

June 19, 2008

Ms. Margaret Dougherty
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Office of Air Quality Planning and Standards
MC MD-14
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Dear Ms. Dougherty:

Attached is the PDF version of the Annual Data Summary Report for the PM2.5 Chemical Speciation Program.

If you have any questions or comments, please feel free to call me at 541-6483, or e-mail at rkunj@rti.org. Thank you for your continued support.

Sincerely,



R. K. M. Jayanty, Ph.D.
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/dmh

Attachment

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RTI/08858/06ADS
June 19, 2008

Annual Data Summary Report for the Chemical Speciation of PM_{2.5} Filter Samples Project

January 1 through December 31, 2007

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

EPA Contract No. 68-D-03-038

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Executive Summary

Introduction

The U.S. Environmental Protection Agency (EPA) established a PM_{2.5} Chemical Speciation Network (CSN) in 1999. The CSN included the Speciation Trends Network (STN) (a core set of 54 speciation trends analysis sites), as well as some 135 other sites. RTI is assisting in the PM_{2.5} CSN 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, 2007, 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 RTI International (RTI) laboratories were not audited by EPA personnel during 2007; however, RTI received performance audit samples as part of a multi-lab study conducted by EPA's Montgomery Laboratory.

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), 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 to quickly recognize and correct future filter debris problems. This enhanced procedure has continued, and data quality for gravimetric mass results was generally found to be satisfactory during 2007.

Minimal problems with laboratory operations and filter media were reported by the Ion and Organic and Elemental Carbon (OC/EC) laboratories during 2007. Interlaboratory performance comparison results were satisfactory.

The 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 National Air and Radiation Environmental Laboratory were satisfactory.

Operations in RTI's Sampling Handling and Archiving Laboratory (SHAL) proceeded normally during 2007. A small number of samples were missed due to late return of coolers from the field sites. Shipping containers ("coolers") were changed since 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 2007 (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 February 2000 was reloaded with revised uncertainty values. Data continues to be reviewed and posted to a secure Web site 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 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

One Corrective Action Request (CAR) was issued during 2007. 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
0011	SHAL	Coldroom failure	Cooling unit was repaired	None
none	SHAL	Late-arriving coolers	DOPO and others are notified whenever coolers are received late from the field	Data are flagged as missing
none	XRF	Harmonize XRF uncertainty calculations	RTI, 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 February 2000

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 (PM). The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations ($\mu\text{g}/\text{m}^3$ of air) of particles with aerodynamic diameters less than 10 micrometers (the PM₁₀ standard) and less than 2.5 micrometers (the PM_{2.5} 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 PM, 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 Network (CSN) included the Speciation Trends Network (STN) (a core set of 54 speciation trends analysis sites) and some 135 other sites from State and local agencies that are supported by RTI International (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, 2007. Chemical speciation data will be used to support development of emission-mitigation approaches to reduce ambient PM_{2.5} 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 PM_{2.5} and its components, and evaluating potential linkages to health effects.

RTI is supporting the PM_{2.5} CSN 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 CSN 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 energy-dispersive x-ray fluorescence [EDXRF]), soluble anions and cations (by ion chromatography), and

carbonaceous species (using the Sunset Labs thermal-optical transmittance system). Desert Research Institute (DRI) has performed the IMPROVE_A carbon analysis for filters collected by URG 3000N samplers using thermal-optical analysis in both the reflectance and transmittance mode. Analysis of semi-volatile organic compounds and examination of particles by electron or optical microscopy have not been performed.

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 QA/quality control (QC) system. RTI's Quality Management Plan (QMP), 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 RTI's 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, 2007. 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 (XRF) 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 Pyro1C) on quartz filters using thermal optical transmittance. DRI has performed the IMPROVE_A carbon analysis using the thermal optical reflectance for the samples collected by URG 3000N samplers. 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 CSN 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 CSN data set:

- Accuracy. All analyses standardized to reference values that are traceable to the National Institute of Standards and Technology (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 CSN is outside of RTI's control. The CSN sites are generally selected to evaluate population-based health effects and tend to be in populated areas. Because of this, the CSN has relatively little coverage of rural sites in the western United States, where IMPROVE sites predominate.
- Comparability. Intercomparison studies recently conducted by EPA have shown good agreement with programs such as the Federal Reference Methods (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 CSN 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, URG 3000N, PM_{2.5} 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, and iron, 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** of this report.

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 data set:

- 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 CSN and IMPROVE. The appropriate OC correction factor may differ among the four different CSN 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 CSN 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 CSN and other networks. RTI is working with the University of California at Davis (UC Davis) and other experts in XRF to define an acceptable method for determining XRF uncertainty. This work by RTI has resulted in a White Paper that was delivered to EPA in 2006.¹ A peer-reviewed publication is expected on this topic in 2008.
 - Realism of total uncertainty estimates based on statistics from sites with side-by-side collocation of samplers. Collocation results in the 2005 and 2006 reports 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

2.2 Summary of Data Completeness

Data completeness network-wide exceeded 95% for 2007. 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 of this report includes more details of the sampling events and completeness for the Reporting Batches delivered in 2007. **Table B.1** shows the total number of sampling events included in each Reporting Batch. **Table B.2** provides the total number of records

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, “PM_{2.5} 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.

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 AQS 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 AQS 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. One Corrective Action Request was created during 2007 and is discussed in Sections 2.3.5 and 3.6.1.

2.3.1 Gravimetric Mass

No significant quality issues were identified in the Gravimetric Laboratory in 2007. 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 2007 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 CSN contract.

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 Organic Carbon/Elemental Carbon Analysis

There were no corrective actions taken during this reporting period.

2.3.5 Sample Handling and Archiving Laboratory (SHAL)

During 2007, there was one corrective action taken in the SHAL. This concerned a failure of the walk-in cold room used to store sampled filters returned to RTI from the field sites. The CAR was initiated on March 5, 2007, and closed on June 22, 2007. The walk-in cold room was repaired immediately upon discovery of the problem, but RTI determined that having a continuous record of the cold room temperatures would be desirable to document failures of this type in the future. The solution was to place a temperature-monitoring data logger in the cold room. This data will be used to assess the impact of any future failures of the cold room. See Section 3.6.1 for more discussion.

2.3.6 Data Processing

There were no corrective actions taken during this reporting period; however, uncertainties and MDLs for data on the prior contract (2/2000 to 7/2003) were calculated and loaded to AQS. These values had not been required under the prior contract. The uncertainties for the carbon values for the samples collected by URG 3000N have not yet been posted into AQS.

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.** This continues to be an issue with the R&P 2300 samplers, in which sodium carbonate is used in the denuder before the nylon filter. High outliers are sometimes seen in the sodium ion data for this sampler type. High values for certain metals are sometimes seen in the MetOne and Andersen blank data, probably from the filter modules or other sampler components.

3.0 Laboratory Quality Control Summaries

3.1 Gravimetric Laboratory

The RTI Gravimetric Laboratory's two weigh chambers were used to tare 17,127 Teflon filters for the PM_{2.5} speciation program between January 1 and December 31, 2007. During the same time period, the laboratory performed final (post-sampling) weighings of 16,643 Teflon filters for the program. The difference between the number of tared filters and the number of final filters is partly due to the inherent lag time between the initial and final weighing sessions. Determination of PM_{2.5} 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 2007. The laboratory continued to proactively 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 2007 in either this enhanced inspection or in the routine visual inspection in the chamber.

The laboratory identified an issue with the calibration of the Dickson D200 data loggers routinely purchased as a secondary means of monitoring temperature and humidity in the chambers. We have used Dickson calibration services to calibrate our data loggers since we set up the laboratory in 1998, but the D200 data logger is actually manufactured by Veriteq. Dickson discontinued calibration/adjustment support for the Veriteq data logger, so we contacted Veriteq to identify an alternate calibration laboratory. We have scheduled an A2LA-accredited NIST-traceable 3-point calibration of three D200 data loggers in the Veriteq Test and Calibration Laboratory for February 2008. The primary sensors and process board controllers for the chamber temperature and humidity systems are calibrated annually and were calibrated on-site in December 2006 and December 2007. The data loggers in use track with the chamber sensor outputs. In addition, RTI upgraded its building-control system in 2007 to include enhanced monitoring of control systems, including the chamber-control systems. This upgrade allows RTI's Facilities and Maintenance Control Department staff to be notified of chamber temperature and humidity excursions more efficiently.

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 \pm 3 μ g [Standard reference weights initially calibrated by Troemner at purchase. Verified by the laboratory in conjunction with 2007 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 41145 03/07/07 Verification: 99.99805 mg \pm 0.00086 Laboratory Tolerance Interval: 99.994–100.002 mg	Average = 99.997 mg Std Dev = 0.0006 for 469 weighings	Laboratory average falls within tolerance interval.
		100-mg S/N 14056 02/02/06 Verification: 100.0008 mg \pm 0.0025 Laboratory Tolerance Interval: 99.995–100.0062 mg	Average = 99.995 mg Std Dev = 0.0009 for 1278 weighings	Laboratory average falls within tolerance interval.
		200-mg S/N 41147 03/07/07 Verification: 200.00646 mg \pm 0.00086 Laboratory Tolerance Interval: 200.003–200.010 mg	Average = 200.006 mg Std Dev = 0.0008 for 465 weighings	Laboratory average falls within tolerance interval.
		200-mg S/N 14059 02/02/06 Verification: 200.0014 mg \pm 0.0025 Laboratory Tolerance Interval: 199.996–200.007 mg	Average = 199.994 mg Std Dev = 0.0012 for 1279 weighings	Laboratory average falls below lower tolerance interval. The reference weight displayed stable mass over time and was monitored by the laboratory. It is likely the weight received a nick or scratch in handling.
		<u>Chamber 2</u> 100-mg S/N 58096 03/07/07 Verification: 100.00290 mg \pm 0.00086 Laboratory Tolerance Interval: 99.999–100.007 mg	Average = 100.003 mg Std Dev = 0.0007 for 688 weighings	Laboratory average falls within tolerance interval.
		100-mg S/N 58097 03/07/07 Verification: 100.00259 mg \pm 0.00086 Laboratory Tolerance Interval: 99.999–100.006 mg	Average = 100.002 mg Std Dev = 0.0012 for 591 weighings	Laboratory average falls within tolerance interval.

(continued)

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 \pm 3 μ g	200-mg S/N 41146 03/07/07 Verification: 200.00357 mg \pm 0.00086 Laboratory Tolerance Interval: 200.005–200.013 mg 200-mg S/N 58099 03/07/07 Verification: 200.00548 mg \pm 0.00086 Laboratory Tolerance Interval: 200.001–200.009 mg	Mean = 200.008 mg Std Dev = 0.0010 for 688 weighings Mean = 200.004 mg Std Dev = 0.0011 for 590 weighings	Laboratory average falls within tolerance interval. Laboratory average falls within tolerance interval.
Balance calibrations	Auto (internal) calibration daily External calibration annually or as needed	Daily All balances inspected and externally calibrated by Mettler Toledo on August 8, 2007, using NIST-traceable weight	N/A N/A	 Next inspection and external calibration scheduled for August 2008
Balance audits	Annually	Audits of all balances performed by RTI Quality Systems Program personnel on November 15, 2007, 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.
RH/T monitoring devices calibrations	Annually	Chamber temperature and humidity sensors, temperature and humidity controllers, and process alarm control board (mother board) calibrated by Environmental Specialties – LUWA on December 11, 2007 Contacted Veriteq Data Logger Test and Calibration Services for guidance on calibration of Dickson D200 data loggers manufactured by Veriteq	N/A N/A	Chamber sensors, controllers, and process boards are calibrated on-site annually by LUWA-Environmental Specialties Calibration scheduled for February 2008

(continued)

Table 3-1. (continued)

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Laboratory (Filter) blanks	Initial weight \pm 15 μ g	2121 total replicate weighings of 319 individual laboratory blanks	Average difference between final and initial weight = 3 μ g Std Dev = 4.2 Min wt change = 0 μ g Max wt change = 28 μ g	7 total replicate weighings of 2 individual laboratory blank filters (0.3% of the replicate weighings; 0.6% of the individual laboratory blanks) exceeded the 15 μ g criterion. Outliers were split between upper and lower outliers, as expected.
Replicates	Initial weight \pm 15 μ g	17,389 individual filters were weighed as pre-sampling (tared) replicates 6,504 individual filters were weighed as post-sampling replicates	Average = 0.4 μ g Average = 0.5 μ g	30 replicate weighings (0.2% of the weighings) exceeded the 15 μ g criterion on the first pass. Outliers were reweighed in order to confirm a mass value with two weights within 5 μ g of each other. These third weighings brought the number of individual outlier filters down to 2 filters (0.01% of the filters weighed). 40 replicate weighings (0.6% of the weighings) exceeded the 15 μ g criterion on the first pass. Outliers were reweighed to confirm value with two weights within 5 μ g of each other. These third weighings brought the number of individual outlier filters down to 3 filters (0.05% of the filters weighed.)

(continued)

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 6236013 (Rec'd lot two times and ran a lot stability test each time)	24 hours = +2 µg 48 hours = +2 µg 72 hours = +2 µg 96 hours = -3 µg	Weight changes fall within required range
			24 hours = +1 µg 48 hours = 0 µg 72 hours = 0 µg 96 hours = +1 µg	Weight changes fall within required range
		Whatman Lot 7050009	24 hours = -3 µg 48 hours = -3 µg 72 hours = -1 µg 96 hours = +1 µg	Weight changes fall within required range
		Whatman Lot 7072008	24 hours = 0 µg 48 hours = -2µg 72 hours = -1 µg 96 hours = 0 µg	Weight changes fall within required range
		Whatman Lot 7176034	24 hours = +1 µg 48 hours = +1 µg 72 hours = 0 µg 96 hours = 0 µg	Weight changes fall within required range

3.1.3 Summary of QC Results

Internal QC values generated by the laboratory usually met the criteria shown in **Table 3-1**; however, 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 Determination of Uncertainties and Method Detection Limits

The Gravimetric Laboratory's MDL calculations are based on replicate weighings of a large number of filters from filter lot acceptance batches. Because determination of gravimetric mass requires two separate weighings, each of which contributes to the total uncertainty, a 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. MDLs reported to AQS are shown in Appendix A. All balances use the same MDLs.

3.1.5 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	January 17–19, 2008	RTI FRM and CSN Project QA Officers	No significant deficiency findings were reported by the QA Officers. The auditors inspected both chambers with a black light to evaluate chamber cleaning and made the following comment: “By checking for dust with a black light in Chamber 1 immediately after cleaning and in Chamber 2 a little more than a month after its last cleaning, it is clear that our cleaning procedures are effective.”
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 were posted on the EPA AMTIC Web site on March 28, 2007. RTI’s Gravimetric Laboratory performance in the study was good, with the RTI lab agreeing with the EPA NAREL lab within 6 µg. EPA NAREL conducted another study in the fall of 2007. Those results have not yet been received.
Accreditation		Louisiana Environmental Laboratory Accreditation Program (LELAP)	RTI is accredited for the determination of fine particulates in ambient air by the FRM for PM _{2.5} .

3.2 Ions Analysis Laboratory

The Ion Analysis Laboratory used four ion chromatographs to extract and analyze 20,712 cation analyses (sodium, potassium, and ammonium); 22,028 anion analyses (nitrate and sulfate). The analyses were performed on the CSN program during the period January 1 through December 31, 2007.

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 QA/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 and 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 PM_{2.5} 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⁺, NH₄⁺, and K⁺ for cation analyses; NO₃⁻ and SO₄²⁻ 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 PM_{2.5} Quality Control/ Quality Assurance Checks

QA/QC Check	Frequency	Requirements
Calibration Regression Parameters	Daily	$r \geq 0.999$
Initial QA/QC Checks: <ul style="list-style-type: none"> ▪ RTI prepared QC sample at mid- to high-range concentration ▪ RTI prepared QC sample at lower-end concentration ▪ Commercially prepared, NIST traceable QA sample 	Daily, immediately after calibration Daily, immediately after calibration Daily, immediately after calibration	Measured concentrations within 10% of known values Measured concentrations within 10% of known values Measured concentrations within 10% of known values
Periodic QA/QC Checks: <ul style="list-style-type: none"> ▪ Replicate sample † ▪ QA/QC sample ▪ Matrix spiked sample extract ▪ Duplicates ‡ 	Every 20 samples Every 20 samples Every 20 samples At least one per day	RPD = 5% at 100x MDL* RPD = 10% at 10x MDL* RPD = 100% at MDL* Measured concentrations within 10% of known values Recoveries within 90 to 100% of target values No limit set. This data gathered for comparability studies.

(continued)

Table 3-4. (continued)

QA/QC Check	Frequency	Requirements
▪ 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 Percent Difference

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

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

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

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

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

Table 3-5. Minimum Detection Limit* 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 $\mu\text{g}/\text{filter}$

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 the following:

- 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	385	0.6	98.1%	1.0%	0.569	0.606
	QA-CPI_MED-HI	304	3.0	101.1%	1.0%	2.936	3.169
	RTI-QC-HIGH	318	6.0	102.0%	0.7%	5.847	6.238
	RTI-QC-LOW	586	0.6	98.1%	0.9%	0.570	0.618
	RTI-QC-MED	748	1.5	98.9%	0.9%	1.439	1.538
Sulfate	QA-CPI_LOW	385	1.2	100.0%	2.0%	1.138	1.471
	QA-CPI_MED-HI	304	6.0	103.3%	1.3%	5.992	6.412
	RTI-QC-HIGH	318	12.0	103.6%	1.0%	11.912	12.677
	RTI-QC-LOW	586	1.2	100.3%	1.1%	1.166	1.247
	RTI-QC-MED	748	3.0	101.8%	1.1%	2.940	3.268

(continued)

Table 3-7. (continued)

Analyte	Sample ID	Cnt	Conc. $\mu\text{g/mL}$	Avg % Rec *	SD	Min	Max
Sodium	GFS 0.4 PPM QA	608	0.4	102.1%	1.9%	0.386	0.450
	GFS 4.0 PPM QA	592	4.0	99.9%	1.2%	3.797	4.185
	RTI 2.0 PPM QC Reg Std	427	2.0	100.4%	1.3%	1.928	2.127
	RTI 5.0 PPM QC	367	5.0	100.6%	1.2%	4.856	5.265
Ammonium	GFS 0.4 PPM QA	608	0.4	101.2%	3.6%	0.342	0.456
	GFS 4.0 PPM QA	592	4.0	101.5%	1.9%	3.681	4.937
	RTI 2.0 PPM QC Reg Std	427	2.0	101.4%	2.0%	1.882	2.175
	RTI 5.0 PPM QC	367	5.0	102.8%	2.0%	4.823	6.039
Potassium	GFS 0.4 PPM QA	608	0.4	99.3%	1.8%	0.335	0.415
	GFS 4.0 PPM QA	592	4.0	98.7%	1.4%	3.726	4.186
	RTI 2.0 PPM QC Reg Std	427	2.0	99.0%	1.5%	1.917	2.170
	RTI 5.0 PPM QC	367	5.0	99.2%	2.0%	4.625	5.548

* Acceptance criteria for average percent recovery is $\pm 10\%$.

Average recoveries for the QC samples ranged from 98.1 to 103.6% for the year. Average recoveries for the QA samples ranged from 98.1 to 103.3% for the year.

Table 3-8 shows percent recovery for all analyte spikes for the year. Average recoveries for the spikes ranged from 100.0 to 100.9%.

Table 3-8. Average Percent Recovery for Spikes

Analyte	Avg Recovery *	StDev	Count	Min	Max
Nitrate	100.4%	1.7%	702	92.6%	108.6%
Sulfate	100.7%	1.4%	702	92.9%	107.8%
Sodium	100.6%	1.9%	678	87.9%	109.7%
Ammonium	100.9%	2.1%	678	89.4%	108.7%
Potassium	100.0%	1.8%	678	88.3%	111.2%

* Acceptance criteria for average percent recovery is $\pm 10\%$

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 (N) and Reagent Blank Values (ppm) for all Analytes

Analyte	Type	Count	Avg	StDev	Min	Max
Nitrate	N QC	365	0.007	0.010	0.000	0.038
	REAG	712	0.001	0.003	0.000	0.029
Sulfate	N QC	365	0.002	0.006	0.000	0.027
	REAG	712	0.002	0.005	0.000	0.036
Sodium	N QC	374	374	374	-0.007	0.035
	REAG	501	0.000	0.002	-0.009	0.016
Ammonium	N QC	374	0.000	0.000	0.000	0.000
	REAG	501	0.000	0.000	0.000	0.000
Potassium	N QC	374	0.000	0.000	0.000	0.000
	REAG	501	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 µg, 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 two instruments indicates very close results.

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

Table 3-10. Between-instrument Comparability

Analyte	QA/QC Type	Conc., µg/mL	Cnt	Average * Difference	Standard Deviation of Diff.	Minimum Diff.	Maximum Diff.
Nitrate	QA-CPI_LOW	0.6	127	-0.002	0.004	-0.016	0.008
	QA-CPI_MED-HI	3.0	86	-0.004	0.027	-0.080	0.150
	RTI-QC-HIGH	6.0	88	0.009	0.042	-0.182	0.153
	RTI-QC-LOW	0.6	324	-0.005	0.046	-0.586	0.031
	RTI-QC-MED	1.5	496	-0.005	0.012	-0.048	0.056

(continued)

Table 3.10. (continued)

Analyte	QA/QC Type	Conc., µg/mL	Cnt	Average * Difference	Standard Deviation of Diff.	Minimum Diff.	Maximum Diff.
Sulfate	QA-CPI_LOW	1.2	127	-0.004	0.010	-0.048	0.017
	QA-CPI_MED-HI	6.0	86	-0.011	0.054	-0.172	0.290
	RTI-QC-HIGH	12.0	88	0.003	0.088	-0.432	0.300
	RTI-QC-LOW	1.2	322	-0.004	0.010	-0.049	0.062
	RTI-QC-MED	3.0	496	-0.006	0.022	-0.117	0.087
Sodium	GFS 0.4 PPM QA	0.4	337	0.002	0.011	-0.050	0.029
	GFS 4.0 PPM QA	4.0	312	-0.014	0.046	-0.206	0.201
	RTI 2.0 PPM QC	2.0	164	0.001	0.027	-0.095	0.056
	RTI 5.0 PPM QC	5.0	118	-0.009	0.059	-0.185	0.115
Ammonium	GFS 0.4 PPM QA	0.4	337	0.004	0.019	-0.078	0.042
	GFS 4.0 PPM QA	4.0	312	0.000	0.112	-0.419	0.884
	RTI 2.0 PPM QC	2.0	164	0.013	0.049	-0.168	0.106
	RTI 5.0 PPM QC	5.0	118	0.033	0.100	-0.218	0.286
Potassium	GFS 0.4 PPM QA	0.4	337	0.001	0.009	-0.060	0.039
	GFS 4.0 PPM QA	4.0	312	-0.003	0.042	-0.197	0.126
	RTI 2.0 PPM QC	2.0	164	0.001	0.026	-0.134	0.057
	RTI 5.0 PPM QC	5.0	118	0.008	0.058	-0.197	0.141

* 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, Performance Evaluations, Training, and Accreditations

In November 2007, RTI's Ion Analysis Laboratory received 12 filters from NAREL that NAREL had prepared as part of a PE study. No on-site audit was performed by NAREL during 2007; however, PE samples were received and analyzed. A report of these results is in preparation by NAREL, but was not finalized at the time of the preparation of this report.

