

May 27, 2009

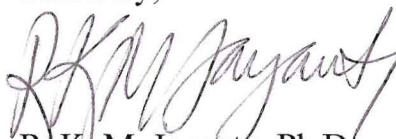
Ms. Margaret Dougherty  
U.S. Environmental Protection Agency  
Office of Air Quality Planning and Standards  
MC MD-14  
Research Triangle Park, NC 27711

Dear Ms. Dougherty:

Attached is the final PDF version of the Annual Data Summary Report for the PM2.5 Chemical Speciation Program, EPA Contract 68-D-03-038.

If you have any questions or comments, please feel free to call me at 541-6483, or e-mail at [rkmj@rti.org](mailto:rkmj@rti.org). Thank you for your continued support.

Sincerely,



R. K. M. Jayanty, Ph.D.  
Program Manager

/dmh

Attachment

cc: 91U-08858  
J. Rice  
S. Ricks  
D. Crumpler

RTI/0208858/07ADS

May 27, 2009

# **Annual Data Summary Report for the Chemical Speciation of PM<sub>2.5</sub> Filter Samples Project**

**January 1 through December 31, 2008**

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

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



*\*RTI International is a trade name of Research Triangle Institute.*

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## TABLE OF CONTENTS

Section	Page
Executive Summary .....	ES-1
1.0 Introduction.....	1-1
1.1 Program Overview .....	1-1
1.2 Project/Task Description .....	1-1
1.3 Major Laboratory Operational Areas .....	1-2
2.0 Quality Issues and Corrective Actions.....	2-1
2.1 Data Quality .....	2-1
2.2 Summary of Data Completeness .....	2-2
2.3 Corrective Actions.....	2-3
2.3.1 Gravimetric Mass.....	2-3
2.3.2 Elemental Analysis .....	2-3
2.3.3 Ion Analysis.....	2-4
2.3.4 Organic Carbon/Elemental Carbon Analysis.....	2-4
2.3.5 Sample Handling and Archiving Laboratory (SHAL).....	2-4
2.3.6 Data Processing .....	2-4
2.4 Other Quality Issues .....	2-4
3.0 Laboratory Quality Control Summaries.....	3-1
3.1 Gravimetric Laboratory .....	3-1
3.1.1 Quality Issues and Corrective Actions.....	3-1
3.1.2 Description of QC Checks Applied .....	3-2
3.1.3 Summary of QC Results .....	3-5
3.1.4 Determination of Uncertainties and Method Detection Limits.....	3-5
3.1.5 Audits, Performance Evaluations, Training, and Accreditations.....	3-5
3.2 Ions Analysis Laboratory .....	3-7
3.2.1 Audits, Performance Evaluations, Training, and Accreditations.....	3-7
3.2.2 Description of QA/QC Checks Applied .....	3-7
3.2.3 Summary of QC Results .....	3-9
3.2.4 Assessment of Between-instrument Comparability.....	3-11
3.2.5 Determination of Uncertainties and MDLs.....	3-12
3.2.6 Audits, Performance Evaluations, Training, and Accreditations.....	3-13
3.3 Organic Carbon/Elemental Carbon Laboratory.....	3-13
3.3.1 Quality Issues and Corrective Actions.....	3-13
3.3.2 Description of QC Checks Applied .....	3-13
3.3.3 Summary of QC Results .....	3-13
3.3.4 Determination of Uncertainties and MDLs.....	3-19
3.3.5 Audits, PEs, Training, and Accreditations.....	3-20
3.4 DRI Carbon Analysis Laboratory.....	3-21
3.4.1 Quality Issues and Corrective Actions.....	3-21
3.4.2 Description of QC Checks Applied .....	3-21
3.4.3 Summary of QC Results .....	3-23
3.4.4 Assessment of Duplicate and Replicate Analyses .....	3-34
3.4.5 Determination of MDLs and LQLs .....	3-34
3.4.6 Audits, PEs, Training, and Accreditations.....	3-35
3.5 X-ray Fluorescence Laboratories .....	3-36
3.5.1 RTI International XRF Laboratory .....	3-36
3.5.2 Chester LabNet X-Ray Fluorescence Laboratory .....	3-44
3.6 Denuder Refurbishment Laboratory.....	3-48
3.6.1 Quality Issues and Corrective Actions.....	3-49
3.6.2 Operational Discussion.....	3-49

## TABLE OF CONTENTS

Section	Page
3.6.3 Description of QC Checks Applied and Results.....	3-50
3.7 Sample Handling and Archiving Laboratory.....	3-51
3.7.1 Quality Issues and Corrective Actions.....	3-51
3.7.2 Description of QC Checks Applied .....	3-51
3.7.3 Summary of QC Results .....	3-51
3.7.4 Summary of Scheduling Problems .....	3-52
3.7.5 Support Activities for Site Operators and Data Users .....	3-53
3.7.6 Audits, PEs, Training, and Accreditations.....	3-54
4.0 Data Processing.....	4-1
4.1 Quality Issues and Corrective Actions .....	4-1
4.2 Operational Summary.....	4-1
4.3 Operational Changes and Improvements.....	4-1
4.4 Monthly Data Postings to Web Site .....	4-2
4.5 Data User Support Activities.....	4-2
4.5.1 Data Change Requests .....	4-2
4.5.2 Requests for Old Data.....	4-6
4.5.3 SDVAT Support .....	4-6
4.5.4 Data User Communications.....	4-6
4.6 Changes in AQS Event Validity Flags .....	4-7
5.0 Quality Assurance and Data Validation.....	5-1
5.1 QA Activities.....	5-1
5.1.1 QAPP Updates .....	5-1
5.1.2 SOP Updates.....	5-1
5.1.3 Internal Surveillance Activities .....	5-1
5.1.4 Data User Support Activities .....	5-1
5.2 Data Validation and Review.....	5-1
5.2.1 Review of Monthly Data Reports to the CSN Web Site.....	5-1
5.2.2 Review of Monthly Data Packages to AQS.....	5-2
5.3 Analysis of Collocated Data .....	5-2
5.3.1 Precision .....	5-9
5.3.2 Bias .....	5-11
5.4 Analysis of Trip and Field Blanks.....	5-11
5.5 Analysis of Trip and Field Blanks for the URG 3000N .....	5-14
6.0 External Audits .....	6-1
6.1 Performance Evaluation Audit Results .....	6-1
6.1.1 Performance Evaluation Audit Sample Resultss for 2007.....	6-1
6.1.2 Performance Evaluation Audit Samples for 2008 .....	6-2
6.2 System Audit Results .....	6-2
7.0 List of References .....	7-1
7.1 List of CSN Documents .....	7-1

## LIST OF APPENDICES

- A. Method Detection Limits
- B. Data Completeness Summary

## LIST OF TABLES

Table	Page
3-1. Summary of QC Checks Applied and Results Achieved in the Gravimetric Laboratory .....	3-2
3-2. Description of Audits, PEs, Training, and Accreditations .....	3-6
3-3. Description of Ion Chromatographic Systems Used for Analysis of PM <sub>2.5</sub> Filter Samples .....	3-7
3-4. Ion Analysis of PM <sub>2.5</sub> Quality Control/ Quality Assurance Checks.....	3-8
3-5. Minimum Detection Limit for Each Instrument and Analyte .....	3-9
3-6. Definitions and Specifications for QA/QC Samples .....	3-9
3-7. Average Percent Recovery for QA and QC Samples.....	3-10
3-8. Average Percent Recovery for Spikes.....	3-11
3-9. Filter Blank (N) and Reagent Blank Values (ppm) for all Analytes .....	3-11
3-10. Between-instrument Comparability .....	3-12
3-11. OC/EC Laboratory QC Checks, Acceptance Criteria, and Corrective Actions .....	3-14
3-12. OC/EC Laboratory-Assigned Data Flags.....	3-15
3-13. OC/EC Instrument Blank Statistics.....	3-15
3-14. OC/EC Three-Point Calibration Statistics.....	3-16
3-15. OC/EC Daily Calibration Check Statistics.....	3-17
3-16. Duplicate OC/EC Analysis Statistics .....	3-18
3-17. Estimated Uncertainties for CSN/TOT Carbon Fractions.....	3-20
3-18. Target MDLs for OC/EC Carbon Fractions .....	3-20
3-19. DRI Carbon Analysis QC Measures .....	3-22
3-20. DRI Carbon Laboratory-Assigned Data Flags .....	3-23
3-21. DRI Carbon Laboratory System Blank Statistics for All Analyzers by Month for the Period 1/1/08 thorough 12/31/08 .....	3-24
3-22. DRI Carbon Laboratory System Blank Statistics for Each Analyzer (1/1/08 through 12/31/08) .....	3-25
3-23. DRI Carbon Analysis Statistics for 24-Hour Field Blanks .....	3-27
3-24. DRI Carbon Analysis Statistics for Backup Filters.....	3-28
3-25. DRI Carbon Analysis Statistics for Trip Blanks .....	3-29
3-26. DRI Carbon Analysis Annual Statistics for CSN Blank Categories .....	3-30
3-27. DRI Multi-Point Calibration Statistics.....	3-31
3-28. DRI Temperature Calibration Statistics .....	3-32
3-29. DRI Oxygen Test Statistics .....	3-32
3-30. Summary of Instrument Maintenance Performed as a Result of Autocalibration Peak Response .....	3-33
3-31. DRI Replicate Analysis Criteria and Statistics.....	3-34
3-32. Estimated MDLs and LQLs for IMPROVE_A Parameters for 2008.....	3-35
3-33. QC Procedures Performed in RTI XRF Elemental Analysis Laboratory.....	3-37
3-34. Summary of RTI XRF 1 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$ , 1/9/2008 through 2/26/2008 .....	3-38
3-35. Summary of RTI XRF 1 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$ , 4/15/2008 through 4/25/2008 .....	3-38
3-36. Summary of RTI XRF 1 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$ , 7/26/2008 through 11/10/2008 .....	3-38
3-37. Summary of RTI XRF 2 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$ , 1/7/2008 through 7/6/2008 .....	3-38
3-38. Summary of RTI XRF 2 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$ , 8/29/2008 through 12/31/2008 .....	3-39
3-39. Summary of RTI XRF 3 Laboratory QC Precision Data, $\mu\text{g}/\text{cm}^2$ , 3/19/2008 through 12/31/2008 .....	3-39
3-40. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 1, 1/1/08 through 12/31/08 .....	3-40
3-41. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 2, 1/1/2008 through 12/31/2008 .....	3-40

## LIST OF TABLES

Table	Page
3-42. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 3, 1/1/2008 through 12/31/2008 .....	3-40
3-43. Replicates for XRF 1, XRF 2, and XRF 3.....	3-41
3-44. Numbers of Round-Robin Filter Analyses Performed during 2008.....	3-42
3-45. Regression Results for 11 Elements RTI XRF Instruments.....	3-43
3-46. Regression Results for 11 Elements CLN XRF Instrument 770.....	3-43
3-47. QC Procedures Performed in Support of XRF Elemental Analysis.....	3-45
3-48A. Summary of Chester XRF 770 Laboratory QC Precision Data 1/1/08 through 12/31/08 .....	3-45
3-48B. Recovery Determined from Analysis of NIST SRMs 1832, 1833, 2708, and 2783 for Chester XRF 770--1/1/08 through 12/31/08.....	3-46
3-49. Replicate Data for Chester CRF 770.....	3-47
3-50. Denuder Refurbishments, January 1, 2008 through December 31, 2008.....	3-49
3-51. Sites with Less than 95% of Filters Run on Intended Sampling Date.....	3-53
3-52. Summary of SHAL Communications with Site Operators and Data Users .....	3-53
3-53. Review of SHAL Technician Processing Filter Modules .....	3-54
4-1. Events Posted to Web Site .....	4-3
4-2. Records Posted to Web Site .....	4-4
4-3. Events Posted to AQS .....	4-5
4-4. Records Posted to AQS.....	4-5
4-5. Change Requests per Report Batch.....	4-5
4-6. New AQS Informational Only Event Flags .....	4-7
5-1. Summary of Validity Status Codes by Delivery Batch Number (percent of data records reported).....	5-3
5-2. Summary of Null Value Codes by Delivery Batch Number (percent of data records reported).....	5-4
5-3. RTI-assigned Flags (not reported to AQS) by Delivery Batch Number (percent of data records reported).....	5-5
5-4. Collocated sites in the CSN during 2008. ....	5-6
5-5. Precision of Collocated Samplers .....	5-10
5-6. Concentration Percentiles for Combined Trip and Field Blanks (Reporting Batches 95-106). ....	5-11
5-7. Concentration Percentiles for 3000N Backup Filter Blanks (Reporting Batches 95-106). ....	5-12

## LIST OF FIGURES

Figure	Page
3-1. DRI Carbon Analyzer Daily Autocalibration Response for the Period 1/1/08 – 12/31/08.....	3-33
3-2. SHAL Technician loading the URG 3000N Cassette. ....	3-51
3-3A. Late Coolers by Site. ....	3-52
3-3B. Late Coolers by FedEx.....	3-52
5-1. Examples of the Comparisons for Organic Carbon, Elemental Carbon, Mass, Nitrate, Sulfate, and Sulfur. ....	5-6

## **Executive Summary**

### ***Introduction***

The U.S. Environmental Protection Agency (EPA) established a PM<sub>2.5</sub> 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<sub>2.5</sub> 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 CSN sites from January 1 to December 31, 2008, 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 team (RTI and DRI) laboratories were not audited by EPA personnel during 2008; however, the RTI team received performance audit samples as part of a multi-lab study conducted by EPA's Montgomery Laboratory. Interlaboratory comparison results for analyses performed in 2007 were received in 2008. These encompassed all the major analyses being performed under the CSN contract, and the RTI team's results compared well with results from the other speciation laboratories and the EPA reference laboratory (EDXRF only).

### ***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 (CSN Organic and Elemental Carbon), 3.4 Organic and Elemental Carbon IMPROVE\_A, and 3.5 (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 2008.

Minimal problems with laboratory operations and filter media were reported by the Ion and Organic and Elemental Carbon (OC/EC) laboratories during 2008. 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 3.5.1 and 3.5.2). 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 3.5.2.4. 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 2008. 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 3.7).

No significant quality issues were reported by the data processing and data validation functions during 2008 (Sections 4.0 and 5.0). 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***

There were no Corrective Action Requests (CARs) issued during 2008. 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.

<b>CAR Number</b>	<b>Lab</b>	<b>Description</b>	<b>Response</b>	<b>Effect on Data</b>
None	SHAL	Late-arriving coolers	DOPO and others are notified whenever coolers are received late from the field	Data are flagged as missing

## **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 PM<sub>10</sub> standard) and less than 2.5 micrometers (the PM<sub>2.5</sub> 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).

Chemical speciation data will be used to support development of emission-mitigation approaches to reduce ambient PM<sub>2.5</sub> 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<sub>2.5</sub> and its components, and evaluating potential linkages to health effects.

This data summary report covers the quality assurance (QA) aspects of the collection and chemical analysis of samples from the CSN sites from January 1 through December 31, 2008. RTI is supporting the PM<sub>2.5</sub> 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 State Agencies, 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 State Agencies.
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, 2008. 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 PyroC) 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<sub>2.5</sub> 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.<sup>1</sup> A peer-reviewed publication has been submitted to the Journal of the Air and Waste Management Association.<sup>2</sup>
  - 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.<sup>3</sup>

## 2.2 Summary of Data Completeness

Data completeness network-wide exceeded 95% for 2008. 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 2008. **Table B.1** shows the total number of sampling events included in each Reporting Batch. **Table B.2** provides the total number of records delivered by type. **Table B.3** shows the percentage of routine exposure records for each delivery batch group that were valid (i.e., not invalidated with an AQS Null Value Code) relative to the

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

<sup>2</sup> Gutknecht, W.F., J.B. Flanagan, A. McWilliams, R.K.M. Jayanty, et al. 2009. Harmonization of uncertainties of X-ray fluorescence data from PM<sub>2.5</sub> air filter analysis. *Journal of the Air and Waste Management Association*, submitted for publication.

<sup>3</sup> Flanagan, James B., R.K.M. Jayanty, E. Edward Rickman, Jr., and Max R. Peterson, “PM<sub>2.5</sub> 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.

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. The following subsections describe corrective actions undertaken in each laboratory area during 2008.

### **2.3.1 Gravimetric Mass**

No significant quality issues were identified in the Gravimetric Laboratory in 2008. 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 2008 in either this enhanced inspection or in routine visual inspection in the chamber. As a result of continuing good results for filters examined, the intensity of filter screening will be reduced to meet the baseline criteria of Section 2.12 guidelines beginning in early 2009.

The RTI Gravimetric Laboratory was dropped from the North Carolina Department of Agriculture and Consumer Services Standards Laboratory appointment and notification queue in 2008 due to a system glitch at the Standards Division. In corrective action follow-up, the Laboratory Supervisor arranged a new calibration schedule for working mass standards for March and July of each year. One 200-mg standard was removed from use at the end of the year pending re-verification by the state.

Chamber 1's steam generator humidification system malfunctioned on Sunday, November 23, 2008. Relative humidity in the chamber fell below 30%. The problem was an electrical short in a relay block. The relay was replaced on Wednesday, November 26. No filters were invalidated or compromised as a result of the failure.

### **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)**

There were no corrective actions taken in the SHAL during 2008.

### **2.3.6 Data Processing**

There were no corrective actions taken during this reporting period. The uncertainties for the carbon values for the samples collected by URG 3000N have not yet been posted into AQS, pending direction from EPA about the method to be used for calculations. Blank-corrected IMPROVE\_A carbon measurements rely on the same set of calculations, and these have also not been posted, pending direction from EPA.

## **2.4 Other Quality Issues**

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 17,089 Teflon filters for the PM<sub>2.5</sub> speciation program between January 1 and December 31, 2008. During the same time period, the laboratory performed final (post-sampling) weighings of 15,440 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<sub>2.5</sub> 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 filter quality issues were identified in the Gravimetric Laboratory in 2008. 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 2008 in either this enhanced inspection or in the routine visual inspection in the chamber. Lot stability tests indicated the three Teflon filter lots used for the program in 2008 did not have issues with debris or outgassing.

The laboratory's environmental chambers experienced little downtime due to system failure in 2008. However, Chamber 1's steam generator humidification system did malfunction on Sunday, November 23, 2008. Relative humidity in the chamber fell below 30%. RTI's on-call HVAC technician was notified by RTI Security when the regular patrol Sunday evening found the chamber in alarm. RTI's HVAC Department could not immediately identify the problem because the system had begun to generate steam by the time the on-call tech arrived at RTI's campus. In follow up, RTI's HVAC Department monitored the chamber systems and the Laboratory Supervisor contacted the chamber vendor, Environmental Specialties, for emergency service. The problem turned out to be an electrical short in a specialty relay block. The relay shorted out completely on November 25 and was replaced by Environmental Specialties on Wednesday, November 26. One batch of filters was post-weighed in Chamber 1 on Monday, November 24. The chamber had been stable and within FRM environmental temperature and humidity ranges for approximately 13 hours prior to weighing. RTI's rationale for weighing the filters early was the unknown nature of the chamber stability and repair situation (how long the chamber would remain stable, whether the chamber would lose both temperature and humidity controls, how quickly the chamber could be repaired, whether repair activities would introduce contamination into the chamber, etc.) and the upcoming Thanksgiving holiday. The samples would have expired on November 29, over the Thanksgiving weekend. As it turned out, the laboratory had a narrow window in which to weigh the samples before the relay shorted out completely.

The RTI Gravimetric Laboratory was dropped from the North Carolina Department of Agriculture and Consumer Services Standards Laboratory appointment and notification queue in 2008 due to a system glitch at the Standards Division. In corrective action follow-up, the Laboratory Supervisor arranged a new calibration schedule for working mass standards for March and July of each year. Splitting the working mass standard calibrations into at least two separate calibration appointments will allow RTI's laboratory to have calibrated weight sets in use while other sets are being calibrated by the state laboratory. The working mass standards routinely used in the laboratory showed good stability in 2008. One 200-mg standard was removed from use at the end of the year pending re-verification by the state.

### 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 $\pm 3 \mu\text{g}$  [Standard reference weights initially calibrated by Troemner. Verified by North Carolina Department of Agriculture and Consumer Services (NCDA&CS) Standards Laboratory in 2007. Verified by the laboratory in conjunction with 2008 internal balance audit performed by RTI Quality Systems Program. 2009 NCDA&CS verifications have already been scheduled for March 2009 and July 2009. ]	<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 = 0.0011 for 1669 weighings	Laboratory average falls within tolerance interval. No weighing exceeded 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 = 200.005 mg Std Dev = 0.0011 for 1673 weighings	Laboratory average falls within tolerance interval. No weighing exceeded tolerance interval.
		<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 = 0.0010 for 1232 weighings	Laboratory average falls within tolerance interval. No weighing exceeded 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 = 100.003 mg Std Dev = 0.0008 for 1731 weighings	Laboratory average falls within tolerance interval. No weighing exceeded tolerance interval.
		200-mg S/N 58098 03/07/07 Verification: 200.00886 mg $\pm$ 0.00086	Mean = 200.007 mg Std Dev = 0.0010 for 1230 weighings	Laboratory average falls within tolerance interval. Six individual

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
		<p>Laboratory Tolerance Interval: 200.005–200.013 mg</p> <p>200-mg S/N 58099 03/07/07 Verification: 200.00548 mg ± 0.00086 Laboratory Tolerance Interval: 200.001–200.009 mg</p>	<p>Mean = 200.005 mg Std Dev = 0.0008 for 1730 weighings</p>	<p>weighings of 200.004 mg fell 1 µg below lower limit. Weight was removed from service.</p> <p>Laboratory average falls within tolerance interval. No weighing exceeded tolerance interval.</p>
Balance calibrations	<p>Auto (internal) calibration daily</p> <p>External calibration annually or as needed</p>	<p>Daily</p> <p>All balances inspected and externally calibrated by Mettler Toledo on August 1, 2008, using NIST-traceable weight</p>	<p>N/A</p> <p>N/A</p>	<p>Next inspection and external calibration scheduled for August 2009</p>
Balance audits	Annually	Audits of all balances performed by RTI Quality Systems Program personnel on November 10, 2008, 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	<p>Chamber temperature and humidity sensors, temperature and humidity controllers, and process alarm control board (mother board) calibrated by Environmental Specialties – LUWA on January 13, 2009</p> <p>Chamber data loggers calibrated by Veriteq Data Logger Test and Calibration Services on March 18, 2008</p>	<p>N/A</p> <p>N/A</p>	<p>Chamber sensors, controllers, and process boards are calibrated on-site annually by Environmental Specialties</p> <p>Next calibration scheduled for March 2009</p>

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Laboratory (Filter) blanks	Initial weight $\pm 15 \mu\text{g}$	1766 total replicate weighings of 294 individual laboratory blanks	Average difference between final and initial weight = $2.6 \mu\text{g}$ Std Dev = $3.9$  Min wt change = $0 \mu\text{g}$ Max wt change = $20 \mu\text{g}$	6 total replicate weighings of 3 individual laboratory blank filters (0.3% of the replicate weighings; 1.1% of the individual laboratory blanks) exceeded the upper $15 \mu\text{g}$ criterion.
Replicates	Initial weight $\pm 15 \mu\text{g}$	17,053 individual filters were weighed as pre-sampling (tared) replicates	Average = $0.4 \mu\text{g}$	17 replicate weighings (0.1% of the weighings) exceeded the $15 \mu\text{g}$ criterion on the first pass. Outliers were reweighed in order to confirm a mass value with two weights within $5 \mu\text{g}$ of each other. The third weighings of all 17 individual outlier filters were within the $15 \mu\text{g}$ acceptance range.
		5,403 individual filters were weighed as post-sampling replicates	Average = $0.4 \mu\text{g}$	23 replicate weighings (0.4% of the weighings) exceeded the $15 \mu\text{g}$ criterion on the first pass. Outliers were reweighed to confirm value with two weights within $5 \mu\text{g}$ of each other. The third weighings of all 23 individual outlier filters were within the $15 \mu\text{g}$ acceptance range.
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 $< \pm 5 \mu\text{g}$	Whatman Lot 7176034	24 hours = $+1 \mu\text{g}$ 48 hours = $+1 \mu\text{g}$ 72 hours = $0 \mu\text{g}$ 96 hours = $0 \mu\text{g}$	Weight changes fall within required range

QC Check	Requirements	QC Checks Applied in RTI Laboratory	Average Value Determined by Lab	Comments
Lot blanks (Lot stability filters) (cont'd)	24-hour weight change < $\pm 5 \mu\text{g}$	Whatman Lot 7317005	24 hours = 0 $\mu\text{g}$ 48 hours = 0 $\mu\text{g}$ 72 hours = 0 $\mu\text{g}$	Weight changes fall within required range
			24 hours = 0 $\mu\text{g}$ 48 hours = 0 $\mu\text{g}$ 72 hours = 0 $\mu\text{g}$ 96 hours = 0 $\mu\text{g}$	Weight changes fall within required range
		Whatman Lot 8084050	24 hours = 0 $\mu\text{g}$ 48 hours = 0 $\mu\text{g}$ 72 hours = 0 $\mu\text{g}$ 96 hours = 0 $\mu\text{g}$	Weight changes fall within required range
			24 hours = +2 $\mu\text{g}$ 48 hours = +1 $\mu\text{g}$ 72 hours = 0 $\mu\text{g}$ 96 hours = -1 $\mu\text{g}$	Weight changes fall within required range
			24 hours = +1 $\mu\text{g}$ 48 hours = 0 $\mu\text{g}$ 72 hours = +2 $\mu\text{g}$ 96 hours = -1 $\mu\text{g}$	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. The six outlier laboratory blank weighings fell above the upper warning limit, suggesting dust fall-out rather than a systematic issue of debris on Teflon. In response, the chamber was wet-wiped monthly. In the case of outlier replicates, Gravimetric Laboratory analysts reweighed outliers to validate weights. Although 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 weights were quite stable in 2008. 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 29, 2008  October 2008 follow-up in preparation for LELAP/ NELAP accreditation audit	RTI FRM Project QA Officer	The auditor noted that balance log books were not current. The issue was corrected by laboratory staff  The auditor also reviewed the laboratory against the National Environmental Laboratory Accreditation Conference (NELAC) quality systems checklist in October 2008. However, being governed by QA Handbook Section 2.12, the Grav Lab scope of work does not fit neatly into the NELAC system.
Proficiency Evaluation (PE)	October 2008 (results received)	EPA National Air and Radiation Environmental Laboratory (NAREL)	EPA NAREL conducted an experimental inter-comparison of speciation laboratories in the fall of 2007. Analyses were performed on real-world samples collected in Montgomery, AL. EPA NAREL staff provided a draft report to RTI on October 24, 2008. RTI's Gravimetric Laboratory performance in the study was good, with the RTI lab agreeing with the EPA NAREL lab within 5 µg on exposed (sampled) filters.
External Audit	November 13-14, 2008	Louisiana Environmental Laboratory Accreditation Program (LELAP)	There were no significant technical findings. Quality systems findings reported by the assessor were generally related to systems requirements of the NELAC Standard, many of which have little application to the laboratory's technical systems (for example, requiring a reference to the 2003 NELAC Standard in the laboratory's FRM QAPP). The auditor noted, "The laboratory appears to be well-organized and has a good security system. ... The staff interviewed was knowledgeable of their assignments."
Accreditation	N/A	Louisiana Environmental Laboratory Accreditation Program (LELAP)	RTI is accredited for the determination of fine particulates in ambient air by the FRM for PM <sub>2.5</sub> . RTI has requested to change from "state" accreditation to National Environmental Laboratory Accreditation Program (NELAP) accreditation and anticipates receiving this accreditation in 2009.

