PROTOCOL FOR INTER – LABORATORY COMPARISON OF MALÉ DECLERATION

Prepared by Dr. Nguyen Thi Kim Oanh
Environmental Engineering and Management
School of Environment Resource and Development
Asian Institute of Technology

Version: Draft 1

March 2007

1. Background

Malé Declaration on Control and Prevention of Air Pollution and Its Likely Trans-boundary Effects for South Asia (Malé Declaration) is an intergovernmental agreement to tackle the issue of transboundary air pollution through regional cooperation in South Asia. Participating countries are Bangladesh, Bhutan, Iran, India, Maldives, Nepal, Pakistan and Sri Lanka. The programme started in 1998 and is now in phase III. Currently the monitoring network is being implemented based on the common methodologies and standards. At this stage, there is a need to establish an inter-laboratory comparison as a required QA measure to ensure the harmonization and quality of the data.

Asian Institute of Technology (AIT) is an international university in Asia, which can serve as the independent laboratory and can perform this QA procedure for the network data. AIT and UNEP RRC.AP had agreed to collaborate in implementing Phase III activities, through a Letter of Exchange. Implementing inter-laboratory comparison was one of the activities agreed upon. The inter-laboratory comparison needs to follow standardized procedures as per accepted standards.

This protocol is prepared to give the specific procedures to be followed for the inter-laboratory comparison project/exercise. This exercise involves a round-robin analysis of uniformly prepared artificial rainwater samples, which will be carried out by the NIA of the Male' Declaration project. The overall objectives of the inter-laboratory comparison is to recognize the analytical precision and accuracy of the data in each participating laboratory and consequently to provide an opportunity to improve data reliability/quality. The protocol consists of the following main contents: 1) Pre-comparison steps, 2) Inter-comparison procedure, 3) Data acquisition and handling, 4) Post-comparison verification, and 5) Dissemination of results. The methodology for this inter-laboratory comparison is developed based on QA/QC procedure for Male's declaration network with reference to the inter-lab comparison reports of the EANET project.

2. Pre-comparison steps

2.1 Review of relevant documents and QA program development

- Review the QA/QC procedures of the Male's network for the information on the DQOs, analytical parameters and equipment
- Review the monitoring data produced by the network to determine the levels of pH, EC and ionic concentrations that should be in the prepared artificial rainwater samples (statistical analysis will be made, tentatively 2-3 levels will be prepared).
- Design and deliver a QA program to participating labs in the inter-lab comparison

2.2 Preparing artificial rainwater samples

- <u>Materials:</u>

All materials which come in contact with the sample must be chemically inert. In this QA/QC exercise, polypropylene bottles will be used to prepare and contain rainwater samples which is the same as the EANET inter-laboratory comparison.

- <u>Cleaning:</u>

Rinse carefully all bottles and other equipment before use with deionized water. All cleaned bottles and utensils will be stored in plastic bags before use.

- **Concentration of artificial rainwater samples:**

At least 2 concentration levels will be prepared (higher concentration and lower concentration, a medium concentration may be considered at a later attempt if necessary) with ten the parameters (10) specified in Male' QA/QC will be prepared based on distribution frequency curves of each parameter from databases of participating laboratories. The 100 time concentrated samples will be prepared. The ranges of each parameter in the prepared samples will be informed to NIA. Examples of the ranges width are presented in Table 1. Summary information on the proposed artificial samples is presented in Table 2.

Table 1: Example of Concentration Ranges to be distributed to NIA

Parameter	Range	Parameter	Range
pH	4-5.5	Na^+	1 – 50 µ mol/L
EC	1-10 mS/m	K^+	1 – 50 µ mol/L
SO_4^{2-}	5 – 100 µ mol/L	Ca^{2+}	1 – 50 µ mol/L
NO_3^-	5 – 100 µ mol/L	Mg^{2+}	1 – 50 µ mol/L
Cl^-	5 – 150 µ mol/L	NH_4^+	3 – 100 µ mol/L

All concentrations are for diluted samples by 100 times (after 100 times dilution)

Table 2: Outline of artificial rainwater samples

Sample name	Amount of sample in a bottle	Container	Number of samples	Note
No. M11 (high concentration) No. M12 (low concentration)	Approximately 150 mL	Polypropylene bottle, 250 mL	One bottle each	Known amount of reagents dissolved in demonized water

- **Chemicals:**

Known amount of reagents will be dissolved in deionized water. The chemicals should be of high purity/analytical grade. Deionized water used should meet the Male' QA/QC criteria (EC<0.15 mS/m).

