sydney	120573002	5	SASS	100	100	100	100	89	100	100	100	100	99	100	89
Univ. of Florida Ag School	120111002	5	SASS			100	100	100	100	100	91	100	100	100	100
Urban League	440070022	5	RAAS	100	86	88	92	100	88	100	100	100	99	100	100
Washington Park	180970078	5	SASS	100	99	68	100	88	89	100	100	100	100	100	100
Woolworth St	310550019	5	SASS	97	97	97	86	88	97	97	97	97	97	97	97
WV - Guthrie Agricultural Center	540390011	5	SASS	100	80	78	83	56	100	78	75	83	82	80	56

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

Monthly Percent Data Completeness by Site – Non-STN Sites

			Sampler	Report Batch											
Location	**AQS Site**	**POC**	**Type**	**71**	**72**	**73**	**74**	**75**	**76**	**77**	**78**	**79**	**80**	**81**	**82**
5 Points	391530023	5	SASS			100	100	100	100	100	100	100	100	100	100
AL - Phenix City	011130001	5	SASS	97	98	100	100	80	100	100	100	80	80	80	100
Alton	171192009	5	SASS	80	100	100	100	100	100	100	100	100	80	100	100
APCD (Barret)	211110048	5	SASS	100	100	100	100	100							
Arendtsville	420010001	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Army Reserve Center	191130037	5	R & P 2300	80	100	100	100	100	100	100	100	100	100	83	100
Arnold	290990012	5	SASS	49	100	100	100	89	90	100	100	100	91	100	100
Ashland Health Department	210190017	5	SASS	100	100	100	100	100	100	100	100	100	100	100	85
Athens	130590001	5	RAAS	100	99	100									
Athens - Met One	130590001	5	SASS			100	100	100	100	85	52	82	45	82	100
Augusta	132450091	5	RAAS	83	100	100									
Augusta - Met One	132450091	5	SASS						100	100	100	100	100	100	100
Bates House (USC)	450790019	5	SASS	100	100	100	100	100	100	100	100	50	83	83	100
Bismarck Residential	380150003	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Bonne Terre	291860005	5	R & P 2300	90	92	100	83	89	90	89	92	90	82	100	89
Bountiful	490110004	5	SASS	100	100	100	71	100	75	100	100	100	100	100	100
Bowling Green-Kereiakes Park	212270007	5	SASS	100	100	100	100	100							
Bristol	515200006	5	SASS	100	100	100	100	100	100	99	100	100	100	100	100
Buffalo	360290005	6	R & P 2300	100	99	71	100	100	100	100	100	100	100	100	40
Buncombe County Board of Education	370210034	5	SASS	80	100	75	100	100	25	85	100	100	100	100	80
Camden	340070003	5	SASS	89	100	100	91	99	87	97	100	63	98	100	100
Canal St. Post Office	360610062	5	SASS	100	100	99	91	100	100	98	94	99	95	92	98
Canton Fire Station	391510017	5	SASS	100	100	100	100	100	100	100	100	100	100	71	
Chester	340273001	5	SASS	100	100	100	100	100	100	100	100	63	90	100	100
Chester (PA)	420450002	5	SASS	100	100	100	100	100	100	85	76	100	60	100	100
Chesterfield	450250001	5	SASS	80	98	100	100	100	100	100	83	100	100	98	100

