

## 6. QUALITY ASSURANCE AND QUALITY CONTROL

**This chapter describes quality assurance and quality control (QA/QC) procedures that are recommended when making precipitation chemistry and wet deposition measurements. Chapters on Siting, Field Protocols, and Laboratory Operations address QA/QC procedures relevant to those activities. This chapter summarizes the most important of these QA/QC procedures and describes several overarching QA activities not presented in previous chapters.**

Quality Assurance (QA) and Quality Control (QC) are extremely important to the collection and reporting of high-quality data. Achieving high-quality precipitation chemistry and wet deposition measurements begins with prescribing Data Quality Objectives (DQOs) that provide the measurement community with specific levels of measurement quality that must be achieved. The following sections describe specific QA/QC procedures that each monitoring station, laboratory, and data center should institute to meet the prescribed DQOs.

### 6.1 Quality Assurance Requirements

This section describes specific QA requirements with subsections on DQOs, the need for a QA Project Plan, and the recommendation for regularly documenting data quality assessments in a QA Report.

#### 6.1.1 Data Quality Objectives

DQOs are defined as follows:

*“Qualitative and quantitative statements of the overall level of uncertainty that a decision-maker will accept in results or decisions based on environmental data. DQOs provide the statistical framework for planning and managing environmental data operations consistent with user’s needs”*  
(U.S. EPA, 1997).

Quantitative DQOs are listed in Table A.1 in [Appendix A](#). These DQOs were developed by the GAW [Scientific Advisory Group for Total Atmospheric Deposition](#) and were based on achievable measures of data quality. The DQOs provide each NMHS or other station sponsor with a specific set of objectives for bias, precision, completeness, detection limits, and calibrations. It is the responsibility of each organization to review Table A.1 and adjust its precipitation chemistry and wet deposition measurements to meet the DQOs listed there.

#### 6.1.2 Quality Assurance Project Plans

The Quality Assurance Project Plan (QAPjP) *“integrates all technical and quality aspects of a project, including planning, implementation, and assessment. The purpose of the QA Project Plan is to document planning results for environmental data operations and to provide a project-specific ‘blueprint’ for obtaining the type and quality of environmental data needed for a specific decision or use. The QA Project Plan documents how quality assurance (QA) and quality control (QC) are applied to an environmental data operation to assure that the results obtained are of the type and quality needed and expected.”* (U.S. EPA, 1998).

Every sponsor of precipitation chemistry and wet deposition measurements should prepare a Quality Assurance Project Plan that describes in detail the QA/QC procedures that are integral to their measurement system. The U.S. Environmental Protection Agency offers [Guidance for Quality Assurance Project Plans](#). Other public-domain guidelines for the preparation of QA Project Plans are equally acceptable. QA Project Plans should be readily available to all staff, especially laboratory technicians. These plans should be reviewed annually and updated as needed.

#### 6.1.3 Quality Assurance Reporting

Each sponsor of precipitation chemistry and wet deposition measurements is responsible for assessing the quality of its precipitation chemistry data against the DQOs listed in Table A.1 in [Appendix A](#). The process of analyzing the quality of data is known as *Data Quality Assessment* and is described in detail in U.S. EPA (2000).

Each sponsor of precipitation chemistry and wet deposition measurements should prepare an annual or biannual QA Report. This report should describe the QA/QC procedures in the measurement system and it should include an assessment of data quality relative to the DQOs. The report should focus on measurement accuracy and precision as well as on data completeness, comparability, and representativeness. These QA Reports should be made available to the data user community. An alternative is to provide a copy for archival at the [GAW Quality Assurance - Science Activity Centre for the Americas](#).

Examples of QA Reports are available at <http://nadp.slh.wisc.edu/lib/qaReports.aspx#CAL>.

## **6.2 QA/QC for Field Operations**

Described below are specific QA/QC activities and procedures for stations where precipitation chemistry and wet deposition measurements are made.

