

# Quality Assurance Guidance Document

Revision 1.2

## Laboratory Analysis and Data Processing/Validation for Chemical Speciation of PM<sub>2.5</sub> Filter Samples

### Quality Assurance Project Plan

### OAQPS Category 2 QAPP

Prepared for:

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

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Prepared by:

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## LIST OF ACRONYMS AND ABBREVIATIONS

ADQ	audit of data quality
AMTIC	Ambient Monitoring Technology Information Center (US EPA)
AQRC	Air Quality Research Center
AQS	air quality system database
CDMS	Chemical Speciation Network data management system
cm <sup>2</sup>	square centimeter
COC	chain-of-custody
COV	coefficient of variation
cps	counts per second
CSN	Chemical Speciation Network
CV	coefficient of variation
DART	data analysis and reporting tool
DAS	Division of Atmospheric Sciences
DDW	distilled-deionized water
DOPO	Delivery Order Project Officer
DQI	data quality indicator
DQO	data quality objective
EAF	Environmental Analysis Facility
EC	elemental carbon
EDXRF	energy dispersive X-ray fluorescence
EPA	U.S. Environmental Protection Agency
FID	flame ionization detector
HIPS	hybrid integrating plate/sphere analysis
IC	ion chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
KHP	potassium hydrogen phthalate
L	liters
L/min	liters per minute
LAN	local area network
m	meter
m <sup>3</sup>	cubic meter
mA	milliamp
MDL	method detection limit
ME-RM	multi-element reference material
µg	micrograms
min	minute
µm	micrometers
MQO	measurement quality objective

MS	mass spectrometry
NAAQS	National Ambient Air Quality Standard
NIST	National Institute of Standards and Technology
NPS	United States of America National Park Service
OAQPS	EPA Office of Air Quality Planning and Standards
OC	organic carbon
PE	performance evaluation
PI	principal investigator
PM	particulate matter
PM <sub>2.5</sub>	particulate matter (with aerodynamic diameter less than 2.5 µm)
PM <sub>10</sub>	particulate matter (with aerodynamic diameter less than 10 µm)
PM <sub>10-2.5</sub>	PM <sub>10</sub> – PM <sub>2.5</sub>
PTFE	polytetrafluoroethylene
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QMP	quality management plan
r	correlation coefficient
RM	reference material
RMSRE	reference material standard relative error
RTI	Research Triangle Institute
SIP	state implementation plan
SLT	state, local, and tribal
STN	speciated trends network
SOP	standard operating procedure
SRM	standard reference material
SVOC	semi-volatile organic compound
TI	technical information document
TOA	thermal/optical analysis
TOR	thermal optical analysis by reflectance
TOT	thermal optical analysis by transmittance
TSA	technical systems audit
UC Davis	University of California at Davis
UCD	University of California at Davis
Urel	relative expanded uncertainty
Wood	Wood PLC
XRF	X-ray fluorescence
z-score	standard score

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## 1. TITLE AND APPROVAL SHEET

The following signatures indicate agreement with the procedures specified within this plan and a commitment to deliver the details of this plan.

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### **3. DISTRIBUTION LIST**

#### **Air Quality Research Center (AQRC)**

Anthony Wexler, AQRC Director  
Nicole Hyslop, Principal Investigator  
Sean Raffuse, Software & Analysis Group Manager  
Katrine Gorham, Program Manager and Data & Reporting Group Manager  
Krystyna Trzepla, Laboratory Manager  
Nicholas Spada, AQRC QA Manager

#### **Research Triangle Institute (RTI)**

Keith Levine, RTI Director of Analytical Sciences  
Tracy Dombek, Program Manager  
Laura Haines, RTI QA Manager

#### **Environmental Protection Agency (EPA)**

Joann Rice, EPA/OAQPS Program Manager  
Jeff Yane, EPA/OAQPS Project Officer  
Greg Noah, EPA/OAQPS Quality Assurance Officer

### **4. PROJECT MANAGEMENT**

#### **4.1 Project/Task Organization**

This QAPP describes the quality assurance plan for contract number EP-D-15-020 with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). Work on this contract in support of the particulate matter (PM) Chemical Speciation Network (CSN) program is performed by staff from the Air Quality Research Center (AQRC) at the University of California – Davis (UC Davis). UC Davis will perform energy dispersive X-ray fluorescence (EDXRF) analysis, hybrid integrating plate/sphere (HIPS) analysis, thermal/optical analysis (TOA), and will process, validate, and deliver the final concentration data. Research Triangle Institute (RTI), a subcontractor to UC Davis, will perform ion chromatography analysis. UC Davis is not responsible for the sample handling laboratory operations (e.g., shipping/handling filters and coordinating field activities); this work is performed by Wood PLC as a separate contract.

Organizational charts for project personnel at UC Davis and RTI are shown in Figure 1 and Figure 2, respectively.

UC Davis coordinates its laboratory and data management activities with EPA/OAQPS. Lab QA auditing and technical assistance are also provided by EPA/OAQPS.

Figure 1. UC Davis organizational chart.

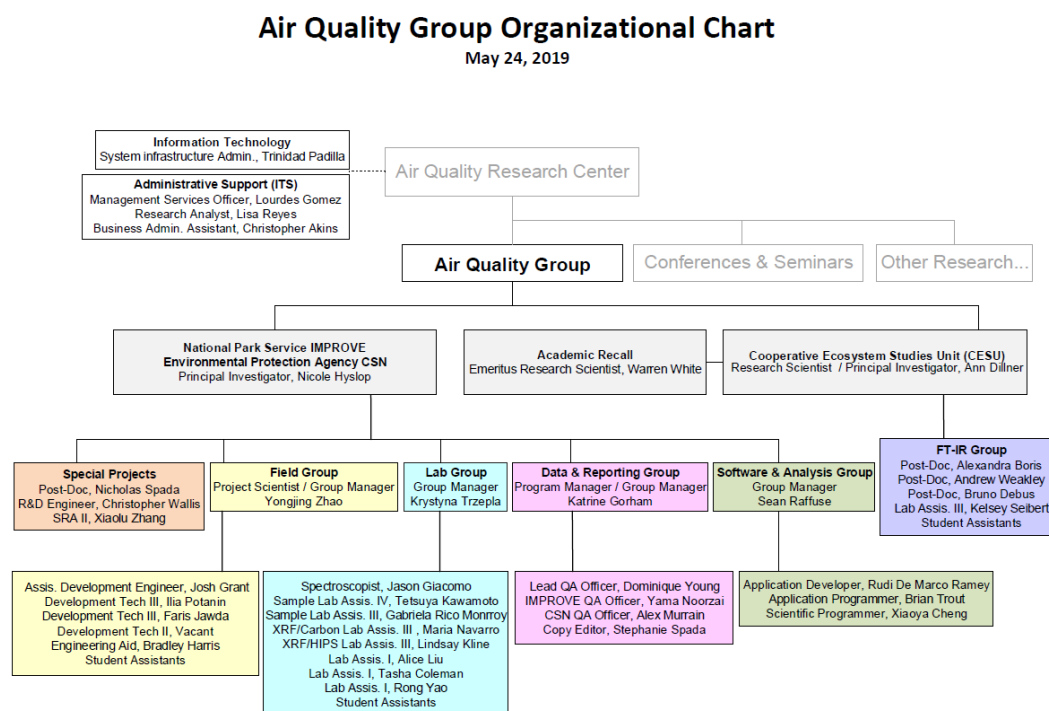
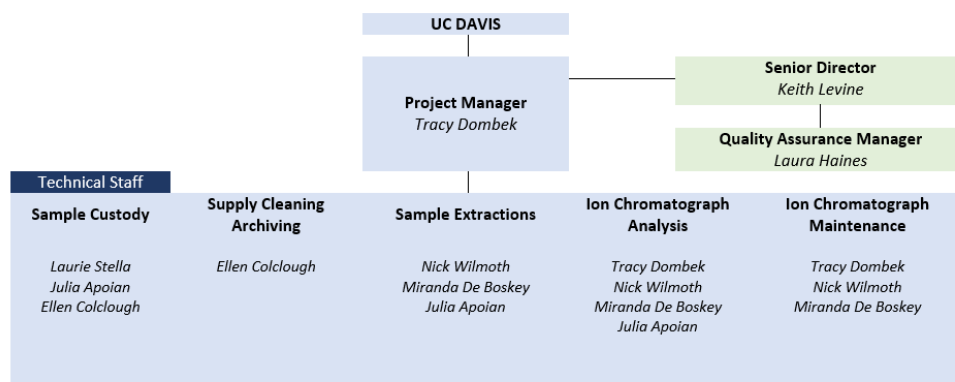


Figure 2. RTI organizational chart.



#### 4.1.1 Position Responsibilities: UC Davis

##### 4.1.1.1 AQRC Director, Dr. Anthony Wexler

The AQRC Director has the overall responsibility, accountability, and authority for all programs operating through the center. Responsibilities include:

1. Determining that the research program adheres to its budget;
2. Facilitating interaction with other AQRC programs, as well as other programs on the UC Davis or other UC campuses;
3. Overseeing personnel performance reviews; and
4. Representing AQRC in any fiscal inquiries.

Dr. Wexler is an aerosol scientist and professor of Mechanical and Aerospace Engineering, Civil and Environmental Engineering, and Land, Air and Water Resources. His work focuses on the role of atmospheric particles in human health and climate change. He works on mathematical modeling of atmospheric aerosol dynamics, development of advanced instrumentation for particle collection and analysis, and response of airways to particle deposition. He has over 31 years of experience in the field of atmospheric science with 19 years at UC Davis. Contact information: [aswexler@ucdavis.edu](mailto:aswexler@ucdavis.edu) and 530-754-6558.

##### 4.1.1.2 Principal Investigator, Dr. Nicole Hyslop

The CSN program at UC Davis is led by the Principal Investigator, who provides overall supervision to ensure that the technical program is being performed in accordance with the EPA statement of work and according to this QAPP. Responsibilities include:

1. Maintaining cooperative working relationships with the EPA Program Manager, Delivery Order Project Officers (DOPO), and AQRC QA Manager in the following ways:
  - a. Conference calls to be held as frequently as needed,
  - b. Meetings with EPA staff as-needed,
  - c. Written communications and e-mails to document planning and decisions;
2. Facilitating interaction among team personnel;
3. Ensuring that proper techniques and procedures are followed;
4. Ensuring the quality and timely delivery of data;
5. Ensuring that reporting requirements are satisfied;
6. Maintaining cost and schedule control;
7. Adjusting schedules to meet client needs; and
8. Reviewing and approving deliverables submitted to the client.

Dr. Hyslop is responsible for managing IMPROVE and CSN operations at UCD including managing the laboratory, field, data validation, and applications development staff. Dr. Hyslop has BS and MS degrees in Chemical Engineering from the University of Wisconsin – Madison and University of Texas – Austin. She has 23 years of experience in the field of atmospheric science with 15 years at UC Davis and five years at Sonoma Technology, Inc. Contact information: nmhyslop@ucdavis.edu and 530-754-8979.

#### 4.1.1.3 AQRC QA Manager, Dr. Nicholas Spada

The AQRC QA Manager monitors quality assurance/quality control (QA/QC) for the CSN program at UC Davis, and in this role Dr. Spada reports to the AQRC Director. As such, the AQRC QA Manager can report problems to AQRC's highest level of management, independent of the CSN project structure. In practice the AQRC QA Manager will work closely with the Principal Investigator with the expectation that most problems can be solved without involvement from the AQRC Director. Responsibilities include:

1. Reviewing the efforts of other AQRC staff to investigate problems identified during data review and to recommend corrective actions;
2. Reviewing control charts and other data quality reports from AQRC and RTI to assess the achievement of MQOs for uncertainties and MDLs;
3. Performing periodic in-lab and data review audits of data quality for the AQRC and RTI laboratories;
4. Conducting an annual review of the Standard Operating Procedures (SOPs), technical information documents (TIs), QAPP, and Quality Management Plan (QMP) for both AQRC and RTI;
5. Hosting external auditors during anticipated visits; and

6. Distributing EPA-provided Performance Evaluation (PE) samples within AQRC and summarizing PE analysis results.

Dr. Spada is a post-doctoral scholar with UC Davis AQRC. His work focuses on the role of metallic species in atmospheric particles in human health and climate change. He works on development of measurement techniques and instrumentation as well as performs local and long-transport field studies. He has 13 years of experience in the field of environmental science with eight years at UC Davis. Contact information: njspada@ucdavis.edu and 530-752-0933.

#### 4.1.1.4 Program Manager and Data & Reporting Group Manager, Dr. Katrine Gorham

The CSN Program Manager reports directly to the Principal Investigator and assists with several facets of the CSN program. Responsibilities include:

1. Preparing monthly, quarterly, and annual reports for the EPA, with input from other project staff;
2. Preparing and editing various project-related documents such as position descriptions, technical reports, and meeting summaries;
3. Assisting in the editing of the SOPs, QAPP, and QMP;
4. Tracking project budgets and submitting monthly budget summaries to the Principal Investigator;
5. Tracking the number of samples analyzed under each Delivery Order as input to the monthly invoices;
6. Coordinating the purchasing of supplies and equipment;
7. Coordinating the recruitment and hiring of new staff, as needed; and
8. Tracking the flow of data through DART and on to final submittal to ensure that schedules for each monthly submittal are met.