## 3.2 Ions Analysis Laboratory

For the CSN program during the period January 1 through December 31, 2008, the Ion Analysis Laboratory performed 20,269 analyses for cations (sodium, potassium, and ammonium) and 21,986 analyses for anions (nitrate and sulfate).

### 3.2.1 Audits, Performance Evaluations, Training, and Accreditations

No on-site audit was performed by NAREL during 2008, and no PE samples were received for analysis. A preliminary report for the November 2007 PE samples was released by the EPA in October 2008. All ion chromatography analyses were found to be satisfactory.

### 3.2.2 Description of QA/QC Checks Applied

Ion chromatographic analyses are performed by personnel from RTI's Environmental Industrial Chemistry Department (EICD). Five of our six available anion chromatographic systems and all four of our cation chromatographic systems were used for performance of the measurements. These instruments are listed in **Table 3-3**. The use of these systems was determined by the workload in the Ion Analysis Laboratory.

**Table 3-3. Description of Ion Chromatographic Systems Used for Analysis of PM<sub>2.5</sub> Filter Samples**

System No.	Dionex IC Model	Ions Measured
A1	DX-500	SO <sub>4</sub> , NO <sub>3</sub>
A2	DX-500	SO <sub>4</sub> , NO <sub>3</sub>
A3	DX-500	SO <sub>4</sub> , NO <sub>3</sub>
A4	DX-600	SO <sub>4</sub> , NO <sub>3</sub>
A5	DX-600	SO <sub>4</sub> , NO <sub>3</sub>
C1	DX-500	Na, NH <sub>4</sub> , K
C2	DX-600	Na, NH <sub>4</sub> , K
C3	ICS-2000	Na, NH <sub>4</sub> , K
C4	DX-600	Na, NH <sub>4</sub> , 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<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and K<sup>+</sup> for cation analyses; NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> 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<sub>2.5</sub> Quality Control/ Quality Assurance Checks**

QA/QC Check	Frequency	Requirements
Calibration Regression Parameters	Daily	$r \geq 0.999$
Initial QA/QC Checks:		
▪ RTI prepared QC sample at mid-to high-range concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values.
▪ RTI prepared QC sample at lower-end concentration	Daily, immediately after calibration	Measured concentrations within 10% of known values
▪ Commercially prepared, NIST traceable QA sample	Daily, immediately after calibration	Measured concentrations within 10% of known values.
Periodic QA/QC Checks:		
▪ Replicate sample †	Every 20 samples	RPD = 5% at 100x MDL* RPD = 10% at 10x MDL* RPD = 100% at MDL*
▪ QA/QC sample	Every 20 samples	Measured concentrations within 10% of known values.
▪ Matrix spiked sample extract	Every 20 samples	Recoveries within 90 to 100% of target values.
▪ Duplicates ‡	At least one per day	No limit set. This data gathered for comparability studies.
▪ Reagent Blanks	One reagent blank per reagent used (DI H <sub>2</sub> O 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
A1	0.059	0.066	na	na	na
A2	0.058	0.090	na	na	na
A3	0.066	0.074	na	na	na
A4	0.070	0.100	na	na	na
A5	0.051	0.068	na	na	na
C1	na	na	0.290	0.160	0.134
C2	na	na	0.290	0.160	0.134
C3	na	na	0.109	0.244	0.228
C4	na	na	0.212	0.014	0.022

\* 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	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 samples (prepared by RTI) 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. $\mu\text{g/mL}$	Avg % Rec *	SD	Min	Max
Nitrate	QA-CPI_LOW	381	0.6	98.3%	1.2%	0.570	0.626
	QA-CPI_MED-HI	325	3.0	101.1%	1.1%	2.932	3.160
	RTI-QC-HIGH	332	6.0	101.4%	0.9%	5.927	6.252
	RTI-QC-LOW	629	0.6	97.9%	1.6%	0.499	0.636
	RTI-QC-MED	757	1.5	98.6%	1.2%	1.431	1.595
Sulfate	QA-CPI_LOW	381	1.2	99.2%	1.4%	1.149	1.249
	QA-CPI_MED-HI	325	6.0	102.2%	1.4%	5.938	6.423
	RTI-QC-HIGH	332	12.0	102.2%	1.5%	11.669	12.718
	RTI-QC-LOW	629	1.2	99.4%	1.6%	1.128	1.285
	RTI-QC-MED	757	3.0	100.6%	1.7%	2.863	3.208
Sodium	GFS 0.4 PPM QA	646	0.4	101.9%	2.8%	0.373	0.468
	GFS 4.0 PPM QA	607	4.0	99.7%	1.2%	3.818	4.434
	RTI 2.0 PPM QC Reg Std	387	2.0	100.3%	1.6%	1.933	2.287
	RTI 5.0 PPM QC	350	5.0	100.3%	1.2%	4.867	5.622
Ammonium	GFS 0.4 PPM QA	646	0.4	101.1%	3.5%	0.352	0.453
	GFS 4.0 PPM QA	607	4.0	100.2%	1.6%	3.741	4.247
	RTI 2.0 PPM QC Reg Std	387	2.0	101.0%	1.9%	1.913	2.175
	RTI 5.0 PPM QC	350	5.0	101.7%	2.0%	4.784	5.575
Potassium	GFS 0.4 PPM QA	646	0.4	99.2%	1.7%	0.375	0.445
	GFS 4.0 PPM QA	607	4.0	98.7%	1.4%	3.828	4.327
	RTI 2.0 PPM QC	387	2.0	99.3%	1.3%	1.871	2.187
	RTI 5.0 PPM QC	350	5.0	99.7%	1.7%	4.830	5.443

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

Average recoveries for the QC samples ranged from 97.9 to 102.2% for the year.  
Average recoveries for the QA samples ranged from 98.3 to 102.2% 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 101.4%.

Table 3-8. Average Percent Recovery for Spikes

Analyte	Avg Recovery *	StDev	Count	Min	Max
Nitrate	101.4%	2.4%	694	85.9%	134.5%
Sulfate	101.4%	2.2%	694	85.9%	143.5%
Sodium	100.3%	2.1%	649	85.8%	111.7%
Ammonium	100.5%	2.1%	649	83.0%	109.5%
Potassium	100.0%	1.9%	649	84.6%	110.2%

\* 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	355	0.010	0.011	0.000	0.040
	REAG	335	0.001	0.004	0.000	0.024
Sulfate	N QC	355	0.002	0.004	0.000	0.028
	REAG	335	0.002	0.005	0.000	0.025
Sodium	N QC	349	0.001	0.005	-0.018	0.031
	REAG	236	0.001	0.005	-0.018	0.034
Ammonium	N QC	349	0.000	0.001	0.000	0.011
	REAG	236	0.000	0.000	-0.004	0.000
Potassium	N QC	349	0.000	0.000	0.000	0.000
	REAG	236	0.000	0.002	0.000	0.030

\* 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  $>1 \mu\text{g}$ , 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 A1, A2, A3, A4, and A5. (Less than 1% were run on A1 and A2.) Cation duplicates were analyzed on instruments C1, C2, C3 and C4. 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	1.2	106	-0.001	0.006	-0.016	0.022
	QA-CPI_MED-HI	6.0	68	0.008	0.028	-0.054	0.073
	RTI-QC-HIGH	12.0	71	0.011	0.045	-0.176	0.082
	RTI-QC-LOW	1.2	259	0.000	0.006	-0.017	0.021
	RTI-QC-MED	3.0	389	0.000	0.012	-0.034	0.040
Sulfate	QA-CPI_LOW	1.2	106	-0.002	0.008	-0.024	0.023
	QA-CPI_MED-HI	6.0	68	0.030	0.056	-0.090	0.202
	RTI-QC-HIGH	12.0	71	0.016	0.105	-0.381	0.171
	RTI-QC-LOW	1.2	259	0.000	0.009	-0.034	0.025
	RTI-QC-MED	3.0	389	0.004	0.022	-0.063	0.066
Sodium	GFS 0.4 PPM QA	0.4	296	0.002	0.013	-0.043	0.069
	GFS 4.0 PPM QA	4.0	253	-0.007	0.051	-0.144	0.468
	RTI 2.0 PPM QC	2.0	116	0.007	0.038	-0.071	0.261
	RTI 5.0 PPM QC	5.0	89	0.006	0.105	-0.193	0.672
Ammonium	GFS 0.4 PPM QA	0.4	296	-0.001	0.019	-0.064	0.042
	GFS 4.0 PPM QA	4.0	253	0.013	0.070	-0.195	0.241
	RTI 2.0 PPM QC	2.0	116	0.004	0.044	-0.101	0.154
	RTI 5.0 PPM QC	5.0	89	0.038	0.116	-0.192	0.423
Potassium	GFS 0.4 PPM QA	0.4	296	0.001	0.007	-0.013	0.050
	GFS 4.0 PPM QA	4.0	253	0.007	0.038	-0.068	0.417
	RTI 2.0 PPM QC	2.0	116	0.003	0.032	-0.060	0.242
	RTI 5.0 PPM QC	5.0	89	0.026	0.084	-0.098	0.574

\* Differences are calculated as Concentration of A3 – Concentration of A4 for Anions and Concentration of C1 – Concentration of C2 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 2008, 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 2008; 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/Elemental Carbon Laboratory

The RTI OC/EC Laboratory staff analyzed 10,571 quartz filter samples by the STN or CSN/TOT method during the period January 1, 2008, through December 31, 2008, and reported the results of those analyses to RTI's Speciation Program Information Management System (SPIMS). Three Sunset Laboratory Carbon Aerosol Analyzers (designated by the letters R, S, and T) were used for CSN/TOT analyses for the entire year.

### 3.3.1 Quality Issues and Corrective Actions

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

### 3.3.2 Description of QC Checks Applied

Quality control (QC) checks, acceptance criteria, and corrective actions for the OC/EC Laboratory are summarized in **Table 3-11**.

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

### 3.3.3 Summary of QC Results

#### 3.3.3.1 Instrument Blanks

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

Table 3-11. 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 0.5 $\mu\text{g C}/\text{cm}^2$	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 0.3 $\mu\text{g}/\text{cm}^2$ , and (2) calibration peak area 90% to 110% of average for the weekly three-point calibration.	Determine if the problem is with the filter or the instrument and, if necessary, initiate corrective action to identify and solve any instrument problem, and run an acceptable instrument blank before analyzing samples.
Three-Point Calibration	Weekly	(1) Correlation Coefficient ( $R^2$ ) 0.998 [with force-fit through 0,0], (2) 93% to 107% recovery for all three standards, and (3) FID response factor is 90% to 110% of the average response factor for all three standards.	Determine the cause of the nonlinearity, and initiate actions that will identify and solve any problem that may have arisen. Then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed.
Calibration Check	Daily	(1) 93% to 107% recovery, (2) calibration peak area 90% to 110% of average for the weekly three-point calibration, and (3) FID response factor is 90% to 110% of average response factor for last three-point calibration.	Initiate corrective action, if necessary, to solve the problem before analyzing samples.
Duplicate Analyses	10% of all samples	(1) TC Values greater than 10 $\mu\text{g C}/\text{cm}^2$ -- Less than 10% RPD, (2) TC Values 5 - 10 $\mu\text{g C}/\text{cm}^2$ -- Less than 15% RPD, (3) TC Values less than 5 $\mu\text{g C}/\text{cm}^2$ -- Within 0.75 $\mu\text{g C}/\text{cm}^2$ .	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
LFD	Filter inspection flag – discoloration	1
LFU	Filter inspection flag - non-uniformity (Duplicate analysis failed applicable duplicate criterion.)	41
Total Number of Analyses Flagged by OC/EC Analysts		44
Total Number of OC/EC Analyses Reported to SPIMS		10,571
Percent of OC/EC Analyses Flagged by Analysts		0.416%

Table 3-13. OC/EC Instrument Blank Statistics

Blank Statistic	CSN/TOT Analyzer		
	R	S	T
Number of Instrument Blanks	258	215	261
Mean Response ( $\mu\text{g C/cm}^2$ )	0.010	0.038	0.017
Standard Deviation	0.017	0.051	0.019
Minimum Response ( $\mu\text{g C/cm}^2$ )	0.000	0.000	0.000
Maximum Response ( $\mu\text{g C/cm}^2$ )	0.233	0.261	0.139

### 3.3.3.2 Calibrations

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

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

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

Variable/Statistic			CSN/TOT Analyzer		
			R	S	T
Number of Full Calibrations Passing All Criteria			54	48	52
Number of Full Calibrations Failing Any Criterion			0	0	0
Slope (counts/μgC), forced through origin (0,0)	Average	Average	8,116	6,750	6,484
		Minimum	7,605	5,496	5,721
		Maximum	8,788	8,184	7,512
Correlation Coefficient (R <sup>2</sup> ) (Criterion: ≥0.998)	Average	Average	0.9994	0.9995	0.9995
		Minimum	0.9985	0.9982	0.9983
		Maximum	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	100.13%	100.31%	100.17%
		Minimum	98.73%	97.37%	97.80%
		Maximum	101.63%	103.74%	101.46%
	Mid Cal	Average	100.01%	99.87%	99.98%
		Minimum	97.51%	95.15%	97.60%
		Maximum	101.11%	103.47%	101.43%
	High Cal	Average	99.86%	99.82%	99.84%
		Minimum	98.39%	95.11%	97.42%
		Maximum	101.13%	102.18%	101.28%
Recovery: Mass of Carbon Measured as a Percent of Mass of Carbon Spiked (Criterion: 93% to 107%)	Low Cal	Average	100.92%	101.20%	101.30%
		Minimum	95.66%	95.39%	96.80%
		Maximum	104.91%	104.89%	104.90%
	Mid Cal	Average	100.54%	100.27%	100.34%
		Minimum	97.76%	97.02%	97.68%
		Maximum	103.92%	104.37%	104.04%
	High Cal	Average	98.53%	98.53%	98.36%
		Minimum	95.75%	95.69%	95.59%
		Maximum	103.73%	102.33%	102.00%
	All 3 Cals	Average	100.00%	100.00%	100.00%
		Minimum	99.98%	99.97%	99.98%
		Maximum	100.02%	100.06%	100.02%
FID Response Factor as a Percent of Average FID Response Factor for 3-Point Cal (Criterion: 90% to 110%)	Low Cal	Average	101.05%	101.51%	102.48%
		Minimum	95.77%	96.17%	95.38%
		Maximum	104.94%	105.77%	106.09%
	Mid Cal	Average	102.21%	101.84%	102.18%
		Minimum	94.56%	95.35%	96.70%
		Maximum	105.42%	106.08%	105.82%
	High Cal	Average	98.40%	98.35%	98.20%
		Minimum	95.69%	95.06%	94.75%
		Maximum	103.35%	100.96%	102.04%

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

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

A calibration check is acceptable only if it meets all three criteria, and all 2008 calibration checks were acceptable.

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

Variable/Statistic		R	S	T
Number of Cal Checks Passing All Criteria		198	158	203
Number of Cal Checks Failing Any Criterion		0	0	0
Internal Standard (IS) Area as a Percent of Average IS Area for 3-Point Cal (Criterion: 90% to 110%)	Average	99.86%	99.81%	99.60%
	Minimum	94.44%	91.06%	92.03%
	Maximum	105.18%	109.95%	106.99%
Recovery: Mass of Carbon Measured as a Percent of Mass of Carbon Spiked (Criterion: 95% to 105%)	Average	99.89%	99.98%	100.25%
	Minimum	95.20%	95.14%	95.00%
	Maximum	104.88%	104.95%	104.97%
FID Response Factor as a Percent of Average Response Factor for 3-Point Cal (Criterion: 90% to 110%)	Average	99.74%	99.77%	99.84%
	Minimum	92.47%	91.35%	91.04%
	Maximum	107.93%	108.66%	108.83%

### 3.3.3.3 Duplicate Analyses

**Table 3-16** gives summary statistics for all duplicate CSN/TOT 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 1,237 duplicate CSN/TOT analyses were run under the laboratory support contract in 2008. OC/EC analysis results for 43 (or 3.48%) of those duplicates failed the applicable duplicate criterion and were flagged as coming from a filter with a non-uniform deposit.

Table 3-16. Duplicate OC/EC Analysis Statistics

Variable/Statistic		Analyzer		
		R	S	T
Total Number of Duplicate Analyses		438	368	431
Number of Analyses Flagged as Failing Duplicate Criteria		15	15	13
Percentage of Duplicate Analyses Failing Duplicate Criteria		3.42%	4.08%	3.02%
OC Sample vs. Dup Plot	Slope	0.994	0.958	0.987
	Intercept	0.041	0.206	0.064
	R <sup>2</sup>	0.980	0.787	0.982
EC Sample vs. Dup Plot	Slope	0.952	0.977	1.000
	Intercept	0.019	0.024	0.011
	R <sup>2</sup>	0.948	0.935	0.903
TC Sample vs. Dup Plot	Slope	0.993	0.966	0.993
	Intercept	0.044	0.211	0.061
	R <sup>2</sup>	0.978	0.817	0.979
Pk1C Sample vs. Dup Plot	Slope	0.981	0.966	0.984
	Intercept	0.012	0.014	0.011
	R <sup>2</sup>	0.983	0.978	0.989
Pk2C Sample vs. Dup Plot	Slope	0.980	0.944	0.988
	Intercept	0.041	0.067	0.016
	R <sup>2</sup>	0.952	0.913	0.969
Pk3C Sample vs. Dup Plot	Slope	0.961	0.855	0.986
	Intercept	0.031	0.169	0.016
	R <sup>2</sup>	0.968	0.313	0.963
Pk4C Sample vs. Dup Plot	Slope	0.980	0.989	0.985
	Intercept	0.016	0.017	0.024
	R <sup>2</sup>	0.976	0.869	0.981
PyrolC Sample vs. Dup Plot	Slope	0.446	0.967	0.973
	Intercept	0.002	0.004	0.001
	R <sup>2</sup>	0.142	0.982	0.988

### 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.<sup>1</sup> 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.

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

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

To assess between-analyzer comparability of OC, EC, TC, and the individual OC Peaks, RTI's OC/EC Laboratory analyzed 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 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.

### 3.3.4 Determination of Uncertainties and MDLs

**Table 3-17** gives estimated constant and proportional components of uncertainty for OC, EC, TC, and the five OC Peaks measured on multiple analyzers in RTI's OC/EC Laboratory.<sup>4,5,6</sup> The constant component of uncertainty appears to be essentially independent of filter loading and can be easily estimated in plots of absolute difference (y-axis) vs. average value (x-axis) for sample-duplicate pairs of analyses run on the same analyzer. The proportional component of uncertainty is most evident in plots of individual measurements of replicate analyses of filter samples across multiple analyzers (y-axis) vs. the average measured values across analyzers for those filter samples (x-axis).

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

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<sup>4</sup> Peterson, M.R., and M.H. Richards. 2006. *Estimation of Uncertainties for Organic Carbon Peaks Data in Thermal-Optical-Transmittance Analysis of PM<sub>2.5</sub> 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.

<sup>5</sup> Peterson, M.R., J.B. Flanagan, and M.H. Richards. 2008. *Estimating Uncertainties for Non-Independent Analytes--Thermal-Optical Analysis of Carbon in PM<sub>2.5</sub>*. Presented at Air & Waste Management Association (A&WMA) 101st Annual Conference & Exhibition, Portland, OR, June 23-27.

<sup>6</sup> Peterson, M.R., and M.H. Richards. 2008. *Evaluating Nonuniformity of Carbon Fractions in PM<sub>2.5</sub> Collected on Quartz Fiber Filters*. Presented at Air & Waste Management Association (A&WMA) Symposium on Air Quality Measurement Methods and Technology, Chapel Hill, NC, November 3-6.

Table 3-17. Estimated Uncertainties for CSN/TOT Carbon Fractions

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

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

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

Carbon 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

### 3.3.5 Audits, PEs, Training, and Accreditations

#### 3.3.5.1 System Audits

RTI's chemical speciation laboratories did not receive an external TSA during 2008.

### 3.3.5.2 Performance Evaluations

RTI's OC/EC Laboratory was one of four laboratories participating in the December 2007 EPA/NAREL interlaboratory comparison study. Both CSN/TOT and IMPROVE\_A analysis results for the PE samples were reported to EPA/NAREL in January 2008.

### 3.3.5.3 Training

No new analysts were trained for the CSN/TOT method; however, three current CSN/TOT-trained analysts were instructed in running the IMPROVE\_A method on both Sunset Laboratory and DRI Model 2001 analyzers.

### 3.3.5.4 Accreditations

There are no accreditation programs for OC/EC analysis.

## 3.4 DRI Carbon Analysis Laboratory

The DRI Carbon Analysis Laboratory, as a subcontractor to RTI for EPA's Chemical Speciation Network (CSN), received 6,087 quartz-fiber filters in batches 28 through 61 during the period January 1, 2008 through December 31, 2008. (Batch numbers refer to sets of quartz filters sent from RTI to DRI approximately twice per month.) DRI analyzed 6,281 quartz-fiber filter samples in these batches using the IMPROVE\_A method (Chow et al. 2007) and reported the results of those analyses to RTI. The statistics included in this report cover only those samples analyzed in 2008. Nine DRI Model 2001 Thermal/Optical Carbon Analyzers (designated as units # 6 – 13 and 16) were used for the CSN IMPROVE\_A analyses.

### 3.4.1 Quality Issues and Corrective Actions

Oxygen tests were performed in April 2008. Subsequent tests were delayed due to the need to repair a component used in the oxygen measurements and scheduling around annual GC/MS calibrations. Additional oxygen tests were completed as soon as possible (January 2009) after repairs and calibrations were completed.

### 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 # 2-216r2, revised in July 2008. Quality control (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 3-20** 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 7,510 runs, there were 433 runs flagged as invalid and 2,190 runs with blank flags. These were flagged based on notes on the sample Petri dish and modified for this report based on data in a spreadsheet later submitted to DRI by RTI. Actual sample blank

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 <sub>4</sub> /He, CO <sub>2</sub> /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 <sub>2</sub>	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 <sub>4</sub> /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 <sub>4</sub> /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. DRI Carbon Laboratory-Assigned Data Flags

Validation Flag Category	Validation Flag Subcategory	Description	No. of Sample Runs
n		Foreign substance on sample	8
s		Suspect analysis result	3
v		Void (invalid) analysis result	433
	v2	Replicate analysis failed acceptable limit	104
	v3	Potential contamination	19
	v5	Analytical instrument error	289
	v6	Analyst error	21
		Total no. of sample runs (incl. blank and replicate flags)	7510

information is not included in the data files RTI sends to DRI at the time the filters are to be analyzed. It was provided to DRI prior to completion of this report for MDL and LQL analysis. For 2007 there were two categories of blank – 24-hour field blank and trip blank. For 2008, there were four categories of blanks with the addition of backup filter and trip blank backup filter. In addition, there were 796 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. 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 AQS null value codes or validity status codes when reporting the data to AQS.

### 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 nine carbon aerosol analyzers used in the program. Specifically, **Table 3-21** gives the system blank values by month for all nine analyzers and **Table 3-22** gives the system blank values for each of the nine carbon analyzers used during this reporting period.

System blanks are run at the beginning of each analysis day for each operating analyzer. They may be rerun until the analyzer gives readings lower than  $0.20 \mu\text{g C}/\text{cm}^2$  of TC. However, they 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.