### **6.2.1 Siting and Instrument Placement**

Reporting precipitation chemistry and wet deposition data that are spatially- and temporally-representative requires that, as a minimum, measurement stations satisfy the siting criteria presented in [Chapter 2](#). Stations should be assessed annually vis-à-vis these siting criteria to determine whether they continue to meet the requirements. An independent audit of sites is recommended every five years. Changes to sites (e.g., instrument make/model, instrument locations/installations, on-site vegetation, surrounding vegetation/potential sampling obstructions, large changes in regional emissions) should be documented as indicated in Section 6 of [Chapter 2](#).

### **6.2.2 Instrumentation**

Described below are QA/QC procedures for the proper instrumentation and recommended operations of field instruments for precipitation chemistry and wet deposition measurements.

#### *6.2.2.1 Satisfying Minimum Operating Specifications*

Precipitation chemistry samplers and standard precipitation gauges must meet the minimum operating specifications listed in Section 3.2.1 of [Chapter 3](#), e.g., sensor sensitivity, chemical inertness of sample containers. Only the samplers and gauges that meet these specifications should be used for reporting precipitation chemistry and wet deposition measurements.

#### *6.2.2.2 Instrument Pretesting*

Repaired and newly-purchased instruments should be pre-tested in the laboratory or repair shop before being deployed for operational use. Adherence to this principle will reduce unexpected instrumental down-time.

#### *6.2.2.3 Spare Parts*

Spare parts and/or spare samplers should be readily available whenever possible to allow for quick instrument repair/replacement, thereby reducing measurement down-time.

## **6.2.3 Sample Collection and Handling**

Provided below is a short summary of the most important QA/QC procedures related to field sample collection and handling. Detailed procedures are described in [Chapter 3](#).

### *6.2.3.1 Sample Container Testing*

All containers (e.g., buckets, bags, funnel-and-bottles) used in precipitation chemistry samplers must be tested for chemical inertness before use. Specific testing must be done to ensure that the container material does not adversely affect the sample chemistry through adsorption or desorption of major ions to or from the container surfaces. Testing should be done with high and low volumes of deionized (DI) water

and with actual rainwater samples of known concentration or with reference solutions having certified concentrations of the major ions within the normal range of precipitation. Testing with low and high volumes will indicate whether adsorption or /desorption effects, if any, are volume-dependent. Testing with rainwater or reference solutions will indicate whether the effects are dependent upon the chemical matrix or concentration.

Old collection vessels should be tested in the foregoing manner at least every 5 years to ensure that absorption and desorption effects have not accumulated or changed with time and use.

#### 6.2.3.2 *Sample Container Cleaning*

All sample containers must be cleaned with DI water, preferably at the analytical laboratory. Alternatively, containers can be cleaned at a clean field laboratory. Where sample containers are cleaned at a field laboratory, the DI water used in the cleaning process must be tested to ensure that it meets predetermined quality specifications, both before and after the sample containers are cleaned (see Section 3.3.1 of [Chapter 3](#)). Methods must include careful cleaning of all surfaces that come in contact with precipitation samples. After cleaning, sample containers that are not used immediately must be air dried in a clean location, covered in clean plastic, and stored in a clean area. See Section 3.3.1 of [Chapter 3](#) for specific sample container cleaning procedures.

#### 6.2.3.3 *Sample Collection*

Specific QC procedures that prevent contamination during sample collection and handling include:

- Inspecting sample containers for visible signs of contamination before installation in the collector
- Standing downwind of the precipitation chemistry sampler when collecting samples
- Wearing disposable plastic gloves when handling sample containers and transferring samples
- Never touching the inside surfaces of sample containers
- Replacing gaskets on the underside of the hood or cover of the precipitation chemistry sampler at frequent and regular intervals (every few months depending on the dirtiness of the location)
- Checking for and documenting sample leakage in the field, during shipping, and upon receipt at the analytical laboratory.

