# Quality Assurance & Quality Control

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# Introduction

# Objectives of a QA/QC programme

**To obtain reliable data**

- For decision support
- To compare data across Malé Network and between Malé Network and other networks

**For data to be reliable, it has to be <u>accurate</u>, <u>precise</u>, <u>representative</u>, <u>complete</u>**

# Definitions

- **Quality control:** The routine use of **procedures** designed to achieve and maintain a **level of quality** for a product or measurement system, ie, QC is a system of activities to obtain a quality product.

- **Quality assurance:** A set of coordinated **actions**—plans, specifications and policies—to assure that a measurement programme is **quantifiable** and can produce **data of known quality** ie, QA is a system of activities that ensures that a QC programme is functioning adequately.

# Responsibilities

**Steering committee:**

- Endorse QA/QC programmes, review their implementation

**Technical committee:**

- Prepare and implement QA/QC programme[1]
- Prepare data report
- Prepare QA/QC implementation report
- Develop and implement training programme
- Compare analysis of QA/QC activities with those of other networks, ie, EANET, EMEP

**NIA:**

- Prepare national monitoring plan
- Prepare and implement national QA/QC programme[2]

**Monitoring agencies:**

- Execute national monitoring plan & QA/QC programme[3]

- Appointment of a QA/QC network manager
- Develop data quality objectives (DQOs)
- Provide information to prepare Standard operating procedures (SOPs)
- Assure that adequate reference material is used
- Implement round robin analysis survey
- Exchange information with and provide technical support for NIAs
- Compare analysis of sampling and analysis methods in the network

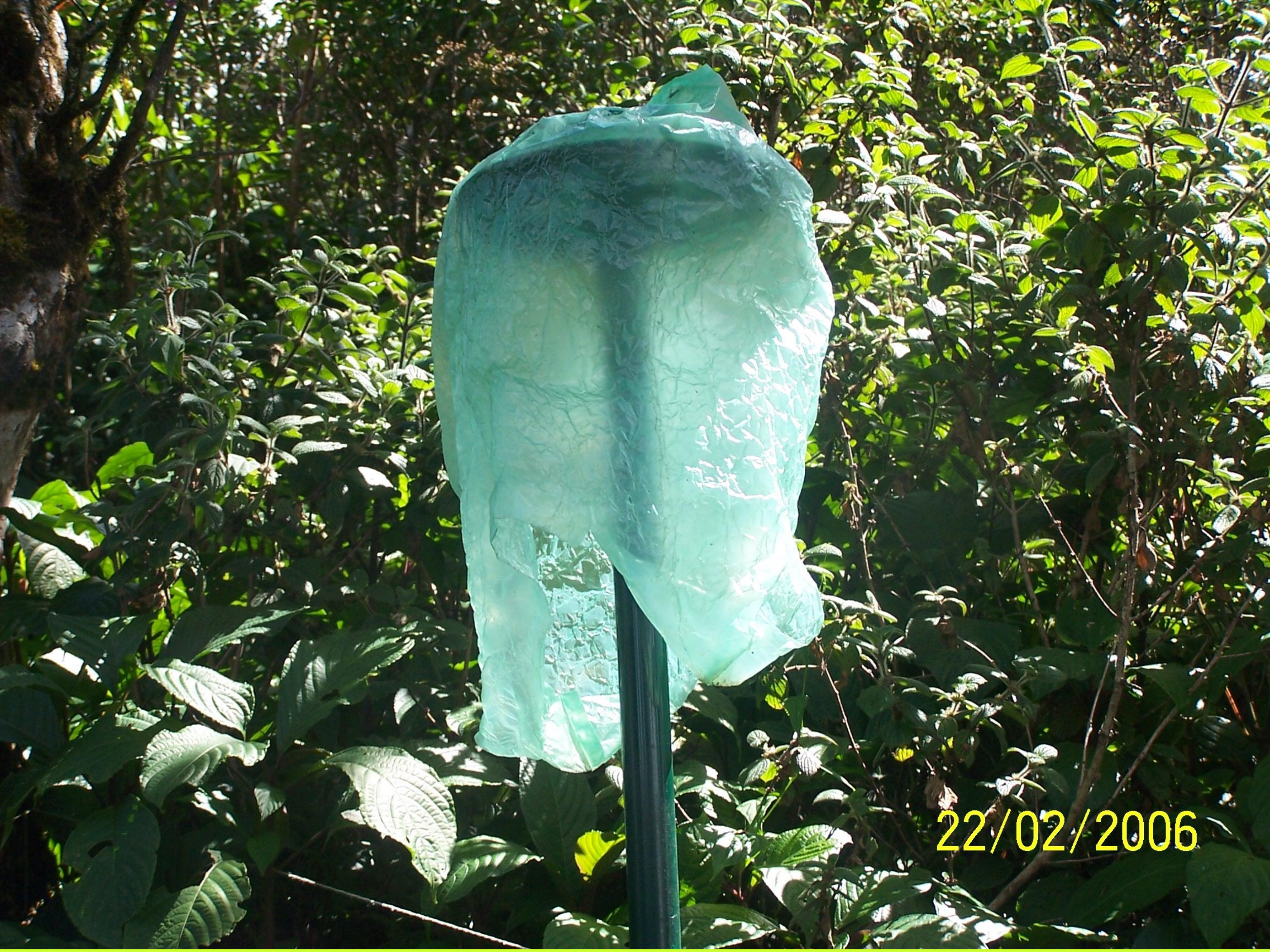
- Appoint a national QA/QC manager
- Provide guidance for preparing SOPs
- Distribute round robin samples, collection of results
- Reporting to the Technical Committee
- Site and laboratory audits
- Comparing sample collection and analysis methods used in a country

- Appoint personnel
- Prepare SOPs for various activities
- Execute routine sample collection and analysis
- Report to NIA
- Participate in QA/QC activities conducted by NIA, eg, round robin analysis

# Requirements of a QA/QC programme

1. **Coverage**

- Should include QA/QC activities for all components of the measurement/ analysis systems, ie, field site, lab, data reporting and management processes