The AQRC Data & Reporting Manager Group Manager oversees data validation and delivery operations, and oversees technical staff (including Dr. Dominique Young, Mr. Yama Noorzai, and Mr. Alex Murrain) responsible for data validation and submission (see Section 7). Responsibilities include:

1. Reviewing the components of the measurements (flow rates, elemental concentration, etc.) in preparation for final data validation;
2. Working with others in laboratory operations to resolve problems or discrepancies encountered during data review;
3. Validating the final data set, with input as needed from data analysts;
4. Submitting the data set to the DART system for SLT review;
5. Communicating with SLT data validators to resolve discrepancies;
6. Formatting the data to meet AQS standards; and

## 7. Submitting the final data sets to AQS.

As the AQRC Program Manager and Data & Reporting Group Manager, Dr. Gorham manages the data validation process, data deliverables, reporting, documentation, internal/external communication, and financial tracking. She has a background in atmospheric chemistry, and 10 years of experience in the field of research management with three years at UC Davis. Contact information: kgorham@ucdavis.edu and 530-752-7119.

### 4.1.1.5 Laboratory Manager, Ms. Krystyna Trzepla

The AQRC Laboratory Manager is responsible for overseeing all aspects of the laboratory, including sample handling, sample analysis by EDXRF, TOA, and HIPS, and analytical data validation. Responsibilities include:

1. Maintaining a smooth flow of filters through the laboratory;
2. Coordinating work with RTI for ions analysis;
3. Maintaining a schedule for sample analysis, quality control tests, data processing, and progress tracking to ensure that schedules are met and sample identification and integrity are not compromised;
4. Reviewing each data set in the context of historical data and of current system conditions, reviewing control charts, identifying abnormalities, and providing recommendations for understanding and rectifying them;
5. Reviewing the SOPs, QAPP, and QMP;
6. Training and mentoring new staff; and
7. Managing tests comparing the AQRC laboratories with other laboratories (through PE sample comparisons or other round-robin studies), working with the other laboratories to establish test protocols, overseeing the analysis of samples at AQRC, analyzing the results, and working with the other laboratories to prepare reports and publications for external distribution.

The AQRC Laboratory Manager oversees technical staff, including:  
A spectroscopist (Dr. Jason Giacomo) responsible for reviewing all of the EDXRF data and performing QC checks, including:

1. Reviewing the EDXRF analysis results and related spectra;
2. Processing and reviewing the data from all EDXRF quality control tests and providing the data to other analysts in final form; and
3. Providing recommendations to the data validation analyst regarding EDXRF data quality.

Two laboratory technicians (Ms. Gabby Navarro and Ms. Lindsay Kline) share the following responsibilities:

1. Organizing the PTFE filters received for analysis and recording filter identification information in the database;
2. Operating the EDXRF, TOA, and optical absorption systems;
3. Maintaining a record of the parameters and conditions associated with each analysis for each analytical system, processing the data, and providing the data to other analysts in final form; and
4. Placing PTFE filters in a permanent archive and maintaining a cataloging system to allow efficient retrieval of archived filters (see Section 5.3.3).

As the Laboratory Manager, Ms. Trzepla is responsible for managing daily laboratory operations including sample preparation, gravimetric analysis, EDXRF analysis, TOA analysis, and optical absorption measurements. She has been the Laboratory Manager since 2010. She led several laboratory changes related to new instrumentation (EDXRF systems, balances) including research, testing and implementation. Ms. Trzepla is also leading the efforts to develop EDXRF calibration materials specifically for particulate matter analysis. She has 33 years of experience in the field of atmospheric science with 29 years at UC Davis. Contact information: [ktrzepla@ucdavis.edu](mailto:ktrzepla@ucdavis.edu) and 530-752-4232.

#### 4.1.1.6 Software & Analysis Group Manager, Mr. Sean Raffuse

The AQRC Software & Analysis Group Manager oversees development of the CSN SQL database and software for laboratory operations, validation, and data analysis. The AQRC Software & Analysis Group Manager oversees technical staff (including Mr. Rudi De Marco Ramey, Mr. Brian Trout, and Ms. Xiaoya Cheng) who share responsibilities for database management and programming. Responsibilities include:

1. Maintaining and upgrading the data management system (see Section 5.10) including the SQL Server database, data processing and visualization tools, and data reporting and data input forms;
2. Working with staff to identify, map, design and implement improvements to the data management system;
3. Testing, verifying, and documenting modifications to the system;
4. Importing and processing new data and associated metadata into the database system; and
5. Designing and maintaining an archival system for all data and metadata records and source files.

As the AQRC Software & Analysis Group Manager, Mr. Raffuse oversees data processing and software development for laboratory operations, validation tools, and data analysis. In addition, his research focuses on developing, improving and

applying fire and smoke models through the use of data sets, research, and information systems, and developing and using satellite-derived data products. He has 17 years of experience in the field of atmospheric science with six at UC Davis. Contact information: [sraffuse@ucdavis.edu](mailto:sraffuse@ucdavis.edu) and 530-752-4225.

#### 4.1.2 The Role of RTI in the Program

RTI performs ion analysis using ion chromatography as a subcontractor to UC Davis. As a subcontractor laboratory providing analytical services, RTI has contributed to this QAPP and provided their SOPs.

The data quality requirements specified in the UC Davis prime contract with EPA flow down contractually through the subcontract to RTI. RTI's ions data are also subject to data validation prior to submittal to AQS (see Section 7). UCD will arrange technical systems audits of the RTI facilities every two to three years.

RTI provides ion analysis for nylon filter samples collected in CSN. Each filter is extracted in distilled-deionized water (DDW) and analyzed for anions and cations by ion chromatography (IC). The sample extracts are archived for a period of six months. The reported anions are sulfate, nitrate, and chloride. The reported cations are ammonium, sodium, and potassium. Detailed description of RTI methods for ion analysis, along with references to the applicable SOP, can be found in Sections 5.4.2.

#### 4.1.3 Position Responsibilities: RTI

##### 4.1.3.1 RTI Senior Director of Analytical Sciences, Dr. Keith Levine

Dr. Keith Levine is responsible for the overall technical, administrative, and business development leadership for a large and diverse team of analytical scientists which includes the staff supporting this project. He manages strategically important projects and overall team budgets and operations. He develops technical staff at many professional levels and drives continuous improvement in operational efficiency and scientific stature. He manages an operation with atomic spectrometry, electron microscopy, X-ray spectrometry, mass spectrometry, and chromatographic instrumentation. Dr. Levine has an extensive track record in developing and applying novel analytical methods for determination of metals/metal species in a variety of media. Contact information: [levine@rti.org](mailto:levine@rti.org), 919-541-8886.

##### 4.1.3.2 RTI Program Manager, Ms. Tracy Dombek

Ms. Tracy Dombek is a Research Chemist in RTI International's Center for Analytical Sciences. In addition to this work, she manages the U.S. National Park Service (NPS) and the Ogawa project. In support of the NPS IMPROVE project



and other related PM<sub>2.5</sub> related tasks, Ms. Dombek serves as the Ion Laboratory Manager and oversees work that involves analyzing filters for inorganic anions and cations by ion chromatography. In this capacity, she is involved with day-to-day laboratory operations, ensuring proper maintenance and troubleshooting for analyzers and other instrumentation and coordinating service needs for instrumentation through the equipment vendor. She trains staff on how to perform routine maintenance and troubleshooting of equipment. Ms. Dombek also coordinates work assignments that involve ions analysis for the National Toxicology Program. She is responsible for ensuring that completed work meets compliance and provides updates to the task leader for National Toxicology Program. Ms. Dombek reviews and analyzes data for Level 1 compliance. She is also responsible for developing maintenance plans and records of changes. She ensures that all RTI SOPs and QA documents are updated, as needed.

Ms. Dombek is responsible for the overall performance of RTI on this program and for technical communications with the client. She is ultimately responsible for ensuring that only fully qualified and trained staff members perform work under this contract. She also works closely with the RTI QA Manager to ensure implementation of the quality system, ensure that necessary resources are available for performing the required analyses, and ensure that effective corrective actions are taken when required. Contact information: [tdombek@rti.org](mailto:tdombek@rti.org), 919-541-5934.

#### 4.1.3.3 RTI Quality Assurance Manager, Ms. Laura Haines

Ms. Laura Haines is a Chemist in the Center for Analytical Sciences at RTI International. In this capacity, she manages several commercial projects and is responsible for sample preparation, digestion and analytical techniques, including inductively coupled plasma–mass spectrometry, XRF, ultra-performance liquid chromatography, inductively coupled plasma–optical emission spectroscopy, Lachat flow injection analysis and IC. She is experienced in nanomaterials and sensor engineering and nanofiber filtration fabrication and testing, electrospinning, electrolysis, electrochemistry techniques, liquid-phase deposition, dynamic light scattering, laser diffraction particle size analysis, transmission electron microscopy and scanning electron microscopy, solution and thin-film preparation, biochemical analyses, volatile organic compound testing, and data analysis. She has provided internal quality assurance and quality control to a number of projects. Her work has included projects subject to U.S. Food and Drug Administration Good Laboratory Practice and Good Manufacturing Process regulations. Performs QC duties to ensure Good Laboratory Practice compliance for regulatory projects and tasks. Prepares and reviews data packets and reports for the National Toxicology Program and commercial projects.

As QA Manager, she has primary responsibility for overseeing and coordinating all QA activities. She has authority to declare any report, data, or analytical result as unacceptable and does not participate in laboratory activities over which she has QA responsibilities. Contact information: lhaines@rti.org, 919-541-1277.

#### **4.2 Problem Definition/Background**

In 1997, the EPA promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The regulations (40 CFR Parts 50, 53, and 58) apply to the mass concentrations ( $\mu\text{g}/\text{cubic meter of air}$ ) of particles with aerodynamic diameters less than 10 micrometers (the  $\text{PM}_{10}$  standard) and to particles with aerodynamic diameters less than 2.5 micrometers (the  $\text{PM}_{2.5}$  standard). To support these standards, a 1500-site mass measurements network and a smaller  $\text{PM}_{2.5}$  CSN were established.

The CSN consists of a set of core and non-core sites. Chemically speciated data are used to serve needs associated with development of emission mitigation approaches to reduce ambient PM 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 and its components, evaluating potential linkages to health effects, and support for setting a secondary NAAQS for PM.

#### **4.3 Project/Task Description**

The UC Davis laboratory contract involves three broad areas:

1. Receiving field samples from the filter handling contractor (Wood PLC) and analyzing the sample media for chemical constituents including elements, soluble anions and cations, and carbonaceous species as well as measuring filter optical absorption.
2. Assembling validated sets of data from the analyses, preparing data reports for EPA management and SLT, and entering data into the AQS.
3. Establishing and applying a comprehensive QA/QC system. The UC Davis and RTI CSN SOPs and QMPs and this QAPP provide the documentation for the quality system for this study.

UC Davis will provide all the staff, facilities, analytical instrumentation, computer hardware and software, and consumable supplies necessary to carry out tasks from these work areas and will ensure that all contractual specifications are met. The contractual requirements for UC Davis flow down to RTI through the subcontract that UC Davis has established with RTI.

#### 4.3.1 Schedule

The current contract is active September 16, 2015 to September 15, 2020 (sample collection dates). After receipt of all filters and associated filter data, the analysis laboratories analyze the filters for elements, ions, carbon, and optical absorption. Levels 0 and 1 data validation is conducted prior to delivering the data to an interim password protected website or file transfer protocol (FTP) site (DART) for review by state, local, and tribal agencies. After the data has returned from DART, UC Davis uploads the data into AQS. Data is delivered to AQS within 120 days from when the analytical laboratories receive all monthly filters from Wood PLC.

#### 4.3.2 Sample Types and Quantities

Samples are analyzed on three types of filters: polytetrafluoroethylene (PTFE), nylon, and quartz. PTFE and quartz filters (elements, absorption, and carbon) are shipped to UC Davis and the nylon filters (ions) are shipped directly to RTI (see Section 5.3). Approximately 13,400 filters of each type are anticipated to be analyzed each year. This level of activity is expected to continue for the remainder of the contract unless program funding is reduced.

### 4.4 Quality Objectives and Criteria for Measurement Data

#### 4.4.1 Data Quality Objectives Process

The data quality objectives (DQO) process is a strategic planning approach used to achieve data of adequate quality to support decision making. The DQO process helps to ensure that the type, quantity, and quality of environmental monitoring data will be sufficient for the data's intended use, while simultaneously ensuring that resources are not wasted collecting unnecessary, redundant, or overly precise data. The formal DQO process consists of seven steps for development of an experimental design to meet decision criteria specified by stakeholders, as described in EPA QA/G-4, *Guidance for the Data Quality Objectives Process* (EPA, 1994).