### 6.2.4 **Sample Storage and Shipping**

Proper storage and shipping methods must be used to preserve the chemical and physical integrity of precipitation chemistry samples. QC procedures for this purpose include:

- Maintaining a sample temperature of  $\sim 4^{\circ}\text{C}$  during periods of on-site storage, during shipment to the analytical laboratory, and prior to analysis in the analytical laboratory
- Weighing samples to determine sample volume at the field laboratory and again on arrival at the analytical laboratory to detect sample loss in transit
- Instituting procedures to eliminate leakage during sample handling and transit

### 6.2.5 **Blanks**

Field blanks are to be collected at every station on a regular basis to ensure that sampling methods and materials do not interfere with precipitation chemistry. Where samples are collected daily, 2 to 4 blanks should be collected randomly throughout the month. For weekly sampling, 1 to 2 blanks should be collected each month. Prepare a field blank by pouring a prescribed volume of DI water into a dry sample container (e.g., bucket, bag, funnel-and-bottle) that was installed in the precipitation chemistry sampler throughout a sampling period that had no precipitation. (In the absence of a dry sampling period, an alternative is to install a container in the sampler for a prescribed period, simulating a dry period.) The field blank should be handled and shipped to the laboratory following the same procedures as if it were a precipitation sample. Field blank data should be reviewed regularly for evidence of contamination. (Section 3.3.2.3 in [Chapter 3](#) provides a comprehensive description of the preparation and handling of field blanks.)

IMPORTANT: Care must be taken to label all field blank samples. Blank data must be stored separately from precipitation sample data.

### **6.2.6 Data Reporting at the Field Sites**

A sample history form must be filled out for every sampling period and this form should accompany the sample to the analytical laboratory. (See figures 3.1 and 3.2 in [Chapter 3](#) for examples of sample history forms.) Specific QA/QC items related to field data reporting include:

- Checking for legible, accurate and thorough completion of sample history forms
- Contacting the station operator when questionable, problematic, or incorrect entries are found on the sample history form to clarify the problem and correct errors
- Reviewing the information on every sample history form to ensure adherence to standard operational procedures and identify potential problems with the sampler and gauge

### **6.2.7 Routine Instrument Checks**

Below is a list of routine checks that the station operator must make when collecting a precipitation chemistry sample and servicing the standard precipitation gauge. The operator must check that:

- The sampler has electrical power and the switch is in the “on” position
- Upon wetting the sensor, it triggers the hood or cover to open the collector
- The hood or cover returns to the ‘closed’ position when the sensor is no longer wet
- The hood or cover makes a tight seal with no visible gaps over the sampling orifice
- The standard precipitation gauge does not leak and, if a recording gauge, that it has responded to the occurrence of precipitation

### **6.2.8 Preventive Maintenance**

Preventive maintenance on the precipitation chemistry sampler and standard gauge reduces the likelihood of instrumental breakdowns and should be performed at regular intervals.

### **6.2.9 Regular Site Visits and Inspections**

NMHS staff or a representative of the sponsoring agency should visit the station once per year. The purpose of this visit is to offer support and guidance to the station operator, review standard operating procedures, inspect the condition and operation of the field instruments, and check for any changes in on-site and near-site conditions. The visitor/inspector should check for the following:

- Proper precipitation chemistry sampler operation (hood or cover opens when sensor is wet and closes and seals the sampler when sensor is dry)
- Cleanliness of the gasket on the underside of the sampler hood or cover
- Cleanliness of sample containers
- Cleanliness of field laboratory or area where samples are handled
- Correct adherence to Standard Operational Procedures (SOPs)
- Proper storage and shipping of samples
- Confirmation that instruments comply with siting criteria (See [Chapter 2](#))

### **6.2.10 Corrective Actions**

Corrective actions must be taken as soon as practical after an instrument malfunctions or sampling irregularities are detected. Rapid response can reduce data loss and help ensure that the data set for the station meets the GAW annual data completeness criterion of 95%. As mentioned in Section 6.2.2.3, data loss is reduced if spare parts and extra instruments are available and ready for use.

### 6.3 QA/QC for Laboratory Operations

Laboratory operations ([Chapter 4](#)) cover a wide range of activities including sample reception, field sampling support, sample transfer, storage and analysis, QA, QC, and data reporting. QA/QC related to laboratory operations can be broken down into three parts: (1) setting DQOs, (2) adopting good QA/QC practices, and (3) regularly summarizing and reporting QA/QC results.

