Quality Assurance
Guidance Document

Revision 1.0

IMPROVE:
Interagency Monitoring of Protected Visual Environments

Quality Assurance Project Plan

OAQPS Category 1 QAPP

March 2016

LIST OF ACRONYMS AND ABBREVIATIONS

BLM	US Bureau of Land Management
C	Celsius
CAA	Clean Air Act
cm^2	square centimeter
CESU	Cooperative Ecosystem Studies Unit
CIRA	Cooperative Institute for Research in the Atmosphere, Colorado State University
CNL	Crocker Nuclear Laboratory
COTR	Contracting Officer's Technical Representative
DQO	Data Quality Objective
DRI	Desert Research Institute, University of Nevada
EC	elemental carbon
EPA	US Environmental Protection Agency
FID	flame ionization detector
FLM	Federal Land Manager
FTP	file transfer protocol
FWS	US Fish and Wildlife Service
HIPS	Hybrid Integrating Plate/Sphere
L	liters
LIPM	Laser Integrating Plate Method
IC	Ion Chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
L/min	liters per minute
m	meter
m^3	cubic meter
MDL	minimum detectable limit
min	minute
Mm^{-1}	inverse megameters (a unit of visibility)
MQL	minimum quantifiable limit
MQO	measurement quality objectives
MSR	Management System Reviews
NAAQS	National Ambient Air Quality Standard
ng	nanograms
NIST	National Institute of Standards and Technology
NPS	US National Park Service
OAP	EPA Office of Atmospheric Programs
OAQPS	EPA Office of Air Quality Planning and Standards
OAR	EPA Office of Air and Radiation
OC	organic carbon

OMC	organic mass from carbon analysis
PE	performance evaluation
$PM_{2.5}$	particulate matter (with aerodynamic diameter less than 2.5 μm)
PM_{10}	particulate matter (with aerodynamic diameter less than 10 μm)
PTFE	polytetrafluoroethylene, tradename Teflon®
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RHR	Regional Haze Rule
RTI	Research Triangle Institute
SIP	State Implementation Plan
SOP	standard operating procedure
TC	total carbon
TI	technical instruction
TOR	Thermal Optical Reflectance Carbon Combustion Analysis
TOT	Thermal Optical Transmittance Carbon Combustion Analysis
TSA	Technical Systems Audit
μm	micrometers
USFS	USDA Forest Service
XRF	x-ray fluorescence

LIST OF TABLES

Table 1. IMPROVE Project Organizations and Responsibilities 8
Table 2. CNL IMPROVE Project Organization. 16
Table 3. IMPROVE Measurement Quality Objectives for Random and Systematic Errors. 31
Table 4. Flow Rate and Analytical Bias 32
Table 5. QAPP structure mapped to g5 requirements...35
Table 6. IMPROVE Sampler Modules and Filter Media: Module (Filter), Analysis Performed, and Parameters Measured. 40
Table 7. IMPROVE Module Sample Media. 44
Table 8. Days the filter is in shipment, in storage at the site, or in the sampler. 49

LIST OF FIGURES

Figure 1. Organization for IMPROVE program. 9
Figure 2 16
Figure 3. Monitoring Sites: Growth by Year from 1988 to 2013. 21
Figure 4. Monitoring Sites in 2013. 22
Figure 5. IMPROVE Sampler Modules: A (PTFE), B (Nylon), C (Quartz), and D (PTFE). 40
Figure 6. IMPROVE Sampler Control Module. 42
Figure 7. IMPROVE $PM_{2.5}$ Sampler Module. 43
Figure 8. IMPROVE Network Field Sample Log Sheet and custody form..........46
Figure 9. IMPROVE Sampler Handling of Filters. 47

1. TITLE AND APPROVAL SHEET

The Interagency Monitoring of Protected Visual Environments (IMPROVE) project began in 1987 and continues to protect visibility in Class I Areas from existing and future man-made air pollution. This quality assurance project plan (QAPP) was developed by the IMPROVE Steering Committee and Crocker Nuclear Laboratory (CNL) to document the quality assurance (QA) and quality control (QC) activities of the IMPROVE project. The following signatures of key officials indicate agreement with the procedures specified within this plan and a commitment to deliver the details of this plan to personnel on this project.

Crocker Nuclear Laboratory

11/1/16
Anthony Wexler, CNL Director — Date

11/1/16
Nicole Hyslop, Principal Investigator — Date

Xiaoya Cheng — 12/30/16
Xiaoya Cheng, QA Officer — Date

11/16/16
Krystyna Trzepla, Laboratory Manager — Date

Nov 11, 2016
Yongjing Zhao, Field Manager — Date

Research Triangle Institute

Tracy L Dombek — 11/1/16
Tracy Dombek, Laboratory Manager — Date

Desert Research Institute

Judith Chow 11/1/16

Judith Chow, Laboratory Manager Date

Environmental Protection Agency

Laurie Trinca 11/1/16

Laurie Trinca, EPA Project Officer Date

Jenia McBrian Tufts 2/7/17

Jenia McBrian Tufts, EPA Quality Assurance Lead Date

Cooperative Institute for Research in the Atmosphere, Colorado State University

11/1/16

Scott Copeland, Steering Committee Chair Date

Derek Day 11/1/16

Derek Day, Field Audit Coordinator, Quality Assurance Lead Date

National Park Service (Contract Agency)

11/1/2016

John Vimont, Branch Chief, Research and Monitoring,
NPS Air Resources Division Date

2. TABLE OF CONTENTS

List of Acronyms and Abbreviations i
List of Tables iii
List of Figures iv
1. Title and Approval Sheet 1
2. Table of Contents 3
3. Distribution List 6
4. Project Management 7
    4.1. Project/Task Organization 7
        4.1.1. Roles and Responsibilities 7
    4.2. Project /Task description by organization 10
        4.2.1. The IMPROVE Steering Committee 10
        4.2.2. EPA 10
        4.2.3. National Park Service 12
        4.2.4. U.S. Forest Service 12
        4.2.5. U.S. Fish and Wildlife Service 13
        4.2.6. Research Triangle Institute (RTI) 13
        4.2.7. Desert Research Institute (DRI) 13
        4.2.8. Cooperative Institute for Research in the Atmosphere (CIRA) 14
        4.2.9. Crocker Nuclear Laboratory 14
    4.3. Problem Definition / Background 19
    4.4. Project/Task Description 22
        Tasks that CNL is responsible for include: 23
    4.5. Data Quality Objectives 26
        4.5.1 Network Mission 26
        4.5.2 RHR metrics and their calculations. 27
        4.5.3 Stability of the RHR Algorithm 29
    4.6. Measurement Quality Objectives 30
        4.6.1. Tracking Precision 31
        4.6.2. Tracking Bias 31
        4.6.3. Tracking Minimum Detectable Limits 32
        4.6.4. Recovery Rate and Completeness 32
        4.6.5. Class I Area Representativeness 33
        4.6.6. Data Comparability 33
    4.7. Special Training and Certification 34
        4.7.1. Purpose / Background 34
        4.7.2. Training 34
        4.7.3. Certification 34
    4.8. Documents and Records 34
        4.8.1. Structure of the Quality Assurance Project Plan 34
        4.8.2. Contents of the Data Report Packages 35

4.8.3. Process of Producing Final Datasets 36
5. Data Generation and Acquisition 39
5.1. Sampling Process Design (Experimental Design) 39
5.1.1. IMPROVE Sampler Configuration 39
5.1.2. IMPROVE Sampler Site Selection 40
5.2. Sampling Methods 41
5.2.1. IMPROVE Sampler 41
5.2.2 Sampling Media 43
5.2.3 Sampling Operations 44
5.3 Sample Handling and Custody 47
5.3.1 Purchasing Filters and Acceptance Testing 48
5.3.2 Load Clean Filters 48
5.3.3 Transport and On-Site Storage 49
5.3.4 Handling Onsite 49
5.3.5 Receiving Boxes and Log Sheet Information 49
5.3.6 Unloading Nylon and Quartz Filters 50
5.3.7 IC and TOR/TOT 50
5.3.8 Unloading PTFE filters 50
5.3.9 XRF and HIPS 50
5.4 Analytical Methods 51
5.5 Quality Control 51
5.5.1 IMPROVE Sampler Quality Control 51
5.5.2 Gravimetric Quality Control 52
5.5.3 HIPS Quality Control 53
5.5.4 XRF Quality Control 54
5.5.5 Ion Chromatography Quality Control 54
5.5.6 Thermal Optical Reflectance/Thermal Optical Transmittance Quality Control 55
5.5.7 Field Blanks 56
5.5.8 Site Collocation 56
5.6 Instrument/Equipment Testing, Inspection, and Maintenance 57
5.6.1 IMPROVE Sampler Testing and Maintenance 57
5.6.2 Gravimetric Laboratory Maintenance 57
5.6.3 HIPS Maintenance 58
5.6.4 XRF Maintenance 58
5.6.5 Ion Chromatography Maintenance 58
5.6.6 Thermal Optical Reflectance/Thermal Optical Transmittance Maintenance 58
5.7 Instrument/Equipment Calibration and Frequency 59
5.7.1 IMPROVE Sampler Calibration 59
5.7.2 Gravimetric Calibration 59
5.7.3 HIPS Calibration 59

5.7.4 XRF Calibration ... 60
5.7.5 Ion Chromatography Calibration ... 60
5.7.6 Thermal Optical Reflectance/Thermal Optical Transmittance Calibration ... 61
5.8 Calculation of Concentration, Uncertainty, and MDL ... 62
5.9 Inspection/Acceptance of Supplies and Consumables ... 62
5.10 Non-direct Measurements ... 62
5.11 Data Management ... 62
6. Assessment and Oversight ... 64
6.1 Overview ... 64
6.2 Types of Assessments ... 65
6.2.1 Assessment of the Quality System ... 65
6.2.2 Network Reviews ... 67
6.2.3 Technical Systems Audits of Field Operations ... 67
6.2.4 Performance Audits of Field Operations ... 68
6.2.5 Performance Evaluations of Laboratory Operations ... 70
6.2.6 Audits of Data Quality ... 70
6.2.7 Data Quality Assessments ... 70
6.3 Reports to Management ... 71
7. Data Validation and Usability ... 72
7.1 Data Review, Verification, and Validation ... 72
7.2 Verification and Validation Methods ... 72
7.3 Reconciliation with User Requirements ... 75
8. References ... 76
9. Appendix ... 77
9.1 Introduction ... 77
9.1 Data Quality Objectives ... 78
9.2 Sampling Design Error ... 79
9.3 Decision Performance ... 82
9.4 Implementation Plans ... 87
9.5 Estimated Measurement Error ... 91
9.6 Conclusions ... 92
9.7 References ... 92

3. DISTRIBUTION LIST

Crocker Nuclear Laboratory (CNL)

Anthony Wexler, CNL Director
Nicole Hyslop, Principal Investigator
Xiaoya Cheng, QA Officer
Krystyna Trzepla, Laboratory Manager
vice Jose Mojica, Field Manager
Sean Raffuse, Data Manager

Research Triangle Institute (RTI)

Tracy Dombek, Laboratory Manager

Desert Research Institute (DRI)

Judith Chow, Laboratory Manager

Environmental Protection Agency (EPA)

Laurie Trinca, EPA Project Officer
Jenia McBrian Tufts, EPA Quality Assurance Lead

Cooperative Institute for Research in the Atmosphere (CIRA)

Derek Day, Quality Assurance Lead, Field Audit Coordinator

National Park Service (Contract Agency)
John Vimont, Branch Chief, Research and Monitoring, Air Resources Division

4. PROJECT MANAGEMENT

4.1. Project/Task Organization

4.1.1. Roles and Responsibilities

This section identifies individuals and organizations working on the IMPROVE (Interagency Monitoring of Protected Visual Environments) project and discusses their specific responsibilities which are summarized below in Table 1. The organization for the IMPROVE Aerosol Monitoring Network is shown in Figure 1. Gray boxes within the chart represent Quality Assurance (QA) organizations.

Three distinct types of activities are performed as part of the IMPROVE program. Field activities include filter shipping and activities at IMPROVE sites. Laboratory activities include analyses, QA, and data reporting at contracted labs. Data compilation, analysis and reporting includes higher level QA performed at CNL, and QA, data synthesis, and reporting done by NPS and CIRA. NPS administers the contracts/agreements with CNL, DRI, RTI, and CIRA. EPA provides oversight of the program to be sure it meets the objectives of tracking progress under the RHR and fine particle speciation. The Steering Committee is an advisory body comprised of stakeholders which provides feedback to EPA and NPS consistent with the goals of the member organizations. The Steering Committee also provides an effective “independent” QA oversight role by reviewing reports of QA audits, laboratory inter-comparisons, data quality assessments and network performance annually. The Steering Committee also coordinates the team that conducts the periodic quality system reviews.

Table 1. IMPROVE Project Organizations and Responsibilities

Organization	Responsibilities
US Environmental Protection Agency,	
■ Office of Air Quality Planning and Standards, (OAQPS)	Primary funding source; voting delegate on the Steering Committee; technical and policy consultation on regional haze, monitoring methods, and associated analytical methods; advise on QA implementation; coordinate network analytical laboratory technical systems audit and laboratory inter-comparison assessment.
■ Office of Atmospheric Programs	Provide site operators at CASTNET Sites.
■ EPA Regional Offices	Provide technical systems audits of field operations in some circumstances.
US National Park Service (NPS)	Administer contracts, provide site operators, coordinate field technical systems audits program.
US Fish and Wildlife Service (FWS)	Provide site operators, provide independent auditors as available.
USDA Forest Service (USFS)	Provide site operators, provide independent auditors as available.
State, Tribe, Local, and International affiliates	Provide site operators, provide independent auditors as available.
Crocker Nuclear Laboratory at University of California, Davis (CNL)	Provide field support, process filters, ship quartz filters to DRI and nylon filters to RTI, provide analysis of polytetrafluoroethylene (PTFE) filters for mass, elemental concentrations, and optical absorption, process filter data from all three contractors, perform data validation through Level 2, provide final data to CIRA and EPA Air Quality System (AQS).
Desert Research Institute (DRI)	Provide analysis of quartz filters for carbon.
Research Triangle Institute (RTI)	Provide analysis of nylon filters for ions.
Cooperative Institute for Research in the Atmosphere (CIRA)	Perform additional level 2 validation, data quality assessments, coordinate field technical systems audits, maintain IMPROVE website, periodic data reports.

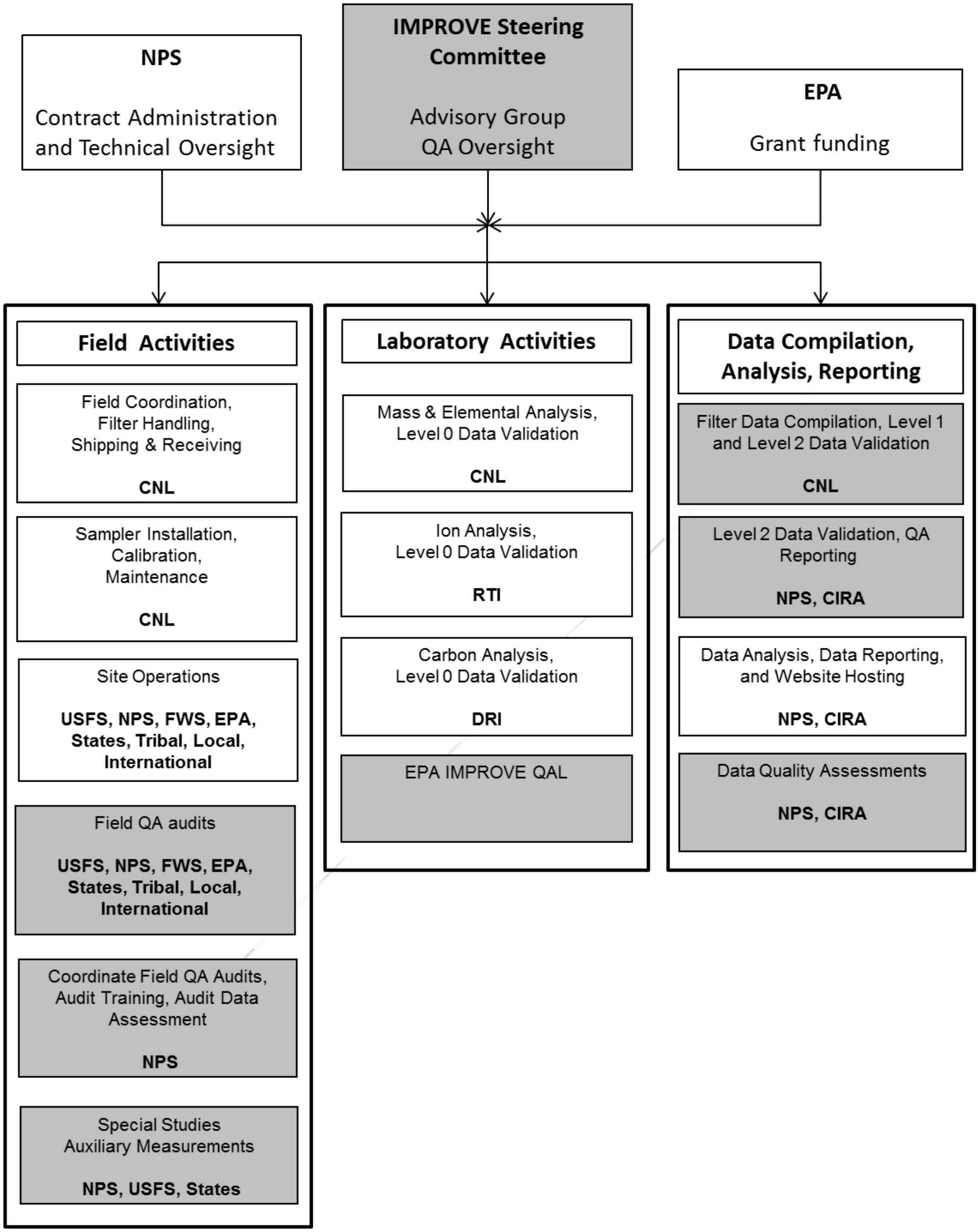

Figure 1. Organization for IMPROVE program.

4.2. Project /Task description by organization

4.2.1. The IMPROVE Steering Committee

This committee makes policy recommendations as needed and reviews QA information at least annually. The voting members of the committee are representatives from:

- EPA
- NPS
- BLM
- USFS
- FWS
- NESCAUM (Northeast States for Coordinated Air Use Management)
- WESTAR (Western States Air Resources Council)
- MARAMA (Mid-Atlantic Regional Air Management Association)
- NOAA (National Oceanic and Atmospheric Administration)
- NACAA (National Associating of Clean Air Agencies)

These representatives meet annually and provide oversight to the IMPROVE program. They interact with the Quality Assurance Lead and the organizations involved in field, laboratory, analysis, and reporting activities.

There are currently three associate members (non-voting), including the State of Arizona, Environment Canada, and the Republic of Korea Ministry of Environment.

The Chair of the IMPROVE Steering Committee is selected by vote of the members of the Steering Committee. Chair coordinates with all IMPROVE QA staff to arrange for information to be presented to Steering Committee at annual meetings.

4.2.2. EPA

The EPA’s tasks are distributed among two offices under the Office of Air and Radiation (OAR) and multiple EPA Regions.

- The Office of Air Quality Planning and Standards (OAQPS)
- The Office of Atmospheric Programs, and
- The EPA Regional ambient monitoring (or sometimes QA staff)

4.2.2.1. Office of Air Quality Planning and Standards

OAQPS responsibilities are distributed over two divisions:

- The Air Quality Policy Division provides policy and technical consultation regarding regional haze and visibility regulations.
- The Air Quality Assessment Division:
    - Allocates funding from Congress under the State and Tribal Assistance Grants
    - Provides technical consultation on monitoring and associated analytical procedures
    - Provides review and comment on emissions data reports and data quality assessments
    - Provides technical input and participates in the assessment of the quality system
    - Provides a voting delegate to the Steering committee
    - Provides an independent QA function for the supporting analytical laboratories as follows:
        - Reviews SOPs and QAPP of each supporting analytical laboratory in support of laboratory Technical Systems Audits (TSAs)
        - Produces and distributes Performance Evaluation (PE) samples for analytes quantified by Network laboratories and reports comparative results to the participating laboratories and NPS
        - Perform on-site TSAs of network analytical laboratories.
        - Report significant TSA findings, monitor corrective actions; and reports resolutions or significant unresolved issues to NPS, EPA OAQPS Management and the IMPROVE Steering Committee.
        - Maintain a repository of PE samples that could be used for PE retrials and diagnostic tools by laboratories, etc.

4.2.2.2. Office of Atmospheric Programs

Provide contractors who will operate 8 CASTNET (speciation) sites as well as other EPA sponsored sites.

- Receive and store sampler shipping box.
- Perform weekly sample change.
- Return sampler shipping box to CNL.
- Consult with CNL concerning problems.

  - Perform calibration and maintenance as directed by CNL.

4.2.2.3. EPA Regional Office ambient monitoring and/or QA Staff

Some Regions have considerable interest in the implementation of the IMPROVE monitoring network due to its integration into State, local or Tribal monitoring plans. As a consequence, they may task EPA staff to perform technical systems audits of field operations or they may also commission contract auditors to perform such audits from which the Region may construct audit reports. The audit personnel are trained under the IMPROVE audit training coordinated by the NPS, EPA and the Steering Committee.

4.2.3. National Park Service

The National Park Service (NPS) is the key operational agency of the IMPROVE Program. The agency is responsible for implementing the recommendations of the Steering Committee; operating a large number of IMPROVE sites; issuing and administering the primary IMPROVE contracts; performing final QA on all data; performing data analyses; and distributing the data, analyses, and project information through the IMPROVE and FED web sites.

The responsibilities of the NPS include:

- Participate in the IMPROVE Steering Committee.
- Issue and administer the following IMPROVE support contracts and agreements:
  - Prime Contractor: Operational support, mass and elemental speciation
  - Ion filter analysis
  - Carbon filter analysis
  - Data quality assurance, analysis, and reporting
- Provide technical oversight to all aspects of the IMPROVE program.
- Operate samplers at NPS sites.
- Perform detailed data analyses including the preparation of scientific papers and presentations.
- May provide technical systems audits of field operations.
- Ensures that the QAPP is implemented.
- Compiles QA and QC reports outlined in this document.

4.2.4. U.S. Forest Service

The U.S. Forest Service (USFS) is a member of the IMPROVE Steering Committee and serves as one of the agencies that will perform the field work for the program. The responsibilities of the USFS include:

- Participate in the IMPROVE Steering Committee.
- Operate samplers at USFS sites.
- May provide technical systems audits of field operations.