A DQO Workgroup was established by the EPA to develop and document DQOs for the Speciated Trends Network portion of CSN. The primary DQO, detection of trends in the chemical speciation data, was defined as follows ([https://www.epa.gov/sites/production/files/2017-01/documents/dqos\\_for\\_pm2.5\\_trends\\_and\\_speciation\\_monitoring\\_network\\_1998.pdf](https://www.epa.gov/sites/production/files/2017-01/documents/dqos_for_pm2.5_trends_and_speciation_monitoring_network_1998.pdf)):

“To be able to detect a 3%–5% annual trend in the concentrations of selected chemical species with 3–5 years of data on a site-by-site basis after adjusting for seasonality, with power of 0.80.” (EPA, 1999a)

The DQO study concluded that with sampling every third day for five years, trends greater than 5 % (or less than minus 5 %) per year can be detected for sulfate, calcium, and total carbon on a single-site basis. For nitrate, however, the annual trend must exceed  $\pm 6.3$  % to be detected with a power of 80 %. The workgroup members concluded that this was not sufficiently different from the 5 % goal to require adjustment to the sampling design. Sampling daily instead of every third day provides little improvement in the ability to detect trends; however, the model showed that cutting the sampling rate to every sixth day begins to impair the ability to detect concentration trends within five years.

Several secondary objectives for data collected at the CSN sites and other chemical speciation sites were identified, but these were not evaluated quantitatively by the workgroup. Five important secondary data uses are as follows:

1. Model evaluation, verification, and/or validation
2. Emission inventory
3. Source attribution
4. Spatial and seasonal characterization of aerosol distributions
5. State Implementation Plan (SIP) attainment and strategy development

The desirable data quality characteristics for these secondary objectives are significantly different from those applicable to trend assessment.

Further development of quantitative DQOs will inform refinement of quality objectives for CSN; subsequent versions of this QAPP will include updates as they become available. The DQOs described are only applicable to the portion of CSN that is a part of the Speciated Trends Network (STN).

#### **4.5 Measurement Quality Objectives**

Measurement Quality Objectives (MQOs) are performance requirements established to meet the DQOs for CSN. They are based on the coefficient of variation (COV) between collocated measurements of selected target species. Specifically, the COV of collocated measurement pairs must be less than or equal to the following requirements for each parameter category:

- Ions: 10 %
- Total Carbon: 15 %
- Elements: 20 %

To meet the MQO requirements, data quality indicators (DQIs) are continuously monitored as part of routine laboratory procedures: precision, bias, representativeness, comparability, completeness, and detectability.

**Precision** – is a measure of the “repeatability of the measurement process under specified conditions” (EPA, 1983). Precision represents the random component of the error term.

**Bias** – is a measure of a systematic offset which skews data results in a single direction, either positive or negative, from an accepted value.

**Representativeness** – is the extent to which measurement results represent the locations, conditions, and times of sampling. This aspect is controlled by network design, siting, and probe locations.

**Comparability** – is the agreement between similar and related data sets. Comparability can be determined using collocated sampling techniques with the same or similar analytical methods and quantifying the difference for a statistically significant number of collocated sample pairs.

**Completeness** – is the yield of valid measurement results from an expected set of measurements under normal conditions. The data completeness goal for each parameter reported is 75 %, consistent with 40 CFR Part 50.

**Detectability** – is the lowest result value that a specific analytical method can reliably discern.

The DQIs that are used to support the MQOs for laboratory analyses are discussed in detail in Section 5.5 and shown in Tables 5 through 7. DQI criteria are summarized in Table 1. The existing CSN DQOs were based on IMPROVE data, and the MQOs for CSN are specified by the same DQIs as for IMPROVE.

Table 1. QC criteria summary.

QC Activity	Frequency
<b>Ion Chromatography (Anions and Cations)</b>	
Multipoint Calibration	Daily
MDL (Nylon Lab Blank)	Initially, then annually or after major instrument change (e.g., conductivity detector or column change)
Deionized Water Blank	Two at the beginning analysis before calibration
Method Blank and Laboratory Control Spikes	One for every 25 samples
QC Standards	Daily or every run
Check Standards	Every 10 samples
Replicates	Three per batch of 50 samples
<b>EDXRF (Elements)</b>	
Calibration Verification (SRM2783)	Following calibration
Calibration Verification (SRM2783)	Monthly
PTFE Blanks, Instrument Stability/ Precision (Repeatability)	Daily
Multi-element RMs, Instrument Stability/ Precision (Repeatability)	Daily & weekly
Reanalysis (Reproducibility)	Monthly
<b>IMPROVE_A TOR/TOT (Carbon)</b>	

QC Activity	Frequency
Laboratory Blank Check	Beginning of analysis day
System Leak Check	Before every analysis
Laser Performance Check	Beginning of analysis day
Calibration Peak Area Check	After every analysis
Sucrose Calibration Check	Beginning of analysis day
Instrument Blank Check	Beginning of analysis day
Sample Replicates (on the same or a different analyzer)	Every 20 network sample analyses
Inter-instrument Comparison Check	Weekly
Multiple Point Calibrations	Every six months or after major instrument repair or change of calibration gas cylinder
Temperature Calibrations	Every six months, or after major instrument repair
Inter-laboratory comparisons	Once per year or as scheduled
External systems audits	Initiated by UC Davis once every two to three years
Carrier Gas Cylinder Leak Check	Every time after a gas cylinder is replaced
<b>HIPS (filter optical absorption)</b>	
Filter Verification Check	Beginning of analysis day
Registration Filter Check	After every 200 samples
Filter Reanalysis Check	Beginning of analysis day

## 4.6 Special Training and Certification

### 4.6.1 Purpose / Background

This section describes any specialized training requirements necessary to complete the project and the procedures are summarized to ensure that specific training skills can be verified, documented, and updated as necessary.

### 4.6.2 Training

The Laboratory Manager trains laboratory technicians in sample handling and preparation for analysis at the time of employment. Physical records of training are maintained by the Laboratory Manager, who closely oversees all operations.

Analysts new to the CSN program are required to have experience with basic measurement techniques relevant to the analyses being performed. These techniques include operation of an EDXRF, IC, TOA, and/or optical absorption instruments.

Prior to training, analysts will read and understand the relevant SOP(s). Under the direction the Laboratory Manager or designated technician, the analyst will follow the SOP to analyze samples and, if available, samples that have been analyzed previously by an experienced analyst. The Laboratory Manager will audit performance of the analyst, checking operations such as calibration, data treatment, system maintenance, and record keeping. With both acceptable analytical results and a successful audit, the analyst will be approved to perform program sample analyses. Ongoing performance will be monitored by the Laboratory Manager through review of analytical data.

#### 4.6.2.1 Experience and Training of Current Personnel

Permanent employees at UC Davis and RTI are eligible to attend training courses relevant to this program. Both in-house and extramural training opportunities are available to employees. Project staff are encouraged to attend courses such as manufacturers' training sessions or method-specific courses.

#### 4.6.2.2 Training and Qualification of New Personnel

New personnel will be hired as necessary to meet the needs of this program. UC Davis utilizes student employees who are replaced by new employees when they graduate. These personnel are typically involved with routine, but important, activities such as receiving exposed samples and data entry. It is critical that errors in these areas be held to an absolute minimum; therefore, an in-house training program is used to ensure full proficiency.

The approach for assessing and training new hires (and cross-training of existing employees) is as follows:

- Candidate credentials are carefully assessed with regard to prior experience and aptitude, and are interviewed by a panel including at least one senior-level project participant.
- Candidates are assessed on a case-by-case basis by the Laboratory Manager, and are expected to have experience or aptitude equivalent to two years of experience. Many student employees have science or engineering majors and have gained laboratory experience through their studies. References are contacted to verify that candidates have appropriate laboratory skills and aptitude.
- For permanent employee hires, there is a six-month probationary period, during which time the employee may be terminated for failing to meet required job standards; temporary employees may be dismissed at any time.
- All SOPs are written in sufficient detail to provide new employees with the requisite training and experience to perform the task. Any departures from the written SOPs require consultation with the Laboratory Manager. Departures from SOPs necessitated by systematic or recurring problems result in corrective actions, which may include revision of the SOP.
- All new employees work under close supervision by the Laboratory Manager or a designated technician.

#### 4.6.3 Certification

UC Davis regulations require that staff who operate EDXRF instrumentation are certified in radiation safety by the UC Davis Environmental Health and Safety Department. Records are maintained by UC Davis Environmental Health and Safety. This has no impact on the quality of the CSN data.

#### **4.7 Documents and Records**

The following sections describe the required documentation for the program. Data records associated with all field sampling and analytical results will be retained for a minimum of five years following sample analysis. Documents related to data quality and training are listed in Table 2. These documents will be retained for a period of ten years after contract completion as specified in *EPA Records Schedule 1035 Item c* (EPA, 2017). If additional contracts are awarded, all of the documentation will be retained as specified in the contract. All of the electronic records will be maintained on servers dedicated to the AQRC at UC Davis. Data records and QA documentation for the subcontract laboratory will be obtained from RTI as needed.

Some of the documents listed in Table 2 will be made available to UC Davis and RTI project staff for training and reference. These include this QAPP, the QMPs (UC Davis and RTI), SOPs and TIs, and forms and logbooks related to each analytical method or data processing function. Documents will be made available to staff in hardcopy and/or shared drive electronic versions.

The QAPP, QMPs, SOPs and TIs, and forms will be reviewed annually and revised as needed, as scheduled by the UC Davis Program Manager. Documents that are maintained and revised at RTI will be sent to UC Davis for review and archiving. Project staff will be notified when new/updated documents are available by the AQRC QA Manager.

##### Document Amendment Practices

In the course of sample analysis and data validation, new information may become available that supports modifying operational practices. Any proposed changes will be discussed in detail with the EPA, clarifying the expected impacts on data results and historical trends. Proposed actions that have received support from the EPA will be documented in the monthly reports to the EPA, in a memo describing the actions to be taken, and in the CSN Annual Quality Report. All affected QA documents (e.g., QAPP, QMP, SOPs, and TIs) will be given a new revision number, distributed to the appropriate personnel, and notification will be sent to the EPA in a memo as well as the monthly and annual reports.

##### Document Management at RTI

Hardcopies of controlled project documents such as this QAPP and SOPs are limited and managed by the Principal Investigator. Current versions are available in both .pdf and .doc format, with the signed PDF version as the official one. To the extent possible, RTI maintains copies of all SOPs, project-related documents such as reports and deliverables, QA-related documents, such as QAPPs, QMPs,



audit of data quality (ADQ) results, and technical systems audits (TSAs) for at least ten years after project completion and generally, indefinitely.

The Principal Investigator reviews relevant project material annually as part of internal audits of quality systems.

#### 4.7.1 Management Records

A summary of the management documentation and records maintained for this program is shown in Table 2.

Table 2. Management records.

Document Name	Description	Format	Storage Location
Monthly Reports	Monthly progress reports to EPA, indicating data delivered and problems encountered.	Electronic; delivered to EPA	AQRC
Quarterly Metadata Reports	Changes and issues that impact data quality. Dates for samples affected or invalidated.	Electronic; delivered to EPA	AQRC
CSN Annual Quality Report	Annual summary of data quality and analysis issues	Electronic; delivered to EPA	AQRC
Correspondence	Contractual correspondence with EPA & RTI	Electronic	AQRC
Purchase Requisitions	Copies of all approved purchase requisitions and purchase orders	Electronic	AQRC
Conference Call Notes	Notes made during conference calls and other project-related calls	Electronic	AQRC
E-mail	All project-related e-mail correspondence	Electronic	UCD server

#### 4.7.2 QA/QC Records

A summary of QA/QC records that are maintained for this program is shown in Table 3.

Table 3. QA/QC records.

Document Name	Description	Format	Storage Location
Training Files	Records of training for lab analysts	Electronic; web-based records for online training	AQRC & RTI
Internal audits, questionnaires, & results	Results of internal QA surveys & audits	Electronic	AQRC & RTI

Document Name	Description	Format	Storage Location
External audits, questionnaires, & results	Results of audits conducted by outside parties (ADQs, TSAs, audits of sample custody)	Electronic	AQRC & RTI
QAPP	Master version of QAPP, including pending revisions	Electronic & hardcopy	AQRC
QMPs	Master versions of UCD and RTI QMPs, including pending revisions	Electronic & hardcopy	AQRC & RTI
SOPs	Current versions of all SOPs	Electronic & hardcopy	AQRC & RTI
Intercomparison Study Results	Results of comparisons of two or more laboratories	Electronic	AQRC & RTI
Corrective Action Response Memos	Results of identified QA problems & their resolutions	Electronic	AQRC & RTI

#### 4.7.3 Analytical Laboratories' Records

UC Davis and RTI analytical laboratories maintain the records listed in Table 4.

Table 4. Laboratory records.