3.3 Organic Carbon/Element Carbon Laboratory

The RTI OC/EC Laboratory analyzed 13,831 quartz filter samples by the STN method during the period January 1, 2007, through December 31, 2007, 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 CSN analyses. The R, S, and T analyzers were used for the CSN program throughout 2007, whereas the F analyzer was used for the CSN program from January 1, 2007, through June 26, 2007, at which time it was devoted to other research work.

As a subcontractor to RTI, the DRI Carbon Analysis Laboratory received 3,683 quartz-fiber filters during the period May 17, 2007, through December 26, 2007 (excluding special study samples). As of December 31, 2007, DRI analyzed 3,305 quartz-fiber filter samples using the IMPROVE_A method and reported the results of those analyses to RTI,³ using eight DRI Model 2001 Thermal/Optical Carbon Analyzers.

3.3.1 Quality Issues and Corrective Action

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

3.3.2 Description of QC Checks Applied

QC checks, acceptance criteria, and 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 SHAL or the QA Officer may have assigned additional flags to the quartz filter samples based on field data or additional data validation checks. See Section 5.2.1 for a summary of all flags reported to AQS.

³ Chow, J.C., J.G. Watson, L.W. Chen, M.C. Chang, N.F. Robinson, D. Trimble, and S. Kohl. 2007. The IMPROVE_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database. *J. Air Waste Manage. Assoc.*, **57**:1014–1023.

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	$MDL \leq 0.5 \mu\text{g C/cm}^2$	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 $\leq 0.3 \mu\text{g/cm}^2$, and (2) Calibration peak area 90 to 110% of average for the weekly 3-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.
3-Point Calibration	Weekly	(1) Correlation Coefficient (R^2) ≥ 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 3-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 3-point calibration, and (3) FID response factor is 90 to 110% of average response factor for last 3-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 $10 \mu\text{g C/cm}^2$ — less than 10% RPD, (2) TC Values 5 - $10 \mu\text{g C/cm}^2$ — less than 15% RPD, (3) TC Values less than $5 \mu\text{g C/cm}^2$ — within $\pm 0.75 \mu\text{g C/cm}^2$.	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
LFW	Filter inspection flag – filter sampled on wrong side	2
LFU	Filter inspection flag – non-uniformity (Duplicate analysis failed applicable duplicate criterion.)	62
Total Number of Analyses Flagged by OC/EC Analysts		64
Total Number of OC/EC Analyses Reported to SPIMS		13,831
Percent of OC/EC Analyses Flagged by Analysts		0.448%

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 the following:

1. FID response to the internal standard (expressed as a percentage of the average FID response to the internal standard for the 3-point calibration),
2. Recovery (mass of carbon measured expressed as a percentage of the mass of carbon in the spiked volume of standard used), and
3. FID response factor (expressed as a percentage of the average FID response factor for the 3-point calibration).

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

1. Internal standard area (as a percentage of the average internal standard area for the last 3-point calibration),
2. Recovery (mass of carbon measured expressed as a percentage of the mass of carbon in the spiked volume of standard used), and
3. FID response factor (as a percentage of the average response factor for the last 3-point calibration).

A calibration check is acceptable only if it meets all three criteria. All 2007 calibration checks were acceptable.

Table 3-13. OC/EC Instrument Blank Statistics

Blank Statistic	OC/EC Analyzer			
	R	S	T	F
Number of Instrument Blanks	252	257	273	146
Mean Response ($\mu\text{g C}/\text{cm}^2$)	0.012	0.029	0.021	0.028
Standard Deviation	0.013	0.027	0.023	0.041
Minimum Response ($\mu\text{g C}/\text{cm}^2$)	0.000	0.000	0.001	-0.114
Maximum Response ($\mu\text{g C}/\text{cm}^2$)	0.120	0.226	0.157	0.265

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 1,572 duplicate STN analyses were run under the laboratory support contract in 2007. OC/EC analysis results for 62 (or 3.94%) of those duplicates failed the applicable duplicate criterion and were flagged as coming from a filter with a non-uniform deposit.

3.3.3.4 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, by back-diffusion from the oxidizer oven (immediately downstream from the sample oven), or from some type of carry-over from the preceding analysis is not known.

¹The 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.

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

Variable/Statistic		OC/EC Analyzer				
		R	S	T	F	
Number of Full Calibrations Passing All Criteria		50	53	52	26	
Number of Full Calibrations Failing Any Criterion		0	0	0	0	
Slope (counts/ μgC), forced through origin (0,0)	Average	8,282	5,523	6,667	10,053	
	Minimum	7,592	4,775	6,057	9,477	
	Maximum	8,766	6,527	7,100	10,457	
Correlation Coefficient (R^2) (Criterion: ≥ 0.998)	Average	0.9996	0.9996	0.9997	0.9997	
	Minimum	0.9981	0.9985	0.9989	0.9984	
	Maximum	1.0000	1.0000	1.0000	1.0000	
FID Response to Internal Standard as a Percent of Average Internal Standard FID Response for 3-Point Cal (Criterion: 90 to 110%)	Low Cal	Average	100.21%	100.22%	100.12%	100.09%
		Minimum	99.31%	99.10%	98.35%	98.51%
		Maximum	101.42%	102.19%	102.18%	104.27%
	Mid Cal	Average	99.96%	99.95%	99.92%	99.81%
		Minimum	98.97%	98.16%	98.13%	97.07%
		Maximum	101.25%	102.28%	101.78%	101.22%
	High Cal	Average	99.83%	99.84%	99.96%	100.10%
		Minimum	98.73%	98.44%	97.61%	95.16%
		Maximum	101.11%	101.61%	101.97%	103.79%
Recovery: Mass of Carbon Measured as a Percent of Mass of Carbon Spiked (Criterion: 93 to 107%)	Low Cal	Average	101.43%	101.31%	101.91%	102.06%
		Minimum	96.70%	96.14%	96.99%	97.93%
		Maximum	104.97%	104.76%	104.90%	104.72%
	Mid Cal	Average	100.04%	99.70%	99.43%	99.58%
		Minimum	97.49%	95.65%	95.86%	97.17%
		Maximum	104.18%	103.90%	103.68%	102.76%
	High Cal	Average	98.51%	98.94%	98.65%	98.35%
		Minimum	95.21%	95.06%	95.93%	95.03%
		Maximum	100.93%	104.53%	101.88%	100.73%
	All 3 Cals	Average	99.99%	99.98%	100.00%	100.00%
		Minimum	99.91%	99.16%	99.98%	99.98%
		Maximum	100.02%	100.16%	100.02%	100.02%
FID Response Factor as a Percent of Average FID Response Factor for 3-Point Cal (Criterion: 90 to 110%)	Low Cal	Average	101.65%	101.54%	102.03%	102.17%
		Minimum	96.51%	96.63%	96.90%	96.86%
		Maximum	105.28%	104.97%	105.63%	106.09%
	Mid Cal	Average	101.71%	100.91%	100.77%	100.96%
		Minimum	96.72%	94.52%	95.90%	98.06%
		Maximum	105.90%	105.50%	104.72%	104.98%
	High Cal	Average	98.35%	98.79%	98.61%	98.45%
		Minimum	95.22%	95.73%	95.98%	94.60%
		Maximum	101.02%	104.44%	101.21%	100.94%

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

Variable/Statistic		R	S	T	F
Number of Cal Checks Passing All Criteria		185	184	203	98
Number of Cal Checks Failing Any Criterion		0	0	0	0
Internal Standard (IS) Area as a Percent of Average IS Area for 3-Point Cal (Criterion: 90 to 110%)	Average	99.97%	99.59%	99.77%	100.07%
	Minimum	94.37%	90.08%	90.04%	92.65%
	Maximum	103.91%	105.25%	105.97%	107.76%
Recovery: Mass of Carbon Measured as a Percent of Mass of Carbon Spiked (Criterion: 95 to 105%)	Average	100.76%	100.54%	100.49%	99.99%
	Minimum	95.42%	95.21%	95.03%	95.16%
	Maximum	104.99%	104.98%	104.95%	104.82%
FID Response Factor as a Percent of Average Response Factor for 3-Point Cal (Criterion: 90 to 110%)	Average	100.74%	100.15%	100.25%	100.04%
	Minimum	92.82%	90.83%	92.42%	91.56%
	Maximum	107.37%	109.03%	109.20%	108.08%

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 continue the assessment of between-analyzer comparability of OC, EC, TC, and the individual OC Peaks, RTI's OC/EC Laboratory has analyzed a total 294 filters by the STN/TOT method on three Sunset Laboratory Carbon Aerosol Analyzers over a 3-year period. Because carbon fractions are defined by the conditions (temperature, oxygen concentration, and time) under which they evolve from the sample during analysis, carbon fractions (except for TC) are not independent analytes, and the usual statistical approaches to measurement uncertainty are not adequate and may be misleading. As a result, RTI's OC/EC Laboratory has developed an empirical procedure to estimate reasonable uncertainties for all of the reported carbon fractions based on replicate (across-analyzers) analysis data. The results are presented in Section 3.3.5.

Table 3-16. Duplicate OC/EC Analysis Statistics

Variable/Statistic		Analyzer			
		R	S	T	F
Total Number of Duplicate Analyses		460	491	502	119
Number of Analyses Flagged as Failing Duplicate Criteria		19	24	13	6
Percentage of Duplicate Analyses Failing Duplicate Criteria		4.13%	4.89%	2.59%	5.04%
OC Sample/Dup Plot	Slope	0.983	0.803	0.979	0.971
	Intercept	0.072	0.634	0.075	0.077
	R ²	0.983	0.881	0.986	0.990
EC Sample/Dup Plot	Slope	0.959	0.942	0.967	1.010
	Intercept	0.038	0.040	0.015	-0.007
	R ²	0.902	0.947	0.964	0.995
TC Sample/Dup Plot	Slope	0.983	0.840	0.982	0.983
	Intercept	0.097	0.610	0.071	0.046
	R ²	0.980	0.903	0.984	0.993
Pk1C Sample/Dup Plot	Slope	0.988	0.960	0.988	0.935
	Intercept	0.007	0.030	0.007	0.043
	R ²	0.991	0.955	0.987	0.985
Pk2C Sample/Dup Plot	Slope	0.938	0.707	0.961	0.942
	Intercept	0.077	0.296	0.040	0.043
	R ²	0.956	0.777	0.970	0.965
Pk3C Sample/Dup Plot	Slope	0.887	0.482	0.955	0.958
	Intercept	0.078	0.351	0.038	0.020
	R ²	0.924	0.690	0.964	0.963
Pk4C Sample/Dup Plot	Slope	0.985	0.841	0.950	1.001
	Intercept	0.011	0.123	0.035	0.012
	R ²	0.978	0.908	0.971	0.986
PyrolC Sample/Dup Plot	Slope	1.004	0.899	1.102	0.892
	Intercept	0.005	0.005	0.000	0.000
	R ²	0.980	0.963	0.993	0.930

3.3.3.5 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.⁴ 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

⁴ Peterson, M.R., and M.H. Richards. 2006. *Estimation of Uncertainties for Organic Carbon Peaks Data in Thermal-Optical-Transmittance Analysis of PM_{2.5} 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.

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 ($\mu\text{gC}/\text{cm}^2$)
OC	$\pm(0.20 + 0.05 \cdot \text{OC})$
EC	$\pm(0.20 + 0.05 \cdot \text{EC})$
TC	$\pm(0.30 + 0.05 \cdot \text{TC})$
Pk1 C	$\pm(0.20 + 0.05 \cdot \text{Pk1 C})$
Pk2 C	$\pm(0.20 + 0.05 \cdot \text{Pk2 C})$
Pk3 C	$\pm(0.30 + 0.05 \cdot \text{Pk3 C})$
Pk4 C	$\pm(0.30 + 0.10 \cdot \text{Pk4 C})$
Pyrol C	$\pm(0.20 + 1.40 \cdot \text{Pyrol C})$

Table 3-18 gives target MDLs for all reported carbon fractions. MDL values for the five OC Peaks were taken from the absolute uncertainties in **Table 3-17**. This same approach was used to determine reasonable target MDLs for OC, EC, and TC, all of which have proven to be attainable when an analyzer is functioning properly and all operating conditions are under control.

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

Fraction	Target MDL ($\mu\text{gC}/\text{cm}^2$)
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

3.3.3.6 Audits, PEs, Training, and Accreditations

System Audits

RTI's chemical speciation laboratories were not audited in 2007.

Performance Evaluations

RTI's OC/EC Laboratory was one of four laboratories participating in the December 2007 EPA/NAREL interlaboratory comparison study. Analysis results for the PE samples have been reported to EPA/NAREL.

Training

One new analyst was trained during the reporting period. 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 part-time second-shift analyst since August 2007.

Accreditations

There are no accreditation programs for OC/EC analysis.

3.4 DRI Carbon Analysis Laboratory

As a subcontractor to RTI, the DRI Carbon Analysis Laboratory received 3,683 quartz-fiber filters during the period May 17, 2007, through December 26, 2007 (excluding special study samples). As of December 31, 2007, DRI analyzed 3,305 quartz-fiber filter samples for EPA's CSN using the IMPROVE_A method and reported the results of those analyses to RTI.³ Eight DRI Model 2001 Thermal/Optical Carbon Analyzers (designated as units # 6 – 13) were used for the CSN IMPROVE_A analyses.

3.4.1 Quality Issues and Corrective Actions

No quality issues arose, and no corrective actions were needed.

3.4.2 Description of QC Checks Applied

Samples received at the DRI Carbon Laboratory follow the chain-of-custody procedure specified in DRI SOP #2-111.4. Samples are analyzed following DRI SOP # 2-216.1. QC measures for the DRI carbon analysis are summarized in **Table 3-19**. It specifies the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions.

Table 3-19. DRI Carbon Analysis QC Measures

Requirement	Frequency	Calibration Standard	Performed By	Acceptance Criteria	Corrective Action
Temperature Calibration	1/6 months, or after major instrument repair	6 Tempilaq G temperature-indicating liquids	Analyst	Slope within 5% of 1; intercept <15, and $r^2 > 0.98$	Troubleshoot instrument, especially position of thermocouple, and repeat calibration until results are satisfactory
Multipoint Calibrations	1/6 months, or after major instrument repair	CH ₄ /He, CO ₂ /He, sucrose, and KHP QC standards	Analyst	All slopes \pm 5% of average	Troubleshoot instrument and repeat calibration until results are satisfactory
Oxygen Test	1/6 months, or after major instrument repair	N/A	GC/MS Analyst	<100 ppm O ₂	Troubleshoot instrument and repeat test until results are satisfactory
Minimum Detection Limit (MDL)	Initially, then annually or after major instrument change	Lab blanks	Carbon Lab Supervisor, Project Mgr, QA Mgr	Within \pm 10% of previous limits	Troubleshoot instrument and repeat calibration until results are satisfactory
Lower Quantifiable Limit (LQL)	Annually	Field blanks	Carbon lab Supervisor, Project Mgr, QA Mgr	Within \pm 10% of previous limits	Troubleshoot instrument and check samples
System Blank Check	Beginning of analysis day	N/A	Analyst	$\leq 0.2 \mu\text{g C/cm}^2$	Check instrument and filter lots; bake oven
Leak Check	Beginning of analysis day	N/A	Analyst	Oven pressure drops <0.01 psi per sec.	Locate leaks and fix
Laser Performance Check	Beginning of analysis day	Clean blank filter	Analyst	Reflectance 1400–2000 mv; Transmittance 800–1300 mv; both consistent with previous days values	Check laser and filter holder position; adjust potentiometer
Auto-Calibration Check	Beginning of analysis day	NIST 5% CH ₄ /He gas standard	Analyst	Three calibration peak areas should compare and be >20,000	Troubleshoot and correct system before analyzing samples
Calibration Peak Area Check	Every sample	NIST 5% CH ₄ /He gas standard	Analyst	Counts >20,000 and 95–100% of average calibration peak area for the day	Discard analysis result and repeat analysis with second filter punch

Table 3-20 contains a list of quality-related data flags assigned to carbon analysis data and the number of filter analysis results assigned each flag by the DRI Carbon Laboratory during the reporting period. Out of 4,110 runs, there were 387 runs flagged as invalid and 534 runs with blank flags. These were flagged based on notes on the sample Petri dish. Actual sample blank information is not included in the data files sent to DRI by RTI, but was provided to DRI prior to completion of this report for MDL and LQL analysis. In addition, there were 409 runs with replicate (and duplicate) flags. In many cases, there was more than one flag for a sample run. The

flag categories “s” and “v” will generally result in additional runs so that valid results can be reported for the filter. Only flags assigned in DRI Carbon Laboratory data reports to RTI are included in the table. RTI interprets the DRI Carbon Laboratory validation flags and assigns null or quality codes when reporting the data to AQS.

Table 3-20. DRI Carbon Laboratory-Assigned Data Flags

Validation Flag Category	Validation Flag Subcategory	Description	No. of Sample Runs
N		Foreign substance on sample	37
S		Suspect analysis result	4
V		Void (invalid) analysis result	173
	V2	Replicate analysis failed acceptable limit	61
	V3	Potential contamination	12
	V5	Analytical instrument error	44
	V6	Analyst error	56
		Total no. of sample runs (including blank and replicate flags)	4,110

3.4.3 Summary of QC Results

3.4.3.1 Blanks

Tables 3-21 and 3-22 contain the number of instrument system blanks run during the reporting period and the average, standard deviation, maximum, minimum, and median measured blank values for the eight carbon aerosol analyzers used in the program. Specifically, **Table 3-21** gives the system blank values by month for all eight analyzers, and **Table 3-22** gives the system blank values for each of the eight carbon analyzers used during this reporting period.

System blanks are run at the beginning of each analysis day for each operating analyzer, and may be rerun until the analyzer gives readings lower than 0.20 µg C/cm² of TC. However, system blanks are also run to check instrument performance after repairs and adjustments. In addition, system blanks are assigned to the instrument and not to the project. The data in **Tables 3-21 and 3-22** include all reported system blank data that met the blank criterion for TC before reported samples were analyzed using the IMPROVE_A method for this and other projects.

In addition, **Tables 3-23 and 3-24** give the analysis results for the 24-hour (field) and trip blanks, respectively, based upon the blank list provided to DRI by RTI. Average TC concentrations for the 278 field blanks was 1.74 ± 1.2 µg/cm², about 20% higher than the average trip blank of 1.37 ± 0.57 µg/cm² (n=96). No trip blank was run on carbon analyzer #13 due to maintenance. There is no instrument to instrument variation among the 24-hour (field) or trip blanks. Nearly all the TC was in OC, with negligible quantities of EC.

Table 3-21. DRI Carbon Laboratory System Blank Statistics for All Analyzers by Month (5/2007 through 12/2007)

Month	No.	Statistic	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$)													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
May	158	Mean	0.000	0.005	0.012	0.001	0.000	0.000	0.018	0.018	0.000	0.000	0.002	0.003	0.003	0.021
		StdDev	0.002	0.009	0.013	0.006	0.000	0.000	0.021	0.021	0.002	0.003	0.011	0.013	0.013	0.028
		Max	0.017	0.046	0.050	0.054	0.000	0.000	0.086	0.086	0.025	0.038	0.109	0.119	0.119	0.179
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.007	0.000	0.000	0.000	0.011	0.011	0.000	0.000	0.000	0.000	0.000	0.011
Jun	246	Mean	0.001	0.004	0.014	0.001	0.000	0.002	0.019	0.021	0.000	0.002	0.007	0.009	0.008	0.028
		StdDev	0.009	0.009	0.021	0.004	0.000	0.011	0.028	0.031	0.005	0.009	0.023	0.026	0.024	0.041
		Max	0.146	0.056	0.120	0.039	0.006	0.128	0.146	0.172	0.076	0.062	0.171	0.171	0.171	0.196
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.002	0.000	0.000	0.000	0.005	0.005	0.000	0.000	0.000	0.000	0.000	0.008
Jul	287	Mean	0.003	0.005	0.021	0.001	0.000	0.002	0.029	0.031	0.000	0.002	0.007	0.009	0.007	0.038
		StdDev	0.016	0.011	0.023	0.004	0.000	0.010	0.033	0.035	0.003	0.008	0.020	0.023	0.021	0.044
		Max	0.200	0.065	0.113	0.040	0.000	0.096	0.200	0.196	0.034	0.067	0.146	0.159	0.159	0.200
		Min	0.000	0.000	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.018	0.000	0.000	0.000	0.021	0.022	0.000	0.000	0.000	0.000	0.000	0.023
Aug	233	Mean	0.001	0.006	0.017	0.003	0.001	0.001	0.028	0.028	0.000	0.003	0.007	0.009	0.009	0.037
		StdDev	0.005	0.012	0.021	0.010	0.011	0.004	0.036	0.035	0.001	0.009	0.024	0.027	0.029	0.048
		Max	0.060	0.055	0.118	0.090	0.112	0.044	0.183	0.164	0.009	0.057	0.139	0.160	0.160	0.197
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.013	0.000	0.000	0.000	0.016	0.016	0.000	0.000	0.000	0.000	0.000	0.018
Sep	184	Mean	0.000	0.004	0.007	0.001	0.000	0.001	0.012	0.013	0.000	0.000	0.003	0.003	0.002	0.015
		StdDev	0.001	0.009	0.012	0.007	0.001	0.009	0.019	0.022	0.001	0.001	0.014	0.014	0.010	0.025
		Max	0.011	0.042	0.073	0.095	0.010	0.120	0.098	0.151	0.006	0.011	0.120	0.120	0.102	0.159
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.003
Oct	232	Mean	0.000	0.001	0.004	0.000	0.001	0.000	0.006	0.006	0.000	0.001	0.002	0.002	0.003	0.009
		StdDev	0.001	0.004	0.011	0.004	0.010	0.000	0.017	0.014	0.000	0.010	0.010	0.011	0.014	0.021
		Max	0.021	0.040	0.079	0.057	0.152	0.000	0.152	0.103	0.004	0.149	0.078	0.082	0.152	0.152
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nov	215	Mean	0.000	0.001	0.010	0.000	0.001	0.000	0.013	0.012	0.000	0.001	0.004	0.004	0.005	0.017
		StdDev	0.001	0.005	0.016	0.003	0.013	0.000	0.023	0.019	0.000	0.012	0.018	0.018	0.022	0.030
		Max	0.008	0.056	0.092	0.050	0.182	0.000	0.182	0.142	0.005	0.182	0.181	0.181	0.182	0.187
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.005
Dec	255	Mean	0.000	0.005	0.012	0.003	0.000	0.000	0.020	0.020	0.000	0.001	0.001	0.001	0.002	0.022
		StdDev	0.001	0.014	0.022	0.009	0.002	0.001	0.040	0.040	0.001	0.006	0.008	0.010	0.010	0.043
		Max	0.019	0.068	0.166	0.061	0.027	0.012	0.194	0.194	0.006	0.082	0.120	0.123	0.123	0.199
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
May - Dec	1810	Mean	0.001	0.004	0.013	0.001	0.000	0.001	0.019	0.019	0.000	0.001	0.004	0.005	0.005	0.024
		StdDev	0.008	0.010	0.019	0.006	0.007	0.007	0.030	0.031	0.002	0.008	0.018	0.019	0.020	0.038
		Max	0.200	0.068	0.166	0.095	0.182	0.128	0.200	0.196	0.076	0.182	0.181	0.181	0.182	0.200
		Min	0.000	0.000	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.001	0.000	0.000	0.000	0.004	0.004	0.000	0.000	0.000	0.000	0.000	0.006