4.2.5. U.S. Fish and Wildlife Service

The U.S. Fish and Wildlife Service (FWS) is a member of the IMPROVE Steering Committee and serves as one of the agencies that will perform the field work for the program. The responsibilities of the FWS include:

- Participate in the IMPROVE Steering Committee.
- Operate samplers at FWS sites.
- May provide technical systems audits of field operations.

4.2.6. Research Triangle Institute (RTI)

Under contract to the NPS, RTI will perform ion chromatography (IC) on all IMPROVE Module B nylon filters. Specifically, RTI will:

- Receive all Module B nylon filters and associated files with sample identification information.
- Perform IC on all sample filters and blanks.
- Report all results to CNL as micrograms per filter.
- Validate to Level-0 all Module B ion analyses data.
- Prepare and maintain all IC laboratory SOPs.
- Verify that all laboratory QA procedures are met.
- Review QA documentation by staff members.
- Prepare annual report of ion measurement QA, forward to CNL, and present to Steering Committee.

4.2.7. Desert Research Institute (DRI)

Under contract to the NPS, DRI will analyze all IMPROVE Module C quartz filters for carbon. Specifically, DRI will:

- Pre-fire all Module C quartz filters and forward them to CNL.
- Receive all Module C filters and associated files with sample identification information.
- Perform carbon fraction analyses on all sample filters and blanks.
- Report all results to CNL as micrograms per filter.

- Perform scientific analyses of IMPROVE data as directed by the NPS, and prepare scientific papers and presentations.
- Validate to Level-0 all Module C carbon analysis data.
- Prepare and maintain all carbon laboratory SOPs.
- Verify that all laboratory QA procedures are met.
- Review QA documentation by staff members.
- Prepare annual report of carbon measurement QA, forward to CNL, and present to Steering Committee.

4.2.8. Cooperative Institute for Research in the Atmosphere (CIRA)

Through a Cooperative Agreement with the NPS, the Cooperative Institute for Research in the Atmosphere at Colorado State University performs the following field audit, data QA, database management, analysis, and reporting functions for IMPROVE:

- Receives Level-2 validated data from CNL and performs independent Level-2 data validation.
- Maintains all IMPROVE data, reports, and program documentation on the IMPROVE Web site.
- Develops, maintains, and hosts the IMPROVE Web site.
- Verify that all data and documentation posted on the IMPROVE Web site meets all QA standards.
- Performs scientific analyses of IMPROVE data as directed by the NPS, and prepares scientific papers and presentations, including video presentations.
- Performs visibility research as directed by the NPS.
- Prepares and maintains SOPs for Level-2 validation.
- Prepares and maintains SOPs for data, reporting, and documentation distribution.
- Coordinates field audit program, audit training, prepares annual report of field audits and presents to Steering Committee.

4.2.9. Crocker Nuclear Laboratory

Crocker Nuclear Laboratory (CNL) at UC Davis is the coordinating laboratory for all field operations and speciation work. CNL will coordinate filter pre-sampling, shipping, sampling, and post-sampling activities. CNL will also perform gravimetric analysis on the Module A and D PTFE filters and absorption and elemental analysis on the Module A PTFE filters. Using the information from the contract laboratories and from its own analytical laboratory, CNL will calculate concentrations and uncertainties for all reported parameters. Some of the QA activities of CNL are listed below:

- Track and keep records of all samples as they move through the program.
- Participate in all Technical Systems Audits(TSAs) and Management System Reviews (MSRs).
- Analyze the laboratory inter-comparison samples when received from the EPA OAQPS QA laboratory and report the results to EPA OAQPS.
- Perform gravimetric, absorption, and elemental analysis on sample filters and blanks.
- Coordinate with other contract laboratories (DRI and RTI) and assure that good laboratory practices and QA are performed.
- Maintain adequate internal documentation and quality control.
- Perform Level 0, Level 1 and some Level 2 validation of the data.
- Perform precision and bias analyses on collected data.
- Prepare and maintain field, sample handling, XRF, HIPS, and data validation/delivery SOPs.
- Perform biennial (once every two years) calibrations, adjustments, and major repairs of the field samplers.
- Install instrumentation at new monitoring sites/remove instrumentation from discontinued sites.
- Coordinate the manufacturing of IMPROVE samplers.
- Perform scientific analyses of IMPROVE data as directed by the NPS, and prepare scientific papers and presentations.
- Perform research as directed by the NPS.

Organizational Structure of Crocker Nuclear Laboratory

The organizational chart for CNL is provided in Figure 2. The responsibilities for the various CNL positions are defined in Table 2.

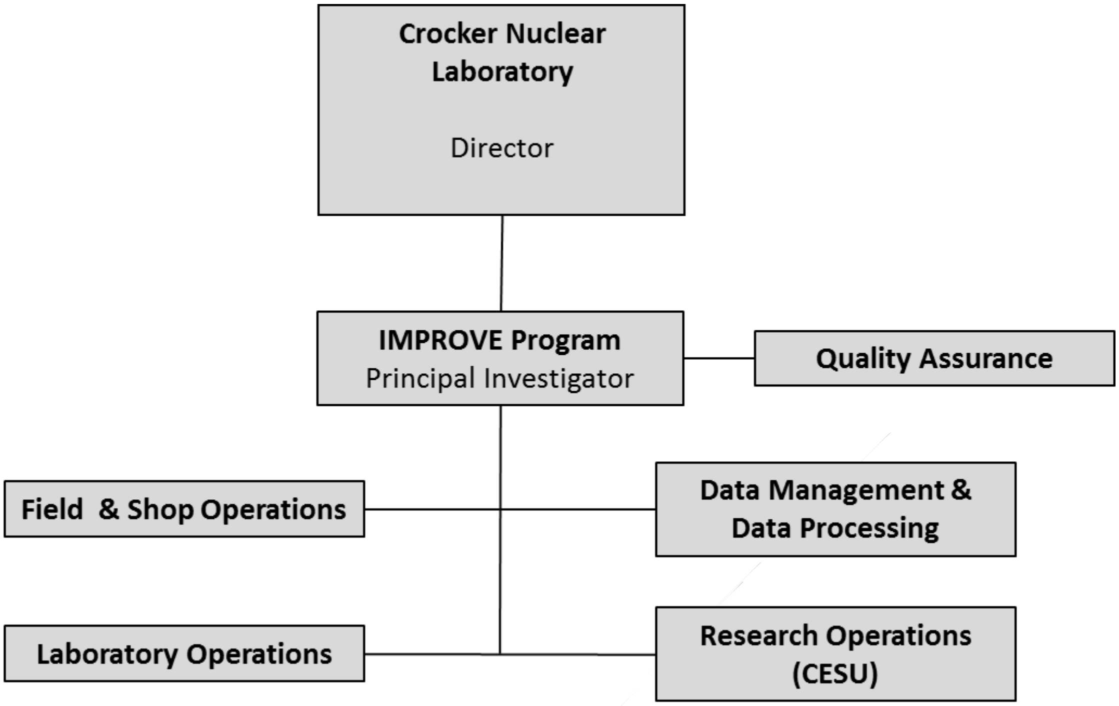

Figure 2. Organizational chart for Crocker Nuclear Lab

Table 2. CNL IMPROVE Project Organization.

Role	Responsibilities
CNL Director	• Ensuring that the research program adheres to its budget. • Determining that the program interacts with other CNL programs properly. • Overseeing personnel performance reviews. • Representing CNL in any fiscal inquiries.

Role	Responsibilities
Principal Investigator	• Determining that all program objectives and contractual requirements are being met on schedule and within budget. • Preparing cost and budget analysis of the program. • Preparing reviews, work plans, and revisions to work plans in accordance with contract requirements. • Overseeing program reviews, approving program work plans, and approving revisions to work plans in accordance with contract and COTR requirements. • Representing CNL in any technical inquiries. • Serving as point of contact with the COTR and IMPROVE Steering Committee Chair. • Reviewing all QA procedures with the QA Manager and ensuring overall compliance. • Periodic reviewing of field operations, sample handling, sample analysis, and sampler testing with the various managers. • Preparing the annual report, presenting to Steering Committee. • Preparing other reports as needed. • Maintaining the Standard Operating Procedures (SOPs) for all CNL operations. • Preparing and maintaining the QAPP sections related to CNL operations. • Coordinating printed and HTML documentation for the particulate monitoring program.

Role	Responsibilities
Quality Assurance Officer	• Reviewing the quality assurance procedures of all aspects of the program, in cooperation with the Principal Investigator. • Verifying that all quality assurance procedures are being met. • Reviewing quality assurance documentation by staff members. • Supervising all quality assurance/quality control studies, including those conducted at the Davis field station. • Validating the analytical results of gravimetric, absorption, and XRF analysis. • Validating the final data set. • Conducting internal audits of CNL operations. • Preparing the quality assurance annual report. • Preparing other reports as needed. • Performing management tasks as assigned by the Principal Investigators.
Laboratory Operations	• Directing the activities of the workers in the sample handling laboratory. • Maintaining a smooth flow of filters through the laboratory. • Purchasing filter supplies. • Overseeing gravimetric measurements, and maintaining the quality assurance records. • Supervising the entry of the field data in the database. • Coordinating with external contractors on the transport of filters. • Preparing the instruction files for the analyses. • Operating the absorption system and providing the data to the QA Officer. • Operating the XRF system and providing the data to the QA Officer. • Reviewing the quality assurance procedures with the QA Officer. • Maintaining records of quality assurance procedures as advised by the QA Officer.

Role	Responsibilities
Data Management and Data Processing	• Calculating artifact values and analytical precisions. • Calculating concentrations, uncertainties, and minimum detectable limits. • Performing data validation procedures. • Maintaining the database. • Preparing seasonal summaries. • Communicating with the IMPROVE website webmaster. • Maintaining records of quality assurance procedures as advised by the QA Officer.
Field and Shop Operations	• Coordinating the annual site visits. • Coordinating with site operators and responding to sampler problems. • Reviewing sampler flow rates and calibrations. • Maintaining records of all field equipment. • Maintaining records of site descriptions. • Repairing malfunctioning sampling equipment. • Maintaining all samplers in storage at Davis. • Overseeing all tests at the Davis field station. • Overseeing fabrication of new samplers.
Research Operations (CESU)	• Conducting research programs designed to advance IMPROVE. • Publishing research results in peer-reviewed journals. • Presenting results at scientific conferences. • Preparing proposals for future research projects.

4.3. Problem Definition / Background

Section 169A of the 1977 amendments to the Clean Air Act (CAA) established as a national goal the “prevention of any future, and the remedying of any existing, impairment of visibility in mandatory Class I Federal areas, which impairment results from manmade air pollution.” Mandatory Class I Federal areas are national parks greater in size than 6000 acres, international parks, and wilderness areas greater in size than 5000 acres, all of which were in existence on August 7, 1977. There are 156 such areas. The responsibility of protecting the air quality at these areas was given to the Federal Land Managers (FLMs): National Park Service (NPS), USDA Forest Service (USFS), Fish and Wildlife Service (FWS), and Bureau of Land Management (BLM).

The NPS Visibility Monitoring Program started in 1978 without particulate measurements. A program administered by the Las Vegas office of the EPA began monitoring particulate concentrations in 1979 at several Class I NPS areas in the Rocky Mountain region. CNL was the contractor for this program. The protocols for remote area sampling were developed at this time. Using the samplers and protocols from the EPA network, the NPS Visibility Monitoring Program added a particulate component in 1981.

In 1985, the EPA established Federal Implementation Plans for states without approved visibility provisions in their State Implementation Plans. To assist states in meeting Clean Air Act (CAA) objectives, in 1987, Federal Land Managers joined with the EPA in a collaborative monitoring program called IMPROVE. The IMPROVE committee originally consisted of representatives of the four Federal Land Managers and the EPA.

The 1990 amendments to the CAA reaffirm the importance of visibility protection. Section 169B includes provisions for the EPA to conduct visibility research with the National Park Service and other federal agencies, to develop an interim findings report on visibility research, to develop a Report to Congress on expected visibility improvements due to implementation of other air pollution programs, and to provide periodic reports to Congress on trends in visibility improvements.

In 1991, three organizations were formally added to IMPROVE: the State and Territorial Air Pollution Program Administrators (this membership is now the NACAA seat), the Western States Air Resources Council, and the Northeast States for Coordinated Air Use Management. A fourth state organization, the Mid-Atlantic Regional Air Management Association, was added later. Ten sites in the Eastern US were added to the IMPROVE network in 1991.

In 1997, EPA published proposed amendments to the 1990 regulations (62 FR 41138) to set forth a program to address visibility impairment due to regional haze. Between 1999 and 2002, the IMPROVE network underwent a major expansion, increasing from 89 to 162 sites. Of these, 110 “Regional Haze Tracking Sites” represent 155 of the 156 mandatory Class I Wilderness Areas and are used to track progress towards the national visibility goal. The 52 sites not directly representing class I areas are sponsored by FLMs, states, tribes, local, and international agencies. These sites use the same instrumentation, monitoring, and analysis protocols as the IMPROVE sites and are informally referred to as “IMPROVE Protocol sites.” In 2000, the sampling frequency changed from every Wednesday and Saturday to 1-day-in-3. These changes required the design and fabrication of the Version II IMPROVE sampler, installed throughout the network in 1999 and 2000.

The growth of the IMPROVE network from 1988 through 2013 is shown in Figure 3. The “Year” on the horizontal axis represents the extent of the network on the final sampling day of that year. Since the major expansion ending in 2002 the size of the network has remained fairly constant. The number of IMPROVE sites has remained at 110 and the number of Protocol sites has fluctuated slightly, with a handful of sites added or dropped within a typical year. A map of the IMPROVE network in 2013 is shown in Figure 4. An interactive map of the network can be found on the Federal Environmental Database (FED) website at: http://views.cira.colostate.edu/fed/

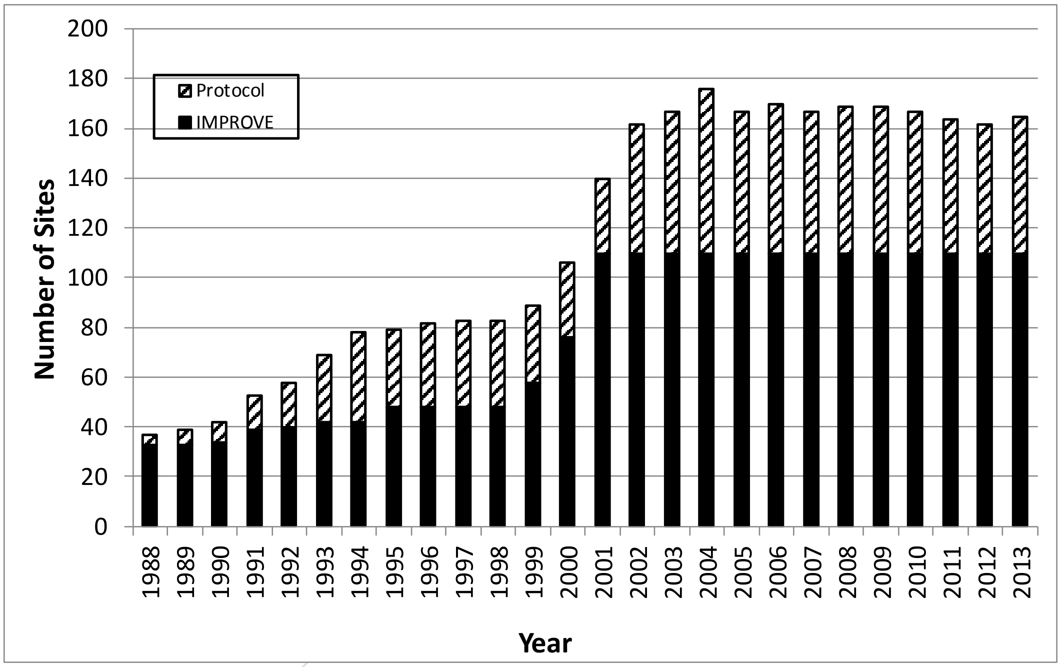

Figure 3. Monitoring Sites: Growth by Year from 1988 to 2013.

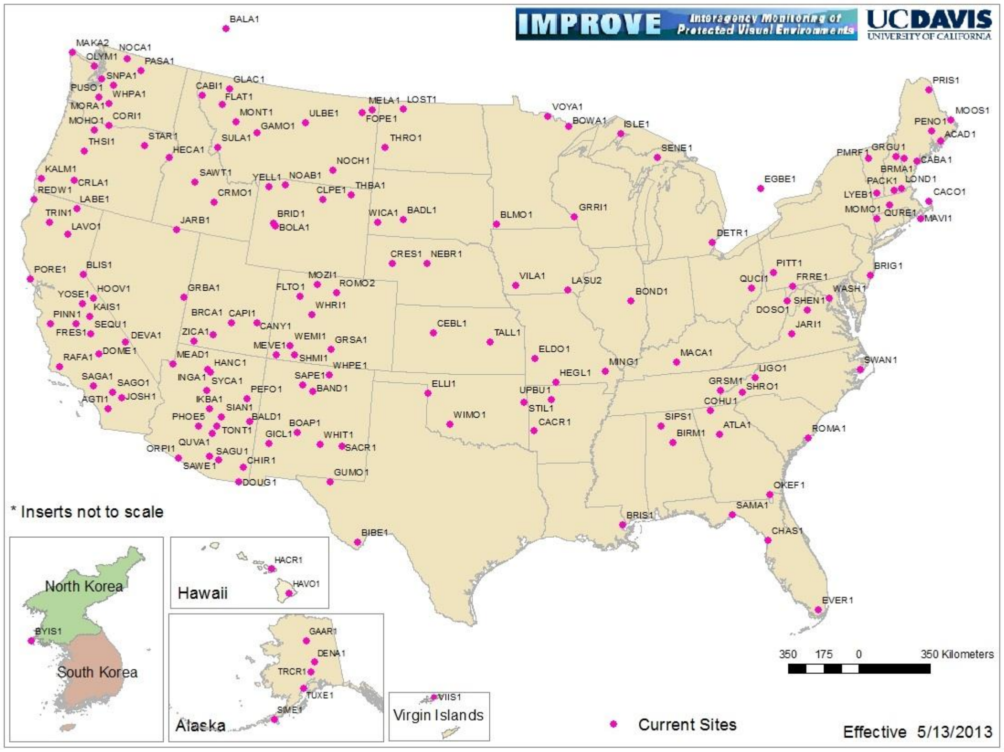

Figure 4. Monitoring Sites in 2013.

4.4. Project/Task Description

The primary objective of the IMPROVE Visibility Monitoring Program is to measure the concentrations of particles affecting visibility in class I areas. With the RHR, the specific species for this primary objective have been defined as those used to calculate reconstructed extinction: sulfate (sulfate ion or elemental sulfur), nitrate, soil, organic matter, light-absorbing (elemental) carbon, sea salt, and coarse mass. The last is the difference between PM_{10} mass and $PM_{2.5}$ mass.

This primary objective affects only the IMPROVE sites at class I areas and only a portion of the species measured.

Secondary objectives include:

- Monitoring the species used to calculate reconstruction extinction at the Protocol sites in order to understand the transport of visibility-impairing species into class I areas. In many cases, this information is also used by states in developing State Implementation Plans (SIPs).
- Monitoring trace elements in order to understand possible sources of the visibility-impairing species.

The original objectives of the particulate component of the Visibility Monitoring Program as stated in 1987 are still appropriate. These were (Joseph, et al., 1987):

- To establish the background visibility levels necessary to assess impacts of potential new sources through the development and operation of a long-term background monitoring network,
- To determine the sources and levels of reasonably attributable visibility impairment through the design and implementation of special source attribution studies, relationship between visibility impairment and various atmospheric particulate constituents.
- To collect data useful for assessing progress toward the national visibility goal, and determine the existing sources of particles producing visibility impairment.
- To promote the development of improved visibility monitoring technology and the collection of comparable visibility data by the evaluation of candidate monitoring methods and the development of quality assurance, data processing and documentation procedures.

The operation of the IMPROVE network is performed by three contractors. The prime contractor is CNL, and has been the prime contractor since the start of the program in 1987. There are two additional contractors for part of the sample analysis. Research Triangle Institute (RTI) is responsible for the analysis of the nylon filters and Desert Research Institute (DRI) is responsible for the analysis of the quartz filters. CNL is responsible for all other project activities. The quality assurance objectives of RTI and DRI are included in this plan. In order to meet these objectives, the particulate contractors for IMPROVE must perform the following tasks.

Tasks that CNL is responsible for include:

1. Designing and fabricating the samplers used in the network.
2. Supervising the selection of sites and installing the samplers.
3. Overseeing the field operation at all ambient monitoring stations by:
    - Providing training and support to IMPROVE site operators,
    - Maintaining flow rates, calibrations, site records, and sampler equipment on biennial site visits.
4. Acquiring and acceptance testing the PTFE and nylon filters:
    - Running acceptance tests on the collection properties of each new batch of PTFE and nylon filters,
    - Performing elemental analysis on a set of filters from each new batch,
    - Shipping a set of nylon filters from each new batch to RTI and analyzing the results to verify that the artifact values are acceptable.
5. Handling all samples by:

  - Loading filters into cassettes and cartridges, and shipping to site operators along with the field log sheet,
  - Receiving samples from site operators,
  - Logging the collection parameters from memory card into the computer data base and checking the data for consistency,
  - If the collection information is not available on memory cards, logging the collection parameters from the field log sheets into the computer data base twice, and checking the data for consistency,
  - Logging all comments from the field operator in the database,
  - Logging all sample-handling actions into the computer database to track actions at laboratory workstations, performing immediate quality control checks, and verifying complete data entry,
  - Distributing the filters to the appropriate analytical custodian: Module A PTFE to the CNL XRF operator, Module B nylon to the Ions Contractor, Module C quartz to the Carbon Contractor, and Module D PTFE to the archives. All relevant information is sent electronically with the samples to improve efficiency and maintain quality control.
6. Performing and/or supervising all filter analyses, by:
    - Analyzing all PTFE filters for gravimetric mass,
    - Analyzing a set of gravimetric controls at the beginning of every morning and afternoon session,
    - Analyzing the Module A PTFE filters by Hybrid Integrating Plate/Sphere (HIPS) and X-ray Fluorescence (XRF).
    - Reanalyzing a set of filters each month to track measurement stability,
    - Reviewing all quality control and assurance data from the various analytical methods: gravimetric analysis, HIPS, and XRF by CNL; IC by the Ions Contractor; and Thermal Optical Reflectance/Thermal Optical Transmittance (TOR/TOT) by the Carbon Contractor.
7. Processing and validating data by:
    - Combining field sampling and analytical data.
    - Calculating sample volumes by applying flow rate calibration factors to pressure transducer and temperature measurements.
    - Generating a mass database to contrast pre- and post- sampling filter mass values, as well as descriptive statistics for mass gains of control and field blank filters.
    - Monitoring analytical precision through standard reference materials and replicate analyses.
    - Performing Level 0 (for gravimetric mass, HIPS and XRF), Level 1 and Level 2 data validation.