Document Name	Description	Format	Storage Location
<b>EDXRF Laboratory Records</b>			
Laboratory Notebooks	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	EDXRF Lab
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	EDXRF Lab
Method Specific Application	Includes x-ray generation information and other information required to automate the EDXRF analyses	Computer files on each XRF instrument	EDXRF Lab
Instrument User's Manual and SOP	Information for setting up, using, and troubleshooting the EDXRF instrument	Electronic & hardcopy	EDXRF Lab
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	EDXRF Lab
QAPP	Current copy of this QAPP	Electronic & hardcopy	EDXRF Lab
Analytical Results Database (Raw Data Records)	Results of EDXRF elemental analyses	Electronic (database)	EDXRF Lab
Analytical QC Records	Results of calibrations, SRM recoveries, QC checks, replicate analyses	Electronic	EDXRF Lab
<b>IC Laboratory Records</b>			

Document Name	Description	Format	Storage Location
Laboratory Notebooks and Worksheets	Analysts' comments, instrument operations and maintenance logs	hardcopy	IC Lab & Project Managers Office
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	IC Lab Computers & IC Prep Lab
Method Database	Information for automating the analyses	Computer files	IC Lab Computers
Instrument User's Manuals & SOP	Information for setting up, using, and troubleshooting the instruments	Electronic & hardcopy	IC Lab & Vender website
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	IC Lab & Prep Lab
QAPP	Current copy of this QAPP	Electronic & hardcopy	IC Lab
Analytical Results Database (Raw Data Records)	Results of ions analyses	Electronic (database)	Instrument PC Analyst PC IC Lab Database
Analytical QC Records	Results of calibrations, QC recoveries, and replicate precision	Electronic	IC Lab Database
<b>Carbon Laboratory Records</b>			
Laboratory Notebooks and Files	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	Carbon Lab
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	Carbon Lab Network project files
Method Parameter Files	Information required to run the analysis	Electronic & hardcopy	Carbon Lab Database Hardcopies & Archive
Instrument User's Manuals	Information for setting up, using, and troubleshooting the instruments	Hardcopies	Carbon Lab
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	Carbon Lab
QAPP	Current copy of this QAPP	Electronic & hardcopy	Carbon Lab
Analytical Results Database (Raw Data Records)	Results of carbon analyses	Electronic (database)	Instrument PC Computer Database
Analytical QC Records	Results of instrument blanks, calibrations, standard recoveries and replicate precision	Electronic and hardcopy	Carbon Lab Database
<b>HIPS Laboratory Records</b>			
Laboratory Notebooks and Files	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	HIPS Lab

Document Name	Description	Format	Storage Location
Method Parameter Files	Information required to run the analysis	Electronic & hardcopy	HIPS Lab Database Hardcopies & Archive
Instrument User's Manuals	Information for setting up, using, and troubleshooting the instruments	Hardcopies	HIPS Lab
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	HIPS Lab
QAPP	Current copy of this QAPP	Electronic & hardcopy	HIPS Lab
Analytical Results Database (Raw Data Records)	Results of HIPS analyses	Electronic (database)	Instrument PC Computer Database
Analytical QC Records	Results of instrument blanks, verification, and reanalysis samples	Electronic and hardcopy	HIPS Lab Database

Electronic records at UCD and RTI are backed up according to the storage practices described in the QMP and the associated SOP/TIs.

## 5. DATA GENERATION AND ACQUISITION

### 5.1 Sampling Process Design (Experimental Design)

The experimental design, including design of the sampling network and sampling locations, is outside the scope of this QAPP. Refer to EPA planning documents available on the EPA AMTIC Web site.

### 5.2 Sampling Methods Requirements

Collection of samples is conducted by the SLT agencies and is outside the purview of the UC Davis contract and this QAPP. For more information, please see the Chemical Speciation – Field SOPs:  
<https://www3.epa.gov/ttn/amtic/spectraining.html>.

### 5.3 Sample Handling and Custody

This section describes the procedures for sample handling, chain of custody, and archiving of the filters.

### 5.3.1 Sample Handling and Chain of Custody

#### 5.3.1.1 UC Davis Laboratories

The flowcharts for receiving and inventorying the PTFE (elements and optical absorption) and quartz (carbon) filter samples are shown in Figures 3 and 4. The filter samples are shipped in coolers from Wood PLC to UC Davis, accompanied with chain-of-custody forms (COC). Upon receipt of the samples the technician signs and dates the COC, and stores the samples in a refrigerator.

The UCD CSN Data Management Site stores electronic data associated with all the sample types (quartz, nylon, and PTFE). Electronic records provided by Wood PLC are ingested into the CSN database via the UCD CSN Data Management Site.

An integrity check is performed by verifying the filter count and the number of samples on the COC and in the queue file, and a detailed inventory is done when loading samples into the EDXRF, TOA, and HIPS instruments. Shipments from Wood PLC are assigned batch numbers, with each batch containing multiple boxes of Petri trays. Each Petri box can hold two Petri trays, and each tray contains 50 Petri slides. The samples are organized in numerical order based on the COC. Wood PLC is responsible for labeling the boxes and each Petri Tray with the set numbers. The samples are identified by the Lab Analysis ID barcode (F#####) on the bottom of the Petri slide.

Figure 3. Flowchart of PTFE sample receiving and inventorying at UC Davis.

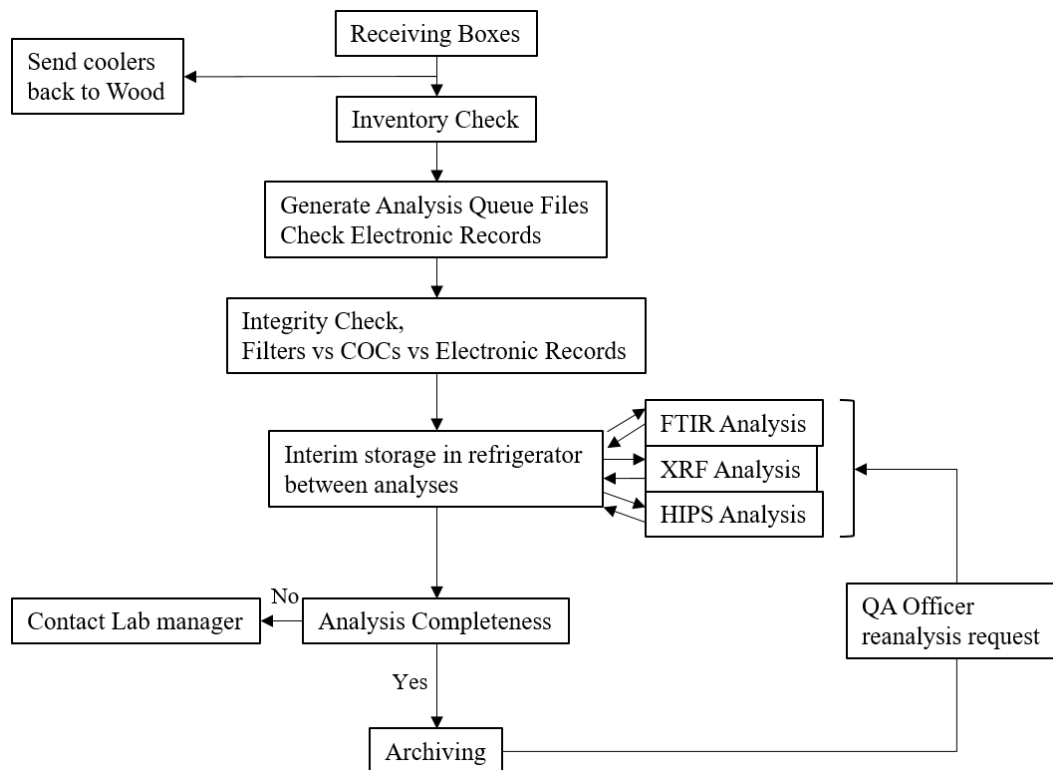
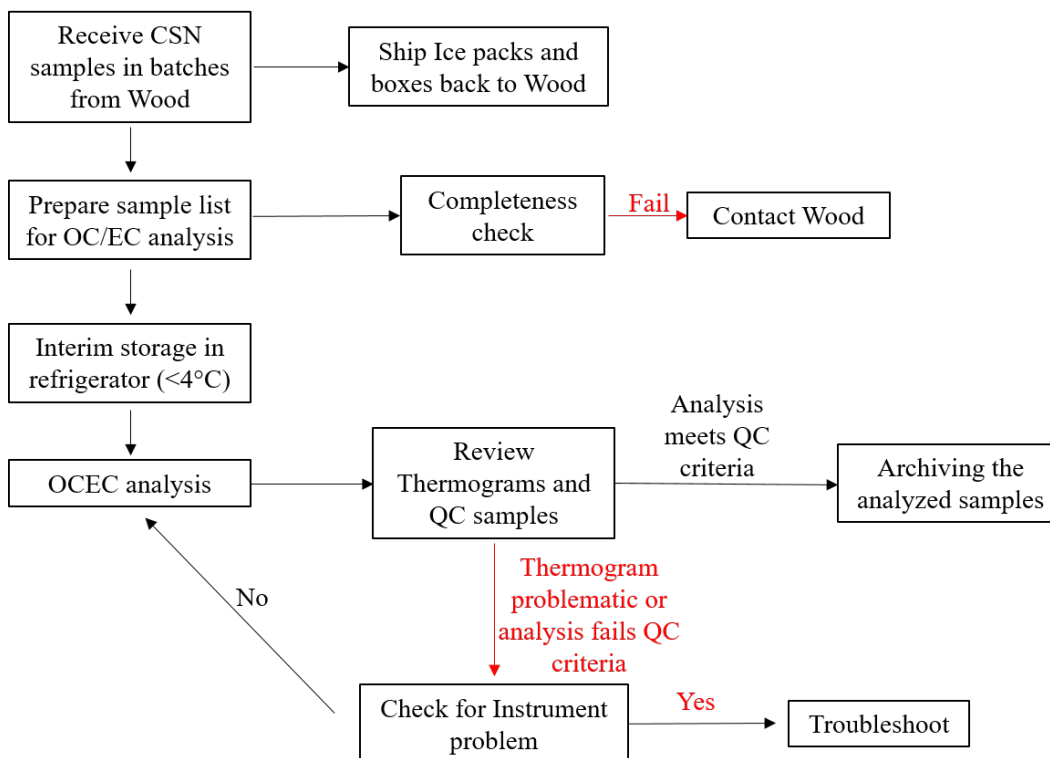


Figure 4. Flowchart of quartz sample receiving and inventorying at UC Davis.



### 5.3.1.2 Ion Analysis Laboratory (RTI)

Nylon filters, along with COC, are received by RTI from Wood PLC packaged in coolers. Using the COC, receipt of the filters is confirmed and any discrepancies are noted. The filter IDs are recorded in RTIs Sample Tracking and Extraction log. The nylon filters are then stored below freezing until processing for analysis.

Refer to the RTI SOP for further details:

*RTI SOP, Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)*

### 5.3.2 Internal Tracking of Analytical Samples

Filters are analyzed within 40 days of receipt from the sample handling laboratory. See Section 4.3.1 for more details.

For EDXRF, TOA, and HIPS analysis at UC Davis, queue files are used in conjunction with barcode scanners to load sample information into each instrument. Filters are transferred from Petri slides into their respective sample holders for each analysis immediately after scanning the barcode associated with

each sample. For EDXRF, the sample holders (cups) are placed into one of six 8-position trays (as assigned at the time of scanning). The instrument name and assigned tray and position number are written on the COC. The trays are placed into the EDXRF instrument sample changer compartment, then the samples are queued in the software. After analysis is complete, trays are removed and filters are transferred back into labeled Petri slides. For TOA, sample punches are taken from the quartz filters and immediately loaded into the instrument. The sample filter remains in the labeled Petri slide. For HIPS, samples are loaded into custom filter holders and loaded into analysis trays. After analysis is complete the filters are transferred back into their labeled Petri slides.

At RTI, samples are tracked internally by batch or sub-batch. Analysis lists are prepared, and barcode labels are used to program and track Petri slides and extract vials through the analysis process.

#### 5.3.3 Archiving of Filters and Extracts

Refer to the UC Davis SOP for details:

*UCD CSN SOP #901: Long-Term Archiving of Filters.*

### 5.4 Analytical Methods Requirements

#### 5.4.1 EDXRF Analysis for Elements

Analysis of CSN PTFE filter samples is performed at UC Davis using energy dispersive X-ray fluorescence (EDXRF) for analysis of elements, specifically using PANalytical Epsilon 5 systems, per the UC Davis SOP:

*UCD CSN SOP #302: CSN Standard Operating Procedure for the X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*

#### 5.4.2 Extraction and Analysis of Anions and Cations

Analysis of CSN nylon filter samples is performed at RTI using ion chromatography (IC) for analysis of water-soluble ions, specifically using Dionex 2000, 3000, and Integrion systems, per the RTI SOP:

*RTI CSN SOP #Ions1: Determination of Anions and Cations Extracted from Nylon Filters by Ion Chromatography (IC)*



#### 5.4.3 Carbon Analysis

Analysis of CSN quartz filter samples is performed at UC Davis using thermal optical analysis (TOA) for analysis of carbon, specifically using Sunset Laboratory thermal-optical OC/EC analyzers following the IMPROVE\_A carbon analysis protocol, per the UC Davis SOP:

*UCD CSN SOP #402: Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer*

#### 5.4.4 Optical Absorption Analysis

Analysis of CSN PTFE filter samples is performed at UC Davis using the AQRC custom hybrid integrating plate/sphere (HIPS) system for optical absorption, per the UC Davis SOP:

*UCD CSN SOP #277: Optical Absorption Analysis of PM<sub>2.5</sub> Samples*

### 5.5 Quality Control Requirements

#### 5.5.1 Quality Criteria for Ion Analysis

Data quality objectives for analysis of ions are listed in Table 5. The multipoint calibration is discussed in detail in Section 5.7.1.

