Quality Assurance & Quality Control

Sagar Dhara

Objectives of a QA/QC programme

To obtain reliable data

Definitions

- **Quality control:** The routine use of procedures designed to achieve and maintain a level of quality for a 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 can be quantifiable and produce data of known quality ie, QA is a system of activities of activities that ensures that a QC programme is functioning adequately.

Responsibilities

Steering committee:

- **O** Endorse QA/QC programmes, review their implementation

Technical committee:

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

NIA:

- **O** Prepare national monitoring plan
- **O** Prepare and implement national QA/QC programme

Monitoring agencies:

- **O** Execute national monitoring plan & QA/QC programme

Fundamentals of a QA/QC programme

- **Must include all activities** of the technical committee, the NIA and the monitoring agencies.

- **Each country must 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.

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

- **Standard operating procedures (SOPs) should be prepared** for the sample collection, analysis and data management areas. This will ensure uniformity of the procedures adopted in various countries. The SOP should cover aspects related to:

1. Sample collection

· Appointment of personnel
· Changes in sampling sites
· Sampling instruments
· Sampling methods

2 Sample storage and transport

- Storage
- Transport

3. Measurement and chemical analysis

- Appointment of personnel
- Training plan
- Deionized water/distilled water
- Measurement by instruments (calibration, measuring conditions)
- Operating procedures for measurements (repeated measurements, instrument fluctuations)
- Treatment of results (concentration computations, ion balance, comparison of measured and calculated EC)

4. QA/QC

- Evaluation of sample collection (comparison of precipitation amount with standard rain gauge, comparison of ion balance and conductivities)

- Evaluation of reliability (repeated measurements, instrument fluctuations, field blanks)

. Evaluation of results (sample validity, sample representativeness, completeness of sampling period, determination of precision)

5. Management of equipment, laboratory, consumables

- Equipment (documentation of instrument details—type, manufacturer, year of manufacture, …, instrument maintenance and inspection, equipment and consumables)

- Laboratory management practices, including inventory methods

- Management of consumables glassware cleaning methods and storage of

6. External audits

- Sampling sites
- Field blanks
- Operational check of equipment and analytical procedures
- Evaluation of QC
- Evaluation of results

Data quality objectives (DQOs)

DQO values define the desirable levels of **accuracy, precision** 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:

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

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.

1. **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.

2. **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 $4^{o}C$.

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%

- **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.

DDQO for precipitation, P>90% on an annual basis for the wet only collector

- **Completeness:** The percent of the total precipitation that is associated with a valid sample during a given monitoring period.

Percent coverage length: The percent of measurement period in a given period. Eg, if monitoring has been done for 11 months in a year, percent coverage length = 11/12 = 91.7%.

Percent total precipitation: Percent valid sample amount out of the total precipitation in a given period. Eg, if valid samples are available for 700 mm out of a total precipitation of 800 mm, percent total precipitation = 700/800 = 87.5%.

Percent valid sample length: Percent period holding valid samples in a given period. Eg, if valid samples are available for 10 months in a given year, percent valid sample length = 10/12 = 83.3%.

Percent valid sample with measured precipitation: Percent of precipitation samples with valid analysis. Eg, if of the 700 mm sampled (out of a total precipitation of 800 mm), valid analysis was available for 650 mm, percent valid sample with measured precipitation = 650/700 = 92.9%.

In the above problem, completeness = 650/800 = 81.3%, which satisfies the DQO given below.

DQO for completeness should be >80%.

Site

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

- **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.

Quality control

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:

- **Operational checks for equipment:**

Operations of the samplers should be checked as follows:

1. For the wet only collector:
   - The response sensitivity of the sensor and its response time should be as prescribed;
   - Collection bucket and should be clean;
   - 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).

