

## 6. QUALITY ASSURANCE AND QUALITY CONTROL

This chapter describes the major Quality Assurance and Quality Control procedures that should be incorporated within the GAW Precipitation Chemistry Programme. Previous chapters on Siting, Standard Operating Procedures, Laboratory Procedures and Data Management contain many of the QA/QC procedures relevant to those activities, so this chapter summarizes the most important of these procedures and describes several overarching quality assurance activities not yet presented.

Quality assurance and quality control are now common terms that are understood by many in the precipitation chemistry measurement community. However, within the field of QA/QC, there is much terminology that might not be familiar to some readers. Those readers are referred to the following Web-based glossary of terminology called the *Terminology Reference System* operated by the United States Environmental Protection Agency (U.S. EPA, 2002) <http://www.epa.gov/trs/>.

Quality assurance and quality control are extremely important to the collection and reporting of high quality GAW data. For this reason, this chapter begins with a review of GAW Data Quality Objectives for precipitation chemistry measurements, thereby providing the measurement community with specific levels of measurement quality that must be achieved by every NMHS making GAW precipitation chemistry measurements. The following sections describe specific QA/QC procedures that should be instituted by NMHSs at their monitoring stations, laboratories and data centres in order to meet the prescribed Data Quality Objectives.

### 6.1 Quality Assurance Requirements

This section describes the specific Quality Assurance procedures recommended for adoption by the NMHSs involved in the GAW Precipitation Chemistry Programme. It includes subsections on Data Quality Objectives, the requirement for a Quality Assurance Officer, and the need for proper Quality Assurance documentation.

#### 6.1.1 Data Quality Objectives

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. They provide the statistical framework for planning and managing environmental data operations consistent with user's needs (U.S. EPA, 1997).

Quantitative Data Quality Objectives for the GAW Precipitation Chemistry Programme are shown in Table 1.1 and described in detail in Appendix A. These DQOs have been developed by the GAW Scientific Advisory Group for Precipitation Chemistry based on published achievable measures of data quality. The DQOs provide each NMHS with a specific set of objectives for bias, precision, completeness, detection limits, and calibrations. **It is the responsibility of each and every NMHS to review these DQOs and adjust their GAW precipitation chemistry measurements to meet the DQOs.**

#### 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).

It is recommended that each NMHS prepare a Quality Assurance Project Plan for its GAW Precipitation Chemistry Programme. The QAPjP should describe in detail the QA/QC procedures incorporated into the measurement system. Guidelines for the preparation of QA Project Plans can be found in U.S. EPA (1998). Other public-domain guidelines for the preparation of QA Project Plans are equally acceptable. The QAPjPs should readily available to laboratory staff and updated at least annually.

### **6.1.3 Quality Assurance Reporting**

Each NMHS is responsible for assessing the quality of its precipitation chemistry data against the Data Quality Objectives stated in Table 1.1. The process of analyzing the quality of the data is known as *Data Quality Assessment*, which is described in detail in a U.S. EPA (2000).

It is recommended that each NMHS prepare an annual or biannual Quality Assurance Report that includes a description of the QA/QC procedures used in the GAW precipitation chemistry measurement system and a formal assessment of data quality relative to the Data Quality Objectives. The report should focus, in particular, on the accuracy, precision, completeness, comparability and representativeness of the data. All QA Reports should be submitted to the GAW Quality Assurance - Science Activity Centre for the Americas for archiving. An outline of a QA Report suitable for adaptation to precipitation chemistry measurements can be found under the "Metadata details" worksheet at the following web site: [http://cdiac.esd.ornl.gov/programs/NARSTO/NARSTO\\_template\\_atmospheric\\_measurements.xls](http://cdiac.esd.ornl.gov/programs/NARSTO/NARSTO_template_atmospheric_measurements.xls). Statistical methods for the assessment of data quality are described in documents accessible from the following US Environmental Protection Agency web site: [http://www.epa.gov/quality/qa\\_docs.html](http://www.epa.gov/quality/qa_docs.html).

## **6.2 Quality Assurance and Quality Control for Field Operations**

Described below are specific QA/QC activities and procedures recommended for use at GAW Precipitation Chemistry Programme measurement sites.

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

To ensure collection of spatially- and temporally-representative GAW data, all precipitation chemistry sites must satisfy the siting criteria presented in Chapter 2 for "Global" and "Regional" GAW sites. GAW sites should be assessed annually with respect to the siting criteria to determine whether they continue to meet the minimum GAW siting requirements. An independent audit of sites is recommended every five years. Changes to sites should be documented as indicated in Section 2.6.