				Report Batch											
Chickasaw	010970003	5	SASS	100	85	100	100	60							
Children's Park	040191028	5	SASS	100	100	100	100	100	100	100	100	60	100	83	100
Chiwaukee Prairie Site	550590019	5	SASS	100	100	75									
Clio	010050002	5	SASS	100	100	100	100	80							
Columbus	132150011	5	RAAS	100	100	100									
Columbus - Met One	132150011	5	SASS			100	100	100	100	100	100	100	100	100	100
Courthouse Annex-Libby	300530018	5	SASS	100	100	100	100	80	100	100	100	100	80	87	100
Covington - University College	211170007	5	SASS	100	100	77	100	100	100	100	82	100	100	100	100
Crown Z	530630016	5	RAAS	85	100	100	100	100	100	100	100	100	98	100	100
Dearborn	261630033	5	SASS	100	100	50	88	100	100	67	100	100	80	100	100
Del Norte	350010023	5	R & P 2300	100	100	100	100	100	100	99	100	100	100	69	80
Douglas	130690002	5	RAAS	85	100	98									
Douglas - Met One	130690002	5	SASS			100	83	98	100	100	100	99	100	100	100
Duwamish	530330057	6	RAAS	100	100	100	100	100	100	83	100	100	100	100	100
Elkhart Pierre Moran	180390003	5	SASS	100	100	100	100	85	100	100	100	100	100	100	100
Ellis County WMA	400450890	5	SASS	100	100	100	100	100	100	100					
Ellyson	120330004	6	SASS	100	100	100	100	100	50						
Elmwood	421010136	5	SASS	100	100	100	83	80	100	100	100	100	80	17	0
Erie	420490003	5	SASS	100	100	100	100	80	100	100	100	100	100	85	100
Essex - Met One	240053001	5	SASS	100	100	100	99	91	100	88	90	100	100	88	100
Evansville - Mill Road	181630012	5	SASS	100	99	75	100	100	100	100	100	100	100	100	100
Fairbanks State Bldg	020900010	6	SASS	100	100	92	92	100	100	100	100	100	100	100	100
Florence	421255001	5	SASS	80	100	100	100	80	100	100	100	100	80	100	100
Freemansburg	420950025	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Gary litri	180890022	5	SASS	100	100	100	100	99	100	80	100	100	85	83	100
General Hospital	390870010	5	SASS	60	100	100	100	100	100	100	100	80	80	100	85
Grand Junction - Powell Building	080770017	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Grand Rapids	260810020	5	SASS	100	100	100	100	100	100	100	100	100	100	83	100
Greensburg	421290008	5	SASS	60	100	100	100	100	100	100	100	100	100	100	100
Grenada	280430001	5	SASS	80	80	100	100	100							
Hammond Purdue	180892004	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Harrisburg	420430401	5	SASS	80	100	100	100	100	100	100	100	100	100	100	100
Hattie Avenue	370670022	5	SASS	100	100	100	100	100	75	100	100	60	80	100	100

				Report Batch											
Hattiesburg	280350004	5	SASS	100	80	100									
Haynes Pt.	110010042	6	RAAS	100	86	86	100	100	100	91	100	88	100		
Hazard - Perry County Horse Park	211930003	5	SASS	100	100	100	100	100	100	100	100	100	100	88	100
Head Start	390990014	5	SASS	100	100	77	100	100	100	100	100	100	80	100	100
Hendersonville	471650007	5	SASS	100	100	100	100	100	100						
Hickory	370350004	5	SASS	100	100	100	88	100	100	100	83	100	85	100	80
Holland	260050003	5	SASS	100	85	100	100	100	75						
Houghton Lake	261130001	5	SASS	100	100	80	98	100	25	83	100	100	40	83	100
HU-Beltsville	240330030	5	RAAS	100	80	100	100	98	100	100	100	82	80	100	100
Huntsville Old Airport	010890014	5	SASS	100	100	100	100	100	100	88	100	100	100	100	100
IL - Decatur	171150013	5	SASS	100	100	75	100	100	100	100	100	100	100	100	100
IS 52	360050110	5	R & P 2300	100	93	99	100								
IS 52 - Met One	360050110	5	SASS				100	100	100	100	100	100	100	90	100
Jackson Hinds Co.	280490018	5	SASS	100	100	100	67	100	100	100	60				
Jasper Post Office	180372001	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Jefferson Elementary (10th and Vine)	191630015	5	R & P 2300	40	41	11	100	100	100	89	100	100	73	80	98
Kalamazoo	260770008	5	SASS	99	100	100	83	60	25	100	80	100	80	83	100
Kelo	460990006	5	SASS	100	100	100	100	100	100	100	100		100	100	100
Kingsport	471631007	5	SASS	100	100	100	83	100	100	100	100	100	100	100	100
Lake Forest Park	530330024	6	RAAS	100	100	50									
Lancaster	420710007	5	SASS	100	80	100	100	100	100	100	100	100	100	100	100
Laurel	280670002	5	SASS	100	100	100									
Lawrence County	470990002	5	SASS	65	100	100	83	82	100	100	80	100	100	100	100
Lenoir Community College	371070004	5	SASS	100	100	100	83	100	100	98	80	100	100	100	40
Lexington (NC)	370570002	5	SASS	100	100	100	100	100	100	83	100	100	100	100	100
Lexington Health Department	210670012	5	SASS	100	100	100	83	100	98	100	100	100	100	83	100
Liberty	290470005	5	R & P 2300	100	89	92	100	100	100	100	100	89	91	100	100
Liberty (PA)	420030064	6	SASS	100	100	50	100	99	100	100	83	99	78	100	100
Lockeland School	470370023	5	RAAS	100	100	100	100	100	100	100	100	100	100	88	100
London-Laurel County	211250004	5	SASS	100	100	100	100	100							
Lorain	390933002	5	SASS			100	83	100	100	100	100	100	100	100	100