After analysis, each chromatogram is reviewed for the following: 1) correct peak identification, 2) correct peak shapes and integration windows, 3) peak overlaps, 4) calibration acceptability, and 5) to ensure data quality objectives are met. Individual samples with unusual peak shapes, overlapping peaks, or samples impacted by failure to meet data quality objectives outlined in Table 5 are reanalyzed.

The instrument will be set up to analyze a complete calibration curve at the beginning of the run. Deionized water blanks will be analyzed prior to the calibration curve for sample loop rinsing. QC samples are analyzed at the beginning and end of the sample queue and after every ten samples to ensure instrument stability. Typically, 50 samples complete an analytical batch. Three replicates and two matrix spikes (prepared by spiking 0.2 mL of a known concentration into 3 mL of sample) are included with each batch of 50 samples. The Dionex Chromeleon® software is set up using quadratic functions for the calibration of all anions and cations except for ammonium which is a cubic fit function. Dionex recommends using a cubic function for the calibration of ammonium.

The upper and lower control limits for QC standards and matrix spikes are set at  $\pm 10\%$  for ions with concentrations above 0.050 mg/L. When ion concentrations are below 0.050 mg/L, the acceptable range is  $\pm 35\%$ . If a QC standard fails, a second QC standard may be analyzed to verify the calibration. If this standard fails, samples bracketed by the failed QC standard are reanalyzed.

The acceptance criterion for replicates is based on the sample concentration. Near the detection limit, variability will increase and therefore the limits are  $\pm 200\%$ . For sample concentrations greater than ten times the detection limit, acceptable ranges are  $\pm 10\%$ . For sample spikes, recoveries within 90 to 110 % of target values are acceptable. When QC criteria fail for replicate or matrix spikes, the sample impacted is reanalyzed as are 5 % of the samples analyzed within the entire sample queue to verify precision and ascertain if more than one sample was impacted. If other samples reanalyzed fail to meet the replicate criteria, the entire set is reanalyzed.

Table 5. RTI QC criteria for ions (anions and cations) by ion chromatography.

QC Activity	Frequency	Acceptance Criteria (MQO)	Response/ Action
Calibration regression	Daily	$R^2 \geq 0.999$	Investigate; Repeat calibration
Continuing calibration verification check standard	Daily, immediately after calibration and at every 10 samples	Measured concentrations < 0.050 mg/L within 35 % of known values.	Investigate; reanalyze samples
RTI dilution of a commercially prepared, NIST-traceable QC sample		Measured concentrations > 0.050 mg/L within 10 % of known values.	
Replicate	3 per batch of 50 samples	RPD = 10 % at 10x MDL RPD = 200 % at MDL	Investigate; reanalyze
Spiked sample extract	2 per batch of 50 samples	Recoveries within 90 to 110 % of target values	Investigate; reanalyze
Reagent blanks	One reagent blank per reagent used (DI H <sub>2</sub> O and/or eluent) At least one per day	No limit set. The data is compiled for comparability studies.	Investigate; reanalyze
Round Robin (External QA by USGS)	4/month	Not applicable; data reported and compared annually	Investigate
Re-analysis	5 % per batch reanalyzed on different day and as requested	MDL-10 times MDL Percent differences up to 200 %, 10 – 100 times MDL Percent differences < 20 %, > 100 times MDL differences within 10 %	Investigate from batch reanalyze samples if needed

### 5.5.2 Quality Criteria for Element Analysis

Quality criteria for EDXRF analysis are shown in Table 6. The inspection parameters selected for the criteria are defined as:

- Correlation coefficient (r; Equation 1): a measure of the relative mutual dependence of two variables, equal to the ratio of their covariances to the positive square root of the product of their variances.

$$r = \frac{\sum_{i=1}^n (c_{std,i} - \bar{c}_{std,i})(I_{cor,i} - \bar{I}_{cor,i})}{\sqrt{\sum_{i=1}^n (c_{std,i} - \bar{c}_{std,i})^2} \sqrt{\sum_{i=1}^n (I_{cor,i} - \bar{I}_{cor,i})^2}} \quad \text{Eqn. 1}$$

where,  $c_{std,i}$  is the loading ( $\mu\text{g}/\text{cm}^2$ ) of calibration standard i ( $\mu\text{g}/\text{cm}^2$ ) for any given element,  $I_{cor,i}$  is the blank subtracted intensity of X-rays emitted by the standard i (cps/mA),  $\bar{c}$  and  $\bar{I}$  denote the mean; and n is the number of the standards included in the calibration.

- Relative Expanded Uncertainty (Urel; Equation 2): The ratio of uncertainty estimated by the summation of contributions of each factor effective on the measurement to the result of measurement (%). Urel of calibration function is estimated following an international method as detailed in the *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement* published by the Joint Committee for Guides in Metrology (JCGM, 2008).

$$\begin{aligned} C_{std,i} = E_i * I_{cor,i} \rightarrow U_{rel}(C_{std,i}) &= k \frac{u(C_{std,i})}{C_{std}} = k \frac{\sqrt{\sum \left( \frac{\partial C_{std,i}}{\partial x} u(x) \right)^2}}{C_{std}} \\ &= k \frac{\sqrt{(E_i * u(I_{cor,i}))^2 + (I_{cor,i} * u(E_i))^2 + (u(C_{std}))^2}}{C_{std}} \quad \text{Eqn. 2} \end{aligned}$$

where,  $c_{std,i}$  is the re-constructed loading ( $\mu\text{g}/\text{cm}^2$ ) of calibration standard i ( $c_{std}$ ) using the calibration factor (E, in  $[(\mu\text{g}/\text{cm}^2)/(\text{cps}/\text{mA})]$ ) and  $I_{cor}$  is the blank subtracted intensity of X-rays emitted by the standard i (cps/mA). Although the uncertainty of  $c_{std}$ ,  $u(c_{std})$ , is not a part of the  $c_{std,i}$  calculation, it is added to the uncertainty equation for a conservative approach. The coverage factor, k, considers the distribution of uncertainties possible for a given measurement. In this work, a coverage factor of 2 is used to give approximately the 95 % confidence interval on the uncertainty value (k=1.96 at 95 % confidence level for a normal distribution).

- Bias (Equation 3): The ratio of difference between measured and certified loading of NIST SRM2783 to certified loading (%).

$$Bias = 100 * \frac{C_{E5} - C_{cer}}{C_{cer}} \quad \text{Eqn. 3}$$

where,  $c_{E5}$  and  $c_{cer}$  are the loadings by E5 and certified loadings of NIST SRM2783, respectively.

- z-score (Equation 4): The ratio of the difference between each result from monthly reanalysis and reference value to accompanying uncertainty.

$$z = \frac{C_{E5} - C_{ref}}{\sqrt{U_{C_{E5}}^2 + U_{C_{ref}}^2}} \quad \text{Eqn. 4}$$

where,  $c_{E5}$  is the mass loading measured ( $\mu\text{g}/\text{cm}^2$ ),  $c_{ref}$  is the reference mass loading,  $U_{c_{E5}}$  and  $U_{c_{ref}}$  are the expanded uncertainties of measured ( $c_{E5}$ ) and reference ( $c_{ref}$ ) mass loadings. The expanded uncertainties are estimated following an international method, defined above.

- Acceptance limits:
  - PTFE blanks: Analyzed daily, and determined as three times the standard deviation plus the median of a set of lab blanks.
  - Multi-element samples: Analyzed daily and weekly, and determined as  $\pm 10\%$  of the reference loadings (calculated as the mean of ten measurements after calibration).
  - SRM: Analyzed monthly, are element-specific and determined as root-mean-squared-relative-errors (RMSREs) plus three times standard deviations from 44 measurements, January 2013 through July 2016.

Table 6. UC Davis QC criteria for element analysis by EDXRF.

QC Activity	Inspection Frequency	Inspection Parameter	Acceptance criteria (MQO)	Corrective Action
Calibration Verification	Following calibration	<ul style="list-style-type: none"> <li>- Correlation coefficient (r)</li> <li>- Bias from certified loadings of SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb</li> </ul>	<ul style="list-style-type: none"> <li>- <math>r \geq 0.98</math></li> <li>- Bias within element-specific acceptance limits</li> </ul>	<ul style="list-style-type: none"> <li>- Check calibration line and spectra</li> <li>- Check standard(s) for damage/contamination</li> <li>- Exclude standard(s) from calibration line</li> <li>- Further cross-instrumental testing</li> <li>- Recalibration with current or new standards</li> </ul>
	Monthly	Bias from certified loadings of SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	Bias within element-specific acceptance limits	
Instrument Stability/ Precision (repeatability)	Daily	PTFE Blank	$\leq$ acceptance limits with exceedance of any element not to occur in more than two consecutive days	<ul style="list-style-type: none"> <li>- Change/clean blank if contaminated/damaged</li> <li>- Clean the diaphragm, if necessary</li> <li>- Further cross-instrumental testing</li> </ul>
	Daily & weekly	multi-element RMs (ME-RMs) for elements: Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb.	Within $\pm 10\%$ of reference mass loadings with exceedance of any element not to occur in more than two consecutive days	<ul style="list-style-type: none"> <li>- Check sample for damage/contamination</li> <li>- Further cross-instrumental testing</li> <li>- Replace filter sample as necessary</li> </ul>
Reproducibility	Monthly	z-score based on reanalysis of 16 ME-RM samples for elements: Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb.	z-score within $\pm 1$ for selected elements	Investigate and reanalyze set of samples as needed

Control charts displaying z-scores for monitored elements as a function of analysis time are reviewed by the laboratory manager on a monthly basis. Measurements exceeding the acceptance criteria specified in Table 6 are investigated.

### 5.5.3 Quality Criteria for Carbon Analysis

Quality criteria for carbon analysis are shown in Table 7, assuming 12 hours per day, 5 days per week operation of the laboratory.

Daily checks include an instrument blank analysis to check for system contamination and evaluate laser response and a single-point sucrose standard check to evaluate FID response. Each is performed at the beginning of the analysis day. An instrument blank check uses a filter punch that has been previously analyzed to check for instrument contamination. If the measured TC level is not less than  $0.3 \mu\text{g C/cm}^2$ , then the instrument needs to be checked and possibly baked clean. If the reflected and/or transmitted laser reading is less than 5000 with a clean filter punch placed in the sample spoon, adjust laser position and examine oven and spoon for possible frosting. For the single-point sucrose calibration check,  $10 \mu\text{L}$  of  $1.0525 \mu\text{g C}/\mu\text{L}$  sucrose solution ( $10.525 \mu\text{g carbon}$ ) is injected onto a previously analyzed clean filter and analyzed for carbon content. If the resulted total carbon (TC) is over  $\pm 7 \%$  different from the calculated value, then a second analysis is performed or a new sucrose solution is generated and analyzed before analyzing samples.

For every analysis the oven pressure is checked for leak and the calibration peak area is checked with an internal  $5 \%$   $\text{CH}_4/\text{He}$  gas standard. If the leak check indicates that the oven pressure is below the pressure criteria determined for each instrument and does not stabilize, then the cause of the leak is identified and the leak is fixed. If the calibration peak area is over  $\pm 10 \%$  different from the average calibration peak area for the previous two weeks, then the analysis result is voided; the flowrates and sample oven pressure are checked; and the analysis is repeated using a second filter punch.

Sample replicates are performed on randomly selected filters and assigned randomly to the same or different analyzer at a frequency of one for every twenty network sample analyses. If the acceptance criteria in Table 7 are not met, then the instrument and sample anomalies are investigated and another replicate is rerun on a third analyzer. One 37 mm quartz sample collected on UC Davis campus is analyzed every Wednesday on all five analyzers for inter-instrument comparison. If the acceptance criteria in Table 7 are still not met, then the instrument and sample anomalies are investigated and another sample is rerun on all the analyzers.

A multi-point calibration is performed every six months, after a major instrument repair or after replacement of calibration gas ( $\text{CH}_4/\text{He}$ ) cylinder. The calibrations use sucrose standards at five different concentration levels. The calibration constant in the instrument parameter file is updated if the measured and calculated sucrose concentrations deviate from the 1:1 line. A temperature calibration is

performed every six months (usually along with a multi-point calibration) or after a major instrument repair. The sample oven temperature is set to various temperatures ranging from 140 °C to 930 °C. A temperature calibration protocol is run with a Sunset temperature calibration device in place and the temperature offsets are calculated and updated in the instrument parameter file.