### **6.2.2 Instrumentation**

Described below are QA/QC procedures that ensure the correct installation and operation of GAW Precipitation Chemistry Programme monitoring instrumentation. Where appropriate, the methods are referenced back to specific sections in the Field and Laboratory Chapters.

#### **6.2.2.1 Satisfying Minimum Operating Specifications**

Precipitation chemistry collectors and standard precipitation gauges must meet the minimum operating specifications listed in Chapter 3, e.g., sensor sensitivity, chemical inertness. Only those precipitation chemistry samplers and standard precipitation gauges that meet the specifications should be purchased and used in the GAW Precipitation Chemistry Programme. (**Section 3.2.1**)

#### **6.2.2.2 Instrument Pretesting**

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

### 6.2.2.3 Spare Parts

Spare parts and/or spare collectors should be stored at GAW precipitation chemistry sites whenever possible to allow quick instrument repair/replacement, thereby reducing measurement down-time.

### 6.2.3 Sample Collection and Handling

A short summary of the most important QA/QC procedures related to field sample collection and handling is given below. Detailed procedures are described in Chapter 3.

#### 6.2.3.1 Sample Container Testing

Precipitation sample containers (e.g., buckets, bags, funnel-and-bottles) used in precipitation chemistry samplers must be tested for chemical inertness before being deployed to the field. Specific testing must be done to ensure that the collection vessel material does not adversely affect precipitation through the adsorption/desorption of major ions to/from the vessel walls. Testing should be done with high and low volumes of deionised water and real rainwater samples of known concentrations or reference solutions (where reference solutions have known certified concentrations of the major ions within the normal range of real precipitation samples). The different volumes will indicate whether the material adsorption/desorption effects, if they exist, are volume-dependent and the different rainwater or reference solutions will indicate whether the effects are matrix- or concentration-dependent.

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

#### 6.2.3.2 Sample Container Cleaning

All sample containers (including funnels and bottles) must be cleaned with deionised water between uses – preferably at the analytical laboratory but, if necessary, at the field sites. At GAW sites where the collection vessels are cleaned on-site, the deionised 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). Methods must include careful cleaning and rinsing of the bucket and/or funnel rims since they are in direct contact with the collector hood. After being cleaned, sample containers that are not used immediately must be air dried in a clean location, sealed or covered in plastic, and stored in a clean area before being placed in the precipitation chemistry collector. See Sections 3.3.1 and 4.3.1.3 for specific sample container cleaning procedures.

#### 6.2.3.3 Sample Collection

Specific quality control procedures that prevent contamination from occurring during sample collection and handling include:

- Inspecting the collection vessels for visible signs of contamination **before they are placed in the collector**
- Standing on the downwind side of the precipitation chemistry samplers when collecting samples in order to reduce the potential for contamination
- Wearing disposable plastic gloves whenever handling precipitation sample containers and transferring samples
- Instructing operators never to touch the inside of sample containers
- Replacing dirty gaskets on the underside of the sampler hood at frequent and regular intervals (every few months depending on the dirtiness of the site)
- Checking for, and documenting, sample leaks in the field, during shipping, and upon receipt at the laboratory. (**Section 3.2.1**)

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

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

- Maintaining sample temperature at 4°C during periods of storage on-site, in the laboratory, and in shipment.
- Weighing samples to determine sample volume at the GAW precipitation chemistry station and at the laboratory in order to detect leaks in transit
- Instituting procedures to eliminate leaks during transit. **(Section 3.3)**

#### **6.2.5 Blanks**

Field blanks are to be collected on a regular basis to ensure that sampling methods and materials do not interfere with sample chemistry. It is recommended that, for daily sampling, 2 to 4 blanks be collected randomly per month and, for weekly sampling, 1 to 2 blanks per month. This should be done at every site. The blanks are to be collected by pouring an aliquot of deionised water into a dry sample container (e.g., bucket, bag, funnel-and-bottle) that was installed in the precipitation chemistry sampler for a sampling period during which no precipitation occurred (or for a short period which simulates the sampling period). The aliquot should be submitted to the laboratory in the same manner as precipitation samples. Blank sample data should be checked regularly for evidence of contamination and should be routinely control-charted. **(Section 3.3.2.3)**