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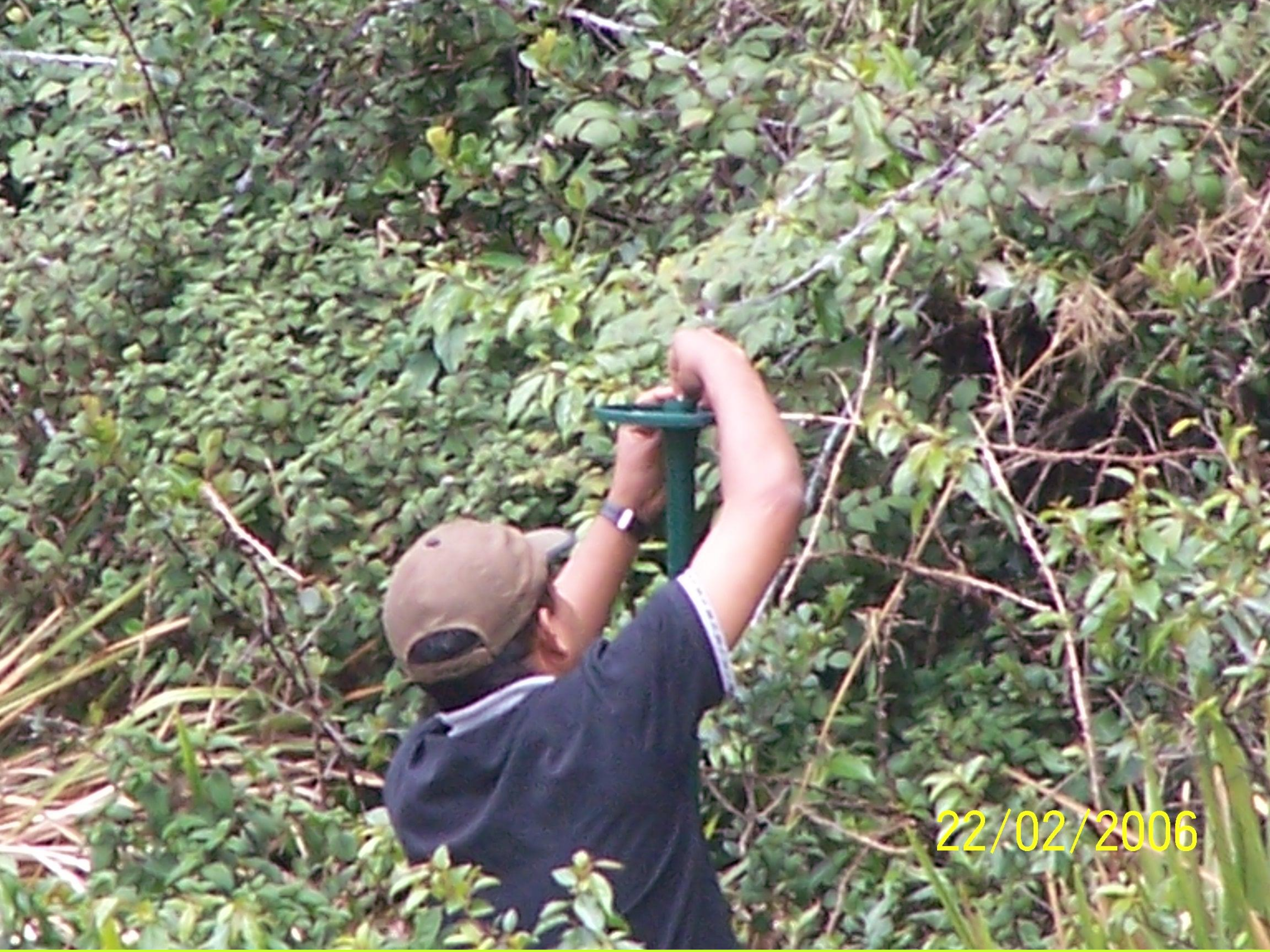
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- QA/QC programmes should cover all activities of the Technical Committee, NIAs, and monitoring organizations

- NIAS and monitoring organizations should do various QA/QC activities, including development of QA/QC programmes and SOPs.

## 2. National programmes

- Each country should develop its QA/QC programme (based on the model given in the technical manual or otherwise) and revise it periodically, using possibly the same format provided in the technical manual.

### Items to be covered in the national QA/QC program

**1.0 Objectives**

**2.0 Definition and importance of the QA/QC programs**

**3.0 Roles and responsibilities of relevant entities**

**4.0 Requirements of a QA/QC programme**
4.1 Standard operating procedures
4.2 Sampling and chemical analytical methods
4.3 Data quality objectives

**5.0 Sampling sites**
5.1 Criteria for selection of sampling sites
5.2 Documentation of site conditions
5.3 Assessment and documentation of representativeness
5.4 Site audit

**6.0 Collection and handling of samples**
6.1 Sampling apparatus
6.2 Operation check of samplers
6.3 Handling and transportation of samples
6.4 On-site inspection
6.5 Parallel sampling

**7.0 Measurement and chemical analysis of samples**
7.1 Standard materials and solutions
7.2 Storage and pretreatment of samples
7.3 Adjustment of instruments
7.4 Fluctuation of instruments
7.5 Calculation of detection limits and determination limits
7.6 Duplicate and repeated analysis
7.7 Ion balance
7.8 Comparison of calculated and measured conductivity

**8.0 Data management**
8.1 Data check at laboratories
8.2 Treatment of extraordinary data, and data validation
8.4 Assessment of data quality by NIA
8.5 Assessment of adequacy of sampling sites, and completeness of data collection

**9.0 Data reporting**
9.1 Site information
9.2 Sample collection
9.3 Chemical analysis
9.4 QA/QC activities

**10.0 Training programmes**

3. **Assignment of responsibility**

A A clear assignment of responsibility should be done for all personnel working in the programme.