Specific QC practices and procedures at a well-controlled laboratory include:

- Good laboratory practices
- Good sample handling practices
- Documentation of analytical procedures
- Preventive maintenance of laboratory instrumentation
- Analyst training and upgrading
- Provision of appropriate facilities, instrumentation, and reagents
- Inspections and/or audits
- Appropriate safety measures
- Well-defined chain-of-custody of samples
- Traceability of calibration standards
- Control charting
- Accuracy checks (calibration controls, spikes, blinds, reagent blanks)
- Precision checks (within-run and between-run duplicates)

#### 6.3.1 Laboratory Data Quality Objectives

Laboratory DQOs are listed in Table A.1 of [Appendix A](#). It is the responsibility of each laboratory to implement an appropriate set of operational and QA/QC activities to ensure that these objectives are met or exceeded.

#### 6.3.2 Laboratory Sample Handling QA/QC

QC procedures related to sample handling at the laboratory include the following:

- Sample Reception, Logging and Custody. Correct sample logging and chain-of-custody procedures must be implemented at the laboratory to ensure that no samples are lost, mixed up, or misplaced. Samples should be stored at 4°C until they enter the analysis stream.
- Sample Handling, Labelling, and Transferring. After reception, logged-in samples should be weighed (to check for leakage during transit and to confirm the field weight) and inspected for visible contamination. Problems should be documented, the information verified, and corrective actions taken, as needed.

#### 6.3.3 Chemical Analyses QA/QC

Laboratories that analyze precipitation samples are expected to meet the GAW DQOs. This requires adherence to Standard Operating Procedures and to QA/QC procedures throughout the analytical system. Specific QA/QC procedures are described below.

##### 6.3.3.1 Calibration Control and Verification

All laboratories must implement QC procedures that guarantee the accuracy of calibrations. Recommended procedures include:

- Using ultra-pure reagents traceable to Certified Reference Materials for producing calibration standards
- Checking that the slope, intercept and correlation coefficient of each calibration curve are within acceptable ranges (use of control charts is recommended)
- Using calibration standards that range from 2% to 98% of all precipitation sample concentrations

- Using extra calibration standards in non-linear portions of calibration curves
- Calibrating at the beginning and end of each analytical run
- Analyzing and control-charting the measurement of a QC solution (QCS), having a concentration at the 10<sup>th</sup>, 50<sup>th</sup>, or 90<sup>th</sup> percentile of precipitation samples, in every batch of 10 samples; when this QCS measurement exceeds the control limit, the entire batch of 10 samples must be reanalyzed.

#### 6.3.3.2 Replicate Analyses

Replicate analyses of precipitation samples provide a measure of analytical precision. There are two types of replicate analyses: within-run and between-run. A “run” is a set or batch of consecutive measurements with the analytical instrument operating within fixed calibration settings and control limits. In general, between-run replicates are more important than within-run replicates because they capture the day-to-day and batch-to-batch variability of the analyses.

At least 2% to 5% of the sample load should be analyzed as between-run replicates. Select these samples randomly from the sample stream with the condition that they have adequate volume for two analyses. Replicate analysis results should be control-charted immediately, and when control limits are exceeded, the entire batch of samples should be reanalyzed.

Replicate analysis data can be used to determine analytical precision, which can be compared with the DQOs for laboratory precision listed in Table A.1 ([Appendix A](#)). No fewer than 30 replicate samples should be used when calculating analytical precision.

#### 6.3.3.3 Laboratory Blanks

DI water and reagent blanks should undergo the same chemical analyses as precipitation samples. Analyze one DI water and one reagent blank per analytical batch. Control-chart the results and take corrective actions when control limits are exceeded, e.g., replace the DI water and/or reagents.

#### 6.3.3.4 Blind Samples

Blind samples composed of DI water, acidified DI water, simulated rainwater, or certified reference materials should be inserted into the sample stream on a weekly basis. Control-chart the measurements to ensure that the system is in-control.