- Preparing quarterly data summaries.

Tasks that RTI is responsible for include:

1. Analyzing the laboratory blanks for ions from new nylon batches when sent by CNL.
2. Analyzing the filter samples sent by CNL.
3. Calibrating the analytical system and running quality assurance standards.
4. Performing replicate analyses as specified by their SOP's.
5. Sending the analytical results for samples and field blanks to CNL.
6. Report results of QA work to Steering Committee annually.

Tasks that DRI is responsible for include:

1. Pre-firing the quartz filters and shipping to CNL.
2. Analyzing laboratory and field blanks as specified by their SOP's.
3. Analyzing the samples sent by CNL.
4. Calibrating the analytical system and running quality assurance standards.
5. Performing replicate analyses as specified by their SOP's.
6. Sending the analytical results for samples, blanks, and secondary filters to CNL.
7. Report results of QA work to Steering Committee annually.

CNL, RTI, and DRI have separate SOP's for Network Operations and PTFE Filter Analyses, for Ion Chromatography Analysis, and for TOR/TOT Analysis, respectively. The SOP's are available on the IMPROVE web site at the following URL's:

CNL SOP's:
http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdsop.asp

DRI SOP's:
http://vista.cira.colostate.edu/improve/Publications/SOPs/CarbonSOP.asp

RTI SOP’s:
http://vista.cira.colostate.edu/improve/Publications/SOPs/RTIsop.asp.

4.5. Data Quality Objectives

4.5.1 Network Mission

Data quality objectives for IMPROVE are based on the central mission of the network: tracking changes in concentrations of key light scattering and absorbing components of particulate matter (“species”). The long term goal of the Clean Air Act is to eliminate “man-made” visibility impairment by 2064. EPA’s 1999 Regional Haze Rule defines progress towards the CAA goal by setting the goal of a linear reduction in the haze index (in deciview) on the “most impaired” days, while preventing increases in the haze index on the “least impaired” days. The implications of the goal are that the IMPROVE network needs to be able to quantify changes in concentrations of haze forming species and that it is necessary to understand which portions of haze forming species are anthropogenic.

As of this QAPP revision, IMPROVE samples measure the total amount of haze forming particulate matter with very good precision and at least some components of haze are known to have low long term bias. The sampling techniques provide little information about what fraction of each haze component is anthropogenic, though when combined with emission inventories and atmospheric transport and chemistry models some estimates can be made. DQOs for IMPROVE are more limited by this inability to segregate anthropogenic haze from natural haze than by the analytical uncertainties described in 4.6 below. Research into new analytical techniques should focus on those which would facilitate this separation of haze forming particles.

It is nevertheless important to define the criteria for determining trends in the parameters that are measured, whether the trends are caused by natural variation or changes in anthropogenic emissions.

Based on the 2000-2004 data set and default assumptions about the 2064 target natural conditions, and based on the RHR assumption that the haziest days are the “most impaired” days, the lowest rate of change in atmospheric extinction on the haziest days for a class I area to ensure linear progress would be about 4% per decade, with typical rates around 10% to 30% per decade. Thus, the DQO is to be able to reject the null hypothesis (no change in total extinction on the most impaired days) for situations with actual reductions in haze forming pollutants which would correspond to a 4% decrease in calculated light extinction. Comparisons are to be made between any two non-overlapping 5 year periods. The statistical certainty with which the null hypothesis could be rejected is key, but not quantified at this time.

Individual light scattering components at some sites are already considered equivalent to or below natural conditions on the most impaired days. In those situations, as with the case of clearest days, the DQO would be to be able to rule out increasing trends with reasonable statistical certainty. The table below summarizes each of the six primary light scattering components along with the range of hypothetical decreases in most-impaired-days' concentrations over the lifespan of the Rule.

Component	Lowest concentration change for a site by 2064 (ug/m3)	Highest concentration change for a site by 2064 (ug/m3)
Coarse Mass	0	20.7
Fine Soil	0	5.5
Elemental Carbon	0.06	1.1
Organic Mass	0	14.8
Fine Particle Nitrate	0	6.7
Fine Particle Sulfate	0.5	13.2

There are also complex relationships between IMPROVE's DQOs and the network's performance, independent of the analytical uncertainties. Seasonal gaps in data completeness can create a false signal in certain measured parameters, as can relocating a site. IMPROVE's historically high data collection efficiency of 90%+ has minimized the data completeness uncertainties, but individual cases still remain where data loss has affected trends. Efforts to prevent data loss need to remain a priority for the network.

Section 4.6 states that "random errors are negligible when averaged over multiple years", which may be true even in the case of less-well-measured parameters, but to estimate the actual statistical power of the network for every site and parameter with varying data completeness will require rigorous statistical simulations.

4.5.2 RHR metrics and their calculations.

The coefficient of extinction in Mm^{-1} was originally defined by the RHR as

$$b_{ext} = 3f(RH)[Sulfate] + 3f(RH)[Nitrate] + (4)[OMC] + (10)[LAC] + (1)[Soil] + (0.6)[CM] + (Rayleigh) \quad \text{(Equation 1)}$$

where [Sulfate] = (4.125)[S] or (1.375)[$SO_4^{=}$],
[Nitrate] = (1.29)[NO_3^-]
[OMC] = (1.4)[OC] {OC = sum of organic fractions}

[LAC] is elemental carbon = sum of elemental fractions
[Soil] = sum of Al, Si, K, Ca, Ti, Fe plus oxides
[CM] = [PM_{10}] – [$PM_{2.5}$] (called “coarse mass”)
f(RH) = relative humidity growth factor.

The *Rayleigh* term represents scattering from air molecules and is 10 Mm^{-1} in this equation.

The relative humidity factor f(RH) is specific for each site and month. It varies from 1 to 5, with an average value of 2.6. Generally, the annual average is from 1.5 to 3 in most of the west, 3.0 to 3.6 in the east, and 3.6 to 4.2 in most of Oregon and Washington and a few other marine sites.

The RHR algorithm above was revised in 2006 and the current version of the equation is shown below with revised terms in bold font. The total sulfate, nitrate and organic carbon compound concentrations are each split into two fractions, representing small and large size distributions of those components. Though not explicitly shown in the equation, the organic mass concentration used in this new algorithm is 1.8 times the organic carbon mass concentration, changed from 1.4 times carbon mass concentration as used for input for the prior IMPROVE algorithm. New terms have been added for sea salt (important for coastal locations) and for absorption by NO_2 (only used where NO_2 data are available). Site-specific Rayleigh scattering is calculated for the elevation and annual average temperature of each of the IMPROVE monitoring sites.

$$\begin{aligned}
b_{ext} \approx\ & \mathbf{2.2 \times f_S(RH) \times [Small\ Sulfate] + 4.8 \times f_L(RH) \times [Large\ Sulfate]} \\
& \mathbf{+ 2.4 \times f_S(RH) \times [Small\ Nitrate] + 5.1 \times f_L(RH) \times [Large\ Nitrate]} \\
& \mathbf{+ 2.8 \times [Small\ Organic\ Mass] + 6.1 \times [Large\ Organic\ Mass]} \\
& + 10 \times [Elemental\ \ Carbon] \\
& + 1 \times [Fine\ Soil] \qquad\qquad \text{(Equation 2)} \\
& \mathbf{+ 1.7 \times f_{SS}(RH) \times [Sea\ Salt]} \\
& + 0.6 \times [Coarse\ Mass] \\
& \mathbf{+ Rayleigh\ Scattering\ (Site\ Specific)} \\
& \mathbf{+ 0.33 \times [NO_2\ (ppb)]}
\end{aligned}$$

The apportionment of the total concentration of sulfate compounds into the concentrations of the small and large size fractions is accomplished using the following equations.

$$[Large\ \ Sulfate] = \frac{[Total\ Sulfate]}{20\mu g/m^3} \times [Total\ Sulfate],\ \ for\ [Total\ Sulfate] < 20\mu g/m^3$$

$$[Small\ Sulfate] = [Total\ Sulfate] - [Large\ Sulfate]$$

$$[Large\ Sulfate] = [Total\ Sulfate] \quad for\ [Total\ Sulfate] \geq 20 \mu g/m^3$$

The same equations are used to apportion total nitrate and total organic mass concentrations into the small and large size fractions.

$f_s(RH)$ is the relative humidity factor for the small size fraction, $f_l(RH)$ is the relative humidity factor for the large size fraction and $f_{ss}(RH)$ is the relative humidity factor for seas salt.

Sea salt is calculated as 1.8 × [*Chloride*], or 1.8 × [*Chlorine*] if the chloride measurement is below detection limits, missing or invalid.

The extinction in Mm^{-1} is converted to deciviews using the formula

$$dv = 10 \ln\left(\frac{b_{ext}}{10}\right) \qquad \text{(Equation 3)}$$

The deciview is calculated for each sample and ranked for the calendar year. Annual averages are calculated for the 20% clearest days (lowest dv) and 20% haziest days (highest dv). The values are combined for specific five-year periods (2000-2004, 2005-2009, etc), by averaging the five annual values. The trends in the five-year values will be used to measure progress for SIPS. The goal of the RHR is that most impaired conditions will improve steadily until achieving natural conditions in 2064, while clearest days are not to degrade.

4.5.3 Stability of the RHR Algorithm

Changes in atmospheric chemistry and corresponding changes in light scattering efficiencies for the principal species may justify modifying the reconstructed extinction algorithm described above.

Direct measurements of the optical properties of pollutants in the atmosphere have been routinely made since roughly 1990 as auxiliary measurements of the IMPROVE program. Nephelometers, which directly measure ambient light scattering, operate near roughly 10 IMPROVE sites as of 2016. One additional site operates a transmissometer which measures light extinction over a path. Comparisons between these direct optical measurements and measured species concentrations is the primary means of tracking the stability of the reconstructed extinction algorithm.

4.6. Measurement Quality Objectives

As noted above, "the DQO is to be able to reject the null hypothesis … for situations with actual reductions in haze forming pollutants which would correspond to a 4% decrease in calculated light extinction." and "to rule out increasing trends with reasonable statistical power" on clearest days and when individual species are at or below the target condition.

These targets:

(i) identify tracking change as the primary objective,
(ii) quantify the rate of change that is relevant, and
(iii) clarify that the objective applies to each of the major particle fractions and not just the aggregate haze metric.

The implications of trend targets for IMPROVE data and measurement quality objectives (MQOs) were analyzed in a 2005 report, "Tracking progress with imperfect measurements: data quality and the Regional Haze Rule", which was reviewed by the IMPROVE Steering Committee at their July 2005 meeting in Acadia National Park and is included in the Section 9 of this QAPP. Two findings emerge clearly from this analysis:

- Because natural weather factors are notoriously irregular, concentrations can be expected to vary from one multi-year period to the next even if emissions remain constant and the climate is stationary (i.e., without overall trend).
- Time-varying biases are the dominant source of error in measuring air-quality trends. The precision of IMPROVE measurements is well characterized by collocated sampling and replicate measurements, and observed levels of random error are negligible when averaged over multiple years. **The focus of quality assurance efforts for regional haze tracking should thus be on the consistent minimization of measurement bias.**

Measurement quality objectives for random error are bounds for the root-mean-square (rms) scatter of individual replicate measurements about their mean value for moderately loaded filters. Objectives for systematic error are bounds for the mean error in multiple replicate measurements of a standard reference such as a metallic weight for gravimetric mass. Table 3 presents the MQOs for both types of error. These MQOs are designed to support the DQO stated above.

Table 3. IMPROVE Measurement Quality Objectives for Random and Systematic Errors.

Method	Parameters	Random Error (rms)	Systematic Error (limit)
Gravimetric	Mass	± 5 µg/filter	± 5 µg/filter
HIPS	F_{abs}	± 10%	± 5%
XRF	Al,Si,S,K,Ca,Ti,Fe	± 10%	± 5%
IC	NO_3^{-}, $SO_4^{=}$, Cl^{-}	± 10%	± 5%
TOR/TOT	OC, EC	± 10%	± 5%

The metrics for determining and tracking measurement quality are precision, accuracy, minimum detectable limit (MDL), completeness, representativeness, and comparability. These factors are described in the following subsections.

4.6.1. Tracking Precision

Precision is a measure of random error based on the differences between independent measurements of the same quantity. The overall precision can be determined from collocated samplers. IMPROVE uses single collocated modules (either A, B, C, or D) at different sites to achieve collocated sampling. Phoenix has a complete duplicate sampler.

Precision is expressed as the relative error for samples with values at least three times the detection limit. For major components, the precisions observed in collocated IMPROVE measurements range from 3% for sulfate to 130% for the third elemental carbon fraction.

4.6.2. Tracking Bias

Bias is systematic error, the difference between a sample reading and the true value of the sample that remains even after averaging over multiple independent measurements. Bias is determined by measuring reference materials traceable to an external standard or authority, such as the National Institute of Standards and Technology (NIST). The reference standard for flow rate and each analytical method is listed in Table 4.

Table 4. Flow Rate and Analytical Bias

Method	Bias Reference
Flow Rate	NIST-traceable Dry-Cal Nexus DC-2 Flow-Calibrator
Gravimetric	NIST-traceable Ultra Class mass standards
HIPS	Unloaded PTFE filters
XRF	Commercial elemental foils, NIST traceable reference standards, lab-developed reference filters
IC	NIST-traceable solutions of each ion
TOR/TOT	CH_4 gas, CO_2 gas, samples spiked with KHP and sucrose, none NIST-traceable.

4.6.3. Tracking Minimum Detectable Limits

Minimum detectable limits are provided with each concentration value in the IMPROVE database. A concentration is considered meaningful only if it is greater than the MDL. For IC and TOR/TOT OC/EC analyses the MDL is based on the standard deviation of the field blanks. For mass and light absorption, the MDL is based on laboratory blanks (mass) or low-absorbing controls (light absorption). Beginning in 2011, the MDL for XRF (using the PANalytical Epsilon 5 instrument) is based on field blanks. Prior to 2011, the MDL for XRF was based on standard theoretical formulas for photon counting statistics.

4.6.4. Recovery Rate and Completeness

Recovery rate and completeness are both defined as the ratio of the number of valid samples divided by the number of possible samples. Recovery rate considers only the $PM_{2.5}$ PTFE filter while completeness considers all four filters. Since the $PM_{2.5}$ PTFE filter contributes the fine mass and most of the fine species, the recovery rate is appropriate if these variables are being considered. However, for a full characterization of reconstructed extinction, it is necessary to have valid measurements from all four filters. This is represented by completeness.

Objectives. The objective for recovery rate for the total IMPROVE network is 90% of all possible samples. The objective for completeness for each site reflects the criteria established by the RHR – at least 75% completeness within a calendar year, at least 50% completeness within each calendar quarter, and no more than 10 consecutive samples lost.

Recovery Rate. Prior to implementation of the RHR, a sample was considered valid if the elemental concentrations from the $PM_{2.5}$ PTFE filter (Module A) were valid, independent of the validity of the remaining filters. Recovery rate is defined as the ratio of samples with valid elemental concentrations divided by the number of possible samples. A recovered sample has at least sulfur, soil elements, trace elements, the coefficient of absorption. Because the Module A PTFE filter has a central role in the data validation procedures, if the Module A

PTFE filter is invalid, then the entire sampling period is considered invalid, and data from the other filters is not included in the RHR database. Thus the recovery rate indicates the upper limit for the number of samples in the database.

Completeness. The parameter of interest for the RHR is reconstructed extinction, which is calculated from the following $PM_{2.5}$ concentrations: sulfate and soil from Module A, organic and elemental carbon from Module C, and nitrate from Module B. (Sulfate could also be calculated from Module B.) Reconstructed extinction also has a component calculated from the coarse mass, which is the difference between PM_{10} mass (from Module D) and $PM_{2.5}$ mass (from Module A). The most conservative definition for completeness is to require all that all parameters above must have valid measurements for the sample to be valid.

Since the expansion of the network completed in 2002 the network-wide averages for both recovery rate and completeness have exceeded 90% every year.

4.6.5. Class I Area Representativeness

Representativeness is based on the relationship between monitoring objectives and the geographical location of monitoring stations. The locations of the sites have been determined according to IMPROVE site selection criteria (section 5.1.2). These criteria ensure that sites avoid non-representative meteorology, avoid local sources of pollution, avoid obstructions, and represent class I areas within specified spatial parameters.

Fundamental to the IMPROVE program is the notion that trends in class I area visibility can be determined by collecting 1-in-3 day 24-hour samples at locations within certain spatial parameters relative to those class I areas. Modeling efforts suggest that nearly all class I areas are well characterized by the current network configuration. New sources or modeling efforts could cause some class I areas to fall out of the “well characterized” category.

Network Reviews need to consider relocated sites, decommissioned sites, and class I areas not adequately represented by the current network.

4.6.6. Data Comparability

Comparability is defined as the measure of confidence with which one data set can be compared to another. An important factor is that all operations are coordinated by one contractor (CNL), and each analysis for a given parameter is conducted by a single contractor.

4.7. Special Training and Certification

4.7.1. 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.

4.7.2. Training

Site operators are trained in equipment operations, sample collection, and log recording. A training session is conducted during new site installation and repeated during the biennial maintenance. This training session consists of all the steps needed to change filters, plus how to change the date and time. Training videos are available at http://airquality.crocker.ucdavis.edu/improve/resources-operators/ . The operators are given a brief summary on how to calibrate the sampler flow rate. (The operators are given a detailed step-by-step manual whenever they are asked to calibrate the sampler.) The field manager keeps current records of trained site operators.

The laboratory manager trains laboratory technicians in sample handling and gravimetric analysis at the time of employment. This is done in a series of sessions, each one on a specific station in the sample handling procedure. Maintaining a record of training is unnecessary as the laboratory manager closely oversees all operations.

Field staff for various organizations that perform technical systems audits receive training from audit coordinator. This training includes the calibration and use of flow audit devices, sampler design, and IMPROVE siting requirements.

4.7.3. Certification

University regulations require that CNL staff are certified in radiation safety by UC Davis Environmental Health and Safety (EH&S). Records are maintained by UC Davis EH&S.

There are no additional specific certification requirements for the IMPROVE project.

4.8. Documents and Records

The following sections describe the structure of the QAPP, the contents of the data report packages, and the process of producing final datasets.

4.8.1. Structure of the Quality Assurance Project Plan

The structure of this QAPP is directly adapted from the EPA QA/G-5 document covering all 24 elements. See Table 4a below.

Group A. Project Management	**Corresponding Section in this QAPP**	**Group B. Data Generation and Acquisition**	**Corresponding Section in this QAPP**	**Group C. Assessment and Oversight**	**Corresponding Section in this QAPP**
A1 Title and Approval Sheet	1	B1 Sampling Process Design (Experimental Design)	5.1	C1 Assessments and Response Actions	6.1, 6.2
A2 Table of Contents	2	B2 Sampling Methods	5.2	C2 Reports to Management	6.3
A3 Distribution List	3	B3 Sample Handling and Custody	5.3		
A4 Project/Task Organization	4.1, 4.2	B4 Analytical Methods	5.4, 5.8	**Group D. Data Validation and**	
A5 Problem Definition and Background	4.3	B5 Quality Control	5.5	D1 Data Review, Verification, and	7.1
A6 Project/Task Description	4.4	B6 Instrument/ Equipment Inspection, and Maintenance Testing,	5.6	D2 Verification and Validation Methods	7.2
A7 Quality Objectives and Criteria	4.5, 4.6	B7 Instrument/Equipment Calibration and Frequency	5.7	D3 Reconciliation with User Requirements	7.3
A8 Special Training/Certifications	4.7	B8 Inspection/Acceptance of Supplies and Consumables	5.9		
A9 Documentation and Records	4.8	B9 Non-direct Measurements	5.10		
		B10 Data Management	5.11		

Table 5. QAPP structure mapped to g5 requirements.

Numerous SOPs and TIs are referenced below. All of the IMPROVE SOPs and TIs can be found on the IMPROVE website:

http://vista.cira.colostate.edu/improve/Publications/IMPROVE_SOPs.htm

This QAPP documents a process to ensure early detection of problems and timely feedback when corrective actions are necessary. It also provides a blueprint of all operations and coordination of the entire project. Since it is a working document, it will be revised as needed to incorporate changes to the program. Document revisions will be approved by and distributed to members of the QAPP signature list.

4.8.2. Contents of the Data Report Packages

All original data are archived at CNL. Data are typically reviewed on a quarterly basis as they are produced. In addition, data produced in a given month are compared to data produced in the same month in prior years to identify systematic irregularities.

Data packages are typically delivered quarterly to CIRA by CNL for posting on the FED data website. 24-hour ambient concentrations of all measured species are provided in units of ng/m^3. The data packages also identify sites that have been added or removed from the network during the quarter and identify problems that were found during data validation.

Quarterly and annual site completeness reports are provided to the IMPROVE Steering Committee members and to other interested participants. These reports list data completeness for each site, including performance against the RHR completeness criteria. The reports also include a detailed discussion of sites that have experienced noteworthy problems, including a summary of corrective actions planned or taken.

All IMPROVE contractors submit monthly invoices to the National Park Service, indicating their spending during the month as well as cumulatively to date.

4.8.3. Process of Producing Final Datasets

IMPROVE data pass three levels of validation before becoming a part of the final dataset.

Level 0 Validation

Data at this level are, in essence, raw data, obtained directly from the data-acquiring instruments. These data can be reduced or reformatted, but are unedited and unreviewed, without any adjustments for known biases or problems that might have been identified during preventative maintenance checks or audits. These data may monitor instrument operations on a frequent basis. Averaging times represent the minimum intervals recorded, and these data may need to be aggregated to obtain averages for the sampling periods. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline shifts, span changes, or known problems been applied.

Level 1 Validation

Level 1 validation involves a review of field operations, instrumentation performance, and questionable data being coded for evaluation.

- Review of the field operations database for problems that occurred during the season.
- Review of flow rates for the season. This includes a comparison of flow rates measured by the two system methods and identification of any cases with questionable validity.
- Review of the QA documentation accompanying the external contractor data.
- Review of field blanks, secondary filters, chosen artifact values and analytical precision.

- Review of the calibration and controls for gravimetric, XRF, and HIPS analyses for the season.

Level 2 Validation

Level 2 validation verifies sample concentrations by contrasting with expected values.

The QA Officer reviews the individual concentrations and means for a standard set of parameters for each site. A set of time series and correlation plots are used to compare related variables at each site.

Discrepancies are investigated and, when necessary, samples are reanalyzed in an attempt to resolve the issues.

Whenever a value is changed in the database, a note is attached to that location indicating the change and the reason. When a sample is invalidated, the concentrations are flagged as invalid, but the original parameters are retained in the database.