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Lorain County - OH	390930016	5	SASS	100	40	50									
Luna Pier	261150005	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Luray Airport	511390004	5	SASS	98	100	100	83	100	100	100	100	100	100	100	100
Macon	130210007	5	RAAS	80	100	100									
Macon - Met One	130210007	5	SASS			100	100	100	100	98	100	80	100	100	99
Manchester	330110020	5	RAAS	100	100	100									
Maple Canyon	390490081	6	SASS	100	100	100	100	100	100	100	100	80	40	0	0
Mayville Hubbard Township site	550270007	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Mendenhall	370810013	5	SASS	100	100	100	100	98	100	100	100	100	100	99	50
Middletown	390171004	5	SASS	100	99	100	100	100	100	100	100	100	100	83	100
Millbrook	371830014	5	SASS	100	90	100	100	100	91	75	82				90
MN - Rochester	271095008	5	SASS	80	100	100	83	100	100	100	80			100	100
MOMS	011011002	5	SASS	100	98	100	100	100	100	100	60	60	100	100	80
Moundsville Armory	540511002	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Naperville	170434002	5	SASS	100	100	100	100	100	100	100	100	100	100	100	99
New Garden	420290100	5	SASS	85	100	100	83	100	100	96	67	85	100	100	100
NLR Parr	051190007	5	SASS	100	100	75	83	100	100	100	80	100	100	100	100
North Los Angeles	060371103	5	SASS	100	100	100	100	83	100	100	98	85	100	100	100
Northbrook	170314201	5	SASS	100	99	100	100	100	100	100	100	97	100	100	100
OCUSA Campus	401091037	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Olive Street	530330048	6	RAAS	100	100	100	33	100	85	75	100	100	100	80	0
Owensboro Primary	210590005	5	SASS	100	100	100	83	100							
Paducah Middle School	211451004	5	SASS	100	100	100	100	100							
Pearl City	150032004	5	SASS	100	100	100	83	100	100	100	100	100	100	100	100
PerkinstownCASNET	551198001	5	SASS	100	100	100	100	100	100	100	100	100	80	100	100
Perry County	420990301	5	SASS	100	100	100									
Pinnacle State Park	361010003	5	R & P 2300	99	90	89	100	100	100	70	84	90	100	90	89
Platteville	081230008	5	SASS	100	80	100	100	100	100	100	100	60	100	100	100
Pleasant Green (Central MO)	290530001	5	R & P 2300	100	100	100	83	80	100	100	100	100			
Providence	010731009	5	SASS	100	100	100	99	99	100	97	100	75			
Public Health Building	191530030	5	R & P 2300	100	100	100	76	100	100	100	100	100	100	100	100