**Table 3-22. DRI Carbon Laboratory System Blank Statistics for Each Analyzer
(5/2007 through 12/2007)**

Analyzer No.	No.	Statistic	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$)													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
6	181	Mean	0.001	0.001	0.008	0.000	0.001	0.002	0.010	0.011	0.000	0.001	0.003	0.003	0.002	0.013
		StdDev	0.011	0.003	0.014	0.003	0.011	0.012	0.021	0.022	0.002	0.011	0.016	0.016	0.016	0.027
		Max	0.146	0.021	0.064	0.036	0.152	0.120	0.152	0.151	0.025	0.149	0.139	0.139	0.152	0.154
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
7	226	Mean	0.001	0.006	0.016	0.001	0.000	0.002	0.024	0.026	0.000	0.004	0.003	0.007	0.005	0.031
		StdDev	0.004	0.013	0.022	0.004	0.000	0.008	0.031	0.034	0.001	0.012	0.011	0.019	0.017	0.040
		Max	0.037	0.059	0.113	0.040	0.000	0.061	0.147	0.163	0.006	0.067	0.117	0.117	0.117	0.172
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.014	0.014	0.000	0.000	0.000	0.000	0.000
8	203	Mean	0.000	0.001	0.006	0.000	0.001	0.000	0.008	0.007	0.000	0.000	0.002	0.001	0.002	0.009
		StdDev	0.000	0.004	0.017	0.002	0.011	0.001	0.024	0.021	0.001	0.001	0.014	0.009	0.014	0.027
		Max	0.001	0.042	0.166	0.030	0.112	0.014	0.168	0.168	0.006	0.009	0.120	0.123	0.123	0.181
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
9	237	Mean	0.000	0.001	0.007	0.000	0.000	0.000	0.009	0.009	0.000	0.000	0.002	0.002	0.002	0.011
		StdDev	0.001	0.006	0.011	0.003	0.000	0.002	0.015	0.015	0.000	0.001	0.014	0.014	0.014	0.022
		Max	0.010	0.055	0.052	0.050	0.000	0.021	0.108	0.108	0.001	0.019	0.171	0.171	0.171	0.196
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000
10	307	Mean	0.001	0.001	0.013	0.002	0.000	0.000	0.017	0.017	0.000	0.002	0.011	0.013	0.012	0.029
		StdDev	0.005	0.005	0.021	0.008	0.000	0.004	0.029	0.030	0.000	0.006	0.028	0.031	0.031	0.048
		Max	0.060	0.065	0.118	0.095	0.000	0.044	0.146	0.160	0.005	0.057	0.181	0.181	0.181	0.197
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
11	275	Mean	0.000	0.003	0.014	0.001	0.001	0.000	0.019	0.018	0.001	0.001	0.004	0.004	0.005	0.023
		StdDev	0.001	0.008	0.015	0.005	0.011	0.005	0.024	0.022	0.005	0.011	0.015	0.016	0.019	0.031
		Max	0.017	0.056	0.079	0.054	0.182	0.084	0.182	0.130	0.076	0.182	0.126	0.126	0.182	0.189
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.012	0.000	0.000	0.000	0.000	0.013	0.013	0.000	0.000	0.000	0.000	0.014
12	260	Mean	0.000	0.013	0.018	0.004	0.000	0.000	0.035	0.035	0.000	0.002	0.001	0.003	0.003	0.038
		StdDev	0.001	0.016	0.019	0.012	0.003	0.000	0.042	0.041	0.001	0.008	0.007	0.012	0.013	0.045
		Max	0.005	0.068	0.084	0.090	0.051	0.000	0.194	0.194	0.009	0.082	0.082	0.119	0.119	0.199
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.004	0.015	0.000	0.000	0.000	0.000	0.021	0.021	0.000	0.000	0.000	0.000	0.024
13	121	Mean	0.005	0.001	0.021	0.000	0.000	0.003	0.027	0.030	0.000	0.000	0.008	0.008	0.005	0.035
		StdDev	0.024	0.004	0.030	0.001	0.001	0.016	0.037	0.042	0.003	0.001	0.023	0.023	0.018	0.044
		Max	0.200	0.024	0.120	0.013	0.006	0.128	0.200	0.196	0.027	0.009	0.131	0.131	0.129	0.200
		Min	0.000	0.000	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.006	0.000	0.000	0.000	0.000	0.013
6 - 13	1810	Mean	0.001	0.004	0.013	0.001	0.000	0.001	0.019	0.019	0.000	0.001	0.004	0.005	0.005	0.024
		StdDev	0.008	0.010	0.019	0.006	0.007	0.007	0.030	0.031	0.002	0.008	0.018	0.019	0.020	0.038
		Max	0.200	0.068	0.166	0.095	0.182	0.128	0.200	0.196	0.076	0.182	0.181	0.181	0.182	0.200
		Min	0.000	0.000	0.000	0.000	0.000	-0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.004	0.004	0.000	0.000	0.000	0.000	0.006

**Table 3-23. DRI Carbon Analysis Statistics for 24-Hour Field Blanks
(5/2007 through 12/2007)**

Analyzer No.	No.	Statistic	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$)													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
6	20	Mean	0.254	0.537	0.504	0.021	0.000	0.004	1.316	1.321	0.005	0.000	0.000	0.005	0.000	1.321
		StdDev	0.125	0.225	0.223	0.051	0.000	0.014	0.520	0.526	0.014	0.000	0.000	0.014	0.001	0.526
		Max	0.507	1.163	1.067	0.181	0.000	0.046	2.592	2.634	0.046	0.000	0.000	0.046	0.006	2.634
		Min	0.000	0.224	0.144	0.000	0.000	0.000	0.546	0.546	0.000	0.000	0.000	0.000	0.000	0.546
		Median	0.275	0.531	0.434	0.000	0.000	0.000	1.290	1.290	0.000	0.000	0.000	0.000	0.000	1.290
7	47	Mean	0.367	0.589	0.595	0.042	0.000	0.006	1.593	1.598	0.013	0.000	0.000	0.014	0.008	1.606
		StdDev	0.243	0.289	0.198	0.047	0.000	0.024	0.617	0.618	0.046	0.001	0.000	0.046	0.026	0.623
		Max	1.474	1.411	1.116	0.187	0.000	0.145	3.035	3.035	0.289	0.010	0.000	0.289	0.144	3.035
		Min	0.000	0.210	0.310	0.000	0.000	0.000	0.613	0.613	0.000	0.000	0.000	0.000	0.000	0.613
		Median	0.332	0.496	0.550	0.038	0.000	0.000	1.473	1.473	0.000	0.000	0.000	0.000	0.000	1.473
8	36	Mean	0.524	0.696	0.612	0.055	0.000	0.023	1.887	1.910	0.022	0.003	0.000	0.026	0.003	1.913
		StdDev	0.716	0.459	0.188	0.055	0.000	0.035	1.270	1.268	0.033	0.012	0.003	0.042	0.013	1.269
		Max	4.484	3.045	1.122	0.232	0.000	0.128	8.700	8.700	0.128	0.058	0.018	0.185	0.076	8.700
		Min	0.099	0.252	0.277	0.000	0.000	0.000	1.015	1.015	0.000	0.000	0.000	0.000	0.000	1.015
		Median	0.354	0.594	0.578	0.051	0.000	0.003	1.540	1.549	0.001	0.000	0.000	0.008	0.000	1.549
9	57	Mean	0.408	0.532	0.850	0.071	0.004	0.031	1.864	1.891	0.044	0.021	0.004	0.065	0.037	1.929
		StdDev	0.242	0.258	1.089	0.184	0.030	0.114	1.384	1.444	0.201	0.139	0.025	0.310	0.234	1.620
		Max	1.438	1.649	5.437	1.319	0.224	0.794	9.081	9.651	1.488	1.046	0.184	2.309	1.739	11.390
		Min	0.122	0.065	0.244	0.000	0.000	0.000	0.694	0.694	0.000	0.000	0.000	0.000	0.000	0.694
		Median	0.349	0.464	0.524	0.024	0.000	0.000	1.446	1.446	0.000	0.000	0.000	0.000	0.000	1.446
10	32	Mean	0.435	0.377	0.556	0.045	0.000	0.033	1.412	1.445	0.029	0.007	0.012	0.048	0.015	1.460
		StdDev	0.188	0.181	0.492	0.164	0.000	0.123	0.759	0.864	0.107	0.023	0.048	0.135	0.064	0.871
		Max	1.021	0.872	2.987	0.927	0.000	0.682	4.775	5.457	0.588	0.094	0.270	0.682	0.357	5.457
		Min	0.169	0.129	0.253	0.000	0.000	0.000	0.686	0.710	0.000	0.000	0.000	0.000	0.000	0.710
		Median	0.420	0.344	0.418	0.000	0.000	0.000	1.185	1.185	0.000	0.000	0.000	0.000	0.000	1.185
11	47	Mean	0.439	0.555	0.647	0.155	0.000	0.035	1.796	1.831	0.028	0.007	0.002	0.036	0.001	1.832
		StdDev	0.319	0.324	0.343	0.684	0.000	0.088	1.176	1.248	0.065	0.028	0.006	0.091	0.005	1.250
		Max	1.810	1.695	1.911	4.669	0.000	0.458	6.326	6.681	0.291	0.177	0.033	0.491	0.033	6.681
		Min	0.135	0.160	0.256	0.000	0.000	0.000	0.673	0.673	0.000	0.000	0.000	0.000	0.000	0.673
		Median	0.353	0.469	0.545	0.008	0.000	0.000	1.427	1.427	0.000	0.000	0.000	0.000	0.000	1.427
12	37	Mean	0.354	0.774	0.581	0.069	0.006	0.010	1.784	1.788	0.033	0.005	0.000	0.032	0.027	1.816
		StdDev	0.391	0.369	0.265	0.119	0.036	0.064	0.947	0.965	0.049	0.026	0.001	0.044	0.037	0.972
		Max	1.960	1.770	1.778	0.714	0.218	0.386	5.370	5.539	0.228	0.159	0.004	0.169	0.138	5.539
		Min	0.000	0.323	0.232	0.000	0.000	0.000	0.556	0.556	0.000	0.000	0.000	0.000	0.000	0.556
		Median	0.278	0.650	0.537	0.053	0.000	0.000	1.515	1.515	0.000	0.000	0.000	0.000	0.000	1.515
13	2	Mean	0.131	0.504	0.453	0.000	0.000	0.000	1.088	1.088	0.000	0.000	0.002	0.002	0.002	1.090
		StdDev	0.180	0.071	0.032	0.000	0.000	0.000	0.283	0.283	0.000	0.000	0.003	0.003	0.003	0.279
		Max	0.258	0.554	0.476	0.000	0.000	0.000	1.288	1.288	0.000	0.000	0.005	0.005	0.005	1.288
		Min	0.003	0.454	0.431	0.000	0.000	0.000	0.888	0.888	0.000	0.000	0.000	0.000	0.000	0.893
		Median	0.131	0.504	0.453	0.000	0.000	0.000	1.088	1.088	0.000	0.000	0.002	0.002	0.002	1.090
All	278	Mean	0.404	0.581	0.644	0.071	0.002	0.022	1.702	1.722	0.027	0.007	0.003	0.035	0.015	1.737
		StdDev	0.365	0.330	0.568	0.303	0.019	0.081	1.059	1.100	0.105	0.065	0.020	0.155	0.110	1.151
		Max	4.484	3.045	5.437	4.669	0.224	0.794	9.081	9.651	1.488	1.046	0.270	2.309	1.739	11.390
		Min	0.000	0.065	0.144	0.000	0.000	0.000	0.546	0.546	0.000	0.000	0.000	0.000	0.000	0.546
		Median	0.334	0.518	0.531	0.017	0.000	0.000	1.439	1.445	0.000	0.000	0.000	0.000	0.000	1.460

**Table 3-24. DRI Carbon Analysis Statistics for Trip Blanks
(5/2007 through 12/2007)***

Analyzer No.	No.	Statistic	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$)													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
6	13	Mean	0.315	0.312	0.337	0.002	0.000	0.000	0.966	0.980	0.014	0.000	0.000	0.015	0.000	0.981
		StdDev	0.136	0.148	0.164	0.004	0.000	0.000	0.297	0.312	0.049	0.000	0.001	0.049	0.001	0.312
		Max	0.617	0.522	0.665	0.011	0.000	0.000	1.566	1.566	0.177	0.000	0.003	0.177	0.003	1.566
		Min	0.119	0.093	0.113	0.000	0.000	0.000	0.515	0.515	0.000	0.000	0.000	0.000	0.000	0.518
		Median	0.274	0.252	0.308	0.000	0.000	0.000	0.930	0.930	0.000	0.000	0.000	0.000	0.000	0.930
7	16	Mean	0.372	0.368	0.614	0.043	0.000	0.000	1.397	1.397	0.016	0.002	0.000	0.018	0.018	1.415
		StdDev	0.153	0.156	0.338	0.066	0.000	0.000	0.538	0.538	0.045	0.006	0.000	0.046	0.046	0.550
		Max	0.750	0.665	1.233	0.252	0.000	0.000	2.513	2.513	0.178	0.025	0.000	0.178	0.178	2.513
		Min	0.102	0.149	0.256	0.000	0.000	0.000	0.669	0.669	0.000	0.000	0.000	0.000	0.000	0.669
		Median	0.370	0.357	0.499	0.016	0.000	0.000	1.353	1.353	0.000	0.000	0.000	0.000	0.000	1.382
8	19	Mean	0.330	0.322	0.520	0.041	0.000	0.000	1.213	1.231	0.017	0.000	0.001	0.018	0.000	1.231
		StdDev	0.149	0.100	0.304	0.085	0.000	0.000	0.448	0.468	0.033	0.000	0.003	0.033	0.000	0.468
		Max	0.681	0.539	1.643	0.366	0.000	0.000	2.661	2.699	0.119	0.000	0.014	0.119	0.000	2.699
		Min	0.104	0.166	0.257	0.000	0.000	0.000	0.659	0.659	0.000	0.000	0.000	0.000	0.000	0.659
		Median	0.277	0.319	0.415	0.003	0.000	0.000	1.169	1.169	0.000	0.000	0.000	0.000	0.000	1.169
9	16	Mean	0.414	0.376	0.497	0.039	0.000	0.000	1.325	1.345	0.022	0.003	0.000	0.025	0.005	1.351
		StdDev	0.201	0.203	0.173	0.063	0.000	0.000	0.518	0.538	0.028	0.011	0.001	0.034	0.018	0.543
		Max	0.870	0.821	0.870	0.234	0.000	0.000	2.345	2.458	0.069	0.044	0.004	0.113	0.069	2.458
		Min	0.159	0.157	0.233	0.000	0.000	0.000	0.638	0.638	0.000	0.000	0.000	0.000	0.000	0.638
		Median	0.389	0.319	0.498	0.004	0.000	0.000	1.162	1.162	0.003	0.000	0.000	0.003	0.000	1.162
10	1	Mean	0.709	0.195	0.524	0.000	0.000	0.000	1.427	1.458	0.031	0.000	0.000	0.031	0.000	1.458
		StdDev														
		Max	0.709	0.195	0.524	0.000	0.000	0.000	1.427	1.458	0.031	0.000	0.000	0.031	0.000	1.458
		Min	0.709	0.195	0.524	0.000	0.000	0.000	1.427	1.458	0.031	0.000	0.000	0.031	0.000	1.458
		Median	0.709	0.195	0.524	0.000	0.000	0.000	1.427	1.458	0.031	0.000	0.000	0.031	0.000	1.458
11	15	Mean	0.321	0.433	0.730	0.100	0.000	0.000	1.584	1.658	0.070	0.005	0.001	0.075	0.001	1.659
		StdDev	0.149	0.176	0.363	0.083	0.000	0.000	0.562	0.627	0.084	0.012	0.003	0.088	0.003	0.627
		Max	0.568	0.822	1.467	0.324	0.000	0.000	2.763	2.954	0.265	0.044	0.010	0.265	0.010	2.954
		Min	0.104	0.233	0.384	0.000	0.000	0.000	0.819	0.819	0.000	0.000	0.000	0.000	0.000	0.819
		Median	0.300	0.371	0.528	0.084	0.000	0.000	1.428	1.470	0.043	0.000	0.000	0.043	0.000	1.481
12	16	Mean	0.361	0.517	0.576	0.063	0.000	0.000	1.517	1.517	0.027	0.005	0.000	0.032	0.032	1.549
		StdDev	0.137	0.178	0.403	0.115	0.000	0.000	0.610	0.610	0.063	0.015	0.001	0.071	0.071	0.676
		Max	0.581	0.764	1.953	0.457	0.000	0.000	3.383	3.383	0.247	0.059	0.006	0.261	0.261	3.644
		Min	0.103	0.196	0.369	0.000	0.000	0.000	0.736	0.736	0.000	0.000	0.000	0.000	0.000	0.736
		Median	0.378	0.493	0.429	0.027	0.000	0.000	1.373	1.373	0.000	0.000	0.000	0.001	0.001	1.375
All	96	Mean	0.357	0.386	0.549	0.048	0.000	0.000	1.340	1.360	0.027	0.002	0.000	0.030	0.009	1.370
		StdDev	0.159	0.173	0.319	0.081	0.000	0.000	0.529	0.551	0.055	0.009	0.002	0.058	0.036	0.567
		Max	0.870	0.822	1.953	0.457	0.000	0.000	3.383	3.383	0.265	0.059	0.014	0.265	0.261	3.644
		Min	0.102	0.093	0.113	0.000	0.000	0.000	0.515	0.515	0.000	0.000	0.000	0.000	0.000	0.518
		Median	0.334	0.360	0.459	0.014	0.000	0.000	1.279	1.291	0.000	0.000	0.000	0.000	0.000	1.291

*Carbon analyzer no. 13 was removed from service July 24, 2007.

3.4.3.2 Calibrations

Table 3-25 provides summary statistics for full multipoint calibrations by analyzer for the period during which the project samples were analyzed. The next scheduled multipoint calibrations are due in February 2008. The multipoint calibrations are performed semiannually or whenever major repairs or changes are made to the instruments. Separate calibrations are performed using four different sources of carbon: methane (CH₄), carbon dioxide (CO₂), sucrose (C₁₂H₂₂O₁₁), and potassium hydrogen phthalate (KHP). The average of the regression slopes through zero is obtained and used for converting counts to µg C. The slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation and methanator zones and sensitivity of the FID.

Table 3-26 provides summary statistics for the multipoint temperature calibrations of each carbon analyzer. The temperature calibrations are performed every six months or after a major instrument repair. Criteria for an acceptable calibration include a slope within 5% of 1, an absolute value of the intercept <15, and an R² >0.98. As shown in **Table 3-26**, performance for the calibrated analyzers was well within the specified criteria.

Table 3-27 provides a summary of the oxygen-leak tests that are performed every six months or after major instrument repairs. The results are considered acceptable if the O₂ concentration is <100 ppm. The O₂ contents were generally low, in the range of 10 to 30 ppm.

Figure 3-1 shows the daily autocalibration response during the reporting period for each analyzer. Using the Carle valve, the methane standard is injected once in a He-only atmosphere, once in a He/O₂ atmosphere, and finally the normal calibration peak at the end. The three peaks should have similar peak areas if the catalysts are in good condition and the calibration factor holds. Thermogram peaks are compared, and the calibration peak area is examined. Counts that fall below 20,000 result in instrument maintenance. Details of instrument maintenance performed during the reporting period as a result of the autocalibration check are included in **Table 3-28**.

3.4.3.3 Replicate and Duplicate Analyses

Replicate analysis results are from two or more punches from the same sample run on different analyzers. Duplicate analysis results are from two punches from the same sample run on the same analyzer. Table 3-29 gives the criteria and summary statistics for replicate and duplicate IMPROVE_A carbon analyses run on all analyzers for the CSN filter samples during the reporting period. A replicate or duplicate analysis was selected randomly from every group of 10 samples. A total of 409 replicate or duplicate analyses were analyzed during the reporting period. Of the 409 replicates or duplicates, 31 contained f, g, h, or i analysis flags. These were not included in the replicate and duplicate statistical summary. Of the 378 remaining, 35 were duplicate analyses and 343 were replicate analyses.