The QA Officer prepares a summary of the Level 1 and Level 2 validation results and presents it to the Data Manager and Principal Investigator. If judged acceptable by the PI the data are considered validated. The data are sent to CIRA, who is responsible for updating the database on the FED web site.

The following information is retained:

All Level 0 raw data. Some examples are

- 15-minute averaged pressure transducer and temperature data downloaded from the sampler flashcards before automated validation tests
- balance measurements before automated validity tests
- XRF raw spectra

Level 1 validation of sampler flow rate calibration

- Electronic calibration log sheets for calibration devices
- Electronic calibration log sheets for samplers
- Flow rate calibrations database (with historic values)
- Biennial maintenance notes

Level 1 validation of collection

- Hardcopy field log sheets are archived for 5 years
- Data recorded from field log sheets

Level 1 validation of gravimetric analysis

- Electronic results of gravimetric lab blanks

Level 1 validation of absorption analysis

- Log book of maintenance

- Log book of HIPS control filters

Level 1 validation of elemental analysis

- Calibration data
- Reanalysis data
- Electronic and handwritten logs of analysis

Level 1 validation of external contractor analysis

- External contractors' quality assurance documents
- Original electronic data delivery files

Level 2 validation of data processing

- Data processing software with changes tracked by source control software

5. DATA GENERATION AND ACQUISITION

5.1. Sampling Process Design (Experimental Design)

The IMPROVE network is designed to provide data for the RHR and to show baseline, temporal, and spatial trends in ambient air quality in class I areas throughout the United States. To accomplish this, we focus on obtaining a partial chemical signature of the composition of the airborne particles.

Twenty-four hour samples are collected every third day from midnight to midnight. Sampling is continuous throughout the year.

5.1.1. IMPROVE Sampler Configuration

The standard IMPROVE sampler has four sampling modules, as shown inFigure 5. Each module collects a single filter for each sample date. Module A (PTFE), B (Nylon), and C (Quartz) collect fine particles (0-2.5 µm). Module D (PTFE) collects PM_{10} particles (0-10 µm). Module A (PTFE) provides $PM_{2.5}$ mass, certain elements, and the coefficient of optical absorption. Module B (Nylon), with a denuder before the nylon filter to remove acidic gases, is used for anions. Module C (Quartz) measures carbon in eight temperature fractions. The properties of the four modules are summarized in Table 6. The inlets are normally horizontally spaced 0.6 meters apart. Selected sites have an additional collocated module for quality assurance.

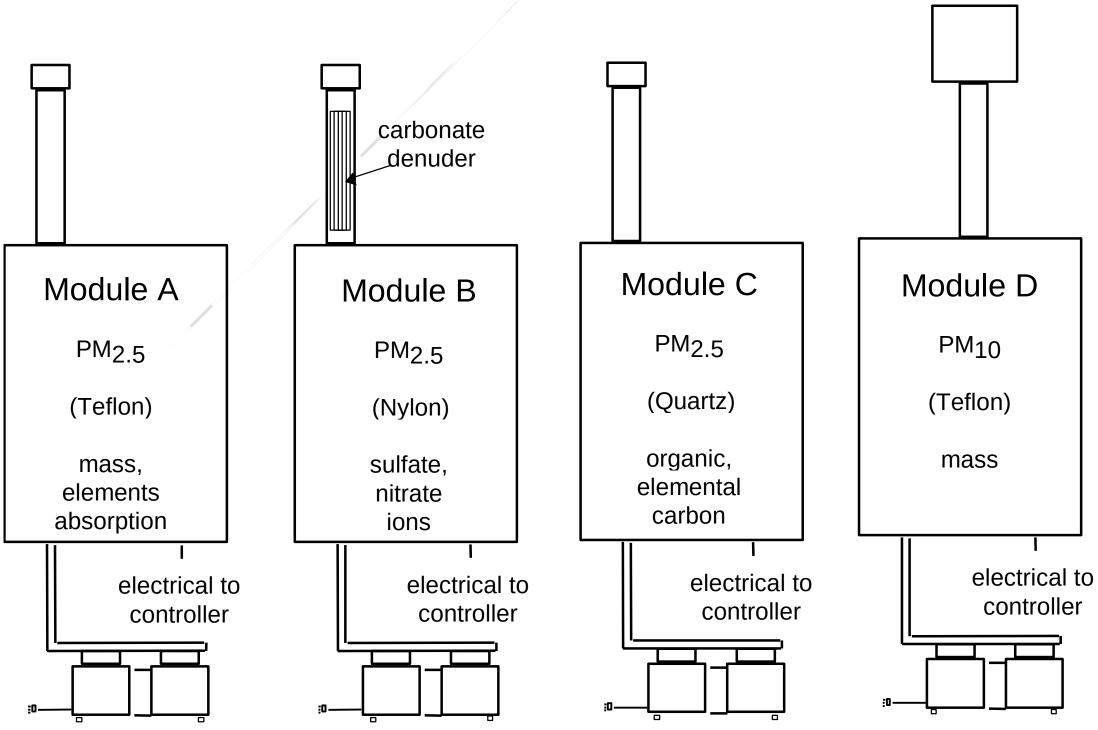

Figure 5. IMPROVE Sampler Modules: A (PTFE), B (Nylon), C (Quartz), and D (PTFE).

Table 6. IMPROVE Sampler Modules and Filter Media: Module (Filter), Analysis Performed, and Parameters Measured.

Module (Filter)	Analysis Performed	Parameters Measured
A (PTFE)	Gravimetric, HIPS, XRF	$PM_{2.5}$ mass, coefficient of absorption (f_{abs}) Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Pb
B (Nylon)	IC	Nitrate, Nitrite, Sulfate, Chloride
C (Quartz)	TOR/TOT combustion	Carbon in 8 temperature fractions
D (PTFE)	Gravimetric	PM_{10} mass

Hybrid Integrating Plate/Sphere (HIPS); X-ray Florescence (XRF); Ion Chromatography (IC), Thermal Optical Reflectance/Thermal Optical Transmittance (TOR/TOT)

5.1.2. IMPROVE Site Selection

Sites are selected to provide regionally representative samples with minimal influence from local emission sources. Distance and elevation criteria were used: all class I areas should be within 100 km of a current or potential site, whose elevation lies between the highest and lowest elevations of each area represented by the site, with a permitted variance of 100 feet or 10%. The siting criteria are described in detail in SOP 126 (http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdavis_sops/select22.pdf).

Once potential sites have been found to meet the siting criteria, the local FLM, or other persons leading the initial search send photos, sketches, and siting information for each potential site to CNL. CNL distributes summaries to all parties involved in the selection.

FLMs, air quality agencies, and CNL make a joint decision on where to locate the sampling site. If significant disagreements exist between the concerned parties, CNL prepares a summary for the IMPROVE Steering Committee that discusses each siting alternative and the tradeoff between them. The IMPROVE Steering Committee will work with the parties to reach a decision.

The local FLM/agency completes the necessary paperwork required to use the site, installs power, and builds a suitable structure. This includes obtaining any needed permission to use the property, preparing and submitting any environmental impact reports, and obtaining any needed authorization to install and use electrical power.

5.2. Sampling Methods

5.2.1. IMPROVE Sampler

The IMPROVE sampler operates with a flow rate of 22.8 L/min at local temperature and pressure for modules A, B, and C. The D module flow rate is 16.9 L/min.

In September of 1999, IMPROVE sites began conversion to the version II sampler. The version II IMPROVE sampler measures the flow rate and volume more accurately, is more flexible, and is easier to operate than the original sampler, while retaining the same collection characteristics.

The version II IMPROVE controller is shown in Figure 6Figure 6. It includes a microprocessor and a keypad with display. The flow rate and temperature are read every minute and a 15-minute average is recorded on a removable memory card. The memory card is shipped between the site and the central laboratory with each shipping container.

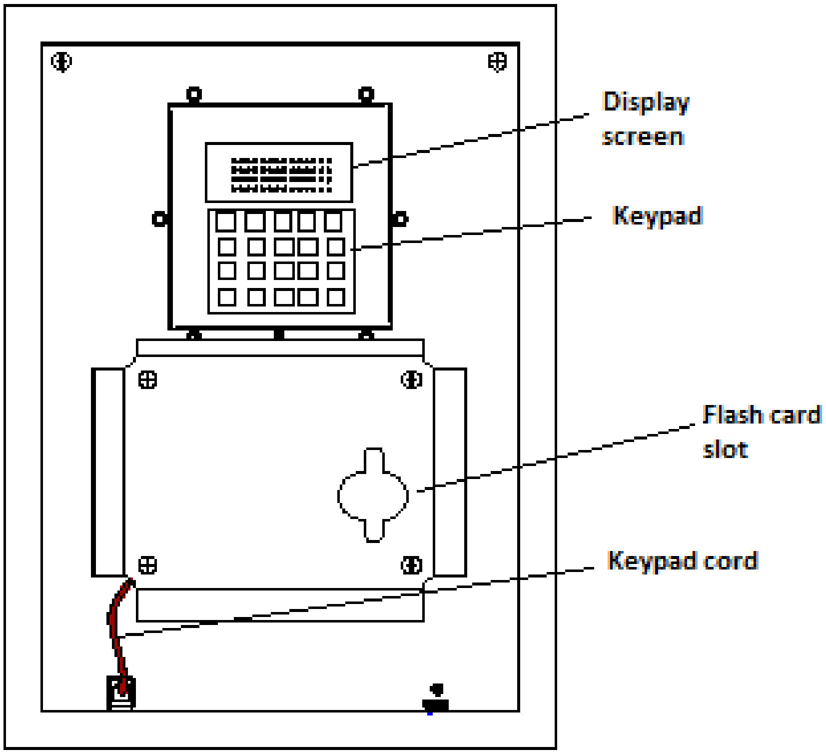

Figure 6. IMPROVE Version II Control Module.

PM$_{2.5}$ Sampler (Module A, B, and C)

The PM$_{2.5}$ module is shown in Figure 7. Each PM$_{2.5}$ module contains a cyclone (to separate out particles larger than 2.5 µm), 4 solenoids, a critical orifice flow controller, 2 flow gauges, an inlet stack, and associated electronics. The Nylon module (B) inlet contains a denuder to remove nitric acid vapor. Each module measures 16” × 12” × 7” and weighs 40 pounds. The air stream at the filters goes vertically up. Four vacuum pumps provide airflow through the filters. All the filters are pre-loaded into cassettes and the cassettes into cartridges at the CNL sample laboratory. Each module has a separate color-coded cartridge.

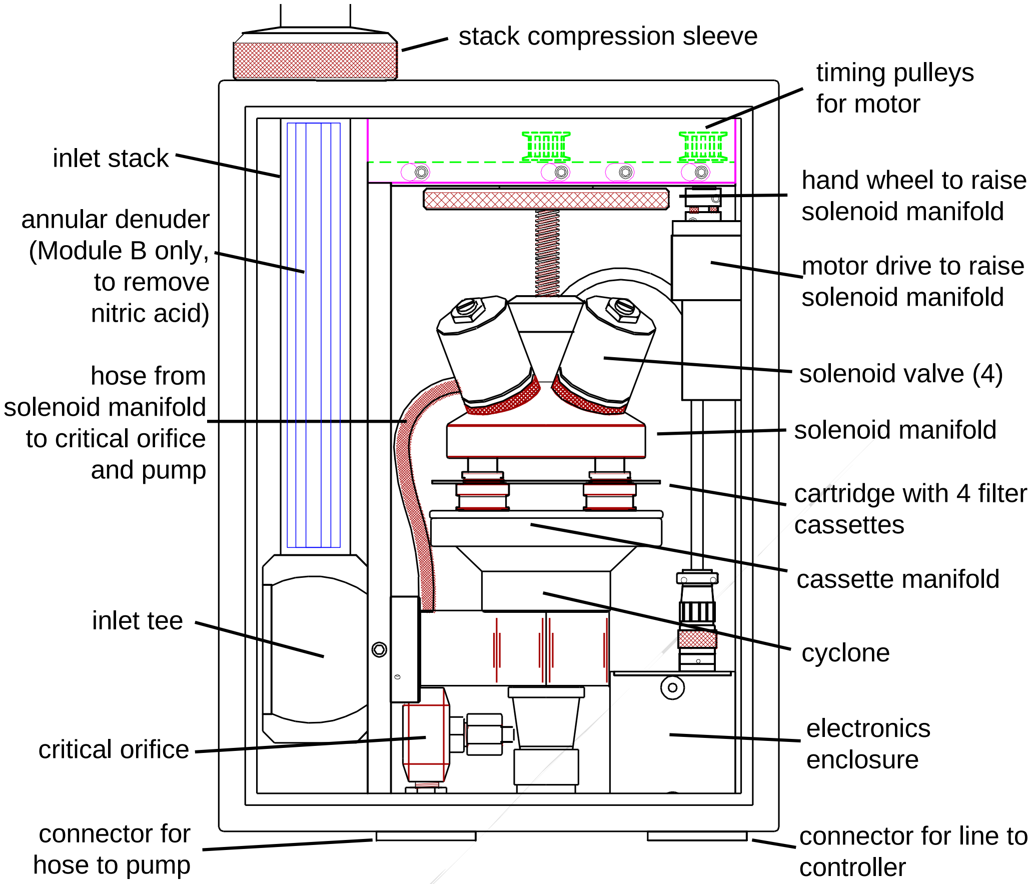

Figure 7. IMPROVE $PM_{2.5}$ Sampler Module.

PM_{10} Sampler (Module D)

The PM_{10} module is the same as a $PM_{2.5}$ module, except that the inlet and cyclone are replaced by a commercial PM_{10} inlet and the air stream at the PM_{10} filters goes vertically down.

5.2.2 Sampling Media

The filter media are summarized in Table 1Table 7. Section 5.3.1 covers purchasing and acceptance testing.

Table 7. IMPROVE Module Sample Media.

Module (Filter)	Media	Diameter	Supplier
A or D (PTFE)	Teflo™	25 mm	Pall Corp.
B (Nylon)	Nylasorb™	37 mm	Pall Corp.
C (Quartz)	QAT-UP quartz-fiber	25 mm	Pall Corp.

PTFE filters

Teflo™ Filters (for Gravimetric, HIPS, and XRF analysis) are supplied in packs of fifty. The filters are 25mm stretched PTFE mesh filters with pore size 3.0 μm, and a rigid olefin ring support.

Nylon filters

Nylasorb™ filters (for Ion Chromatography analysis) are 37mm in diameter with a 1.0μm pore size. Filter media are contained in plastic bags and stored in a refrigerator.

Quartz filters

QAT-UP quartz-fiber filters (for TOR/TOT combustion analysis) are supplied in boxes of approximately one hundred. The quantity in each box varies because filters with holes or manufacturing defects are discarded. DRI purchases and pre-fires the quartz filters at 900°C for at least four hours in accordance with in-house procedures. DRI tests a portion of the pre-fired filters for contamination. DRI ships the carbon filters to CNL in a cooled container. The filters are shipped in plastic containers and stored in a freezer.

5.2.3 Sampling Operations

The instructions for changing samples are detailed in SOP 201, Sampler Maintenance by Site Operators. The instructions include a troubleshooting guide to diagnose and fix common sampler problems.

The controller reads the sensors and displays the values for the operator to record on the log sheet, shown in Figure 8. The operator removes the cartridges with exposed filters and installs the new cartridges. Every third week the operator removes one cassette from the old cartridge and places it in the new cartridge. The controller then displays the new flow values for recording.

The general duties for the site operator are:

- To receive a shipping box containing 3 re-sealable, labeled bags, each containing filters for one week and the corresponding log sheet. Each bag contains a color-coded cartridge for each module; each box contains a data storage memory card.

- To verify the correct dates on the boxes and bags; and initiate the sample changing sequence via the controller's keypad.
- To record Final Readings for each of the filters; and to log additional information including date, time, temperature reading, operator's initials, and comments on any anomalous events (i.e. pump noises, extreme sampler pressure values, equipment malfunction, missed sample changes, or sample interference such as forest fires).
- To remove the old cartridges and replace with the current cartridge.
- To remove the old memory card and replace with the current memory card when needed.
- To record Initial Readings of the newly installed filters.

If there are any questions or difficulties with regular sampling, site operators call the CNL field operations group. Operators also call if there are any equipment malfunctions, improper labeling of cassettes, or if readings are outside of site-specific, acceptable ranges.

The telephone number for the CNL sample-handling laboratory is provided both on the sampler manual and on the Field Sample Log sheet. We provide a person for telephone response from 8 a.m. to 5 p.m. Pacific time every workday. A voice-mail system is available at other times. The site operators receive prompt and courteous responses to any questions or problems, from procedures to sampler malfunctions.

IMPROVE Network Field Log

Preweighed by:ABC
12/25/1999

INSTALL ON --> **ACAD1 01/18/2000**

CurTemp_____C

INITIAL READINGS **FINAL READINGS**

Operator's Initials______ **Date:____/____/1999**
Time:________

Init____ **Date:____/____/1999**
Time:________

SamDate	StrTim		MxVac	Cass	Vac	Mag	Vac	Mag	ET
**********	**********	**********	**********	**********	**********	**********	**********	**********	**********
01/19/2000	0000			1	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
		Mod A	__ __ __						
01/22/2000	0000			2	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
01/25/2000	0000			3	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
**********	**********	**********	**********	**********	**********	**********	**********	**********	**********
01/19/2000	0000			1	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
		Mod B	__ __ __						
01/22/2000	0000			2	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
01/25/2000	0000			3	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
**********	**********	**********	**********	**********	**********	**********	**********	**********	**********
01/19/2000	0000			1	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
		Mod C	__ __ __						
01/22/2000	0000			2	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
01/25/2000	0000			3	__ __ __	__ __ __	__ __ __	__ __ __	__ __ __ __
**********	**********	**********	**********	**********	**********	**********	**********	**********	**********
01/19/2000	0000			1	__ __ __		__ __ __		__ __ __ __
		Mod D	__ __ __						
01/22/2000	0000			2	__ __ __		__ __ __		__ __ __ __
01/25/2000	0000			3	__ __ __		__ __ __		__ __ __ __

Lab Use Only
TFF M11681
10.911
10.822
10.302

comments:

For Help Call (530) 752-1123

Figure 8. IMPROVE Network Field Sample Log Sheet and custody form.

5.3 Sample Handling and Custody

The filter preparation and sample handling is done in a dedicated sample handling facility at CNL. A flow diagram of the sample-handling process is shown in Figure 9. The sample handling procedures are described in detail in SOP 251 (Sample Handling).

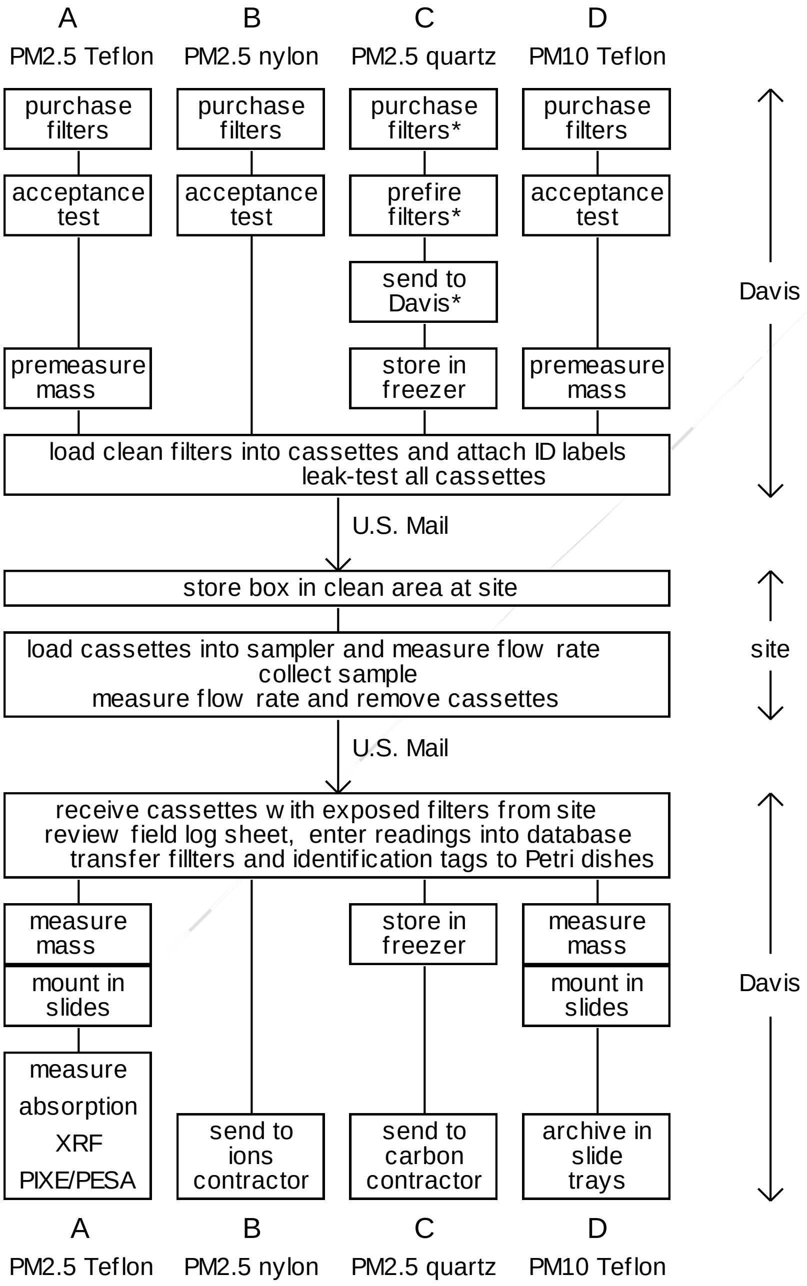

Figure 9. IMPROVE Sample Handling.

5.3.1 Purchasing Filters and Acceptance Testing

PTFE and nylon filters are purchased by CNL and quartz filters are purchased by DRI. Each sampling module requires around 20,000 filters per year for network operations, including blanks. Filters are purchased approximately once a year so that a year's worth of filters will come from a single manufacturing lot.

All filters undergo acceptance testing before a new lot is used to ensure minimal contamination as well as physical consistency. About a dozen filters of each type are selected for each test. The flow resistance of each new PTFE filter lot is measured at CNL, as well as XRF and HIPS analysis to check for contamination. The flow resistance of nylon filters is measured at CNL and RTI also subjects nylon filters to ion chromatography analysis to check for contamination. DRI purchases the quartz filters and they analyze some from each lot both before and after pre-firing to check for contamination.

The details of filter purchasing and testing are provided in Technical Information document TI 251C (Filter Inventory and Acceptance).

