Quality Assurance/Quality Control in Acid Deposition Monitoring

Acid Deposition and Oxidant Research Center
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Introduction

- **Wet deposition data are used for**

-assessments of spatial distributions and temporal trends,

-research into wet deposition processes,

-research into aquatic and terrestrial effects of wet deposition,

-the development and evaluation of long range transport computer models

Why QA/QC ?

There has been a strong demand by the scientific community for the quantification of data quality, particularly data uncertainty.

- **The relatively new field of `quality assurance/quality control for wet deposition measurements' have been evolved.**
- **Many of the philosophies , principles and procedures in this area have been adapted from QA/QC practices for air pollution measurements and analytical laboratories.**

The difference between QA and QC

- **The US EPA differentiates between QC and QA in the following way:**

  **** QC is a `system of activities to provide a quality product ' and QA is a `system of activities to provide assurance that the QC system is performing adequately. In other words, QA is QC for QC'.****
- **QC ensure that the analytical system is 'in control '(i.e. operating within specified limits).**
- **QA ensure that the quality control procedures are working correctly.**

The five QA/QC elements

QA programs generally address five QA/QC elements, namely:

1. ***Accuracy*** **-the degree of agreement of a measurement with an accepted reference or true value.**
2. ***Precision*** **- a measure of the mutual agreement among individual measurements of the property, usually under prescribed similar conditions.**

3. ***Completeness*** **- 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.**
4. ***Representativeness*** **-the degree to which data accurately and precisely represent a characteristic of a population or parameter variations at a sampling point, a process condition, or an environmental condition.**
5. ***Comparability*** **-the confidence with which one data set may be compared to another**

1. Accuracy

- Because the absolute accuracy of wet deposition measurements cannot be defined, most QA program do not asses `overall accuracy'. In stead, they break the measurement system into component parts and determine the measurement uncertainty with each.
- Methods for assessing uncertainty of component parts,

- they include:

-submission of field blanks for defining errors due to sampling and sample handling procedures,

-routine collection of field information for use in validating chemistry data,

-special studies using standard reference solutions to determine errors induced by evaporation and dry deposition,

-routine audits of the field, laboratory and data management systems,

-submission of blind samples to the laboratory,

-analysis of ultra pure water samples by the laboratory.

2. Precision

- **'Overall precision', i.e. precision of the entire measurement system, is measured by co-locating two precipitation chemistry collectors.**
- **The two sets of instruments are operated independently and the precipitation samples are analyzed separately at the laboratory.**
- **The laboratory precision is measured by running duplicate analyses of the same samples, both within and between analytical runs.**

3. Completeness

There are four major data completeness issues of concern to wet deposition sampling. They are:

(1) the portion of the data summary period(season or year) with complete records of the amount of precipitation that fell (%PCL: Percent precipitation coverage length),

%PCL = ((Number of days in the summary period)-(Number of days with missing or unknown precipitation))/(Number of days in the summary period)*100

(2)the potion of the precipitation associated with valid chemical analysis and valid sample collection (%TP: Percent total precipitation),

%TP = (Sum of precipitation amounts for samples with valid sample component measurements)/(Sum of precipitation amounts for all samples)*100

(3)the fraction of the total number of sampling periods(daily, weekly, monthly etc.) having valid concentration data (%VSMP), and

(4)the percentage of time in the summary period represented by samples having valid concentrations (%VSL).

4. Representativeness

- **Site representativeness can be assured and controlled by auditing the sites and their surrounding at regular intervals. This ensures that the program's siting criteria are not being violated without the knowledge of the data users. Timely modification or relocation of sites can be used to correct violations of the siting criteria.**
- **Sample representativeness can be assured by minimizing sample contamination and maximizing collection efficiency of the precipitation chemistry collectors. Quality control measurers such as wearing gloves during sample changes and adjusting collector sensors to maximize sensitivity can be used.**

5. Comparability

- **Comparability is often referred to as `relative accuracy'.**
- **There are two methods used to address comparability in wet deposition measurement programs.**
- **One is to carry out co-located sampling of several measurement programs at the same site, and the other is carry out laboratory inter-comparison studies.**
- **The former focuses on overall measurement comparability while the latter addresses laboratory comparability.**

QA/QC for Field Operations
-Sample Collection and Handling (1)

- ***Collection vessel preparation***

  -Cleanness of collection funnel, tubes and bottles should be noted, e.g. conductivity tests on rinse water, wearing plastic gloves when placing new sampling bottles.

- ***Sample collection***

  -Samples should be collected from the precipitation chemistry collector without contamination, e.g. approaching the collector from the downwind side, keeping fingers out of collector vessels.

