QAQC in Water Quality Monitoring & Analysis

by
Dr. V. A.Mhaisalkar
Professor & Head
Department of Civil Engineering
Visvesvaraya National Institute of Technology (VNIT), Nagpur

Data Validation and Analysis

Validation of water quality data involves checking and assessment of the data to see if there have been any errors made during sampling or analysis of the water quality sample or data entry.

Specific Data Validation Tests

A series of data checks should be carried out to identify any problems in the data. A number of tests is described below including:

- Absolute checking/Data entry

- Checking if data is within the detection limits of a particular method

- Checking if the data is within the expected ranges for a parameter

- Checking if there are too many (or too few) significant digits reported

- Checking if data are physically or scientifically possible (general checks)

- Checking correlation of parameters (Some conditional checks)

- Checking the correlation between EC and TDS

- Checking the cation-anion balance

Aspects of Data Analysis

The specific analyses to be conducted depend on the water quality information desired, or the specific questions about water quality being asked. For example:

1. What is the water quality at any specific location or area?
2. What are the water quality trends in the region: is the quality improving or getting   worse?
3. How do certain water quality parameters relate with one another at given sites
4. For surface water (rivers): how do certain water quality parameters relate to   stream discharge?
5. What are the total mass loadings of materials moving in and out of water systems,   and from what sources and in what quantities do these originate?
6. Are sampling frequencies adequate and are sampling stations suitably located to   represent water quality conditions in an area?

Types of Data Analysis

There are a number of ways that water quality data can be made more meaningful to a non-technical audience including the following:

• Comparing the data with national water quality standards
• Comparing the data to international standards
• Calculating water quality indices, such as Water classification index
• Determining the water quality classification and comparing to desired classification
• Comparing the data derived from one area to data from another similar area
• Calculation of trends showing how water quality has changed at one or more sampling points either over time or due to a particular event (e.g., the construction of a power station on a river reach)
• Calculating how much mass of a substance has travelled down a river (i.e. mass fluxes).

Graphical techniques

There are a number of advantages associated with the data analysis using graphical
techniques as follows:

- trends in the data are often easier to spot
- outlying data points are normally obvious
- many people find visually presented data more acceptable and more readily understandable

Time Series Graphs

Histograms (bar charts)

Pie Charts

Profile Plots

Geographical Plots

Advanced Techniques

• **Linear trend analysis** –
Trend analysis can be important for the analysis of water quality data as it can aid understanding of the variability of data and also allow predictions to be made of likely future water quality

• **Regression and correlation analysis** –
Regression and correlation analysis are related techniques which are used to assess the association between two or more variables; both can be useful techniques for establishing the factors which regulate the variability of a particular water quality parameter.

• **Autocorrelation analysis:**
To assess the association between two or more measurements of the same variable at different times.

• **Hypothesis testing**:
Statistical analysis to check for relationships within the data (e.g. a step trend)

• **Mathematical modeling**
A technique for representing and predicting, by means of mathematics, the behaviour of a system;

Quality Assurance Programme

The objective of a water quality monitoring programme is to produce data and information on the quality of water resources, so that appropriate management can take place.

The goal of a laboratory Quality Assurance Programme is:

• To ensure meaningful water quality assessment
• To have confidence in results, based on standardized procedures for all components of water quality monitoring

Quality Assurance in Water Quality Monitoring

The full set of activities for QA in WQM which should be documented are:

- monitoring network design,
- sample collection (including field measurements, bottle labeling, proformae, preservation, treatment and transport).
- sample control and documentation in the laboratory
- maintenance of equipment
- laboratory AQC
- Data validation, reduction, and reporting

1 Monitoring network

Monitoring network is to be designed depending on the objective of the programme. It may be flexible.

2 Sample collection

Sample collection includes the following activities:

•collecting the sample in the correct manner, in the correct container
•field measurements of water quality: e.g. Temperature, pH, EC, DO
•labeling sample bottles and completing sample proformae
•preservation (if necessary) and transport to the laboratory

3 Control Samples

•Field check samples to provide routine checks on sample stability. Checks can be done by dividing a real sample in two and making a known addition to one portion. The recovery is a check that conservation, sample transport and storage are satisfactory.
• Duplicate samples to provide checks on variability.

Sample control and documentation – Sample receipt register

Each laboratory should have a bound register, which is used for registering samples as they are received.