5.3.2 Load Clean Filters

The sample handling computer code maintains a record of how each cassette should be loaded, including field blanks and secondary quartz filters. The computer also maintains a record of every action, the time, and the name of the technician. Following the explicit instructions on the computer screen, the clean filters are loaded into the appropriate cassette within the sampling cartridge. Each cassette is identified with a unique tag: five-digit alphanumeric site code, sample date, and module type. The labels are prepared by the computer and placed on the cartridge next to the appropriate cassette. This is the method used to maintain the identity of each filter/sample.

Each cartridge is identified with a color-coded label to indicate module type (A, B, C or D). The cassette tags on the cartridge also indicate the correct module and date.

The cartridges for a given sample week are placed in a re-sealable bag that is labeled by the site code and date of installation, which is generally a Tuesday. This is generally different than the sample dates on the labels attached to the cartridges. The field log sheet is included in the bag. The three bags for a given cycle are placed inside shipping boxes. Prior to shipment, the laboratory manager checks the contents and dates of each box against the correct information listed by the computer.

A shipping container was specifically designed to transport a three week supply of sampling materials between CNL and the sampling sites. On the front there is a mailer with a reversible prepaid mailing label. The CNL address is on one side of the mailer, while the site address is on the other. Each shipping box is assigned to a given site. For each site there are two shipping boxes in the system. A few sites with long transit times have three boxes.

5.3.3 Transport and On-Site Storage

Each shipping box is identified with a site ID and with the dates the cartridges are to be installed. The container is received one to two weeks prior to the first installation date.

Most shipments are by United Parcel Service (UPS), but a few remote locations without UPS service use First Class US Mail. The boxes are not shipped with cold packs.

The site operators receive and store the shipping boxes in a clean location, either near the office or close to the field site. Acceptable storage locations are either indoor office space or onsite sampler housing units.

The number of days that the clean and exposed filters are either in shipment, stored at the site, or are in the sampler are listed in Table 8.

Table 8. Days the filter is in shipment, in storage at the site, or in the sampler.

filter in cycle	clean filter	exposed filter
filter 1	15 days	22 days
filter 2	18 days	19 days
filter 3	21 days	16 days
filter 4	24 days	13 days
filter 5	27 days	10 days
filter 6	30 days	7 days
filter 7	33 days	4 days

5.3.4 Handling Onsite

Each shipping box contains the filters for three weekly changes. All three installation dates are labeled on the box. Inside the box are three labeled, sealed bags, one for each sample change date. In each bag are four cartridges, one for each module, and one field log sheet. The operator always brings the box with the clean filters. On two out of every three weeks, this box also contains the empty bag with the date of last week's installation. Every third week, the operator must bring a second box, one for the exposed filters and one with the clean filters. A detailed description of the onsite sample changing procedure can be found in SOP 201 (Sampler Maintenance by Site Operators).

5.3.5 Receiving Boxes and Log Sheet Information

When exposed cassettes are delivered from the site to CNL, a lab technician arranges the boxes on the countertop in the IMPROVE shop area, opens each box, removes the log sheets, checks that the dates on the log sheets match the dates on the filter cassettes. All of these materials are placed in a plastic tub, one for each site, and are transported to the sample handling laboratory. The shipping boxes, often dusty from the field, are not taken into the clean sample handling laboratory.

The lab manager downloads the collection data from the memory card. The computer checks for incorrect data and allows the lab manager to delete or correct specific values. The lab manager then compares the field log sheet with the data from the memory card, displayed to look like the log sheet. If the memory card is missing or damaged, the data from the log sheet is entered in the computer. If there are any errors or problems, they are noted in a comment field or documented in the Jira® ticketing system. If necessary, the site operator is called.

Lab technicians clean the outside of the shipping boxes and verify that a 1-1/2" × 3" white tag is mounted on the right side of the box to allow postal authorities to affix required postage. Prepaid mail labels are reversed, exposing the 'send to' address. Shipping boxes remain at CNL awaiting the next shipment to the field.

5.3.6 Unloading Nylon and Quartz Filters

Nylon and quartz filters are removed from their cassettes and are shipped for analysis to RTI and DRI, respectively. Each filter is placed in its own Petri dish and the Sample Identification label is transferred from the cassette to the Petri dish. The Petri dishes are placed into a white Petri shipping tray that contains fifty Petri dishes. Each tray is labeled with the site and sample date of the first and last filters in the box and the filter type: B (Nylon) or C (Quartz).

5.3.7 IC and TOR/TOT

The quartz and nylon filters are shipped to the respective contractors approximately once a week, in batches of approximately 400 filters. Sample lists with the site and date of each filter in the tray are printed and included with the filters. Electronic sample lists are emailed to the analysis contractor and samples are shipped via UPS or Federal Express.

5.3.8 Unloading PTFE filters

The A and D module (PTFE) filters are weighed and placed in Petri dishes. A module filters undergo subsequent non-destructive analysis by XRF and HIPS. After all analyses of the A filters are completed, the A and D filters are archived indefinitely in a clean, but not climate controlled, environment.

5.3.9 XRF and HIPS

A module (PTFE) filters in their Petri dishes are placed in 50-position trays and are taken for analysis to the XRF lab and then to the HIPS lab. “Tray files” (computerized records of filter ids and position in a lot or batch) are created in the sample handling lab listing the position of each filter in the tray. These tray files are transferred to the XRF and HIPS computer systems to maintain the identification of each filter through each step of the analysis.

5.4 Analytical Methods

The analytical methods used for IMPROVE filters are described in detail in the various SOPs, which can be accessed through the IMPROVE website:

http://vista.cira.colostate.edu/improve/Publications/IMPROVE_SOPs.htm

The methods applied to the filters from each module are listed below.

A Module (PTFE filter)

- Gravimetric mass – contained in SOP 251 (Sample Handling) and related TI documents
- X-Ray Fluorescence analysis for 24 reported elements – SOP 301 (X-Ray Fluorescence Analysis) and related TI documents
- Hybrid Integrating Plate/Sphere (HIPS) analysis for optical absorption of filter samples – SOP 276 (Optical Absorption Analysis) and related TI documents

B Module (Nylon filter)

- Ion Chromatography analysis for four reported anions – RTI Ion SOP

C Module (Quartz filter)

- Thermal Optical Reflectance/Thermal Optical Transmittance analysis for the components of organic and elemental carbon – DRI Method IMPROVE_A SOP

D Module (PTFE filter)

- Gravimetric mass – contained in SOP 251 (Sample Handling) and related TI documents

5.5 Quality Control

5.5.1 IMPROVE Sampler Quality Control

Sampler airflow precision is monitored in three ways.

(1) The history of flow rates for each pressure transducer located in the air flow path is examined at least once a month to monitor for changes in performance. The baseline value, typically expressed in units of millivolts for the calibrated flow rate, is established when the field technician recalibrates the samplers every two years, or when a calibration is required due to a sampler malfunction or the observation of significant drift from the original baseline setting.

  a. Transducer readings are recorded on a memory card and inspected by a lab technician upon return to CNL.
  b. The operator also logs key performance parameters for each sampling cartridge exchange. These values are reviewed for indicators of malfunction

(2) The comparison of equivalent measurements by different modules is performed once a quarter as part of data validation. Disagreements among variables can sometimes be traced to flow rate irregularities. The most precise test is the comparison of sulfur from Module A with sulfate from Module B. A less precise comparison is between $PM_{2.5}$ mass from Module A and PM_{10} mass from Module D.

(3) Field flow calibrations are conducted by a CNL field technician at least once every two years during site maintenance visits, and when there is a potential problem with flow measurements. The calibration device is an orifice meter used to measure the pressure drop across the orifice. All calibrations consist of comparison of the system transducer readings with the flow rates of the calibration device at four different flow rates covering the normal range encountered. If the correlation between the calibration and system flow rates has an R^2 value less than 0.99, then the calibration is redone. If the nominal flow rate (flow rate with a normal clean filter) is not within 5% of the desired nominal values, the nominal flow rate is adjusted and a new calibration is performed.

If the calibration results are not within 5% of the previous calibration results, the past data are reviewed to determine when the change occurred. This is determined by examining the comparisons between similar concentrations measured by separate modules (sulfur vs. sulfate). If no change date can be identified, the samples collected between the two calibrations will be flagged as QD (questionable data) and will be examined further during data validation. The new calibration is applied to all samples collected after that change.

Sampler calibration accuracy is maintained by referencing all field calibration devices to a DryCal Nexus DC-2 Flow Calibrator that is certified NIST traceable. The results are verified using a dry gas meter. The field manager maintains a set of calibration orifice meters for field and mail calibrations. All calibration devices are calibrated at UCD using the same reference flow calibrator. The calibration of each calibration device is verified before and after each calibration.

5.5.2 Gravimetric Quality Control

Temperature control is through a central heating/air conditioning unit used for the entire building. The temperature is set at or near 22˚C and stays mostly within a ±3˚C range.

Due to the central air processing system, relative humidity is not a controlled parameter and usually ranges between 20-50%.

Temperature and relative humidity in the weighing room are monitored but there are no strict acceptance criteria. The data are collected as 5-minute averages, 24 hours a day. The 5-minute averaged data can be used to calculate the mean and standard deviation of the temperature and humidity during each 24-hour period. Large excursions from the ranges quoted above are extremely rare.

Lab blank filters check the performances of the gravimetric analysis systems over the typical period between pre- and post-weighing of filter samples. Lab blank filters monitor the artifact collection of filters in cassettes. They also provide a twice daily check of the correlation between the two microbalances used in filter processing.

A fresh control filter is weighed on both balances in the morning and afternoon twice a week after test weights are measured. It is then placed in a cassette and stored for 33 days. A second control filter, weighed 33 days previously and stored in a cassette, is removed from the cassette and also weighed on both balances. More detailed instructions can be found in TI 251B.

The lab blank filters facilitate determination of the following:

- Any change in the equivalency of the two balances. The balances should produce filter weights that are within ±0.003mg of each other. If the weights do not agree well, the problem is noted and metallic test weights are checked.
- Any change in either microbalance between morning and afternoon.
- Any shift in readings between the pre-weights and post-weights for an ambient sample. As pre and post weights are performed about five weeks apart, a drift or shift in either balance could lead to erroneous gravimetric measurements. Lab blank filters provide a daily record of balance consistency.
- The uncertainty of the analysis. The difference between the morning weights and the afternoon re-weights provides an estimate of the precision of each microbalance.

At the beginning of every work week, ten lab blanks and four filters sampled in Davis (containing particle deposits) are weighed on both balances. The weights are recorded in the SQL database. These filters are tracked to see how the mass differs over time for clean and sampled filters.

5.5.3 HIPS Quality Control

Several checks throughout the laser analysis process ensure that the laser data are as accurate as possible.

Before the filters are analyzed by the HIPS system, they are checked to ensure that the integrity of the filters remains acceptable and that any terminal status filters have been removed. The electronic tray files are compared to the contents of the slide trays to confirm that the order of filters is correct before the filters undergo analysis.

A reference filter tray is run before reanalysis and routine analysis can occur. The values for the reference filters must be within ±3% of their reference values before the process can continue. After this, a reanalysis tray is analyzed. The coefficient of determination (r^2) between the assigned reference values of the reanalysis set and the results obtained from running the reanalysis set should be at least 0.90 for each independent variable (T, R and calculated b). For details refer to TI 276D, "Quality Assurance and Quality Check of Analysis of $PM_{2.5}$ Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption." Once the criteria for both the reference and reanalysis filters have been met, routine HIPS analysis of IMPROVE samples can begin.

After every five trays of routine filters, the HIPS system is readjusted using position 3 of the standards tray in order to maintain accurate results throughout analysis.

Files are reviewed by the technician and the laboratory manager before being released for upload to the SQL server.

5.5.4 XRF Quality Control

Quality control for the XRF analyzers consists of the following checks (see the details in TI 301E):

- Checking the performance of each analyzer against a multi-element reference material which is analyzed daily,
- Checking the performance of each analyzer with selected PTFE and Nuclepore blanks which are analyzed daily,
- Re-analyzing selected IMPROVE samples (currently 16) and one NIST SRM 2783 on each analyzer on a monthly basis and following each element calibration to evaluate long-term reproducibility and inter-analyzer performance, and
- Performing regular analysis of field blanks (FBs).

Control charts of the daily checks for PTFE blanks, Nuclepore blanks, field blanks and ME reference materials are updated automatically and inspected routinely. The reanalysis charts are updated monthly, after the reanalysis is performed.

5.5.5 Ion Chromatography Quality Control

Two different sources of NIST traceable certified standards are purchased for the preparation of calibration and quality control (QC) standards. Calibration and QC standards are prepared by conducting serial dilutions of the concentrated standards purchased from outside vendors. QC samples are analyzed at the beginning and end of the sample queue and after every ten samples to ensure instrument stability. A matrix spike is a separate aliquot of a sample spiked with known concentrations of analytes of interest. Three duplicates and two matrix spikes are included with each batch of 50 samples. Upper and lower control limits for QC standards and matrix spikes are set at ± 10%. The acceptance criterion for duplicates is based on the sample concentration. Near the detection limit variability will increase and therefore limits are ± 100%. For sample concentrations greater than ten times the detection limit acceptable ranges are ± 10%. If QC standards fail limits, samples bracketed within the failed QC standards will be reanalyzed. QC fails occur infrequently: roughly 1% of analysis batches fail.

The concentration of all variables is determined from the measured mass, the median artifact from designated field blanks, and the volume. The uncertainty includes volume uncertainty, instrument calibration uncertainty, and the standard deviation of the field blanks.

The best estimate of the total analytical precision is the standard deviation of the difference between the measured values of the QA standards and the predicted values, recoveries of spiked samples, and differences between duplicate samples.

5.5.6 Thermal Optical Reflectance/Thermal Optical Transmittance Quality Control

The concentration of all variables is determined from the measured mass, the monthly median artifact from field blanks, and the volume. The uncertainty includes volume uncertainty, analytical normalization uncertainty, and the standard deviation of the field blanks.

The precision of carbon analysis has been reported as 5% for total carbon (TC; Chow et al., 1993). For analysis of actual ambient and source filters, homogeneity of the deposit is most important for reproducible results. This can be demonstrated by the precision of CH_4 standard injection (by computer-controlled auto-injections), which is always better than sample analysis. For homogeneous deposits containing > 5 µg/cm^2 (~10 times MDL) TC, precision is generally 10% or better; for inhomogeneous deposits replicates may differ by as much as 30%.

The precision of the laser-dependent split between OC and EC fractions depends upon particle loadings and particle composition. Typically, relative laser split times are reproducible within 10 seconds and deviations in calculated splits are < 5% of the total measured carbon. If the laser split is greater than 10 seconds and deviations are > 5%, the analysis is investigated for sample anomalies (e.g., inhomogeneous loading, low or high loading, etc.), instrument laser noise, or O_2 contamination. Most of the uncertainty for low concentration samples is from the standard deviation of the field blanks. Poor laser precision is also found for heavily loaded samples while the initial laser response is relatively unstable. Uncertainty is not determined by precision at these levels.

The relative analytical precision of TOR/TOT is determined by the analysis of a second punch in the sample. This precision depends on the normalization of the analysis, and on the uncertainty in the temperature and in the optical measurement. For total carbon, there is no temperature/optical separation and the precision depends on the ratio of the flame ionization detector (FID) response to a reference level of methane (CH_4) automatically injected at the end of each sample analysis cycle. The separation into organic and elemental carbon also involves the uncertainty in optical measurements. Because the concentrations of elemental carbon are much less than for organic carbon, the effect of the uncertainty in the optical measurements on elemental carbon is larger than on organic carbon. Most of the uncertainty for organic carbon is from the normalization. Most of the uncertainty for elemental carbon is from the optical measurement. The goal is to achieve a 10% relative analytical precision for organic and total organic carbon, and 20% for elemental carbon.

5.5.7 Field Blanks

Field blanks are used to estimate the background contamination on sample filters. With the introduction of the PANalytical XRF instruments in 2011, the median monthly PTFE field blank loading for each element is subtracted from the sample loadings to correct for background contamination. Prior to that only spectral background subtraction was performed by the XRF software. The nylon field blanks are used to estimate the artifacts of the ionic species, and the quartz field blanks are used to estimate the artifacts of the carbonaceous aerosol. The blank values are generally small compared to those on ambient filters, but are not negligible.

The field blank cassette is identical to the normal cassette and placed in the same cartridge. The controller does not allow any air to pass through the field blank. No special treatment for field blanks is needed at the site. The field blanks go through normal sample handling and analysis.

Field blanks for all four modules are prepared at a rate of at least 2% of the normal field samples. This provides about 100 field blanks per quarter for 160 sites.

5.5.8 Site Collocation

The IMPROVE aerosol samplers consist of four modules within a given sampler—referred to as A, B, C, and D. Beginning in 2003, IMPROVE installed single collocated modules (either A, B, C, or D) at different sites. Phoenix has a complete duplicate sampler. Prior to 2013 there were seven duplicate modules of each type (A, B, C, and D); since IMPROVE operates approximately 164 sites, this was equivalent to collocation at 4% of the sites. In 2013, due to budget cuts the number of collocated modules was cut to four of each type, about a 2% collocation percentage.

5.6 Instrument/Equipment Testing, Inspection, and Maintenance

5.6.1 IMPROVE Sampler Testing and Maintenance

When a malfunction occurs, the CNL field staff will first try to isolate the problem over the telephone. When possible, they will suggest methods for remedying the problem. The components in the IMPROVE sampler are generally easily removable. If the problem is a malfunction of any of these removable components, the CNL field staff will ship a new component to the site via express mail and have the defective item returned to CNL. The next step is to ship a complete new sampling module. As a final resort, a staff member will travel to the site to make appropriate repairs.

On biennial site visits, a field technician checks all sampler functions, including solenoid action, vacuum pressure, keypad function, and electronic control. The technician also cleans the inlet head, inlet stack, internal cyclone and resets system clocks. Any worn or damaged parts are replaced. The flow rates are calibrated, and if necessary adjusted. The field technician also reviews the sampler procedures with the site operator and trains new operators where needed.

Equipment testing is performed at the CNL Field Test Station on the UCD campus. Any modification of the sampler is tested before being used in the network.

5.6.2 Gravimetric Laboratory Maintenance

To reduce dust levels in the sample handling room and to prevent filter contamination, inlet air coming through the vents into the room must pass through high efficiency filters that are changed every 4-6 months. Air deflectors are placed on the vents to direct the air away from the balances. Entrance into the laboratory requires walking over a clean room floor mat to capture dust and foreign particles. The room is cleaned twice a week. This includes cleaning the floors with a high efficiency HEPA vacuum and wiping down all counter surfaces with reagent grade alcohol and Kimwipes™. One day a week the floor is also cleaned with a Swiffer® to help eliminate any residue that cannot be removed with the vacuum. These procedures reduce the possibility for contamination should a filter fall to the work surface. Following the cleaning, no analysis shall occur for at least 12 hours to reduce the potential for contamination of filters by compounds used in the cleaning process.

5.6.3 HIPS Maintenance

No special maintenance is required. Instrumentation is cleaned and repaired if precision check is not within data quality objectives.

5.6.4 XRF Maintenance

No special maintenance is required by CNL staff. CNL maintains a service contract with the instrument manufacturer, PANalytical, and a PANalytical service technician visits CNL twice a year to perform routine maintenance and cleaning of the instruments.

5.6.5 Ion Chromatography Maintenance

Analytical instrumentation used in this project will be carried through preventative maintenance procedures and schedules as recommended by the manufacturer. The following checks are completed for each day that instruments are operated:

- Check for leaks at all valves and column fittings.
- Wipe-up liquid spills and salted-out chemicals.
- Record the background conductivity and pump pressure and check it against previous days in the log book.
- Verify that helium pressure is stable and that the tank is not empty.
- Compare standard chromatographs and verify peak resolution by calculating the recovery of standards. The recovery should be within 10% for all analytes.

5.6.6 Thermal Optical Reflectance/Thermal Optical Transmittance Maintenance

Regular maintenance for the carbon analyzer involves daily checking of compressed gas supplies, cleaning the punching tool, glass disc, and tweezers between each sample with dry KimWipes (Kimberly-Clark Corporation), performing twice daily calibrations based on the SOP calibration schedule, performing leak and flow checks, and backing up data files on a daily basis. Checks of laser and FID response (physical and electrical) are made daily; and full analyzer calibrations are performed every six months or after major maintenance or repairs. All calibrations and repairs must be recorded in the individual analyzer log book and documented in on-line maintenance tracking system.

5.7 Instrument/Equipment Calibration and Frequency

5.7.1 IMPROVE Sampler Calibration

The sampler's flow rates are adjusted and calibrated at the time of installation, during biennial maintenance, and whenever flow rate problems dictate a new calibration. The calibration device is an orifice meter, which consists of an orifice and Magnehelic® gauge to measure the pressure drop across the orifice. The orifice is contained in a probe that is inserted at the base of the inlet stack. The calibration system is calibrated at CNL using a DryCal Nexus DC-2 Flow Calibrator that is certified NIST traceable.

At the time of installation, the nominal flow rates are adjusted to provide a flow rate of 22.8 L/min at 20°C with a typical filter in the cassette. Before any later re-adjustment, a 4-point calibration is performed. If the regression of the logs of these four points yields a correlation coefficient (R^2) less than 0.99, the system is recalibrated.

5.7.2 Gravimetric Calibration

The Mettler balances have been programmed using the proFACT function to automatically do an internal calibration every morning. During an internal calibration, the balances generate a 3-point calibration equation with two internal masses. The weights of these internal masses combined are in the range of 5-6 grams. At the start of the work day, lab personnel manually redo the internal calibration. Detailed information can be found in TI 251A.

The balances are calibrated annually by Mettler technicians, who compare the internal calibration weights against Mettler's own traceable weights and make adjustments to the electronics as needed.

5.7.3 HIPS Calibration

To initially calibrate the system, the HIPS reflectance sphere detector was adjusted to give the same value of reflectance, R, for a reference filter as the research sphere in the reflectance mode. The HIPS plate detector was adjusted to give the same value of transmittance, T, as the research sphere in the transmittance mode. This procedure ensured that the new HIPS system was equivalent to the old LIPM system and to the 6" research integrating sphere system for a wide variation of sample loadings and aerosol types.

The HIPS system was calibrated relative to a 6" research model integrating sphere (Labsphere). The research sphere was used to calibrate a set of 20 filters having mass loadings and compositions representative of those found in the IMPROVE aerosol sampling network. These 20 filters are used to perform a calibration check prior to each monthly run of IMPROVE field samples.

5.7.4 XRF Calibration

The 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.

The reference materials (standards) used for calibrating the Epsilon 5 consist of 47 mm Micromatter thin film foils on Nuclepore membranes (prepared by vacuum deposition), $PM_{2.5}$ deposits on PTFE membranes, and NIST Standard Reference Material (SRM) 2783 air particulate on polycarbonate filter membranes. Each type of reference material medium has a corresponding blank membrane that must be analyzed and used for blank subtraction.