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Queens College	360810124	6	R & P 2300	73	67	92	91	100	100	100	100	100	100	100	100
RBD	080410011	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Reading	420110009	5	SASS				100	100	100	83					
Reading (temporary)	420110010	5	SASS								60	100	80	100	100
Rochester Primary	360551007	5	R & P 2300	100	99	89	100	78	80	100	100	98	100	83	100
Rockwell	371590021	5	SASS	80	100	100	100	100	100	83	100	100	100	100	100
Rome	131150005	5	RAAS	100	100	100									
Rome - Met One	131150005	5	SASS			100	100	100	100	100	100	100	100	100	100
Rossville	132950002	5	RAAS	100	100	100									
Rossville - Met One	132950002	5	SASS			100	100	100	100	100	80	100	100	100	100
Sault Ste Marie	260330901	5	SASS	100	99	100	100	99	60	0					
Scranton	420692006	5	SASS	100	100	100	100	100	75	100	100	100	100	100	100
Senior Center	040137020	5	SASS	100	100	100	100	100	100	100	100	99	100	100	80
Shenandoah High School	180650003	5	SASS	85	100	100	100	85	100	100	79	100	100	100	100
Shreveport Airport	220150008	5	MASS	84	100	78	100	82	75	100	67		99	40	0
Skyview	121030026	5	SASS	89	100	100	100	100	89	100	93	100	100	100	86
South Charleston Library	540391005	5	SASS	100	100	75	100	100	100	100	100	80	100	100	60
Southwick Community Center	211110043	5	SASS	100	100	100	88	100	100	100	100	100	100	100	100
Spring Hill Elementary School	470931020	5	RAAS	60	80	100	100	60	80	96	100	100	96	83	100
St Johns	040137003	5	SASS	100	100	100	100	100	60	80	100	100	100	100	100
St Theo	390350038	6	SASS	100	100	100	100	100	100	100	80	100	100	100	100
State College	420270100	5	SASS	100	100	100	100	85	100	100	80	100	100	100	100
Steubenville	390810017	5	SASS	100	80	82	100	100	75	100	100	100	100	83	100
Sunrise Acres	320030561	5	SASS	100	100	100	100	100	100	100	100	100	80	100	100
Tacoma	530530029	5	RAAS				100	80	100	100	100	100	100	100	100
Taft	390610040	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Tallahassee Community College	120730012	5	SASS	100	85	100	100	100	100	100	88	100	100	100	100
Taylors Fire Station	450450009	5	SASS	100	90	78	100	100	100	67	100	100	100	100	100
Toledo Airport	390950026	5	SASS	100	80	97	100	100	99	99	100	100	100	83	100
TRNP - NU	380530002	5	SASS	100	100	100	69	100	100	100	100	100	100	100	85
UTC	470654002	5	SASS	100	100	100	100	100	100	100	100	80	100	33	60
VEI - Phoenix	040139998	5	SASS	100	80	100									

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Waukesha, Cleveland Ave. Site	551330027	5	SASS	100	100	100	100	100	100	100	100	99	100	100	100
West Phoenix	040130019	5	SASS	100	100	100									
Whiteface	360310003	5	R & P 2300	90	100	100	100	100	100	100	100	100	100	100	80
Wichita Dept. of Environmental Health	201730010	5	R & P 2300	80	80	100	100	100	75	60	73	51	60	100	80
Wilbur Wright Middle School	391130031	5	SASS	100	40	100	100	100	100	100	99	99	100	84	100
Wylam	010732003	5	SASS	100	100	100	100	98	97	85	100	100	100	100	100
York	421330008	5	SASS	100	100	100	100	100	100	100	100	100	80	100	100
Ypsilanti	261610008	5	SASS	100	82	100	100	98	100	100	100	100	100	100	100