Work Assignment and Personal Registers

The laboratory incharge should maintain a bound register for assignment of work. This register would link the lab. sample number to the analyst who makes specific analyses, such as pH, EC, BOD, etc.

An estimate of time needed for performing the analyses may also be entered in the register.

Each laboratory analyst should have his/her own bound register, where all laboratory readings and calculations are to be entered.

When analysis and calculations are completed, the results must be recorded in a register containing data record sheets described in the next section.

4. Maintenance of Equipment

Regular maintenance of laboratory equipment is key to making controlled analyses of water samples.

Calibration procedures: In analyses where an instrument has to be calibrated, the procedure for preparing standard solutions and making a standard curve must be specified, e.g., the minimum number of different dilutions of a standard to be used, method detection limit (MDL), range of calibration, verification of the standard curve during routine analyses, etc. Recommendations

The primary goal of the Quality Assurance Programme in water quality monitoring is that the information obtained from the monitoring system meets the required quality criteria. Those using the data must have confidence in the data.

Quality Assurance/Quality Control (QA/QC)

These are the measures to ensure that the data are accurate and useful. Even the best water quality data will have errors, and it is the goal of the QA/QC program to measure and minimize these errors.

Data quality is described by its accuracy, precision, completeness, representative ness, and comparability.

Accuracy is the difference between measured value and the "true" value.

It is one of the most difficult QA/QC parameters to measure, since you usually don't know what the true value is. The most common way to estimate accuracy is to test your methods with a sample that has a known chemical concentration (this kind of sample is known as a **reference sample**). Accuracy is then the difference between the measured value and the true value, expressed as a percentage of the true value:

Accuracy = 100. x (Measured Value - True Value)/True Value If a method's accuracy is 10%, you would expect your measurements to be within 10% of the true value.

Precision describes the repeatability of methods.

A method is precise if you get the same result every time you analyze similar samples, and imprecise if you get widely-differing results.
Precision is measured by analyzing two duplicate water samples that are taken at the same location and time. It is expressed as the **Relative Percent Difference (RPD)** between the chemical concentrations measured from the two duplicates:

RPD = 100. x (Duplicate 1 - Duplicate 2)/(Average of the two duplicates) where Average = (Duplicate 1 + Duplicate 2)/2

Completeness measures how well you finished all of the sampling that you originally planned to do. Completeness is expressed as the percentage of samples you measured relative to the number that were planned.

For instance, if you were supposed to take 10 samples at a location and were only able to take 9, your data completeness would be 90 percent. Few monitoring programs can achieve 100% completeness; bad weather, equipment problems, and budget problems all result in some loss of data.

Representativeness describes how well your sample represents the environmental condition you are trying to measure. It is controlled primarily by how you choose your sampling locations and timing.

For instance, a sample collected just after an oil spill would not be representative of typical conditions in the river. A sample collected downstream of a sewage treatment plant would not be representative of background (or natural) water quality.

Comparability describes how well your data can be compared with other data. To maintain comparability, the methods you use to collect and analyze samples should remain consistent - you should not switch methods in the middle of a study without good reason.

If you are trying to compare your results to data from an earlier study, you should sample at the same locations and at the same times of year.

SOURCES OF ERROR

A typical sample goes through a lot of steps before it becomes part of your water quality data set, and there is potential for error at each of these steps. The major sources of error are measurement error, sample handling error, and natural variability.
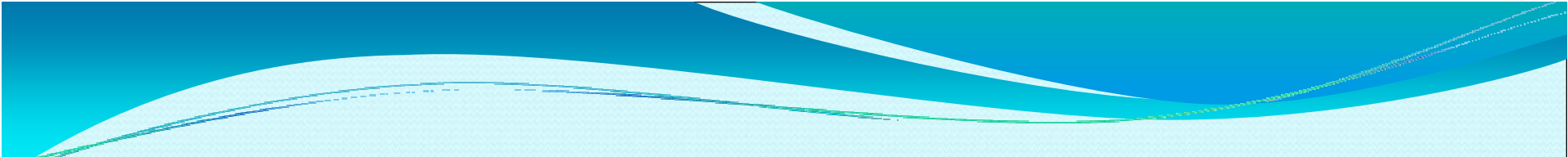
Measurement errors result because none of the methods (field kits, calibrated instruments, or laboratory analysis) provide perfect water quality measurements. Measurement error can be reduced by instrument calibration, proper training, and equipment maintenance, but it never goes away entirely.