Table 3-21. DRI Carbon Laboratory System Blank Statistics for All Analyzers by Month for the Period 1/1/08 through 12/31/08

Month	No.	Statistic	IMPROVE_A Parameter (units are µg C/cm <sup>2</sup> )													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
Jan	262	Mean	0.000	0.001	0.008	0.000	0.001	0.000	0.010	0.009	0.000	0.001	0.002	0.001	0.002	0.011
		StdDev	0.001	0.005	0.018	0.001	0.010	0.007	0.024	0.022	0.000	0.007	0.012	0.010	0.012	0.026
		Max	0.011	0.040	0.134	0.006	0.116	0.120	0.184	0.174	0.003	0.108	0.127	0.127	0.116	0.184
		Min	0.000	0.000	0.000	0.000	-0.006	-0.006	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
Feb	269	Mean	0.000	0.001	0.011	0.001	0.000	0.002	0.012	0.015	0.000	0.001	0.003	0.005	0.003	0.017
		StdDev	0.002	0.004	0.023	0.005	0.006	0.016	0.028	0.031	0.001	0.008	0.016	0.020	0.015	0.038
		Max	0.015	0.026	0.120	0.045	0.071	0.146	0.192	0.192	0.017	0.083	0.148	0.154	0.154	0.199
		Min	0.000	0.000	0.000	0.000	-0.045	-0.045	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
Mar	265	Mean	0.001	0.002	0.021	0.002	0.000	0.001	0.026	0.026	0.001	0.002	0.003	0.005	0.005	0.031
		StdDev	0.007	0.006	0.030	0.009	0.009	0.014	0.038	0.039	0.003	0.013	0.018	0.022	0.020	0.045
		Max	0.074	0.040	0.146	0.080	0.113	0.162	0.198	0.197	0.036	0.132	0.182	0.182	0.182	0.198
		Min	0.000	0.000	0.000	0.000	-0.073	-0.073	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.004	0.000	0.000	0.000	0.006	0.006	0.000	0.000	0.000	0.000	0.000	0.008
Apr	205	Mean	0.000	0.002	0.009	0.001	0.000	0.000	0.012	0.012	0.000	0.000	0.002	0.003	0.003	0.015
		StdDev	0.004	0.006	0.021	0.005	0.009	0.013	0.027	0.028	0.001	0.002	0.016	0.016	0.013	0.035
		Max	0.047	0.040	0.166	0.037	0.098	0.163	0.166	0.175	0.006	0.029	0.163	0.163	0.119	0.175
		Min	0.000	0.000	0.000	0.000	-0.037	-0.037	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
May	225	Mean	0.000	0.002	0.014	0.000	0.000	0.000	0.016	0.016	0.000	0.000	0.001	0.001	0.001	0.017
		StdDev	0.001	0.006	0.029	0.001	0.001	0.001	0.033	0.033	0.001	0.002	0.005	0.006	0.006	0.035
		Max	0.005	0.045	0.162	0.012	0.002	0.005	0.186	0.186	0.020	0.021	0.059	0.064	0.064	0.186
		Min	0.000	0.000	0.000	0.000	-0.010	-0.010	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
Jun	204	Mean	0.000	0.005	0.013	0.000	0.000	0.000	0.019	0.019	0.000	0.000	0.002	0.003	0.003	0.022
		StdDev	0.002	0.016	0.025	0.000	0.000	0.000	0.039	0.039	0.000	0.001	0.015	0.015	0.015	0.041
		Max	0.018	0.085	0.128	0.003	0.000	0.000	0.190	0.190	0.004	0.011	0.163	0.163	0.163	0.190
		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
Jul	185	Mean	0.000	0.003	0.015	0.000	0.000	0.000	0.018	0.019	0.000	0.000	0.002	0.002	0.002	0.020
		StdDev	0.002	0.009	0.025	0.001	0.000	0.004	0.032	0.033	0.000	0.003	0.012	0.012	0.012	0.034
		Max	0.026	0.054	0.172	0.006	0.000	0.041	0.172	0.172	0.000	0.037	0.114	0.114	0.114	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	0.002	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.005
Aug	198	Mean	0.000	0.004	0.027	0.000	0.000	0.000	0.032	0.032	0.000	0.000	0.001	0.001	0.001	0.033
		StdDev	0.002	0.010	0.031	0.001	0.004	0.001	0.040	0.039	0.000	0.001	0.009	0.008	0.009	0.041
		Max	0.031	0.057	0.140	0.004	0.062	0.007	0.192	0.192	0.005	0.019	0.109	0.109	0.109	0.192
		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	0.019	0.000	0.000	0.000	0.019	0.019	0.000	0.000	0.000	0.000	0.000	0.019
Sep	182	Mean	0.001	0.003	0.022	0.000	0.000	0.000	0.026	0.026	0.000	0.000	0.004	0.005	0.005	0.031
		StdDev	0.004	0.010	0.028	0.001	0.001	0.000	0.034	0.033	0.002	0.001	0.017	0.017	0.017	0.041
		Max	0.037	0.085	0.178	0.013	0.014	0.000	0.190	0.190	0.016	0.015	0.118	0.118	0.118	0.194
		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	0.016	0.000	0.000	0.000	0.018	0.018	0.000	0.000	0.000	0.000	0.000	0.018
Oct	168	Mean	0.002	0.007	0.020	0.000	0.000	0.000	0.028	0.028	0.001	0.001	0.002	0.003	0.003	0.032
		StdDev	0.006	0.014	0.024	0.002	0.000	0.000	0.035	0.035	0.003	0.005	0.013	0.015	0.015	0.041
		Max	0.046	0.066	0.119	0.030	0.000	0.003	0.188	0.188	0.028	0.045	0.149	0.149	0.149	0.188
		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	0.014	0.000	0.000	0.000	0.018	0.018	0.000	0.000	0.000	0.000	0.000	0.018
Nov	292	Mean	0.003	0.009	0.019	0.001	0.000	0.000	0.032	0.032	0.000	0.001	0.005	0.006	0.006	0.038
		StdDev	0.011	0.017	0.023	0.003	0.002	0.000	0.042	0.042	0.001	0.003	0.022	0.023	0.022	0.048
		Max	0.071	0.097	0.137	0.028	0.034	0.006	0.185	0.185	0.011	0.021	0.169	0.169	0.169	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	0.012	0.000	0.000	0.000	0.016	0.016	0.000	0.000	0.000	0.000	0.000	0.018
Dec	228	Mean	0.002	0.009	0.018	0.001	0.000	0.001	0.031	0.032	0.000	0.000	0.001	0.002	0.001	0.033
		StdDev	0.011	0.019	0.026	0.003	0.001	0.009	0.042	0.043	0.001	0.003	0.010	0.010	0.006	0.044
		Max	0.139	0.112	0.185	0.033	0.009	0.129	0.185	0.185	0.010	0.031	0.129	0.129	0.071	0.185
		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	0.015	0.015	0.000	0.000	0.000	0.000	0.000	0.015
2008	2683	Mean	0.001	0.004	0.016	0.001	0.000	0.000	0.022	0.022	0.000	0.001	0.002	0.003	0.003	0.025
		StdDev	0.006	0.012	0.026	0.004	0.005	0.008	0.036	0.036	0.002	0.006	0.015	0.016	0.015	0.040
		Max	0.139	0.112	0.185	0.080	0.116	0.163	0.198	0.197	0.036	0.132	0.182	0.182	0.182	0.199
		Min	0.000	0.000	0.000	0.000	-0.073	-0.073	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	0.004

Table 3-22. DRI Carbon Laboratory System Blank Statistics for Each Analyzer (1/1/08 through 12/31/08)

Analyzer No.	No.	Statistic	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$ )												
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCOTRC	OCOTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC
6	397	Mean	0.001	0.004	0.013	0.000	0.000	0.000	0.018	0.018	0.000	0.000	0.001	0.002	0.002
		StdDev	0.004	0.013	0.024	0.004	0.003	0.004	0.033	0.033	0.000	0.001	0.008	0.010	0.010
		Max	0.044	0.112	0.120	0.045	0.003	0.041	0.173	0.173	0.005	0.025	0.098	0.098	0.098
		Min	0.000	0.000	0.000	0.000	-0.045	-0.045	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	0.002
7	292	Mean	0.001	0.002	0.016	0.000	0.000	0.000	0.020	0.020	0.000	0.000	0.001	0.002	0.002
		StdDev	0.006	0.009	0.030	0.002	0.001	0.001	0.037	0.037	0.001	0.002	0.010	0.011	0.011
		Max	0.074	0.067	0.172	0.033	0.000	0.000	0.197	0.197	0.011	0.029	0.114	0.114	0.114
		Min	0.000	0.000	0.000	0.000	-0.017	-0.017	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	0.002
8	383	Mean	0.000	0.003	0.020	0.000	0.000	0.000	0.024	0.024	0.000	0.001	0.002	0.003	0.003
		StdDev	0.002	0.008	0.027	0.002	0.001	0.001	0.033	0.033	0.002	0.003	0.012	0.013	0.013
		Max	0.022	0.051	0.185	0.030	0.002	0.001	0.192	0.192	0.019	0.045	0.150	0.150	0.150
		Min	0.000	0.000	0.000	0.000	-0.022	-0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.008	0.000	0.000	0.000	0.010	0.010	0.000	0.000	0.000	0.000	0.013
9	403	Mean	0.000	0.001	0.006	0.000	0.000	0.002	0.007	0.009	0.000	0.000	0.003	0.003	0.001
		StdDev	0.003	0.004	0.016	0.001	0.001	0.012	0.019	0.024	0.001	0.003	0.015	0.016	0.010
		Max	0.037	0.052	0.115	0.013	0.006	0.146	0.158	0.192	0.016	0.057	0.182	0.182	0.182
		Min	0.000	0.000	0.000	0.000	-0.010	-0.010	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
10	253	Mean	0.001	0.005	0.017	0.000	0.000	0.002	0.023	0.026	0.000	0.001	0.004	0.005	0.003
		StdDev	0.005	0.015	0.027	0.001	0.006	0.018	0.040	0.043	0.001	0.006	0.022	0.023	0.015
		Max	0.047	0.085	0.146	0.015	0.098	0.163	0.190	0.190	0.016	0.083	0.163	0.166	0.160
		Min	0.000	0.000	0.000	0.000	-0.015	-0.011	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	0.004	0.005	0.000	0.000	0.000	0.000	0.006
11	395	Mean	0.000	0.002	0.017	0.000	0.001	0.000	0.020	0.019	0.000	0.000	0.005	0.004	0.005
		StdDev	0.001	0.008	0.027	0.001	0.009	0.007	0.032	0.031	0.001	0.006	0.020	0.019	0.020
		Max	0.013	0.092	0.166	0.012	0.116	0.129	0.184	0.174	0.009	0.108	0.169	0.169	0.169
		Min	0.000	0.000	0.000	0.000	-0.007	-0.006	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	0.003	0.002	0.000	0.000	0.000	0.000	0.004
12	386	Mean	0.001	0.005	0.019	0.002	0.000	-0.001	0.027	0.026	0.000	0.002	0.002	0.004	0.005
		StdDev	0.008	0.012	0.024	0.008	0.009	0.006	0.036	0.034	0.002	0.012	0.014	0.019	0.021
		Max	0.139	0.085	0.153	0.080	0.113	0.038	0.198	0.172	0.036	0.132	0.163	0.163	0.163
		Min	0.000	0.000	0.000	0.000	-0.073	-0.073	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Median	0.000	0.000	0.011	0.000	0.000	0.000	0.014	0.014	0.000	0.000	0.000	0.000	0.015
13	109	Mean	0.002	0.012	0.026	0.001	0.000	0.000	0.041	0.041	0.001	0.001	0.003	0.004	0.003
		StdDev	0.008	0.021	0.034	0.003	0.001	0.003	0.051	0.051	0.004	0.004	0.009	0.011	0.011
		Max	0.049	0.091	0.178	0.024	0.014	0.028	0.190	0.190	0.028	0.041	0.053	0.060	0.060
		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
		Median	0.000	0.000	0.013	0.000	0.000	0.000	0.020	0.020	0.000	0.000	0.000	0.000	0.020
16	65	Mean	0.014	0.018	0.038	0.003	0.000	0.000	0.073	0.073	0.000	0.002	0.003	0.006	0.005
		StdDev	0.020	0.019	0.028	0.006	0.000	0.003	0.052	0.052	0.001	0.006	0.010	0.012	0.012
		Max	0.071	0.068	0.116	0.028	0.000	0.026	0.180	0.180	0.006	0.025	0.073	0.073	0.073
		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
		Median	0.002	0.012	0.035	0.000	0.000	0.000	0.066	0.066	0.000	0.000	0.000	0.000	0.068
6-13 & 16	2683	Mean	0.001	0.004	0.016	0.001	0.000	0.000	0.022	0.022	0.000	0.001	0.002	0.003	0.003
		StdDev	0.006	0.012	0.026	0.004	0.005	0.008	0.036	0.036	0.002	0.006	0.015	0.016	0.015
		Max	0.139	0.112	0.185	0.080	0.116	0.163	0.198	0.197	0.036	0.132	0.182	0.182	0.182
		Min	0.000	0.000	0.000	0.000	-0.073	-0.073	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	0.004

In addition, **Tables 3-23** through **3-25** give the analysis results by analyzer for the 24-hour (field), backup filter, and trip blanks, respectively, based upon the blank list provided to DRI by RTI. There were only 7 trip blank backup filters, so there is no table showing their analysis results by analyzer. However, **Table 3-26** summarizes the results for all analyzers for each type of blank, including trip blank backup filters. Average TC concentration for the 908 field blanks was  $1.6 \pm 1.3 \mu\text{g}/\text{cm}^2$ , while it was  $3.8 \pm 1.9 \mu\text{g}/\text{cm}^2$  for the 885 backup filters,  $1.4 \pm 1.0 \mu\text{g}/\text{cm}^2$  for the 187 trip blanks, and  $2.7 \pm 2.2 \mu\text{g}/\text{cm}^2$  for the seven trip blank backup filters. No trip blanks were run on carbon analyzer #16 because it was put into service late in 2008. There is little instrument to instrument variation among the 24-hour (field), backup filters, or trip blanks. Differences were typically within one standard deviation. Some differences may be due to samples incorrectly labeled as blanks. Nearly all the TC was in OC, with negligible quantities of EC.

### 3.4.3.2 Calibrations

**Table 3-27** provides summary statistics for full multi-point calibrations by analyzer for the period during which the project samples were analyzed. The next scheduled multi-point calibrations are due in January 2009. The multipoint calibrations are performed semi-annually or whenever major repairs or changes are made to the instruments. Separate calibrations are performed using four different sources of carbon: methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), and potassium hydrogen phthalate (KHP). The average of the regression slopes through zero is obtained and used for converting counts to  $\mu\text{g C}$ . 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 3-28** provides summary statistics for the multi-point 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  $r^2 > 0.98$ . As shown in **Table 3-27**, performance for the calibrated analyzers was well within the specified criteria.

**Table 3-29** 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 O<sub>2</sub> concentration is < 100 ppm. The O<sub>2</sub> contents were well below 100 ppm, in the range of 10-30 ppm. Measurements were not taken semi-annually due to the failure of components used in the test and the subsequent need to perform the annual calibration on the GC/MS before the tests could be done. They were completed in January 2009.

**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/O<sub>2</sub> 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 3-30**.

Table 3-23. DRI Carbon Analysis Statistics for 24-Hour Field Blanks

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
6	111	Mean	0.346	0.467	0.755	0.102	0.012	0.020	1.681	1.689	0.029	0.002	0.000	0.020	0.012
		StdDev	0.770	0.428	1.053	0.300	0.098	0.102	1.784	1.791	0.107	0.017	0.001	0.054	0.047
		Max	7.101	2.813	8.780	2.525	1.011	1.011	10.877	10.877	1.011	0.178	0.009	0.378	0.378
		Min	0.000	0.000	0.035	0.000	0.000	0.000	0.168	0.168	0.000	0.000	0.000	0.000	0.000
		Median	0.205	0.348	0.481	0.007	0.000	0.000	1.161	1.164	0.000	0.000	0.000	0.000	0.000
7	112	Mean	0.206	0.517	0.687	0.076	0.000	0.032	1.486	1.518	0.036	0.005	0.001	0.041	0.009
		StdDev	0.273	0.460	0.533	0.132	0.004	0.080	1.070	1.115	0.077	0.026	0.005	0.086	0.035
		Max	2.605	3.719	3.575	0.695	0.038	0.395	7.450	7.564	0.395	0.202	0.056	0.395	0.213
		Min	0.000	0.114	0.232	0.000	0.000	0.000	0.403	0.403	0.000	0.000	0.000	0.000	0.000
		Median	0.159	0.394	0.505	0.011	0.000	0.000	1.156	1.156	0.000	0.000	0.000	0.000	0.000
8	131	Mean	0.401	0.528	0.649	0.104	0.005	0.038	1.686	1.719	0.036	0.011	0.002	0.045	0.012
		StdDev	0.559	0.467	0.437	0.169	0.036	0.097	1.332	1.369	0.085	0.048	0.015	0.103	0.053
		Max	4.702	3.709	2.593	0.929	0.357	0.707	10.076	10.282	0.677	0.409	0.117	0.707	0.420
		Min	0.000	0.140	0.230	0.000	0.000	0.000	0.380	0.380	0.000	0.000	0.000	0.000	0.000
		Median	0.296	0.370	0.534	0.060	0.000	0.000	1.328	1.354	0.000	0.000	0.000	0.000	0.000
9	176	Mean	0.297	0.473	0.731	0.100	0.001	0.025	1.602	1.626	0.029	0.004	0.000	0.032	0.008
		StdDev	0.897	0.402	0.594	0.196	0.009	0.081	1.622	1.667	0.083	0.020	0.002	0.090	0.047
		Max	11.638	4.404	5.207	1.554	0.120	0.691	17.962	18.092	0.714	0.166	0.018	0.705	0.511
		Min	0.000	0.000	0.083	0.000	0.000	0.000	0.215	0.215	0.000	0.000	0.000	0.000	0.000
		Median	0.182	0.401	0.554	0.039	0.000	0.000	1.260	1.260	0.000	0.000	0.000	0.000	0.000
10	80	Mean	0.416	0.422	0.644	0.058	0.004	0.022	1.544	1.562	0.020	0.001	0.002	0.018	0.000
		StdDev	0.373	0.262	0.631	0.098	0.027	0.054	0.940	0.956	0.050	0.007	0.011	0.050	0.003
		Max	2.583	1.465	5.635	0.511	0.197	0.297	6.588	6.678	0.297	0.050	0.097	0.297	0.022
		Min	0.003	0.090	0.208	0.000	0.000	0.000	0.546	0.546	0.000	0.000	0.000	0.000	0.000
		Median	0.356	0.356	0.523	0.016	0.000	0.000	1.398	1.398	0.000	0.000	0.000	0.000	0.000
11	135	Mean	0.225	0.462	0.703	0.081	0.007	0.033	1.479	1.504	0.028	0.003	0.003	0.028	0.002
		StdDev	0.175	0.270	0.629	0.177	0.028	0.073	1.038	1.074	0.062	0.016	0.016	0.056	0.009
		Max	0.972	1.717	4.082	1.168	0.171	0.367	6.635	6.786	0.323	0.155	0.155	0.269	0.058
		Min	0.000	0.086	0.134	0.000	0.000	0.000	0.358	0.358	0.000	0.000	0.000	0.000	0.000
		Median	0.194	0.382	0.533	0.010	0.000	0.000	1.182	1.192	0.000	0.000	0.000	0.000	0.000
12	113	Mean	0.161	0.537	0.730	0.102	0.002	0.018	1.532	1.548	0.028	0.002	0.000	0.028	0.013
		StdDev	0.171	0.308	0.384	0.120	0.015	0.066	0.782	0.811	0.073	0.012	0.001	0.073	0.035
		Max	1.046	1.761	2.348	0.601	0.110	0.511	4.085	4.242	0.581	0.100	0.005	0.581	0.246
		Min	0.000	0.000	0.254	0.000	0.000	0.000	0.366	0.366	0.000	0.000	0.000	0.000	0.000
		Median	0.129	0.470	0.643	0.072	0.000	0.000	1.340	1.340	0.000	0.000	0.000	0.000	0.000
13	39	Mean	0.149	0.639	0.673	0.083	0.007	0.022	1.551	1.566	0.040	0.003	0.003	0.039	0.025
		StdDev	0.120	0.389	0.356	0.119	0.025	0.061	0.917	0.926	0.062	0.012	0.008	0.069	0.047
		Max	0.714	2.196	1.864	0.478	0.105	0.341	5.056	5.082	0.302	0.071	0.030	0.341	0.194
		Min	0.000	0.290	0.276	0.000	0.000	0.000	0.683	0.683	0.000	0.000	0.000	0.000	0.000
		Median	0.129	0.545	0.529	0.027	0.000	0.000	1.233	1.271	0.000	0.000	0.000	0.000	0.000
16	11	Mean	0.240	0.357	0.669	0.078	0.000	0.026	1.344	1.370	0.050	0.011	0.000	0.061	0.035
		StdDev	0.054	0.113	0.245	0.053	0.000	0.046	0.351	0.391	0.093	0.022	0.001	0.097	0.060
		Max	0.313	0.592	1.143	0.204	0.000	0.124	2.061	2.159	0.292	0.071	0.003	0.292	0.193
		Min	0.144	0.210	0.439	0.029	0.000	0.000	0.905	0.905	0.000	0.000	0.000	0.000	0.000
		Median	0.250	0.320	0.584	0.053	0.000	0.000	1.232	1.232	0.004	0.000	0.000	0.004	0.004
All	908	Mean	0.282	0.493	0.701	0.091	0.004	0.027	1.572	1.595	0.030	0.004	0.001	0.032	0.009
		StdDev	0.557	0.384	0.619	0.181	0.040	0.080	1.282	1.312	0.079	0.025	0.009	0.078	0.040
		Max	11.638	4.404	8.780	2.525	1.011	1.011	17.962	18.092	1.011	0.409	0.155	0.707	0.511
		Min	0.000	0.000	0.035	0.000	0.000	0.000	0.168	0.168	0.000	0.000	0.000	0.000	0.000
		Median	0.201	0.396	0.537	0.036	0.000	0.000	1.258	1.263	0.000	0.000	0.000	0.000	0.000

\* Excludes replicates

Table 3-24. DRI Carbon Analysis Statistics for Backup Filters

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	105	Mean	0.802	1.138	1.326	0.407	0.062	0.134	3.736	3.808	0.121	0.020	0.000	0.078	0.007	3.814
		StdDev	0.720	0.550	0.773	0.315	0.178	0.223	1.803	1.867	0.176	0.058	0.001	0.115	0.020	1.868
		Max	4.316	2.541	4.948	1.841	1.438	1.676	9.670	9.893	1.204	0.473	0.010	0.734	0.133	9.893
		Min	0.000	0.030	0.172	0.000	0.000	0.000	0.202	0.202	0.000	0.000	0.000	0.000	0.000	0.202
		Median	0.636	1.039	1.170	0.300	0.000	0.072	3.529	3.589	0.076	0.000	0.000	0.044	0.000	3.589
7	105	Mean	0.570	1.168	1.318	0.334	0.029	0.112	3.419	3.502	0.113	0.013	0.001	0.098	0.015	3.517
		StdDev	0.470	0.593	0.836	0.291	0.083	0.173	1.741	1.819	0.146	0.051	0.009	0.157	0.068	1.824
		Max	2.643	2.681	4.969	1.689	0.542	1.044	9.479	9.898	0.809	0.361	0.095	1.044	0.600	9.898
		Min	0.000	0.000	0.103	0.000	0.000	0.000	0.124	0.124	0.000	0.000	0.000	0.000	-0.009	0.124
		Median	0.453	1.084	1.143	0.286	0.000	0.058	3.075	3.138	0.073	0.000	0.000	0.046	0.000	3.161
8	133	Mean	0.926	1.099	1.350	0.434	0.024	0.196	3.835	4.007	0.179	0.036	0.001	0.191	0.019	4.026
		StdDev	0.592	0.509	1.282	0.372	0.102	0.348	2.150	2.422	0.365	0.063	0.004	0.403	0.091	2.484
		Max	3.958	3.140	14.305	3.281	0.955	3.553	20.296	23.849	3.981	0.493	0.042	4.474	0.921	24.769
		Min	0.000	0.227	0.267	0.000	0.000	0.000	0.725	0.725	0.000	0.000	0.000	0.000	0.000	0.725
		Median	0.795	1.081	1.201	0.353	0.000	0.118	3.600	3.720	0.117	0.000	0.000	0.122	0.000	3.720
9	165	Mean	0.572	1.070	1.497	0.423	0.020	0.109	3.581	3.671	0.094	0.025	0.002	0.101	0.012	3.683
		StdDev	0.486	0.452	0.748	0.285	0.071	0.132	1.623	1.688	0.107	0.053	0.020	0.116	0.050	1.695
		Max	2.606	2.981	4.191	1.678	0.634	0.847	10.214	10.427	0.756	0.440	0.254	0.592	0.527	10.451
		Min	0.000	0.105	0.191	0.000	0.000	0.000	0.439	0.439	0.000	0.000	0.000	0.000	0.000	0.439
		Median	0.413	1.059	1.371	0.364	0.000	0.068	3.456	3.541	0.070	0.000	0.000	0.062	0.000	3.541
10	62	Mean	0.964	0.811	0.995	0.239	0.068	0.131	3.077	3.140	0.105	0.030	0.001	0.069	0.006	3.145
		StdDev	0.529	0.437	0.489	0.225	0.247	0.251	1.596	1.628	0.181	0.083	0.010	0.079	0.015	1.632
		Max	2.172	2.370	3.221	1.115	1.717	1.678	8.715	8.860	1.215	0.517	0.082	0.329	0.066	8.860
		Min	0.093	0.155	0.182	0.000	0.000	0.000	0.668	0.668	0.000	0.000	0.000	0.000	0.000	0.668
		Median	0.911	0.716	0.883	0.180	0.000	0.057	2.842	2.887	0.061	0.000	0.000	0.046	0.000	2.894
11	133	Mean	0.594	1.174	1.533	0.447	0.099	0.194	3.846	3.942	0.151	0.042	0.004	0.098	0.002	3.945
		StdDev	0.511	0.553	0.957	0.346	0.211	0.257	1.916	1.945	0.184	0.105	0.020	0.128	0.012	1.947
		Max	3.249	2.811	5.895	1.889	1.883	2.217	10.092	10.178	1.427	0.956	0.166	0.956	0.111	10.180
		Min	0.000	0.131	0.391	0.000	0.000	0.000	0.712	0.712	0.000	0.000	0.000	-0.004	-0.006	0.712
		Median	0.447	1.100	1.340	0.403	0.000	0.116	3.567	3.727	0.101	0.003	0.000	0.061	0.000	3.727
12	134	Mean	0.444	1.262	1.513	0.437	0.066	0.107	3.722	3.763	0.121	0.024	0.000	0.078	0.037	3.800
		StdDev	0.386	0.620	0.786	0.308	0.156	0.180	1.684	1.708	0.155	0.051	0.001	0.099	0.066	1.727
		Max	2.415	3.641	4.616	1.411	1.242	1.242	9.110	9.502	1.014	0.436	0.012	0.587	0.371	9.502
		Min	0.000	0.000	0.347	0.000	0.000	0.000	0.347	0.347	0.000	0.000	0.000	0.000	-0.001	0.347
		Median	0.343	1.121	1.315	0.337	0.000	0.056	3.348	3.398	0.079	0.000	0.000	0.045	0.000	3.407
13	42	Mean	0.400	1.464	1.421	0.392	0.099	0.184	3.777	3.862	0.157	0.049	0.000	0.108	0.023	3.885
		StdDev	0.495	0.724	0.685	0.292	0.440	0.463	1.982	2.031	0.372	0.118	0.002	0.136	0.051	2.050
		Max	2.691	4.444	3.827	1.326	2.838	2.988	12.166	12.315	2.393	0.595	0.010	0.553	0.208	12.315
		Min	0.000	0.247	0.384	0.000	0.000	0.000	0.708	0.708	0.000	0.000	0.000	0.000	-0.003	0.708
		Median	0.251	1.283	1.305	0.306	0.000	0.070	3.257	3.422	0.061	0.000	0.000	0.073	0.000	3.445
16	6	Mean	1.819	1.344	1.572	0.603	0.023	0.477	5.361	5.816	0.470	0.136	0.000	0.583	0.129	5.945
		StdDev	0.658	0.451	0.328	0.212	0.056	0.425	1.154	1.316	0.368	0.064	0.000	0.437	0.104	1.303
		Max	2.715	2.144	1.923	0.810	0.136	1.180	6.647	6.999	1.038	0.223	0.000	1.215	0.267	7.090
		Min	0.738	0.845	1.077	0.325	0.000	0.000	3.251	3.251	0.096	0.062	0.000	0.158	0.005	3.409
		Median	1.775	1.344	1.637	0.676	0.000	0.351	5.472	6.153	0.309	0.134	0.000	0.440	0.125	6.396
All	885	Mean	0.664	1.141	1.403	0.405	0.053	0.146	3.666	3.759	0.131	0.029	0.001	0.109	0.016	3.775
		StdDev	0.565	0.559	0.889	0.317	0.177	0.251	1.823	1.916	0.219	0.072	0.013	0.201	0.058	1.935
		Max	4.316	4.444	14.305	3.281	2.838	3.553	20.296	23.849	3.981	0.956	0.254	4.474	0.921	24.769
		Min	0.000	0.000	0.103	0.000	0.000	0.000	0.124	0.124	0.000	0.000	0.000	-0.004	-0.009	0.124
		Median	0.489	1.063	1.259	0.327	0.000	0.078	3.424	3.502	0.080	0.000	0.000	0.062	0.000	3.517