4. **Prepare standard operating procedures (SOPs)**

**SOPshould be prepared** for the sample collection, analysis and data management. This will ensure uniformity of the procedures adopted in various countries. The SOP should cover aspects related to:

# 1.0 Sampling

## 1.1 Appointment of sampling staff and their supervisors

## 1.2 Check of possible changes around the sampling sites

- Local situation (new construction of emission and contamination sources etc.)
- On-site situation

## 1.3 Check of sampling instruments apparatus

- Appearance of sampler (check for corrosion etc.)
- Operation of sampler (rain sensor, moving of lid, documentation of repair of sampler)
- Collection efficiency (comparison with standard rain gauge)
- Cleaning of sampling parts

## 1.4 Sampling methods

- Sampler (involving the documentation of check and maintenance)
- Sampling interval (sampling dates)
- Change of sample vessels
- Addition of biocide

# 2.0 Sample transportation and storage

## 2.1 Transportation of samples

## 2.2 Sample storage

- On-site storage
- Laboratory storage

# 3.0 Measurement and chemical analysis

## 3.1 Appointment of staff and supervisors

## 3.2 Development of training plan

## 3.3 Deionized water

- Daily maintenance
- Documentation of maintenance

## 3.4 Measurement by instruments

- Measuring conditions of instruments
- Calibration
- Performance tests (sensitivity, stability, interference and its removal, documentation of repair)
- Calculation of lowest detection limits and lowest determination limits
- Documentation of maintenance

## 3.5 Operating procedures for measurements

- Preparation of calibration curves
- Measurement/analysis of samples
- Repeated measurements/analyses
- Check of sensitivity fluctuation

## 3.6 Treatment of measurement results

- Calculation of concentrations
- Measurement of sensitivity fluctuation
- Repeat measurements/analyses
- Calculation of ion balances
- Comparison of measured and calculated conductivity

# 4.0 Quality assurance and quality control

## 4.1 Evaluation of sample collection

- Comparison of precipitation amount with standard rain gauge
- Evaluation of ion balance
- Evaluation of conductivities

## 4.2 Evaluation of reliability

- Evaluation of sensitivity fluctuations
- Evaluation of repeated measurements/analyses
- Evaluation of field blanks
- Comparison between measured data and lowest detection and lowest determination limits

## 4.3 Evaluation of results

- Representativeness of sampling sites
- Evaluation of sample validity
- Evaluation of completeness for the sampling period
- Determination of total precision

# 5.0 Management of instruments, reagents & glassware

## 5.1 Management of sampling instruments

- Appointment of management staff and their supervisors
- Documentation of names of manufactures, types, manufacture dates and operation methods
- Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)

## 5.2 Laboratory management

- Appointment of management staff and their supervisors
- Daily and regular maintenance and inspection methods (including items and recording format)

## 5.3 Management of measurement/analysis instruments

- Appointment of responsible staff for each instrument, and overall measurement
- Documentation of names of manufactures, types, manufacture dates and operation methods
- Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)

## 5.4 Management of reagents, standard materials, etc

- Appointment of management staff and their supervisors
- Receiving and disposal of reagents (recording format of dates, manufacture names, dealers, purity, degree of standard and valid period)

## 5.5 Management of glassware and polyethylene vessels

- Appointment of management staff and their supervisors
- Cleaning methods
- Storage
- Confirmation of cleanness

# 6.0 External audit

- Check of sampling sites
- Measurement of field blank values
- Operation check of samplers
- Evaluation of the results of quality control
- Evaluation of the measured results

# Data quality objectives (DQOs)

DQO values define the desirable levels of **accuracy, precision, precipitation** and **completeness** required for a programme.

**Accuracy:** The ability of the measurement procedure to produce results those are close to the true value. Lower systematic and random errors (refer to notes on basic statistics) allow for higher accuracy of measurement.

The accuracy of measurement achieved by a laboratory is determined by having the reference laboratory send samples (artificial wet deposition and $SO_2$ and $NO_2$ precipitation samples) to all participating laboratories. The accuracy of the analysis is determined by computing it as follows:

$$\text{Accuracy, } A = \frac{\text{(certified value - analytical value)}}{\text{(certified value)}} \times 100$$

Certified values are those which are certified by the reference laboratory/ technical committee.

**DQO for accuracy, A is ±15%.**

**Precision:** The ability of the measurement procedure to reproduce a result as closely as possible.

***Sampling precision:*** should be established by duplicate sampling, from time to time, with co-located samplers or collectors. The samplers should follow identical procedures-collection, handling and storage.

***Analytical precision:*** To estimate the contribution of analytical variability, duplicate analysis should be performed on 5% of routinely analyzed samples. Half these samples should be analyzed immediately and the other half within 1 week, after being refrigerated at $4^oC$.

**Analytical precision, $S_i = (\Sigma d_i^2/2N_i)^{0.5} \times 100/Av$**

where, $d_i$ = difference between the duplicate analyses

$N_i$ = number of sample pairs during the reporting period

Av = mean of the duplicate analyzed samples

**DQO for analytical precision, $S_i$ should be 15%**

***Example:*** *Precision is computed for the following duplicately analyzed data set:*

*Chloride concentrations in samples duplicately analyzed:*

| *S #* | *Result 1 (mg/L)* | *Result 2 (mg/L)* | *Difference d (mg/L)* | *Average Av (mg/L)* |
|---|---|---|---|---|
| *1.* | *50* | *46* | *4* | *48.0* |
| *2.* | *37* | *36* | *1* | *36.5* |
| *3.* | *22* | *19* | *3* | *20.5* |
| *4.* | *17* | *20* | *3* | *18.5* |
| *5.* | *32* | *34* | *2* | *33.0* |

$\Sigma d_i^2 = 4^2+1^2+3^2+3^2+2^2 = 39$

$N_i = 5$

$$Av = \frac{48+36.5+20.5+18.5+33}{5} = 31.5$$

$S_i = (\Sigma d_i^2/2N_i)^{0.5} \times 100/Av = 6.27\%$, *which meets the DQO*

**Precipitation:** Precipitation, P is computed for wet deposition samples as the percent of rain water collected by the wet only collector as a fraction of the total precipitation as measured by a standard rain gauge. In areas with high precipitation, the 5 L collection bottle provided with the wet only collector and bulk sampler may be replaced with a 10 L bottle.

$$\text{Precipitation, P} = \frac{\text{Vol of precipitation measured by the collector x 100}}{\text{Vol of precipitation measured by standard rain gauge}}$$

**DQO for precipitation, P>90% on a monthly and annual basis for the wet only and bulk collectors**

**Completeness (C):** The ratio of the time or volume for which valid samples total are available to the total time or total volume for which samples could have been collected.

C ≥ 80% for precipitation and diffusive samples
C ≥ 60% for HVS samples

$$\textbf{\% valid sample time (PVST)} = \frac{\text{Sampling time for which valid samples are available}}{\text{Total time}} \times 100$$

PVST is a measure that can be used to compute completeness for precipitation and AAQ samples

***Example:*** *In a year, if diffusive samplers were used for 11 months, but one sampler gave a result which was an outlier, the rest giving valid results for 10 months*

*PVST = 10/12 × 100 = 83.3%*

***The above sample meets the DQO requirements.***

**% valid sample volume (PVSV)** = $\frac{\text{Vol of valid precipitation sample}}{\text{Total time}} \times 100$

PVSV is a measure that can be used to compute completeness for precipitation samples

***Example:*** *Of the total precipitation of 800 mm in a year, 700 mm was collected by a bulk collector. But, valid results were obtained for only 600 mm,*

$PVSP = 600/800 \times 100 = 75\%$

***The above sample does not meet the DQO requirement of 80% for precipitation samples.***

Precipitation samples must satisfy Completeness DQO for both PVST and PVSV. If it does not, it has not satisfied this DQO.