Calibration of the Epsilon 5 XRF analyzers is performed using a subset of the available standards, selected for the elements reported for IMPROVE. First, the standards are selected in the instrument 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 then performs least-squares regression with the theoretical and measured intensities forcing the intercept to zero for each element. At least two standards for each element are required, preferably spanning the range of concentrations expected in the IMPROVE samples. The calibration factors (slopes of linear regression) for the elements are stored within the application on the XRF computer.

After each calibration, the element calibration factors must be copied and provided to the Database Manager for ingestion into the IMPROVE SQL Server database.

5.7.5 Ion Chromatography Calibration

The system is first flushed with eluent. Then a daily multipoint calibration is performed over the range 0.05 to 25.0 ppm Cl^-, NO_2^-, NO_3^-, and SO_4^{2-} followed by control/quality assurance (QC/QA) samples listed below:

- QC sample containing concentrations of Cl^-, NO_2^-, NO_3^- and SO_4^{2-} typical of those found in the mid-range of actual filter extract concentrations.
- QC sample containing concentrations of Cl^-, NO_2^-, NO_3^- and SO_4^{2-} typical of those found at the lower end of actual filter extract concentrations.

- Commercially prepared, NIST-traceable QA sample containing known concentrations of Cl^-, NO_2^-, NO_3^- and SO_4^{2-}.

If the observed values for Cl^-, NO_2^-, NO_3^- and SO_4^{2-} differ by more than 10 percent from the known values, the problem is identified and corrected before analyzing samples.

5.7.6 Thermal Optical Reflectance/Thermal Optical Transmittance Calibration

Four types of standards are used to calibrate the carbon analyzers: 5% nominal CH_4 in He, 5% nominal CO_2 in He, KHP (potassium hydrogen phthalate), and sucrose. Only the calibration gases are used on a daily basis as analyzer performance monitors. KHP and sucrose are used in conjunction with CH_4 and CO_2 semiannually to establish the calibration curve of each analyzer.

The calibration procedures for the carbon analyzers are of four types: 1) the end-of-run calibration peak; 2) the routine beginning and end-of-day calibration injections of He/CH_4 and He/CO_2 (or the auto calibration check using the *cmdAutoCalibCheck* command); 3) full instrument calibration, performed every six months, using KHP, sucrose, and the two calibration gases; and 4) temperature calibrations performed every six months using temperature-sensitive indicating liquids with different melting points.

The end-of-run calibration consists of a set quantity of He/CH_4 calibration gas which is automatically injected by the carbon program. All FID readings during the analysis run are normalized to this peak to minimize the effects of FID performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis run and requires no operator intervention. The integrated calibration peak counts should be checked by the operator immediately after each run to confirm that the analyzer is operating satisfactorily. Calibration peak area counts should be within an acceptable range (typically between 20,000 and 30,000 with minimal change between runs) for the specific analyzer. Check daily records to compare peak area counts and determine analyzer performance and stability.

Routine calibrations must be performed at the beginning and end of each day, either manually or by using the automated routine calibration command (*cmdAutoCalibCheck*) in the *CarbonNetWork* database Command table.

Full instrument calibration, performed semiannually or after major maintenance or repairs, establishes the calibration slope used in converting counts to µg of carbon, as explained in the next section. Instrument calibration involves spiking pre-fired quartz punches with 5.0 to 20.0 µl of the 1800 ppm KHP and sucrose solutions and injecting 200 to 1000 µl of the CH4 and CO2 gases.

Temperature calibrations are performed semiannually on all instruments to verify that the sample temperature is as accurate as possible. Since it is not possible to sense the temperature of the sample directly, materials were sought that: 1) could be placed where the sample would normally be located, and 2) would cause sharp reactions when known temperatures were achieved. Quick-drying temperature-indicating liquids of different melting points, Tempilaqº G (Tempil, Inc., South Plainfield, NJ, USA), were used as temperature indicators in muffle furnaces. A Tempilaqº G set contains long-chain hydrocarbons suspended in an organic solvent, which change their appearance at 44 specific temperatures spanning 80-1000 °C. The accuracy of Tempilaq° G is certified within ±1% of its designated temperature and is traceable to the National Institute of Standards and Technology (NIST). Tempilaqº G is bottled in liquid form and dries quickly to a dull, opaque film when applied to a surface. As the surface is heated to the designated temperature, the film liquefies and is accompanied by a change of appearance that can be optically monitored to determine sample temperature.

5.8 Calculation of Concentration, Uncertainty, and MDL

CNL combines the analytical results, flow rate data, and elapsed time data to calculate ambient concentrations, uncertainties and MDLs for every parameter of every sample and records them in the database. These final values are determined from volumetric flow rates established from the measured temperature and atmospheric pressure estimated based on the elevation of each monitoring site. Full details, including the equations used for each type of variable, can be found in SOP 351 (Data Processing and Validation).

5.9 Inspection/Acceptance of Supplies and Consumables

The details of filter purchasing and testing are provided in Technical Information document TI 251C (Filter Inventory and Acceptance).

Acceptance testing is also performed on filter slide frames with each new batch ordered. Slide frames must close securely to ensure that filters do not fall out of the frames when they are handled.

5.10 Non-direct Measurements

Data required from non-direct measurements include site operator observations made each week. These observations are recorded on log sheets and entered into the database comments field.

5.11 Data Management

All IMPROVE data are housed and maintained in an SQL database at CNL. This database is fully relational. Data are added automatically through laboratory software and dynamic connections to laboratory instrumentation. Edits to the database are performed through software interfaces; only a few selected staff at CNL have permission to manually add or edit data. Additions and edits are recorded and time-stamped electronically in the database so there is a permanent history of all transactions.

The SQL database includes all primary IMPROVE data such as individual filter weights, sampler flow rate transducer voltages (15 minute averages), analytical results, and operator comments. Laboratory analytical results not produced at CNL (ions from RTI and carbon from DRI) are added to the SQL database once they are received at CNL.

Data analysts and laboratory staff at CNL use a variety of applications to interact with the database. Some applications are used to add data to the database, such as the laboratory software that interfaces the balances to the database and records the weighing results. Other applications query the database to produce plots and statistical summaries for use in quality control analysis and data validation. The database can also be queried in read-only mode through standard tools such as Excel.

Details of the data management system can be found in SOP 351 (Data Processing and Validation).

6. Assessment and Oversight

6.1 Overview

Regular assessments of the IMPROVE program are implemented to ensure that the data are meeting the primary objective of the IMPROVE program; namely, making high quality measurements of the concentrations and compositions of particles affecting visibility in class I areas. The specific chemical species related to this objective are described in Section 4.4. More detailed descriptions of each of these assessments are given in Section 6.2, with examples of specific attributes to be examined with each assessment. These criteria are subject to change over time based upon new QC measures and recommendations of the IMPROVE Steering Committee.

Table 6.1. Summary of Assessments

Assessment Type	Frequency	Focus of the Assessment	Organization Performing Assessment	To whom the results will be reported
Assessment of the Quality System	Every 5 years	Management of the QA program	Working Group identified by the IMPROVE Steering Committee (SC) Chair. Joint Report signed by Feds	EPA, IMPROVE SC
Network Reviews	Every 5 years	Size and spatial distribution of IMPROVE monitors	Working Group identified by the IMPROVE SC Chair. Joint report signed by Feds	EPA; IMPROVE SC
Technical Systems Audits of Field Operations	Subset of sites are audited annually	Monitoring Sites: Technical	NPS oversees auditing; Partners and independent contractors carry out audits	EPA; IMPROVE SC

Performance Audits of Field Operations	Annually	Monitoring Sites: Performance	NPS reviews data; IMPROVE Operations Contractor prepares report	NPS; EPA; IMPROVE SC
TSA of Laboratory operations	Every 3 years	Analytical Processes and procedures	EPA OAQPS	IMPROVE Contractors (laboratories), NPS and EPA OAQPS
Performance Evaluations of Laboratory Operations	Annually	Analytical Systems	EPA OAQPS	Contractors (laboratories), NPS and EPA OAQPS
Audits of Data Quality	ADQs were carried out during implementation phase of IMPROVE. No longer performed independently.	Quality of the Measurements	NPS; CIRA; SC Chair. [If an audit, report should be under supporting Fed(s) signature(s).]	EPA; IMPROVE Operations contractor; IMPROVE SC
Data Quality Assessments	Annually for data quality; Every 5 Years for program goals	Overall Data Quality, DQOS	NPS; CIRA; IMPROVE SC Chair; Contactor	Contractors; EPA; IMPROVE SC

6.2 Types of Assessments

Seven different types of assessments are implemented within the IMPROVE Program. Each assessment focuses on a specific aspect of the program, and combined the assessments evaluate all aspects of the quality system. A summary of assessments is given in Table 6.1; detailed descriptions are given below.

6.2.1 Assessment of the Quality System

Periodic assessments are carried out of the quality system described in the Quality Management Plan and QAPP. Assessments of the quality system emphasize organizational activities, and as such focus primarily on management policies and procedures used to plan, implement, assess, and correct the technical activities for IMPROVE. These assessments are intended to provide systematic reviews of all of the quality control measures of the IMPROVE program, in order to ensure that the quality assurance program is effective as implemented. These assessments place a high priority on ensuring that the Quality Control measures which are in place are fully documented. The final product of the Assessment of the Quality System will identify good practices within the existing quality system and will provide suggestions for improving quality assurance measures.

Although an Assessment of the Quality System may be broader in scope, it should at a minimum address the following questions:

- Are all quality control measures documented, up-to-date, and available (Includes SOPs, QAPP, QMP)?
- Have laboratory staff been trained to carry out the relevant QA/QC measures?
- Have site operators been trained to carry out the relevant QA/QC measures in the field?
- Are data that do not meet minimum QC standards identified in the released data sets?
- Does each contractor have a QA program in place and a QA manager to oversee their QA program?
- Have all of the assessments that are identified in Table 6.1 been carried out on their prescribed schedules?
- Have appropriate actions been taken to correct for weaknesses identified in any of the assessments given in Table 6.1?
- Is there adequate communication within the groups represented by the Steering Committee?
- Are sufficient resources available to carry out a robust Quality Assurance Program?

Assessments should include an objective grading system (e.g. Exceptional; Very Good; Average; Marginal; Poor) which is utilized for each area described above. The process, carried out by a working group of federal, regional and state shareholders, is overseen by the IMPROVE Steering Committee Chair and is conducted approximately every five years. Signatures on QSR reports will need to be by the supporting Federal Agencies due to this review being an inherent Governmental Function. The working group should consist of a minimum of two members who are familiar with the IMPROVE Program. The product of the Assessment of the Quality System is either a written report or a summary presentation using PowerPoint (or comparable software). In either case, results from Assessments of the Quality System will be presented to the Steering

Committee at the annual Steering Committee Meeting. It is the responsibility of the Steering Committee to utilize these data and to determine whether to recommend that IMPROVE implement any suggested changes.

6.2.2 Network Reviews

Network Reviews are intended to serve as a high level review of the IMPROVE Program, with a focus on evaluating the number and location of IMPROVE monitors. These reviews involve analysis of long term monitoring data from all sites, and intercomparison of these data to ensure that all class I areas (except Bering Sea Wilderness) are being effectively monitored as part of the IMPROVE Program. Regulatory objectives take highest priority, but other constraints, primarily related to budget, are also considered. For example, previous assessments have been carried out in response to budget cuts, with the goal of determining if the network could be reduced in size and still provide sufficient data to determine state compliance with the RHR. These assessments also evaluate potential relocation, removal, or addition of sites due to changes in pollution and meteorological conditions or shifts in people or resources affected by pollution. This process involves establishing a number of network criteria to rank the monitoring sites to determine which sites would have the least impact on national particulate matter and haze monitoring and compliance with the RHR. The process, carried out by a working group of federal, regional and/or state shareholders, is overseen by the IMPROVE Steering Committee Chair and is conducted approximately every five years. The working group should consist of a minimum of two members who have a technical knowledge of the IMPROVE Network and the necessary expertise to conduct a statistical assessment of the existing network. The product of the Network Reviews may either be a written report or a summary presentation. Results from Network Reviews are presented to the Steering Committee at the annual Steering Committee Meeting. It is the responsibility of the Steering Committee to use these data to determine if changes to the network configuration are warranted, and the responsibility of the Steering Committee, in conjunction with NPS, to ensure that any recommended changes are carried out.

6.2.3 Technical Systems Audits of Field Operations

Technical Systems Audits (TSAs) of Field Operations are intended to assess whether the IMPROVE sampling sites are run in compliance with the QAPP and incorporated SOPs. For the IMPROVE Network, these TSAs focus primarily on evaluating the sampling sites and the particle samplers in the field. In conducting a TSA, the auditor:

- Assesses whether the sampling site still meets siting criteria for an IMPROVE sampler (see SOP 126-2; Site Selection for IMPROVE), such as whether the site is still removed from local sources;

- Evaluates the integrity of the sampling structure, to ensure that samplers are securely mounted and that all electrical connections are insulated and securely fastened;
- Checks the flow of each sampling module using a NIST certified flow meter, to ensure flows fall within QAPP specifications;
- Observes and critiques the technique of the site operator collecting and retrieving samples, and resetting the sampler for the routine sampling events; and
- Asks the site operator to complete a questionnaire to ensure that (s)he has been trained, that all safety concerns have been addressed, and that the current IMPROVE Operations Contractor (currently UC Davis) is providing adequate support to run the site.

TSAs are conducted by IMPROVE partners (e.g. USFS, FWS, or EPA staff) and independent contractors (i.e. contractors other than three primary IMPROVE contractors, currently UC Davis, DRI, and RTI), and through 2014 these data were compiled and assessed by EPA. Beginning in 2015, NPS will oversee the TSAs; NPS will work with one of its collaborators (CIRA) to manage the TSAs and compile the data. TSAs are to be conducted each year on a subset of IMPROVE sampling sites. A goal is to complete TSAs at all sites over a 10 year time period, although some sites may be subject to multiple TSAs during this time period, especially sites exhibiting unusual samples/data. Results are summarized in an electronic format and shared with the IMPROVE Operations contractor as data become available, and presented annually to the IMPROVE Steering Committee and EPA. It is the responsibility of IMPROVE Operations contractor to address any minor problems noted in the audit. Major problems found during the audit will be addressed by a joint committee including the PI of the IMPROVE Operations contractor, the Steering Committee Chair, and Contracting Officer Representative at NPS.

6.2.4 Performance Audits of Field Operations

Performance Audits of Field Operations evaluate if data are being collected at each of the sites of a sufficient quantity to satisfy regulations. For the audit, recovery rate and completeness are examined for all sites in the network. As noted above, both are defined as the ratio of the number of valid samples divided by the number of possible samples. Recovery rate considers only the $PM_{2.5}$ PTFE filter while completeness considers all four filters. The recovery rate goal for the IMPROVE network is 90%; the completeness goal is consistent with the RHR, which is at least 75% completeness within a calendar year, at least 50% completeness within each calendar quarter, and no more than 10 consecutive samples lost for any given site. Recovery rate and completeness data are compiled by the IMPROVE Operations contractor, and the contractor reports these data to NPS quarterly for review. The contractor also presents an annual report at the IMPROVE Steering Committee Meeting. It is the responsibility of the contractor and NPS to identify sites which are not meeting data recovery goals. It is the responsibility of the contractor and the relevant FLM to identify causes for any collection shortfalls, and to find a remedy for problems.

6.2.5 Technical Systems Audits of Laboratory Operations

Laboratory TSAs are conducted by OAQPS triennially and involve a thorough, systematic, on-site, qualitative audit of facilities, equipment, personnel, training, procedures, record keeping, data validation, chain of custody, data management, and reporting aspects of a system. TSAs may also include the analysis of audit samples during the audit period. Network laboratories will be provided with a TSA checklist prior to the on-site audit that is based upon their approved QAPP and SOPs. Following the completion of the TSA, the OAQPS auditors will provide verbal feedback to the laboratory with suggested corrective actions, if required. A written report with findings and corrective actions will be provided to the laboratory within 30 days of audit completion. OAQPS will follow up with the laboratory to ensure any findings and corrective actions are implemented by the laboratory.

System Audit Components

- Assessment of Staff:
    - Background and education,
    - Chain of command regarding description of assignments and specific duties,
    - Continued training, and
    - Level of staffing.
- Assessment of Facilities:
    - Laboratory and support facilities,
        - Extraction and analysis procedures
        - Sample handling
    - Calibration and audit frequency, and
    - Documentation.
- Assessment of Data and Document Control:
    - Chain of custody,
    - Validation and processing procedures,
    - Reporting formats,
    - Storage, and
    - Documentation.

- Assessment of the Quality Control Programs:
    - Adequacy of procedures, and
    - Adherence to procedures.

6.2.6 Performance Evaluations of Laboratory Operations

A Performance Evaluation (PE) is a quantitative audit in which analytical results are generated by a measurement system for a sample that originates outside of a project. PEs of Laboratory Operations for IMPROVE are used to determine if the analytical systems used to analyze filter samples produce results that are within the measurement quality objectives specified in the QAPP. PEs are performed annually. A PE sample mimics the analysis of routine field samples in all possible aspects, except that its composition is unknown to the analyst and known to the auditor. For PEs of IMPROVE Laboratory Operations, OAQPS will assume responsibility for producing and distributing PE samples to the laboratories that analyze filter samples. OAQPS will report comparative results to the participating laboratories and NPS. Results will be presented annually at the IMPROVE Steering committee. EPA OAQPS will maintain a repository of these IC and XRF PE samples so that samples can be reanalyzed by the laboratories within 6 months following the PE event.

It is the responsibility of contractors to address any discrepancies identified as part of the PE. Upon correction of any noted problems, the contractor shall perform a follow up PE and the EPA OAQPS QAL shall again report results to the laboratory doing the reanalysis, NPS and EPA OAQPS.

6.2.7 Audits of Data Quality

Audits of Data Quality (ADQ) are examinations of data after they have been collected and verified by the contractors to determine whether the data were reported and transcribed correctly. ADQs include tracing data through their processing steps and duplicating intermediate calculations. For IMPROVE, ADQs are meant to verify that Level 1 and Level 2 validation have been applied to all data before it is released, thereby ensuring that the reported sample concentrations are accurate within the specifications described in this QAPP. ADQs occurred during the implementation phase of IMPROVE and are no longer performed. Data Quality Assessments, described next, have replaced ADQs.

6.2.8 Data Quality Assessments

Data Quality Assessments (DQAs) are statistical evaluations to determine whether the validated data obtained from the network are of the right type, quality, and quantity to support their intended use. DQAs help to determine the usability of the data and provide information on the effectiveness of the measurement systems used.

As described in Sections 4.8.3 and 7.1, intercomparisons are routinely conducted on the data to ensure self-consistency utilizing different measurement techniques, sometimes from separate laboratories, to compare similar parameters. For example, all data is examined to ensure that the elemental sulfur measurement made using XRF is comparable to the sulfate ion measured using ion chromatography within prescribed limits (section 7.2). Finally, as noted above, there are collocated samplers of each module type located across the network, allowing for direct comparison of parallel measurements. Data from each of these QC measures, as well as others described throughout the QAPP, are analyzed on an ongoing basis. Results of these analyses are summarized by the contactor and presented to NPS and the Steering Committee Chair twice per year, and are presented to the Steering Committee at the annual meeting.

A separate cooperator (CIRA) performs the same checks on all data submitted to the archive as part of the DQA. DQAs include comparisons of IMPROVE aerosol measurements to other networks' similar measurements and IMPROVE's optical monitoring data. DQAs also assess whether the DQO is being met; namely whether the data are of sufficient quality to measure a 4% change in b_{ext} between any two non-overlapping 5 year averages (see Section 4.5.1). These assessments are led by the IMPROVE Steering Committee Chair, in collaboration with NPS, CIRA, and CNL, and are typically done every 5 years. Results are reported to the Steering Committee. If the DQO is not being met, it is the responsibility of the Steering Committee to formulate a new strategy for meeting this objective.

6.3 Reports to Management

Results from the assessments described in Section 6.1 are primarily documented through PowerPoint presentations, which are presented to the IMPROVE Steering Committee and EPA at the annual IMPROVE Steering Committee Meeting. Other assessments involve short written reports or surveys, which beginning in 2015 will be archived by NPS. Details for the frequency and types of reports are given in Section 6.1.

7. DATA VALIDATION AND USABILITY

7.1 Data Review, Verification, and Validation

Data are reviewed at every step of the measurement process. Flow rate data are reviewed by the CNL field measurements group as soon as the transducer memory cards are received, once every three weeks for each site. Unusual data trigger further review, leading to diagnosis and repair of instrument problems as needed. Data from each analysis are reviewed by technical staff in each laboratory. This review includes flagging or invalidating data if problems are identified. Analytical data undergo thorough review and final validation before they are released to be added to the CNL database.

Once all of the sampler data and analytical data have been entered into the CNL database for a given period, then the ambient concentrations are calculated and the results undergo final validation by the QA Officer at CNL. This final validation includes several cross-comparisons of related variables designed to identify problems that may not be apparent in the review of each type of data independently. Final data validation is typically performed in three month batches so that time series analysis might reveal problems that might not be evident in a shorter snapshot of the data. Data that are determined during validation to be suspect or incorrect are flagged or invalidated, respectively. Once validation is complete a data package is delivered to NPS to be made available for public access on the FED website and ingested into the EPA AQS database.

7.2 Verification and Validation Methods

Samplers are installed, tested and maintained by the CNL field staff. Operational flow rates are expected to remain within 5% of target values. If flow rates slightly exceed these values, audits performed by site operators or field staff may be used to back-calculate accurate flow rates. If flow rates still do not meet the data quality objectives, the samples are marked with appropriate data quality flags.

After collection log sheets are reviewed and each sample is coded with a status flag, typically “normal” (NM). Data coded as “questionable data” are subject to additional validation checks to determine data validity.

Cases in which the measured mass (postweight minus preweight) is substantially larger or smaller than expectations are generally resolved before entering the database, often by reweighing the sampled filter. If no resolution is found, the A module (PTFE) mass data is flagged as questionable (QD), but is entered into the database. Later data validation procedures resolve the problem. For D module (PTFE) filters, unresolved large negative masses are changed in status to invalid (XX), while unresolved large positive masses are flagged as QD, but kept and entered into the database for further analysis.