\* Excludes replicates

Table 3-25. DRI Carbon Analysis Statistics for Trip Blanks

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	26	Mean	0.343	0.281	0.428	0.020	0.000	0.000	1.072	1.072	0.001	0.000	0.012	0.013	0.013	1.085
		StdDev	0.179	0.119	0.147	0.036	0.000	0.000	0.391	0.391	0.005	0.000	0.042	0.042	0.042	0.399
		Max	0.827	0.551	0.739	0.132	0.000	0.000	1.779	1.779	0.022	0.000	0.183	0.183	0.183	1.827
		Min	0.000	0.126	0.171	0.000	0.000	0.000	0.361	0.361	0.000	0.000	0.000	0.000	0.000	0.361
		Median	0.314	0.235	0.438	0.000	0.000	0.000	0.987	0.987	0.000	0.000	0.000	0.000	0.000	1.013
7	10	Mean	0.204	0.221	0.381	0.005	0.000	0.002	0.810	0.811	0.009	0.000	0.000	0.009	0.007	0.818
		StdDev	0.116	0.068	0.132	0.015	0.000	0.004	0.228	0.228	0.019	0.000	0.000	0.019	0.019	0.235
		Max	0.348	0.345	0.631	0.047	0.000	0.011	1.037	1.037	0.062	0.000	0.000	0.062	0.062	1.098
		Min	0.000	0.108	0.189	0.000	0.000	0.000	0.408	0.408	0.000	0.000	0.000	0.000	0.000	0.408
		Median	0.244	0.219	0.373	0.000	0.000	0.000	0.890	0.893	0.000	0.000	0.000	0.000	0.000	0.897
8	32	Mean	0.383	0.334	0.542	0.067	0.000	0.018	1.327	1.345	0.017	0.003	0.000	0.020	0.002	1.347
		StdDev	0.133	0.179	0.358	0.140	0.000	0.038	0.636	0.666	0.032	0.011	0.001	0.039	0.012	0.666
		Max	0.758	0.854	2.111	0.696	0.000	0.148	3.779	3.927	0.097	0.055	0.008	0.148	0.066	3.927
		Min	0.083	0.066	0.173	0.000	0.000	0.000	0.533	0.533	0.000	0.000	0.000	0.000	0.000	0.533
		Median	0.380	0.305	0.454	0.020	0.000	0.000	1.200	1.208	0.000	0.000	0.000	0.000	0.000	1.208
9	32	Mean	0.321	0.468	0.750	0.118	0.010	0.036	1.667	1.692	0.038	0.003	0.001	0.032	0.006	1.698
		StdDev	0.164	0.586	0.907	0.314	0.059	0.102	1.746	1.790	0.099	0.009	0.003	0.082	0.017	1.792
		Max	0.602	3.488	4.150	1.577	0.332	0.443	9.554	9.587	0.426	0.046	0.015	0.443	0.075	9.604
		Min	0.002	0.111	0.137	0.000	0.000	0.000	0.512	0.512	0.000	0.000	0.000	0.000	0.000	0.512
		Median	0.327	0.350	0.526	0.024	0.000	0.000	1.236	1.236	0.000	0.000	0.000	0.000	0.000	1.236
10	22	Mean	0.520	0.349	0.507	0.044	0.001	0.019	1.421	1.438	0.014	0.004	0.000	0.017	0.000	1.438
		StdDev	0.372	0.166	0.368	0.079	0.007	0.049	0.722	0.734	0.030	0.021	0.000	0.048	0.000	0.734
		Max	1.969	0.696	1.475	0.318	0.032	0.220	3.172	3.212	0.121	0.099	0.002	0.220	0.000	3.212
		Min	0.170	0.109	0.199	0.000	0.000	0.000	0.489	0.489	0.000	0.000	0.000	0.000	0.000	0.489
		Median	0.507	0.303	0.383	0.000	0.000	0.000	1.131	1.134	0.000	0.000	0.000	0.000	0.000	1.134
11	35	Mean	0.302	0.348	0.702	0.090	0.007	0.022	1.448	1.463	0.018	0.002	0.002	0.015	0.000	1.464
		StdDev	0.142	0.155	0.804	0.245	0.040	0.065	1.179	1.196	0.058	0.009	0.009	0.041	0.001	1.196
		Max	0.667	0.805	5.042	1.449	0.238	0.322	7.619	7.704	0.268	0.054	0.054	0.216	0.003	7.704
		Min	0.000	0.136	0.212	0.000	0.000	0.000	0.605	0.605	0.000	0.000	0.000	0.000	0.000	0.608
		Median	0.300	0.318	0.516	0.003	0.000	0.000	1.133	1.133	0.000	0.000	0.000	0.000	0.000	1.133
12	19	Mean	0.204	0.401	0.554	0.068	0.006	0.000	1.233	1.227	0.012	0.001	0.000	0.007	0.012	1.240
		StdDev	0.093	0.240	0.357	0.158	0.025	0.000	0.787	0.767	0.038	0.003	0.000	0.016	0.038	0.801
		Max	0.439	1.275	1.578	0.696	0.111	0.000	3.900	3.790	0.163	0.012	0.000	0.052	0.163	3.952
		Min	0.081	0.208	0.264	0.000	0.000	0.000	0.690	0.690	0.000	0.000	0.000	0.000	0.000	0.690
		Median	0.205	0.364	0.489	0.012	0.000	0.000	0.956	0.956	0.000	0.000	0.000	0.000	0.000	0.963
13	11	Mean	0.220	0.526	0.670	0.089	0.000	0.022	1.505	1.527	0.031	0.002	0.002	0.034	0.013	1.539
		StdDev	0.111	0.175	0.406	0.151	0.000	0.054	0.696	0.730	0.058	0.005	0.004	0.062	0.032	0.740
		Max	0.459	0.870	1.642	0.497	0.000	0.173	3.132	3.196	0.173	0.017	0.013	0.173	0.101	3.234
		Min	0.036	0.335	0.339	0.000	0.000	0.000	0.729	0.729	0.000	0.000	0.000	0.000	0.000	0.729
		Median	0.194	0.464	0.484	0.009	0.000	0.000	1.242	1.242	0.000	0.000	0.000	0.000	0.000	1.242
16	0	Mean	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		StdDev	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Max	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Min	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Median	-	-	-	-	-	-	-	-	-	-	-	-	-	-
All	187	Mean	0.330	0.366	0.588	0.069	0.004	0.017	1.357	1.370	0.018	0.002	0.002	0.019	0.006	1.375
		StdDev	0.203	0.292	0.576	0.191	0.031	0.058	1.023	1.045	0.055	0.010	0.016	0.050	0.023	1.048
		Max	1.969	3.488	5.042	1.577	0.332	0.443	9.554	9.587	0.426	0.099	0.183	0.443	0.183	9.604
		Min	0.000	0.066	0.137	0.000	0.000	0.000	0.361	0.361	0.000	0.000	0.000	0.000	0.000	0.361
		Median	0.305	0.315	0.450	0.006	0.000	0.000	1.112	1.118	0.000	0.000	0.000	0.000	0.000	1.121

\* Excludes replicates

Table 3-26. DRI Carbon Analysis Annual Statistics for CSN Blank Categories

Type of Blank	No.*	Statistic*	IMPROVE A Parameter (units are $\mu\text{g C/cm}^2$ )													
			O1TC	O2TC	O3TC	O4TC	OPTRC	OPTTC	OCTRC	OCTTC	E1TC	E2TC	E3TC	ECTRC	ECTTC	TCTC
24-Hour Field	908	Mean	0.282	0.494	0.702	0.091	0.004	0.027	1.573	1.595	0.030	0.005	0.001	0.032	0.009	1.605
		StdDev	0.557	0.384	0.617	0.180	0.040	0.080	1.279	1.309	0.079	0.026	0.009	0.078	0.040	1.316
		Max	11.638	4.404	8.780	2.525	1.011	1.011	17.962	18.092	1.011	0.409	0.155	0.707	0.511	18.092
		Min	0.000	0.000	0.035	0.000	0.000	0.000	0.168	0.168	0.000	0.000	0.000	0.000	0.000	0.168
		Median	0.201	0.399	0.537	0.037	0.000	0.000	1.261	1.264	0.000	0.000	0.000	0.000	0.000	1.267
Backup	885	Mean	0.664	1.141	1.403	0.405	0.053	0.146	3.666	3.759	0.131	0.029	0.001	0.109	0.016	3.775
		StdDev	0.565	0.559	0.889	0.317	0.177	0.251	1.823	1.916	0.219	0.072	0.013	0.201	0.058	1.935
		Max	4.316	4.444	14.305	3.281	2.838	3.553	20.296	23.849	3.981	0.956	0.254	4.474	0.921	24.769
		Min	0.000	0.000	0.103	0.000	0.000	0.000	0.124	0.124	0.000	0.000	0.000	-0.004	-0.009	0.124
		Median	0.489	1.063	1.259	0.327	0.000	0.078	3.424	3.502	0.080	0.000	0.000	0.062	0.000	3.517
Trip	187	Mean	0.330	0.366	0.588	0.069	0.004	0.017	1.357	1.370	0.018	0.002	0.002	0.019	0.006	1.375
		StdDev	0.203	0.292	0.576	0.191	0.031	0.058	1.023	1.045	0.055	0.010	0.016	0.050	0.023	1.048
		Max	1.969	3.488	5.042	1.577	0.332	0.443	9.554	9.587	0.426	0.099	0.183	0.443	0.183	9.604
		Min	0.000	0.066	0.137	0.000	0.000	0.000	0.361	0.361	0.000	0.000	0.000	0.000	0.000	0.361
		Median	0.305	0.315	0.450	0.006	0.000	0.000	1.112	1.118	0.000	0.000	0.000	0.000	0.000	1.121
Trip Backup	7	Mean	0.202	0.348	1.593	0.344	0.015	0.244	2.502	2.731	0.096	0.148	0.000	0.229	0.000	2.731
		StdDev	0.118	0.144	1.406	0.390	0.040	0.397	1.879	2.157	0.106	0.366	0.000	0.394	0.000	2.157
		Max	0.460	0.454	3.196	0.830	0.105	1.097	4.592	5.664	0.288	0.976	0.000	1.097	0.000	5.664
		Min	0.111	0.103	0.210	0.000	0.000	0.000	0.512	0.512	0.000	0.000	0.000	0.000	0.000	0.512
		Median	0.168	0.419	1.000	0.140	0.000	0.127	1.703	1.830	0.121	0.000	0.000	0.127	0.000	1.830

\* Excludes replicates

Table 3-27. DRI Multi-Point Calibration Statistics

Analyzer No.	Date	Slope	Scatter	Correlation
6	09/07/07	20.56	0.54	0.9819
	02/29/08	20.61	0.62	0.9813
	03/10/08	21.26	0.24	0.9947
	10/02/08	21.83	0.33	0.9974
	12/23/08	20.71	0.63	0.9919
7	09/07/07	22.37	0.43	0.9926
	02/29/08	22.37	0.43	0.9926
	03/10/08	21.83	0.43	0.9942
	04/20/08	21.96	0.55	0.9929
	05/01/08	21.78	0.15	0.9982
	06/21/08	22.52	0.65	0.9946
	08/08/08	22.26	0.27	0.9968
	11/11/08	21.46	0.34	0.9971
8	09/07/07	20.54	0.86	0.9908
	03/14/08	20.80	0.28	0.9979
	08/01/08	21.52	0.53	0.9968
	12/23/08	20.66	0.61	0.9884
9	09/07/07	21.16	0.54	0.9928
	03/24/08	21.32	0.27	0.9968
	06/19/08	23.66	0.30	0.9973
	09/23/08	21.50	0.30	0.9974
10	08/07/07	20.34	0.61	0.9893
	02/29/08	20.32	0.71	0.9892
	06/04/08	21.14	0.47	0.9949
11	11/09/07	22.20	0.51	0.9809
	02/29/08	21.86	0.26	0.9978
	03/05/08	21.81	0.23	0.9983
	08/03/08	21.99	0.28	0.9979
	08/12/08	21.06	0.56	0.9908
12	09/07/07	21.09	1.21	0.9719
	02/29/08	21.86	0.66	0.9935
	03/12/08	22.21	1.14	0.9840
	09/10/08	22.73	0.27	0.9991
13	06/01/07	21.77	0.54	0.9923
	03/10/08	21.54	0.35	0.9960
	10/28/08	21.57	0.37	0.9954
	11/03/08	21.70	0.34	0.9965
16	10/20/08	21.88	0.69	0.9929

Table 3-28. DRI Temperature Calibration Statistics

Date	Param.	Units	Analyzer No.								
			6	7	8	9	10	11	12	13*	16**
Jul/Aug 2007	Slope	° C	1.036	1.014	1.020	1.014	1.022	1.024	1.024		
	Intercept		9.698	7.235	10.764	4.419	6.096	8.513	1.025		
	r <sup>2</sup>		0.9997	0.9996	0.9995	0.9993	0.9997	0.9990	0.9996		
Feb/Mar 2008	Slope	° C	1.019	1.015	1.007	1.013	1.015	1.016	1.025	1.010	
	Intercept		11.143	6.879	3.639	8.095	4.247	8.588	0.955	2.015	
	r <sup>2</sup>		0.9995	0.9993	0.9982	0.9989	0.9993	0.9996	0.9996	0.9993	
Jun-Oct 2008	Slope	° C		1.013	1.014	1.010	1.016	1.016	1.019	1.007	1.007
	Intercept			6.181	4.804	6.350	8.131	3.244	3.613	11.536	14.201
	r <sup>2</sup>			0.9995	0.9990	0.9997	0.9993	0.9997	0.9996	0.9977	0.9989
Dec 2008	Slope	° C			1.019						
	Intercept				11.312						
	r <sup>2</sup>				0.9989						

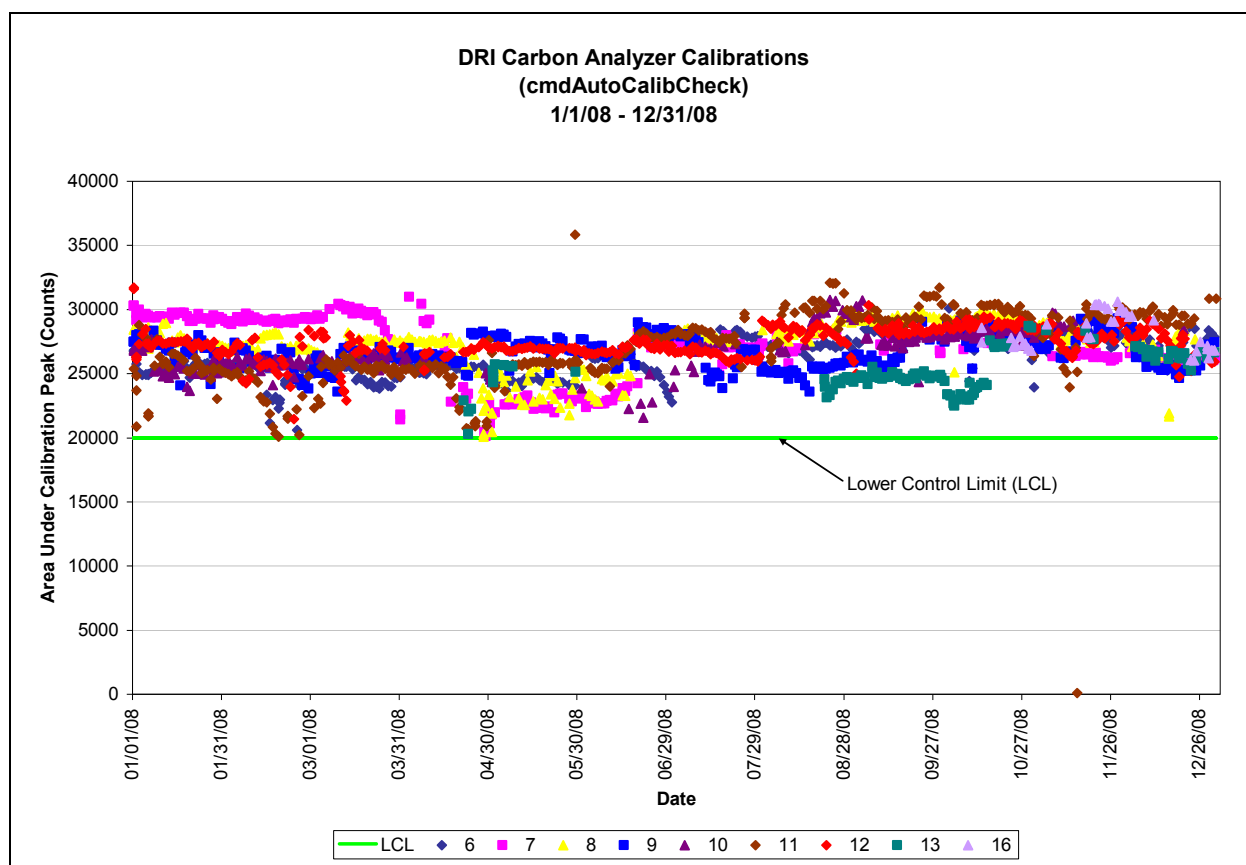
\* Returned to service 3/08 and to CSN analysis 9/08

\*\* New analyzer entered into service 10/08 and to CSN analysis 11/08

Table 3-29. DRI Oxygen Test Statistics

Date	Temp (°C)	Analyzer No.																	
		6		7		8		9		10		11		12				13	
		Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)	Mean O <sub>2</sub> (ppm)	Std Dev (ppm)
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	Out of Service 8/07 - 3/08			
	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				
Apr 2008	140	20.4	n/a	20.3	n/a	30	n/a	23	n/a	21	n/a	21.4	n/a	23.1	n/a	17.6	n/a	Brought into Service 10/08	
	580	21	n/a	21	n/a	31.3	n/a	28.7	n/a	21.8	n/a	20.4	n/a	23.6	n/a	18.2	n/a		
Jan 2009*	140	14.5	0.4	14.3	0.1	6.5	0.2	10.5	0.3	16.0	0.7	5.1	0.4	8.9	0.6	21.6	0.4	6.4	0.2
	580	12.0	0.5	15.5	0.4	6.7	0.3	10.7	0.3	10.2	0.2	5.6	0.3	4.5	0.1	12.4	0.2	5.7	0.1

\* Measurements not made until January 2009 due to measurement component failure and the need to calibrate the GC/MS.



**Figure 3-1. DRI Carbon Analyzer Daily Autocalibration Response for the Period 1/1/08 – 12/31/08**

**Table 3-30. Summary of Instrument Maintenance Performed as a Result of Autocalibration Peak Response**

Analyzer No.	Date	Resolution
11	11/14/08	Replaced methanator

### 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 3-31** 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 795 replicate or duplicate analyses were analyzed during the reporting period. Of the 795 replicates or duplicates, 11 contained f, g, h, or i analysis flags. These were not included in the replicate and duplicate statistical summary. Of the 784 remaining, 38 were duplicate analyses and 746 were replicate analyses.

Table 3-31. DRI Replicate Analysis Criteria and Statistics

Range	Criteria	Replicates				Duplicates				Units
		Statistic	No.	TC	OC	EC	No.	TC	OC	EC
All		Count	746				38			
TC, OC, & EC < 10 µg C/cm <sup>2</sup>	< ±1.0 µg C/cm <sup>2</sup>	Count		132	161	516		4	4	13
		No. Fail		4	3	21		0	0	0
		%Fail		3.0	1.9	4.1		0.0	0.0	0.0
		Mean		0.370	0.335	0.346		0.253	0.252	0.214
		StdDev		0.322	0.278	0.369		0.269	0.269	0.275
		Max		1.691	1.355	3.037		0.631	0.631	0.800
		Min		0.003	0.003	0.000		0.020	0.020	0.000
		Median		0.286	0.269	0.246		0.181	0.178	0.102
TC, OC, & EC ≥ 10 µg C/cm <sup>2</sup>	TC, OC %RPD < 10% EC %RPD < 20%	Count		614	585	230		34	34	25
		No. Fail		4	18	5		0	1	0
		%Fail		0.7	3.1	2.2		0.0	2.9	0.0
		Mean		3.31	4.05	6.91		2.24	2.89	4.55
		StdDev		2.34	2.84	5.88		1.86	2.69	4.41
		Max		10.49	13.32	32.61		9.57	14.24	19.11
		Min		0.03	0.01	0.00		0.09	0.06	0.01
		Median		2.96	3.55	5.43		1.90	2.16	3.44

### 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/cm<sup>2</sup>. 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 cm<sup>2</sup>) 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 3-32** gives estimated minimum detection limits (MDLs) for IMPROVE\_A parameters for 2008. The MDLs are determined as three times the standard deviation of laboratory blanks. **Table 3-32** 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, backup filters, and trip blanks, based on information provided to DRI after the analyses were completed.

Table 3-32. Estimated MDLs and LQLs for IMPROVE\_A Parameters for 2008

Type of Blank	No.*	Statistic*	IMPROVE_A Parameter (units are $\mu\text{g C}/\text{cm}^2$ )													
			O1TC	O2TC	O3TC	O4TC	OPTTC	OPTTC	OCTTC	OCTTC	E1TC	E2TC	E3TC	ECTTC	ECTTC	TCTC
Lab	617	Mean	0.004	0.022	0.142	0.008	0.000	0.008	0.175	0.183	0.009	0.003	0.002	0.014	0.006	0.189
		StdDev	0.018	0.044	0.185	0.045	0.005	0.043	0.248	0.266	0.060	0.021	0.021	0.074	0.061	0.304
		Max	0.153	0.398	2.407	0.705	0.118	0.431	3.189	3.189	1.242	0.319	0.371	1.405	1.405	4.594
		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	0.091	0.000	0.000	0.000	0.097	0.097	0.000	0.000	0.000	0.000	0.000	0.097
		MDL	0.055	0.133	0.556	0.135	0.015	0.129	0.745	0.797	0.179	0.062	0.062	0.221	0.184	0.913
24-Hour Field	908	Mean	0.282	0.494	0.702	0.091	0.004	0.027	1.573	1.595	0.030	0.005	0.001	0.032	0.009	1.605
		StdDev	0.557	0.384	0.617	0.180	0.040	0.080	1.279	1.309	0.079	0.026	0.009	0.078	0.040	1.316
		Max	11.638	4.404	8.780	2.525	1.011	1.011	17.962	18.092	1.011	0.409	0.155	0.707	0.511	18.092
		Min	0.000	0.000	0.035	0.000	0.000	0.000	0.168	0.168	0.000	0.000	0.000	0.000	0.000	0.168
		Median	0.201	0.399	0.537	0.037	0.000	0.000	1.261	1.264	0.000	0.000	0.000	0.000	0.000	1.267
		LQL	1.670	1.153	1.850	0.541	0.120	0.241	3.837	3.927	0.237	0.077	0.028	0.235	0.121	3.947
Backup	885	Mean	0.664	1.141	1.403	0.405	0.053	0.146	3.666	3.759	0.131	0.029	0.001	0.109	0.016	3.775
		StdDev	0.565	0.559	0.889	0.317	0.177	0.251	1.823	1.916	0.219	0.072	0.013	0.201	0.058	1.935
		Max	4.316	4.444	14.305	3.281	2.838	3.553	20.296	23.849	3.981	0.956	0.254	4.474	0.921	24.769
		Min	0.000	0.000	0.103	0.000	0.000	0.000	0.124	0.124	0.000	0.000	0.000	-0.004	-0.009	0.124
		Median	0.489	1.063	1.259	0.327	0.000	0.078	3.424	3.502	0.080	0.000	0.000	0.062	0.000	3.517
		LQL	1.696	1.676	2.667	0.952	0.532	0.752	5.468	5.749	0.656	0.216	0.038	0.604	0.175	5.805
Trip	187	Mean	0.330	0.366	0.588	0.069	0.004	0.017	1.357	1.370	0.018	0.002	0.002	0.019	0.006	1.375
		StdDev	0.203	0.292	0.576	0.191	0.031	0.058	1.023	1.045	0.055	0.010	0.016	0.050	0.023	1.048
		Max	1.969	3.488	5.042	1.577	0.332	0.443	9.554	9.587	0.426	0.099	0.183	0.443	0.183	9.604
		Min	0.000	0.066	0.137	0.000	0.000	0.000	0.361	0.361	0.000	0.000	0.000	0.000	0.000	0.361
		Median	0.305	0.315	0.450	0.006	0.000	0.000	1.112	1.118	0.000	0.000	0.000	0.000	0.000	1.121
		LQL	0.610	0.876	1.727	0.572	0.093	0.173	3.068	3.134	0.164	0.030	0.049	0.150	0.070	3.145
Trip Backup	7	Mean	0.202	0.348	1.593	0.344	0.015	0.244	2.502	2.731	0.096	0.148	0.000	0.229	0.000	2.731
		StdDev	0.118	0.144	1.406	0.390	0.040	0.397	1.879	2.157	0.106	0.366	0.000	0.394	0.000	2.157
		Max	0.460	0.454	3.196	0.830	0.105	1.097	4.592	5.664	0.288	0.976	0.000	1.097	0.000	5.664
		Min	0.111	0.103	0.210	0.000	0.000	0.000	0.512	0.512	0.000	0.000	0.000	0.000	0.000	0.512
		Median	0.168	0.419	1.000	0.140	0.000	0.127	1.703	1.830	0.121	0.000	0.000	0.127	0.000	1.830
		LQL	0.353	0.433	4.217	1.170	0.119	1.190	5.636	6.472	0.319	1.097	0.000	1.182	0.000	6.472

\* Excludes replicates

### 3.4.6 Audits, PEs, Training, and Accreditations

#### 3.4.6.1 System Audits

EPA/NAREL conducts a Technical System Audit (TSA) approximately once every two years. EPA/NAREL last conducted a TSA of DRI's Environmental Analysis Facility (EAF), including its Carbon Laboratory, on May 15, 2007. 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. Another TSA is anticipated in 2009.

#### 3.4.6.2 Performance Evaluations

DRI's Environmental Analysis Facility (EAF), including its Carbon Laboratory, was one of several laboratories participating in the December 2007 EPA/NAREL inter-laboratory comparison study. The final results of the Performance Evaluation (PE) have not been released yet. The 2008 PE study was begun December through February 2008 and the results are undergoing review by EPA/NAREL.

### 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 two students from the University of Nevada, Reno are fully trained in carbon analysis. All new technicians undergo a rigorous two-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.

### 3.5.6.4 References

Chow, J.C.; Watson, J.G.; Chen, L.W.; Chang, M.C.; Robinson, N.F.; Dana Trimble; Steven 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.

## 3.5 X-ray Fluorescence Laboratories

The two XRF laboratories, RTI and CLN used 3 and 1 XRF instruments, respectively, to analyze an estimated 14,506 filters for 48 elements during the period January 1 through December 31, 2008.

### 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:**

- 2/14/2008 – Replaced pump oil, defragment hard drive, calibration verified
- 3/06/2008 – Replaced E/I board and workstation computer, calibration required
- 3/14/2008 – Replaced tube and calibrated detector, calibration required
- 5/08/2008 – Replaced detector, ran stability and resolution tests, calibration required
- 7/15/2008 – PM performed, checked voltages, resolution, and stability

**The following repairs and maintenance were performed for XRF 2:**

- 2/14/2008 – PM performed, checked voltages, resolution, and stability
- 4/02/2008 – Replaced fan in Q box, checked stability, verified calibration
- 7/10/2008 – Replaced tube and calibrated detector, calibration required

**The following repair and maintenance was performed for XRF 3:**

- 1/04/2008 – Replaced tube and calibrated detector, calibration required
- 8/26/2008 – PM performed, checked voltages, resolution, and stability

No changes were made in the analytical procedures used by the RTI XRF Laboratory.

### 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 3-33**.

**Table 3-33. QC Procedures Performed in RTI XRF Elemental Analysis Laboratory**

QC Check	QC Frequency	Control Limits	Comments/ Corrective Action
Calibration	as needed	—	—
Calibration verification <sup>1</sup>	weekly	90–110% recovery	check calibration
Instrument precision <sup>2</sup>	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

<sup>1</sup> Using NIST SRM

<sup>2</sup> 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 3-34 through 3-39**. The percent coefficient of variation (%CV) for the average of all data for each of the six elements ranged between 0.13 and 0.56% for XRF 1, between 0.17 and 0.42% for XRF 2, and between 0.22 and 0.38% for XRF 3.