In addition, inter-laboratory comparisons are performed once a year. The results are reviewed and procedures verified. External systems audits initiated by the EPA are typically performed once every two or three years. Actions are taken to correct any deficiencies noted in the audit report.

Table 7. UC Davis QC criteria for carbon analysis by TOA using the IMPROVE\_A TOR/TOT carbon analysis method.

Type	Calibration Standards and Range	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank Check	NA	Beginning of analysis day	< 1.0 µg C/cm <sup>2</sup>	Repeat analysis. If same result, check filter lot for possible contamination and perform pre-firing
Instrument Blank Check	NA	Beginning of analysis day	< 0.3 µg C/cm <sup>2</sup>	Repeat analysis. If same result, check instrument and gas lines for possible contamination
Single-point Sucrose Standard Check	10 µL of 1.0525 µgC/µL Sucrose solution	Beginning of analysis day	Within ± 7 % of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform full 5-point calibration to determine new calibration constant.
Calibration Peak Area Check	5 % CH <sub>4</sub> /He gas standard injected into a fix-volume loop; 20 µg equivalent carbon mass	Every analysis	Within ± 10 % of the average value for a specific instrument	Void analysis result; Repeat analysis with second filter punch

System Leak Check	NA	Every analysis	Meet minimum oven pressure (criterion is instrument-specific)	Re-adjust the oven seal and check oven temperatures before analyzing samples
Laser Performance Check	NA	Beginning of analysis day	Laser Transmittance signal for Instrument blank > 5000	Adjust laser position and examine oven for frosting
Network Sample Replicates	NA	Every 20 <sup>th</sup> network sample analyses	$\pm 10\%$ when TC $\geq 10 \mu\text{g C/cm}^2$ $\pm 20\%$ when EC $\geq 2.5 \mu\text{g C/cm}^2$ or $< \pm 1 \mu\text{g/cm}^2$ when TC $< 10 \mu\text{g C/cm}^2$ $< \pm 0.5 \mu\text{g/cm}^2$ when EC $< 2.5 \mu\text{g C/cm}^2$ .	Investigate instrument and sample anomalies Analyze the third punch on a difference analyzer
Inter-instrument Comparison Check	NA	Once per week	Measurement bias for a given analyzer should be $\leq 10\%$ for TC and OC and $\leq 20\%$ for EC.	Investigate instrument and sample anomalies and rerun replicate when criterion is not met
Multi-point Sucrose Standard Check	10 $\mu\text{L}$ of 0.211 - 10.525 $\mu\text{gC/}\mu\text{L}$ Sucrose solutions	Every six months or after major instrument repair or change of calibration gas cylinder	NA	Calculate new calibration constant based on calibration slope and update in the parameter file
Temperature Calibrations	NA	Every six months or after major instrument repair	NA	Change the temperature offset values in IMPROVE_A.par files accordingly
Carrier Gas Cylinder Leak Check	NA	Every time when a gas cylinder is replaced	Regulator pressure reading should not decrease overnight with tank valve closed	Correct for the leak in the gas line and/or fitting

#### 5.5.4 Quality Criteria for Filter Optical Absorption Analysis

Quality criteria for HIPS optical absorption analysis are shown in Table 8.



Daily checks incorporate 15 verification filters and 22 reanalysis filters collected by the IMPROVE network, which span an order of magnitude in absorption values. The first tray includes a registration filter to which the detector response is normalized, thus establishing continuity with historical measurements. Both sets are analyzed at the beginning of each day of analysis. The results are plotted by the spectroscopist alongside previous measurements and with the expected linear relationship between transmittance and reflectance. The results of the verification and reanalysis filters must meet the acceptance criteria in Table 8 before analysis of samples can proceed. If the verification or reanalysis filter results are out of bounds, the analytical system is investigated by the spectroscopist and the verification and reanalysis sets are reanalyzed. Sample analysis does not proceed until the QC process has completed successfully.

Table 8. UC Davis QC criteria for filter optical absorption analysis using the HIPS analysis method.

Type	Calibration Standards and Range	Frequency	Acceptance Criteria	Corrective Action
Verification Filter Check	Reference values of verification filter set	Beginning of analysis day	$\leq 3 \%$	Repeat analysis. If same result, investigate analysis system for error
Reanalysis Filter Check	Reference values of reanalysis filter set	Beginning of analysis day	Accuracy: within expanded uncertainty of reference Linearity: $R^2 > 0.95$ and slope within 0.95 to 1.0 Long-term stability: $-1 \leq z\text{-score} \leq 1$	Check detector registration and repeat analysis. If same result, investigate analysis system for error

#### 5.5.5 Disaster Recovery Plan for Data

Refer to the UC Davis SOP for details:

*UCD SOP #801: Processing and Validating Raw Data*

#### 5.5.6 Uncertainty Determination

There are no absolute standards by which to develop uncertainty estimates for particulate matter measurements. Therefore, uncertainties must be estimated from either theoretical or empirical approaches. Three options to estimate uncertainties are: 1) a bottom-up method which involves identifying and combining the uncertainty estimates from individual measurement components, 2) a top-down

empirical method using duplicate measurements, or 3) a combination of 1) and 2). The previous uncertainty estimates (reported through November 20<sup>th</sup>, 2015) were based on bottom-up estimates of uncertainties in the measurement components (Flanagan et al., 2006). After November 20<sup>th</sup>, 2015, uncertainties are based on a combination of the two approaches by utilizing the collocated measurements in the CSN network and the uncertainty in the blank measurements to estimate an overall uncertainty. These reported uncertainties only capture the variability in the measurements themselves and do not reference any outside or absolute measurement standards. These estimates are limited by the fact that collocated measurements are only available at a small fraction of the CSN sites, and these sites may not be representative of the entire network. The uncertainty estimates include both an additive (analytical uncertainty) and multiplicative (fractional uncertainty) terms as shown in Equation 5: the additive term is dominant at low concentrations, and the fractional term is dominant at high concentrations.

$$\sigma(c) = \sqrt{(S_{FB})^2 + (fC)^2} \quad \text{Eqn. 5}$$

Where,

C = Ambient concentration ( $\mu\text{g}/\text{m}^3$ )

f = Fractional uncertainty

S<sub>FB</sub> = analytical uncertainty

Refer to the UC Davis SOP for details:

*UCD SOP # 801B: CSN Data Processing*

#### 5.5.7 Method Detection Limits

The method detection limits (MDLs) for the CSN analytes are reported with each concentration measurement. The MDLs are calculated on a monthly basis using field blank filters collected during the respective month when possible; if an adequate number of blanks weren't collected in the respective month, blanks from the prior month(s) are included.

Refer to the UC Davis SOP for details:

*UCD SOP # 801B: CSN Data Processing*

#### 5.5.8 Programmatic Uncertainty

Effort during prior CSN contracts helped to identify additional quality issues that were incorporated into the program as they were recognized:

- Shipping/handling components of uncertainty – The laboratory component of random error is typically much smaller than the total random error observed with paired field samples. Thus, improving the precision of laboratory measurements beyond a certain point (e.g., better than +/- 5 % for most species) does not appreciably help overall uncertainty.
- Sensitivity issues – The majority of the PM<sub>2.5</sub> PTFE samples for CSN have been collected using the MetOne SASS sampler, which operates at a flow rate of 6.7 liters per minute and uses 46.2 mm filters. Compared with the IMPROVE program, this relatively low flow rate and large filter size results in a sensitivity deficit of up to 11- fold. This sensitivity difference is immaterial for gravimetric mass and species present in large amounts, such as sulfate and nitrate. Many trace elements analyzed by EDXRF are usually detectable at high levels, including iron, sulfur, and silicon.
- OC artifact – The OC artifact is thought to be the result of adsorbed SVOCs from the gas phase and represents a non-particulate source of carbon. CSN data are reported with artifact correction. The OC artifact for samples taken with the URG 3000N typically range between 0 and 1 µg/m<sup>3</sup> based on field blank measurements.
- Uncertainty definitions – Work with receptor modelers during prior CSN contracts highlighted the importance of consistent definitions of uncertainty to be reported to the AQS database. The original formulation of uncertainty was based on the IMPROVE program's propagation of errors approach and relied on uncertainty values provided by the analytical instruments' software (for EDXRF and TOA). To meet the needs of receptor modeling, it was important that the uncertainties be calculated in a consistent way across all analyzers. An approach was developed for harmonizing the uncertainties reported between different EDXRF instruments (Gutknecht et al., 2010). In the process, it was also ensured that the total uncertainties for the other CSN analytical techniques (gravimetry, ion chromatography, TOA, optical absorption) were comparable with those for EDXRF and were realistic, based on the collocation results.

## **5.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements**

### **5.6.1 Ion Chromatography Laboratory**

Refer to RTI SOP for details:

*RTI SOP, Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)*

Table 9. Inspection criteria for RTI IC Laboratory.

Item	Frequency	Parameter	Action if Failed	Documentation
IC column back pressure	Daily	Compare against previous back pressure	1) Check for blockage 2) Replace column if necessary	Record pressure in instrument log and on level 0 review.
IC background conductivity	Daily	Compare against previous conductivity	1) Check eluent flow 2) Check suppressor 3) Contact supervisor or call Dionex tech support if necessary	Record conductivity in instrument log and on level 0 review.
IC column back pressure	Daily	Compare against previous back pressure	1) Check for blockage 2) Replace column if necessary	Record pressure in instrument log and on level 0 review.

Table 10. RTI IC Laboratory maintenance schedule and responsibility.

Item	Frequency	Parameter	Responsible Party
IC system preventive maintenance	Yearly	Check all valves, fittings, flows and replace as needed; replace piston seals, gaskets and check valves on pump head	IC Lab supervisor or Dionex service representative
Check for leaks at valves and column fittings	Daily	Check for leaks	IC analyst

### 5.6.2 EDXRF Laboratory

Refer to UC Davis SOP for details:

*UCD CSN SOP # 302: CSN Standard Operating Procedure for the X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*

Table 11. Inspection criteria for the UC Davis EDXRF Laboratory.

Item	Frequency	Parameter	Acceptance Criteria (MQO)	Action if Failed	Documentation
Energy Calibration	Weekly	Wavelength/energy alignment of the instrument	Instrument resolution < 140 keV	This is an automated process; manufacturer contacted if failed	Documented in instrument's run log book and computer files
Instrument Stability/Precision	Daily and weekly	Loadings of blank and ME-RMs	Acceptance limits	Investigate, correct, and possibly recalibrate	Results are stored in the EDXRF database and in designated computer files
Ongoing Calibration Verification	Monthly	Loadings of SRM 2783	Absolute bias $\leq$ limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	Investigate and recalibrate if needed	Results are stored in the EDXRF database and in designated computer files
Long-term Reproducibility	Monthly	z-score based on reanalysis of a set of 16 ME-RM samples.	z-score within $\pm 1$ for selected elements	Investigate, correct, and possibly reanalyze affected samples	Results are stored in the EDXRF database and in designated computer files

Table 12. UC Davis EDXRF Laboratory maintenance schedule and responsibility.

Item	Frequency	Responsible Party
Instrument maintenance including vacuum pump maintenance and oil change	Every 6 months	Manufacturer (PANalytical)
State-mandated radiation safety checks	Yearly	UC Davis Environmental Health & Safety Department

### 5.6.3 TOA Laboratory

Refer to UCD SOP for details:

*UCD CSN SOP #402: Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer*

Table 13. Inspection criteria for the UC Davis TOA Laboratory.

Item	Frequency	Parameter	Action if Failed	Documentation
Laser response	Daily	Initial laser reading for a clean filter	1) Check for dirty spoon and/or oven 2) Adjust laser or photodetector position to maximize signal	Documented in instrument's run log book and computer files
Carbon instrument background	Daily	Compare total carbon (TC) against criteria	1) Check baseline 2) Check oven seal 3) Check gas lines for possible contamination. Contact supervisor or call Sunset tech support if necessary	Results are stored in the carbon database and in designated computer files
Single-point calibration	Daily	Compare TC against calculated value	1) Check for system leak or contamination 2) Make new sucrose standard and rerun	Documented in instrument's run log book and computer files
Inter-instrument comparison	Weekly	Compare network replicate pairs and weekly QC PC sample results	1) Check sample for inhomogeneity 2) Rerun a sample punch on a different analyzer 3) Check oven for frosting sign	Results are stored in the carbon database and in designated computer files

Table 14. UC Davis TOA Laboratory maintenance schedule and responsibility.

Item	Frequency	Responsible Party
Carbon analyzer	As needed (daily checks are performed on key components)	Carbon lab supervisor and/or manufacturer (Sunset)
Sucrose standard	semi-annually or as needed	Carbon lab supervisor
Muffle furnace	As needed	Carbon lab supervisor
Sample oven	As needed	Carbon lab supervisor and/or Sunset tech support

#### 5.6.4 HIPS Laboratory

Refer to UCD SOP for details:

*UCD CSN SOP #277: Optical Absorption Analysis of PM<sub>2.5</sub> Samples*

Table 15. Inspection criteria for the UC Davis HIPS Laboratory.