Completeness for **diffusive samplers** is defined as the percent time in a whole year for which valid results are available.

Completeness for the **PM10 sampler** is defined as the actual monitirong time expressed as a percent of the 2880 hours (24 hrs/day × 10 days/mth × 12 mths/yr) of sampling time required under the monitoring protocol of this programme.

***Example:*** *If valid $SO_2$ samples obtained for a total time of 200 hrs in a year,*

$$Completeness = \frac{2000\ hrs}{2880\ hrs} \times 100 = 69\%$$

The completeness percent in this example satisfies the DQO of 60% for a $PM_{10}$ sample. Completeness for diffusive samplers is defined as the percent time in a whole year for which valid results are available.

**Valid sample:** Sample falls within an expected range of values.

**Invalid sample:**

- Sample contamination or error in sample collection, handling, storage or analysis.

- For an HVS (only), the sample has been collected for ≤60% in a 24 hr sampling period, or less than 14.5 hrs.
- The result is an outlier which is outside the expected range of values by a margin which is very large

# *Quality control*

# Site

**Site characteristics:** Deposition and ecological sites should meet criteria for remote sites.

**Site selection criteria for acidic gas deposition by the Malé Network**

- Two types of sites are required for monitoring transboundary air pollution—**deposition monitoring sites** for monitoring wet and dry deposition, and **ecological monitoring sites** where soils, vegetation, water bodies and aquatic ecology would be monitored. Deposition monitoring should not be done in forests as vegetation will absorb a part of the pollutants, thus giving erroneous results.

- The **sites for monitoring the ecological parameters should be in a good natural forest** which is likely to remain undisturbed in future. Ecological sites should also have a fresh water lake or stream that does not receive liquid or solid pollutants.

- Monitoring of transboundary air pollutants should be done at **remote sites** as close as is practically feasible to the international border. The monitoring sites should be at least 25 km away from the nearest town/ large industry and 10 km away from the nearest highway/ small industry .

- To the extent possible, there should be **no human habitation/ activity or other emission sources close to the sites.** Population density around the sites should be low and should be expected to remain low in future.

- The site should be **representative** of other remote areas in its proximity.

- The sites should be **downwind of major emission sources in neighbouring countries and upwind of major emission sources in the country in which the monitoring is being done.**

- Unless unavoidable, the sites should be sufficiently inland to **avoid the influence of coastal breezes.**

- The **terrain between the emission sources in the neighbouring country and the monitoring sites should preferably be flat.**

- The **sites should be secure.** They should be accessible to sample collectors. They should have a power connection and be habitable for short periods, if necessary.

  - The sites should preferably have a **meteorological station within about 50** km of them. The terrain between the monitoring site and the meteorological station should be flat.

  - The **site should be within 12-15 hours travel time from the place where the samples (other than passive samplers) will be analyzed.**

  - **A few of the ecological monitoring sites should be in areas which are at high risk to acidification impacts.**

  - For best results, these criteria should be met to the extent possible. However, it is probable that all the above criteria will not be met at all the monitoring sites. A judicious choice must be made, and to the extent possible, the first six criteria should be met.

- **Site information:** Site information—location, monitored parameters, site information (physical features, land use of the area, human activity—farming, vehicular traffic, human habitats, etc), emission sources around the site—should be documented as described in the technical manual.

# Sample collection and handling

- **Equipment information:** Information regarding equipment—brand, manufacture date, technical specifications, maintenance record, etc—should be maintained by the NIA.

**Gantt charts for monitoring schedule:** A duplicate set of Gantt charts detailing the monitoring schedule as per the schedule set by the NIA, and completed monitorings, flagged as required (using the flag system in the technical manual), should be maintained at the field site and the laboratory. The Gantt charts should be used to plan the monitoring schedule as well as keep track of completed work, with explanations for deviations from the planned schedule. A simple example of a Gantt chart for the use of the $PM_{10}$ sampler is given below:

| Dt | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Planned monitoring | | | | | | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | | | | | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | | | | |
| Actual monitoring | | | | | | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | | | | | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | | | |
| Flags | | | | | | | | | | | 667 | | | | 649 | | | | | | | | | |

- **Operational checks for equipment:**

Operations of the samplers should be checked as follows:

1. For the wet only collector:
    - o The response sensitivity of the sensor and its response time should be as prescribed;
    - o Collection bucket and should be clean;
    - o Sensor heating should be as required by the technical specifications of the collector; etc.

2. Clean wet only containers should be available at the site. The deionized water used for cleaning the containers should have an electrical conductivity <0.15 mS/m.

3. For wet deposition monitoring, a field blank should be collected every month to determine any possible contamination of the collector, leading tubes and sampling bottles. After sample collection, the funnel should be cleaned thoroughly and wiped with clean tissue paper. Then, 100 ml of deionized/ distilled water should be added to the collector and collected in the same manner as a sample. The field blank and the remaining deionized/ distilled water should be analyzed for the same parameters as rainwater samples. If the concentrations of chemical species are significantly higher than that of usual field blank values, the funnel and tubes should be cleaned or replaced.

If a fresh plastic bag is not used inside the bulk collector-sampling bottle for collecting the sample, the same procedure as above for the wet only collector may be adopted for the bulk collector.

4. For the $PM_{10}$ sampler,

- The sampler should be periodically leak tested;
- Filter paper should inspected for pin holes;
- Filter conditioning should be done at 20-25$^{o}$C;
- Rotameter and impinger manifolds should be cleaned once in two months;
- Flow readings should be taken five minutes after the machine is switched on;
- Flow meters should be calibrated periodically, as required;
- Water in manometer should be changed every fortnight with distilled water;
- Deformed O-rings, if any, should be replaced;
- Blower speed should be constant;

- Filter paper should be placed properly;
- Initial water level in the manometer should be at zero level and there should be no residue;

Timer should be properly set; hose connected to the blower should be tight;

- Top cover should be tightened sufficiently;
- Cyclone should be properly cleaned and the cup fitted properly;
- Ice/ cold water should be put into the ice tray;
- Impingers should be greased after cleaning;
- Float in the rotameter should be freely moving;

- **Handling and transport of samples:** The following measures should be taken while storing and transporting samples:

1. Precipitation samples (wet only collector and bulk sampler) should be handled with disposable gloves.
2. Samples (precipitation, $SO_2$, $NO_2$ samples) should be stored at $4^oC$, for a maximum period of 2-3 weeks before analysis.
3. Transport of samples (precipitation, $SO_2$, $NO_2$ samples) should be done in ice boxes filled with ice to last the entire period of transport.
4. Sample bottles should be sealed tightly to avoid leakage or contamination by atmosphere.