#### 6.3.3.5 Dilution Checks

Dilution is often used to increase the volume of small precipitation samples to obtain sufficient sample for a complete chemical analysis and/or to reduce high concentrations into the normal operating range of the analytical instruments. It is recommended that the method for diluting samples be tested routinely on ~1% of the samples. An accepted method for testing dilutions is to analyze aliquots of large precipitation samples or certified reference materials both before and after dilution. Control-chart the differences and where they exceed 10% of the undiluted concentrations, correct the dilution procedures as needed.

### 6.3.4 Control Charting

Control charts are statistical tools used to evaluate whether a measurement system is in control. Using control charts should be a standard practice in all GAW laboratories. Section 4.3.5 ([Chapter 4](#)) describes how to prepare and use control charts in analytical laboratory operations. Details on control chart methods can be found in Taylor (1987) and ASTM (2002).

### 6.3.5 Data Quality Control and Reporting

Data QA/QC procedures must be applied routinely to ensure the accuracy of analytical results. Specific QA/QC procedures include:

- Verifying that satisfactory and timely corrective actions are taken to address every exceedance of a control limit (e.g., sample re-analyses)
- Verifying that extremely high measurements as well as values below the detection limit are correct

- Identifying (i.e., flagging) invalid or questionable analytical results, e.g., cases of laboratory contamination and instrumental malfunctions
- Identifying and re-analyzing samples that failed ion balance criteria.

### 6.3.6 Inter-laboratory Comparison Studies

The WMO/GAW [Science Advisory Group for Total Atmospheric Deposition \(SAG-TAD\)](#) requires every laboratory that makes precipitation chemistry and wet deposition measurements to participate in the Inter-laboratory Comparison Studies (LIS) conducted by the [Quality Assurance Science Activity Centre – Americas \(QA/SAC\)](#).

The SAG-TAD authorizes the World Data Centre for Precipitation Chemistry (WDCPC) to make the precipitation chemistry and wet deposition data from laboratories that participate in the LIS studies accessible from the [WDCPC website](#) and to sequester data from laboratories that do not participate in these studies. The SAG-TAD has set this requirement so that LIS results are available as an indicator of laboratory performance (accuracy/comparability) to a data user who is accessing precipitation chemistry and wet deposition data. To facilitate the evaluation of laboratory performance, WDCPC-accessible data are accompanied by links to the appropriate laboratory's [Study Results posted on the QA/SAC website](#).

Inter-laboratory Comparison Studies are conducted two times per year. The QA/SAC sends participants a set of simulated rain samples for analysis. Analytical results must be reported to the QA/SAC within a prescribed time limit. Results are compiled, statistically summarized, and reported under the [Study Results tab of the QA/SAC website](#).

**Contact the [QA/SAC Manager](#) to register for LIS participation.**

Participation in laboratory studies outside of the WMO/GAW is encouraged. Such studies include the [Acid Deposition Monitoring Network in East Asia Interlaboratory Comparison Project](#) and [European Monitoring and Evaluation Programme Laboratory Intercomparisons](#).

Laboratory managers should use LIS results to assess laboratory measurement biases. A method for calculating laboratory biases is given in [Appendix A](#). Once calculated, the values should be compared with the DQOs for Laboratory Inter-Network Bias listed in Table A.1 ([Appendix A](#)).

Corrective actions are imperative for unsatisfactory LIS performance. Suggested actions for improving performance include:

- Improving internal laboratory QC
- Routinely analyzing and control-charting Certified Reference Materials (CRMs)
- Analyzing split samples provided by a collaborating 'in-control' laboratory
- Arranging for an expert visit/audit by another GAW precipitation chemistry laboratory manager.

### 6.3.7 Laboratory QA Reporting

All laboratories making precipitation chemistry and wet deposition measurements should produce an annual QA Report that documents the quality of the data generated by the laboratory. Copies of the report should be made available to data users upon request.

## 6.4 QA/QC for Data Management

Sponsors of each precipitation chemistry and wet deposition station should have a carefully designed and managed data handling system that encompasses site, laboratory, and office data activities. Key elements of the QA/QC system for data management are described in the following subsections.