Table 3-25. DRI Multi-Point Calibration Statistics

Analyzer				
No.	Date	Slope	Scatter	Correlation
6	03/31/07	20.10	0.44	0.9948
	06/01/07	20.11	0.48	0.9946
	08/14/07	20.61	0.62	0.9813
	09/07/07	20.56	0.54	0.9819
7	03/31/07	21.04	0.60	0.9929
	06/01/07	21.09	0.71	0.9926
	08/09/07	22.25	0.30	0.9940
	09/07/07	22.37	0.43	0.9926
8	03/31/07	21.21	0.40	0.9944
	06/01/07	21.24	0.45	0.9941
	08/08/07	20.49	0.75	0.9920
	09/07/07	20.54	0.86	0.9908
9	03/31/07	21.36	0.64	0.9911
	06/01/07	21.28	0.48	0.9926
	08/08/07	21.15	0.53	0.9930
	09/07/07	21.16	0.54	0.9928
10	03/31/07	20.88	0.49	0.9956
	06/01/07	20.78	0.31	0.9964
	08/07/07	20.34	0.61	0.9893
11	03/31/07	21.08	0.73	0.9860
	06/01/07	21.16	0.96	0.9838
	08/14/07	22.45	0.89	0.9788
	09/07/07	22.14	0.48	0.9814
	11/09/07	22.20	0.51	0.9809
12	03/31/07	21.93	0.74	0.9808
	06/01/07	22.06	1.08	0.9769
	08/13/07	21.14	1.39	0.9718
	09/07/07	21.09	1.21	0.9719
13	3/31/2007	21.71	0.42	0.9933
	5/11/2007	21.74	0.48	0.9927
	6/1/2007	21.77	0.54	0.9923

Table 3-26. DRI Temperature Calibration Statistics

Date	Param.	Units	Analyzer No.							
			6	7	8	9	10	11	12	13
Mar 2007	Slope		1.026	1.025	1.021	1.006	1.016	1.030	1.025	1.016
	Intercept	° C	7.247	7.526	7.937	11.515	10.365	5.557	-1.364	11.525
	R ²		0.9859	0.9994	0.9990	0.9990	0.9990	0.9993	0.9994	0.9995
Jul/Aug 2007	Slope		1.036	1.014	1.020	1.014	1.022	1.024	1.018	Removed from Service (7/24/07)
	Intercept	° C	9.698	7.235	10.764	4.419	6.096	8.513	4.916	
	R ²		0.9997	0.9996	0.9995	0.9993	0.9997	0.9990	0.9996	

Table 3-27. DRI Oxygen Test Statistics

Date	Temp (°C)	Analyzer No.															
		6		7		8		9		10		11		12		13	
		Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)	Mean O ₂ (ppm)	Std Dev (ppm)
Apr 2007	50	11.6	0.7	20.8	1.6	8.1	2.1	11.4	2.8	11.0	1.8	19.8	3.3	7.9	2.3	9.7	1.8
	480	13.1	0.6	25.2	0.7	10.4	0.7	12.3	0.5	11.8	0.4	30.4	1.4	8.3	0.5	19.8	0.4
	580	14.8	0.5	25.8	1.0	11.5	0.6	13.3	0.3	11.8	0.4	30.8	0.7	8.5	0.3	20.5	1.2
Nov 2007	140	25.5	0.2	17.2	0.6	14.8	0.2	19.9	0.4	13.7	0.1	7.8	0.3	14.3	0.3	Removed from Service 7/24/07	
	580	25.1	0.2	15.1	0.2	15.0	0.2	20.6	0.3	14.7	0.3	7.4	0.2	12.8	0.3		

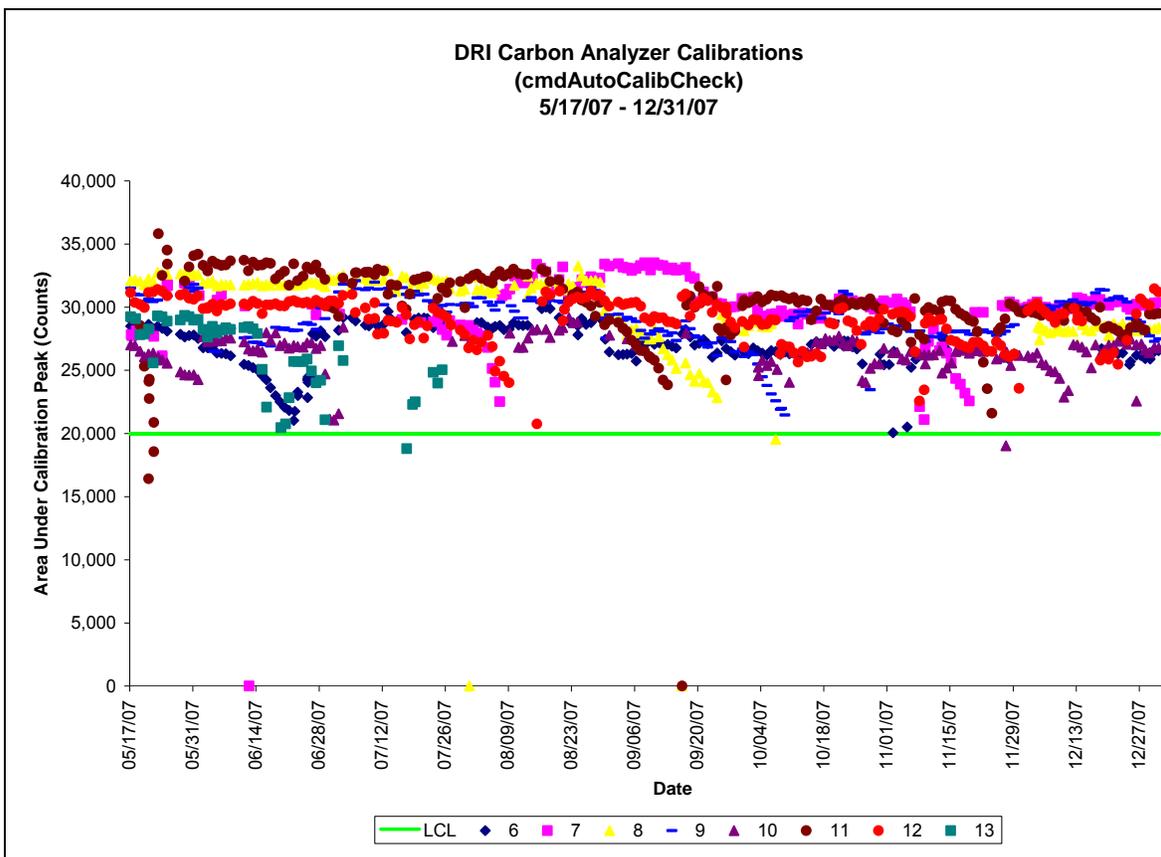


Figure 3-1. DRI Carbon Analyzer Daily Autocalibration Response for the period 5/17/2007 through 12/31/2007.

Table 3-28. Summary of Instrument Maintenance Performed as a Result of Autocalibration Peak Response

Analyzer #	Date	Resolution
7	6/12/07	General instrument maintenance
8	9/16/07	Replaced back valve
8	10/7/07	Replaced Carle valve
10	11/27/07	Replaced thermocouple
11	5/21/07–5/22/07	Replaced Ni catalyst, reducing ferrule, and back valve
11	9/16/07	Rebalanced and checked flow rates
13	7/17/07–7/24/07	General instrument maintenance, instrument removed from service as of 7/24/07

Table 3-29. DRI Replicate Analysis Criteria and Statistics

Range	Criteria	Statistic	Replicates			Duplicates			Units
			No.	TC	OC	EC	No.	TC	
All		Count	343			35			
TC, OC, & EC < 10 µg C/cm ²	< ±1.0 µg C/cm ²	Count	65	70	204	9	9	21	
		No. Fail	6	7	19	1	1	0	
		%Fail	9.2	10.0	9.3	11.1	11.1	0.0	%
		Mean	0.415	0.399	0.398	0.337	0.329	0.140	µg C/cm ²
		StdDev	0.404	0.383	0.410	0.352	0.325	0.181	µg C/cm ²
		Max	2.033	1.934	1.924	1.090	1.070	0.663	µg C/cm ²
		Min	0.001	0.002	0.000	0.069	0.082	0.000	µg C/cm ²
		Median	0.312	0.299	0.293	0.198	0.211	0.084	µg C/cm ²
TC, OC, & EC ≥ 10 µg C/cm ²	TC, OC %RPD < 10% EC %RPD < 20%	Count	278	273	139	26	26	14	
		No. Fail	3	22	16	0	0	0	
		%Fail	1.1	8.1	11.5	0.0	0.0	0.0	%
		Mean	3.40	4.64	8.94	2.28	2.71	3.40	%RPD
		StdDev	2.53	3.67	7.86	2.17	2.01	2.16	%RPD
		Max	14.39	20.39	36.59	8.47	8.03	6.83	%RPD
		Min	0.00	0.02	0.01	0.02	0.25	0.30	%RPD
		Median	3.03	3.68	6.23	1.73	2.14	3.56	%RPD

3.4.4 Assessment of Duplicate and Replicate Analyses

Duplicate and replicate analysis results for TC, OC, and EC agree well, with higher relative percent differences (RPD) at loading levels below 10.0 µg C/cm². Replicate analyses results are more variable than duplicate analyses, but remain within acceptable limits. The small size (25 mm) of the filter used in the IMPROVE_A carbon analysis method does not permit more than three punches (each ~0.5 cm²) to be taken from the filter. Samples not meeting replicate criteria (TC and OC <10% and EC <20% RPD) are re-analyzed or examined for inhomogeneities. Instrument performance is also verified to eliminate instrument issues as a source of replicate or duplicate variation. Higher percent errors in OC and TC may be due to inhomogeneous sample deposit and organic artifact. Higher percent error in EC may be due to the low EC loadings on the samples.

3.4.5 Determination of MDLs and LQLs

Table 3-30 gives estimated MDLs for IMPROVE_A parameters for 2007, which are determined as three times the standard deviation of laboratory blanks. The table also gives estimated lower quantifiable limits (LQLs) for the IMPROVE_A parameters. These LQLs are determined as three times the standard deviation of the 24-hour (field) blanks and trip blanks, based on information provided to DRI after the analyses were completed.

Table 3-30. Estimated MDLs and LQLs for IMPROVE_A Parameters

Type of Blank	No.	Statistic	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$)													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
Lab	670	Mean	0.008	0.025	0.122	0.005	0.000	0.003	0.160	0.163	0.003	0.001	0.002	0.006	0.003	0.166
		StdDev	0.034	0.059	0.139	0.050	0.000	0.022	0.185	0.188	0.017	0.005	0.022	0.029	0.020	0.195
		Max	0.337	0.502	1.132	1.163	0.000	0.399	1.370	1.370	0.189	0.080	0.399	0.399	0.224	1.370
		Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.080	0.000	0.000	0.000	0.000	0.094	0.094	0.000	0.000	0.000	0.000	0.000
		MDL	0.101	0.177	0.416	0.149	0.000	0.065	0.554	0.564	0.050	0.016	0.067	0.087	0.059	0.584
24-Hr	278	Mean	0.404	0.581	0.644	0.071	0.002	0.022	1.702	1.722	0.027	0.007	0.003	0.035	0.015	1.737
		StdDev	0.365	0.330	0.568	0.303	0.019	0.081	1.059	1.100	0.105	0.065	0.020	0.155	0.110	1.151
		Max	4.484	3.045	5.437	4.669	0.224	0.794	9.081	9.651	1.488	1.046	0.270	2.309	1.739	11.390
		Min	0.000	0.065	0.144	0.000	0.000	0.000	0.546	0.546	0.000	0.000	0.000	0.000	0.000	0.546
		Median	0.334	0.518	0.531	0.017	0.000	0.000	1.439	1.445	0.000	0.000	0.000	0.000	0.000	1.460
		LQL	1.096	0.989	1.703	0.910	0.056	0.242	3.177	3.300	0.316	0.195	0.060	0.465	0.330	3.454
Trip	96	Mean	0.357	0.386	0.549	0.048	0.000	0.021	1.340	1.360	0.027	0.002	0.000	0.030	0.009	1.370
		StdDev	0.159	0.173	0.319	0.081	0.000	0.049	0.529	0.551	0.055	0.009	0.002	0.058	0.036	0.567
		Max	0.870	0.822	1.953	0.457	0.000	0.265	3.383	3.383	0.265	0.059	0.014	0.265	0.261	3.644
		Min	0.102	0.093	0.113	0.000	0.000	0.000	0.515	0.515	0.000	0.000	0.000	0.000	0.000	0.518
		Median	0.334	0.360	0.459	0.014	0.000	0.000	1.279	1.291	0.000	0.000	0.000	0.000	0.000	1.291
		LQL	0.478	0.518	0.956	0.244	0.000	0.147	1.588	1.653	0.164	0.028	0.006	0.174	0.109	1.702

3.4.6 Audits, PEs, Training, and Accreditations

The audit report is available on the AMTIC website:

http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/DRI_TSA_Report_2007.pdf

(accessed June 19, 2008).

3.4.6.1 System Audits

On May 15, 2007, EPA/NAREL conducted a Technical Systems Audit (TSA) of DRI's Environmental Analysis Facility (EAF), including its Carbon Laboratory. Its audit report, dated August 21, 2007, found that DRI's Carbon Laboratory was a modern facility with state-of-the-art instrumentation, good documentation, and well-qualified staff and that it met or exceeded compliance with good laboratory practices and SOPs.

3.4.6.2 Performance Evaluations

DRI's EAF, including its Carbon Laboratory, was one of several laboratories participating in the December 2007 EPA/NAREL inter-laboratory comparison study. The results of the PE have not been released yet. In the 2006 PE, DRI's Carbon Laboratory compared favorably with the EPA/NAREL's data.

3.4.6.3 Training

DRI's carbon analysis laboratory currently operates 24 hours a day, 7 days a week. Four full-time technicians and one student from the University of Nevada, Reno, are fully trained in carbon analysis. All new technicians undergo a rigorous 2-week training program, which includes a complete review of SOPs; filter analysis training and documentation; filter shipping and receiving; and basic equipment maintenance and operation.

3.4.6.4 Accreditations

There are no accreditation programs for thermal/optical carbon analysis.

3.5 X-ray Fluorescence Laboratories

The two XRF laboratories, RTI and CLN used 3 and 2 XRF instruments, respectively, to analyze a total of 15,905 filters for 48 elements during the period January 1 through December 31, 2007.

3.5.1 RTI International XRF Laboratory

3.5.1.1 Quality Issues and Instrument Maintenance and Repairs

The following repairs and maintenance were performed for XRF 1:

- 2/14/2007 – Replaced E/I board and repaired tube cable, calibration verified
- 7/11/2007 – PM performed, checked voltages, resolution, and stability
- 3/14/2007 – Replaced tube and detector due to high resolution, calibration required.

The following repairs and maintenance were performed for XRF 2

- 2/26/2007 – Replaced E/I board and repaired tube cable, calibration verified
- 7/10/2007 – PM performed, checked voltages, resolution, and stability
- 8/14/2007 – Replaced PC and upgraded Thermo software, calibration verified.

The following repair and maintenance was performed for XRF 3:

- 3/14/2007 – Replaced high-voltage power supply, calibration verified
- 7/12/2007 – PM performed, checked voltages, resolution, and stability.

No changes were made in the analytical procedures used by the RTI XRF Laboratory, but the ThermoNoran XRF software was upgraded on XRF 2 to be the same as XRF 1; therefore, this instrument required calibration. XRF 3 did not have any major issues during 2007.

3.5.1.2 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 3-31**.

Table 3-31. 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

3.5.1.3 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 3-32 through 3-37**. The percent coefficient of variation (%CV) for the average of all data for each of the six elements ranged between 0.17 and 0.53% for XRF 1, between 0.12 and 0.70% for XRF 2, and between 0.14 and 0.53% for XRF 3.

Table 3-32. Summary of RTI XRF 1 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$, 1/1/2007 through 2/13/2007

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	93	5.18	5.28	5.24	0.02	0.39	-0.1
Ti	93	5.37	5.44	5.40	0.02	0.29	-0.1
Fe	93	6.36	6.45	6.40	0.01	0.21	0.1
Cd	93	5.46	5.55	5.50	0.02	0.35	-0.2
Se	93	3.95	4.04	4.00	0.02	0.53	0.3
Pb	93	10.0	10.2	10.1	0.03	0.33	0.3

Table 3-33. Summary of RTI XRF 1 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$, 7/27/2007 through 12/31/2007

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	294	5.06	5.14	5.10	0.01	0.27	-0.0
Ti	294	6.70	6.79	6.74	0.02	0.31	-0.0
Fe	294	6.78	6.85	6.81	0.01	0.17	-0.1
Cd	294	5.50	5.65	5.54	0.02	0.39	0.0
Se	294	3.79	3.86	3.81	0.01	0.35	-0.1
Pb	294	8.99	9.06	9.02	0.02	0.18	-0.1

Table 3-34. Summary of RTI XRF 2 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$, 1/1/2007 through 2/19/2007

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	108	5.17	5.29	5.20	0.02	0.39	-0.2
Ti	108	6.70	6.79	6.74	0.02	0.33	0.2
Fe	108	6.97	7.06	7.01	0.02	0.28	0.1
Cd	108	5.95	6.06	6.01	0.02	0.39	0.2
Se	108	3.95	4.05	4.00	0.02	0.53	-0.1
Pb	108	9.29	9.39	9.34	0.02	0.17	-0.0

Table 3-35. Summary of RTI XRF 2 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$, 3/15/2007 through 8/15/2007

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	455	5.06	5.14	5.10	0.02	0.32	0.0
Ti	455	6.70	6.79	6.74	0.02	0.31	0.1
Fe	455	6.96	7.05	7.00	0.02	0.23	-0.1
Cd	455	5.62	6.07	6.00	0.04	0.70	0.1
Se	455	4.15	4.24	4.20	0.02	0.43	0.1
Pb	455	9.40	9.49	9.44	0.02	0.20	-0.0

Table 3-36. Summary of RTI XRF 2 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$, 8/23/2007 through 12/31/2007

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	225	5.25	5.33	5.30	0.02	0.30	0.0
Ti	225	6.70	6.98	6.74	0.03	0.46	0.3
Fe	225	6.97	7.05	7.00	0.02	0.22	0.0
Cd	225	5.96	6.05	6.01	0.02	0.27	0.0
Se	225	4.17	4.24	4.20	0.01	0.32	-0.1
Pb	225	9.39	9.46	9.42	0.01	0.12	0.1

Table 3-37. Summary of RTI XRF 3 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$, 1/1/2007 through 12/21/2007

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	720	9.61	9.79	9.71	0.05	0.48	1.27
Ti	720	8.87	9.04	9.00	0.01	0.14	-0.0
Fe	720	10.3	10.5	10.4	0.03	0.30	-0.2
Cd	720	5.60	5.99	5.65	0.03	0.45	-0.1
Se	720	3.94	4.05	4.00	0.02	0.53	-0.0
Pb	720	10.3	10.8	10.6	0.04	0.38	-0.4

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 NIST Standard Reference Material (SRM) filter. Recovery is calculated by comparisons of measured and expected values. **Tables 3-38 through 3-40** show recovery for 7 elements of the 48 elements normally measured. The recovery values for all the elements ranged between 96 and 105% for XRF 1; between 95 and 104% for XRF 2; and between 96 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. In early 2007, NIST SRM 2783 (unmounted SRM) developed inconsistency and was removed from the program. Only NIST SRM 1832 is being reported for the 2007 report; however, every month, 18 elements spanning the atomic mass range of the 48 Micromatter calibration standards are analyzed as unknowns to verify calibration.

Table 3-38. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 1, 1/1/2007 through 12/31/2007

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	98.3	101	99.8	0.11	0.73	1.2
Si	96.3	98.2	97.5	0.18	0.53	0.7
Co	102	104	102	0.01	0.50	-0.2
Ca	99.4	102	101	0.10	0.51	0.7
V	103	105	104	0.02	0.32	0.5
Mn	100	101	101	0.01	0.28	0.1
Cu	98.3	99.7	99.1	0.01	0.29	0.3

Table 3-39. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 2, 1/1/2007 through 12/31/2007

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	96.2	102	98.9	0.25	1.66	3.0
Si	95.0	99.8	96.6	0.52	1.52	1.9
Co	97.1	101	99.7	0.01	0.71	-1.5
Ca	95.0	99.5	98.0	0.23	1.15	-0.7
V	101	104	102	0.03	0.71	1.0
Mn	98.0	99.8	98.9	0.02	0.43	-0.7
Cu	94.7	99.1	97.7	0.03	1.04	-2.4

Table 3-40. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 3, 1/1/2007 through 12/31/2007

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	97.2	100	98.5	0.12	0.81	-1.1
Si	98.0	100	99.4	0.14	0.39	0.8
Co	98.9	102	100	0.01	0.85	2.0
Ca	96.6	97.3	96.9	0.04	0.18	-0.4
V	103	105	104	0.02	0.39	0.3
Mn	98.1	100	99.3	0.02	0.39	-0.4
Cu	96.5	98.5	97.8	0.01	0.42	-0.7

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 3-41** shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients for XRF 1 range from 0.9993 to 1.0000, the correlation coefficients for XRF 2 range from 0.9993 to 1.0000, and the correlation coefficients for XRF 3 range from 0.9999 to 1.0000, indicating acceptable replication with all three instruments. Also, for the six elements, the average RPD on XRF 1 was less than 3%, the average RPD for the six elements on XRF 2 was less than 2%, and the average RPD for the six elements on XRF 3 was less than 2%.

3.5.1.4 Assessment of Between-Instrument Comparability

Overview of Round-Robin Samples Run During 2007

In addition to passing internal QC samples as described in the sections above, the RTI laboratories and CLN 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.

Table 3-41. 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	187	0.9994	-0.98	Si	363	0.9993	-1.85
S	187	0.9999	-0.95	S	363	1.0000	0.21
K	187	0.9998	-0.13	K	363	0.9999	-0.36
Ca	187	0.9997	-0.90	Ca	363	0.9994	0.47
Fe	187	1.0000	-0.20	Fe	363	0.9999	0.24
Zn	187	0.9993	-2.95	Zn	363	1.0000	-0.30

XRF 3			
Element	n	Correlation Coefficient	Average RPD
Si	345	1.0000	-1.40
S	345	0.9999	-0.01
K	345	1.0000	0.13
Ca	345	1.0000	-0.47
Fe	345	1.0000	-0.50
Zn	345	1.0000	-0.41

In the round-robin program, previously analyzed CSN filters are recycled through all the instruments in the two laboratories. **Table 3-42** summarizes the number of round-robin filters analyzed during 2007.

Table 3-42. Numbers of Round-Robin Filter Analyses Performed during 2007

Laboratory	Instrument	Filters*
CLN	Kevex 770	36
CLN	Kevex 771	9
RTI	XRF 1	36
RTI	XRF 2	36
RTI	XRF 3	27

* Kevex 771 and XRF 3 report low counts due to instrument down time for repair.

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. 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. Interlaboratory 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 3-43 and 3-44** show linear regression results when the data for the filters are regressed versus the median for the five instruments for each filter. The median value is used as the reference value, since the “true” value is unknown for these filters. Each instrument in the program reported zeros or low-level detections in some of the elements (especially Ni, Cu, 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 into account when doing the regression (i.e., no weighting factors were used).

**Table 3-43. Regression Results for 11 Elements
RTI XRF Instruments**

Element	RTI #1				RTI #2			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	36	0.9994	1.0087	0.0082	36	0.9990	0.9534	0.0214
S	36	0.9995	1.0135	0.0455	36	0.9989	0.9768	0.0035
K	36	0.9965	1.0213	0.0213	36	0.9961	0.9539	-0.0352
Ca	36	0.9998	0.9713	0.0110	36	0.9997	0.9969	-0.0428
Mn	36	0.9996	0.9974	0.0060	36	0.9997	0.9986	0.0016
Fe	36	0.9997	0.9926	0.0414	36	0.9997	0.9915	-0.0124
Ni	36	0.9988	1.0125	-0.0010	36	0.9983	0.9764	0.0032
Cu	36	0.9934	1.0917	-0.0084	36	0.9947	0.9689	0.0091
Zn	36	0.9998	0.9944	0.0020	36	0.9994	0.9737	0.0114
Se	36	0.9457	1.0781	0.0047	36	0.9654	0.8715	-0.0023
Pb	36	0.9655	0.9688	0.0065	36	0.9712	1.0228	-0.0113

Note: Units for intercept are $\mu\text{g}/\text{filter}$; correlation coefficient and slope are dimensionless.

Element	RTI #3			
	n	Correlation Coefficient	Slope	Intercept
Si	27	0.9995	0.9855	-0.0221
S	27	0.9997	1.0063	0.0434
K	27	0.9990	1.0264	-0.0203
Ca	27	0.9996	1.0209	-0.0153
Mn	27	0.9994	0.9767	-0.0117
Fe	27	0.9995	1.0125	0.0134
Ni	27	0.9970	0.9955	0.0044
Cu	27	0.9964	0.9932	0.0021
Zn	27	0.9998	0.9960	0.0029
Se	27	0.9737	0.8801	0.0002
Pb	27	0.9315	1.1024	-0.0084

**Table 3-44. Regression Results for 11 Elements
CLN XRF Instruments**

Element	CLN 770				CLN 771			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	36	0.9966	1.0555	0.0479	9	0.9990	0.9620	-0.1136
S	36	0.9968	0.9580	0.1635	9	0.9997	1.0018	-0.1951
K	36	0.9954	0.9895	0.0262	9	0.9936	1.0132	-0.1152
Ca	36	0.9992	1.1083	-0.0018	9	0.9998	1.1668	-0.1322
Mn	36	0.9973	1.0340	-0.0034	9	0.9916	1.0095	0.0001
Fe	36	0.9979	0.9872	-0.0338	9	0.9997	1.0012	-0.0225
Ni	36	0.9937	1.1068	-0.0056	9	0.9933	1.0247	0.0014
Cu	36	0.9892	0.9837	-0.00055	9	0.9941	0.9226	-0.0042
Zn	36	0.9987	1.0574	-0.0331	9	0.9989	1.0519	-0.0140
Se	36	0.9427	1.0619	0.0034	9	0.8629	1.0228	0.0023
Pb	36	0.9500	0.8774	0.0161	9	0.9839	1.1076	-0.0053

Note: Units for intercept are $\mu\text{g}/\text{filter}$; correlation coefficient and slope are dimensionless.