- **On-site inspection:** The NIA should periodically conduct on-site audits to check:

1. Operation of equipment
2. Cleanliness of equipment, vessels and work areas
3. Data management

- **Data reporting:** Agencies responsible for data collection will maintain records regarding:

1. Sampling instruments details.

2. Conditions of sample collection (sampling date, meteorological data).

3. Records of on-site data (field blank data, sample volume, standard gauge precipitation, etc).

4. Sample contamination (suspended particulate matter, bird droppings, insects).

5. Sample history (shipping data, packing procedures, etc).

6. Performance of all prescribed in the SOP.

7. Routine instrument check and maintenance, record of instrument adjustment (calibration of instrument).

8. Names of producers and traceability of standard materials, etc, institution of measurement conditions of analytical instruments and its results.

9. Sensitive variability of analytic instruments.

10. Results of site audits/ inspections

# Measurement and analysis

- **Sequence of analysis:** It should be checked that the sequence of analysis of parameters for the precipitation samples should as given in the technical manual.

- **Deionized/ distilled water:** Water with electrical conductivity <0.15 mS/m is acceptable for use in the laboratory.

- **Sample analysis:** Samples should be analyzed as soon as possible after arrival. After electrical conductivity and pH are measured, precipitation samples should be filtered with clean membrane filters and stored at 4$^{o}$C, until they are analyzed. If the samples are diluted, this should be flagged and the purity of the water should be checked before dilution. Diluted samples may not be used in the measurement of electrical conductivity and pH.

- **Fundamental measurement and analysis matters:**

1. Apparatus, materials and reagents should be free from contamination.

2. Well-trained persons should conduct measurement and analyses.

3. To maintain high quality of analytical results, SOPs should be prepared for management of apparatus, materials and reagents.

4. Instruments should be calibrated periodically as per prescribed schedule.

- **pH meter:** The following measures should be taken:

1. pH measurement is recommended at 25$^{o}$C.

2. The pH meter should be calibrated with certified solutions soaked in a temperature-controlled water bath

3. It should be confirmed that the water bath could control temperature fluctuations to with ±0.5$^{o}$C. If a temperature water bath is not available, use a 5 L water bath without temperature control.

1. Tests of reproducibility and linearity should be carried out to assure reliable measurement.

2. The temperature reading on the pH meter should be compared with a certified thermometer.

3. It is recommended to measure the concentration of a series of HCl solutions made with pH values in the range 4-5 once a month.

4. At least once every 20 samples, reference solutions should be measured 3 times to confirm that their values are within ±0.05. If the sensitivity fluctuates over this range, the reasons should be found and removed, and then the reference material should be measured again.

- **Electrical conductivity meter:** The following measures should be taken:

1. Electrical conductivity measurement is recommended at 25$^o$C.

2. The electrical conductivity meter should be calibrated with certified solutions soaked in a temperature-controlled water bath.

3. It should be confirmed that the water bath could control temperature fluctuations to with ±0.5$^o$C. If a temperature water bath is not available, use a 5 L water bath without temperature control.

4. Tests of reproducibility and linearity should be carried out to assure reliable measurement.

5. At least once every 20 samples, reference materials should be measured 3 times to confirm that their values are within ±0.2 mS/m. If the sensitivity fluctuates over this range, the reasons should be found and removed, and then the reference material should be measured again.

6. The temperature reading on the electrical conductivity meter should be compared with a certified thermometer.

- **Spectrophotometer and atomic absorption spectrometer:** The following measures should be adopted:

1. The instrument should be re-calibrated every 30 sample measurements.

2. Reference material should be measured after the calibration.

3. Control charts should be applied for the measurement of the reference material.

4. Standard solutions and reference solutions should be prepared from different stock solutions in order to be independent.

5. If the results of the control solutions are outside 3 standard deviations, or 15% from the expected value, the reasons should be found and corrections made, and reference solution measured again.

- **Ion balance:** An ion balance should be done as given in the data control section. If the ion balance is out of the acceptable limits, some additional ions relevant to the ion balance, such as fluoride, bicarbonate, nitrite and organic acids, are recommended to be identified and measured, as appropriate, though such measurements are not mandatory.