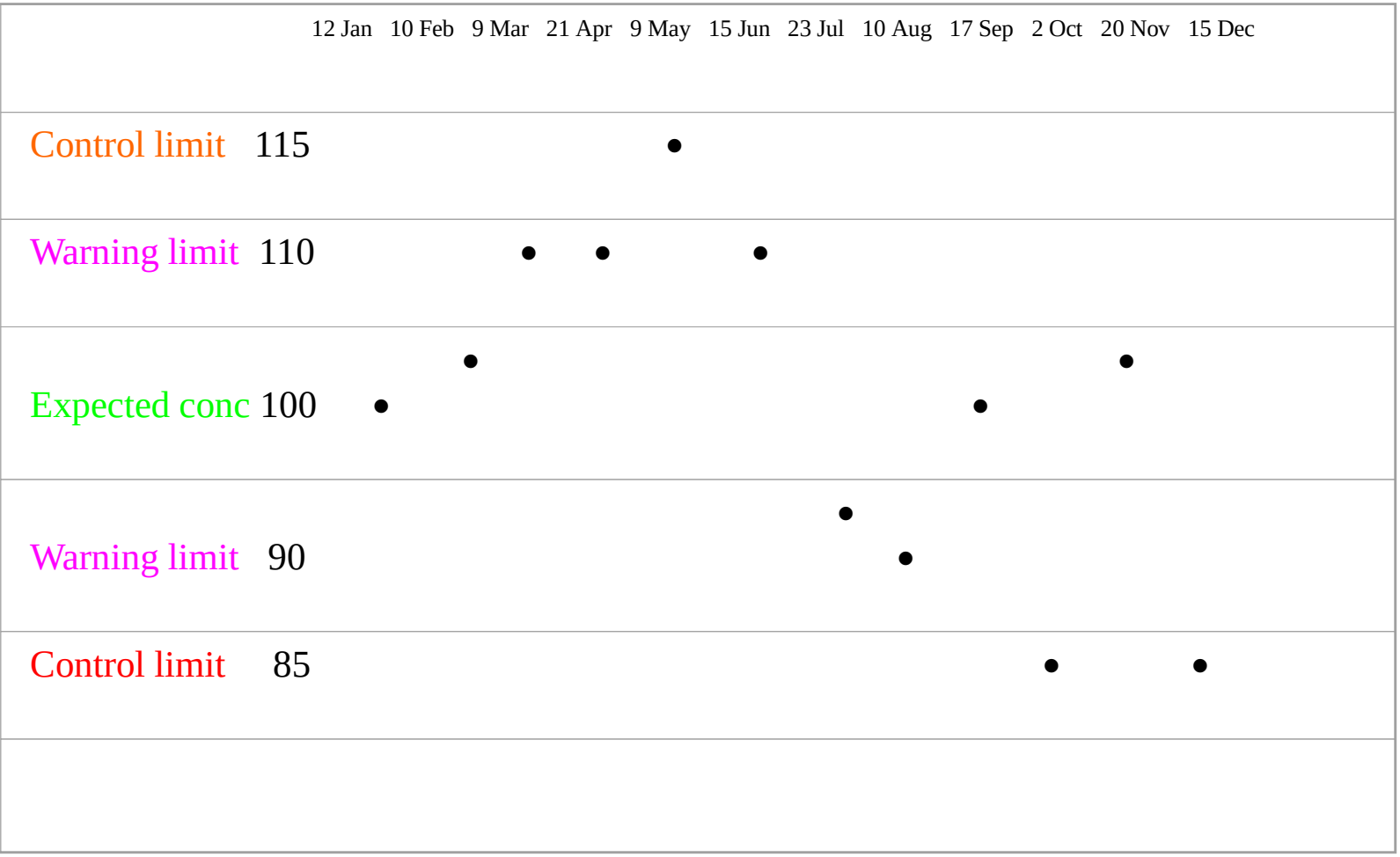
10. Results of laboratory audits/ inspections.

- **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.

Quality assurance

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.

3.Certify 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.
-

•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.

If **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.

- **Judgment of valid data:** All measured data should be checked for ion balance and a comparison made between theoretically computed and measured electrical conductivity.

1. Comparison between computed and measured electrical conductivity

For dilute solutions ($<10^{-3}$ M), total conductivity can be computed as:

$$\mathbf{\Lambda_{calc}\ (mS/m) = \Sigma\ c_i\ x\ \Lambda_i^{O}\ x\ 10^{-4}}$$

where, c_i = ionic concentration of the i^{th} ion in μmol/L
Λ_i^{O} = molar conductivity in Scm^2/mol at infinite dilution

$$R_2 = (\Lambda_{calc} - \Lambda_{meas}) / (\Lambda_{calc} + \Lambda_{meas}) \times 100$$

Required criteria for R_2

Λ_{meas} (mS/m)	R_2 (%)
<0.5	+20
0.5-3	+13
>3	+9

- **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.

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.

Capacity building

Appropriate refresher courses, information exchange websites, email lists will be used for continuous capacity building of the Malé Network team.

QA/QC implemented by Technical Committee

Management of the network's QA/QC activities: The TC will provide participating countries guidance and advice regarding on QA/QC programmes.

- **Preparation of a report of the network's QA/QC activities:** The TC will prepare reports on the results of round robin analysis, duplicate analysis, parallel analysis, comparison of sampling and analytic methods and QA/QC methods of other networks and circulate these to the Malé Network members.

Provide technical support for NIAs: The TC will provide technical support to NIAs to attain such objectives as follows:

1. The TC will review QA/QC activities carried out by each NIA to ensure that the measurements are carried and reported with the expected precision and accuracy, and that all measurements activities are accurately documented and stored.

2. The TC will, where appropriate, recommend changes to improve accuracy, precision and completeness of measurements.

3. The TC will provide useful information for the preparation of national-level SOPs.

• **Round robin analysis:** To review the accuracy of chemical analysis, the TC will send artificial precipitation samples to all participating laboratories once a year. The TC will evaluate statistically the results of the analysis and samples, and prepare reports about the results. The results should be used to study and find solutions for existing problems and improve the quality of laboratory analysis.

• **Comparative analysis of sampling and analysis methods:** The TC will compare the precision and accuracy of the field sampling and laboratory measurements, based on parallel measurements and duplicate sample analysis and grasp the overall precision and accuracy of deposition monitoring of the network.

- **Comparative analysis of the precision and accuracy achieved by the Malé Network and other networks:** The TC will assess and compare the measurement methodology and QA data of the Malé Network data and other networks and submit reports to the Steering Committee.

- **Reference material:** The TC will ensure that the NIAs have adequate reference material.