Uncertainty Reporting

The effort to harmonize uncertainties within all the XRF analyzers used under the CSN program was completed during 2006. Background discussion of the problem is found in the 2005 Data Summary Report.⁵ White Papers 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>.

After approval of the revised approach by EPA, RTI proceeded to upload revised uncertainty values for all the XRF data posted to AQS after February 2000. 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 CLN and RTI are sufficiently comparable to be combined for such applications as source-apportionment modeling.

3.5.1.5 Determination of Uncertainties and MDLs

MDLs are determined periodically by obtaining data from the analysis of 10 laboratory blanks. The MDLs are calculated as three times the average counting uncertainty for each 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 some laboratories 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 3-45**. Network-wide MDLs are summarized in Appendix A.

⁵ 2005 Annual Data Summary Report. RTI/08858/004QAS, July 19, 2006.

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 an uncertainty value for when the concentration is zero, the following formula is used:

$$\text{Uncertainty} = \text{slope} * A * \text{sqrt}(3 * \text{sqrt}(B * t) + B * t) / t$$

Where

A = scaling factor

B = background counts (cps) is incorporated during the importing of the data into the RTI XRF database

t = livetime.

Table 3-45. 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	0.53948	0.39811	0.33700	Sr	0.02146	0.26452	0.01723
Mg	0.16704	0.68174	0.10702	Y	0.02266	0.02399	0.01981
Al	0.41007	0.35504	0.28584	Zr	0.38407	0.26929	0.03308
Si	0.20850	0.17624	0.13628	Nb	0.05345	0.04228	0.03527
P	0.16143	0.14180	0.11497	Mo	0.06486	0.04389	0.04411
S	0.10913	0.09421	0.07099	Ag	0.27143	0.14408	0.12847
Cl	0.08024	0.07522	0.05226	Cd	0.23207	0.15129	0.13900
K	0.06204	0.06484	0.03884	In	0.24721	0.15511	0.18588
Ca	0.07468	0.06972	0.04675	Sn	0.53068	0.27461	0.26306
Sc	0.11276	0.09915	0.06506	Sb	0.47414	0.31460	0.33031
Ti	0.04850	0.05595	0.04326	Cs	0.12961	0.16963	0.19014
V	0.03776	0.04062	0.03160	Ba	0.09352	0.15454	0.10770
Cr	0.02134	0.02446	0.02202	La	0.08517	0.07950	0.08411
Mn	0.01737	0.02085	0.01732	Ce	0.10332	0.09959	0.07383
Fe	0.01591	0.01683	0.01394	Sm	0.04885	0.05601	0.05037
Co	0.01486	0.01341	0.01157	Eu	0.04479	0.04793	0.04422
Ni	0.01411	0.01355	0.01044	Tb	0.03870	0.13656	0.03764
Cu	0.02127	0.01568	0.01291	Hf	0.10614	0.10489	0.03954
Zn	0.02222	0.01779	0.01435	Ta	0.10983	0.10435	0.09697
Ga	0.02632	0.02717	0.02613	W	0.07965	0.08209	0.07031
As	0.01972	0.01888	0.01677	Ir	0.07163	0.07450	0.07119
Se	0.02035	0.01943	0.01828	Au	0.04716	0.04502	0.04240
Br	0.02126	0.01771	0.01575	Hg	0.12261	0.11757	0.08687
Rb	0.01684	0.02992	0.01566	Pb	0.04817	0.04061	0.04580

3.5.1.6 Audits, PEs, Training, and Accreditations

In November 2007, RTI's XRF laboratory received eight 47mm Teflon filters from NAREL. These eight samples were prepared by NAREL and were part of a PE study. No on-site audit was performed by NAREL during 2007; however, PE samples were received and analyzed. A report of these results is in preparation by NAREL, but was not finalized at the time of the preparation of this report.

In November 2007, Andrea McWilliams, Eric Poitras, and William Gutknecht attended a 3-day on-site training by Thermo on RTI's XRF hardware and software systems. The training was specific to work being performed for the CSN program.

3.5.2 CLN X-Ray Fluorescence Laboratory

CLN was the original XRF contractor laboratory used for the CSN program. During the period covered by this report, CLN operated two Kevex XRF instruments designated 770 and 771 analyzing 2,211 samples and 20 round robins for 48 elements.

3.5.2.1 Quality Issues and Instrument Repair and Maintenance

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

- 2/22/07 – Replaced vacuum pump.
- 4/25/07 – QS standard was damaged. Another Micromatter multi-element standard (Si, Ti, Fe, Se, Cd, Pb) was characterized.
- 4/30/07 – Replaced detector. Slight Ar peak indicates “incomplete” vacuum behind window. After calibration and Teflon blank analysis, it was determined that MDLs were met with normal counting times.
- 7/16/07 – Replaced detector after complete loss of vacuum of detector installed on 4/30/07.
- 11/26/07 – Removed X-ray tube to clear blockage in coolant line. Installed and realigned X-ray tube and ran QS standard to insure calibration.

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

- 5/1/07 – Replaced detector.
- 5/29/07 – Reset the atm threshold to 20,000 due to faulty pressure sensor.
- 11/5/07 – Replenished X-ray tube coolant.

3.5.2.2 Description of QC Checks Applied

QC activities for the analysis of elements by EDXRF for CLN, their frequency of application and control limits, comments, and corrective actions are shown in **Table 3-46**.

Table 3-46. 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 SRMs² Micromatter QC

3.5.2.3 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 3-47 and 3-48**, for the 770 and 771 instruments, respectively. The percent coefficient of variation (%CV) for the average of all data for each of the 6 elements ranged between 1.91 and 4.50% for the 770 and between 0.75 and 2.11% for the 771.

**Table 3-47. Summary of CLN XRF 770 Laboratory QC Precision Data,
1/1/2007 through 12/31/2007**

Element	N	Percent of Expected				%CV	Slope (%/year)
		Min	Max	Average	Std Dev		
Si	151	90.1	111.5	98.6	4.44	4.50	-0.001
Ti	151	93.8	107.9	99.8	2.36	2.36	0.003
Fe	151	95.3	108.0	100.4	1.91	1.91	0.004
Cd	151	92.2	106.2	99.5	2.62	2.63	0.006
Se	151	91.9	107.2	100.0	3.24	3.24	-0.013
Pb	151	93.9	107.6	100.1	3.17	3.16	-0.012

**Table 3-48. Summary of CLN XRF 771 Laboratory QC Precision Data,
7/31/2007 through 12/31/2007**

Element	N	Percent of Expected				%CV	Slope (%/year)
		Min	Max	Average	Std Dev		
Si	27	94.8	102.0	99.1	2.09	2.11	-1.019
Ti	27	96.8	102.6	100.0	1.45	1.45	0.003
Fe	27	99.0	101.7	100.4	0.76	0.75	0.002
Cd	27	96.1	104.1	100.6	1.63	1.62	0.005
Se	27	94.9	102.9	99.1	1.95	1.97	-0.029
Pb	27	93.8	102.4	99.2	1.79	1.80	-0.022

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 3-49 and 3-50** show recovery for 12 elements spanning the atomic mass range of the 48 elements normally measured. The minimum and maximum recovery values for all the elements ranged between 85.2 and 122.9% for the 770 and between 89.2 and 115.9% for the 771. Analysis of NIST Particle Standard SRM2783 yielded a Ca recovery of 99.1% for the 770 and 103.7% for the 771, 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 3-49 and 3-50** 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 3-49. Recovery Determined from Analysis of NIST SRMs 1832, 1833, and 2708 for CLN XRF 770, 1/1/2007 through 12/31/2007

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	91.1	112.3	100.3	4.40	4.38	0.008
Si	94.3	108.7	101.0	3.68	3.65	-0.003
Si	91.9	106.4	99.2	4.06	4.10	-0.010
S	85.2	109.8	97.0	4.63	4.78	0.008
K	87.8	105.1	96.7	4.45	4.60	0.028
Ca	100.1	122.9	107.1	4.30	4.01	-0.001
Ti	92.0	109.1	98.3	4.07	4.14	0.020
V	91.5	106.9	97.7	3.42	3.50	-0.018
Mn	94.7	108.4	100.4	3.36	3.34	-0.006
Fe	92.1	108.5	97.5	3.19	3.27	-0.002
Cu	89.4	108.2	97.3	4.76	4.89	0.010
Zn	87.6	108.4	100.0	3.73	3.73	0.007
Pb	94.8	107.6	102.3	3.33	3.26	-0.0002

Table 3-50. Recovery Determined from Analysis of NIST SRMs 1832, 1833 and 2708 for CLN XRF 771 , 7/31/2007 through 12/31/2007

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	91.2	101.5	96.5	2.58	2.67	0.027
Si	93.7	103.6	99.9	2.41	2.41	0.019
Si	93.7	103.1	100.2	2.35	2.35	0.019
S	91.8	101.3	96.5	2.73	2.83	-0.017
K	89.2	97.0	93.0	1.96	2.11	-0.012
Ca	107.4	115.9	111.8	2.49	2.22	-0.013
Ti	93.9	97.8	95.5	1.28	1.34	-0.012
V	98.8	109.3	104.2	2.77	2.66	-0.023
Mn	101.3	107.7	104.7	1.90	1.82	-0.005
Fe	96.3	101.7	98.0	1.38	1.41	-0.020
Cu	90.9	106.3	97.0	4.37	4.50	-0.017
Zn	92.4	105.4	97.7	3.63	3.72	-0.002
Pb	93.4	109.8	99.6	3.82	3.84	-0.0001

Reproducibility

Replicate analyses 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 3-51** shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients for the 770 range from 0.9986 to 0.9998, and the correlation coefficients for the 771 range from 0.9645 to 0.9998, indicating acceptable replication on both instruments.

Table 3-51. Replicate Data for CLN XRF 770 and 771

KeveX 770				KeveX 771			
Element	N	Correlation Coefficient	Average RPD	Element	n	Correlation Coefficient	Average RPD
Si	169	.9986	-1.59	Si	10	.9963	-0.83
S	169	.9994	-0.39	S	10	.9998	1.16
K	69	.9986	-1.18	K	9	.9671	-2.00
Ca	169	.9986	-0.75	Ca	10	.9872	-3.49
Fe	168	.9997	0.43	Fe	10	.9976	-3.23
Zn	135	.9998	3.14	Zn	9	.9645	1.94

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 CLN'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.

3.5.2.4 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 3.5.1.4 for comparative performance of both laboratories.

Since the inception of the PM_{2.5} Speciation project, CLN has performed numerous comparisons between instruments via replicate analysis for a number of clients, but much of this data is proprietary and cannot be shared in this report.

3.5.2.5 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 12/01/07 and are shown in **Table 3-52**. MDLs used during 2007 across analyzers are shown in Appendix A.

3.5.2.6 Audits, PEs, Training, and Accreditations

CLN has not received any audit visits from EPA on the CSN program since the beginning of the speciation project and would welcome any PE samples or other oversight, which the EPA might deem appropriate.

CLN began training Ms. Rachel Mori in mid-April of 2007. Her training has included sample log-in, sample preparation for XRF, XRF analysis, QA/QC of XRF spectral data, data entry, and sample shipping. Ms. Mori came to CLN with approximately 2 years' experience performing XRF analysis on Teflon filters for the IMPROVE network at UC Davis.

Table 3-52. MDL Values for Kevex 770 and Kevex 771, µg/filter

Element	770	771	Element	770	771
Na	0.94106	0.42693	Sr	0.02024	0.01899
Mg	0.31163	0.21334	Y	0.02556	0.01905
Al	0.14728	0.10663	Zr	0.03179	0.02065
Si	0.09287	0.08748	Nb	0.03905	0.02306
P	0.05433	0.06964	Mo	0.04745	0.03032
S	0.04848	0.05347	Ag	0.14472	0.11715
Cl	0.09816	0.14881	Cd	0.14719	0.12535
K	0.05095	0.08954	In	0.16248	0.13383
Ca	0.03357	0.08608	Sn	0.18349	0.18425
Sc	0.02539	0.08131	Sb	0.19950	0.17245
Ti	0.02141	0.05423	Cs	0.05102	0.14750
V	0.01589	0.04721	Ba	0.07384	0.21757
Cr	0.02472	0.03973	La	0.04679	0.21346
Mn	0.03134	0.04296	Ce	0.05864	0.19366
Fe	0.03085	0.04128	Sm	0.09167	0.11682
Co	0.02281	0.03062	Eu	0.16555	0.21894
Ni	0.02103	0.02895	Tb	0.12465	0.12321
Cu	0.03268	0.02537	Hf	0.08534	0.12610
Zn	0.02686	0.02466	Ta	0.08734	0.12828
Ga	0.02293	0.03734	W	0.09307	0.12983
As	0.01940	0.04207	Ir	0.03951	0.06058
Se	0.01629	0.02387	Au	0.04380	0.06381
Br	0.01489	0.02178	Hg	0.03928	0.06296
Rb	0.01724	0.01893	Pb	0.05029	0.06163

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 CSNs operated by EPA and various State, local, and tribal agencies, which utilize the RTI/EPA contract. The laboratory follows these SOPs, 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. Generally, this could not be discerned, and the denuder laboratory account covered the cost of repairs. Fewer Andersen and URG samplers are in use at field sites; their use will be phased out entirely in 2008. Thus, the breakage of glass denuders will no longer be an issue since the MetOne sampler uses aluminum honeycomb denuders rather than glass denuders.

Personnel have been cross-trained to be able to process denuders. At present, there are four persons trained to refurbish denuders. RTI is also capable of coating denuders in a glove cabinet so that exposure of denuders to ambient air is minimized and the denuders can later be extracted to quantify the mass of acidic or basic gases collected.

3.6.2 Operational Discussion

3.6.2.1 Numbers of Each Type of Denuder Serviced

Table 3-53 lists the type of denuders refurbished and the number of refurbishments completed in 2007.

Table 3-53. Denuder Refurbishments, 1/2007 through 12/2007

Denuder Type	Total Refurbished
R&P	1657
MetOne	6920
URG	745
Andersen	29

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 3-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.

3.7 Sample Handling and Archiving Laboratory

3.7.1 Quality Issues and Corrective Actions

There were no major quality issues in the SHAL during 2007. One Corrective Action was undertaken. During one weekend, the walk in cold room malfunctioned. RTI's HVAC technicians responded immediately upon discovery of the malfunction on Monday morning, and repairs were implemented. The temperature was restored by 10 a.m. on Monday. The cause of the outage was a spider getting inside a relay. The relay was replaced, and the unit was cooling again. The corrective action instituted was that a datalogger was placed inside the cold room to monitor the temperature and provide the time duration of any outage.

One major change in SHAL operations during 2007 was the implementation of the URG 3000N filter cassette. In May, the URG 3000N sampler was deployed at 55 locations in the network, and samples are processed by RTI. Prior to the deployment, all SHAL staff were trained in the handling of the 25 mm quartz filter and the new cassette for the URG 3000N sampler. By the time the samplers were phased into the network, the SHAL staff processed the new cassettes without interruption of service to the field sampling locations. A photograph of the URG 3000N cassette being loaded with a filter is shown in Figure 3-2.



Figure 3-2. SHAL technician loading the URG 3000N cassette.

3.7.2 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 6 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.

3.7.3 Summary of QC Results

During calendar year 2007, the SHAL shipped out and received back more than 16,000 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** in **Appendix B**).

3.7.4 Summary of Scheduling Problems

With the introduction of the URG 3000N samplers into the network, the scheduling of shipments from RTI to the field sampling locations and back necessitated that two additional schedules be created. This meant that four shipping and receiving schedules were prepared for the CSN. One schedule is for those sites sampling on the 1-in-3 day frequency using the URG 3000N, and a second schedule is for those sites sampling on the 1-in-6 day frequency and using the URG 3000N. A third schedule is for those sites sampling on the 1-in-3 day frequency and using a sampler other than the URG 3000N, and the fourth schedule is for those sites sampling on the 1-in-6 day frequency and using a sampler other than the URG 3000N. 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 2007 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 3-54** lists those sites with less than 95% of their filters run on the intended sampling date.

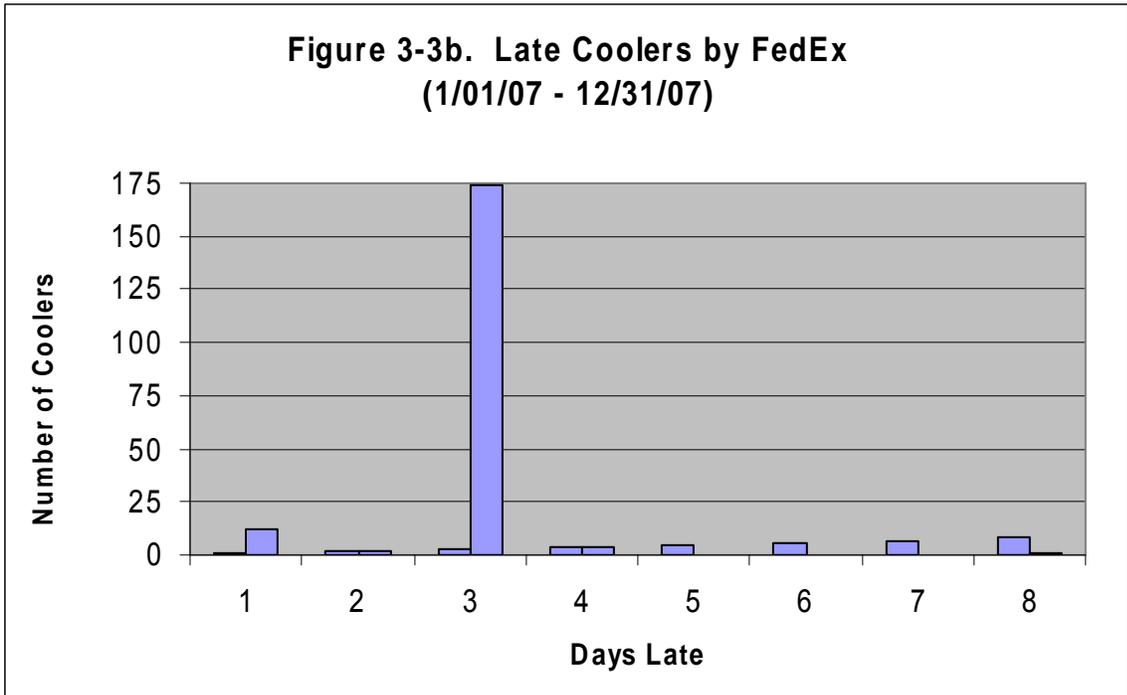
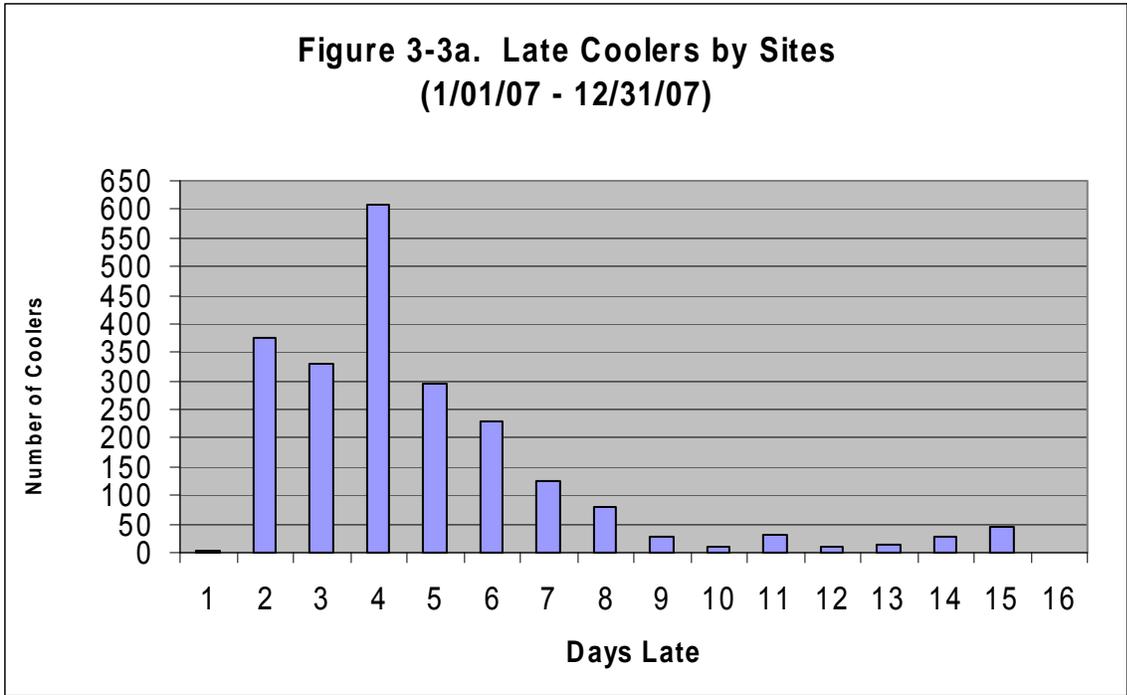


Table 3-54. Sites with Less than 95% of Filters Run on Intended Sampling Date

Airs Code	POC	Location	Events	On Date	Pct.
261630001	5	Allen Park	122	101	83
330150014	5	Portsmouth	43	36	84
080010006	5	Commerce City	156	135	87
040137020	5	Senior Center	8	7	88
040137003	5	St Johns	17	15	88
471570024	5	Alabama (TN)	117	104	89
080410011	5	RBD	9	8	89
470370023	5	Lockeland School	29	26	90
481130069	5	Hinton	104	95	91
360551007	5	Rochester Primary – MET ONE	13	12	92
040139997	7	Phoenix Supersite	122	113	93
060290014	6	Bakersfield (Collocated)	111	104	94
340070003	5	Camden	156	147	94
060190008	5	Fresno – First St	122	115	94
060658001	6	Riverside – Rubidoux (Collocated)	122	115	94

3.7.5 Support Activities for Site Operators and Data Users

SHAL staff provided support to site operators and data users throughout 2007. A summary of email and phone communications with site operators and data users is presented in **Table 3-55**.

Table 3-55. Summary of SHAL Communications With Site Operators and Data Users

Description	Number of Communications
Site will send cooler late	127
Site needs schedule	51
Site did not receive cooler	49
Change of operator/site information	66
Sampler problems/questions	90
Field Blank/Trip Blank ran as routine sample	7
Request change of ship date from RTI	26
Site is stopping	15
Miscellaneous QA Issues	135
Data questions/reporting	114
Other	100

3.7.6 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 SOP and instruction by senior staff in filter handling. A record of this training is kept on file.
- SHAL staff periodically review the SOP and a record of this review is added to their training file.
- All SHAL staff were trained in the handling of the 25mm quartz filters used in the URG 3000N sampler and the proper installation and removal of the new quartz filter using the URG 3000N cassette.
- 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 2007 is shown in **Table 3-56**.