Sample Collection and Handling (2)

- ***Sample handling*** **-Samples should be handled and stored on-site without contamination or chemical change.**
- ***Field data reporting*** **-Complete and accurate data reporting are important.**
- ***Sample shipping*****-Shipping procedures are also important to arrive at the laboratory within specified times and without spilling and chemical change, e.g. the use of curie systems to minimize travel time and the use of ice-pack.**

QA/QC for Laboratory Operations

QA/QC for Laboratory Operations can be broken down into next functions:

-laboratory support for field operations

-laboratory sample handling (e.g. weighing samples upon arrival to check the field weight),

-chemical analysis (e.g. calibration checks, replicate analyses, blank checks, control charting),

-sample keeping,

-corrective action,

-data reporting,

-inter laboratory inter comparisons, and

-quality assurance reporting.

Major QC in laboratories

- **Many laboratory quality control procedures exist.**
- **Some are qualitative and some are quantitative.**

The qualitative procedures

- **Include:**
  - **-Good laboratory practice(GLP)**
  - **-Good sample handling practice**
  - **-Definition of standard operating procedures(SOPs)**
  - **-Preventive maintenance of instruments**
  - **-Analyst training and upgrading**
  - **-Appropriate facilities and instrumentation**
  - **-Proper documentation**
  - **-Laboratory inspections or audits**
  - **-Laboratory safety**
  - **-Well-defined chain-of-custody**
  - **-Traceability of standards**

The quantitative procedures
Control charting (1)

A statistical technique designed to ensure that a laboratory analysis system is in statistical control.

Control charts are plots on which quality control data are plotted (ideally on a real-time basis) against historically-determined statistical limits which identify 'in-control', 'warming', and 'out-of-control' situation. In most cases, control chart data come from the analysis of calibration control solutions, within-run and between-run replicate samples, reagent blanks, and so on.

Control charting (2)

- **The control limits are determined from the mean(Xbar) and standard deviation(σx) of repeat measurements of these samples.**
- **The warning limits at Xbar ±2σ**
- **The control limits at ±3σ**
- **This is done by plotting the QC sample results against the predetermined control limits after each analytical run.**
- **If the control limits are exceeded, then the analytical run is repeated.**

Instrument calibration and calibration checks (1)

It should be kept in mind,

-making all calibration solutions from ultra-pure or reagent grade chemicals traceable to reference standards

-checking that the slope, intercept, and correlation co-efficient of the calibration curve are within acceptable range

-using calibration standards that cover a concentration range of at least 95% of the expected sample concentrations, and using more standards in non-linear section of the calibration curve;

-calibrating at the beginning of each analytical run, and at the end of each run;

-analyzing and control-charting one or more calibration check solutions in each batch of samples (note that these check solutions are normally secondary in-house reference standards)

Instrument calibration and calibration checks (2)

Calibration checks by standard reference material

- **Instrument calibrations are quality controlled by analyzing standard reference materials(SRMs) at regular intervals.**
- **The accuracy of the analytical system is normally reported as the deviation from the true value, i.e.**

  %Error=(Xbar-X_{srm})/X_{srm} , where

  Xbar: mean value of repeated measurements of the SRM,

  X_{srm}:certified value of SRM

Replicate sample analyses

- **Replicate analysis of samples provides a measure of analytical precision.**
- **Two types of replicate analyses are carried out -within-run and between-run.**
- **Both within-run and between-run precision are calculated as the standard deviation(SD) of replicate analyses X and Y of samples i from 1 to n. When the standard deviation is independent of concentration, it is calculated as $SD=\{\Sigma(Xi-Yi)^2/2n\}^{1/2}$**
- **Precision is frequently expressed as the coefficient of variation of the replicate analyses, i.e. the SD/mean concentration. The frequency of replicate analyses varies from laboratory to laboratory, but normally represents about 4 to 5 % of the sample load.**

Major QA in laboratories

Quality assurance procedures ensure that the quality control system is in working correctly.

Two QA procedures are of particular note:

- Blind audits

  Blind audits are programs in which standard reference solution(or precipitation samples of known concentration) are submitted to the chemical laboratory without the knowledge of the laboratory staff (i.e. blindly).
- Laboratory inter comparison studies

  This studies are used to determine the comparability (or relative accuracy) of several laboratories.

Quality Assurance Reporting

- The final deliverable of every quality assurance program is the assessment and reporting of data quality.
- This is achieved in many different ways, one of the most common of which is the publication of formal Quality Assurance Reports.
- The second methods of reporting is the journal or report publication that focuses on a specific aspect of quality.

Summary

- In without quality control procedures in place, laboratories cannot hope to remain in-control, and without quality assurance procedures in place, they cannot ensure that they are in-control.
- Also, without formal reporting of the QA/QC results, laboratories cannot demonstrate to data users that they are producing high quality analytical data. It is therefore very important that Quality Assurance Programs adopt QA/QC reporting as a regular laboratory function.