**Table 3-34. Summary of RTI XRF 1 Laboratory QC Precision Data,  $\mu\text{g}/\text{cm}^2$ ,  
1/9/2008 through 2/26/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	123	5.08	5.12	5.10	0.01	0.19	0.0
Ti	123	6.70	6.81	6.74	0.02	0.29	0.1
Fe	123	6.79	6.84	6.81	0.01	0.15	0.0
Cd	123	5.50	5.58	5.54	0.02	0.39	0.0
Se	123	3.78	3.84	3.81	0.01	0.24	-0.1
Pb	123	8.99	9.04	9.01	0.01	0.13	-0.1

**Table 3-35. Summary of RTI XRF 1 Laboratory QC Precision Data,  $\mu\text{g}/\text{cm}^2$ ,  
4/15/2008 through 4/25/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	45	5.07	5.12	5.10	0.01	0.27	-1.1
Ti	45	6.89	6.92	6.90	0.01	0.15	-0.2
Fe	45	6.89	6.94	6.90	0.01	0.16	-0.2
Cd	45	5.60	5.83	5.63	0.02	0.36	-0.9
Se	45	3.88	3.93	3.91	0.01	0.32	1.0
Pb	45	9.21	9.27	9.25	0.01	0.16	0.3

**Table 3-36. Summary of RTI XRF 1 Laboratory QC Precision Data,  $\mu\text{g}/\text{cm}^2$ ,  
7/26/2008 through 11/10/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	199	5.08	5.17	5.12	0.02	0.37	0.1
Ti	199	6.64	6.89	6.83	0.03	0.40	-0.1
Fe	199	9.21	9.28	9.25	0.02	0.18	0.0
Cd	199	5.60	5.69	5.64	0.02	0.37	0.0
Se	199	3.89	3.98	3.93	0.02	0.56	-0.1
Pb	199	9.21	9.28	9.25	0.02	0.18	0.0

**Table 3-37. Summary of RTI XRF 2 Laboratory QC Precision Data,  $\mu\text{g}/\text{cm}^2$ ,  
1/7/2008 through 7/6/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	468	5.25	5.34	5.30	0.02	0.31	0.0
Ti	468	6.70	6.79	6.74	0.02	0.29	0.0
Fe	468	6.97	7.05	7.00	0.02	0.22	0.0
Cd	468	5.84	6.08	6.01	0.02	0.40	0.0
Se	468	4.16	4.23	4.20	0.01	0.35	0.0
Pb	468	9.38	9.48	9.41	0.02	0.17	0.1

**Table 3-38. Summary of RTI XRF 2 Laboratory QC Precision Data,  $\mu\text{g}/\text{cm}^2$ , 8/29/2008 through 12/31/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	270	5.26	5.34	5.30	0.02	0.32	0.0
Ti	270	6.60	6.68	6.64	0.02	0.29	0.0
Fe	270	6.89	6.96	6.92	0.01	0.21	0.0
Cd	270	5.81	5.99	5.92	0.02	0.32	0.0
Se	270	3.94	4.04	4.00	0.02	0.42	0.0
Pb	270	9.40	9.50	9.44	0.02	0.17	0.0

**Table 3-39. Summary of RTI XRF 3 Laboratory QC Precision Data,  $\mu\text{g}/\text{cm}^2$ , 3/19/2008 through 12/31/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	652	9.95	10.2	10.1	0.04	0.37	-0.3
Ti	652	9.09	9.19	9.14	0.02	0.22	0.2
Fe	652	10.5	10.7	10.6	0.03	0.28	0.0
Cd	652	5.78	5.92	5.84	0.02	0.35	0.1
Se	652	4.05	4.14	4.09	0.02	0.38	0.1
Pb	652	10.6	10.8	10.7	0.04	0.36	-0.2

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 3-40 through 3-42** show recovery for 7 elements of the 48 elements normally measured. The recovery values for all the elements ranged between 94 and 104% for XRF 1; between 94 and 104% for XRF 2; and between 94 and 104% 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 2008, NIST SRM 2783 (unmounted SRM) developed inconsistency and was removed from the program. Only NIST SRM 1832 is being reported for the 2008 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 3-40. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 1,  
1/1/2008 through 12/31/2008**

**Table 3-41. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 2,  
1/1/2008 through 12/31/2008**

**Table 3-42. Recovery Determined from Analysis of NIST SRM 1832 for RTI XRF 3,  
1/1/2008 through 12/31/2008**

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 3-43** shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients for XRF 1 range from 0.9982 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 0.9984 to 0.9999, indicating acceptable replication with all three instruments. Also, for the six elements, the average RPD on XRF 1 was less than 1%, 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 1%.

**Table 3-43. 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	177	0.9982	-0.33	Si	355	0.9993	1.40
S	177	0.9999	-0.08	S	355	0.9999	0.04
K	177	1.0000	-0.33	K	355	0.9995	-0.06
Ca	177	0.9994	-0.51	Ca	355	0.9997	0.87
Fe	177	0.9999	-0.21	Fe	355	1.0000	0.20
Zn	177	0.9986	0.06	Zn	355	0.9995	-0.28

XRF 3			
Element	n	Correlation Coefficient	Average RPD
Si	320	0.9991	-0.17
S	320	0.9999	-0.06
K	320	0.9999	0.09
Ca	320	0.9997	0.29
Fe	320	0.9999	-0.11
Zn	320	0.9984	-0.67

## Assessment of Between-Instrument Comparability

### Overview of Round-Robin Samples Run During 2008

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.

In the round-robin program, previously analyzed CSN filters are recycled through all the instruments in the two laboratories. **Table 3-44** summarizes the number of round-robin filters analyzed during 2008.

**Table 3-44. Numbers of Round-Robin Filter Analyses Performed during 2008**

Laboratory	Instrument	Filters
CLN	KeveX 770	31
CLN	KeveX 771	0
RTI	XRF 1	9
RTI	XRF 2	31
RTI	XRF 3	31

The KeveX 771 XRF instrument of the CLN Laboratory did not analyze any CSN filters during 2008; therefore no round robin filter results are reported for this instrument. XRF 1 of the RTI Laboratory reported a limited amount of round robin filter results due to the instrument being inoperable for the majority of 2008.

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 3-45 and 3-46** show linear regression results when the data for the filters are regressed versus the median for the three 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 Mn, 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).

**Note:** KeveX 771 and XRF 1 were not included in the statistical analysis due to too few samples analyzed for meaningful correlation. Two instruments from RTI and one from CLN were used in the calculations for the regression results.

**Table 3-45. Regression Results for 11 Elements  
RTI XRF Instruments**

Element	RTI #1				RTI #2			
	n	Correlation Coefficient	Slope	Intercept	n	Correlation Coefficient	Slope	Intercept
Si	31	0.9976	1.0138	-0.0352	31	0.9968	0.9936	0.0044
S	31	0.9997	1.0066	-0.0221	31	0.9996	1.0022	0.1043
K	31	0.9966	1.0956	-0.0673	31	0.9984	1.0116	-0.0153
Ca	31	0.9981	0.9862	-0.0130	31	0.9996	0.9998	-0.0039
Mn	31	0.9805	0.9664	0.0031	31	0.9947	1.0512	-0.0016
Fe	31	0.9988	1.0006	0.0187	31	0.9994	1.0103	-0.0060
Ni	31	0.9973	0.9882	0.0032	31	0.9960	0.9434	-0.0005
Cu	31	0.9801	1.0579	-0.0005	31	0.9878	1.0200	-0.0040
Zn	31	0.9973	0.9797	0.0194	31	0.9997	1.0055	0.0009
Se	31	0.9748	1.0311	-0.0041	31	0.9883	0.9541	0.0002
Pb	31	0.9805	1.0184	-0.0026	31	0.9803	0.9463	0.0036

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

**Table 3-46. Regression Results for 11 Elements  
CLN XRF Instrument 770**

Element	CLN 770			
	n	Correlation Coefficient	Slope	Intercept
Si	31	0.9970	1.0078	0.0332
S	31	0.9982	0.9640	0.0397
K	31	0.9978	0.9638	0.0378
Ca	31	0.9975	1.0391	0.0020
Mn	31	0.9370	0.9419	-0.0020
Fe	31	0.9978	1.0058	-0.0409
Ni	31	0.9893	0.9892	0.0027
Cu	31	0.9619	0.9581	0.0022
Zn	31	0.9978	1.0497	-0.0397
Se	31	0.9776	0.9426	0.0060
Pb	31	0.9747	0.9491	0.0074

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

### 3.5.1.4 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 Appendix 2 of the RTI Quality Assurance Project Plan for Chemical Speciation of PM<sub>2.5</sub> Filter Samples.

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.

### 3.5.1.5 Audits, PEs, Training, and Accreditations

No on-site audit was performed by NAREL during 2008.

## 3.5.2 Chester LabNet X-Ray Fluorescence Laboratory

During the period covered by this report, Chester operated one Kevex 770 XRF instrument analyzing 2,126 samples for 48 elements.

### 3.5.2.1 Quality Issues and Instrument Repair and Maintenance

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

- 5/28/08 - replaced analysis chamber lid interlock solenoid.
- 7/8/08 – peak shift due to low liquid nitrogen level. Recalibrated peak energies, and performed NIST standard check to ensure calibration was valid.
- 7/14/08 – recalibrated peak energies due to shifting. Checked calibration with QS standard.
- 8/23/08 - replaced vacuum pump.

- 10/6/08 – recalibrated excitation condition 3. Increased calibration factors by an average of 1.10x.

### 3.5.2.2 Description of QC Checks Applied

QC activities for the analysis of elements by EDXRF for the Chester LabNet XRF laboratory, their frequency of application and control limits, comments and corrective actions are shown in **Table 3-47**.

**Table 3-47. 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 <sup>1</sup>	Once per week	± 2 sigma	Recalibrate
Instrument precision <sup>2</sup>	Per 10 to 15 samples	± 10%	Re-analyze
Excitation condition check	Per 10 to 15 samples	± 10%	Re-analyze
Sample replicate precision	Per 10 samples	RPD < 2x uncertainty	Re-analyze if necessary

1 - Using NIST SRMs

2 – Micromatter QC

### 3.5.2.3 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 **Table 3-48A**. The percent coefficient of variation (%CV) for the average of all data for each of the six elements ranged between 1.39 and 2.53%.

**Table 3-48A. Summary of Chester XRF 770 Laboratory QC Precision Data 1/1/2008 through 12/31/2008**

Element	n	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Si	186	92.1	105.7	98.1	2.48	2.53	4.07
Ti	186	93.4	104.9	99.2	1.59	1.60	-0.24
Fe	186	94.3	103.2	99.2	1.38	1.39	2.92
Cd	186	93.4	103.4	99.1	2.03	2.04	-16.64
Se	186	94.4	104.5	98.5	2.03	2.06	-7.29
Pb	186	93.0	104.9	98.4	2.19	2.22	-5.70

### 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. Table 3-21A show recovery for 12 elements spanning the atomic mass range of the 48 elements normally measured. The min and max recovery values for all the elements ranged between 88.4 and 122.6% . Analysis of NIST Particle Standard SRM2783 yielded a Ca recovery of 94.2% . Averages over the reporting period were within the recovery goal of twice the standard deviation; 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 **Table 3-48B** 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 3-48B. Recovery Determined from Analysis of NIST SRMs 1832, 1833, 2708 and 2783 for Chester XRF 770 -- 1/1/2008 through 12/31/2008**

Element	Min	Max	Average	Std Dev	%CV	Slope (%/year)
Al	97.0	122.6	101.9	3.57	3.50	- 0.006
Si	98.4	105.4	101.5	1.35	1.33	-0.005
Si	96.2	101.8	99.7	1.26	1.26	-0.004
S	88.6	103.2	95.4	2.81	2.94	-0.012
K	95.3	110.0	102.5	3.01	2.94	0.014
Ca	88.4	104.9	94.2	4.12	4.37	0.027
Ti	97.6	107.9	102.6	2.49	2.43	-0.018
V	90.6	105.7	96.0	3.91	4.07	-0.005
Mn	96.2	106.4	101.2	2.06	2.04	-0.008
Fe	96.1	104.2	100.9	1.93	1.91	-0.001
Cu	89.9	115.6	104.4	4.30	4.11	0.023
Zn	95.5	107.2	99.7	2.40	2.41	-0.003
Pb	98.3	107.3	101.8	2.22	2.18	-0.004

## **Reproducibility**

Replicate analysis of field samples are used to assess reproducibility of the analytical system. Replicates were analyzed at a frequency of 5% of the filters analyzed. Six elements were selected for comparison through regression analysis. **Table 3-49** shows the correlation coefficient and average RPDs for the replicate analysis. The correlation coefficients range from 0.9953 to 0.9997.

**Table 3-49. Replicate Data for Chester XRF 770**

KeveX 770			
Element	n	Correlation Coefficient	Average RPD
Al	175	.9953	-0.31
Si	198	.9993	-1.79
S	198	.9990	0.11
K	197	.9997	-0.35
Ca	198	.9994	-0.60
Fe	197	.9993	0.01
Zn	165	.9997	0.94

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 Chester's position that re-analysis of particle deposits on filters received from the field represents the degree of confidence the client may expect more accurately than precision calculated from the uniformly distributed deposits from the Micromatter QC standard.

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

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

### **3.5.2.4 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 3.4.2.4 for comparative performance of both laboratories.

Since the inception of the PM2.5 Speciation project, Chester has performed numerous comparisons between instruments via replicate analysis of a number of clients, but much of this data is proprietary and cannot be shared in this report.

### **3.5.2.5 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 instrument on 12/26/05. The calculated MDLs are presented in Appendix 2 of the RTI Quality Assurance Project Plan for Chemical Speciation of PM2.5 Filter Samples.

### **3.5.2.6 Audits, PEs, Training, and Accreditations**

Chester LabNet 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.

Chester LabNet began training 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. Rachel came to Chester LabNet with approximately 2 years experience performing XRF analysis on Teflon filters for the IMPROVE network at UC Davis. In 2008, Rachel Mori was named technical director of Chester's Gravimetry Department. She now splits her time between XRF and Gravimetry.

Another Chester client provides quarterly PE samples in the form of Micromatter vapor deposited standards for elements: Cr, Cu, Zn, Ga, As, Se, Cd, Te, and Pb. However, these PE samples were analyzed using instrument XRF 772, which is not currently approved for use on the CSN program.

## **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
- Standard Operating Procedure for Coating and Extracting Denuders for Capture of Ammonia and Its Analysis (New SOP; Draft).

### 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. All SOPs were reviewed and signed by responsible personnel in early 2009. Revisions mainly concerned glassware use and volumes of slurry; no revisions affected the quality of the actual denuder-coating process.

A new SOP, "Standard Operating Procedure for Coating and Extracting Denunders for Capture of Ammonia and Its Analysis" was prepared in 2008. This SOP was assembled in anticipation of the need for collection of the basic gas, ammonia, using the denuder technique with the MetOne SASS system. This SOP is subject to significant revisions when the final edition of the glass, parallel plate design denuder is accepted by EPA and put into use at field sites.

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 beginning 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 3-50** lists the type of denuders refurbished and the number of refurbishments completed in 2008.

**Table 3-50. Denuder Refurbishments, January 1, 2008 through December 31, 2008**

Denuder Type	Total Refurbished
R&P	617
MetOne	565
URG	24
Andersen	14

### 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 2008.

#### 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 8 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.



**Figure 3-2. SHAL Technician Loading the URG 3000N Cassette.**

- 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 2008, the SHAL shipped out and received back more than 31,000 packages of filters. By employing the QC checks described in Section 3.7.2, 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

RTI prepares shipping schedules for the CSN and distributes these to all field sampling locations through the EPA DOPO's. 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 2008 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 3-51** lists those sites with less than 95% of their filters run on the intended sampling date.

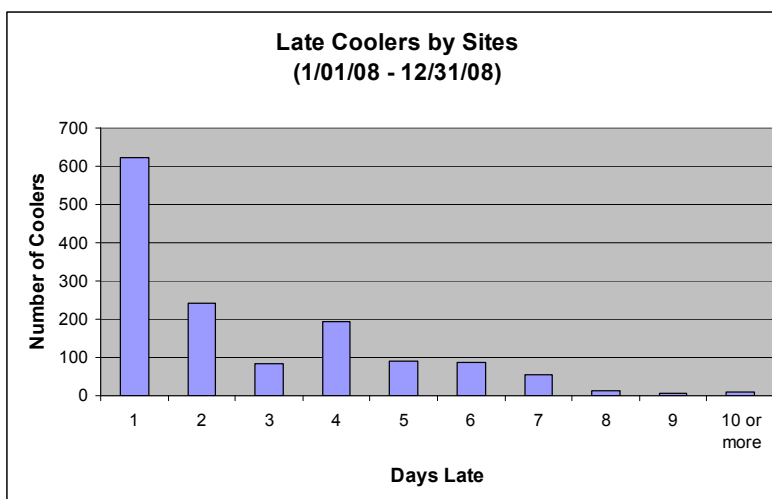


Figure 3-3A. Late Coolers by Site.

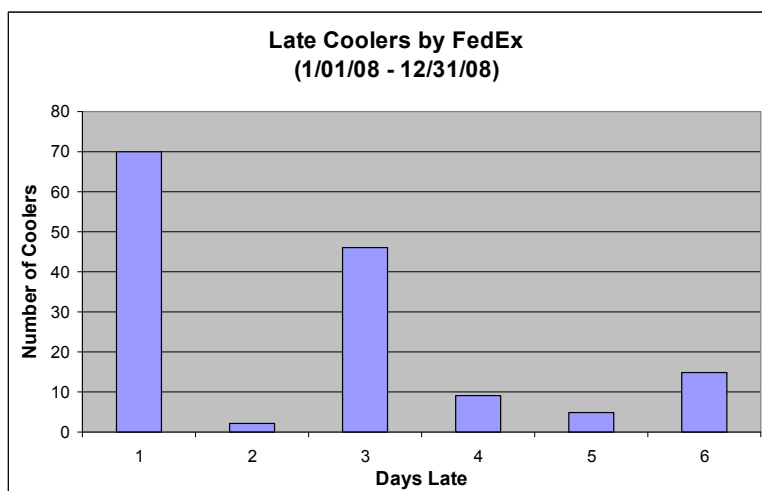


Figure 3-3B. Late Coolers by FedEx.

**Table 3-51. Sites with Less than 95% of Filters Run on Intended Sampling Date**

Airs Code	POC	Location	Events	On Date	Pct.
280670002	5	Laurel	12	10	83
471570024	5	Alabama (TN)	121	101	83
350010023	5	Del Norte	41	36	88
171190024	5	Granite City	122	109	89
080010006	5	Commerce City	190	172	91
261630001	5	Allen Park	122	112	92
180390003	5	Elkhart Pierre Moran	13	12	92
481130069	5	Hinton	104	97	93
391510020	5	Canton Health Dept	32	30	94
530110013	5	VAN4PLN2	16	15	94
060290014	6	Bakersfield-California Ave (Collocated)	120	113	94

### 3.7.5 Support Activities for Site Operators and Data Users

SHAL staff provided support to site operators and data users throughout 2008. A summary of email and phone communications with site operators and data users is presented in **Table 3-52**.

**Table 3-52. Summary of SHAL Communications with Site Operators and Data Users**

Description	Number of Communications
Site will send cooler late	92
Site needs schedule	25
Site did not receive cooler	43
Change of operator/site information	55
Sampler problems/questions	68
Field Blank/Trip Blank ran as routine sample	0
Request change of ship date from RTI	31
Site is stopping	18
Miscellaneous QA Issues	169
Data questions/reporting	103
Other	139

### 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 are trained in the handling of the 25mm quartz filters used in the URG 3000N sampler and the proper installation and removal of the quartz filter using the URG 3000N cassette.
- Throughout the year, senior SHAL staff will 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 2008 is shown in **Table 3-53**.

**Table 3-53. Review of SHAL Technician Processing Filter Modules**

Module Type	Number Observed	Findings	Findings Reviewed with Technician
MET ONE	103	7	7
Andersen	1	0	0
URG	3	0	0
R&P Spec	2	0	0
URG 3000N	27	0	0

## **4.0 Data Processing**

### **4.1 Quality Issues and Corrective Actions**

Late in 2008, a software problem was found that could cause an incorrect AQS validity code to be applied to some parameters when both a URG 3000 N sampler and another sampler ran at the same site and the same date. A review of data found that a total of 62 events had been affected. The problem only occurred when the first channel of either paired sampler was flagged with a validity flag or null value code but the other paired sampler's channel was not similarly flagged. Parameters measured on the nylon channel (anions and cations) were never affected. RTI has revised its processing code to prevent this from happening in the future and has reposted the corrected data to AQS.

No other significant quality issues arose during the period of this report that affected reportable data.

### **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 2008).

#### 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. In addition, the totals in table 4-1 exclude backup filters (which are always run as part of another event) to prevent double counting of events.

#### 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).

EPA has recently modified the Code of Federal Regulations (40 CFR 58.16) to require that all chemical speciation data be certified by before the end of the next calendar quarter. The reporting schedule, described above, results in a few events that sampled in one quarter but returned to RTI after the end of that quarter being reported to AQS up to 105 days after the end of the quarter. Addressing this discrepancy will require working with EPA to reduce the time sites have for data review before posting to AQS.

#### 4.5 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.

##### 4.5.1 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 4-1. Events Posted to Web Site

Report		Sampling Date		Total <sup>1</sup>	Routine	Blanks			Backup Filters <sup>3</sup>	
Batch	Date	Earliest	Latest			Field	Trip	24 Hour <sup>2</sup>	Routine	Trip Blank
96	1/14/2008	11/14/2007	12/15/2007	1,407	1,100	134	73	100	99	1
97	2/14/2008	12/8/2007	1/13/2008	1,350	1,211	59	25	55	52	2
98	3/14/2008	1/7/2008	2/15/2008	1,363	1,168	66	28	101	95	3
99	4/15/2008	2/6/2008	3/13/2008	1,306	1,001	56	171	78	75	1
100	5/15/2008	3/7/2008	4/12/2008	1,349	1,142	119	12	76	74	
101	6/12/2008	4/12/2008	5/13/2008	1,224	1,121	23	4	76	75	
102	7/15/2008	5/6/2008	6/11/2008	1,393	1,203	43	72	75	75	
103	8/13/2008	6/5/2008	7/14/2008	1,298	1,165	53	5	75	74	1
104	9/12/2008	7/11/2008	8/13/2008	1,471	1,219	173	5	74	73	
105	10/14/2008	8/10/2008	9/12/2008	1,426	1,178		177	71	70	
106	11/14/2008	9/8/2008	10/12/2008	1,297	1,150	66	7	74	73	
107	12/12/2008	10/9/2008	11/14/2008	1,326	1,246		2	78	79	

1) Counts for Routine Events and Total Events do not include backup filters or 24-hour blanks.

2) Backup filters are only used with the URG 3000N samplers. Only results for OC/EC analysis by the IMPROVE\_A method are reported for these samples.

3) 24 hour blanks are only used for URG 3000N samplers. Only results for OC/EC analysis by the IMPROVE\_A method are reported.

Table 4-2. Records Posted to Web Site

Report		Sampling Date		Routine	Blanks			Backup Filters <sup>1</sup>	
Batch	Date	Earliest	Latest		Field	Trip	24 Hour <sup>1</sup>	Routine	Trip Blank
96	1/14/2008	11/14/2007	12/15/2007	123,683	14,880	8,143	2,300	1,386	14
97	2/14/2008	12/8/2007	1/13/2008	136,038	5,325	2,817	1,265	728	28
98	3/14/2008	1/7/2008	2/15/2008	130,992	6,866	3,162	2,323	1,330	42
99	4/15/2008	2/6/2008	3/13/2008	112,199	4,961	19,222	1,794	1,050	14
100	5/15/2008	3/7/2008	4/12/2008	128,250	13,462	1,246	1,748	1,036	
101	6/12/2008	4/12/2008	5/13/2008	125,959	2,026	410	1,748	1,050	
102	7/15/2008	5/6/2008	6/11/2008	135,014	4,790	7,985	1,725	1,050	
103	8/13/2008	6/5/2008	7/14/2008	130,637	4,672	537	1,725	1,036	14
104	9/12/2008	7/11/2008	8/13/2008	136,555	18,253	521	1,702	1,022	
105	10/14/2008	8/10/2008	9/12/2008	131,632		19,789	1,633	980	
106	11/14/2008	9/8/2008	10/12/2008	128,435	6,841	747	1,702	1,022	
107	12/12/2008	10/9/2008	11/14/2008	139,485		224	1,794	1,106	
<b>Total</b>				1,830,544					

1) URG 3000 N samplers only.

Table 4-3. Events Posted to AQS

Report Batch	Routine	Blanks			Backup Filters <sup>1</sup>
		24 Hour <sup>1</sup>	Field	Trip	
95	1,753	53	54	10	128
96	1,491	101	137	99	100
97	1,645	55	59	35	53
98	1,598	101	66	36	98
99	1,386	78	56	230	77
100	1,543	76	122	17	76
101	1,489	76	23	5	76
102	1,566	75	44	96	75
103	1,558	75	53	7	74
104	1,598	74	178	7	74
105	1,550	73		235	73
106	1,503	74	66	9	73
<b>Total</b>	18,680	911	858	786	977

1) URG 3000 N samplers only.

Table 4-4. Records Posted to AQS

Report Batch	Routine	Blanks			Backup Filters <sup>1</sup>
		24 Hour <sup>1</sup>	Field	Trip	
95	92,896	689	3,254	491	1,664
96	77,374	1,313	9,167	5,192	1,300
97	86,766	715	3,575	1,739	689
98	83,854	1,313	4,283	1,935	1,274
99	71,964	1,014	3,367	12,191	1,001
100	80,397	988	8,186	844	988
101	78,361	988	1,380	278	988
102	83,794	975	2,956	4,980	975
103	81,426	975	3,180	349	962
104	85,149	962	11,567	351	962
105	81,927	949		12,404	949
106	79,264	962	4,276	485	949
<b>Total</b>	983,172	11,843	55,191	41,239	12,701

1) URG 3000 N only.

Table 4-5. Change Requests per Report Batch

Report Batch											
95	96	97	98	99	100	101	102	103	104	105	106
8	8	18	6	3	6	5	3	3	6	5	5

1) Number of site data contact changes. Multiple data changes by one site contact are counted as one request.

## 4.5.2 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.

## 4.5.3 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.

## 4.5.4 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 does 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. Recent changes (as discussed in Section 4.5) to the data posting requirements in the CFR have not yet resulted in significant increase in questions from sites about data availability.
- **Site Changes.** Several sites indicated that they had stopped, started, or relocated samplers during the past year. RTI prepares a monthly report on site and sampler changes to EPA to keep them informed of all changes.
- **Data Questions.** A number of sites had questions about individual data values. These were evaluated and the data flagged as appropriate.

## 4.6 Changes in AQS Event Validity Flags

AQS validity flags are used to indicate valid data that has unusual characteristics that might influence data use. There are two types of validity flags; event flags and QA flags. In response to the Exceptional Event Rule (EER), which was issued in connection with the new NAAQS for ozone and particulate matter, AQS implemented several changes to their event flags. These changes required RTI to make several changes to our system of flagging data. These changes were made in mid-2008, beginning with delivery batch 99. At the same time, revised forms containing the new flags were sent to site operators.