**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**

*Sample History Forms* must be filled out at GAW precipitation chemistry stations for every sampling period (see examples in Figures 3.1 and 3.2). Specific QA/QC items related to field data reporting are:

- Check for legible, accurate and thorough completion of sample history forms. Whenever problem entries are found, contact the station operator promptly to correct the problem and obtain accurate data.
- Based on information contained on the sample history forms, assess the quality of the sample data, for example, to identify problems with the operation of the sampling instruments and adherence or non-adherence to the standard operating procedures. **(Section 3.5)**

#### **6.2.7 Routine Instrument Checks**

When site operators collect precipitation chemistry samples, they must check that the precipitation chemistry samplers and standard gauges are operating correctly. Specific checks include:

- The sampler has electrical power and the switch is in the “on” position
- The sensor, upon being wetted or triggered, opens the hood
- The hood or cover returns to the ‘closed’ position when the sensor is no longer wet
- The hood makes a tight seal on the rim of the sample container with no visible gaps between the hood and the rim
- The standard precipitation gauge is mounted correctly and does not leak. **(Section 3.2.1.4)**

### **6.2.8 Preventive Maintenance**

In order to reduce instrument breakdowns, preventive maintenance to the precipitation chemistry collectors should be performed at regular intervals. **(Section 3.2.1.4)**

### **6.2.9 Regular Site Inspections**

Sites should be inspected once per year by NMHS staff to detect problems with the instrumentation and sample handling procedures as well as continued conformance to siting criteria. The inspector should check for the following:

- Proper precipitation chemistry sampler operation
- Lid moves properly and completely seals the precipitation sample container in dry weather
- Lid gasket is clean
- The sensor activates the sampler lid to open and close as designed
- The sample containers are clean
- The sample handling area is clean
- Correct adherence to Standard Operating Procedures (SOPs)
- Proper storage and shipping of samples
- Proper placement of instrumentation
- Confirmation that GAW siting criteria are satisfied. **(Section 2.6.)**

### **6.2.10 Corrective Action**

Corrective action must be taken as quickly as possible after an instrument breaks down or sampling irregularities are detected. Such immediate response will ensure the site meets the GAW Precipitation Chemistry Programme annual data completeness objective of 95%. As mentioned in Section 6.2.2.3, corrective action times are reduced if spare parts or extra instruments are already on-site.

## **6.3 QA/QC for Laboratory Operations**

Laboratory operations, as discussed in Chapter 4, cover a wide range of activities including sample reception, field sampling support, sample transfer, storage and analysis, quality assurance, quality control, and data reporting. QA/QC related to these laboratory operations can be broken down into 3 parts, namely:

- 1) Setting laboratory data quality objectives
- 2) Adopting good laboratory QA/QC practices
- 3) Regular QA/QC reporting.

Specific quality control procedures in the laboratory include:

- Good laboratory practice
- Good sample handling practice
- 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 sample chain-of-custody
- Traceability of calibration standards
- Control charting
- Accuracy checks (calibration controls, spikes, blinds, reagent blanks)

- Precision checks (within-run and between-run duplicates)

All of these activities must be considered when operating a well-controlled laboratory facility.

### 6.3.1 Laboratory Data Quality Objectives

The Data Quality Objectives of all GAW precipitation chemistry laboratories are presented in Table 1.1 and in 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

Quality control 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 samples should be weighed (to check for leakage during transit and to confirm the field weight) and inspected for visible contamination. Problem samples should be noted and the information verified.

### 6.3.3 Chemical Analyses QA/QC

Chemical laboratories involved in the analysis of precipitation samples are expected to meet the Data Quality Objectives. This can be done only through strict adherence to SOPs and QA/QC procedures within the analytical system. Specific QA/QC procedures are described below.

#### 6.3.3.1 Calibration Control and Verification

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

- Using ultra-pure reagents traceable to Certified Reference Materials for the production of calibration *standards*
- Checking that the slope, intercept and correlation coefficient of each calibration curve are within acceptable ranges (the use of control charts is recommended)
- Using calibration standards that cover a range from 2% to 98% of all precipitation sample concentrations
- Using extra calibration standards in non-linear portions of the calibration curves;
- Calibrating at the beginning and end of each analytical run
- Analyzing and control-charting one or more *quality control check solutions* in each batch of samples. It is recommended that *calibration check solutions* correspond to the 10<sup>th</sup>, 50<sup>th</sup> and 90<sup>th</sup> percentiles of all sample concentrations for the NMHS. When a calibration check solution exceeds the control limits, the entire batch of samples should 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. Here a “run” is defined as a set or batch of consecutive measurements with the analytical instrument operating within fixed calibration settings and within 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.