A special kind of measurement error comes from the method's **detection limit.** As chemical concentrations approach zero it becomes more and more difficult to get accurate measurements. The point where the method is no longer able to detect a chemical is called the method detection limit.

For instance, if a field kit cannot measure nitrate concentrations below 5 mg/l; this method's detection limit is therefore 5 mg/l. The important idea here is that you never report a value of zero concentration, since all you really know is that the concentration is less the detection limit. Instead of writing zero as the result, you write the detection limit with a less-than symbol (for example, nitrate concentration = <5 mg/l).

Sample handling errors come from the ways in which you collect and handle your samples. Samples may be contaminated from your hands, or because air is trapped in the sample bottle when you close it. Improper storage and transportation of the sample are other sources of handling error. This kind of error is minimized by closely following proper handling procedures.

Natural variability is often the biggest source of imprecision, and is unfortunately largely out of your control. When you are measuring water quality in a river, you are really only sampling the small piece of the river that you are able to fit into your sample bottle. During the few seconds it takes you to fill your 1-liter sample bottle, literally thousands of cubic feet of water have flowed past you. Every parcel of this water will have different water quality characteristics than what you measure in your sample. Natural variability is a basic feature of a river, and cannot be controlled. The best approach is therefore to quantify this variability by taking as many samples as you can afford.
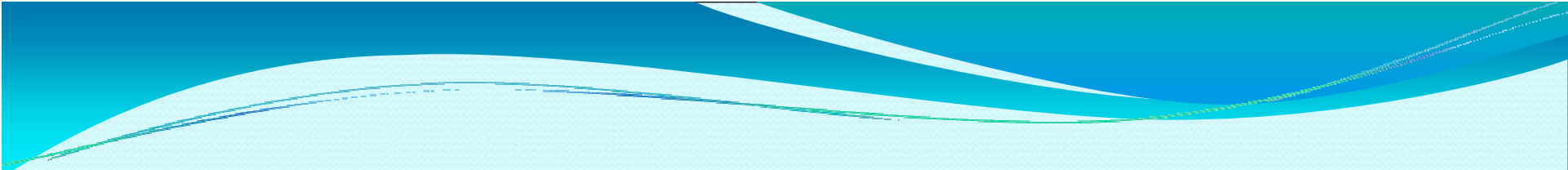
QUALITY CONTROL CHECKS

Every sampling program should have a set of tests and checks that measure data quality. Common checks include duplicate samples, blanks, reference samples, and performance audits.

Duplicate samples are simply two identical samples collected and handled in the same way. They measure the precision of your methods. **Field duplicates** are two samples collected in the field from the same location at the same time; these measure the precision of your entire procedure (sampling, storage and handling, and laboratory analysis). **Laboratory duplicates** are two samples split from a single sample once it has arrived at the laboratory. These test the precision of the laboratory methods only.

Blanks are samples containing pure, uncontaminated water. Blanks contain none of the chemical you are trying to measure, and are used to identify contamination that might occur in the field or laboratory. If your laboratory measures a positive chemical concentration in a blank, you then know that there is a source of contamination somewhere in your procedure. A **field blank** is a blank sample that is placed in a sample bottle at the field site, and is handled the same as a normal sample. It identifies contamination that might occur in your entire procedure (from field sampling to laboratory analysis). A **laboratory blank** is prepared at the laboratory, and tests for laboratory contamination only.

Reference samples are prepared by an independent laboratory, and contain a known concentration of the chemical you are measuring. They are similar to the standards used in instrument calibration, except that the actual concentration is kept secret from your laboratory people. Reference samples measure the accuracy of your laboratory procedures.

A **performance audit** is an independent review of your sampling and laboratory methods, conducted by someone who is familiar with your project but is not a part of your day-to-day project team. The idea is to have your work reviewed by a qualified person who has no stake in the outcome of your project. The performance auditor will check to see how well you are following your sampling and QA/QC plans.

QUALITY ASSURANCE/QUALITY CONTROL PLANS

Every water quality sampling program should have a detailed **Quality Assurance/Quality Control Plan** that describes:
•Data quality objectives
•Equipment maintenance and calibration
•Chain of custody for samples
•Quality control checks
•Data reduction, validation, and reporting

Data quality objectives are your goals for accuracy, precision, completeness, representativeness, and comparability.