**Data reporting:** Agencies responsible for data collection will maintain records regarding:

1. Instruments details.

2. Sample contamination (suspended particulate matter, bird droppings, insects).

3. Sample history (shipping data, packing procedures, etc).

4. Performance of all prescribed in the SOP.

5. Routine instrument check and maintenance, record of instrument adjustment (calibration of instrument).

5. Results of analysis of lowest detection and determination limits.

6. Sensitive variability of analytic instruments.

7. Duplicate analysis and repeat analysis.

8. Evaluation of ion balance and conductivity difference.

9. Evaluation of data (accuracy, precision, completeness, representativeness).

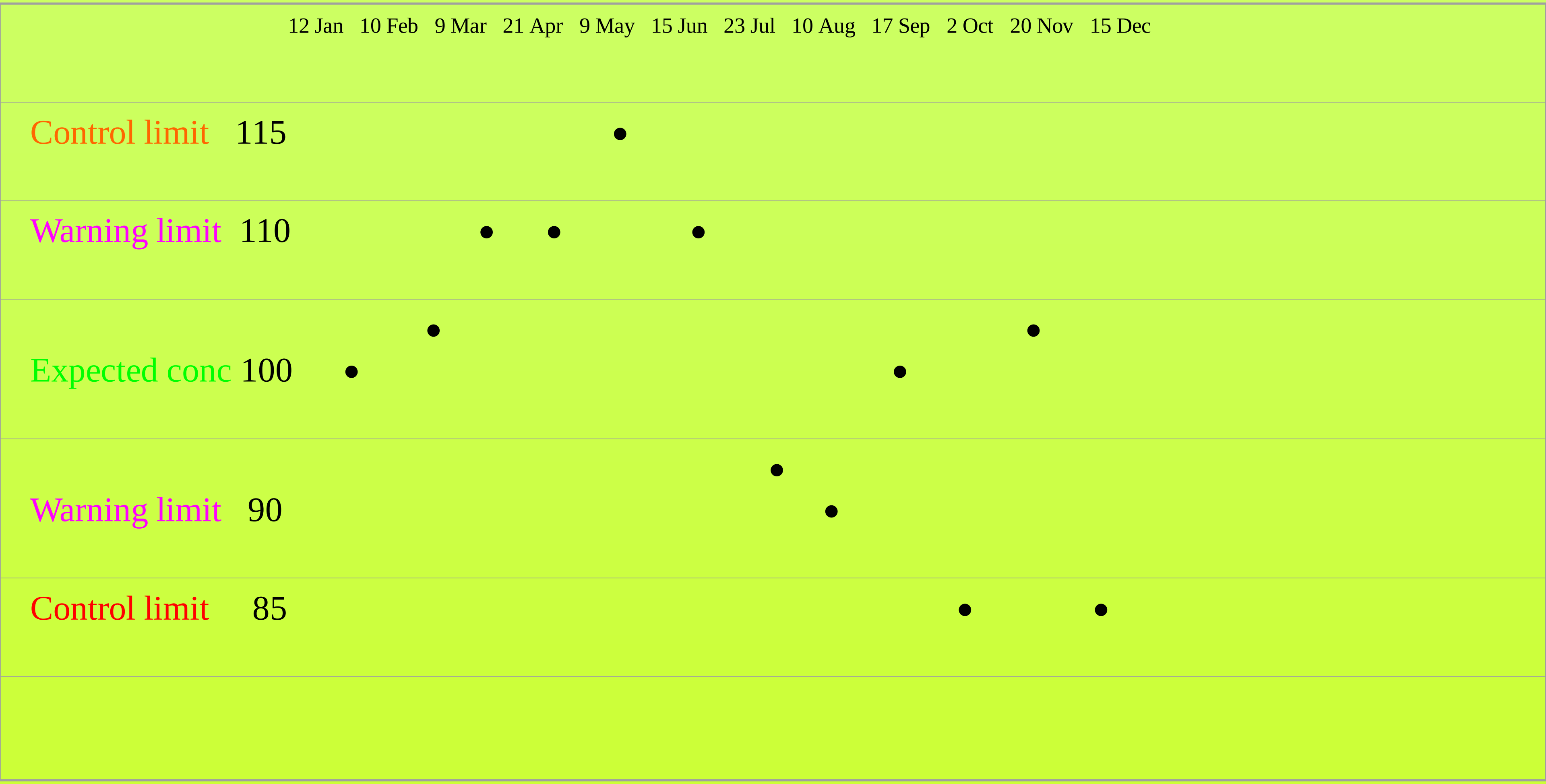
10. Results of laboratory audits/ inspections.

- **Shewhart control charts:** Shewhart control charts may be used to determine whether the measurement of dry and wet deposition samples are within statistical control, variation in the results of analysis of a control sample is only due to random variability.

A control sample is analyzed in the same way as routine samples at fixed intervals, once or twice every week or after 20-50 routine samples.

Assuming that the results for a control sample follow the normal frequency distribution, only 0.3% of the results are expected to fall outside the lines drawn at 3 standard deviations above or below the mean value.

# Shewhart control chart



The values at 3 standard deviations from the mean are known as the upper and lower control limits, respectively.

The lines drawn at 2 standard deviations above and below the mean value are known as the upper and lower warning limits.  If the analytical method is under control, 4.5% of the results are expected to fall outside the warning limits.

The following action should be taken based on analysis results:

1. **Control limit:** If one measurement exceeds the limits, repeat the analysis of the control sample. If the repeat is within the UCL and LCL, continue routine analysis of samples; if it exceeds the control limits, discontinue the analysis and correct the problem.

2. **Warning limit:** If 2 of 3 successive points exceed the limits, analyze another control sample. If the next point is within the UWL and LWL, continue routine analysis; if the next point exceeds the warning limits, discontinue the analysis and correct the problem.

3. **Standard deviation:** If 4 out 5 successive points exceed one standard deviation, or are in increasing or decreasing order, analyze another sample. If the next point is less than one standard deviation, or changes the order, continue routine analysis; otherwise discontinue the analysis and correct the problem.

**4.** **Central line:** If 6 successive points are on one side of the mean line, analyze another sample. If the next point changes side, continue with routine analysis; otherwise discontinue analysis and correct the problem.

# Audits

**Site audit by NIA:** An annual site audit should be done by the NIA. The format for the audit may be drawn by the NIA and should include the following:

- **1. Check operations of the samplers**

  ***For the wet collector:*** the response sensitivity of the sensor and its response time; cleanliness of the bucket; sensor heating; etc.

***For the PM$_{10}$ sampler:*** the instrument is leak tested; the flow meters are calibrated periodically; water in manometer is changed every fortnight with distilled water; deformed O-rings, if any, have been replaced; blower speed is constant, etc.

1. **Check the availability of wet only containers at the site, and the procedure for cleaning containers.** The deionized water used for cleaning the containers should have an electrical conductivity <0.15 mS/m.

2. **Review site procedures and data documentation to see whether all routine site operations are being observed,** including sample handling, instrumentation procedures, data reporting, operator training, etc.

1. **Review the monitoring schedule** to see whether the prescribed monitoring protocol (monitoring frequency and data management) is being observed.

2. **Review operating procedures** to see whether the SOP is being observed.

3. **Check data management:** Check whether data is being maintained as per SOP or as per the formats in the technical manual.

- **Laboratory audit:** An annual laboratory audit should be done by the NIA. The format for the audit may be drawn by the NIA and should include the following:

1. **Check operations of instruments:**

- The working condition of the instruments should be checked.

- The calibration of the instruments should be checked.

## 1. **Check laboratory operations:**

- Cleanliness and housekeeping of the laboratory should be checked.

- Availability of spares and consumables should be ascertained.

- The training and capability of the laboratory staff should be ascertained.

- The availability of deionized/ distilled water should ascertained.

- The working condition of local exhaust ventilation system should be ascertained.

- Check whether routine QA/QC measures are being followed

**3. Check data management:**

- Check whether data is being maintained as per SOP or as per the formats in the technical manual.