It is recommended that 2% to 5% of the sample load be analyzed as between-run replicates and that all replicate samples be randomly selected from the sample stream. The replicate analysis results should be control-charted immediately and, whenever the control limits are exceeded, the entire batch of samples should be reanalyzed. At the end of each year the replicate analysis data can be used to determine the analytical precision, which, in turn, can be compared against the Data Quality Objective for laboratory precision as stated in Table A.1 (see Appendix A for calculation methods). No less than 30 replicate samples should be used when calculating the analytical precision.

#### **6.3.3.3 Laboratory Blanks**

Deionised water and reagent blanks should undergo the same chemical analyses as the precipitation samples. One deionised water and one reagent blank should be analyzed per analytical batch. The analysis results should be control charted and corrective action taken when the control limits are exceeded, i.e., replacement of the deionised water and/or reagents.

#### **6.3.3.4 Blind Samples**

Blind samples composed of deionised water, acidified deionised water, simulated rainwater or certified reference materials should be inserted into the sample stream on a weekly basis. The results should be control charted 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 (in order to obtain enough sample for full chemical analyses) and/or to reduce high concentration samples to the normal operating range of the analytical instruments. It is recommended that the dilution method be tested routinely on 1% of the samples. The accepted method for testing dilutions is to analyze aliquots of large precipitation samples both before and after dilution (certified reference materials are acceptable as well). Before- and after- differences that exceed 10% of the undiluted concentrations should trigger a review of the dilution system. Such checks should be carried out routinely and continuously control charted.

### **6.3.4 Control Charting**

Quality control charts are statistical tools used to ensure that a measurement system is in control. Using control charts should be a standard practice in all GAW laboratories. See Section 4.3.2.2 for further discussion of control charts. 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 that analytical results are accurate and complete. Specific QA/QC procedures include:

- Verification that all control limit exceedences on laboratory control charts have been dealt with in a timely and satisfactory manner (e.g., re-analysis)
- Verification that all extreme values and below detection limit values are correct
- Identification (flagging) of invalid or questionable analytical results, e.g., cases of laboratory contamination and instrument malfunctions
- Identification and re-analysis of samples that failed ion balance criteria.

### **6.3.6 Laboratory Intercomparison Studies**

**All laboratories that analyze GAW precipitation chemistry samples must participate in the WMO/GAW Laboratory Intercomparison Studies.** NMHS personnel in every country are required to register their chemical laboratory (or laboratories if there is more than one involved) with

the manager of the GAW Precipitation Chemistry Programme Laboratory Intercomparison Studies at the QA SAC for the Americas (see laboratory registration form in Appendix G). Twice per year, intercomparison samples will be sent to each laboratory for analysis and the analytical results must be reported to the QA SAC within the prescribed time interval.

**Precipitation chemistry data from countries that do not participate in the WMO/GAW Laboratory Intercomparison Studies will not be archived within the World Data Centre for Precipitation Chemistry.** Such data will be sequestered in data files separate from the main archive. It is the intention of the WDCPC to include in the data archive an indicator of laboratory performance based upon the WMO/GAW Laboratory Intercomparison Studies.

Participation in laboratory intercomparisons outside of the WMO/GAW is encouraged. Such studies include the EMEP Laboratory Intercomparison Studies, the Canadian Laboratory Intercomparison Studies and the East Asian Network Intercomparison Studies. Details of these studies can be obtained by contacting the GAW Precipitation Chemistry Programme Quality Assurance Science Activity Centre in Albany, NY, USA.

Results of the WMO/GAW Laboratory Intercomparison studies should be used by each NMHS to assess its *Between Network Laboratory Bias*. A proposed methodology for calculating the Laboratory Bias is given in Appendix A. Once calculated, the laboratory bias values should be compared against the stated Data Quality Objectives for Inter-laboratory Bias in Table 1.1 (see Appendix A for details).

#### **6.3.6.1 Corrective Action for Unsatisfactory Performance in One or More GAW Precipitation Chemistry Programme Laboratory Intercomparison Studies**

Unsatisfactory performance by a GAW precipitation chemistry laboratory reduces the overall quality of the GAW Precipitation Chemistry Programme. Immediate corrective action must be taken to upgrade the performance of an under-performing laboratory to a satisfactory level. Suggested actions include:

- Improving the internal laboratory quality control programme
- Setting up a routine system of 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.