The **chain of custody** identifies who is responsible for collecting, transporting, and analyzing each sample. This helps to ensure that your project team knows their responsibilities, and makes it easier to identify the sources of problems.

Data reduction, validation, and reporting describes how you will store and report your results. All data should be filed in an organized database, and should be checked to make sure that numbers are entered correctly.

WHAT IS MEANT BY QUALITY ASSURANCE AND QUALITY CONTROL?

Quality Assurance and Quality Control (QAQC), when explained in terms of a sample of water from a lake, river or stream, means that the analysis of the sample is carefully controlled to guarantee that the results are assured to be accurate within acceptable limits and recognized standards.

HOW DOES A LABORATORY ACHIEVE QAQC STATUS?

The first step is to adopt **standard methods** for each parameter to be tested.

Secondly, all workers in the laboratory must be carefully **trained** so that they understand the importance of each step in the analysis procedure.

Thirdly, all **steps must be properly logged and continuously reviewed** to be sure no hitch occurs.

Selecting sampling sites

A sampling site is the general area of a water body from which samples are to be taken. The exact place at which the sample is taken is commonly referred to as a sampling station.

Selection of sampling sites requires consideration of the monitoring objectives and some knowledge of the geography of the water-course system, as well as of the uses of the water and of any discharges of wastes into it.

Example 1

Objective   : Identification of baseline conditions in the water-course
                   system.

Key question : What are the background levels of variables in the water?

Monitoring   :

- Analyze for dissolved oxygen, major ions and nutrients.
- Characterize seasonal or annual concentration patterns.
- Determine annual mean values of water quality variables .

Information expectations:

•A description of the quality of water in the water-course system before it
is   affected by human activities.

Example 2

Objective   : Detection of any signs of deterioration in water quality.

Key question : Are any new water quality problems arising?

Monitoring   : Detect any short-term trends. Detect any long-term trends.

Information expectations:

•Description and interpretation of water quality changes with respect to time.

Example 3

Objective   :   Identification of any water bodies in the water-course system that do not meet the desired water quality standards.

Key questions: What are the designated uses?
        What are the water quality standards for the designated uses?

Monitoring   : Survey for presence of contaminants. Determine extreme values of contaminating variable(s).

Information expectations:

•Description of the contaminating variable(s), the extreme values measured, when and where they occur and how they conflict with the standards.

•Evaluation of the hazards to human health, damage to the environment and any other adverse effects.

•Interpretation of the general state of the water bodies relative to the established standards.

Example 4

Objectives   : Identification of any contaminated areas.

Key questions   : What are the indicators of contamination?
                      What are the contaminating substances?
                       Where are the possible sources?

Monitoring
- Detect contamination.
- Determine the concentration of the variables that indicate contamination.
- Determine the areas affected by the contaminants and whether these areas are increasing.
- Detect the main pollution source(s).

Information expectations :

• Maps or charts showing the distribution of contaminants.
• Classification charts, maps and/or lists showing the contaminated areas in order of severity in relation to the source(s) of pollution.
• Classification is usually made in four or five classes.

Example 5

Objective : Determination of the extent and effects of specific waste discharges.

Key questions : How far away from the point of discharge does the effluent affect the receiving water?
     What changes are being made to the ambient water quality?
      How does the effluent affect the aquatic ecosystem?

Monitoring : Determine the spatial distribution of pollutants
   Measure the effects of pollutants on aquatic life and various
   water uses.

Information expectations :

•The extent to which water quality has changed compared with baseline conditions.
• Cause-and-effect relationships at different levels of the water ecosystem, e.g. basic nutritional requirements of fishes and fish population.
• Maps showing the distribution of pollution.
• Comparison with water quality guidelines.

Example 6

Objective : Evaluation of the effectiveness of a water quality management intervention.

Key question: What are the positive and negative results of a particular water quality management intervention in terms of its effects on the concentration of polluting substances in the water?

Monitoring :
- Determine whether the particular water quality management intervention has resulted in significant changes in water quality.
- Compare mean values of contaminant concentration before and after the intervention.
- Detect short- and long-term trends.

Information expectations:
- Evidence that mean concentration of contaminants was higher before the management intervention. Contaminant concentrations are decreasing with time.

Thanks