# External QA programme

- The technical committee should design an external QA programme to:

  1. Verify that the measurements are being carried out and reported with the expected precision and accuracy and that all measurements activities are accurately documented.

- 2. Identify sources of variability and recommend changes and controls that would improve the accuracy, precision, and completeness of the measurements.

3Certify the NIAs’ assessment of precision and accuracy.

4.Assess and compare the measurement methodology and quality assurance data of the Malé Network with other networks.

# Data control

There are 3 purposes concerning quality assurance of data control:

- Assure that all sample data will be stored in the database in an adequate manner.
- Mark with flags the data whose accuracy and representativeness is doubted.
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- Recognize and describe samples, that were measured without standard methods, ie, with contamination, instrument trouble, bulk sampling, etc.

- **Treatment of abnormal and unrecorded data:**

1. **Abnormal data:** Abnormal data is expected when:

- The sensitivity of instruments is not stable.
- The results of duplicate analysis or re-measurement are significantly different.
- When the ratio of the theoretical value to that of the measured one is significantly different from 1.

If abnormal data is obtained, measurement should be repeated.

I**Unrecorded data:** When samples seem obviously contaminated, these data should be treated as unrecorded data.

When abnormal or unrecorded data appear, the process should be carefully reviewed to prevent repetition of the same problem.

# *Quality assurance*

**Preliminary QA for data sets:** Data should be assessed for accuracy, precision and completeness. These parameters should be quantitatively evaluated before an assessment is made regarding data quality. Accuracy and precision are assessed with respect to chemical analysis. Data completeness is assessed as a ratio of the valid sample to the total precipitation as measured by a rain gauge. Data completeness should >80%.

Data should also be assessed for representativeness and comparability. Representativeness can be evaluated on the basis of site descriptions provided by the NIA and site audits. Comparability should be assessed by comparing the results of diffusive samplers with that of the high volume sampler, and wet only collector with bulk collector. Comparability may also be done for results obtained from paired stations, provided the stations are within proximity and have the same meteorological and terrain conditions.

# Judgment of valid data

All precipitation data should be checked for ion balance and difference between computed and measured electrical conductivity (EC).

## Ion balance (computation of $R_1$)

***Equivalence:*** of an element or radical is the number of hydrogen atoms that it can hold in combination or can replace in a reaction.

In most cases, equivalence = absolute value of valence

***Equivalent*** of an element or radical = gram molecular mass

***Example:*** *How many grams of Ca are required to combine with 90 gms of $CO_3$ to form $CaCO_3$?*

*$CO_3^{2-}$ has a valence of -2, $Ca^{2+}$ has an equivalence of +2.*

*One equivalent of $CO_3^{2-}$ = $\frac{12 + 3(16)}{2}$ = 30 gm/equiv*

*One equivalent of $Ca^{2+}$ = $\frac{40}{2}$ = 20 gm/equiv*

*90 gms of $CO_3^{2-}$ (3 equivs) will combine with 3 equivs of $Ca^{2+}$, ie, 20 x 3 = 60 gms.*

**Major constituents of dissolved in natural waters:** Na, Ca, Mg, K, $NH_4$, $NO_3$, $SO_4$, Cl

**Secondary constituents:** Fe, Sr, $CO_3$, $HCO_3$, F, B, Si

The major constituents are often sufficient to characterize the dissolved contents of water. They are measured individually and summed up on an equivalent basis to represent the approximate TDS.

As a check, **the sum of the anion equivalents should equal the sum of the cation equivalents**, as electro neutrality must be preserved.

**Significant imbalance** in the ion balance **suggests that additional constituents are present or that an error has been made in the analysis** of one or more of the ions.

Total anion (Aeq) of equivalent concentration (μeq/L) is calculated by summing the concentration of all anions (C: μmol/L).

Aeq (μeq/L) = $\Sigma n \bullet CAi$ (μmol/ L) = $2C(SO_4^{2-}) + C(NO_3^-) + C(Cl^-)$

where n = electric charge of ion

CAi = concentration (μmol/L) of anion ‘i’.

Total cation (Ceq) equivalent concentration (μeq /L) is calculated by summing the concentration of all cations (C: μmol/L).

Ceq (μeq/L) = $\Sigma n \bullet Ci$ (μmol/L) = $10^{(6\text{-}pH)} + C(NH_4^+) + C(Na^+) + C(K^+) + 2C(Ca_2^{2+}) + 2C(Mg^{2+})$

$$R_1 = \frac{(Ceq-Aeq) \times 100}{(Ceq+Aeq)}$$

Allowable ranges of $R_1$ in diff conc ranges

| Ceq + Aeq (μeq/L) | R1 (%) |
|---|---|
| <50 | ±30 |
| 50-100 | ±15 |
| >100 | ±8 |

If $R_1$ is out of range, re-measurement or a check with standard samples may be necessary. Otherwise, flags that indicate unsatisfactory data should be marked in the database.

- When pH >6 and $R_1$ is significantly greater than zero, bicarbonate ($HCO_3^-$) concentration should be evaluated to compute R1 and R2 again to include bicarbonate contribution.

- The flags should be marked as follows.

| | |
|---|---|
| 999 | Missing measurement, reason not specified. |
| 899 | Measurement not defined, reason not specified. |
| 783 | Low precipitation, concentration unknown. |
| 782 | Low precipitation, value is obtained from diluted sample |
| 781 | Below detection limit. |
| 701 | Less accurate than usual, reason not specified. |
| 699 | Mechanical problem, reason not specified. |
| 599 | Contamination not specified. |

***Example:*** *A sample had the following ions at pH 5.5:*

$Ca^{2+}$ = 25 mg/L
$Mg^{2+}$ = 8 mg/L
$Na^{+}$ = 48 mg/L
$K^{+}$ = 35 mg/L

$SO_4^{2-}$ = 90 mg/L
$Cl^{-}$ = 125 mg/L
$NO_3^{-}$ = 85 mg/L
$NH^{4+}$ = 15 mg/L

*Converting to μmol L-1,*
$Ca^{2+}$ = 45 mg/L = 45/40 mmol/l = 1,125 μmo/Ll , *where the molecular weight is 40*
$Mg^{2+}$ = 28 mg/L =2 8/24.3 mmol/L = 1,152 μmol/L
$Na^{+}$ = 68 mg/L = 68/23 mmol/L = 2,956 μmol/L
$K^{+}$ = 35 mg/L = 35/39 mmol/L = 897 μmol/L
$NH_4^{+}$ = 15 mg/L = 15/18mmol/L = 833 μmol/L
$SO_4^{2-}$ = 120 mg/L =120/96 mmol/ L = 1250 μmol/L
$Cl^{-}$ = 125 mg/L = 125/35.5 mmol/L = 3521 μmol/L
$NO_3^{-}$ = 85 mg/L = 85/62 mmol/L = 1370 μmol/L