### 6.4.1 GAW Data Management Objectives

- (1) Every station reporting precipitation chemistry and wet deposition data submits final validated data in one-year increments no later than one year after the year in which the data were collected; for example, data for 1 January through 31 December of year 1 are delivered by 31 December of year 2.

- (2) (a) For a station that belongs to a network with a centralized data management system, data are delivered to a system manager, who combines the data for all network stations, making it available to the user community through the network's data management system; or (b) for a station that is not served by a centralized data management system as in (a), data are delivered to the WDCPC, which loads the data into the WDCPC data management system, making it available to the user community via the [WDCPC website](#). The WDCPC makes data from stations that belong to a network (as in 2a) accessible on the [WDCPC website](#) by posting links to these network data management systems.
- (3) Each measurement reported to the WDCPC is accompanied by a "validity flag" that indicates whether the measurement is missing ("M" flag), invalid ("X" flag), valid and above the limit of detection ("V" flag), or valid and at or below the limit of detection ("L" flag for a measurement below the limit of detection or "D" flag for a measurement at or below the limit of detection that is set equal to the limit of detection). Assigning flags is the responsibility of the agency reporting the data.

#### **6.4.2 Data Custody**

Data custody in each measurement system must follow a well-defined protocol. Each person involved, from the site operator to the laboratory analyst to the data manager, must understand and follow this protocol carefully. Every staff member must be trained to detect data flow problems and initiate suitable corrective actions when there is a breach of protocol.

#### **6.4.3 QC of Field Data**

Field data reported on the sample history forms (examples described at the end of [Chapter 3](#)) consist of measurement data (e.g., rain gauge depth, sample weight/volume, etc.) and sampling information (e.g., comments on malfunctioning instrumentation, contamination, etc.). To ensure proper data management, these forms must be reviewed upon receipt of the sample from the field: 1) to identify inaccurate and/or missing data so that prompt actions can be taken to correct errors and address missing values, and 2) to identify operational problems at the site so that actions can be taken to restore the site to correct operations as soon as practical. Experience has shown that the most efficient way to accomplish this is to assign a person the task of inspecting each sample history form as it arrives from the field station. This person's responsibility is to find and correct errors, collect missing information or samples, and initiate corrective actions. Forms are examined for:

- missing entries and transcription or recording errors
- evidence of poor collection efficiency of the sampler
- missing samples
- instrument malfunctions or problems.

#### **6.4.4 QC of Laboratory Data**

Laboratory data should be quality controlled to identify problems and inaccuracies. A laboratory staff member should be responsible for reviewing and releasing the data. Section 4.3 of [Chapter 4](#) provides a comprehensive description of laboratory QA/QC procedures.

#### **6.4.5 QC of Merged Field/Laboratory Data**

Field and laboratory data must be merged into a single database. It is essential that the field and laboratory data match exactly. There can be no mismatched samples or sampling dates. To ensure correct matching, both data sets should contain the same sample identification numbers and sampling dates. Computerized checks provide an efficient way to ensure matching.

#### **6.4.6 Commenting and Flagging of Data**

Every data management system should include a data QC officer whose duty is to review all data before delivery to the network data manager or WDCPC. The data QC officer should conduct a set of data validation, verification, and assessment checks before signing off on the annual data set. Checks include outlier tests, ion balance checks, detection limit verification, and graphical time series plots. Data that fail the assessment process should be flagged appropriately.

Data delivered to the WDCPC should comply with the formatting and flagging described in [Chapter 5](#).

## **6.5 Documentation and Document Control**

All elements of a precipitation chemistry and wet deposition measurement program must maintain a current set of documents and manuals. This includes such documents as a Field Station Description, Field Operators Manual, Field and Laboratory Instrument Manuals, Laboratory Operations Manual, Data Management Manual, QA Project Plan, QA Reports, Data Reports, and personnel job descriptions. Each document should contain a document control system whereby pages are indexed properly and dates of new/updated pages are indicated.