Table 3-56. Review of SHAL Technician Processing Filter Modules

Module Type	Number Observed	Findings	Findings Reviewed with Technician
MET ONE	85	5	5
Andersen	7	1	1
URG	6	1	1
R&P Spec	6	1	1
URG 3000N	21	0	0

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 the following:

- Accepting data entered from field forms
- Accepting data from the laboratories
- Backing up and maintaining the database
- 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 the following:

- Modifications to add new URG 3000 N sampler and associated IMPROVE_A carbon analytes. Blanks and backup filters have been added, but artifact correction has not been implemented pending EPA approval of correction method.
- Modifications to mass balance QA checks to use URG 3000 N sampler.
- Modifications to report calculations to use new “harmonization” factors for XRF uncertainty. Historical AQS data uncertainties were updated under a new work assignment (finishing in February 2007).

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	
84	1/11/2007	11/13/2006	12/13/2006	1,068	70	53	1,191
85	2/13/2007	12/13/2006	1/15/2007	1,298	178	107	1,583
86	3/14/2007	1/15/2007	2/11/2007	1,154	68	48	1,270
87	4/12/2007	1/24/2007	3/14/2007	1,050	175	118	1,343
88	5/14/2007	3/13/2007	4/12/2007	1,264	69	162	1,495
89	6/15/2007	4/14/2007	5/16/2007	1,164	173	28	1,365
90	7/16/2007	5/12/2007	6/14/2007	1,165	67	51	1,283
91	8/15/2007	6/11/2007	7/11/2007	1,063	53	28	1,144
92	9/13/2007	6/29/2007	8/14/2007	1,216	143	7	1,366
93	10/15/2007	8/10/2007	9/12/2007	1,157	53	177	1,387
94	11/13/2007	9/3/2007	10/15/2007	1,120	44	11	1,175
95	12/13/2007	10/9/2007	11/14/2007	1,348	54	7	1,409
96	1/14/2008	11/14/2007	12/15/2007	1,122	135	73	1,330

Table 4-2. Records Posted to Web Site

Report Batch		Sample Date		Field Samples	Blanks		Total
Batch	Date	Earliest	Latest		Field	Trip	
84	1/11/2007	11/13/2006	12/13/2006	120,694	7,855	6,103	134,652
85	2/13/2007	12/13/2006	1/15/2007	146,855	20,203	12,210	179,268
86	3/14/2007	1/15/2007	2/11/2007	130,518	7,678	5,500	143,696
87	4/12/2007	1/24/2007	3/14/2007	118,643	19,844	13,404	151,891
88	5/14/2007	3/13/2007	4/12/2007	142,823	7,762	18,602	169,187
89	6/15/2007	4/14/2007	5/16/2007	133,319	19,580	3,231	156,130
90	7/16/2007	5/12/2007	6/14/2007	138,091	7,507	5,725	151,323
91	8/15/2007	6/11/2007	7/11/2007	126,042	6,041	3,713	135,796
92	9/13/2007	6/29/2007	8/14/2007	135,920	15,572	757	152,249
93	10/15/2007	8/10/2007	9/12/2007	129,549	4,672	19,845	154,066
94	11/13/2007	9/3/2007	10/15/2007	125,195	4,508	1,211	130,914
95	12/13/2007	10/9/2007	11/14/2007	151,094	4,810	745	156,649
96	1/14/2008	11/14/2007	12/15/2007	125,681	14,880	8,143	148,704
97	2/14/2008	12/8/2007	1/13/2008	140,585	5,461	2,817	148,863

4.5 Postings to AQS

After data have been posted to the external Web site, 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	
83	1,260	183	59	1,502
84	1,085	71	53	1,209
85	1,316	181	108	1,605
86	1,164	68	48	1,280
87	1,064	176	120	1,360
88	1,280	70	164	1,514
89	1,193	175	28	1,396
90	1,183	67	51	1,301
91	1,074	53	28	1,155
92	1,230	144	7	1,381
93	1,173	53	178	1,404
94	1,133	44	11	1,188

Table 4-4. Records Posted to AQS

Batch	Field Samples	Blanks		Total
		Field	Trip	
83	84,518	12,271	3,959	100,748
84	72,781	4,767	3,557	81,105
85	88,268	12,137	7,246	107,651
86	78,076	4,564	3,220	85,860
87	71,380	11,804	8,052	91,236
88	85,858	4,765	10,996	101,619
89	81,512	11,735	1,878	95,125
90	84,343	4,497	3,468	92,308
91	75,801	3,551	2,190	81,542
92	84,849	9,513	479	94,841
93	80,799	3,180	12,238	96,217
94	78,084	2,858	775	81,717

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, whereas 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	83	84	85	86	87	88	89	90	91	92	93	94
Requests	13	8	5	6	10	10	7	11	2	9	7	5

4.6.2 Requests for Old Data

RTI keeps draft data reports on its internal Web 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 because 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. In December 2007, EPA provided a work assignment to update the SDVAT to use data from the URG 3000 N. Although EPA no longer provides funding for SDVAT user support, RTI continues to provide limited support to current CSN sites.

4.6.4 Data User Communications

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

- **Data Availability at End of Calendar Year.** Several calls were received from state or regional personnel inquiring on data availability after the end of the calendar year. RTI explained the process and deadlines under the current process and provided estimates of when data would be available (typically in the April 15 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 15) and reported on by RTI on or before February 15. The site would have until April 1 to review their data, and RTI would have until April 15 to post data to AQS.
- **Site Changes.** Several sites indicated that they had stopped, started, or relocated samplers during the past year. A monthly report has been prepared and submitted to EPA.
- **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.
- **SDVAT Questions.** Several sites had problems with URG 3000N data in the SDVAT. A new version of the SDVAT is now being prepared and should eliminate most of these problems.

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5.0 Quality Assurance and Data Validation

5.1 QA Activities

5.1.1 QAPP Updates

RTI's QAPP for CSN was not updated during 2007. No significant changes have been made to RTI's procedures and objectives.

5.1.2 SOP Updates

RTI's SOPs were not updated during 2007, but new SOPs have been prepared. Although new procedures were developed for analyzing quartz filters from the URG 3000N samplers, none of the analysis data generated by RTI was posted to AQS.

5.1.3 Internal Surveillance Activities

Internal surveillance activities during 2007 included walkthroughs of all the laboratories to verify compliance with the SOPs. An internal audit of the Gravimetry Laboratory was performed in January, 2007. Outstanding quality issues are discussed at monthly project meetings, and any new changes required were implemented.

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 and other project personnel responded to a number of questions and requests for data during 2007. These originated from both network participants (state agency personnel and EPA), as well as data users who were not affiliated with the CSN program.

5.2 Data Validation and Review

5.2.1 Review of Monthly Data Reports to the CSN Web Site

Each month, RTI reviews data completed during the previous month. These 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 (e.g., barometric pressure, temperature)

- Level 1 checks (e.g., 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.

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 CSN 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, and 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 the following:
 - 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.

5.3 Analysis of Collocated Data

The CSN program operated six sites with collocated samplers during 2007, shown in **Table 5-4**. Two of these sites included the new URG 3000N IMPROVE-type sampler on both the primary and collocated sampler. 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.

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

Flag	Description	AQS Validity Status Codes												
		83	84	85	86	87	88	89	90	91	92	93	94	95
2	Operational Criteria Not Met								0.08%	0.01%				
3	Possible field contamination													0.00%
5	Outlier-cause unknown	6.36%	7.42%	5.20%	4.35%	3.31%	3.98%	7.06%	6.84%	4.89%	4.81%	7.18%	6.76%	6.71%
A	High Winds	0.15%	0.08%			0.07%	0.13%	0.14%	0.15%		0.22%	0.07%		0.29%
D	Sandblasting				0.07%		0.06%			0.08%				
E	Forest Fire				0.08%	0.07%	0.07%	0.21%	0.69%	0.08%	0.67%	1.07%	0.40%	0.79%
F	Structural Fire			0.06%			0.07%							
H	Chemical Spills						0.07%							
I	Unusual Traffic Congestion									0.08%			0.08%	
J	Construction/Demolition	0.75%	0.58%	0.56%	0.94%	1.03%	0.73%	0.28%	0.36%	0.49%	0.43%	0.28%	0.42%	0.64%
K	Agricultural Tilling	0.13%												
L	Highway Construction	0.13%						0.07%	0.07%	0.16%	0.29%	0.14%		
M	Rerouting of Traffic	0.17%	0.73%						0.07%					
N	Sanding/salting of Streets	0.07%				0.07%								
O	Infrequent Large Gatherings							0.21%	0.07%	0.16%		0.07%		
P	Roofing Operations				0.06%	0.15%								
Q	Prescribed Burning			0.06%	0.23%	0.15%							0.08%	
W	Flow Rate Average out of specs	0.26%			0.20%	0.23%	0.29%	0.13%	0.31%		0.48%	0.14%		0.06%
X	Filter Temperature Diff. out of spec	0.80%	0.83%	0.37%	0.16%	0.85%	0.73%	0.29%	0.56%	0.27%	0.60%	0.35%	0.42%	0.21%
Y	Elapsed Sample Time out of specs					0.07%	0.13%	0.04%	0.07%		0.02%	0.12%		

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

Flag	Description	AQS Validity Status Codes												
		83	84	85	86	87	88	89	90	91	92	93	94	95
AB	Technician Unavailable	0.45%	0.24%	0.31%	0.08%	0.29%	0.07%	0.16%	0.18%	0.02%	0.32%	0.14%	0.08%	0.43%
AC	Construction/Repairs in Area	0.07%			0.08%									
AD	Shelter Storm Damage					0.22%		0.01%						
AF	Scheduled but not Collected	0.84%	1.46%	1.22%	0.75%	0.80%	0.89%	0.66%	0.61%	1.29%	0.95%	0.55%	0.65%	0.40%
AG	Sample Time out of Limits	0.65%	0.78%	0.43%	0.12%	1.58%	0.62%	0.41%	0.68%	0.71%	0.89%	1.01%	0.44%	0.35%
AH	Sample Flow Rate Out of Limits	0.56%	0.32%	0.37%	0.42%	0.19%	0.96%	0.37%	0.68%	0.61%	0.97%	0.66%	0.31%	0.46%
AI	Insufficient Data (Can't Calculate)	0.07%	0.17%	0.26%	0.15%	0.36%	0.07%	0.24%	0.03%	0.11%	0.05%	0.13%	0.11%	0.08%
AJ	Filter Damage	0.19%	0.18%	0.11%	0.17%	0.16%	0.16%	0.08%	0.26%	0.33%	0.27%	0.12%	0.02%	0.18%
AK	Filter Leak				0.06%	0.13%	0.02%			0.03%				
AL	Voided by Operator	0.20%	0.25%	0.60%	0.11%	0.13%	0.08%	0.31%	0.56%	0.40%	0.27%	0.26%	0.08%	0.14%
AM	Miscellaneous Void	0.17%	0.08%	0.13%	0.15%	0.08%	0.08%	0.15%	0.15%	0.03%	0.01%	0.12%	0.02%	0.07%
AN	Machine Malfunction	1.05%	0.65%	1.07%	0.94%	2.20%	1.05%	0.97%	1.43%	0.85%	0.60%	0.38%	0.61%	0.19%
AO	Bad Weather		0.25%	0.12%	0.16%	0.14%	0.07%		0.15%		0.15%	0.07%		
AP														0.07%
AQ	Collection Error	0.67%	0.10%	0.12%	0.16%	0.31%	0.21%	0.26%	0.39%	0.01%	0.54%	0.45%	0.14%	0.10%
AR	Lab Error	0.02%	0.09%	0.19%	0.02%	0.02%	0.08%	0.04%	0.09%	0.06%	0.03%	0.06%	0.03%	0.12%
AS	Poor Quality Assurance Results		0.17%			0.07%	0.07%		0.07%					
AU	Monitoring Waived			0.12%	0.07%		0.05%				0.43%	0.05%		
AV	Power Failure (POWR)	0.69%	0.79%	0.79%	0.44%	0.49%	0.38%	0.50%	0.56%	0.89%	0.54%	0.91%	0.43%	0.60%
AW	Wildlife Damage									0.02%				
AZ	QC Audit (AUDIT)											0.07%		
BA	Maintenance/Routine Repairs		0.01%	0.12%	0.06%	0.09%	0.11%		0.20%	0.15%	0.11%	0.19%	0.07%	0.14%
BB	Unable to Reach Site		0.08%		0.08%	0.07%	0.26%		0.07%	0.02%	0.23%			
BE	Building/Site Repair	0.07%		0.06%	0.08%			0.07%				0.27%	0.09%	
BI	Lost or Damaged in Transit	0.07%		0.06%		0.07%		0.07%			0.14%		0.08%	0.07%
BJ	Operator Error					0.07%			0.07%					

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

Flag	Description	AQS Validity Status Codes												
		83	84	85	86	87	88	89	90	91	92	93	94	95
ANB														0.15%
APB	analysis partly billable	0.34%	0.49%	0.38%	0.55%	1.11%	0.88%	1.23%	1.42%	0.57%	1.05%	1.34%	0.85%	0.76%
DFM	Filter missing	0.01%	0.03%	0.01%	0.03%	0.01%	0.04%	0.01%						
DSI	Module condition invalid			0.06%				0.07%						
DST	Receipt temperature >4C	29.83%	35.51%	25.77%	24.55%	25.63%	43.13%	56.16%	68.66%	76.52%	80.43%	84.28%	69.65%	52.85%
FBS	Field or Trip Blank appears to be actual sample			0.06%										
FCE	Field Environmental Substituted	1.51%	1.90%	1.63%	2.10%	1.19%	0.91%	1.84%	1.29%	0.97%	1.96%	1.86%	1.59%	1.79%
FES	Pickup holding time exceeded	0.06%	0.07%	0.05%	0.04%	0.19%	0.05%	0.04%	0.11%	0.03%	0.14%	0.23%	0.09%	0.05%
FHT	Sample lost or damaged in shipment	12.24%	14.16%	12.85%	5.72%	19.31%	14.23%	5.42%	14.37%	15.82%	13.22%	5.07%	18.36%	14.74%
FSL	Sample Lost					0.07%		0.07%						
LBD	Laboratory blank duplicate outside limits													
LFA	Filter inspection flags - filter wet	0.05%	0.04%	0.13%	0.06%	0.14%	0.04%	0.00%			0.01%	0.02%	0.03%	0.05%
LFH	Filter inspection flags - Holes in filter	0.00%				0.04%								0.03%
LFL	Filter inspection flags -Loose Material	0.07%					0.02%							
LFO	Filter inspection flags -Other			0.00%										
LFP	Filter inspection flags -Pinholes						0.04%							
LFT	Filter inspection flags - Tear						0.01%					0.04%		0.01%
LFU	Filter inspection flags -Non-uniformity													
LHT	Lab holding times exceeded					0.07%								
QAC	Anion/Cation ratio out of limits	0.09%		0.18%	0.16%	0.11%	0.14%	0.23%	0.16%	0.12%	0.22%	0.23%	0.17%	0.38%
QL1	Sulfur/Sulfate ratio out of limits	0.05%	0.05%	0.04%	0.03%	0.04%	0.04%	0.02%	0.03%	0.04%	0.06%	0.06%	0.06%	0.04%
QMB	Mass balance ratio out of limits	6.26%	7.16%	5.01%	4.18%	3.18%	3.83%	6.85%	6.67%	4.76%	4.57%	6.94%	6.58%	6.35%
SNB	Sample not billable	0.40%	0.74%	0.40%	0.08%	0.35%	0.13%		0.08%		0.29%	0.13%	0.24%	
SPB	Sample partly billable	3.99%	3.47%	4.35%	3.05%	4.49%	3.51%	2.99%	4.86%	4.46%	4.57%	3.41%	2.42%	2.66%

Table 5-4. Collocated sites in the CSN

Location Name	State	AQS Code	Sampler Type	URG 3000N
Bakersfield-California Ave	California	60290014	MetOne SASS	Yes*
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	Yes*
Roxbury (Boston)	Massachusetts	250250042	MetOne SASS	

* Both primary and collocated samplers operated with URG 3000N sampling module beginning in May 2007.

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 2007. For statistical analysis, the data presented in this section for the SASS and MASS samplers have 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 organic and elemental carbon, PM_{2.5} mass, nitrate, sulfate, and sulfur. Invalid points have been removed, but data with Airs Validity Status codes set are retained. The oblique line on each chart indicates perfect agreement (slope=1.000).

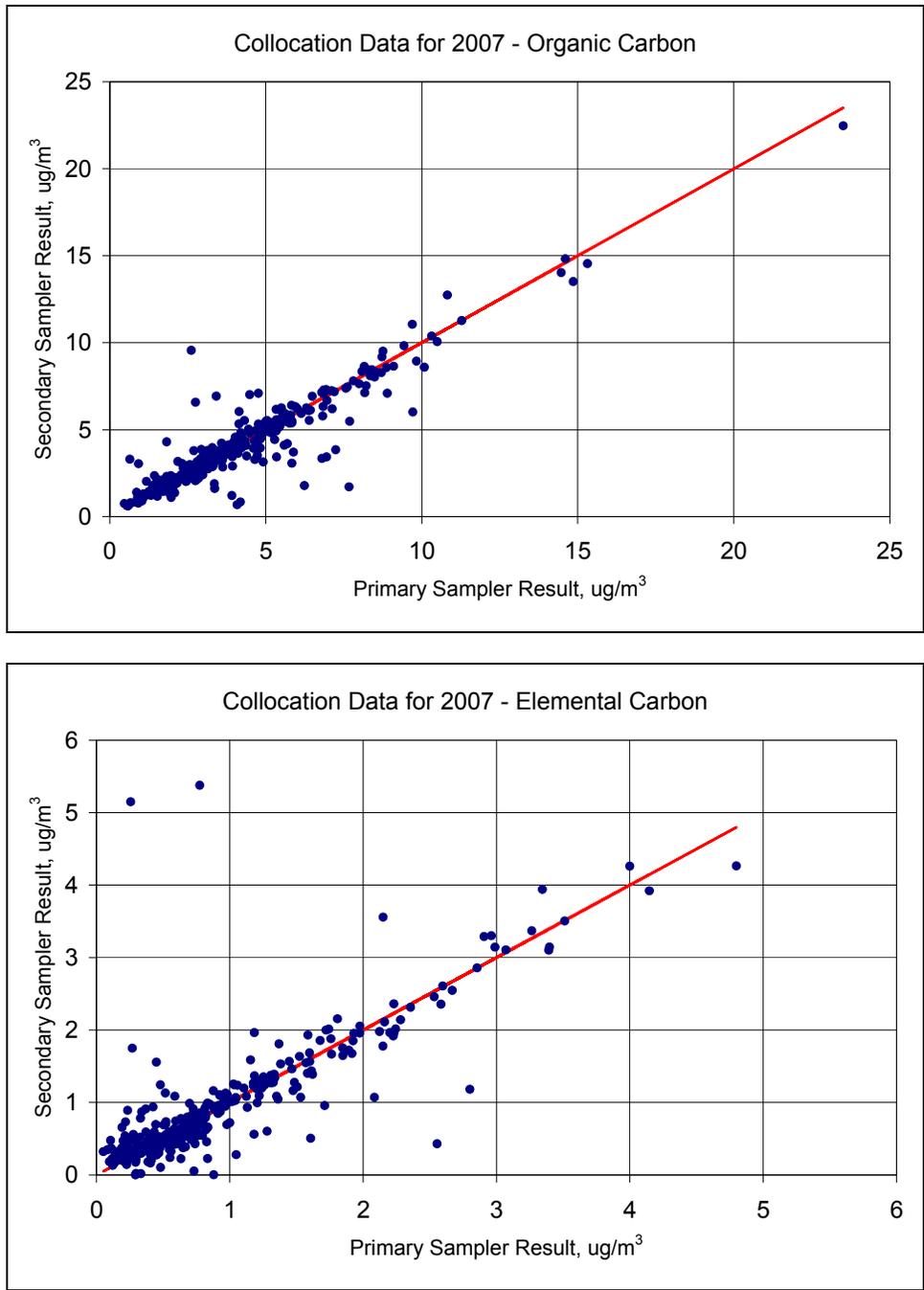


Figure 5-1. Examples of the comparisons for organic carbon, elemental carbon, mass, nitrate, sulfate, and sulfur.

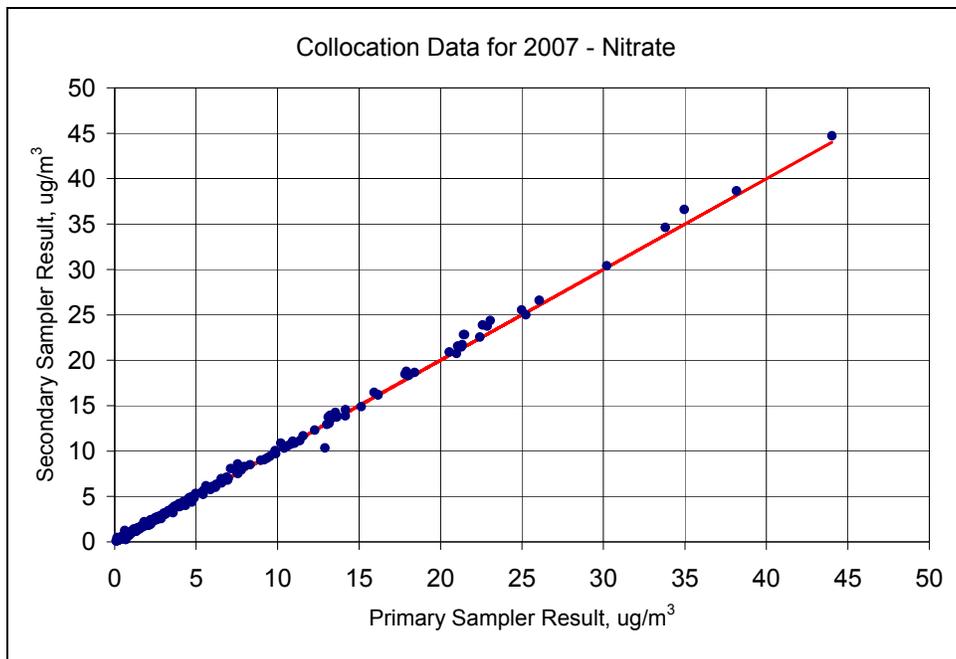
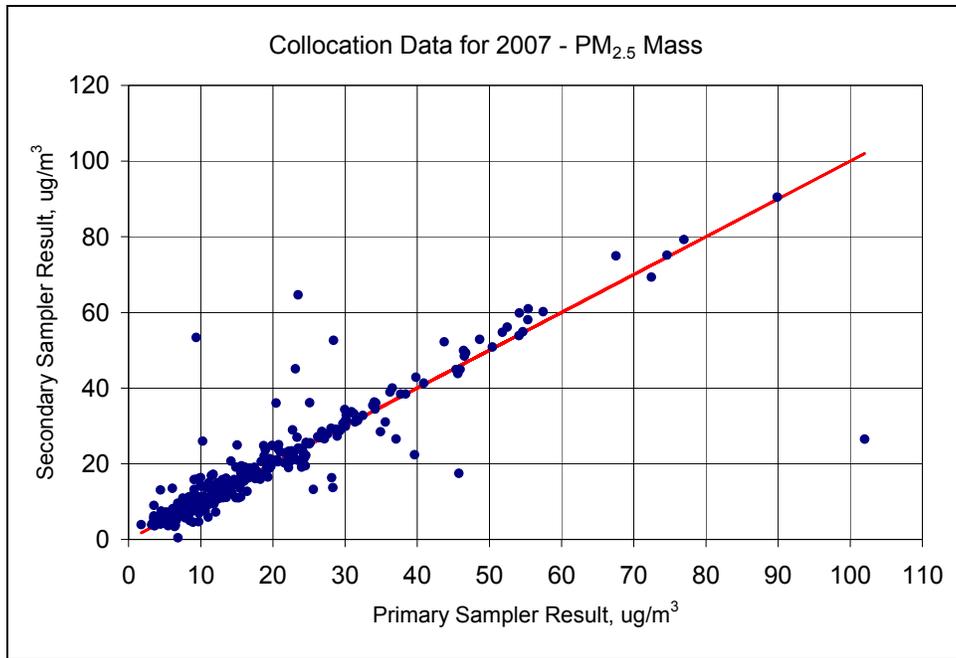


Figure 5-1. (continued).