Laboratories with unsatisfactory performance that wish to arrange an expert visit should contact the WMO Secretariat or the QA SAC Americas.

#### **6.3.7 Laboratory QA Reporting**

It is recommended that all GAW precipitation chemistry laboratories produce an annual Laboratory Quality Assurance Report, which documents the quality of the data generated by the laboratory. Copies of the report should be made available to GAW data users upon request.

### **6.4 QA/QC for GAW Precipitation Chemistry Programme Data Management**

Each NMHS should have a carefully designed and managed data handling system that encompasses site, laboratory and office data activities. Key elements of the QA system for data management are described in the following subsections.

#### **6.4.1 The GAW Precipitation Chemistry Data Management Objective**

The data management objective of the GAW Precipitation Chemistry Programme is as follows: **To submit final validated precipitation chemistry data in one year blocks to the GAW World Data Centre for Precipitation Chemistry (WDCPC) once per year, no later than 1 year after the year in which the data were collected.** For example, data for January 1 to December 31, 2002 should be submitted to the WDCPC by December 31, 2003.

It is a GAW requirement that each measured data value be accompanied by a “validity flag” which indicates whether the datum is valid (a “V” flag) or invalid (an “M2” flag). These flags must be assigned to the measurement data by the NMHS staff member responsible for the collection and reporting of the data. Details of the flagging system are given in Chapter 5 and Appendix F.

#### **6.4.2 Data Custody / Data Flow**

Data custody and data flow within each NMHS must be well-defined and carefully followed. Each person involved in the GAW Precipitation Chemistry Programme from the site operator to the laboratory analyst to the data manager, must understand and carry out data activities with great care and precision. All staff must be trained to detect data flow problems and initiate suitable corrective action.

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

Field data reported on Sample History Forms will 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, the Sample History Forms must be reviewed immediately upon receipt from the field in order to: 1) identify inaccurate and/or missing data, 2) identify operational problems at the site and 3) initiate immediate corrective action. It is recommended that a designated individual be assigned the responsibility of inspecting the Sample History Forms as they arrive from the field sites for:

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

It is the responsibility of this person to correct errors, collect missing information/samples and initiate corrective action.

#### **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. Suggested quality control procedures are identified in Sections 4.3 and 6.3.5.

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

Field and laboratory data must be merged into a single database. It is critical that the field and laboratory data match exactly, i.e., no mismatched samples and sampling dates. To ensure correct matching of field and laboratory data, both data sets should contain the same sampling date information and sample identification numbers. These numbers should then be used by a computer programme to do the matching.

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

Each NMHS should flag the GAW Precipitation Chemistry Programme data in a manner that clearly identifies the data as *Valid* or *Invalid* (see Section 5.6.1). A data quality control officer should review all data to ensure that measurement problems are identified and flagged in the data sets. When reporting data to the GAW World Data Centre for Precipitation Chemistry, care must be taken to conform to the GAW Precipitation Chemistry Programme data flagging system (see Section 5.6 and Appendix F).

#### **6.4.7 Data Quality Assessment**

Each NMHS should carry out a set of data validation, verification and assessment checks before signing off on the data for each year. These checks include outlier tests, ion balance checks, graphical time series plots and detection limit verification. Data that fail the assessment process should be flagged appropriately. Statistical methods for the assessment of environmental data are described in documents at the following U.S. Environmental Protection Agency web site: [http://www.epa.gov/quality/ga\\_docs.html](http://www.epa.gov/quality/ga_docs.html).

### **6.5 Documentation and Document Control**

All elements of the GAW Precipitation Chemistry Programme must be documented and kept current. Each NMHS is responsible for producing a set of manuals including manuals for field, laboratory and data handling operations as well as for quality assurance. Ideally, this includes: Field Operators Manual, Instrumentation Manuals, Laboratory Manual, Data Management Manual, Quality Assurance Project Plan, annual Quality Assurance Reports, detailed job descriptions of personnel, Site Descriptions, and Data Reports. 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 and upgrading are key to the success of the GAW Precipitation Chemistry Programme. All field and laboratory personnel should be trained and certified prior to the start of sampling at a GAW site. New operators must be trained immediately. Refresher training should be done routinely, e.g., every 2 years, to ensure that the field and lab personnel maintain correct up-to-date practices and procedures. Whenever new protocols are instituted, formal training should take place in the field and/or laboratory.