$Aeq = (2 \times 1250) + 3521 + 1370 = 7121$ μeq/L
$Ceq = 100.5 + (2 \times 1125) + (2 \times 1152) + 2956 + 833 = 8346$ μeq/L

$$R1 = \frac{(Ceq-Aeq) \times 100}{(Ceq+Aeq} ) = \frac{1225 \times 100}{15467} = 7.92$$

***R1 is within the permissible range.*** *Hence, the ion balance is valid.*

# Comparison between measured and computed electrical conductivity

The electrical conductivity of water can me theoretically approximated as follows:

**$\Lambda$calc = $\Sigma$(Ci•fi)**

Where, Ci = concentration of ionic species i in solution, expressed in µmol/L
And fi = molar conductivity factor of ionic species i (given in manual)

If $\Lambda$calc is expressed in mS/,
Ci is expressed in µmol/L at 25°C,
and fi = is expressed in $Scm^2/mol$

Total electric conductivity ($\Lambda$calc) should be calculated as follows:

**$\Lambda$calc (mS/m)** = $\{[349.7 \times 10^{(6\text{-pH})}] + [80.0 \times 2C(S0_4^{2-})] + [71.5 \times C(NO_3^-)] + [76.3 \times C(Cl^-)] + [73.5 \times C(NH_4^+)] + [50.1 \times C(Na^+)] + [73.5 \times C(K^+)] + [59.8 \times 2C(Ca_2^+)] + [53.3 \times 2\,C(Mg_2^+)]\}/10000$

**$R_2 = 100 \times (\Lambda calc - \Lambda meas)/(\Lambda calc + \Lambda meas)$**
expressed as a %

Where Λmeas in measured value of electric conductivity in the sample.

If R2 is out of range, a) re-measurement of the ionic concentrations of the sample, b) measurement of a standard sample whose ionic concentrations are known

If after taking the above measures, the R2 is still out of range, an appropriate flag that indicate unsatisfactory data should be marked in the database.

| **Λ meas (mS/m)** | **R2 (%)** |
|---|---|
| <0.5 | ±20 |
| 0.5-3 | ±13 |
| >3 | ± 9 |

The flags should be marked as follows

| | |
|---|---|
| 999 | Missing measurement, reason not specified.. |
| 899 | Measurement not defined, reason not specified.. |
| 783 | Low precipitation, concentration unknown. |
| 782 | Low precipitation, value is obtained from diluted sample |
| 781 | Below detection limit. |
| 701 | Less accurate than usual, reason not specified. |
| 699 | Mechanical problem, reason not specified.. |
| 599 | Contamination not specified. |
| 477 | Inconsistency between measured and estimated conductivity. |

**Example:** *In the example given in the ion balance section, the concentrations of various ions is:*

*Ca2+ = 45 mg/L = 45/40 mmol/l = 1,125 μmo/Ll ,*
*Mg2+ = 28 mg/L =2 8/24.3 mmol/L = 1,152 μmol/L*
*Na+ = 68 mg/L = 68/23 mmol/L = 2,956 μmol/L*
*K+ = 35 mg/L = 35/39 mmol/L = 897 μmol/L*
*NH4+ = 15 mg/L = 15/18mmol/L = 833 μmol/L*
*SO42- = 120 mg/L =120/96 mmol/ L = 1250 μmol/L*
*Cl- = 125 mg/L = 125/35.5 mmol/L = 3521 μmol/L*
*NO3- = 85 mg/L = 85/62 mmol/L = 1370 μmol/L*

*By applying the formula,* $\Lambda calc\ (mS/m) = \{[349.7 \times 10^{(6-pH)}] + [80.0 \times 2C(S0_4^{2-})] + [71.5 \times C(NO_3^-)] + [76.3 \times C(Cl^-)] + [73.5 \times C(NH_4^+)] + [50.1 \times C(Na^+)] + [73.5 \times C(K^+)] + [59.8 \times 2C(Ca^{2+})] + [53.3 \times 2C(Mg^{2+})1152\}/\ 10000$

$= \{[349.7 \times 3.16] + [80 \times 2 \times 1250] + [71.5 \times 1370] + [76.3 \times 3521] + [73.5 \times 833] + [50.1 \times 2956] + [73.5 \times 897] + [59.8 \times 2 \times 1125] + [53.3 \times 2 \times 1152]\}/1000$

**=110.03 mS/m**

*If the measured electrical conductivity is 100 mS/m,*

$$R2 = \frac{100 \times (\Lambda calc - \Lambda meas)}{(\Lambda calc + \Lambda meas)}$$

$= 100 \times (110.03 - 100)/(110.03 + 100) = 4.8\%$

***This meets the criteria***

# Audit

The technical committee should conduct an annual audit of the activities being done in each country, including of the monitoring sites, laboratories and with respect to data management and reporting. The technical committee may design an appropriate audit format. The audits must cover the following points:

- Review whether the site meets the minimum requirement for being classified as a remote site.
- Review operation of the samplers and laboratory instruments
- Review whether monitoring protocol is being followed
- Review quality of chemicals
- Review whether SOPs are being followed
- Review sample handling, storage and transport
- Review sample analysis
- Review data documentation and management
- Review QA/QC activities
- Review human resources and organizational functioning

## Round robin analysis

The TC should send to all chemical analysis laboratories artificial precipitation and AAQ inter-calibration samples once a year through each NIA. The results should be statistically evaluated and a report prepared and circulated in the network. The results should be used to find solutions for existing laboratory problems and to improve the quality of laboratory analyses. The TC may delegate this task to the reference laboratory.

## Comparative analysis of sampling methods and chemical analysis methods

The TC should compare the precision and accuracy of the field sampling and laboratory measurements, based on parallel precipitation measurement and duplicate sample analysis. This task may be delegated to the reference laboratory.

# Comparative analysis between networks

The TC should assess and compare the measurement methodology and quality assurance data of this network with other relevant networks, and submit reports to the SC.

# Reference material

The TC should assure the adequacy of reference materials to be used by the NIAs, field agencies and laboratories of the network.