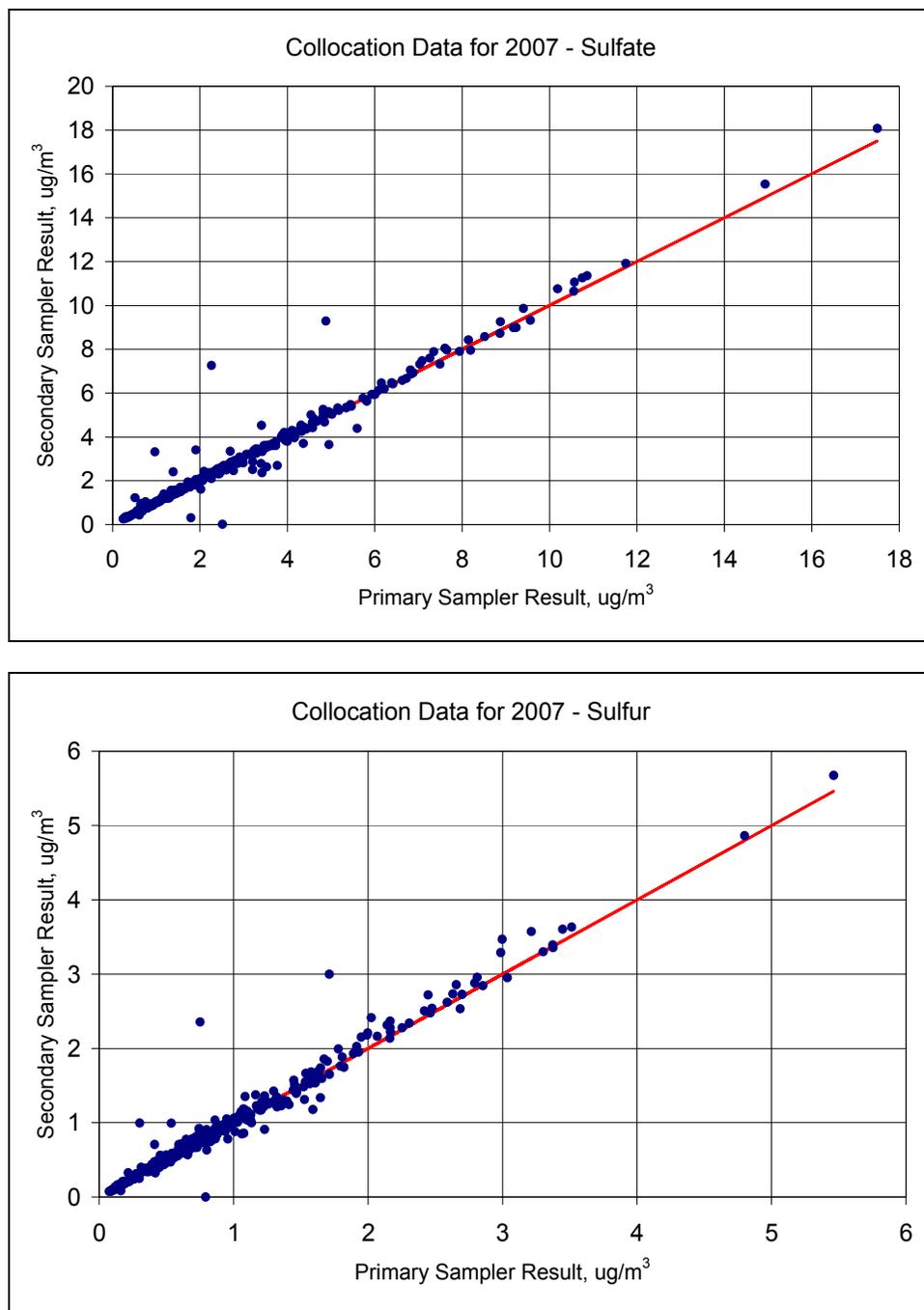


Figure 5-1. (continued).

5.3.1 Precision

Table 5-5 shows 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 (C_1 or C_2) 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. Precision of Collocated Samplers

Analyte	Sampler 1		Sampler 2		Average Relative Diff. ²	Average Rel. AQS Uncert. ³	Ratio AQS/ARD percent ⁴	Counts ⁵
	Average $\mu\text{g}/\text{m}^3$	Standard Dev. $\mu\text{g}/\text{m}^3$ ¹	Average $\mu\text{g}/\text{m}^3$	Standard Dev. $\mu\text{g}/\text{m}^3$ ¹				
Trace Elements by XRF								
Aluminum	0.103	0.132	0.119	0.180	29%	31%	106%	180
Arsenic	0.005	0.004	0.004	0.004	22%	37%	169%	45
Barium	0.024	0.011	0.020	0.006	17%	27%	162%	4
Bromine	0.005	0.003	0.005	0.004	20%	31%	154%	227
Calcium	0.079	0.090	0.088	0.104	22%	16%	70%	331
Cerium	0.027	0.024	0.031	0.030	7%	36%	506%	2
Chlorine	0.083	0.136	0.086	0.154	35%	20%	57%	238
Chromium	0.009	0.012	0.006	0.006	46%	36%	79%	53
Cobalt	0.003	0.001	0.003	0.001	5%	47%	898%	2
Copper	0.013	0.017	0.011	0.021	26%	19%	74%	322
Gallium	0.008	0.005	0.007	0.002	23%	28%	124%	3
Hafnium	0.004		0.005		7%	32%	469%	1
Iron	0.146	0.132	0.152	0.154	18%	11%	62%	348
Lead	0.009	0.006	0.010	0.006	20%	41%	207%	71
Magnesium	0.058	0.074	0.066	0.094	32%	31%	97%	47
Manganese	0.005	0.004	0.006	0.005	22%	33%	152%	141
Nickel	0.003	0.005	0.003	0.003	34%	32%	94%	185
Phosphorus	0.053	0.041	0.020	0.003	51%	29%	58%	2
Potassium	0.111	0.307	0.118	0.329	13%	14%	108%	345
Rubidium	0.001		0.001		1%	65%	5887%	1
Samarium	0.008		0.011		17%	30%	176%	1
Selenium	0.003	0.002	0.003	0.002	19%	47%	249%	24
Silicon	0.162	0.222	0.184	0.299	20%	20%	96%	314
Sodium	0.162	0.131	0.174	0.155	24%	27%	115%	177
Strontium	0.009	0.019	0.009	0.022	25%	46%	183%	24
Sulfur	0.895	0.783	0.925	0.820	5%	11%	208%	348
Titanium	0.013	0.015	0.015	0.017	26%	31%	120%	124
Vanadium	0.007	0.005	0.009	0.006	23%	31%	133%	97
Wolfram	0.008		0.007		13%	61%	484%	1
Yttrium	0.002	0.000	0.002	0.000	6%	69%	1242%	2
Yttrium	0.002	0.001	0.002	0.001	11%	38%	355%	8
Zinc	0.017	0.018	0.017	0.019	15%	20%	133%	301
Zinc	0.024	0.037	0.024	0.037	14%	11%	76%	1497
Zirconium	0.021	0.017	0.019	0.008	25%	21%	85%	2
Zirconium	0.004	0.002	0.004	0.002	20%	32%	158%	59
Silver	0.011	0.006	0.011	0.005	22.6%	32.6%	144.6%	22
Sodium	0.196	0.178	0.202	0.185	20.0%	16.6%	82.8%	567
Strontium	0.003	0.004	0.003	0.005	23.0%	27.6%	119.6%	273

(continued)

Table 5-5. (continued)

Analyte	Sampler 1		Sampler 2		Average Relative Diff. ²	Average Rel. AQS Uncert. ³	Ratio AQS/ARD percent ⁴	Count ⁵ s
Sulfur	1.064	0.861	1.059	0.863	6.0%	7.2%	119.7%	1592
Tantalum	0.012	0.012	0.008	0.006	29.6%	28.4%	96.1%	23
Terbium	0.019	0.015	0.020	0.017	22.3%	30.0%	134.6%	131
Tin	0.020	0.011	0.020	0.011	20.8%	32.6%	156.6%	27
Titanium	0.012	0.012	0.011	0.011	23.6%	19.6%	83.1%	817
Vanadium	0.006	0.004	0.007	0.004	20.1%	20.3%	101.2%	785
Wolfram	0.007	0.005	0.006	0.004	25.3%	31.4%	124.4%	32
Yttrium	0.002	0.001	0.002	0.001	10.7%	38.1%	354.6%	8
Zinc	0.024	0.037	0.024	0.037	14.4%	10.9%	75.7%	1497
Zirconium	0.004	0.002	0.004	0.002	20.2%	32.0%	157.9%	59
Anions and Cations by IC								
Ammonium	2.172	2.528	2.184	2.499	5%	11%	206%	347
Potassium	0.165	0.429	0.167	0.433	10%	12%	122%	191
Sodium	0.239	0.164	0.263	0.200	16%	37%	236%	170
Nitrate	4.521	6.730	4.586	6.849	4%	11%	247%	312
Nitrate	0.427	0.426	0.514	0.385	30%	11%	37%	36
Nitrate	0.449	0.438	0.474	0.448	19%	11%	57%	35
Sulfate	2.764	2.460	2.832	2.542	4%	11%	264%	347
OC/EC								
Elemental carbon	1.202	0.814	1.219	0.878	10%	43%	413%	202
Organic carbon	4.219	2.729	4.146	2.675	10%	20%	192%	317
Total carbon	5.146	3.302	5.117	3.340	9%	22%	232%	327
Particulate Matter (Gravimetry)								
Particulate matter 2.5u	17.111	13.892	17.663	13.903	11%	9%	78%	348

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

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

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

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

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

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 2007. 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:

- Three trace elements having 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. In all three cases, the uncertainty estimates reported to AQS were higher than the estimate from collection.
- Four ionic species— ammonium, sodium, nitrate and sulfate—had reported uncertainties that were slightly over twice the uncertainties estimated from collocation data.
- All the organic and elemental carbon species for the original CSN analysis have reported uncertainties to AQS that are significantly larger than those estimated from the collocated sampler data. This is consistent with reports from previous years.
- The ratio for particulate mass (Table 5-5) is within a factor of two. This is consistent with previous years' results.

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 CSN program, field blanks are run at a frequency of 10% or more, whereas trip blanks are run at approximately 3%. Historical data has shown little difference between the two types of blanks, perhaps because the field SOPs for running them are very similar, the only difference being that the Field Blanks are mounted on the sampler for a few minutes, whereas the Trip Blanks are kept closed. Data 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 5-6** shows the distributions (percentiles) for trip and field blanks during 2007.

Table 5-6. Concentration Percentiles for Combined Trip and Field Blanks Reported During 2007

ANALYTE	MEAN	5	10	25	MEDIAN	75	90	95
Anions and Cations by Ion Chromatography								
Ammonium	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.029
Potassium	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium	0.025	0.000	0.000	0.000	0.000	0.018	0.040	0.089
Nitrate	0.028	0.000	0.000	0.000	0.000	0.041	0.064	0.098
Nitrate	0.028	0.000	0.000	0.017	0.024	0.038	0.051	0.065
Nitrate	0.034	0.017	0.019	0.021	0.026	0.035	0.053	0.085
Sulfate	0.035	0.000	0.000	0.000	0.000	0.039	0.060	0.083
PM _{2.5} Mass by Gravimetry								
PM _{2.5} Mass	0.840	0.000	0.042	0.292	0.729	1.250	1.875	2.396
Organic and Elemental Carbon (OC/EC)								
Elemental carbon	0.031	0.000	0.000	0.000	0.002	0.015	0.062	0.119
Organic carbon	1.049	0.478	0.581	0.752	0.924	1.132	1.463	1.918
Pk1_OC	0.279	0.113	0.141	0.204	0.271	0.334	0.407	0.473
Pk2_OC	0.416	0.159	0.202	0.271	0.347	0.453	0.601	0.807
Pk3_OC	0.260	0.077	0.108	0.153	0.210	0.286	0.395	0.549
Pk4_OC	0.088	0.000	0.010	0.032	0.058	0.093	0.157	0.265
PyroC	0.006	0.000	0.000	0.000	0.000	0.001	0.016	0.029
Total carbon	1.080	0.492	0.603	0.773	0.944	1.151	1.479	1.937
E1 IMPROVE	0.002	0.000	0.000	0.000	0.000	0.003	0.007	0.012
E2 IMPROVE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
E3 IMPROVE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
EC IMPROVE TOR	0.003	0.000	0.000	0.000	0.000	0.003	0.008	0.014
EC IMPROVE TOT	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.005
O1 IMPROVE	0.039	0.013	0.017	0.025	0.034	0.047	0.064	0.072
O2 IMPROVE	0.037	0.015	0.017	0.023	0.034	0.049	0.066	0.072
O3 IMPROVE	0.056	0.023	0.028	0.036	0.046	0.063	0.093	0.130
O4 IMPROVE	0.004	0.000	0.000	0.000	0.000	0.006	0.011	0.020
OC IMPROVE TOR	0.136	0.069	0.074	0.093	0.125	0.158	0.214	0.254
OC IMPROVE TOT	0.138	0.069	0.074	0.093	0.125	0.160	0.214	0.265
OP IMPROVE TOR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
OP IMPROVE TOT	0.002	0.000	0.000	0.000	0.000	0.001	0.005	0.011
TC IMPROVE	0.139	0.069	0.074	0.093	0.125	0.160	0.220	0.268
Trace Elements by XRF								
Aluminum	0.002	0.000	0.000	0.000	0.000	0.001	0.005	0.010
Antimony	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.004
Arsenic	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Barium	0.001	0.000	0.000	0.000	0.000	0.000	0.004	0.007
Bromine	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Cadmium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002

(continued)

Table 5-6. (continued)

ANALYTE	MEAN	5	10	25	MEDIAN	75	90	95
Calcium	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Cerium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cesium	0.001	0.000	0.000	0.000	0.000	0.000	0.003	0.004
Chlorine	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Chromium	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Cobalt	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Copper	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Europium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Gallium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Gold	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Hafnium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Indium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Iridium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Iron	0.005	0.000	0.000	0.000	0.000	0.000	0.004	0.012
Lanthanum	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Lead	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Magnesium	0.001	0.000	0.000	0.000	0.000	0.000	0.002	0.006
Manganese	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Mercury	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Molybdenum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nickel	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Niobium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Phosphorus	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Potassium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Rubidium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Samarium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Scandium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Selenium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Silicon	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.003
Silver	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Sodium	0.004	0.000	0.000	0.000	0.000	0.000	0.003	0.027
Strontium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Sulfur	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Tantalum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Terbium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Tin	0.001	0.000	0.000	0.000	0.000	0.000	0.002	0.004
Titanium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Vanadium	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Wolfram	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.003
Yttrium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Zinc	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Zirconium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001

Note: All units are micrograms per cubic meter.

Trip and Field Blanks during 2007. For XRF analysis, some of the largest values (95 percentile) belong to sodium, silicon, and iron. 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

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 CSN analytes.

5.5 Analysis of Trip and Field Blanks for the URG 3000N

In May, 2007, the new URG 3000N began acquiring quartz filter samples at 57 CSN sites. One important feature is the acquisition of a new type of blank, called “backup filters,” which are intended to help assess the organic carbon artifact. Table 5-7 shows the percentile points of the backup filters for May through December 2007. The median value from the backup filters (shown in the table) are proposed as the value to be used as the artifact correction, similar to what is done in the IMPROVE program.

Table 5-7. Concentration Percentiles for 3000N Backup Filter Blanks Reported during 2007, $\mu\text{g}/\text{m}^3$

ANALYTE	MEAN	5	10	25	MEDIAN	75	90	95
E1 IMPROVE	0.016	0.000	0.000	0.005	0.010	0.019	0.032	0.042
E2 IMPROVE	0.004	0.000	0.000	0.000	0.001	0.006	0.011	0.015
E3 IMPROVE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
EC IMPROVE TOR	0.014	0.000	0.000	0.003	0.011	0.020	0.032	0.042
EC IMPROVE TOT	0.002	0.000	0.000	0.000	0.000	0.000	0.006	0.010
O1 IMPROVE	0.081	0.018	0.025	0.040	0.064	0.100	0.160	0.200
O2 IMPROVE	0.130	0.053	0.067	0.091	0.120	0.160	0.200	0.240
O3 IMPROVE	0.160	0.068	0.079	0.110	0.150	0.200	0.240	0.280
O4 IMPROVE	0.045	0.007	0.012	0.022	0.040	0.061	0.082	0.098
OC IMPROVE TOR	0.420	0.170	0.220	0.310	0.400	0.510	0.630	0.710
OC IMPROVE TOT	0.430	0.170	0.220	0.310	0.420	0.530	0.660	0.740
OP IMPROVE TOR	0.006	0.000	0.000	0.000	0.000	0.000	0.015	0.025
OP IMPROVE TOT	0.019	0.000	0.000	0.004	0.012	0.023	0.039	0.051
TC IMPROVE	0.430	0.180	0.220	0.320	0.420	0.530	0.670	0.750

6.0 External Audits

6.1 Performance Evaluation Audit Results

PE audit samples were received and analyzed by all the analytical laboratories in late 2007, but EPA's final report on the results was not available at the time of this writing.

6.2 System Audit Results

There was no technical systems audit by EPA during 2007.

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7.0 List of References

7.1 List of CSN 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 PM _{2.5} Material	8/14/2003	Hardison, E.	N/A
SOP	XRF Analysis of PM _{2.5} 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 PM ₂₀ and PM _{2.5} 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 PM _{2.5} 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

Type	Title	Date Revised	Author	Document No.
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
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 PM _{2.5} 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
Data	2006 Annual Data Summary Report	2/29/2008	RTI	RTI/8858/06QAS
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

Appendix A

Method Detection Limits

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Appendix A
Method Detection Limits (Network-wide Average)

Analysis	Analyte	Mass (μg)	Concentration ($\mu\text{g}/\text{m}^3$) by Sampler Type				
			MASS	RASS	R and P	SASS	3000N
Cations - PM2.5 (NH4, Na, K)	Ammonium	0.24	0.010	0.026	0.017	0.026	
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	0.030	0.021	0.032	
Mass - PM2.5	Particulate matter 2.5u	7.2	0.32	0.32	0.32	0.83	
Nitrate - PM2.5	Nitrate	0.21		0.0073	0.015	0.023	
Nitrate - PM2.5 (MASS/nylon)	Nitrate	0.21	0.0088				
Nitrate - PM2.5 (MASS/Teflon)	Nitrate	0.070	0.0031				
Organic and elemental carbon	E1 IMPROVE	0.010					0.00032
Organic and elemental carbon	E2 IMPROVE	0.010					0.00032
Organic and elemental carbon	E3 IMPROVE	0.010					0.00032
Organic and elemental carbon	EC IMPROVE TOR	0.034					0.0011
Organic and elemental carbon	EC IMPROVE TOT	0.034					0.0011
Organic and elemental carbon	Elemental carbon	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	O1 IMPROVE	0.014					0.00043
Organic and elemental carbon	O2 IMPROVE	0.34					0.011
Organic and elemental carbon	O3 IMPROVE	1.0					0.032
Organic and elemental	O4 IMPROVE	0.034					0.0011

Analysis	Analyte	Mass (μg)	Concentration ($\mu\text{g}/\text{m}^3$) by Sampler Type				
			MASS	RASS	R and P	SASS	3000N
carbon							
Organic and elemental carbon	OC IMPROVE TOR	1.3					0.042
Organic and elemental carbon	OC IMPROVE TOT	1.3					0.042
Organic and elemental carbon	OP IMPROVE TOR	0.034					0.0011
Organic and elemental carbon	OP IMPROVE TOT	0.034					0.0011
Organic and elemental carbon	Organic carbon	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	Pk1_OC	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	Pk2_OC	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	Pk3_OC	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	Pk4_OC	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	PyroIC	2.4	0.11	0.24	0.17	0.26	
Organic and elemental carbon	TC IMPROVE	1.4					0.045
Organic and elemental carbon	Total carbon	2.4	0.11	0.24	0.17	0.26	
Sulfate - PM2.5	Sulfate	0.10	0.0044	0.010	0.0072	0.011	
Trace elements	Aluminum	0.24	0.0057	0.010	0.0100	0.025	
Trace elements	Antimony	0.40	0.018	0.018	0.017	0.045	
Trace elements	Arsenic	0.026	0.00070	0.0012	0.0011	0.0028	
Trace elements	Barium	0.57	0.0046	0.026	0.025	0.061	

Analysis	Analyte	Mass (μg)	Concentration ($\mu\text{g}/\text{m}^3$) by Sampler Type				
			MASS	RASS	R and P	SASS	3000N
Trace elements	Bromine	0.022	0.00074	0.00098	0.00095	0.0023	
Trace elements	Cadmium	0.18	0.0079	0.0080	0.0078	0.020	
Trace elements	Calcium	0.073	0.0032	0.0032	0.0032	0.0083	
Trace elements	Cerium	0.97	0.0041	0.042	0.040	0.10	
Trace elements	Cesium	0.44	0.014	0.020	0.019	0.047	
Trace elements	Chlorine	0.15	0.0033	0.0063	0.0061	0.015	
Trace elements	Chromium	0.025	0.0011	0.0011	0.0011	0.0028	
Trace elements	Cobalt	0.019	0.00057	0.00085	0.00082	0.0020	
Trace elements	Copper	0.024	0.00069	0.0011	0.0011	0.0028	
Trace elements	Europium	0.11	0.0021	0.0049	0.0047	0.012	
Trace elements	Gallium	0.051	0.0011	0.0022	0.0021	0.0053	
Trace elements	Gold	0.078	0.0023	0.0035	0.0034	0.0083	
Trace elements	Hafnium	0.26	0.0025	0.011	0.011	0.029	
Trace elements	Indium	0.21	0.0093	0.0094	0.0092	0.024	
Trace elements	Iridium	0.075	0.0030	0.0033	0.0032	0.0080	
Trace elements	Iron	0.032	0.00073	0.0014	0.0014	0.0034	
Trace elements	Lanthanum	0.71	0.0036	0.030	0.029	0.073	
Trace elements	Lead	0.061	0.0021	0.0027	0.0026	0.0065	
Trace elements	Magnesium	0.63	0.0050	0.027	0.026	0.065	
Trace elements	Manganese	0.028	0.00081	0.0012	0.0012	0.0030	
Trace elements	Mercury	0.091	0.0040	0.0040	0.0039	0.010	
Trace elements	Molybdenum	0.087	0.0038	0.0038	0.0038	0.0097	
Trace elements	Nickel	0.018	0.00051	0.00080	0.00078	0.0019	
Trace elements	Niobium	0.053	0.0020	0.0024	0.0023	0.0056	
Trace elements	Phosphorus	0.15	0.0068	0.0068	0.0068	0.018	