## **6.6 Training and Upgrading**

Staff training is key to success. Field and laboratory personnel should be trained and certified before beginning their jobs. Refresher training is important, as well, and should be done routinely, e.g., every 2 years, to ensure that all personnel maintain correct up-to-date practices and procedures. Update training should precede the institution of any new field or laboratory procedure.

## **6.7 Corrective Action**

Speedy repair or replacement of a malfunctioning wet deposition sampler is of paramount importance, since failure to collect a wet-only deposition sample leaves a void in the data record. Having a sampling record that is complete is fundamental to having a representative data set. Repairs should be made within a day or two of detecting a problem. Remote stations should have a supply of spare parts or replacement instruments on-site and field site operators should be trained to handle instrument repair.

## **6.8 Calibration and Traceability**

Proper calibration of field and laboratory equipment is essential. All calibrations should be traceable to accepted international standards, such as the U.S. National Institute of Standards and Technology. All calibration procedures should be documented in network manuals and QA Project Plans.

Calibrations at field stations should include weighing balances (where applicable), recording rain gauges, and precipitation sensors. In the laboratory, all instruments including analyzers and the containers and tools for preparing solutions must be properly calibrated.

## **6.9 Audits**

*Performance Audits* and *System Audits* of the field, laboratory, and data management systems are recommended every 5 years. *Performance audits* are defined as systematic checks that are quantitative in nature while *system audits* are systematic qualitative checks that usually consist of reviewing the measurement procedures to ensure that they are consistent with standard operating procedures.

Examples of performance audits include checks of the sensitivity of the sensor on the precipitation sampler and proper operation of the sampler, results of the analysis of Certified Reference Materials, and evaluation of computational checks such as ion balance and conductivity balance and application of these computations to trigger reanalysis and corrective actions.

If possible, audits should be conducted by independent experts.

## **6.10 Routine and Non-Routine Procedures for Assessing Accuracy, Precision, Completeness, Representativeness, and Comparability**

Successful precipitation chemistry and wet deposition measurement programs address five key QA/QC elements: accuracy, precision, completeness, representativeness, and comparability. Below are descriptions of specific activities that address these elements.

### 6.10.1 Accuracy

It is not possible to determine the **absolute accuracy** of precipitation chemistry measurements since the formation and occurrence of precipitation are natural processes and there are no Standard Reference Materials (SRMs) for these natural processes. Lacking SRMs for precipitation, it is especially important to minimize measurement errors by adopting well-designed standard operating procedures and regularly evaluating the accuracy of the various parts of the measurement system. Methods of minimizing measurement errors have already been discussed above. Methods of quantifying the accuracy of components of the measurement system include:

- Comparing the ion concentrations of dynamic field blanks, which represent sources of positive and negative bias, against those of real precipitation samples. Ion concentrations in field blanks generally should be less than or equal to the 15<sup>th</sup> percentile of the ion concentrations of precipitation samples.
- Determining the amount of evaporation, contamination from dry deposition, and change from other sources that occurs while samples sit in the field samplers. This is done by setting a known amount of precipitation of known concentration in a closed sampler and determining the loss of volume and concentration changes by the end of a nominal sampling period.
- Comparing laboratory analysis of certified reference materials to the certified concentrations.
- Audits of the field, laboratory, and data management systems.

The results of these studies can be used to bracket the uncertainties of the overall data set. Further discussion of measurement uncertainties can be found at the following websites:

<http://physics.nist.gov/cuu/Uncertainty/index.html>  
[Quantifying Uncertainty \(eurachem.org\)](http://www.eurachem.org)

### 6.10.2 Precision

Determining the overall precision of precipitation chemistry measurements is best done by operating two precipitation chemistry samplers and standard precipitation gauges simultaneously at the same site for at least one year. The two chemistry samplers must be operated independently but the samples should be analyzed by the same laboratory. Paired sample differences can be evaluated to determine whether they are significantly different from zero and to estimate the magnitude of the differences (which is equal to the precision). [Appendix A](#) contains a recommended method for estimating precision based on this type of data. The results should be compared with the DQOs for Overall Precision as stated in Table A.1 of [Appendix A](#). Publications that describe methods for estimating precision include NILU (1996), Sirois and Vet (1999) and Nilles et al. (1994).