**NOTE: Site operators should always be trained by certified training staff, not by other site operators.**

### **6.7 Corrective Action**

Speedy repair of malfunctioning wet deposition collectors is a necessity since failure to do so will result in unsatisfactory data completeness. NMHS personnel should ensure that corrective action is taken so that repairs to instruments (in the field and laboratory) are done within one to two days of detection. At remote GAW precipitation chemistry sites, spare parts and/or instruments should be kept on site so that faulty parts and instrumentation can be replaced immediately. Specialized training of on-site personnel may be required in such cases.

### **6.8 Calibration and Traceability**

Proper calibration of field and laboratory equipment is essential. All calibrations should be traceable to accepted international standard organizations such as the U.S. National Institute of Standards and Technology and all calibration procedures should be documented in network manuals and quality assurance project plans.

At GAW precipitation chemistry sites, calibration methods should be followed for weighing balances (where applicable), recording rain gauges, and precipitation sensors. In the laboratory, calibrations must be applied to all analytical procedures.

## 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 the standard operating procedures.

Performance audits include checks of the collector sensor sensitivity and operation, laboratory analysis of Certified Reference Materials, and computational checks (e.g., of the ion balance calculation) in the data centre. **Formal audits are ideally carried out by independent experts.** Where this is not possible, auditors from the NMHS can be used.

## 6.10 Routine and Non-Routine QA/QC Procedures for the Assessment of Measurement Accuracy, Precision, Comparability, Completeness and Representativeness

Five elements of quality assurance must be addressed by each NMHS in order to ensure high quality GAW precipitation measurements. The five QA elements are: accuracy, precision, completeness, representativeness and comparability. Specific quality assurance activities that address these issues are described below.

### 6.10.1 Accuracy

**It is not possible to determine the absolute accuracy of precipitation chemistry measurements since there are no Standard Reference Materials falling from clouds at known rates.** As a result, it is important that each NMHS: a) minimizes its measurement errors by adopting well-designed standard operating procedures and b) quantifies the accuracy of certain 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 against those of real precipitation samples. Ion concentrations in field blanks should generally be less than or equal to the 15<sup>th</sup> percentile of the ion concentrations in real precipitation samples.
- For weekly or monthly sampling periods, determining the amount of evaporation and dry deposition contamination to which samples are subject while sitting in the collectors. This can be done by setting a known amount of precipitation of known concentration in a closed collector and determining the lost volume and the increase in concentration by the end of a nominal sampling period.
- Analysis of certified reference materials by the laboratory.
- 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>

<http://www.measurementuncertainty.org/>.

### 6.10.2 Precision

Each NMHS can determine the overall precision of its precipitation chemistry measurements by operating two precipitation chemistry collectors and standard precipitation gauges simultaneously at the same site for at least one year. The two chemistry collectors must be operated independently but the samples should be analyzed by the same laboratory. Paired sample differences can be tested 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 calculation results should be compared against the Data Quality Objectives for Overall Precision as stated in Table 1.1. 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 to be obtained under correct normal conditions (U.S. EPA, 1976). There are two data completeness criteria adopted by the GAW Precipitation Chemistry Programme. These are documented in Olsen et al. (1990) (note that this reference identifies 4 additional completeness criteria which are not used in the GAW programme). The two completeness criteria are:

- 1) **The completeness of rain/snow gauge measurements of precipitation depth.** This is defined 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 or not. In practice, this means the percentage of the time that a standard precipitation gauge was operating properly and reporting whether precipitation occurred or not. If precipitation was known to have occurred but no measurement of precipitation depth was available, then it is assumed that there was no knowledge of precipitation occurrence. Hence, if there were 365 sampling days in a year and a 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.

For the GAW Precipitation Chemistry Programme, the acceptable data completeness levels are as follows (note that a site is required to meet both quarterly and annual completeness criteria to satisfy the annual completeness requirements):

<b>GAW Acceptable Seasonal Data Completeness Measures</b>
%PCL $\geq$ 90%
%TP $\geq$ 70%
<b>GAW Acceptable Annual Data Completeness Measures</b>
%PCL
Annual $\geq$ 90% and
Each quarter $\geq$ 60%
%TP
Annual $\geq$ 70% and
Each quarter $\geq$ 60%.