Item	Frequency	Parameter	Action if Failed	Documentation
Laser and detector verification	Daily	Transmittance and reflectance detector response to verification set of filters	1) check physical condition of verification filters. 2) Repeat detector registration and reanalyze verification filter set.	Documented in instrument's run log book and computer files
Calibration verification	Daily	Optical absorption depth of reanalysis filter set	1) Repeat detector registration and verification set test. Then reanalyze the reanalysis set filters. 2) Stop analysis, notify lab supervisor and troubleshoot system.	Results are stored in the database and in designated computer files
Long-term reproducibility	Daily	Z-score from reanalysis filter set	1) Repeat detector registration and verification set test. Then reanalyze the reanalysis set filters. 2) Stop analysis, notify lab supervisor and troubleshoot system.	Results are stored in the database and in designated computer files

Table 16. UC Davis HIPS Laboratory maintenance schedule and responsibility.

Item	Frequency	Responsible Party
Instrument maintenance	As needed (daily checks are performed for laser and detectors)	Lab supervisor
State mandated radiation safety checks	Yearly	UC Davis Environmental Health & Safety Department

## 5.7 Instrument Calibration and Frequency

### 5.7.1 Ion Chromatography Laboratory

A complete multipoint calibration curve is set up at the beginning of each run and will include at least eight different concentrations. The correlation coefficient of the calibration curve must be  $\geq 0.999$  when the instruments are calibrated up to calibration standard 7. When calibration standard 8 is used to calibrate for samples which exceed calibration standard 7 concentrations, the acceptable coefficient is  $\geq 0.995$ . When measured concentration of any ion exceeds the highest standard, the extract is diluted to bring the ion concentration into the calibration range. Calibration standards are prepared from a commercially purchased National Institute of Standards and Technology (NIST) traceable stock standard (Spex Certiprep or another verified source). QC standards are prepared from commercially purchased NIST traceable stock standards (NSI stock standards or another verified source). Two different sources are always used when

preparing the calibration and QC standards. QC standards are prepared in deionized water at low, mid, and high range as applicable. Laboratory control samples (LCS) are prepared during the extraction of samples by pipetting known concentrations into centrifuge tubes and diluting them with the same volume of deionized water used to extract filters.

#### 5.7.2 EDXRF Laboratory

The PANalytical Epsilon 5 has been shown to be a stable analyzer that does not need frequent calibrations. Calibrations are performed upon first installation, approximately yearly or when the analyzer fails verification tests, and whenever an analysis-critical component (e.g., X-ray source or detector) of the analyzer is maintained or replaced.

Four types of standard reference materials are used for calibrating the analyzers.

1. 47 mm MicroMatter thin film foils on Nuclepore membranes, prepared by vacuum deposition.
2. UC Davis generated single-compound standards on 25 and 47 mm PTFE membranes (sulfur, sodium, potassium, chlorine, aluminum, silicon, titanium, vanadium, calcium, chromium, iron, copper, zinc, lead, and cerium).
3. UC Davis generated multi-element standards on 47 mm PTFE membranes.
4. NIST Standard Reference Material (SRM) 2783 air particulate on polycarbonate filter membranes.

Refer to UC Davis SOP for details:

*UCD CSN SOP # 302: CSN Standard Operating Procedure for the X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*

Calibration of the Epsilon 5 EDXRF analyzers is performed using the standards described above. First, the standards are selected in the application, and the software calculates the theoretical relative intensities of the standards listed in the standards file using the operating and deconvolution parameters in the selected application; this calculation will be most accurate when the full composition of the standards is entered, including elements that are not of interest. Next, the standards are analyzed. The software performs a least-squares regression with the theoretical and measured intensities forcing the intercept to zero for each element.

Correlation coefficient of calibration line is required to be over 0.98 for elements with stoichiometric standards and reference materials used for calibration. Each type of standard sample media has corresponding blank sample media that is



analyzed and utilized for blank subtraction. The number of calibration standards varies from two to 30, depending on the element and the range of mass loadings. At least two standards (low and high) are required for each element, and preferably spanning the range of concentrations expected in the CSN samples (Table 17). The calibration factors (linear regression slope) are stored in the application specific calibration file on the EDXRF computer.

Table 17. Concentration ranges for EDXRF element standards.

Element	Range, $\mu\text{g}/\text{cm}^2$	Element	Range, $\mu\text{g}/\text{cm}^2$	Element	Range, $\mu\text{g}/\text{cm}^2$
Na	0.088-19.4	Mg	0.025-19.9	Al	0.053-49.5
Si	0.151-32.6	P	0.013-14.5	S	0.105-18.1
Cl	0.5-29.9	K	0.053-26.3	Ca	0.053-7.2
Ti	0.005-50.2	V	0.005-41.5	Cr	0.009-52.8
Mn	0.009-47.6	Fe	0.053-19.6	Co	0.02-50.9
Ni	0.005-20.3	Cu	0.005-42.7	Zn	0.005-17.8
As	0.002-25.2	Se	0.009-48	Br	5.6-19
Rb	0.002-18.3	Sr	0.005-37	Zr	0.005-28.6
Ag	0.009-52	Cd	0.005-28.3	In	15.2-48
Sn	17-50	Sb	0.007-54	Cs	9.4-31.6
Ba	0.013-43.8	Ce	3.41-35.9	Pb	0.018-54

### 5.7.3 TOA Laboratory

Four types of calibration procedures are required for the TOA instruments (Table 18):

1. End-of-run calibration peak.
2. Daily single-point sucrose calibration check before analysis of network samples.
3. Full instrument calibration, performed every six months or after major instrument repair or after replacement of calibration gas ( $\text{CH}_4/\text{He}$ ) cylinder, using sucrose solution at different concentration levels.
4. Temperature calibrations performed every six months or after major instrument repair using the manufacturer (Sunset) temperature calibration device.

Table 18. UC Davis carbon laboratory instrument calibrations and frequencies.

Calibration	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria (MQO)	Corrective Action
End-of-Run Internal Calibration Peak Area Check	5 % CH <sub>4</sub> /He gas standard injected into a fix-volume loop; 20 µg equivalent carbon mass	Every analysis	90-110 % of average calibration peak area of the previous two weeks	Void analysis result; check for system leak; repeat analysis with second filter punch
Single-point Sucrose Calibration Check	10 µL of 1.0525 µgC/ µL Sucrose solution	Daily	Within ± 7 % of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform full 5-point calibration to determine new calibration constant.
Multiple Point Calibrations	10 µL of 0.211 - 10.525 µgC/ µL Sucrose solutions	Every six months or after major instrument repair or change of calibration gas cylinder	NA	Calculate new calibration constant based on calibration slope and update in the parameter file
Temperature Calibrations	Sunset temperature calibration device	Every six months or after major instrument repair	NA	Change the temperature offset values in IMPROVE_A.par files accordingly

#### 5.7.4 HIPS Laboratory

There are no traceable standards for the calibration of optical absorption of aerosols collected on filters. Instead calibration of the HIPS instrument is performed on the premise that blank PTFE filters have no absorption. Therefore, HIPS can be calibrated by scaling the response of the transmittance and reflectance detectors such that blank filters read zero absorption.

Refer to UC Davis SOP for details:

*UCD CSN SOP # 377: CSN Standard Operating Procedure for the Optical Absorption Analysis of PM<sub>2.5</sub> Samples*

To properly scale the raw transmittance (T) and reflectance (R) values so the field blanks have zero absorption, a linear regression must be performed on the field blanks and the coefficients, a<sub>0</sub> (y-intercept) and a<sub>1</sub> (slope), must be determined.

This is performed by measuring at least 80 field blanks from the same PTFE filter lot as the samples which are being analyzed. Next, a linear regression of T to R is performed and the coefficients are calculated, which are used for field blank correction of measured samples.

There are many factors which can change the field blank correction coefficients. These include changes to the HIPS system (e.g. replacement of a detector, laser, or optical component, adjusting the alignment of the optics) or changes in the PTFE filter lot or manufacturer. Anytime a change occurs, a set of field blanks of matching PTFE filter material must be analyzed on HIPS and new regression coefficients determined and uploaded to the database. The spectroscopist is responsible for ensuring this is properly done.

## **5.8 Inspection/Acceptance of Supplies and Consumables**

### **5.8.1 Filters**

Filters are purchased and inspected by Wood PLC, outside the purview of the UC Davis contract and this QAPP. The shipping and handling QAPPs and SOPs can be found at <https://www.epa.gov/amtic/csn-shipping-and-handling-quality-assurance-project-plans-qapps-and-standard-operating>.

### **5.8.2 Criteria for Other Materials**

Refer to UC Davis and RTI SOPs.

## **5.9 Data Acquisition Requirements (Non-direct Measurements)**

This work does not directly involve the use of any historical databases, literature files, etc. Any supplemental, non-direct measurement data supplied by the monitoring organizations or subcontractors for inclusion in the database will be subject to limited validation to ensure that data have been correctly entered and identified.

UC Davis has obtained historical CSN data from AQS for comparison to current data and observed trends. This data has undergone limited inspection to ensure compatibility with software applications.

## **5.10 Data Management**

To manage data flow from sample collection, laboratory analysis, concentration processing, validation, and delivery to AQS, UC Davis has developed a custom database and connected applications, referred to collectively as the CSN Data Management System (CDMS). As data management is an area of constant

improvement, the specifics of the CDMS and its individual components are discussed in the relevant SOPs and their associated TI documents.

For additional detail refer to UCD SOP and TIs:

*UCD CSN SOP # 801: Standard Operating Procedure for Processing and Validating the Raw Data*

*UCD CSN TI #801A: CSN Data Ingest*

*UCD CSN TI #801B: CSN Data Processing*

*UCD CSN TI #801C: CSN Data Validation*

*UCD CSN TI #801D: CSN Data Delivery*

For the electronic records associated with sample archive:

*UCD CSN SOP # 901: Long-Term Archiving of Filters*

#### 5.10.1 Data Integrity

The primary goal of the CDMS design is to preserve data integrity, as detailed in the following sections.

##### 5.10.1.1 Relational Database Structure

All CSN sample operational data, site metadata, laboratory analysis results, and final concentrations are contained within a structured relational database. The database structure is normalized, such that each data element is stored in only one location. Tables are joined by primary and foreign keys that disallow duplicates. Referential integrity is enforced to ensure that dependent (child) records cannot be created without first creating parent records, and parent records cannot be deleted creating orphaned child records.

##### 5.10.1.2 Data Entry and Input Validation

All CSN data are ingested to the database through a data upload application. This eliminates the need for manual data entry at UC Davis, which is a common source of data errors. The upload applications perform validation on all inputs, catching errors in input data before they are loaded and preventing duplicate records.

#### 5.10.1.3 Data Editing Restrictions

Data editing is strictly controlled. The UC Davis CSN laboratory staff have access to the web application for applying flags to sample records. The application requires that any flag changes are accompanied by a comment that is also stored in the database. The comments are marked with the user's ID and a time stamp.

In some cases, it may be necessary to change records in the data validation process, typically during Level 0 validation. For example, if a transcription error on the sample date is discovered and confirmed with the operator or sample handling lab (Wood PLC), the sample date would be changed. This is not enabled through the CSN web application and only the Data & Reporting Manager can authorize these changes.

#### 5.10.2 Data Flagging

The CSN database uses extensive flagging to ensure all samples, blanks, and metadata are properly accounted for, calculated, and routed. The most important flag categories are:

1. Filter Purpose: distinguishes a filter as a routine sample, field blank, lab blank, or other irregular filter.
2. AQS Null and Qualifier Flags: the UC Davis CSN internal data flagging system for null and informational flags employs the same list of flags as is available in AQS. The database structure allows for up to one null flag and up to ten informational or quality assurance qualifier flags.
3. Analysis QC Codes: distinguish analysis results as either valid, reanalysis or repetition, or test data.
4. Reporting flags: determine whether specific parameters are to be delivered to DART and/or to AQS. Some parameters are provided to DART for informational purposes even though they are not ultimately delivered to AQS.

#### 5.10.3 Validation of the CDMS

While the CDMS is relatively new code, it borrows extensively from the IMPROVE data management system. Validation of the system is an ongoing process, as new features are added over time and must be tested. The steps for testing and validating new functionality for the CDMS are:

1. Software Testing: new and changed features are tested offline by end users following a test plan designed to exercise all functions of the affected software. Core calculations are covered by unit and regression tests, which are executed whenever code is added or changed to ensure that the new

code does not break existing functionality or change data values unexpectedly.

2. Data Validation Testing: new code that impacts data values is tested by a thorough comparison between records produced by old and new records to ensure either equivalence or changes as expected.
3. Hand Calculation: in the case where no existing vetted analogous calculation is available, results will be confirmed via manual or spreadsheet calculations.
4. Data Completeness and Duplicate Checks: when updates involve new database queries, completeness and duplicate checks are run to ensure that queries are returning all of the intended results.