Analysis	Analyte	Mass (μg)	Concentration ($\mu\text{g}/\text{m}^3$) by Sampler Type				
			MASS	RASS	R and P	SASS	3000N
Trace elements	Potassium	0.11	0.0031	0.0047	0.0046	0.012	
Trace elements	Rubidium	0.025	0.00084	0.0011	0.0011	0.0027	
Trace elements	Samarium	0.096	0.0021	0.0043	0.0042	0.010	
Trace elements	Scandium	0.36	0.016	0.016	0.015	0.040	
Trace elements	Selenium	0.025	0.00083	0.0011	0.0011	0.0029	
Trace elements	Silicon	0.18	0.0047	0.0079	0.0077	0.020	
Trace elements	Silver	0.14	0.0062	0.0063	0.0061	0.016	
Trace elements	Sodium	2.1	0.017	0.092	0.088	0.22	
Trace elements	Strontium	0.030	0.0010	0.0013	0.0013	0.0032	
Trace elements	Sulfur	0.095	0.0042	0.0042	0.0042	0.011	
Trace elements	Tantalum	0.18	0.0042	0.0078	0.0075	0.019	
Trace elements	Terbium	0.097	0.0019	0.0043	0.0042	0.010	
Trace elements	Tin	0.31	0.013	0.014	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	0.12	0.0031	0.0051	0.0050	0.012	
Trace elements	Yttrium	0.036	0.0012	0.0016	0.0016	0.0038	
Trace elements	Zinc	0.034	0.0015	0.0015	0.0015	0.0038	
Trace elements	Zirconium	0.045	0.0019	0.0020	0.0019	0.0049	

Appendix B
Data Completeness Summary

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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	
84	1/11/2007	11/13/2006	12/13/2006	1,068	70	53	1,191
85	2/13/2007	10/14/2006	11/14/2006	1,232	181	59	1,472
86	3/14/2007	11/13/2006	12/13/2006	1,068	70	53	1,191
87	4/12/2007	12/13/2006	1/15/2007	1,298	178	107	1,583
88	5/14/2007	1/15/2007	2/11/2007	1,154	68	48	1,270
89	6/15/2007	1/24/2007	3/14/2007	1,050	175	118	1,343
90	7/16/2007	3/13/2007	4/12/2007	1,264	69	162	1,495
91	8/15/2007	4/14/2007	5/16/2007	1,164	173	28	1,365
92	9/13/2007	5/12/2007	6/14/2007	1,165	67	51	1,283
93	10/15/2007	6/11/2007	7/11/2007	1,063	53	28	1,144
94	11/13/2007	6/29/2007	8/14/2007	1,216	143	7	1,366
95	12/13/2007	8/10/2007	9/12/2007	1,157	53	177	1,387
96	1/14/2008	9/3/2007	10/15/2007	1,120	44	11	1,175
97	2/14/2008	10/9/2007	11/14/2007	1,348	54	7	1,409

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	
84	1/11/2007	11/13/2006	12/13/2006	120,694	7,855	6,103	134,652
85	2/13/2007	12/13/2006	1/15/2007	146,855	20,203	12,210	179,268
86	3/14/2007	1/15/2007	2/11/2007	130,518	7,678	5,500	143,696
87	4/12/2007	1/24/2007	3/14/2007	118,643	19,844	13,404	151,891
88	5/14/2007	3/13/2007	4/12/2007	142,823	7,762	18,602	169,187
89	6/15/2007	4/14/2007	5/16/2007	133,319	19,580	3,231	156,130
90	7/16/2007	5/12/2007	6/14/2007	138,091	7,507	5,725	151,323
91	8/15/2007	6/11/2007	7/11/2007	126,042	6,041	3,713	135,796
92	9/13/2007	6/29/2007	8/14/2007	135,920	15,572	757	152,249
93	10/15/2007	8/10/2007	9/12/2007	129,549	4,672	19,845	154,066
94	11/13/2007	9/3/2007	10/15/2007	125,195	4,508	1,211	130,914
95	12/13/2007	10/9/2007	11/14/2007	151,094	4,810	745	156,649
96	1/14/2008	11/14/2007	12/15/2007	125,681	14,880	8,143	148,704
97	2/14/2008	12/8/2007	1/13/2008	140,585	5,461	2,817	148,863

**Table B-3. Percentage of Routine Exposure Records – CSN Sites
Monthly Percent Data Completeness by Site – CSN Sites**

Location	AQS Site	POC	Sampler Type	Report Batch											
				83	84	85	86	87	88	89	90	91	92	93	94
Alabama (TN)	120861016	5	SASS	100	100	100	100	100	100	100	90	100	82	89	100
Allen Park	471570024	5	SASS	100	100	100	100	91	100	100	100	100	100	100	100
Bakersfield-California Ave	261630001	5	SASS	89	100	89	100	100	100	89	100	100			
Bakersfield-California Ave (Collocated)	060290014	5	SASS	89	100	100	100	100	100	100	100	100			
Beacon Hill - Met One	060290014	6	SASS	100	100	33	100	100	100	100	100	100			
Blair Street	530330080	6	SASS	100	100	100	100	100	100	91	100	100			
Burlington	530330080	6	SASS	91	80	100	100	100	100	100	100	100	100	100	100
Capitol	295100085	6	MASS	82	89	100	100	90	100	100	100	100	91	67	100
Chamizal	500070012	5	MASS	100	100	100	80	100	78	100	86	100	88		100
Chicopee	220330009	5	SASS	75	100	78	100	88	88	100	100	100	100	100	100
Com Ed - Met One	481410044	5	SASS	100	100	89	100	100	100	100	89	100			
Commerce City	250130008	5	SASS	100	100	100	100	100	100	100	100	100			
CPW	170310076	5	SASS	82	100	90	100	100	70	100	90	100	100	80	80
Criscuolo Park	170310076	5	SASS	89	75	78	100	100	100	90	75	100	78	100	100
Deer Park	080010006	5	MASS	91	80	40	70	90	90	91	100	89	100	100	100
Deer Park (Collocated)	450190049	5	MASS	100	100	100	100	100	100	100	100	80	80	100	100
Dover	090090027	5	SASS	100	100	100	100	100	83	100	100	80	100	100	100
El Cajon	482011039	6	SASS	100	89	89	67	100	100	100	100	100			
Elizabeth Lab	482011039	7	SASS	89	100	89	100	100	88	100	100	100	100	100	100
Essex - Met One	100010003	5	SASS	100	100	70	100	88	100	75	100	100			
Fargo NW	060730003	5	SASS	100	90	100	70	50	100	100	100	89	91	100	100
Fresno - First Street	340390004	5	SASS	100	100	90	90	90	90	100	100	100	100	100	100
G.T. Craig	380171004	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
G.T. Craig - Collocated	060190008	5	SASS	80	75	67	40	50	100	100	100	100	100	100	100
Garinger High School	390350060	5	SASS	100	100	100	100	100	100	100	100	89	100	90	100
Gulfport	390350060	6	SASS	100	100	89	89	100	100	100	100	100	100	100	100
Hawthorne	371190041	5	SASS	100	90	20	89	100	100	100	90	100	0		
Henrico Co.	720610001	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Hinton	280470008	5	MASS	100	100	89	88	88	100	100	100	100	100	80	100

				Report Batch											
JFK Center	202090021	5	SASS	89	100	100	100	100	100	100	50			100	100
Lawrenceville	420030008	6	SASS	100	100	100	100	100	100	90	100	88	100	100	100
Lindon	490494001	5	SASS	100	100	100	100	100	83	100	100	100			
McMillan Reservoir	110010043	5	RAAS	100	100	100	100	88	100	100	100	100			
Missoula County Health Dept.	300630031	5	SASS	100	100	100	100	80	100	100	91	100			
MLK	100032004	5	SASS	100	100	100	100	75	100	100	100	100			
New Brunswick	340230006	5	SASS	100	100	78	100	88	88	100	100	100	89	100	100
New Brunswick (Collocated)	340230006	6	SASS	80	100	100	100	75	83	100	100	100	80	100	100
North Birmingham	010730023	5	SASS	100	100	100	100	100	100	100	100	100			
Peoria Site 1127	401431127	5	SASS	100	88	100	100	100	100	100	88	100	100	100	100
PHILA - AMS Laboratory	421010004	7	SASS	91	90	100	100	90	100	100	100	100			
Philips	270530963	5	SASS	100	90	100	100	100	100	100	100	86			
Phoenix Supersite	040139997	7	SASS	100	100	100	90	100	90	100	90	89	100	100	100
Portland - SE Lafayette	410510080	6	SASS			100	90	100	100	100	100	100			
Portland N. Roselawn	410510246	6	SASS	100	100	100									
Portsmouth	330150014	5	RAAS	100	100	100	100	100	75	0					
Reno	320310016	5	SASS	100	100	100	100	100	100	100	100	100	91	100	100
Riverside-Rubidoux	060658001	5	SASS	100	100	100	100	60	80	100	100	100			
Riverside-Rubidoux (Collocated)	060658001	6	SASS	100	100	100	100	80	90	100	100	100			
Roxbury (Boston)	250250042	5	SASS	100	100	100	100	86	100	100	89	100	100	100	100
Roxbury (Boston) - collocated	250250042	6	SASS	100	100	100	100	33	100	100	100	100	100	100	100
Sacramento - Del Paso Manor	060670006	5	SASS	100	100	100	100	100	100	82	100	100	100	100	100
San Jose - Jackson Street	060850005	5	SASS	100	100	100	100	100	100	100	88	100	100	100	100
SER-DNR Headquarters	550790026	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Simi Valley	061112002	5	SASS	100	75	100	100	75	89	91	100	100	100	56	100
South DeKalb - Met One	130890002	5	SASS	100	100	100	100	90	100	100	90	100	100	89	100
Springfield Pumping Station - Met One	170310057	5	SASS	80	100	100	80	100	100	100	100	100			
St. Lukes Meridian (IMS)	160010010	5	SASS	100	100	90	100	100	100	100	100	100			
Sydney	120573002	5	SASS	100	100	90	100	100	90	100	100	100	100	100	80
Univ. of Florida Ag School	120111002	5	SASS	82	100	90	100	90	100	100	90	100	100	100	90
Urban League	440070022	5	RAAS	89	100	89	100	100	100	100	100	100	100	100	100
Washington Park	180970078	5	SASS	100	100	100	100	88	100	100	100	100			
Woolworth St	310550019	5	SASS	89	89	56			100	100	100	100	100	89	100
WV - Guthrie Agricultural Center	540390011	5	SASS	100	80	90	80	80	90	100	91	88			

**Table B-4. Percentage of Routine Exposure Records – Non-CSN Sites
Monthly Percent Data Completeness by Site – Non-CSN Sites**

Location	AQS Site	POC	Sampler Type	Report Batch											
				83	84	85	86	87	88	89	90	91	92	93	94
(NC) - Lexington	370570002	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
(PA) Liberty	420030064	6	SASS	100	100	100	100	100	100	75	83	100			
5 Points	391530023	5	SASS	100	75	100	100	100	100	100	100	0			
AL - Phenix City	011130001	5	SASS	100	100	100	100	100	83	100	100	100			
Albany Co HD	360010005	5	SASS											100	100
Alton	171192009	5	SASS	100	100	100	100	100	83	100	100	100	60	0	
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	83	100	100	100	100	100	100	100	100	100
Arnold	290990012	5	SASS	100											
Arnold - R&P	290990012	5	R & P 2300	75	90	100	100	100	90	100	100	100	100	100	100
Ashland Health Department	210190017	5	SASS	100	100	100	100	50	67	100	100	100	100	80	100
Athens - Met One	130590001	5	SASS	100	100	100	100	100	83	20	60	80	80	20	100
Augusta - Met One	132450091	5	SASS	100	100	100	100	100	100	100	100	100	100	100	80
Bates House (USC)	450790019	5	SASS	80	50	67									
Bismarck Residential	380150003	5	SASS	100	100	100									
Bonne Terre	291860005	5	R & P 2300	91	90	100	80	60	100	89	100	100			
Bountiful	490110004	5	SASS	80	100	100	100	100	100	100	83	100			
Buffalo	360290005	6	R & P 2300	100	100	100	100	100	67	100					
Buffalo - Met One	360290005	6	SASS								80	100	100	100	100
Buncombe County Board of Education	370210034	5	SASS	80	75	100	40	75	83	100	100	100	100	100	80
Camden	340070003	5	SASS	100	100	89	100	63	75	100	100	100			
Canal St. Post Office	360610062	5	SASS	100	100	100	100	100	100						
Canton Fire Station	391510017	5	SASS	100	100	100	100	100	100	100	60	40	80	100	100
Chester	340273001	5	SASS	100	100	78	88	100	100	100	100	88	100	89	100

Location	AQS Site	POC	Sampler Type	Report Batch											
				83	84	85	86	87	88	89	90	91	92	93	94
Chester (PA)	420450002	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Chesterfield	450250001	5	SASS	80	75	100	100	100	100	100	100	100	100	100	100
Children's Park	040191028	5	SASS	80	100	100	100	100	100	100	100	60	20	80	100
Clarksville	471251009	5	SASS			100	100	100	100	100	100	100	100	100	100
Columbus - Met One	132150011	5	SASS	100	100	100	100	100	100	100	83	100			
Courthouse Annex-Libby	300530018	5	SASS	100	75	100	100	75	83	100	100	80	80	80	100
Covington - University College	211170007	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Craig Road	320030020	5	SASS						100	100	100	100	100	100	100
Crown Z	530630016	5	RAAS	100	100	100	100	100	100	100	100	80	100	100	100
Dearborn	261630033	5	SASS	100	100	100	100	100	100	100	100	100			
Del Norte	350010023	5	R & P 2300	100	100	100	100	100	100	100	100	100	100	100	100
Division St.	360610134	5	SASS						86	100	100	90	100		
Douglas - Met One	130690002	5	SASS	100	100	100	100	100	83	100	80	40	80	80	60
Downtown Library	391130032	5	SASS			100	100	100	83	100	100	100	100	100	100
Duwamish	530330057	6	RAAS	100	100	50	100	100	100	100	100	100	80	100	100
Elkhart Pierre Moran	180390003	5	SASS	100	100	100	100	100	100	100	80	100	100	100	100
Elmwood	421010136	5	SASS	75	100	33	100	100	83	100	100	100			
Erie	420490003	5	SASS	100	100	83	100	100	100	60	80	100	80	100	100
Evansville - Mill Road	181630012	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Fairbanks State Bldg	020900010	6	SASS	91	100	90	100	90	100	100	100	100	91	100	100
Florence	421255001	5	SASS	100	100	100	100	100	100	100	100	75			
Freemansburg	420950025	5	SASS	100	100	100	100	100	100	100	100	80	100	100	100
Gary litri	180890022	5	SASS	100	100	100	100	100	100	100	100	100			
General Hospital	390870010	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Grand Junction - Powell Building	080770017	5	SASS	100	100	100	100	100	100	80	80	100	100	100	100
Grand Rapids	260810020	5	SASS	100	100	100	100	75	100	100	100	100	100	80	100
Granite City	171190024	5	SASS												100

Location	AQS Site	POC	Sampler Type	Report Batch											
				83	84	85	86	87	88	89	90	91	92	93	94
Greensburg	421290008	5	SASS	100	75	100	100	100	100	75	100	100			
Hammond Purdue	180892004	5	SASS	100	100	100	100	100	100	100	100	100			
Harrisburg	420430401	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Hattie Avenue	370670022	5	SASS	80	75	100	100	75	100	100	100	100			
Hazard - Perry County Horse Park	211930003	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Head Start	390990014	5	SASS	100	100	100	100	75	100	100	100	100	100	100	100
Hickory	370350004	5	SASS	80	100	100	100	100	100	100	100	80	80	100	100
Houghton Lake	261130001	5	SASS	100	100	100	80	100	67	60	100	100	100	100	100
HU-Beltsville	240330030	5	RAAS	80	100	100	100	75	100	80	80	100	100	100	100
Huntsville Old Airport	010890014	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
IL - Decatur	171150013	5	SASS	80	100	100	100	100	100	100	100	100	100	100	100
IS 52 - Met One	360050110	5	SASS	100	100	90	100	100	100	100	100	100			
Jasper Post Office	180372001	5	SASS	100	100	100	100	100	100	100	100	80	100	100	100
Jefferson Elementary (10th and Vine)	191630015	5	R & P 2300	100	100	90	100	80	100	91	100	89	100	100	90
Kalamazoo	260770008	5	SASS	80	100	100	100	100	100	100	100	100	100	100	100
Kelo	460990006	5	SASS	100	100	100	100	100	67	60	100	100	100	100	100
Kingsport	471631007	5	SASS	100	100										
Lancaster	420710007	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Lawrence County	470990002	5	SASS	100	100	100	100	100	100	100	60	80	100	100	100
Lenoir Community College	371070004	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Lexington Health Department	210670012	5	SASS	80	100	100	100	100	100	100	100	100	80	100	100
Liberty	290470005	5	R & P 2300	73	90	100	90	70	90	100	100	100	100	100	100
Lockeland School	470370023	5	RAAS	100	50	83	80	100	83	75					
Lockeland School - Met One	470370023	5	SASS								100	100	100	100	100
Lorain	390933002	5	SASS	100	100	100	80	100	100	100	100	100			
Luna Pier	261150005	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Macon - Met One	130210007	5	SASS	100	100	100	100	100	100	100	100	100			

Location	AQS Site	POC	Sampler Type	Report Batch												
				83	84	85	86	87	88	89	90	91	92	93	94	
Maple Canyon	390490081	6	SASS	80	100	100	80	100	100	100	100	100				
Mayville Hubbard Township site	550270007	5	SASS	100	100	90	100	100	100	100	100	100	100	100	90	100
Mendenhall	370810013	5	SASS	0	0	0										
Middletown	390171004	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100	
Millbrook	371830014	5	SASS	82	60	100	100	100	100	91	100	100	82	100	100	
Mingo Junction	390811001	5	SASS									100				
MN - Rochester	271095008	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100	
MOMS	011011002	5	SASS	20	75	100	100	75	100	100	80	100	100	80	100	
Moundsville Armory	540511002	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100	
Murray Rd	390618001	5	SASS											100	100	
Naperville	170434002	5	SASS	100	100	100	80	100	100	60	20	100				
New Garden	420290100	5	SASS	100	100	100	100	100	100	60	100	80	100	100	100	
NLR Par	051190007	5	SASS	100	100	100	100	100	100	100	80	100	75	83	100	
North Los Angeles	060371103	5	SASS	100	100	100	100	100	100	75	100	75				
Northbrook	170314201	5	SASS	0	75	100	80	75	100	100	100	100				
OCUSA Campus	401091037	5	SASS	100	100	100	100	100	100	100	80	100	100	100	100	
Olive Street - Met One	530330048	6	SASS			0		100	60	100	100	80	80	80	0	
Pearl City	150032004	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100	
PerkinstownCASNET	551198001	5	SASS	100	100	100	100	100	100	100	100	80	100	100	100	
Pinnacle State Park	361010003	5	R & P 2300	100	100	100	100	100	90	100	100	89	90	90	90	
Platteville	081230008	5	SASS	100	100	67	100	100	100	80	100	100	100	100	100	
Public Health Building	191530030	5	R & P 2300	80	100	100	100	100	100	80	100	100	80	40	100	
Queens College	360810124	6	R & P 2300	100	90	70	100	100	100	100	100	100	100			
Queens College - Met One	360810124	6	SASS										100	100	100	
RBD	080410011	5	SASS	100	100	80										
Reading (temporary)	420110010	5	SASS	100	100	100	100	100	100	100	33					
Reading Airport	420110011	5	SASS								100	100	100	100	100	

Location	AQS Site	POC	Sampler Type	Report Batch											
				83	84	85	86	87	88	89	90	91	92	93	94
Rochester Primary	360551007	5	R & P 2300	100	100	100	100	100	90	100	90	89	91	90	88
Rochester Primary - Met One	360551007	5	SASS												100
Rockwell	371590021	5	SASS	100	100	100	100	100	100	100	100	100	80	100	100
Rome - Met One	131150005	5	SASS	100	100	100	100	100	100	80	100	80	100	100	100
Rossville - Met One	132950002	5	SASS	100	100	100	100	100	100	100	100	0			
Scranton	420692006	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Senior Center	040137020	5	SASS	100	100	100									
Shenandoah High School	180650003	5	SASS	100	75	100	100	100	100	100	100	100	100	100	100
Shreveport Airport	220150008	5	MASS	0	50	0	100	100	100	100	100	100	100	100	100
Skyview	121030026	5	SASS	100	100	100	100	88	100	100	100	88	100	100	100
South Charleston Library	540391005	5	SASS	80	100	100	100	75	67	100	100	100			
Southwick Community Center	211110043	5	SASS	100	100	100	80	75	100	100	100	100			
Spring Hill Elementary School	470931020	5	RAAS	100	50	83	100	75	100	100	100	100			
St Johns	040137003	5	SASS	75	80	100	80	100							
St Theo	390350038	6	SASS	100	100	100	100	100	83	100	100	100			
State College	420270100	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Steubenville	390810017	5	SASS	80	100	100	80	100	100	0					
Sunrise Acres	320030561	5	SASS	100	100	100	100	100							
Tacoma	530530029	5	RAAS	100	100	100	100	100	100						
Tacoma - Met One	530530029	5	SASS						100	100	100	75			
Taft	390610040	5	SASS	100	75	100	100	100	100	100	100	100			
Tallahassee Community College	120730012	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Taylors Fire Station	450450009	5	SASS	80	100	100	100	100	100	100	60	100	100	100	100
Toledo Airport	390950026	5	SASS	100	100	100	100	100	100	80	100	100	100	100	100
TRNP - NU	380530002	5	SASS	100	100	100									
UTC	470654002	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Waukesha, Cleveland Ave. Site	551330027	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100

Location	AQS Site	POC	Sampler Type	Report Batch											
				83	84	85	86	87	88	89	90	91	92	93	94
Whiteface	360310003	5	R & P 2300	100	100	100	100	100	100	100	100	100	100	100	100
Whiteface - Met One	360310003	5	SASS												100
Wichita Dept. of Environmental Health	201730010	5	R & P 2300	40	50	33	60	100	100	100	80	60	60	80	100
Wilbur Wright Middle School	391130031	5	SASS	100	75	100									
Wylam	010732003	5	SASS	100	100	100	100	100	100	100	100	100	100	100	100
York	421330008	5	SASS	100	100	100	60	100	100	100	100	100	100	100	100
Ypsilanti	261610008	5	SASS	100	100	100	100	100	100	100	100	100			