Methods of ensuring that the data completeness criteria are met include:

- repairing malfunctioning instruments as quickly as possible to minimize lost data
- making precipitation depth measurements every day, even if precipitation chemistry samples are not collected
- using large collection vessels so that sample volumes are sufficient for full chemical

- analysis 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**

*Site representativeness* can be assured by carrying out site inspections and audits on a regular basis to verify that the appropriate siting criteria are continually being met. *Sample representativeness* can be assured 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 chemistry samplers and rain gauges of two or more GAW-member countries at a single site. The precipitation chemistry samples from each collector should be sent to their associated GAW precipitation chemistry laboratories (i.e., each collector should operate in the exact manner it would if it were located in its own country). The data from the different countries' samplers should be analyzed to determine their comparability and *overall inter-network bias*. The inter-network bias should be compared against the Data Quality Objectives for Inter-Network Bias as stated in Table 1.1 (see Appendix A for a recommended method for estimating inter-network bias). Examples of published inter-network comparability studies include Sirois et al. (2000), and Areskoug (1988).

Multinational field comparisons are the best method of establishing overall measurement comparability between GAW countries. However, it is recognized that such studies are not feasible for all GAW countries.

#### **6.11 Special Studies**

Special studies should be carried out 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 international basis upon request.

#### **6.12 References**

- American Society for Testing and Materials (ASTM) (2002) Manual 7A Manual on Presentation of Data and Control Chart Analysis, Seventh Edition, pp. 135. ASTM International, West Conshohocken, Pennsylvania, USA.
- Areskoug, H. (1988) In *Expert Meeting on Sampling, Chemical Analysis and Quality Assurance* (edited by Nodop, K. and Leyendecker, W.), Arona, Italy 11-14 Oct. Published by Norwegian Institute of Air Research, Kjeller, Norway.
- Nilles, M. A., Gordon, J. D., and Schroder, L. J. (1994) The precision of wet atmospheric deposition data from National Atmospheric Deposition Programme/National Trends Network sites determined with collocated samplers. *Atmos. Environ.* **24A**, 661-672.

- NILU (1996), EMEP Manual for Sampling and Chemical Analysis. Norwegian Institute for Air Research, Kjeller, Norway.
- Olsen, A. R., Voldner, E. C., Bigelow, D. S., Chan, W. H., Clark, T. L., Lusi, M. A., Misra, P. K. and Vet, R. J. (1990) Unified wet deposition data summaries for North America: data summary procedures and results for 1980-1986. *Atmos. Environ.* **24A**(3), 661-672.
- Sirois, A. and Vet, R. (1999) The precision of precipitation chemistry measurements in the Canadian Air and Precipitation Monitoring Network (CAPMoN). *Environ. Monitor. and Assess.* **57**, 301-329.
- Sirois, A., Vet, R. J. and Lamb, D. (2000) A comparison of the precipitation chemistry measurements obtained by the CAPMoN and NADP/NTN networks. *Environ. Monitor. and Assess.* **62**, 273-303.
- Taylor, J. K. (1987) *Quality Assurance of Chemical Measurements*. Lewis Publishers, Inc., Chelsea, MI, USA.
- U.S. Environmental Protection Agency. (1976) *Quality Assurance Handbook for Air Pollution Measurement Systems – Volume 1 Principles*. EPA-600/9-76-005, Research Triangle Park, NC.
- U.S. Environmental Protection Agency. (1997) *EPA/OA/Office of Communications, Education, and Media Relations: Terms of Environment: Glossary, Abbreviations, and Acronyms (Revised December 1997)*. <http://oaspub.epa.gov/trs/>.
- U.S. Environmental Protection Agency. (1998) *EPA Guidance For Quality Assurance Project Plans, EPA QA/G-5*, Report EPA/600/R-98/018, EPA Office of Research and Development, Washington DC. This document can be downloaded from website: <http://www.epa.gov/swerust1/cat/epaqag5.pdf>.
- U.S. Environmental Protection Agency (2000) *Guidance for Data Quality Assessment – Practical Methods for Data Analysis*, EPA Report QA G-9 QA00 Update, Washington DC, July 2000. This document can be downloaded from website: <http://www.epa.gov/quality/qs-docs/g9-final.pdf>.
- U.S. Environmental Protection Agency. (2002) *Terminology Reference System*. <http://www.epa.gov/trs/>.