The AQS changes replaced the old set of event flags with two new sets of event flags; informational-only (INFORM) and request-exclusion (REQEXC). The first set (INFORM) are used to inform users of exceptional events at the site, while the second set (REQEXC) are also used to request that EPA exclude the unusual event from calculations to evaluate compliance with the NAAQS. As CSN does not report values used to determine NAAQS compliance, only INFORM flags can be reported to AQS by the CSN program.(i.e., REQEXC flags are not permitted for non-criteria pollutants, such as those measured in the CSN). See 72FR 13560 for more information about the EER. Implementation details may be found at <http://www.epa.gov/ttn/airs/airsaqs/memos/> (accessed 2/09).

As a result of the AQS changes, all previous event flags were removed from use when posting new data. A list of new INFORM flags with description and the closest matching former event flag is provided in **Table 4-6**.

**Table 4-6. New AQS Informational Only Event Flags**

Flag	Closest Old Flag	Description
IA	U	African Dust
IB		Asian Dust
IC	H	Chem. Spills and Industrial Accidents
ID	R	Cleanup After a Major Disaster
IE	J	Demolition
IF		Fire - Canadian
IG		Fire - Mexico/Central America
IH		Fireworks
II		High Pollen Count
IJ	A	High Winds
IK	O	Infrequent Large Gatherings
IL		Other
IM	Q	Prescribed Fire
IN	S	Seismic Activity
IO	B	Stratospheric Ozone Intrusion
IP	F	Structural Fire
IQ		Terrorist Act
IR	I	Unique Traffic Disruption
IS	C	Volcanic Eruptions
IT	E	Wildfire-U. S.
IU	E	Wildland Fire Use Fire-U. S.

## **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 2008; however, a revised QAPP was prepared for the new CSN contract, and was submitted in February, 2009.

#### **5.1.2 SOP Updates**

RTI's SOPs were updated in preparation for the procurement of the CSN contract in July 2008. These were finalized in early 2009, after contract award. All SOPs are shown in Section 7 of this report.

#### **5.1.3 Internal Surveillance Activities**

Internal surveillance activities during 2008 included walkthroughs of all the laboratories to verify compliance with the SOPs. An internal audit of the Gravimetry Laboratory was performed in January, 2008. 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 Project Manager, QA Manager, SHAL Supervisors, Data Processing Supervisor and other project personnel responded to a number of questions and requests for data during 2008. 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 2008, 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 (percent of data records reported)

Flag	Description	Delivery Batch Number											
		95	96	97	98	99	100	101	102	103	104	105	106
3	Possible field contamination	0.0%	0.0%	0.0%			0.0%	0.0%					
4	Possible lab contamination									0.0%			
5	Outlier-cause unknown	6.4%	4.0%	4.7%	4.5%	5.0%	5.3%	3.3%	4.4%	4.3%	3.7%	6.2%	8.6%
A	High Winds	0.3%	0.2%	0.1%									
C	Volcanic Eruptions		0.1%										
D	Sandblasting		0.1%										
E	Forest Fire	0.8%											
F	Structural Fire				0.1%								
H	Chemical Spills				0.1%								
J	Construction/Demolition	0.6%	1.0%	0.7%	0.6%	0.1%			0.1%				
K	Agricultural Tilling			0.1%									
P	Roofing Operations		0.1%										
W	Flow Rate Average out of specs	0.1%	0.1%	0.2%	0.0%		0.2%	0.1%					
X	Filter Temperature Diff. out of spec	0.2%	0.1%		0.2%		0.2%	0.3%			0.1%		0.2%
Y	Elapsed Sample Time out of specs			0.0%									
IA	African Dust									0.1%			
IC	Chem. Spills and Industrial Accidents												0.1%
IE	Demolition					0.5%			0.1%	0.1%		0.2%	
IH	Fireworks									0.2%		0.1%	
IJ	High Winds					0.1%	0.1%	0.3%	0.3%			0.2%	1.2%
IK	Infrequent Large Gatherings						0.2%	0.3%	0.2%	0.1%	0.1%	0.1%	
IL	Other					0.1%	0.8%	0.4%	0.1%	0.3%	0.4%	0.3%	0.2%
IM	Prescribed Fire							0.3%					
IN	Seismic Activity										0.1%		
IO	Stratospheric Ozone Intrusion										0.1%		
IP	Structural Fire								0.1%				
IR	Unique Traffic Disruption								0.1%			0.2%	
IT	Wildfire-U. S.									0.7%	0.1%	0.1%	0.2%
IU	Wildland Fire Use Fire-U. S.											0.1%	

Table 5-2. Summary of Null Value Codes by Delivery Batch Number (percent of data records reported)

Flag	Description	Delivery Batch Number											
		95	96	97	98	99	100	101	102	103	104	105	106
AB	Technician Unavailable	0.4%	0.2%	0.1%	0.1%	0.3%	0.2%	0.4%	0.2%	0.1%	0.1%	0.3%	0.1%
AC	Construction/Repairs in Area								0.1%		0.2%	0.3%	0.2%
AD	Shelter Storm Damage			0.1%					0.1%	0.0%			
AF	Scheduled but not Collected	0.4%	0.6%	1.4%	1.3%	1.2%	0.6%	0.4%	0.4%	0.9%	0.4%	0.3%	0.8%
AG	Sample Time out of Limits	0.4%	0.7%	0.8%	0.8%	0.4%	0.6%	0.3%	1.3%	1.2%	0.8%	0.5%	1.2%
AH	Sample Flow Rate out of Limits	0.5%	0.6%	0.6%	1.0%	0.8%	1.2%	0.7%	0.7%	0.8%	0.6%	0.8%	1.2%
AI	Insufficient Data (Can't Calculate)	0.1%	0.1%	0.2%	0.1%	0.6%		0.0%	0.1%	0.1%	0.1%	0.3%	0.1%
AJ	Filter Damage	0.2%	0.0%	0.0%	0.3%	0.1%	0.2%	0.1%	0.0%	0.2%	0.1%	0.1%	
AK	Filter Leak			0.1%									
AL	Voided by Operator	0.4%	0.2%	0.4%	0.4%	0.2%	0.3%	0.0%	0.4%	0.1%	0.3%	0.4%	0.2%
AM	Miscellaneous Void	0.1%	0.3%	0.0%		0.2%	0.1%			0.1%		0.2%	0.1%
AN	Machine Malfunction	0.2%	0.3%	0.3%	0.7%	1.2%	1.5%	0.9%	0.9%	0.8%	0.8%	1.6%	1.0%
AO	Bad Weather			0.1%	0.1%				0.3%	0.2%	0.1%	0.7%	0.4%
AP	Vandalism	0.1%											0.3%
AQ	Collection Error	0.2%	0.4%	0.1%	0.6%	0.1%	0.2%	0.2%	0.3%	0.2%	0.2%	0.1%	0.3%
AR	Lab Error	0.1%	0.1%		0.1%	0.0%		0.0%	0.1%	0.1%	0.1%	0.1%	0.0%
AS	Poor Quality Assurance Results			0.1%			0.0%	0.1%					
AU	Monitoring Waived				0.1%		0.1%					0.2%	0.1%
AV	Power Failure	0.6%	0.3%	0.6%	0.4%	0.5%	0.6%	0.2%	0.9%	0.7%	0.5%	0.5%	1.1%
AW	Wildlife Damage						0.0%				0.1%		0.0%
BA	Maintenance/Routine Repairs	0.1%	0.1%	0.0%	0.4%	0.1%	0.1%	0.2%	0.4%	0.4%		0.2%	0.2%
BB	Unable to Reach Site									0.1%	0.1%		0.1%
BE	Building/Site Repairs					0.1%		0.0%					
BI	Lost or Damaged in Transit	0.1%	0.1%			0.1%		0.1%					
BJ	Operator Error												0.1%

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

Flag	Description	Delivery Batch Number											
		95	96	97	98	99	100	101	102	103	104	105	106
ANB	Analysis not billable	0.2%	0.1%	0.1%	0.1%	0.2%	0.1%	0.0%	0.1%	0.1%	0.1%	0.1%	0.0%
APB	Analysis partially billable	0.8%	1.1%	2.0%	2.4%	1.8%	3.3%	3.4%	2.5%	2.2%	1.8%	2.2%	2.0%
DFM	Filter missing							0.0%	0.0%		0.0%		
DSI	Shipment invalid					0.1%							0.1%
DST	Received Temperature > 4C	52.9%	33.2%	26.4%	36.9%	35.8%	51.9%	58.6%	87.5%	88.1%	64.3%	60.1%	50.9%
FBS	Field or Trip Blank appears sampled											0.1%	
FCE	Corrected - operator data entry error	1.8%	1.7%	1.6%	1.9%	0.9%	1.3%	1.7%	2.4%	1.5%	1.1%	2.6%	0.9%
FES	Field Environmental Data Substituted	0.0%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.2%
FHT	Pickup holding time exceeded	14.6%	8.1%	13.4%	21.7%	14.1%	8.1%	17.7%	21.7%	11.9%	8.8%	13.2%	13.7%
FSB	Sample is blank			0.1%								0.1%	
FSL	Sample lost or damaged in shipment									0.1%			0.1%
LEQ	Lab environ. criteria out of limits								0.0%				
LFA	Filter inspection - Filter wet	0.0%	0.0%	0.1%	0.1%	0.0%	0.1%		0.0%		0.1%	0.1%	0.0%
LFH	Filter inspection - Holes in filter	0.0%										0.0%	
LFL	Filter inspection - Loose Material											0.1%	
LFO	Filter inspection - Other		0.0%										
LFT	Filter inspection - Tear	0.0%											
QAC	Cation/Anion Ratio out of limits	0.4%	0.4%	0.6%	0.4%	0.3%	0.4%	0.2%	0.2%	0.2%	0.2%	0.2%	0.3%
QL1	Invalidated by Level 1 Check	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.1%	0.1%	0.1%
QMB	Reconst. mass balance outside limits	6.1%	3.6%	4.1%	4.1%	4.7%	4.9%	3.0%	4.3%	4.1%	3.5%	6.1%	8.3%
SNB	Sample not billable		0.2%	0.1%	0.3%	0.9%	0.3%				0.2%	0.1%	0.2%
SPB	Sample partially billable	2.7%	2.5%	2.1%	3.6%	2.9%	2.4%	2.1%	3.0%	3.5%	2.3%	3.3%	4.2%

Table 5-4. Collocated Sites in the CSN During 2008.

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.

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 2008. For statistical analysis and plotting, the data from the MetOne and URG 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<sub>2.5</sub> mass, nitrate, sulfate, and sulfur. Events for which one or both concentration values are invalid are not plotted, but data with Airs Validity Status codes set are included in the figures. The oblique line on each chart indicates perfect agreement (slope=1.000).

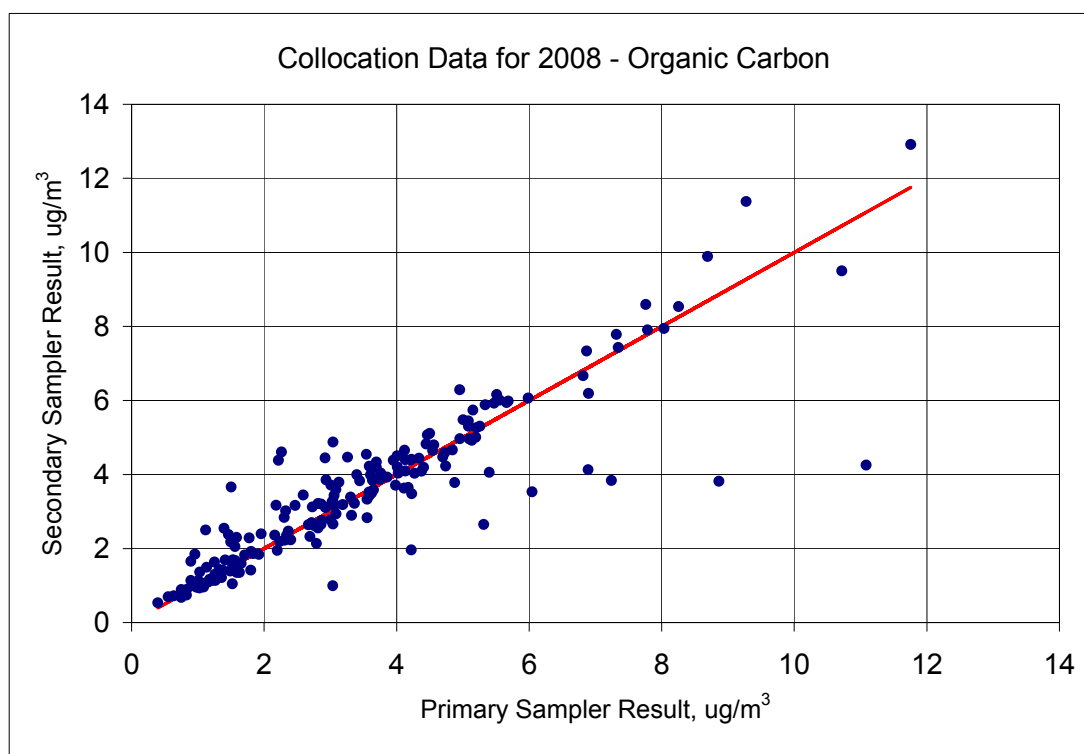


Figure 5-1. Examples of the Comparisons for Organic Carbon, Elemental Carbon, Mass, Nitrate, Sulfate, and Sulfur.

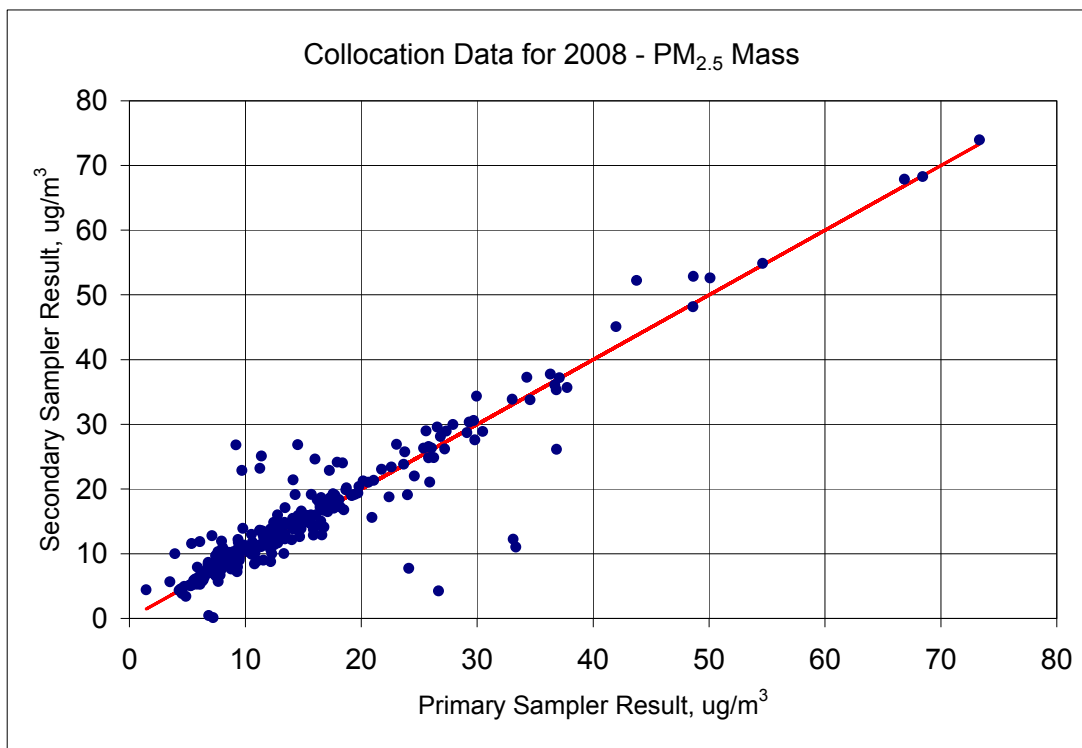
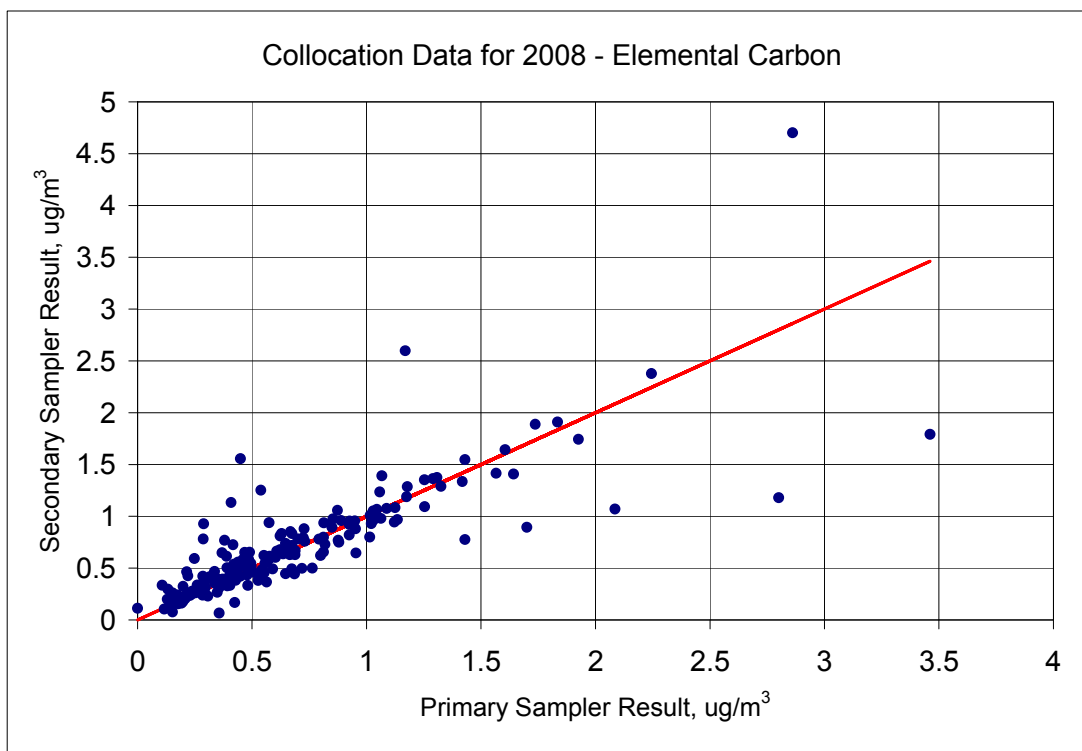


Figure 5-1. (continued).

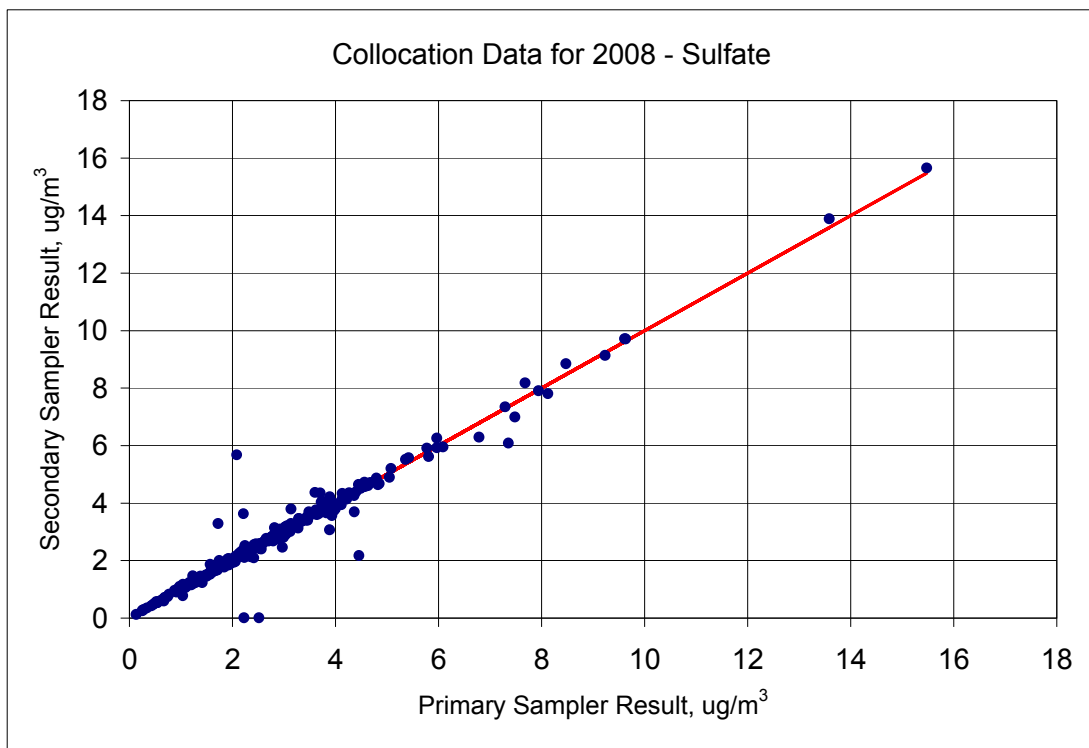
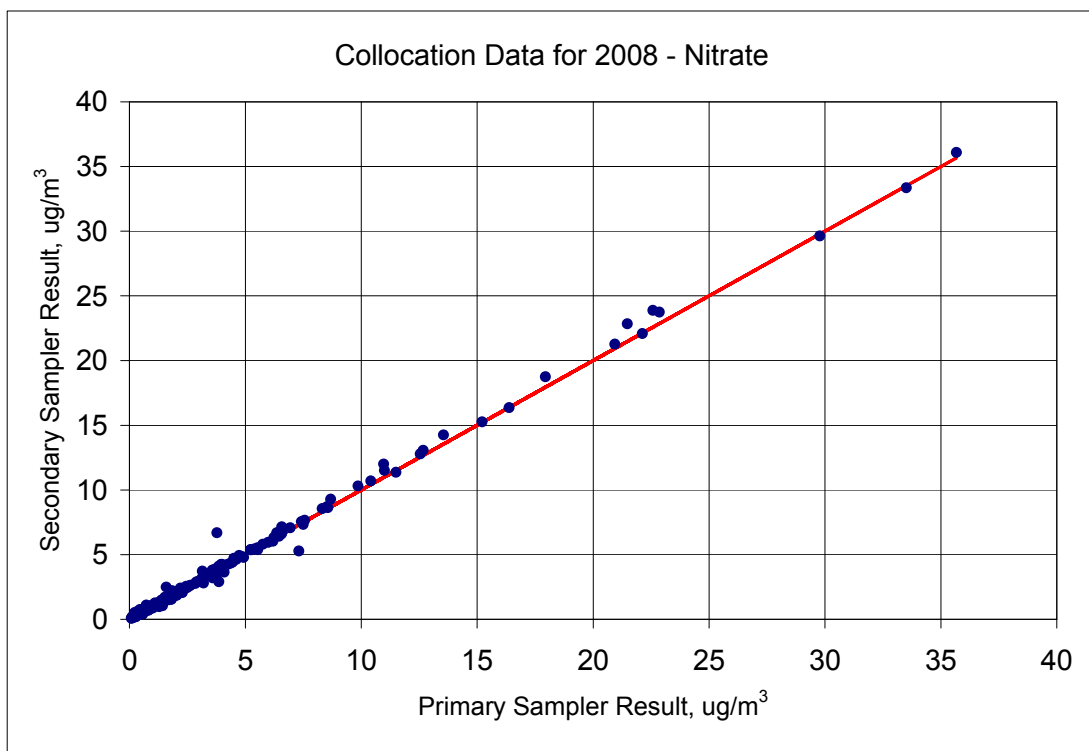


Figure 5-1. (continued).

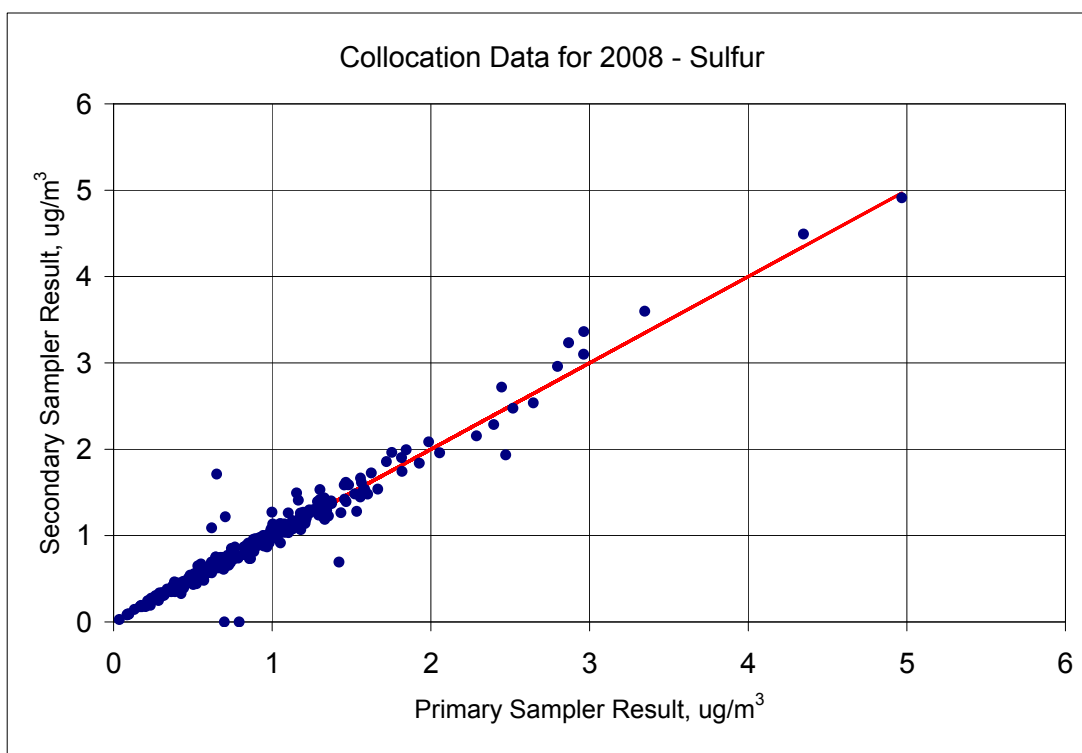


Figure 5-1. (continued).