Each analytical laboratory has its own data validation procedures and tools. The scientists in these laboratories identify and resolve questionable data during their data validation process. Suspect data are flagged and data that are clearly incorrect are invalidated. The laboratories do not release their data for further processing until data validation has been completed. The detailed data validation procedures can be found in the SOPs and related Technical Information documents as follows:

- Gravimetric Mass – SOP 251 (Sample Handling)
- X-Ray Fluorescence – SOP 301 (X-Ray Fluorescence Analysis)
- HIPS Laser Analysis – SOP 276 (Optical Absorption Analysis)
- Ions – RTI Ion SOP
- Carbon (TOR/TOT) – DRI Model 2001, Method IMPROVE_A (SOP 2-216R2)

Once all of the components of the data have been received and assembled at CNL (flow rates, analytical results, etc.) then data analysts at CNL can conduct the final data validation. The first step in the final validation is a review of the flow rate data. A database application is used to calculate a 24-hour average flow rate for each sample and to identify flow rates that exceed the expected flow rate range or that have high flow rate variability within the 24-hour period. In some cases, deviations can be resolved by referring to the operator’s notes or by conferring with the CNL field staff. For cases in which the sample appears to be valid (usually verified by visible sample on the filter) but the transducer memory card data have been corrupted, flow data are obtained from the weekly readings recorded on the operator’s log sheet or by using the nominal flow rate for each module. Data are flagged as invalid if flow rate problems cannot be resolved.

Ambient concentrations are calculated, along with their associated uncertainties and MDLs, prior to the final step in data validation. CNL analysts use database applications to examine plots and statistical summaries that compare values that are expected to have consistent relationships. The principal comparisons are:

- PM_{10} mass (D Module) to $PM_{2.5}$ mass (A Module)
- $PM_{2.5}$ mass (A Module) to reconstructed mass (from the measured components)
- Sulfur (A Module) to sulfate (B Module)
- Optical absorption/HIPS (A Module) to elemental carbon (C Module)

Irregularities observed in these checks are investigated, sometimes requiring a further review of flow rate data, analytical data, or field notes. In a few cases reanalysis or reweighing of suspect filters is required. Samples with problems that cannot be resolved during validation are flagged as invalid.

The data meeting the following conditions are inspected -

- Sulfur by XRF on A (PTFE) (times 3) vs. sulfate by IC on B (Nylon).

3*S / SO4 < 0.667 or 3*S / SO4 > 1.8

- Optical absorption on A (PTFE) vs. light-absorbing carbon on C (Quartz).

  There isn't a quantitative check for comparison since there isn't an expectation of a consistent quantitative relationship between optical absorption and LAC. Time trends between the two parameters are examined to look for general agreement.

- Fine mass (MF) on A (PTFE) vs. reconstructed mass (RCMC)
  - RCMC >> MF

    RCMC > 2*MF

    and

    $$\frac{\mathrm{RCMC} - \mathrm{MF}}{\sqrt{\frac{\mathrm{RCMC\_err}^2 + \mathrm{MF\_err}^2}{2}}} > 3$$

  - RCMC << MF

    $$\frac{\mathrm{RCMC} - \mathrm{MF}}{\sqrt{\frac{\mathrm{RCMC\_err}^2 + \mathrm{MF\_err}^2}{2}}} < -22$$

- Fine mass (MF) on A (PTFE) vs. PM10 mass (MT) on D (PTFE)
  - MF > MT

    $$\frac{\mathrm{MF} - \mathrm{MT}}{\sqrt{\frac{\mathrm{MF\_err}^2 + \mathrm{MT\_err}^2}{2}}} > 1$$

  - MT extremely high

    $$\frac{MF - MT}{\sqrt{\frac{MF\_err^2 + MT\_err^2}{2}}} < -43$$

Full details of the data validation procedures and tools can be found in SOP 351 (Data Processing and Validation).

7.3 Reconciliation with User Requirements

The final validated data are delivered to NPS for posting on the FED website (http://views.cira.colostate.edu/fed/). The FED website is the public portal for public access to the IMPROVE data. Among the principal users are data analysts working under the guidelines of the RHR. Each data point has an associated flag which identifies it as fully valid (the case with most data) or which identifies a known irregularity, such as deviation from the normal midnight-to-midnight sampling schedule. CNL also publishes brief data advisories to alert analysts to potential systematic errors or biases in the data. For example, CNL’s legacy XRF system (used prior to 2011) suffered from interference with the silicon peak when sulfur concentrations were high, and this topic was the subject of a data advisory.

8. REFERENCES

American Society for Quality. 1994. *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs.* ANSI/ ASQC E4-1994. Milwaukee, WI.

Johnson, R.L. 1981. Development and evaluation of a thermal/optical method for the analysis of carbonaceous aerosol. M.S. Thesis, Oregon Graduate Center, Beaverton, Oregon.

Joseph, D. B., J. Metsa, W.C. Malm, M. Pitchford. 1987. Plans for IMPROVE: A federal program to monitor visibility in Class I areas, in *Visibility Protection: Research and Policy Aspects*, P.S. Bhardwaja, ed, 1987.

U. S. Environmental Protection Agency. 1994. *Guidance for Preparing, Conducting, and Reporting the Results of Management Systems Reviews.* Draft EPA Publication No. EPA QA/ G-3. Washington, DC.

U. S. Environmental Protection Agency. 1998a. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1 Ambient Air Quality Monitoring Program Quality System Development.* EPA Publication No. EPA-454/ R-98-004. Washington, DC.

U. S. Environmental Protection Agency. 1998b. *SLAMS/ NAMS/ PAMS Network Review Guidance.* EPA Publication No. EPA-454/ R-98-003. Washington, DC.

U. S. Environmental Protection Agency. 1998c. *Guidance for Data Quality Assessment: Practical Methods for Data Analysis.* EPA Publication No. EPA QA/ G-9. Washington, DC.

U. S. Environmental Protection Agency. 1999. *Guidance on Technical Audits and Related Assessments for Environmental Data Operations.* EPA Publication No. EPA QA/ G-7. Washington, DC.

U. S. Government Accounting Office. 1994. *Government Auditing Standards.* Washington, DC.

W.H. White, L.L. Ashbaugh, N.P. Hyslop, C.E. McDade. 2005. Estimating measurement uncertainty in an ambient sulfate trend. *Atmospheric Environment 39*, 6857-6867.

9. APPENDIX

Tracking Progress with Imperfect Measurements: Data Quality and the Regional Haze Rule

Warren H. White 4/25/05, rev 6/8/05

9.1 Introduction

USEPA supports a variety of measurement programs, and must ensure that they collect data of sufficient quality for their intended uses. To this end the Agency now promotes, in Guidance for the Data Quality Objectives Process (USEPA 2000), the use of a standard analytical framework based on ideas from decision theory. Data users and technical experts are jointly to specify data quality objectives (DQO) that reflect (a) an unambiguous decision rule that will guide regulatory action and (b) tolerable limits on decision errors. The sensitivity of decisions to "sampling design error" and measurement error are then modeled to identify appropriate measurement quality objectives (MQO).

The Regional Haze Rule distinguishes itself from previous air regulatory regimes by framing requirements in terms of "progress" rather than "compliance". The metric in which progress is to be tracked is calculated from data collected by the pre-existing Interagency Monitoring of PROtected Visual Environments (IMPROVE) network. The merits of the DQO process can be debated (e.g. see USEPA 2004, comments of Allen, Chow, Felton, Husar, Ito, and White) along with its applicability to IMPROVE, but the EPA now requires objective performance criteria of some kind for all measurements:

> *When this* [DQO] *Process is not immediately applicable (i.e., the objective of the program is estimation, research, or any other objective that does not select between two distinct conditions), the Agency* [nevertheless] *requires the use of a systematic planning method for defining performance criteria.* (p. i of *Guidance for the Data Quality Objectives Process*, USEPA 2000)

This note examines issues that a DQO process might raise for IMPROVE, exploring how the tracking requirements of the Regional Haze Rule interact with the precision and bias of our measurements.

The following discussion is neither comprehensive nor exhaustive, and seeks only to place the DQO process on the table for discussion by the IMPROVE community. Issues are illustrated with analyses of sulfate concentrations in the eastern U.S., which are a key target of the Regional Haze Rule, are expected to provide early indications of progress, and have already received considerable scrutiny elsewhere (Ames and Malm 2001; Eldred 2001; White et al. 2005; DeBell 2005).

9.1 Data Quality Objectives

> *If progress is not consistent with the visibility and emission reduction goals established in the previous SIP, the State must evaluate the reason for lack of progress and take any appropriate action.* (p. 1-9, Guidance for Tracking Progress Under the Regional Haze Rule, USEPA 2003)

We will treat the guidance quoted above as the decision rule to be supported by our DQO:

"If the measured improvement is less than prescribed,
then the State must take action."

Current IMPROVE documentation combines this rule with a forecast of prescribed improvements to derive a partial DQO:

> *[t]he primary Data Quality Objective (DQO) for IMPROVE is to be able to measure a 5-percent change in b_{ext} in 5 years. The effect of individual components on b_{ext} depends on the site. ... The DQO for IMPROVE will therefore require that a 5-percent change in five years in each of the major components of sulfate, organic carbon, and soil must also be achieved.* (Quality Assurance Project Plan, CNL 2002, pp. 4-30,31)

The above QAPP specification gets the DQO process started, as it

(i) identifies tracking change as the primary objective,
(ii) quantifies the rate of change that is relevant, and
(iii) clarifies that this objective applies to each of the major particle fractions and not just the aggregate haze metric.[1]

---

[1] Note that our test case of fine-particle sulfate in the East is particularly well suited to this identification of haze levels with species concentrations.

However it carries no implications for measurement accuracy. What the DQO process requires as further input is an acceptable probability for making erroneous decisions. It must go beyond (i-iii), to also

(iv) specify a tolerable level for the risk of "false achievement," in which the reported 5-year change attains the prescribed decrement although the true change falls short, and

(v) specify a tolerable level for the risk of "false non-achievement," in which the reported 5-year change falls short although the true change meets the prescription.

Existing guidance on the Regional Haze Rule gives no indication of appropriate values for these tolerances.

9.2 Sampling Design Error

The concentration metric to which the partial DQO of the QAPP applies is the 5-year mean[2] of a species' concentrations on "hazy" days as defined by the Regional Haze Rule. Figure 1 shows 1999-2003 sulfur concentrations at Acadia, highlighting those from the haziest 20% of days in each calendar year. (CIRA-calculated deciviews are the basis for this selection.)

The overall coefficient of variation for hazy-day sulfur concentrations in Figure 1 is 64%. Most of this variability reflects natural fluctuations in the atmosphere; the precision of the sulfur measurement is generally better than 10%, so measurement error can account for less than $(10\%/64\%)^2 < 3\%$ of the total observed variance. Figure 2 shows that Acadia is hardly unique in this respect; the analogous coefficients of variation at 12 other eastern sites are all at least 30%.

---

[2] The difference between the 5-year mean and the average of the 5 annual means is overlooked here because it is negligible relative to other uncertainties that will be considered below.

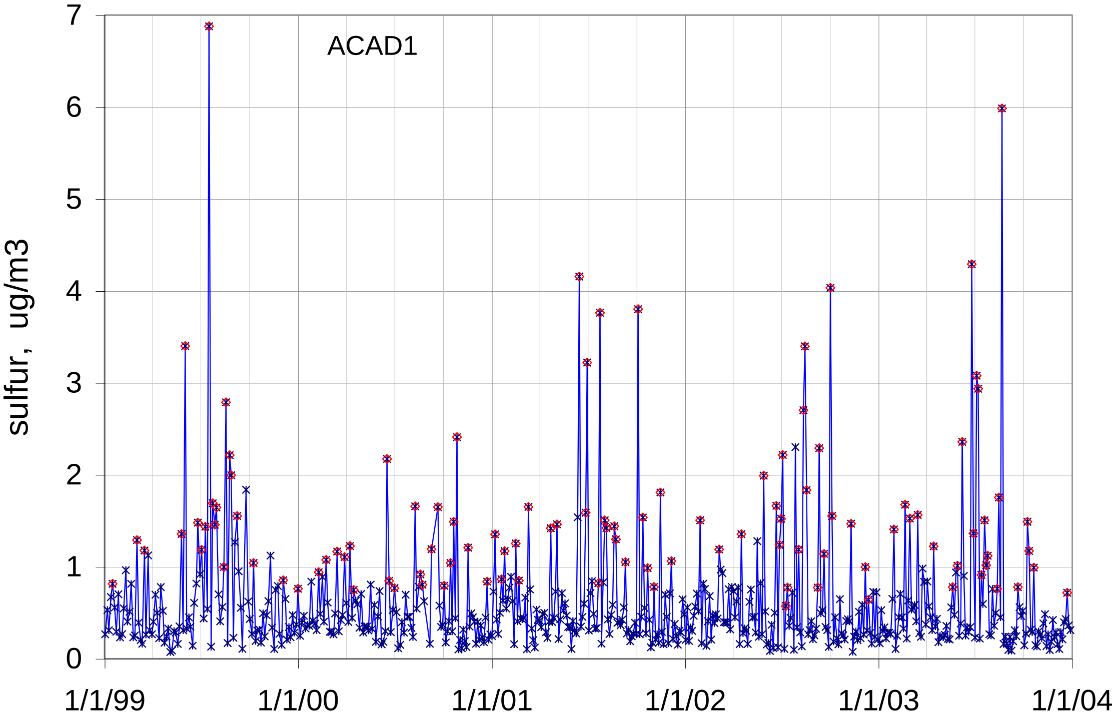

Figure 1. Sulfur concentrations at Acadia National Park, in Maine. The haziest 20% of days in each calendar year are highlighted in red, based on deciviews downloaded from CIRA.

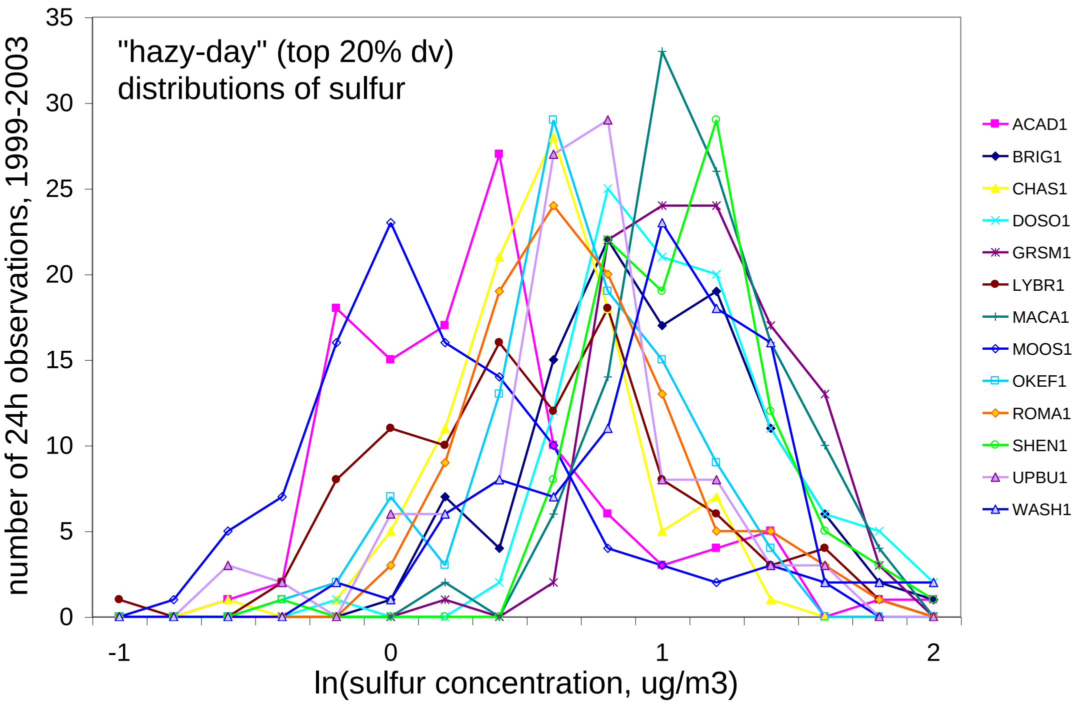

Figure 2. Distribution of hazy-day sulfur concentrations at Acadia (highlighted in Figure 1) and 12 other eastern sites.

Because natural weather factors are notoriously irregular, concentrations can be expected to vary from one 5-year period to the next even if emissions remain constant and the climate is stationary (i.e., without overall trend). These weather-driven variations create noise in the regional haze metric, the "sampling design error" mentioned in the opening paragraph. We approximate this unavoidable uncertainty as the standard error in the 5-year mean of hazy-day concentrations, estimated two different ways in Table 1. Both estimates yield a median of 4 percent across the different sites, and we will take this as a representative value for purposes of illustration. (A full accounting of sampling design error would be quite complex, requiring that the impacts of atmospheric variations on the designation of hazy days also be considered.)

EUS site	geom	arith
ACAD1	4.8%	6.1%
BRIG1	4.0%	3.9%
CHAS1	3.4%	3.3%
DOSO1	3.6%	3.9%
GRSM1	2.9%	2.9%

LYBR1	5.3%	5.6%
MACA1	3.0%	3.0%
MOOS1	5.0%	6.2%
OKEF1	4.2%	3.5%
ROMA1	3.7%	4.2%
SHEN1	3.5%	3.5%
UPBU1	4.4%	4.2%
WASH1	4.6%	4.5%

Table 1. Alternative estimates of the sampling uncertainty in 5-year sulfur means from hazy days in 1999-2003. The geometric estimate is exp((var(ln(**S**))/N)$^{1/2}$) –1 and the arithmetic estimate is (var(**S**)/N)$^{1/2}$/mean(**S**), where **S** represents the collection of all individual 24h sulfur concentrations regarded as a random variable. The number N of hazy days in five years ranges from 98 at CHAS and WASH to 111 at MACA, reflecting differences in data recovery rates.

9.3 Decision Performance

EPA guidance recommends that progress goals take the form of steady declines in the haze metric, so that

$$X(t) \le X_R(t) \equiv X_0 e^{-\beta_R t},$$

where X_0 is the baseline value and $X_R(t)$ is the prescribed value after *t* years. Regulations influence $X(t)$ only indirectly, through the emissions rate $Q(t)$, and it will simplify our discussion to assume that ambient concentrations are proportional to emissions. (If not proportional, they are presumably at least a monotonic function $X = F(Q)$ of emissions. There is then an inverse function $G: X \to Q$ such that $F(G(X)) = X$. We simply target emissions in terms of $G(X)$, to which concentrations *are* proportional.)

The true value of the ambient metric after *t* years will be $X(t) = X_0 e^{-\beta_Q t}(1 + \varepsilon_{weather})$, where β_Q is the rate at which emissions decline and $\varepsilon_{weather}$ is a random variable representing the sampling error discussed in the preceding section. We observe not the true value but $Z(t) = (1 + E)X(t)$, where E is the unknown bias of measurements made during the subject period.

The question posed by the decision rule of the preceding section is whether the observed level $Z(t)=(1+E)X_0e^{-\beta_Q t}\left(1+\varepsilon_{weather}\right)$ is below the prescribed level $X_R(t)=X_0e^{-\beta_R t}$. For a given decline in emissions and a given measurement bias, the answer turns on the value taken by the random variable $\varepsilon_{weather}$; reasonable progress is demonstrated if

$$\varepsilon_{weather} \le (1+E)^{-1}e^{(\beta_Q-\beta_R)t}-1.$$

The probability of success thus depends on the distribution of $\varepsilon_{weather}$, which the preceding section's analysis suggests we model as the normal N(0, σ) with zero mean and standard deviation σ = 0.04. The probability of reaching the prescribed haze level after *t* years is then given by the cumulative normal distribution

$$P\left[Z(t)\le X_R(t)\right]=\frac{1}{\sqrt{2\pi}\left(0.04\right)}\int_{-\infty}^{w} e^{-u^2\big/2(0.04)^2}\,du\,,$$

where

$$w=\frac{e^{(\beta_Q-\beta_R)t}}{1+E}-1. \qquad [1]$$

The blue curve in Figure 3 shows the probability $P\left[Z(t)\le X_R(t)\right]$ that error-free measurements will yield a 5% decrease in reported concentration after $t=5$ years, as a function of the actual decrease in emissions. Inversion of this function yields the emissions trend β_Q needed to have a given probability of demonstrating "reasonable progress" when $t=5$ years, $\beta_R=1$ %/year, and $E=0$. Even with perfect measurements, emissions declines must exceed 2 %/year to generate 95% confidence[3] that ambient progress of 1 %/year will be demonstrated after five years. This "over-control" provides the needed insurance against the possibility that weather conditions in the second five-year period will be less favorable than those in the first. Less of a cushion is needed over longer intervals, as indicated by the green and red curves, because they yield larger signals, a 10% change in 10 years or a 30% change in 30 years.[4] No cushion is needed if one accepts a 50% chance of missing the goal.

---

[3] The more usual statistical terminology for such a probability of detection is "power".

[4] More precisely, a 1 %/year decline produces decreases of $1-e^{-t/100}$ after *t* years, or 4.9%, 9.5%, and 26% after 5, 10, and 30 years.

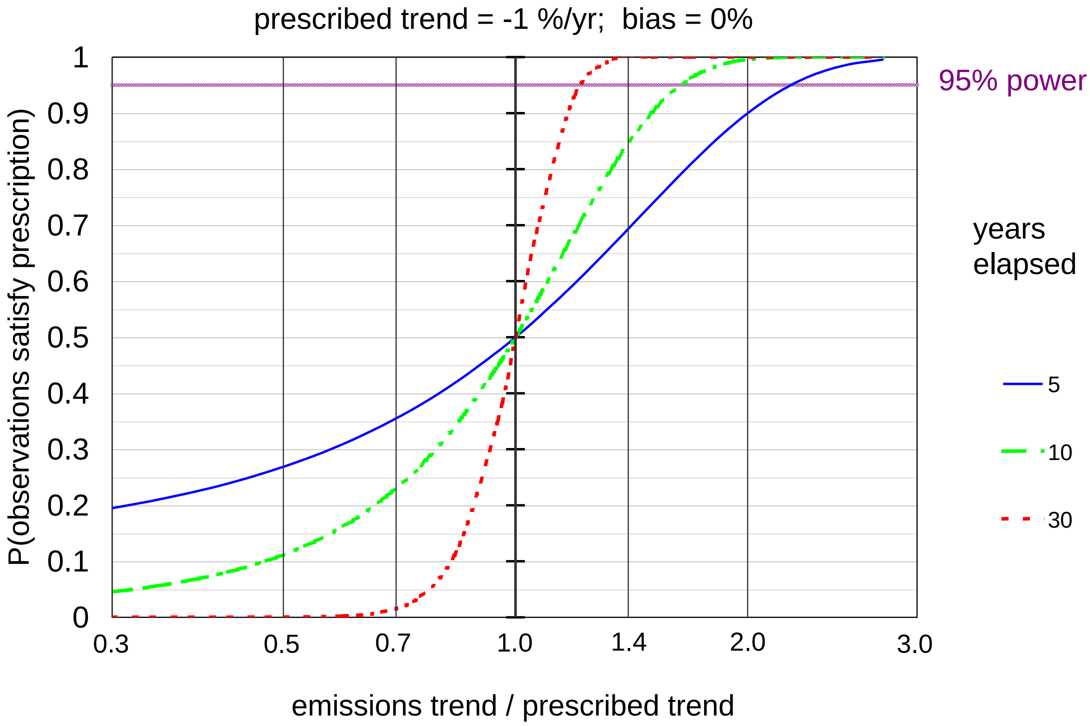

Figure 3. Decision performance curve (c*f*. Figure 6-2 of EPA/600/R-96/055) for error-free measurements and a prescribed haze decline of 1 %/year. In the notation of Equation 1, the horizontal axis is β_Q / β_R and the vertical axis is $P[Z \leq X_R]$. The horizontal axis is what management decisions directly affect; the vertical axis is how they are rewarded.