#### 5.10.4 Facility Recovery

Refer to UCD SOP for details:

*UCD CSN SOP #801: Processing & Validating Raw Data*, see Section 9.1.1.

#### 5.10.5 Hardware Recovery

Refer to UCD SOP for details:

*UCD CSN SOP #801: Processing & Validating Raw Data*, see Section 9.1.2.

#### 5.10.6 Software and Data Recovery

Refer to UCD SOP for details:

*UCD CSN SOP #801: Processing & Validating Raw Data*, see Section 9.1.3.

#### 5.10.7 Data Security

Refer to UCD SOP for details:

*UCD CSN SOP #801: Processing & Validating Raw Data*, see Section 9.1.4.

## 6. ASSESSMENTS AND RESPONSE ACTIONS

UC Davis and RTI will participate in laboratory assessment or proficiency programs established by EPA, and will maintain analyst or laboratory certifications required for the program. The assessments that are planned are described in this section.

## 6.1 Audits of Data Quality

The AQRC QA Manager will perform periodic technical systems audits (TSA) of the UC Davis activities. The RTI QA Manager will perform audits at RTI. Every two to three years, the AQRC QA Manager will initiate and participate in external audits of RTI to ensure RTI is meeting the quality system flow down requirements of the prime contract.

External audits of UC Davis and/or RTI activities will also be performed by the EPA – or designated contractor – as determined and communicated by the EPA Program Manager and EPA Quality Assurance Officer.

Audits will cover all aspects of the CSN work, including sample receipt, custody, sample analysis, and data reduction and reporting. The audits will include a review of all applicable documentation (QAPP, QMP, and SOPs/TIs) along with verification that the SOPs and TIs are being followed by the project staff. The audits will also include verification of calculated values by manually calculating a few selected derived values and comparing them to the values produced by the project software. The types of audits to be conducted are listed in Table 19.

Table 19. Types of audits of data quality.

Type of Audit	
UC Davis	RTI
Sample receipt & chain of custody	Sample receipt & chain of custody
Elemental analysis (EDXRF)	Ions analysis (IC)
Carbon analysis (TOA)	Data processing, validation, & submittal
Filter Optical Absorption (HIPS)	Sample archiving
Data processing, validation, & submittal	
Sample archiving	

Prior to each audit, a checklist will be prepared, based on this QAPP, the QMP, the SOPs/TIs, and applicable guidance documents. After each audit has been completed, the following post-audit activities will be conducted to document the audit finding and corrective actions following details documented in Section 15.3.3 and Section 15.3.4 of the *EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II* (<https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/Final%20Handbook%20Document%2017.pdf>):

- A TSA report will be prepared and delivered to the UC Davis Program Manager and UC Davis Principal Investigator (in the case of an audit of UC Davis) or the RTI Program Manager (in the case of an audit of RTI) within 30 days. The report will include:

- Audit title, number, and any other identifying information;
  - Audit team leaders, audit team participants, and audited participants;
  - Background information about the project, purpose of the audit, dates of the audit, particular measurement phase or parameters that were audited, and a brief description of the audit process;
  - Summary and conclusions of the audit and corrective action requirements; and
  - Attachments or appendices that include all audit evaluations and audit finding forms.
- The organization being audited will have 30 days to respond with TSA report with comments or questions, following which the audit lead team will have 30 days to finalize the TSA report.
- The organization being audited will follow-up on the findings documented in the TSA report within 30 days, providing a corrective actions report (CAR) that summarizes the response to findings for each item identified, as well as an Audit Finding Response Form that documents actions taken, timeline, responsibility, and status for each item.

Descriptions and updates regarding UC Davis corrective actions are also documented in monthly reports to the EPA until the actions have been resolved; resolved actions are further documented in the CSN Annual Quality Report. Any actions that impact delivered data are accompanied by a public data advisory describing the issue, the actions taken, and the anticipated impacts on the measurement data. Data advisories are posted on the AQRC website.

The Principal Investigator and the AQRC QA Manager have the authority to issue stop work orders at any time deemed necessary to preserve data fidelity.

## **6.2 Data Quality Assessments**

Data quality is continually assessed through the tracking of data quality indices and through the data validation process. In addition, a formal data quality assessment will be conducted once a year, led by the Principal Investigator, the Data & Reporting Manager, and the AQRC QA Manager. The data quality assessment is a statistical and scientific evaluation of the data sets to determine the validity and performance of the data and to determine the adequacy of the data set for its intended use. The reliability of each type of data to satisfy its MQOs will be assessed. If any type of data consistently falls short then recommendations for corrective action will be provided. The results of the data quality assessment will be provided in each year's CSN Annual Quality Report.



### **6.3 External Quality Assurance Assessments**

The UC Davis laboratories will participate in external QA assessments as requested by EPA. The AQRC QA Manager will coordinate and oversee external QA assessments of the RTI laboratories every two to three years.

### **6.4 Reports to Management**

The following regularly scheduled technical and quality-related reports will be provided to EPA:

- Monthly Data Reports. Each month UC Davis will provide the latest month of CSN data to EPA (or its designated contractor) in a format suitable for uploading to the Data Analysis and Reporting Tool (DART). UC Davis will also supply an additional monthly report that summarizes delivery status, corrective actions, and issues identified during the laboratory, validation, or DART review processes.
- Quarterly Metadata Reports. UC Davis will prepare quarterly metadata reports to address laboratory changes and any other information that may affect the data reported to AQS. Suspect data points are identified in the UC Davis SQL database, and database queries are used to assess flagged or compromised data. Because CSN is a long-term trends network, changes will be made to laboratory procedures only when necessary. Some events, however, are unavoidable, such as instrument calibrations and routine maintenance, and these events will be documented in the quarterly reports.
- Reporting of Data to AQS. After the SLT agencies have reviewed their data using DART, UC Davis will resolve any remaining data validation issues prior to submitting data to AQS. Submittals will be made on a monthly basis, with each submittal comprising a calendar month of data. The data submittal will consist of final resultant values along with the associated uncertainties, method detection limits, and sampling metadata.
- CSN Annual Quality Report. This report will be prepared as required by the EPA, generally following the example outline for the analysis laboratory presented in Appendix A of the solicitation for this contract. UC Davis will conduct ongoing data validation and review of the data each month throughout the year. The annual report will summarize the validation findings and provide recommendations where changes could improve data quality.
- Data Archival. All laboratory data records associated with each analysis will be stored and archived for a period of five years following sample analyses.

## **7. DATA REVIEW AND VALIDATION**

The following describes the UC Davis approach to data review, validation, and verification. The QC criteria given elsewhere in this QAPP will be used as the

data validation requirements. Any data that fail routine validation checks will be flagged for review by the monitoring agencies. Large or systematic exceedances may also trigger a corrective action investigation by the Data & Reporting Manager or AQRC QA Manager.

Data validation begins with the site operator, who may flag or invalidate samples based on sampling conditions or instrumental errors. Next, the sample handling laboratory examines sample integrity and monitors COC forms for irregularities. The analytical laboratories will again examine sample integrity upon receipt and note any damage that may have occurred during transport.

Analytical data are validated using data from laboratory blanks, calibration checks, and laboratory duplicates. Based on QC verification data, a filter or other sample may be invalidated or specific results flagged prior to submitting results to the UC Davis database. Reasons for invalidation may include, but are not limited to, damaged filter, contamination, and invalid holding times.

Once all data have been ingested in the UC Davis database, the data validation analyst will review analytical pathways individually as well as perform a series of cross-comparisons between analytical methods. Resultant data are compared to any applicable notes recorded by the site operators and questionable data are reported back to the analytical laboratories for re-analysis. After all identified issues have been resolved, the data are delivered to DART for review and validation by the SLT validators. Data returned from DART are reviewed for accuracy and consistency, then reformatted for delivery to AQS. For additional detail refer to,

*UCD CSN SOP # 801: Processing and Validating the Raw Data*

## **7.1 Validation**

Refer to UCD SOP for details:

*UCD CSN TI #351C: CSN Data Validation*

## **7.2 Data Corrections**

The following paragraphs briefly discuss the types of data corrections that are typically encountered in this work.

### **7.2.1 Element Analysis by EDXRF**

EDXRF is subject to interferences and artifacts that are corrected for as follows:

- Spectral interferences with the analyte line intensity determination include elemental peak overlap, escape peak, and sum peak interferences. These interferences are automatically corrected within the specific application. No action is required by the EDXRF operator once these interferences have been addressed within the application.
- No attenuation corrections for light elements (sodium through sulfur) will be applied.
- Filter lot-specific background corrections will be applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).
- Occasional Zn contamination due to mechanical malfunction of the instrument gripper are investigated and corrected.

#### 7.2.2 Ions Analysis by IC

Artifacts and interferences in the analysis of PM<sub>2.5</sub> ions using state-of-the-art IC systems are rare but they can occur. Quality control test samples such as blanks, replicates, and calibration standards will be used to detect the existence of artifacts or interferences. In the event that they occur the most likely remedy will be reanalysis of the affected samples. Month specific background corrections will be applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).

#### 7.2.3 Carbon Analysis by TOA

This method is subject to a number of potential interferences. UC Davis uses best judgment in applying corrections, fully documents any such corrections, and will discuss them with EPA before the data are submitted to AQS.

Carbonates and bicarbonates present in some filter samples may cause interference in the TOA analysis. Two alternative procedures may be used to measure carbonate carbon. The first approach includes analysis of a second portion of the filter sample after it has been acidified (i.e., exposed to hydrochloric acid vapor, which removes carbonate as CO<sub>2</sub>) and takes carbonate carbon as the difference between the pre- and post-acidification results. The second approach estimates carbonate carbon by integrating separately the carbonate peak in the thermogram and using the instrument's software to calculate the mass of carbonate carbon volatilized. Carbonate carbon is not generally present in PM<sub>2.5</sub> on quartz filters at loadings above the absolute error of the measurement; therefore, carbonate carbon was not included in the list of analytes for the current contract. Month specific background corrections will be applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).

#### 7.2.4 Filter Optical Absorption by HIPS

Quality control test samples such as verification and reanalysis filters will be used to detect the existence of abnormalities in the HIPS system. In the event that they

occur the most likely remedy will be reanalysis of the affected samples. The primary source of inconsistency in filter optical absorption is due to the scattering properties of PTFE filters during manufacturing. Differences in the reflectance measurement are observable between filter lots. To reduce these inconsistencies, filter lot specific calibrations are applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).

### **7.3 Reconciliation with User Requirements**

UC Davis will ensure that measurement data meet requirements as expressed in this QAPP and associated SOPs. UC Davis and RTI will work closely with the EPA to ensure that all required performance characteristics are met.

There will be regular communication between the UC Davis Principal Investigator, UC Davis Program Manager, and the EPA Program Manager, the EPA technical leader, and the filter handling contractor (Wood PLC). Communications will include conference calls scheduled monthly or as needed, e-mail and written correspondence, and meetings with EPA/OAQPS personnel in the Research Triangle Park, NC area.

Most programmatic communications with outside participants including EPA/OAQPS, the DOPOs, and the state agencies flow through the UC Davis Principal Investigator. Exceptions are allowable for technical discussions with EPA personnel (e.g., to define data delivery formats for AQS) and with Wood PLC personnel for the purpose of coordinating the transfer of samples and data. No one at UC Davis other than the Principal Investigator is authorized to alter analysis schedules, increase or decrease the number of samples to be analyzed, or change the delivery schedule. All such requests must go through the UC Davis Principal Investigator.

## **8. REFERENCES**

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## 9. APPENDIX

### 9.1 Appendix A: List of RTI SOPs

1. RTI SOP: Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)

### 9.2 Appendix B: List of UC Davis SOPs

1. UCD SOP #277: Optical Absorption Analysis of PM<sub>2.5</sub> Samples
  - UCD TI #277A: HIPS Logs, Tray Checks, and Transferring Filters
  - UCD TI #277B: Performing HIPS Analysis
  - UCD TI #277C: Quality Assurance/Quality Check of Analysis of PM<sub>2.5</sub> Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption

2. UCD SOP #302: X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)
  - UCD TI #302A: LN2 Fills and Detector Calibrations
  - UCD TI #302B: Receiving and Inventorying of CSN Samples
  - UCD TI #302C: Sample Changes for 8-Position Trays
  - UCD TI #302D: Quality Assurance/Quality Checks (QA/QC) of XRF Performance
3. UCD SOP #402: Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer
  - UCD TI #402A: Receiving and Inventorying of Quartz CSN Samples
  - UCD TI #402B: Daily Operation
  - UCD TI #402C: Gas Cylinder Change
  - UCD TI #402D: Troubleshooting
  - UCD TI #402E: Instrument Startup and Shutdown
4. UCD SOP #801: Processing and Validating Raw Data
  - UCD TI #801A: CSN Data Ingest
  - UCD TI #801B: CSN Data Processing
  - UCD TI #801C: CSN Data Validation
  - UCD TI #801D: CSN Data Delivery
5. UCD SOP #901: Long-Term Archiving of Filters