### 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:

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

Table 5-5. Precision of Collocated Samplers

Analyte	Sampler 1		Sampler 2		Average Relative Diff. <sup>2</sup> (pct.)	Average Rel. AQS <sup>3</sup> Uncertainty (pct.)	Ratio AQS to ARD <sup>4</sup> (pct.)	Counts <sup>5</sup>
	Average (ug/m3)	Std. Dev. <sup>1</sup> (ug/m3)	Average (ug/m3)	Std. Dev. <sup>1</sup> (ug/m3)				
Particulate matter 2.5u	15.3355	10.7230	15.7509	10.8720	11%	6%	51%	268
Aluminum	0.0993	0.1401	0.0976	0.1400	29%	20%	68%	132
Arsenic	0.0042	0.0024	0.0028	0.0017	32%	36%	112%	13
Bromine	0.0049	0.0027	0.0048	0.0029	20%	27%	140%	197
Calcium	0.0698	0.1065	0.0672	0.0836	25%	10%	<b>42%</b>	261
Chlorine	0.1085	0.2028	0.1095	0.2055	33%	14%	<b>44%</b>	186
Chromium	0.0259	0.1019	0.0068	0.0097	65%	28%	<b>42%</b>	26
Cobalt	0.0029	0.0019	0.0024	0.0012	26%	37%	143%	22
Copper	0.0164	0.0196	0.0116	0.0128	27%	14%	54%	250
Iron	0.1365	0.1622	0.1323	0.1299	20%	7%	<b>38%</b>	267
Lead	0.0106	0.0050	0.0120	0.0055	18%	31%	167%	19
Magnesium	0.0481	0.0492	0.0411	0.0425	25%	23%	94%	52
Manganese	0.0055	0.0069	0.0053	0.0069	23%	26%	110%	120
Nickel	0.0039	0.0111	0.0028	0.0032	32%	24%	75%	123
Potassium	0.0987	0.2367	0.0995	0.2237	11%	9%	77%	265
Selenium	0.0031	0.0008	0.0030	0.0011	18%	38%	<b>214%</b>	11
Silicon	0.1713	0.2631	0.1695	0.2582	21%	13%	62%	249
Sodium	0.1991	0.1902	0.1945	0.1969	24%	18%	75%	148
Sulfur	0.9191	0.6502	0.9396	0.6675	5%	7%	137%	267
Titanium	0.0124	0.0145	0.0107	0.0127	26%	24%	92%	67
Vanadium	0.0056	0.0031	0.0051	0.0033	24%	28%	120%	76
Zinc	0.0153	0.0193	0.0154	0.0194	16%	13%	86%	237
Ammonium	1.8603	1.9540	1.8935	2.0244	6%	7%	115%	270
Potassium	0.0843	0.2205	0.0816	0.2234	45%	13%	<b>28%</b>	270
Sodium	0.1925	0.1951	0.1932	0.1999	27%	43%	160%	270
Nitrate (MetOne Nylon)	3.6681	5.3691	3.7306	5.4689	6%	7%	131%	229
Nitrate (URG Nylon)	0.3927	0.4060	0.3983	0.4083	24%	7%	<b>31%</b>	41
Nitrate (URG Teflon)	0.3215	0.2628	0.3013	0.2906	18%	7%	<b>41%</b>	41
Sulfate	2.7769	1.9795	2.7904	1.9996	4%	7%	165%	270
Elemental carbon	0.6813	0.5241	0.7041	0.5282	17%	47%	<b>279%</b>	179
Organic carbon	3.5100	2.1342	3.5613	2.0525	11%	13%	115%	179

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

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

<sup>3</sup> Average value of the relative uncertainties as reported to AQS.

<sup>4</sup> 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.

<sup>5</sup> 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.

Where

- $U_{ij}$  and  $C_{ij}$  refer to the uncertainty and concentration for the  $i^{\text{th}}$  exposure with the  $j^{\text{th}}$  sampler ( $j=1$  or  $2$ ).

The criteria for inclusion in the average (index  $i$ ) is the same as in the previous equation.

The next column provides the ratio of AvAQS to ARD defined above. This is essentially the average under- or over-estimate of the uncertainty for each chemical species reported during 2008. 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:

- Five 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 four cases, the uncertainty estimates reported to AQS were higher than the estimate from collocation.
- Three ionic species: nitrate (MASS) and potassium had reported uncertainties that were less than half the uncertainties estimated from collocation data.
- All the organic and elemental carbon species for the original CSN analysis have previously reported uncertainties to AQS that are significantly larger than those estimated from the collocated sampler data. During 2008, only EC differed by more than 2x.
- The ratio for particulate mass (Table 5-5) is barely within a factor of two, indicating that the uncertainties reported to AQS are somewhat low. 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 2008.

**Table 5-6. Concentration Percentiles for Combined Trip and Field Blanks  
(Reporting Batches 95 – 106).**

ANALYTE	MEAN	PERCENTILES OF CONCENTRATION (as ug/m <sup>3</sup> )						
		5	10	25	MEDIAN	75	90	95
Cations and Anions by Ion Chromatography								
Ammonium	0.023	0.000	0.000	0.000	0.000	0.000	0.044	0.136
Potassium	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium	0.037	0.000	0.000	0.000	0.009	0.026	0.057	0.096
Nitrate	0.034	0.000	0.000	0.000	0.023	0.044	0.075	0.125
Nitrate (URG Nylon)	0.033	0.003	0.011	0.017	0.025	0.040	0.066	0.087
Nitrate (URG Teflon)	0.034	0.017	0.019	0.022	0.026	0.037	0.060	0.079
Sulfate	0.032	0.000	0.000	0.000	0.020	0.033	0.055	0.095
Mass by Gravimetry								
PM2.5 mass	0.734	-0.104	0.000	0.208	0.625	1.042	1.667	2.188
Organic and elemental carbon CSN TOT Method								
Elemental carbon	0.033	0.000	0.000	0.000	0.001	0.007	0.073	0.119
Organic carbon	1.379	0.371	0.758	0.964	1.155	1.434	1.936	2.648
Total carbon	1.412	0.371	0.775	0.972	1.170	1.453	1.966	2.754
Pk2_OC	0.587	0.148	0.270	0.382	0.464	0.602	0.864	1.261
Pk3_OC	0.320	0.076	0.102	0.150	0.229	0.355	0.559	0.803
Pk4_OC	0.089	0.002	0.007	0.020	0.042	0.081	0.146	0.242
PyroIC	0.007	0.000	0.000	0.000	0.000	0.001	0.013	0.031
Organic and elemental carbon by IMPROVE_A Method (TOT and TOR)								
E1 IMPROVE	0.002	0.000	0.000	0.000	0.000	0.000	0.004	0.010
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	0.002	0.000	0.000	0.000	0.000	0.001	0.006	0.010
EC IMPROVE TOT	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.002
O1 IMPROVE	0.036	0.009	0.015	0.024	0.035	0.045	0.058	0.066
O2 IMPROVE	0.039	0.014	0.018	0.023	0.033	0.046	0.062	0.074
O3 IMPROVE	0.062	0.022	0.027	0.036	0.048	0.065	0.094	0.133
O4 IMPROVE	0.007	0.000	0.000	0.000	0.000	0.007	0.012	0.022
OC IMPROVE TOR	0.144	0.065	0.075	0.097	0.119	0.157	0.217	0.275
OC IMPROVE TOT	0.146	0.065	0.075	0.098	0.120	0.158	0.219	0.275
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	0.000	0.003	0.010
TC IMPROVE	0.146	0.065	0.075	0.098	0.120	0.161	0.219	0.275

ANALYTE	MEAN	PERCENTILES OF CONCENTRATION (as ug/m³)						
		5	10	25	MEDIAN	75	90	95
Trace elements by XRF								
Aluminum	0.001	0.000	0.000	0.000	0.000	0.000	0.003	0.007
Antimony	0.001	0.000	0.000	0.000	0.000	0.000	0.002	0.006
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	0.002	0.004
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	0.000	0.001
Calcium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Cerium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cesium	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.003
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	0.000	0.001
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	0.000	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	0.003	0.000	0.000	0.000	0.000	0.000	0.002	0.006
Lanthanum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Lead	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Magnesium	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.010
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	0.001	0.001
Molybdenum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nickel	0.000	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	0.000	0.001
Silicon	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Silver	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002
Sodium	0.003	0.000	0.000	0.000	0.000	0.000	0.001	0.015
Strontium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Sulfur	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Tantalum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Terbium	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Tin	0.001	0.000	0.000	0.000	0.000	0.000	0.002	0.003

ANALYTE	MEAN	PERCENTILES OF CONCENTRATION (as ug/m <sup>3</sup> )						
		5	10	25	MEDIAN	75	90	95
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	0.000	0.002
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

**Trip and Field Blanks.** For XRF analysis, the average and 95th percentiles were acceptably low for all elements. Of the ions, nitrate and ammonium were somewhat higher than other chemical species. The high values for organic carbon and total carbon by the CSN TOT method were not unexpected because of the well-known adsorption artifact. The corresponding levels for the IMPROVE\_A method were much lower, when expressed in  $\mu\text{g}/\text{m}^3$ , because of sample volume and filter area differences.

**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

URG 3000N modules began acquiring quartz filter samples at 57 CSN sites in May, 2007, and continued throughout 2008. 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 acquired during 2008. 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; however, RTI has not received a directive to implement such a correction.

Table 5-7. Concentration Percentiles for 3000N Backup Filter Blanks (Reporting Batches 95 – 106).

ANALYTE	MEAN	PERCENTILES OF CONCENTRATION (as $\mu\text{g}/\text{m}^3$ )						
		5	10	25	MEDIAN	75	90	95
EC IMPROVE TOR	0.011	0.000	0.000	0.000	0.007	0.016	0.027	0.036
EC IMPROVE TOT	0.001	0.000	0.000	0.000	0.000	0.000	0.003	0.007
OC IMPROVE TOR	0.394	0.140	0.179	0.261	0.368	0.498	0.624	0.739
OC IMPROVE TOT	0.404	0.141	0.179	0.267	0.378	0.514	0.648	0.756
TC IMPROVE	0.406	0.141	0.179	0.268	0.378	0.514	0.650	0.756
E1 IMPROVE	0.014	0.000	0.000	0.002	0.009	0.017	0.030	0.042
E2 IMPROVE	0.003	0.000	0.000	0.000	0.000	0.004	0.009	0.014
E3 IMPROVE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O1 IMPROVE	0.076	0.004	0.017	0.033	0.056	0.107	0.162	0.198
O2 IMPROVE	0.121	0.044	0.053	0.081	0.112	0.152	0.196	0.228
O3 IMPROVE	0.147	0.055	0.066	0.094	0.133	0.179	0.232	0.286
O4 IMPROVE	0.043	0.005	0.009	0.019	0.036	0.062	0.089	0.106
OP IMPROVE TOR	0.007	0.000	0.000	0.000	0.000	0.002	0.017	0.029
OP IMPROVE TOT	0.017	0.000	0.000	0.001	0.008	0.020	0.037	0.051

## 6.0 External Audits

### 6.1 Performance Evaluation Audit Results

#### 6.1.1 Performance Evaluation Audit Sample Results for 2007

Performance evaluation (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 in time to be included in the 2007 annual report. The PE samples were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. The results were announced in a study report dated October 20, 2008, titled "Experimental Inter-comparison of Speciation Laboratories." This study was similar to studies carried out in 2005 and 2006.

This study was conducted as part of the EPA's quality assurance oversight for the CSN and IMPROVE programs. The purpose of this study was to evaluate specific laboratory performance at those laboratories that routinely analyze PM<sub>2.5</sub> chemical speciation samples. Laboratories included: RTI, Oregon Department of Environmental Quality, Desert Research Institute, the California Air Resources Board, the University of California, Davis (Crocker Nuclear Laboratory); and EPA/NAREL.

This study required each participating laboratory to analyze a set of blind PE filter samples. NAREL prepared replicate filter samples for the study using co-located Met One speciation samplers located in Montgomery, AL. Detailed instructions for analyzing and reporting the PE samples were provided to the laboratories by NAREL. A sufficient number of replicates were prepared so that each laboratory could receive PE filters for the following analyses:

- Gravimetric Mass Analysis
- Ion Chromatography (IC) Analysis
- Carbon by Thermal Optical Analysis (TOA)
- Elemental analysis by X-Ray Fluorescence (XRF)

Five laboratories analyzed a set of PE samples for gravimetric mass, and all results were within the 3-sigma advisory limits established by NAREL. All of the results reported from the participating labs showed good agreement with the gravimetric results reported from NAREL.

Five different laboratories reported IC results from at least one set of PE samples, and three different methods were tested. Both nylon and Teflon® filters were analyzed for selected ions during this study. Good performance was observed from all of the participating labs, and no significant problems were observed in the IC results from this study.

Four laboratories analyzed sets of quartz PE filters by TOT using a variety of instruments and methods. Agreement was good for TC within each method, STN or IMPROVE\_A, results showed relatively good precision for the major carbon fractions and for OC and EC. The study showed good subfraction precision when using the IMPROVE\_A method. The NAREL authors speculated that this might have been due to enhanced temperature calibration procedures now in place at most of the labs.

Six XRF laboratories participated in this study, with EPA's NERL (Research Triangle Park, NC) serving as the reference laboratory. All of the filters used in this study were first analyzed at NERL. Good agreement was found between the laboratories for elements in highest abundance.

### **6.1.2 Performance Evaluation Audit Samples for 2008**

PE samples were received during 2008, but the results were reported to EPA in early 2009. No report has been received as of this writing.

## **6.2 System Audit Results**

There was no technical systems audit of the RTI laboratories performed by EPA during 2008.

## 7.0 List of References

### 7.1 List of CSN Documents

Type	Title	Date Revised	Author	Document No.
SOP	Standard Operating Procedure for Sample Handling and Archiving Laboratory (SHAL)	2/18/2009	O'Rourke	
SOP	Standard Operating Procedure for Shipping Filters to and from an Off-Site Laboratory	2/18/2009	Peterson	
SOP	Standard Operating Procedure for Long-Term Archiving of PM Filters and Extracts	5/13/2008	C. Haas	
SOP	Standard Operating Procedure for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters	2/16/2008	E. Hardison	
SOP	Standard Operating Procedure for Cleaning Nylon Filters Used for the Collection of PM <sub>2.5</sub> Material	5/13/2008	E. Hardison	
SOP	Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis	7/8/2008	Greene	
SOP	Analysis of Elements in Air Particulates by X-Ray Fluorescence (Kevex 770 & 772)	2/3/2009	Chester	
SOP	Kevex XRF Spectrometer Calibration (CHESTER LabNet Proprietary Method)	1/8/2008	Chester	
SOP	Kevex Spectrometer Data Generation, Interpretation and Reporting (CHESTER LabNet Proprietary Method)	1/30/2009	Chester	
SOP	Sample Receipt and Log In Chester LabNet Proprietary Method	6/20/2008	Chester	
SOP	Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters	July 2008	McWilliams	
SOP	Standard Operating Procedure for PM <sub>2.5</sub> Anion Analysis	5/13/2008	E. Hardison	
SOP	Standard Operating Procedure for PM <sub>2.5</sub> Cation Analysis	5/13/2008	E. Hardison	
SOP	DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A	7/1/2008	DRI	
SOP	Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a DRI Model 2001 Analyzer	2/13/2008	Peterson	
SOP	Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory	2/13/2009	Peterson	

Type	Title	Date Revised	Author	Document No.
	or a DRI Model 2001 Carbon Aerosol Analyzer			
SOP	Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer	2/16/2009	Peterson	
SOP	Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a Sunset Laboratory Dual-Mode Analyzer	2/13/2009	Peterson	
SOP	DRI Standard Operating Procedure: Analysis of Semi-Volatile Organic Compound by GC/MS	2/21/2003	DRI	
SOP	Standard Operating Procedure for Sample Preparation and Analysis of PM <sub>10</sub> and PM <sub>2.5</sub> Samples by Scanning Electron Microscopy	7/8/2008	Crankshaw	
SOP	Standard Operating Procedure for Coating and Extracting Annular Denuders with Sodium Carbonate	7/8/2008	Eaton	
SOP	Standard Operating Procedures for Coating Aluminum Honeycomb Denuders With Magnesium Oxide	2/17/2009	Eaton	
SOP	Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin	5/9/2008	Eaton	
SOP	Procedures for Coating R&P Speciation Sampler Chemcomb™ Denuders with Sodium Carbonate	5/21/2008	Eaton	
SOP	Standard Operating Procedure for Coating and Extracting Denuders for Capture of Ammonia and Its Measurement	2/14/2008	Eaton	
SOP	Standard Operating Procedure for Database Operations	5/8/2008	Rickman	
SOP	Standard Operating Procedure for Assigning Data Validation Flags for the Chemical Speciation Network	5/15/2008	Wall	
SOP	Standard Operating Procedure—Speciation Data Processing Disaster Recovery Plan	5/21/2008	Rickman	
SOP	Standard Operating Procedure for the X-Series ICP-MS for the Analysis of Particulate Deposits on Teflon Filters	7/8/2008	Weber	
SOP	DRI Standard Operating Procedure: Procedure for Light Transmission Analysis	7/14/2008	DRI	
SOP	Standard Operating Procedure for Document Control and Storage for the PM <sub>2.5</sub> Chemical Speciation Program	2/18/2009	D. Haas	

Type	Title	Date Revised	Author	Document No.
SOP	Standard Operating Procedure for Corrective Action for the PM <sub>2.5</sub> Chemical Speciation Program	5/21/2008	Flanagan/Haas	
SOP	Standard Operating Procedure for Training for Staff Working on the PM <sub>2.5</sub> Chemical Speciation Program	5/8/2008	D. Haas	
QAPP	QAPP for PM <sub>2.5</sub> of Chemical Speciation Samples	2/29/09	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	2007 Annual Data Summary Report	2/29/2008	RTI	RTI/8858/06QAS
Data	2008 Annual Data Summary Report	2/26/2009	RTI	RTI/8858/07QAS
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
Report	Tests of Acceptance of X-ray Fluorescence Instrument #3 Operated by RTI International	May, 2006	RTI	RTI/0208858/TO2/03D
Report	Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties	8/4/2006	RTI	RTI/0208858/TO2/04D
Report	Reporting Uncertainties for Artifact-Corrected Carbon Data for the URG 3000N Sampler RTI International	10/9/2007	RTI	RTI/0208858/T6B/01D
Report	PM <sub>2.5</sub> Speciation Trends Network -- Measurement Uncertainties and Method Detection Limits	1/8/2008	RTI	RTI/0208858/12/04S

## **Appendix A**

### **Method Detection Limits**

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**Appendix A**  
**Method Detection Limits (Network-wide Maximum)**

Analysis	Analyte	MASS ( $\mu\text{g}$ )	Concentration ( $\mu\text{g}/\text{m}^3$ ) by Sampler Type				
			MASS	R and P	RAAS	SASS	3000N
Cations - PM2.5 (NH <sub>4</sub> , Na, K)	Ammonium	0.24	0.010	0.017	0.024	0.026	
Cations - PM2.5 (NH <sub>4</sub> , Na, K)	Potassium	0.23	0.0095	0.016	0.023	0.025	
Cations - PM2.5 (NH <sub>4</sub> , Na, K)	Sodium	0.29	0.013	0.021	0.030	0.032	
Mass - PM2.5	Particulate matter	7.2	0.33	0.31	0.33	0.83	
Nitrate - PM2.5	Nitrate	0.21		0.015	0.0072	0.023	
Nitrate - PM2.5 (MASS/nylon)	Nitrate	0.21	0.0088				
Nitrate - PM2.5 (MASS/teflon)	Nitrate	0.070	0.0032				
Organic and elemental carbon	E1 IMPROVE	0.010					0.00046
Organic and elemental carbon	E2 IMPROVE	0.010					0.00046
Organic and elemental carbon	E3 IMPROVE	0.010					0.00046
Organic and elemental carbon	EC IMPROVE TOR	0.034					0.0015
Organic and elemental carbon	EC IMPROVE TOT	0.034					0.0015
Organic and elemental carbon	O1 IMPROVE	0.014					0.00061
Organic and elemental carbon	O2 IMPROVE	0.34					0.015
Organic and elemental carbon	O3 IMPROVE	1.0					0.046
Organic and elemental carbon	O4 IMPROVE	0.034					0.0015
Organic and elemental carbon	OC IMPROVE TOR	1.3					0.059
Organic and elemental carbon	OC IMPROVE TOT	1.3					0.059
Organic and elemental carbon	OP IMPROVE TOR	0.034					0.0015
Organic and elemental carbon	OP IMPROVE TOT	0.034					0.0015
Organic and elemental carbon	TC IMPROVE	1.4					0.064
Organic and elemental carbon (NIOSH)	Elemental carbon	2.4	0.098	0.17	0.23	0.27	
Organic and elemental carbon (NIOSH)	Organic carbon	2.4	0.098	0.17	0.23	0.27	
Organic and elemental carbon (NIOSH)	Pk1_OC	2.4	0.098	0.17	0.23	0.27	
Organic and elemental carbon (NIOSH)	Pk2_OC	2.4	0.098	0.17	0.23	0.27	
Organic and elemental carbon (NIOSH)	Pk3_OC	2.4	0.098	0.17	0.23	0.27	
Organic and elemental carbon (NIOSH)	Pk4_OC	2.4	0.098	0.17	0.23	0.27	
Organic and elemental carbon (NIOSH)	PyroIC	2.4	0.098	0.17	0.23	0.27	

Organic and elemental carbon (NIOSH)	Total carbon	2.4	0.098	0.17	0.23	0.27	
Sulfate - PM2.5	Sulfate	0.10	0.0045	0.0072	0.010	0.011	
Trace elements	Aluminum	0.24	0.0091	0.010	0.010	0.026	
Trace elements	Antimony	0.40	0.018	0.017	0.019	0.046	
Trace elements	Arsenic	0.026		0.0011	0.0011		
Trace elements	Barium	0.57	0.0048	0.025	0.025	0.066	
Trace elements	Bromine	0.022					
Trace elements	Cadmium	0.18	0.0080	0.0078	0.0083	0.021	
Trace elements	Calcium	0.073	0.0033	0.0031	0.0033		
Trace elements	Cerium	0.97	0.0042	0.040	0.042	0.11	
Trace elements	Cesium	0.44	0.015	0.019	0.020	0.051	
Trace elements	Chlorine	0.15	0.0034	0.0061	0.0063	0.016	
Trace elements	Chromium	0.025	0.0011	0.0011	0.0011		
Trace elements	Cobalt	0.019					
Trace elements	Copper	0.024	0.0010	0.0011	0.0011		
Trace elements	Europium	0.11	0.0022	0.0047	0.0048	0.013	
Trace elements	Gallium	0.051	0.0011	0.0021	0.0022		
Trace elements	Gold	0.078	0.0023	0.0034	0.0034		
Trace elements	Hafnium	0.26	0.011	0.011	0.011	0.029	
Trace elements	Indium	0.21	0.0094	0.0092	0.0098	0.025	
Trace elements	Iridium	0.075	0.0031	0.0032	0.0033		
Trace elements	Iron	0.032		0.0014	0.0014		
Trace elements	Lanthanum	0.71	0.0037	0.029	0.030	0.078	
Trace elements	Lead	0.061	0.0021	0.0026	0.0027		
Trace elements	Magnesium	0.63	0.0073	0.026	0.027	0.069	
Trace elements	Manganese	0.028		0.0012	0.0012		
Trace elements	Mercury	0.091	0.0040	0.0039	0.0042	0.010	
Trace elements	Molybdenum	0.087	0.0038	0.0038	0.0040	0.010	
Trace elements	Nickel	0.018					
Trace elements	Niobium	0.053	0.0020	0.0023	0.0023		
Trace elements	Phosphorus	0.15	0.0070	0.0066	0.0071	0.018	
Trace elements	Potassium	0.11	0.0044	0.0046	0.0047	0.012	
Trace elements	Rubidium	0.025		0.0011	0.0011		
Trace elements	Samarium	0.096	0.0022	0.0042	0.0042	0.011	
Trace elements	Scandium	0.36	0.016	0.015	0.016	0.041	

Trace elements	Selenium	0.025	0.0011	0.0011	0.0011		
Trace elements	Silicon	0.18	0.0074	0.0077	0.0078	0.020	
Trace elements	Silver	0.14	0.0063	0.0061	0.0065	0.016	
Trace elements	Sodium	2.1	0.022	0.089	0.092	0.23	
Trace elements	Strontium	0.030	0.0010	0.0013	0.0013		
Trace elements	Sulfur	0.095	0.0043	0.0040	0.0043	0.011	
Trace elements	Tantalum	0.18	0.0042	0.0075	0.0078	0.020	
Trace elements	Terbium	0.097	0.0019	0.0042	0.0043	0.011	
Trace elements	Tin	0.31	0.014	0.013	0.014	0.035	
Trace elements	Titanium	0.051	0.0023	0.0022	0.0023		
Trace elements	Vanadium	0.037	0.0017	0.0016	0.0017		
Trace elements	Wolfram	0.12	0.0031	0.0050	0.0051	0.013	
Trace elements	Yttrium	0.036	0.0012	0.0016	0.0016		
Trace elements	Zinc	0.034	0.0015	0.0015	0.0016		
Trace elements	Zirconium	0.045	0.0019	0.0019	0.0020		

## **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		Sampling Date		Total <sup>1</sup>	Routine	Blanks			Backup Filters <sup>3</sup>	
Batch	Date	Earliest	Latest			Field	Trip	24 Hour <sup>2</sup>	Routine	Trip Blank
95	12/13/2007	10/9/2007	11/14/2007	1,426	1,312	54	7	53	126	2
96	1/14/2008	11/14/2007	12/15/2007	1,407	1,100	134	73	100	99	1
97	2/14/2008	12/8/2007	1/13/2008	1,350	1,211	59	25	55	52	2
98	3/14/2008	1/7/2008	2/15/2008	1,363	1,168	66	28	101	95	3
99	4/15/2008	2/6/2008	3/13/2008	1,306	1,001	56	171	78	75	1
100	5/15/2008	3/7/2008	4/12/2008	1,349	1,142	119	12	76	74	
101	6/12/2008	4/12/2008	5/13/2008	1,224	1,121	23	4	76	75	
102	7/15/2008	5/6/2008	6/11/2008	1,393	1,203	43	72	75	75	
103	8/13/2008	6/5/2008	7/14/2008	1,298	1,165	53	5	75	74	1
104	9/12/2008	7/11/2008	8/13/2008	1,471	1,219	173	5	74	73	
105	10/14/2008	8/10/2008	9/12/2008	1,426	1,178		177	71	70	
106	11/14/2008	9/8/2008	10/12/2008	1,297	1,150	66	7	74	73	
107	12/12/2008	10/9/2008	11/14/2008	1,326	1,246		2	78	79	
108	1/13/2009	11/8/2008	12/11/2008	1,414	1,099	178	61	76	76	

1) Counts for Routine Events and Total Events do not include backup filters or 24-hour blanks.

2) Backup filters are only used with the URG 3000N samplers. Only results for OC/EC analysis by the IMPROVE\_A method are reported for these samples.

3) 24 hour blanks are only used for URG 3000N samplers. Only results for OC/EC analysis by the IMPROVE\_A method are reported.

**Table B-2 Total Number of Records Delivered by Type (Records Posted by Report Batch)**

Report		Sampling Date		Routine	Blanks			Backup Filters <sup>1</sup>	
Batch	Date	Earliest	Latest		Field	Trip	24 Hour <sup>1</sup>	Routine	Trip Blank
95	12/13/2007	10/9/2007	11/14/2007	147,744	4,810	745	1,219	1,764	28
96	1/14/2008	11/14/2007	12/15/2007	123,683	14,880	8,143	2,300	1,386	14
97	2/14/2008	12/8/2007	1/13/2008	136,038	5,325	2,817	1,265	728	28
98	3/14/2008	1/7/2008	2/15/2008	130,992	6,866	3,162	2,323	1,330	42
99	4/15/2008	2/6/2008	3/13/2008	112,199	4,961	19,222	1,794	1,050	14
100	5/15/2008	3/7/2008	4/12/2008	128,250	13,462	1,246	1,748	1,036	
101	6/12/2008	4/12/2008	5/13/2008	125,959	2,026	410	1,748	1,050	
102	7/15/2008	5/6/2008	6/11/2008	135,014	4,790	7,985	1,725	1,050	
103	8/13/2008	6/5/2008	7/14/2008	130,637	4,672	537	1,725	1,036	14
104	9/12/2008	7/11/2008	8/13/2008	136,555	18,253	521	1,702	1,022	
105	10/14/2008	8/10/2008	9/12/2008	131,632		19,789	1,633	980	
106	11/14/2008	9/8/2008	10/12/2008	128,435	6,841	747	1,702	1,022	
107	12/12/2008	10/9/2008	11/14/2008	139,485		224	1,794	1,106	
108	1/13/2009	11/8/2008	12/11/2008	123,921	18,833	6,785	1,794	1,092	
<b>Total</b>				1,830,544					

1) URG 3000 N samplers only.