### 6.10.3 Completeness

Completeness is defined as a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected under correct normal conditions (U.S. EPA, 1976). Two data completeness criteria, documented in Olsen et al. (1990), are applied to precipitation chemistry and wet deposition measurements. The two completeness criteria are:

- 1) **The completeness of rain/snow gauge measurements of precipitation depth.** This is identified as the *Percent Precipitation Coverage Length* (%PCL), which is the percent of the summary period (e.g., month, season, year) for which information is available on whether precipitation occurred. In practice, this means the percentage of time that a standard precipitation gauge was operating properly and reporting precipitation measurements. If precipitation was known to have occurred but the gauge failed to record the amount, then there is a loss of precipitation coverage for that measurement period. The %PCL is the number of measurement periods for which the standard rain gauge operated properly to record a precipitation amount divided by the total number of measurement periods. For example, if for the 365 sampling days in a year, the standard rain gauge reported data properly for only 300 of those days, then the %PCL = 82.2%.
- 2) **The completeness of precipitation depth associated with valid chemical analysis and valid sample collection.** This is defined as the *Percent Total Precipitation* (%TP). For a given summary period (e.g., month, season, year), it is the percentage of total precipitation depth measured by a standard gauge that was associated with valid precipitation chemistry data. For example, if a standard precipitation gauge

measured 1000 mm in a year but the total standard gauge depth associated with valid precipitation chemistry samples was 782 mm, then the %TP = 78.2%. Note that the %TP should be calculated for each measured ion since some ion concentrations may be invalid or missing more than others.

Acceptable data completeness criteria are listed in the table below. Note that a station is required to meet both quarterly and annual completeness criteria to satisfy the annual completeness requirements.

<p><b>Acceptable Seasonal Data Completeness Criteria</b></p> <p>%PCL <math>\geq</math> 90% %TP <math>\geq</math> 70%</p> <p><b>Acceptable Annual Data Completeness Criteria</b></p> <p>%PCL Annual <math>\geq</math> 90% and Each quarter <math>\geq</math> 60% %TP Annual <math>\geq</math> 70% and Each quarter <math>\geq</math> 60%.</p>
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Methods of ensuring that the data completeness criteria are met include:

- repairing malfunctioning instruments as quickly as possible to minimize the amount of lost data
- making daily standard precipitation gauge measurements, even if precipitation chemistry samples are not collected
- using collection vessels with ample collection orifices to afford sample volumes that are sufficient for a full set of chemical analyses even with small precipitation events
- diluting low-volume samples in the laboratory to maximize the number of chemical species analyzed
- minimizing the risk of sample contamination, leakage, breakage, or loss through the implementation of good operating procedures.

#### 6.10.4 Representativeness

Representativeness can be ensured by conducting site inspections and audits on a regular basis to verify that the siting criteria are continually being met. Sample representativeness can be ensured by minimizing all possible sources of sample contamination through good sampler design and proper standard operating procedures.

#### 6.10.5 Comparability

Overall measurement comparability can be determined by collocating precipitation chemistry samplers and rain gauges of two or more countries at a specific location. The samples from each precipitation chemistry sampler are sent to their associated precipitation chemistry laboratories. Each sampler operates in the exact manner as if in its own country. Data from the different countries' samplers are analyzed to determine their comparability and overall inter-network bias. This bias is compared with the DQOs for *Inter-Network Bias* as listed in Table A.1 of [Appendix A](#), where there is a method for calculating this statistic. Examples of published inter-network comparability studies include Sirois et al. (2000), and Areskoug (1988).

#### 6.11 Special Studies

Special studies should be conducted to investigate specific measurement problems or the impact of changing measurement methods. Examples include:

- studies to determine whether ions are adsorbed on or desorbed by sample collection vessels
- studies to assess the comparability of new and old sampling procedures and instrumentation
- studies to determine the suitability of various sample preservatives.

The results of these types of special studies should be used to select the best sampling methods and to estimate the uncertainty in the measurement system. Results should be reported in formal reports and made available to the data user community upon request.

## 6.12 References

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