EPA's tracking guidance for the Haze Rule derives the stronger trend of –3 %/year to illustrate reasonable progress in the eastern U.S. (p. 1-7). Figure 4 is the analog of Figure 3 for a prescribed trend of this magnitude.

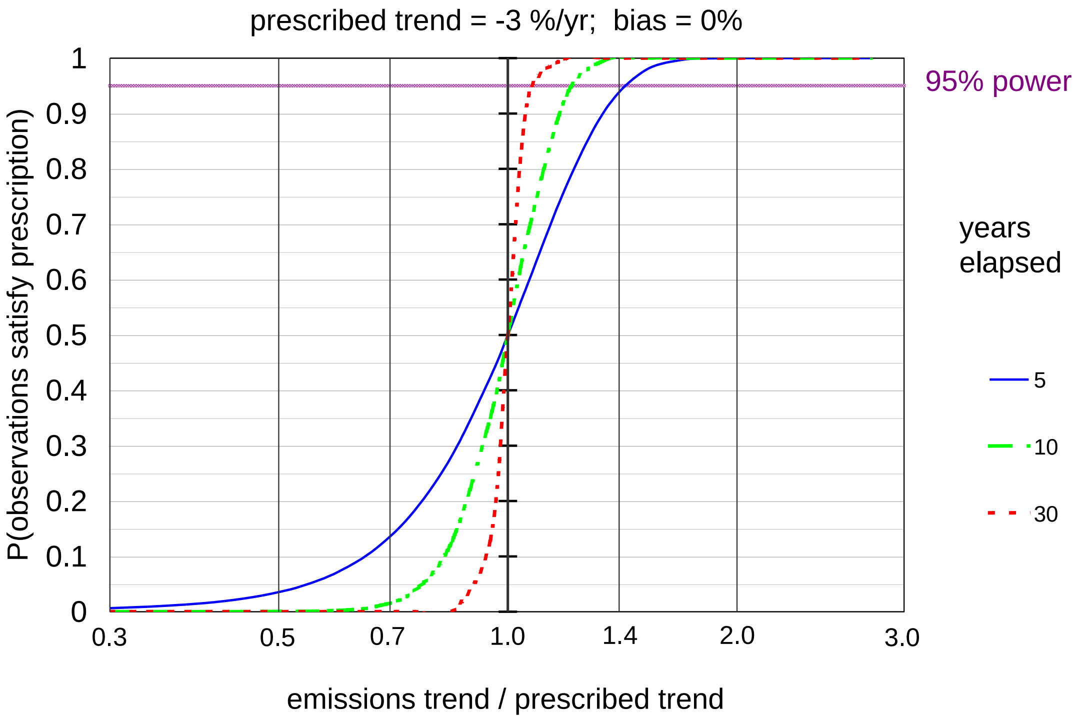

Figure 4. Decision performance curve for error-free measurements and a prescribed haze decline of 3 %/year.

IMPROVE's current accuracy objective is ±5% for all major species (QAPP, p. 4-31). Figures 5 and 6 show the effects of +5% and –5% errors on the decision performance curves of Figure 4. Positive errors in future measurements obscure progress, so that larger reductions in emissions are needed to ensure that reported haze levels meet prescribed goals. Conversely, negative errors inflate progress; a bias of –5% yields a 50% chance of reporting 3 %/year progress after 5 years with emissions reductions of only 2 %/year.

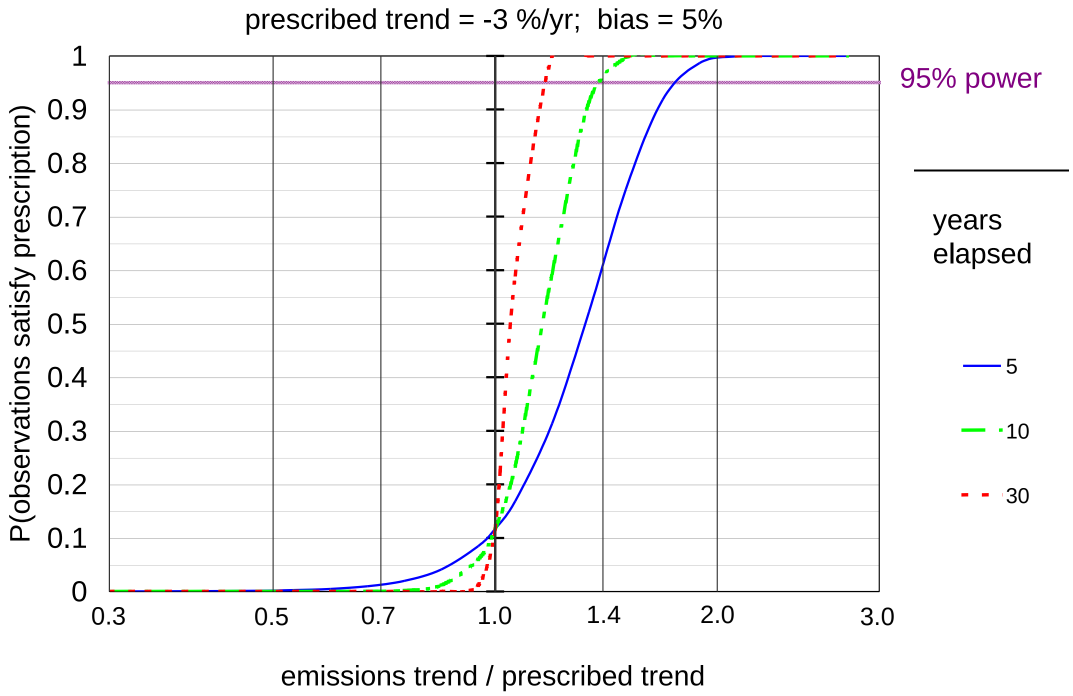
prescribed trend = -3 %/yr; bias = 5%
P(observations satisfy prescription)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.3
0.5
0.7
1.0
1.4
2.0
3.0
emissions trend / prescribed trend
95% power
years elapsed
5
10
30

Figure 5. Decision curves of Figure 4 for a bias of +5% in future measurements relative to baseline.

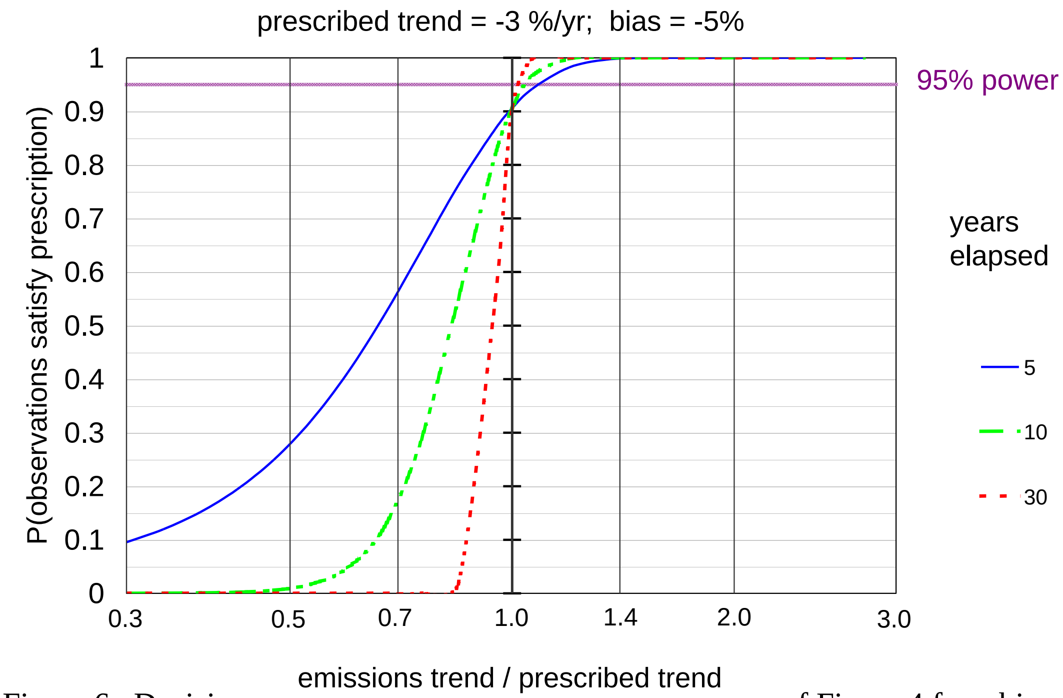

Figure 6. Decision curves of Figure 4 for a bias of -5% in future measurements relative to baseline.

9.4 Implementation Plans

The implications of Figures 3-6 for emissions management depend on how EPA will apply the Haze Rule in actual future situations. The following analysis is based on my understanding of what the Rule requires. This can be phrased as “statistical misfortunes – natural atmospheric variability and measurement errors – are no excuse for failing to show reasonable progress. One deals with statistical uncertainty by making conservative assumptions when calculating the emissions reductions that will be targeted.”

Figure 7 shows the emissions decline required to ensure a 95% chance of reporting a 3 %/year decline in haze, as a function of future measurement bias and the time allowed to demonstrate progress. (For orientation, a vertical ascent of Figure 7 at 0% bias corresponds to a horizontal traverse of Figure 4 at 95% probability.) Emissions must be reduced by more than 3 %/year to ensure that measured progress is 3 %/year even in the favorable situation where future measurements overstate progress by reading 5% low, as could already be seen in Figure 6.

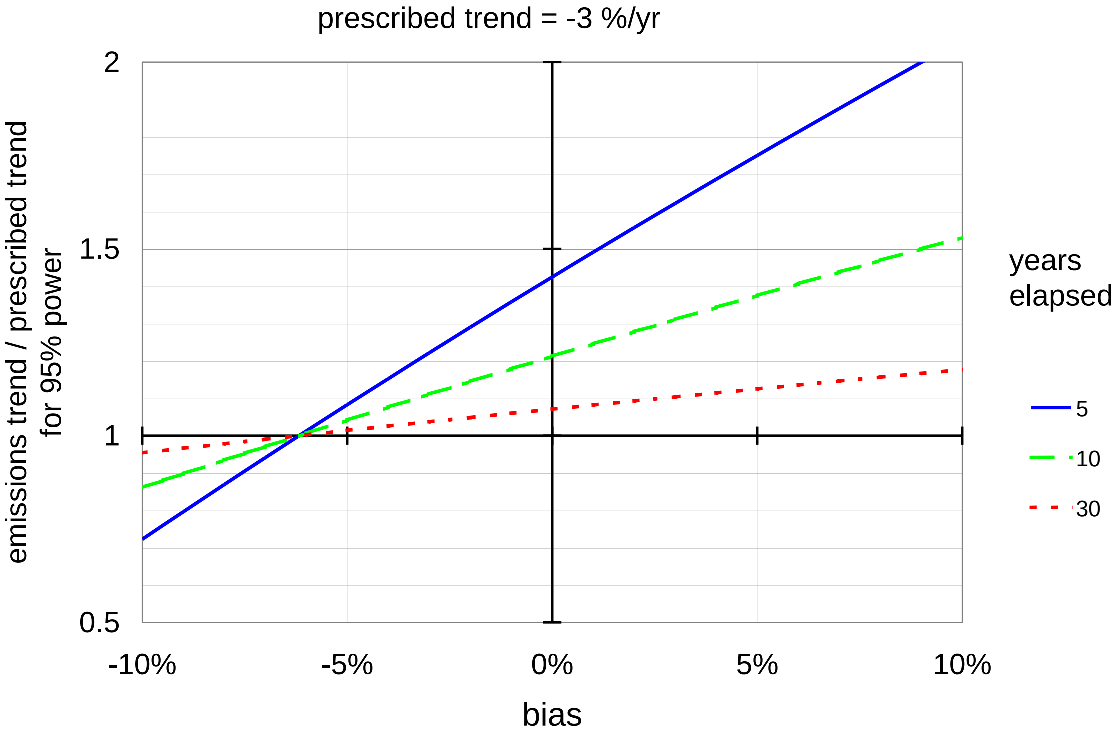

Figure 7. Emissions declines needed to ensure a 95% chance of reporting 3 %/year progress with biased measurements.

Less over-control of emissions is needed if one accepts a greater risk of failing to show progress. Figure 8 shows the emissions decline required for various levels of confidence that a 3 %/year decline in haze will be reported after 10 years. (For orientation, the blue curve in Figure 8 is the same as the green curve in Figure 7.)

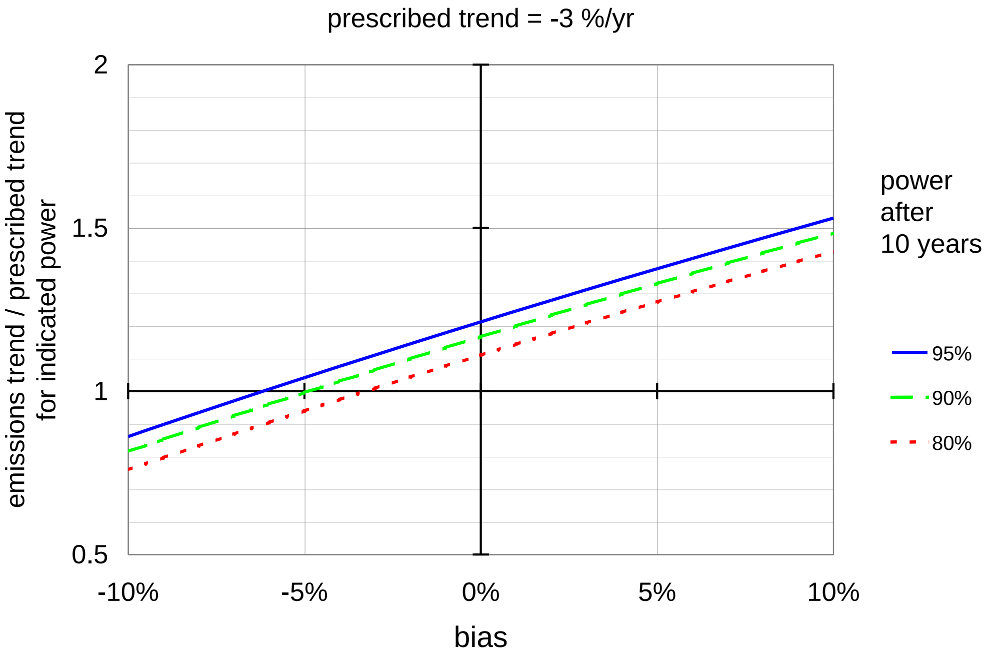

Figure 8. Emissions declines needed for various probabilities of reporting 3 %/year progress after 10 years.

As more time is allowed for demonstrations of progress, the accumulating changes become easier to detect and less over-control is needed to ensure a given probability of success, as illustrated in Figure 9. Some over-control is required even at the end of the program, however, if we desire a better-than-50% chance of success.

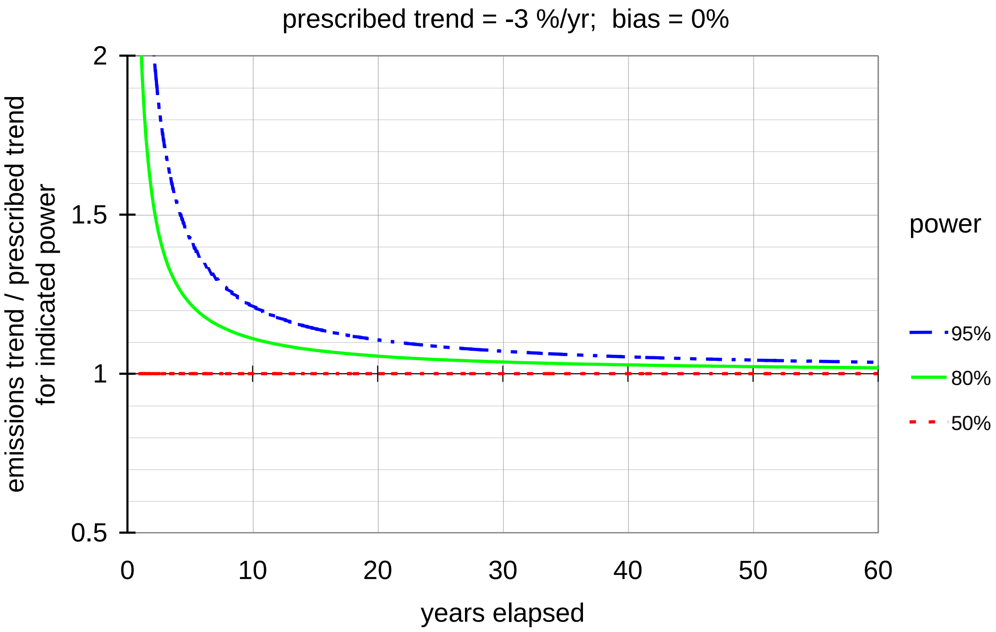

Figure 9. Emissions declines needed to demonstrate 3 %/year progress with error-free measurements.

9.5 Estimated Measurement Error

The empirical uncertainty in IMPROVE's measurement of the haze metric for sulfate can be judged by comparing the 1999-2003 values derived from the X-ray fluorescence analysis of sulfur with those from the ion chromatic analysis of sulfate ion. As summarized in Table 2, the observed differences for our 13 eastern sites range from –5.7% (sulfate higher than 3 times sulfur) to +1.7%. Each individual difference reflects errors in both measurements, which can add or cancel. If these errors can be assumed mutually independent, then $\sqrt{\mathrm{var}(\Delta)} = 2.6\%$ provides an upper bound for the precision of either measurement. This observed value is well within IMPROVE's measurement accuracy objective, but excludes any contribution arising from possible systematic errors.

EUS site	**$\mu(SO_4)$**	**$\mu(3xS)$**	**Δ**
ACAD1	4.90	4.84	-1.2%
BRIG1	8.85	8.42	-5.0%
CHAS1	5.89	5.56	-5.7%
DOSO1	9.31	9.15	-1.7%
GRSM1	9.96	9.91	-0.5%
LYBR1	5.97	5.95	-0.3%
MACA1	9.55	9.71	1.7%
MOOS1	4.16	4.22	1.4%
OKEF1	6.27	6.20	-1.1%
ROMA1	6.91	6.55	-5.4%
SHEN1	9.81	9.32	-5.1%
UPBU1	6.38	6.34	-0.6%
WASH1	9.01	8.62	-4.3%

Table 2. Alternative measurements of 5-year sulfate means ($\mu g/m^3$) from hazy days in 1999-2003. Differences are calculated as $\Delta = \frac{-\mu(SO_4) + \mu(3 \times S)}{(\mu(SO_4) + \mu(3 \times S))/2}$.

The 2.6% precision derived from measurements at different sites in the same 5-year period might also be interpreted as an estimate for the precision of measurements at the same site in different 5-year periods. This would yield a one-sigma measurement uncertainty of $\sqrt{2} \times 2.6\% = 3.7\%$, or ≅ ¾ %/year, for comparisons between adjacent 5-year periods. This is a bit below the 1 %/year uncertainty estimated by White et al. (2005) for 5-year trends, but the latter accounts also for time trends in systematic errors.

9.6 Conclusions

(i) The natural atmospheric variability in the sulfate component of the 5-year haze metric is around 4% in the eastern U.S. This natural variability requires air quality managers to over-control emissions if they wish to have a high probability of meeting progress goals.

(ii) Only slowly varying measurement biases can interfere with the tracking of progress; historical levels of random error have negligible impact. Quality assurance for tracking must ensure accuracy relative to a standard, not just precision in replicate measurements.

(iii) IMPROVE's 5% accuracy objective for sulfate can be defended as follows: To ensure a 95% chance of *falsely* demonstrating progress, *using measurements biased as much as 5% low (e*.g. *by cheating)*, we must reduce emissions enough to produce *true* progress under *normal* atmospheric conditions.

9.7 References

R.B. Ames and W.C. Malm (2001) Comparison of sulfate and nitrate particle mass concentrations measured by IMPROVE and the CDN. *Atmospheric Environment 35*, 905-916.

Crocker Nuclear Laboratory (2002) Quality Assurance Guidance Document, Revision 0.0. http://vista.cira.colostate.edu/improve/Publications/QA_QC/IMPROVE_QAPP_R0.pdf

L. DeBell (2005) Data Validation Historical Report Aerosol Sulfate. Draft manuscript.

R. Eldred (2001) Sulfur-Sulfate History for IMPROVE. http://vista.cira.colostate.edu/improve/Publications/GrayLit/006_Sulfur-Sulfate_History/006_sulfur-sulfate_history.htm.

USEPA (2000) Guidance for the Data Quality Objectives Process. EPA/600/R-96/055, http://www.epa.gov/quality/qs-docs/g4-final.pdf.

USEPA (2003) Guidance for Tracking Progress under the Regional Haze Rule. EPA-454/B-03-004, http://www.epa.gov/ttn/oarpg/t1/memoranda/rh_tpurhr_gd.pdf.

USEPA (2004) Clean Air Scientific Advisory Committee (CASAC)Ambient Air Monitoring and Methods (AAMM)Subcommittee Consultation on Methods for Measuring Coarse-Fraction Particulate Matter (PMc)in Ambient Air (July 2004). EPA-SAB-CASAC-CON-04-005, http://www.epa.gov/sab/pdf/casac_con_04_005.pdf.

W.H. White, L.L. Ashbaugh, N.P. Hyslop, and C.E. McDade (2005) Estimating measurement uncertainty in an ambient sulfate trend. Manuscript submitted to Atmospheric Environment.

The foregoing essay does not systematically explore the effects of the various measurement and regulatory parameters on the decision process. Readers are instead invited to draw their own conclusions, playing with Figures 3-9 via the accompanying spreadsheet DQO_TOY.xls. As a teaser, please try the interactive demo below – just double-click to enter new values in any of the green cells.

years elapsed	5	10	30	[t]
prescribed slope, 1/yr	-2%			[-βR]
measurement bias	0%			[E]
observed 5-yr uncertainty	4%			[σ]

prescribed trend = -2 %/yr; bias = 0%