**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											
				95	96	97	98	99	100	101	102	103	104	105	106
Alabama (TN)	471570024	5	SASS	100	100	100	90	100	100	100	90	100	100	100	100
Allen Park	261630001	5	SASS	100	100	100	100	100	100	100	90	100	100	100	100
Bakersfield-California Ave	060290014	5	URG 3000N	100	100	92	100	100	93	80	100	75	100	93	100
Bakersfield-California Ave	060290014	5	SASS with URG 3000N	99	100	86	100	100	78	67	100	98	95	84	82
Bakersfield-California Ave (Collocated)	060290014	6	SASS with URG 3000N	98	100	100	100	100	100	100	100	100	100	50	28
Bakersfield-California Ave (Collocated)	060290014	6	URG 3000N	100	100	100	100	100	100	100	100	50	100	80	100
Beacon Hill - Met One	530330080	6	SASS with URG 3000N	100	100	100	90	100	99	100	99	90	100	100	100
Beacon Hill - Met One	530330080	6	URG 3000N	100	93	100	83	100	100	100	100	50	92	100	100
Blair Street	295100085	6	SASS with URG 3000N	100	100	91	100	100	100	100	100	100	92	100	100
Blair Street	295100085	6	URG 3000N	65	48	10	83	100	100	100	100	100	100	100	94
Burlington	500070012	5	SASS	100	100	100	92	100	100	100	100	100	100	100	89
Capitol	220330009	5	MASS	99	91	89	97	99	85		87	99	100	52	79
Chamizal	481410044	5	MASS	100	100	100	98	69	0	100	91	99	91	81	80
Chicopee	250130008	5	SASS	41	100	27	72	88	100	63	100	100	100	100	90
Com Ed - Met One	170310076	5	SASS with URG 3000N	89	88	100	100	86	100	88	100	91	100	100	100
Com Ed - Met One	170310076	5	URG 3000N	75	92	100	100	90	67	58	100	100	83	90	92
Commerce City	080010006	5	SASS with URG 3000N	91	100	100	89	100	100	83	100	100	100	100	100
Commerce City	080010006	5	URG 3000N	100	100	100	81	100	100	90	100	100	100	100	100
CPW	450190049	5	SASS	93	100	100	91	100	100	100	80	100	100	100	100
Criscuolo Park	090090027	5	SASS	100	100	100	89	100	100	100	100	100	90	100	100
Deer Park	482011039	6	MASS	93	100	99	91	98	100	100	100	91	100	63	60
Deer Park (Collocated)	482011039	7	MASS	73	97	98	80	78	64	84	100	100	46	100	60
Dover	100010003	5	SASS	100	100	100	100	50	100	98	83	80	100	100	100
El Cajon	060730003	5	URG 3000N	92	100	94	53	58	100	92	100	100	100	100	100
El Cajon	060730003	5	SASS with URG 3000N	100	100	89	75	100	100	100	100	99	97	100	100
Elizabeth Lab	340390004	5	SASS	100	100	100	88	100	100	100	88	100	100	100	100
Essex - Met One	240053001	5	URG 3000N	100	100	100	75	100	100	100	90	100	100	100	100
Essex - Met One	240053001	5	SASS with URG 3000N	100	100	100	78	100	100	99	86	100	100	100	100
Fargo NW	380171004	5	SASS	91	100	100	100	89	100	100	100	99	100	100	100
Fresno - First Street	060190008	5	SASS	100	92	100	100	100	100	100	100	90	100	100	100

Location	AQS Site	POC	Sampler Type	Report Batch											
				95	96	97	98	99	100	101	102	103	104	105	106
G.T. Craig	390350060	5	SASS	91	100	100	75	64	100	100	91	100	100	100	100
G.T. Craig - Collocated	390350060	6	SASS	100	100	100	100	100	80	100	100	100	98	99	100
Garinger High School	371190041	5	SASS	100	100	100	90	100	100	100	100	92	100	99	100
Gulfport	280470008	5	SASS	99	100	100	100	100	100	100	100	88	100	78	100
Hawthorne	490353006	5	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
Hawthorne	490353006	5	URG 3000N	100	100	100	94	100	90	0	100	100	100	100	100
Henrico Co.	510870014	5	SASS	100	100	100	100	100	100	100	100	100	100	89	100
Hinton	481130069	5	MASS	100	90	70	89	100	89	100	100	100	100	100	100
JFK Center	202090021	5	SASS	100	89	100	100	100	100	88	100	88	100	100	88
Lawrenceville	420030008	6	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Lindon	490494001	5	URG 3000N	100	100	100	100	100	100	100	100	100	100	100	88
Lindon	490494001	5	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	84	80
McMillan Reservoir	110010043	5	RAAS with URG 3000N	89	100	98	100	100	100	100	86	100	100	100	100
McMillan Reservoir	110010043	5	URG 3000N	92	100	100	93	100	100	100	100	100	100	100	100
Missoula County Health Dept.	300630031	5	SASS with URG 3000N	100	90	100	92	75	100	90	100	100	90	100	100
Missoula County Health Dept.	300630031	5	URG 3000N	100	93	78	44	92	100	100	75	100	94	75	100
MLK	100032004	5	SASS with URG 3000N	100	60	100	100	75	17	100	100	100	100	100	100
MLK	100032004	5	URG 3000N	100	100	100	100	100	10	13	100	100	100	100	100
New Brunswick	340230006	5	SASS	98	100	99	84	93	97	96	97	85	96	89	99
New Brunswick (Collocated)	340230006	6	SASS	83	100	100	100	100	100	80	100	100	100	100	100
North Birmingham	010730023	5	SASS with URG 3000N	91	100	91	100	100	100	100	100	100	100	100	90
North Birmingham	010730023	5	URG 3000N	94	100	95	100	100	100	100	100	100	100	100	94
Peoria Site 1127	401431127	5	SASS	100	89	100	89	100	100	100	100	100	100	100	100
PHILA - AMS Laboratory	421010004	7	SASS with URG 3000N	100	89	100	91	100	100	100	90	100	100	100	100
PHILA - AMS Laboratory	421010004	7	URG 3000N	95	92	100	94	100	100	93	100	94	100	100	100
Philips	270530963	5	URG 3000N	77	100	100	100	100	100	100	100	100	94	94	100
Philips	270530963	5	SASS with URG 3000N	92	100	100	93	100	100	100	100	100	100	90	100
Phoenix Supersite	040139997	7	SASS	100	90	90	91	100	90	100	100	90	100	91	90
Portland - SE Lafayette	410510080	6	SASS with URG 3000N	100	100	100	100	100	91	100	100	82	100	100	90
Portland - SE Lafayette	410510080	6	URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
Reno	320310016	5	SASS	100	100	99	100	89	100	100	99	100	82	100	100
Riverside-Rubidoux	060658001	5	SASS with URG 3000N	100	100	91	100	89	100	100	100	100	80	100	100
Riverside-Rubidoux	060658001	5	URG 3000N	100	100	50	93	93	100	100	100	100	93	100	100

Location	AQS Site	POC	Sampler Type	Report Batch											
				95	96	97	98	99	100	101	102	103	104	105	106
Riverside-Rubidoux (Collocated)	060658001	6	URG 3000N	100	100	100	100	100	100	100	100	100	100	100	90
Riverside-Rubidoux (Collocated)	060658001	6	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	85
Roxbury (Boston)	250250042	5	SASS	100	100	92	100	100	100	100	100	90	100	100	100
Roxbury (Boston) - collocated	250250042	6	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Sacramento - Del Paso Manor	060670006	5	SASS	100	100	90	99	100	100	100	100	90	100	100	100
San Jose - Jackson Street	060850005	5	SASS	90	100	100	100	100	100	100	75	100	100	100	100
SER-DNR Headquarters	550790026	5	SASS	100	100	100	91	100	100	100	90	100	100	100	100
Simi Valley	061112002	5	SASS	100	100	75	100	100	100	100	100	100	100	100	100
South DeKalb - Met One	130890002	5	SASS	100	100	100	89	100	100	100	100	100	90	100	100
Springfield Pumping Station - Met One	170310057	5	URG 3000N	100	100	100	80	0		100	100	100	90	100	100
Springfield Pumping Station - Met One	170310057	5	SASS with URG 3000N	100	100	100	100	67		100	100	100	85	100	100
St. Lukes Meridian (IMS)	160010010	5	URG 3000N	94	100	100	100	100	100	93	53	79	100	100	100
St. Lukes Meridian (IMS)	160010010	5	SASS with URG 3000N	83	100	83	100	100	100	89	99	100	100	100	100
Sydney	120573002	5	SASS	98	99	99	97	99	99	99	100	90	99	97	96
Univ. of Florida Ag School	120111002	5	SASS	100	90	90	100	89	100	100	80	80	82	90	100
Urban League	440070022	5	RAAS	100	100	100	100	88	75	100	100	100	100	72	88
Washington Park	180970078	5	URG 3000N	83	92	100	100	100	100	100	33	100	100	100	100
Washington Park	180970078	5	SASS with URG 3000N	100	89	99	100	100	100	100	75	100	100	100	100
Woolworth St	310550019	5	SASS	87	97	97	97	97	97	97	97	97	97	97	97
WV - Guthrie Agricultural Center	540390011	5	SASS with URG 3000N	83	100	80	80	80	80	70	78	80	89	100	100
WV - Guthrie Agricultural Center	540390011	5	URG 3000N	78	93	44	86	69	56	44	86	69	61	93	100

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

Location	AQS Site	POC	Site Type	Sampler Type	Report Batch											
					95	96	97	98	99	100	101	102	103	104	105	106
(NC) - Lexington	370570002	5	Other	SASS	100	75	100	100	100	100	100	100	100	100	100	100
(PA) Liberty	420030064	6	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
(PA) Liberty	420030064	6	Other	URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
5 Points	391530023	5	Other	SASS with URG 3000N	100	100	100	98	100	100	100	100	100	100	83	75
5 Points	391530023	5	Other	URG 3000N	100	100	100	100	100	100	100	100	100	100	90	50
AL - Phenix City	011130001	5	Other	SASS with URG 3000N	100	100	100	84	100	80	100	100	84	100	100	100
AL - Phenix City	011130001	5	Other	URG 3000N	100	100	88	88	100	88	100	100	50	100	80	100
Albany Co HD	360010005	5	Other	SASS	100	100	100	91	100	100	100	100	100	100	90	85
Arendtsville	420010001	5	Other	SASS	100	100	83	100	100	100	100	100	100	100	100	99
Army Reserve Center	191130037	5	Other	R & P 2300	100	100	100	100	100	100	100	100	100	100	100	100
Arnold - R&P	290990012	5	Other	R & P 2300	100	100	90	91	75							
Arnold West	290990019	6	Other	R & P 2300					100	100	90	100	100	100	100	100
Ashland Health Department	210190017	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	80	100
Athens - Met One	130590001	5	Other	SASS	100	100	83	100	75	100	100	100	100	20	40	80
Augusta - Met One	132450091	5	Other	SASS	100	75	100	100	100	100	100	67	80	100	100	100
Bonne Terre	291860005	5	Other	URG 3000N	100	93	83	22	54	100	100	100	100	100	75	94
Bonne Terre	291860005	5	Other	R and P with URG 3000N	100	90	100	93	89	80	100	100	100	100	71	100
Bountiful	490110004	5	Other	SASS with URG 3000N	100	100	100	80	100	60	100	100	100	100	100	100
Bountiful	490110004	5	Other	URG 3000N	100	100	100	100	100	88	100	100	100	100	100	100
Buffalo - Met One	360290005	6	Other	SASS	100	100	100	100	100	100	100	100	100	100	80	100
Buncombe County Board of Education	370210034	5	Other	SASS	100	100	69	82	75	100	100	100	100	100	100	100
Camden	340070003	5	Other	URG 3000N	83	100	86	100	67	100	92	100	100	93	93	30
Camden	340070003	5	Other	SASS with URG 3000N	100	99	95	95	71	95	100	100	100	100	100	50
Canton Fire Station	391510017	5	Other	SASS	49	75	20	100						100	100	80
Canton Health Dept.	391510020	5	Other	SASS				50	100	100	100	100	100	100		
Chester	340273001	5	Other	SASS	100	100	100	100	88	88	100	100	100	100	100	100
Chester (PA)	420450002	5	Other	SASS	100	82	100	100	100	92	100	83	60	100	100	100
Chesterfield	450250001	5	Other	SASS	99	100	100	100	100	100	100	100	99	100	100	40
Children's Park	040191028	5	Other	SASS	83	100	100	100	100	100	82	99	100	100	100	100

Location	AQS Site	POC	Site Type	Sampler Type	Report Batch											
					95	96	97	98	99	100	101	102	103	104	105	106
Clarksville	471251009	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Columbus - Met One	132150011	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
Columbus - Met One	132150011	5	Other	URG 3000N	100	13	75	100	100	100	0	0	100	100	100	100
Courthouse Annex-Libby	300530018	5	Other	SASS	100	75	100	100	100	100	98	100	100			
Covington - University College	211170007	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Craig Road	320030020	5	Other	SASS	100	100	100	60	100	100	100	100	100	80	100	100
Crown Z	530630016	5	Other	RAAS	100	82	100	100	100	100	99	100	100	100	100	100
Dearborn	261630033	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	80	80	100	83
Dearborn	261630033	5	Other	URG 3000N	100	100	100	63	0	38	100	88	100	100	100	100
Del Norte	350010023	5	Other	R & P 2300	97	75	100	100	100	60	100	97				
Del Norte - Met One	350010023	5	Other	SASS									100	100	100	100
Division St.	360610134	5	Other	URG 3000N	77	100	90	86	68	94	88	86	75	88	63	88
Division St.	360610134	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	82	64	100
Douglas - Met One	130690002	5	Other	SASS	100	100	100	100	100	98	100	83	84	60	100	40
Downtown Library	391130032	5	Other	SASS	100	100	100	100	57	80	100	100	100	100	100	100
Duwamish	530330057	6	Other	RAAS	88	100	100									
Elkhart Pierre Moran	180390003	5	Other	SASS	100	75	100									
Elkhart Prairie Street	180390008	5	Other	SASS			97	100	100	100	100	100	100	100	100	99
Elmwood	421010055	5	Other	URG 3000N	100	100	100	100	100	100	100	100	88	75	100	100
Elmwood	421010055	5	Other	SASS with URG 3000N	100	100	99	100	99	100	100	100	80	59	100	100
Erie	420490003	5	Other	SASS	100	100	100	80	100	100	100	100	100	100	100	100
Evansville - Mill Road	181630012	5	Other	SASS	99	97	100	98	100	100	99	67	100	100	100	100
Fairbanks State Bldg	020900010	6	Other	SASS	91	100	100	100	100	100	100	100	92	100	90	0
Florence	421255001	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	80	100	83	75	80
Florence	421255001	5	Other	URG 3000N	100	100	100	100	88	100	100	88	100	90	50	50
Freemansburg	420950025	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Gary litri	180890022	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	84	99	100
Gary litri	180890022	5	Other	URG 3000N	100	88	88	100	88	25	88	100	100	100	100	100
General Hospital	390870010	5	Other	SASS	99	99	82	100								
Grand Junction - Powell Building	080770017	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Grand Rapids	260810020	5	Other	SASS	80	75	100	100	100	100	100	83	0	98	100	80
Granite City	171190024	5	Other	URG 3000N	100	100	100	80	67	13	17	0	25	100	100	100
Granite City	171190024	5	Other	SASS with URG 3000N		100	100	84	100	80	25	99	99	99	77	98

Location	AQS Site	POC	Site Type	Sampler Type	Report Batch											
					95	96	97	98	99	100	101	102	103	104	105	106
Granite City	171190024	5	Other	SASS	83	100										
Grayson	210430500	5	Other	SASS									100	100	100	80
Greensburg	421290008	5	Other	SASS with URG 3000N	100	98	100	80	100	100	100	80	82	100	100	80
Greensburg	421290008	5	Other	URG 3000N	100	100	100	100	100	100	100	100	100	100	100	88
Greenville Health Dept	450450008	5	Other	SASS			97	76	0	100	100	100	100	100	100	100
Hammond Purdue	180892004	5	Other	URG 3000N	100	100	100	100	100	100	88	13	100	100	100	75
Hammond Purdue	180892004	5	Other	SASS with URG 3000N	100	100	100	98	98	100	100	80	100	100	100	100
Harrisburg	420430401	5	Other	SASS	100	100	83	100	100	80	100	100	100	100	100	100
Hattie Avenue	370670022	5	Other	URG 3000N	100	100	50	100	100	100	100	100	100	100	88	100
Hattie Avenue	370670022	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	98	99	100	100	100
Hazard - Perry County Horse Park	211930003	5	Other	SASS	100	100	100	100	100	100	98	100				
Head Start	390990014	5	Other	SASS	100	100	100	100	75	98	98	99	100	100	100	100
Hickory	370350004	5	Other	SASS	100	100	100	100	100	100	100	100	80	99	100	60
Houghton Lake	261130001	5	Other	SASS	100	75	100	100	100	100	79	83	80	100	100	100
HU-Beltsville	240330030	5	Other	RAAS	100	100										
HU-Beltsville Met One	240330030	5	Other	SASS		67	100	100	100	100	80	100	100	100	100	100
Huntsville Old Airport	010890014	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	40	80
IL - Decatur	171150013	5	Other	SASS	100	100	67									
IS 52 - Met One	360050110	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	90	100	100	100	90
IS 52 - Met One	360050110	5	Other	URG 3000N	78	92	89	86	69	94	88	93	69	88	94	88
Jasper Post Office	180372001	5	Other	SASS	100	50	100	100	100	85	85	100	80	100	100	100
Jefferson Elementary (10th and Vine)	191630015	5	Other	R & P 2300	100	90	100	100	100	100	80	100	70	91	90	60
Jeffersonville Walnut St	180190006	5	Other	SASS									100	100	100	80
Kalamazoo	260770008	5	Other	SASS	100	100	100	100	100	80	100	99	100			
Kelo	460990006	5	Other	SASS	76	100	100	71	100	65	100	71	100	100	84	100
Lancaster	420710007	5	Other	SASS	100	100	83	100	100	100	100	100	100	100	100	100
Laurel	280670002	5	Other	SASS										100	80	100
Lawrence County	470990002	5	Other	SASS	88	100	100	100	100	100	100	83	100	60	80	100
Lenoir Community College	371070004	5	Other	SASS	100	100	100	100	50							
Lexington Health Department	210670012	5	Other	SASS	100	100	100	100	75	100	100	99	100	60	100	100
Liberty	290470005	5	Other	R & P 2300	91	100	100	99	100	100	100	80	100	100	80	88
Lockeland School - Met One	470370023	5	Other	SASS	96	96	96	96	97	100	100	100	100	100	80	60
Lorain	390933002	5	Other	SASS with URG 3000N	80	75	86	33	80	83	99	100	100	100	0	0

Location	AQS Site	POC	Site Type	Sampler Type	Report Batch											
					95	96	97	98	99	100	101	102	103	104	105	106
Lorain	390933002	5	Other	URG 3000N	58	100	100	25	100	100	100	100	100	100	100	83
Luna Pier	261150005	5	Other	SASS	100	100	100	100	100	33	100	100	100	100	100	80
Macon - Met One	130210007	5	Other	URG 3000N	75	100	100	88	100	100	100	100	100	100	100	100
Macon - Met One	130210007	5	Other	SASS with URG 3000N	100	100	99	100	100	100	100	100	100	100	80	100
Maple Canyon	390490081	6	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	80
Maple Canyon	390490081	6	Other	URG 3000N	75	100	100	100	100	100	100	100	100	100	100	100
Mayville Hubbard Township site	550270007	5	Other	SASS	93	100	100	100	100	100	100	100	100	100	100	100
Middletown	390171004	5	Other	SASS	100	100	98	100	100	85	100	100	100	100	100	80
Millbrook	371830014	5	Other	SASS	91	100	90	100	100	100	100	100	100	91	90	100
Mingo Junction	390811001	5	Other	URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
Mingo Junction	390811001	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	80
MN - Rochester	271095008	5	Other	SASS	100	74	100	96	72	96	100	83	80	100	39	100
MOMS	011011002	5	Other	SASS	100	100	83	100	20	85	100	100	98	100	98	100
Moundsville Armory	540511002	5	Other	SASS	100	100	83	20	50	100	80	100	100	80	100	100
Naperville	170434002	5	Other	URG 3000N	100	88	100	100	100	100	100	100	100	100	100	100
Naperville	170434002	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	99	100	98
New Garden	420290100	5	Other	SASS	100	100	100	97	96	76	94	99	100	80	100	80
NLR Parr	051190007	5	Other	SASS	100	100	100	100	100	80	80	98	100	100	98	100
North Los Angeles	060371103	5	Other	URG 3000N	100	100	90	100	100	100	88	100	100	100	100	100
North Los Angeles	060371103	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	84	100
Northbrook	170314201	5	Other	SASS with URG 3000N	99	100	66	100	100	100	100	100	100	99	100	99
Northbrook	170314201	5	Other	URG 3000N	100	100	50	100	100	88	100	100	25	0	100	100
OCUSA Campus	401091037	5	Other	SASS	100	100	100	85	52	80	100	100	100	100	100	80
ODOT Garage	390870012	5	Other	SASS				100	100	100	100	83	100	80	100	100
Pearl City	150032004	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
PerkinstownCASNET	551198001	5	Other	SASS	99	99	80	98	99	99	100	100	100	100	100	100
Pinnacle State Park - Met One	361010003	5	Other	SASS	99	100	100	99	100	100	100	100	100	100	100	90
Platteville	081230008	5	Other	SASS	88	100	100	100	100	100	100	100	100	100	100	100
Port Huron	261470005	5	Other	SASS									100	100	100	80
Public Health Building	191530030	5	Other	R & P 2300	67	100	100	100	97	100	80	33	0			
Public Health Building - Met One	191530030	5	Other	SASS									100	100	100	100
Queens College - Met One	360810124	6	Other	SASS	99	100	100	100	100	100	93	100	83	100	100	100
Reading Airport	420110011	5	Other	SASS	83	100	100	100	100	100	100	100	100	80	100	100

Location	AQS Site	POC	Site Type	Sampler Type	Report Batch											
					95	96	97	98	99	100	101	102	103	104	105	106
Rochester Primary - Met One	360551007	5	Other	SASS	75	93	78	100	89	77	100	100	100	91	80	89
Rockwell	371590021	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Rome - Met One	131150005	5	Other	SASS	100	100	100	100	100	100	100	67	100	100	100	100
Rossville - Met One	132950002	5	Other	SASS	100	97	98	99	82	81	100	100	100	100	99	100
Scranton	420692006	5	Other	SASS	100	100	100	100	100	100	100	100	100	80	100	100
Shenandoah High School	180650003	5	Other	SASS	100	100	100	100	100	100	100	98	100	100	100	100
Shreveport Airport	220150008	5	Other	MASS	83	75	98	99	99	24	100	100	100	100	80	100
Skyview	121030026	5	Other	SASS	100	89	83	88	88	100	100	100	75	100	89	100
South Charleston Library	540391005	5	Other	URG 3000N	75	100	88	80	100	38	100	100	100	100	100	100
South Charleston Library	540391005	5	Other	SASS with URG 3000N	100	59	80	67	100	100	100	80	100	100	100	100
Southwick Community Center	211110043	5	Other	SASS with URG 3000N	100	100	100	100	100	98	100	80	100	100	100	80
Southwick Community Center	211110043	5	Other	URG 3000N	100	100	75	100	100	50	50	38	38	25	0	13
Spring Hill Elementary School	470931020	5	Other	URG 3000N	100	100	100	50	100	100	100	100	100	100	100	100
Spring Hill Elementary School	470931020	5	Other	SASS with URG 3000N												80
Spring Hill Elementary School	470931020	5	Other	RAAS with URG 3000N	100	78	83	100	100	100	100	84	82	100	100	10
St Theo	390350038	6	Other	URG 3000N	100	100	100	100	100	13	100	88	100	100	100	100
St Theo	390350038	6	Other	SASS with URG 3000N	100	100	100	100	80	100	100	100	100	100	100	100
State College	420270100	5	Other	SASS	100	75	100	100	100	100	100	100	78	100	82	100
SW HS	261630015	5	Other	SASS with URG 3000N											100	100
SW HS	261630015	5	Other	URG 3000N											100	100
SW HS	261630015	5	Other	SASS									100	100	100	
Tacoma - Met One	530530029	5	Other	URG 3000N	100	100	100	83	100	100	100	100	100	100	100	100
Tacoma - Met One	530530029	5	Other	SASS with URG 3000N	100	100	100	78	100	100	100	100	100	100	100	100
Taft	390610040	5	Other	URG 3000N	100	100	100	100	100	13	0	90	0	0	0	17
Taft	390610040	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	100	100	100	100	100
Tallahassee Community College	120730012	5	Other	SASS	100	100	100	100	100	98	100	100	80	80	99	100
Taylor's Fire Station	450450009	5	Other	SASS	99	100	100	100	100	100			100	100	100	100
Tecumseh	260910007	5	Other	SASS						0	80	83	100	100	100	100
Toledo Airport	390950026	5	Other	SASS	100	98	100	65	82	99	96	100	100	100	100	100
UTC	470654002	5	Other	SASS	100	100	83	40	53	100	100	100	100	100	100	100
VAN4PLN2	530110013	5	Other	SASS									33	83	30	80
Waukesha, Cleveland Ave. Site	551330027	5	Other	SASS	100	100	100	100	100	100	100	100	100	100	100	100
Whiteface - Met One	360310003	5	Other	SASS	100	97	100	100	100	100	100	100	100	100	100	98

Location	AQS Site	POC	Site Type	Sampler Type	Report Batch											
					95	96	97	98	99	100	101	102	103	104	105	106
Wichita Dept. of Environmental Health	201730010	5	Other	R & P 2300	67	100	100	100	75	100	100	83	20	40	80	100
Wylam	010732003	5	Other	SASS	100	99	100	100	100	100	100	100	99	100	100	100
Yakima Mental Health	530770009	5	Other	SASS		86	88	100								
Yakima Mental Health	530770009	5	Other	SASS with URG 3000N	100	100		100	100	100	71					0
Yakima Mental Health	530770009	5	Other	URG 3000N	100	93	43	100	75	100	65					100
York	421330008	5	Other	SASS	100	100	100	100	100	100	98	100	100	100	100	100
Ypsilanti	261610008	5	Other	URG 3000N	100	88	20	0	0	38	100	90	0			
Ypsilanti	261610008	5	Other	SASS with URG 3000N	100	100	100	100	100	100	100	83	0			