2.2. Inter-comparison procedure

2.2.1. Sending samples to member laboratories

The artificial rainwater samples (~150 mL) contained in 250 mL polypropylene bottles will be kept with icy box and sent to member laboratories through post by express mail.

2.2.2 Sample analysis

Each laboratory member is expected to analyze samples as soon as received and should be within 1 week after the samples arrive. Before analysis the NIA should dilute the concentrated samples by 100 times using the deionized water (EC < 0.15 mS/m).

(1) Analytical parameters

Ten parameters specified in QA/QC of the Male' Declaration including pH, electric conductivity (EC) (unit - mS/m) and concentrations of ionic species (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} (unit - µmol/L)) will be prepared based on frequency curves of each parameter from databases of participating laboratories. The ranges of each parameter in the prepared samples will be informed to NIA. Examples of the ranges are presented in Table 1. Summary information on the proposed artificial samples is presented in Table 2.

(2) Analytical method

Participating laboratories are expected to use the analytical methods specified in the "Technical Document for Wet and Dry Deposition Monitoring for Malé Declaration" and closely follow the "Quality Assurance/Quality Control (QA/QC) Programme for Wet and Dry Deposition Monitoring for Malé Declaration" protocol.

For ensure the accuracy and precision of the data and for proper assessment of the operation conditions, the persons, who are responsible for measuring wet deposition samples at the NIA, are also required to analyze these artificial rainwater samples of inter-laboratory comparison. The NIA will analyze the diluted samples and report the result in the excel data template. Analytical methods specified in Male' technical document are quoted in Table 3.

Table 3: Analytical methods specified in the Technical Documents for Wet and Dry Deposition monitoring

Parameter	**Instrument method**
Electric Conductivity	Conductivity Cell
pH	Glass electrode (preferably with the electrode of non-leak inner cell)
Chloride	Argentrometric method
Nitrate	Cadmium reduction method
	Spectrophotometry
Sulphate	Spectrophotometry
Ammonium	Spectrophotometry (Indophenol method)*
Sodium	Flame photometry
Potassium	Flame photometry
Calcium	Titrimetry (EDTA method)
Magnesium	Titrimetry

*- no biocide of *Thymol* is expected in the prepared samples hence the method can be used

Each participating laboratory is required to check the data for the ion balance (R_1) and the calculated vs. measured EC (R_2) to ensure the data meeting the criteria. If R_1 and R_2 are out of the specified ranges then re-measurement, check with standard solutions, and/or inspection of calibration curves should be considered as specified in the Male's QA/QC document.

2.3 Data Acquisition and Handling

2.3.1 Data acquisition

A template of data format is prepared for NIA to enter the sample information, operator' information and analytical results, as seen in Table 4. The NIA will send the data to AIT and the UNEP RRC.AP within 1 week after completion of sample analysis, i.e. within 2 weeks after sample arrival. AIT and UNEP RRC.AP will work together to follow up with NIA to get the required data. AIT will notify NIA as soon as data is received. Reporting units of the analytical parameters are followed Male' QA/QC (pH in PH units, EC in mS/m and all ionic components are in µmol/L as seen in Table A1, Appendix).

All laboratories are requested to submit data in the proposed format and the submission of the reports via electronic media, in addition to the documents, is strongly encouraged.

Table 4: Template for data reporting

Organization name					Code		
Department/Section							
Number of staff in charge of measurement							
Year of experience *(if more than 2, a row be added)*			Staff No.1:				
			Staff No.2:				
Name of contact person							
Date of receiving samples							
Samples conditions at received							
Date of measurement							
Postal address							
Contact address			Tel: Fax: Email:				
Note							
Parameter	Measurement /analytical method	Manufacturer /Type of equipment	Detection limits (μmol/l)	Determination limits (μmol/l)	**Concentration**		**Note**
					Sample 1	**Sample 2**	
pH							
Temp*							
EC							
Temp*							
SO_4^{2-}							
NO_3^-							
Cl^-							
NH_4^+							
Na^+							
K^+							
Ca^{2+}							
Mg^{2+}							

** - Temperature readings of the pH and EC meters (recommended value ~ 25°C)*

2.3.2 Data checking procedure

Upon receiving the required information and data AIT will recheck data using the procedures specified in the "Technical Document for Wet and Dry Deposition Monitoring for Malé Declaration" and closely follow the "Quality Assurance/Quality Control (QA/QC) Programme for Wet and Dry Deposition Monitoring for Malé Declaration" protocol.

(1) Calculation of ion balance (R_1)

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

- **A**eq (µeq/L) = S n.C_{Ai} (µmol L^{-1}) = 2C(SO_4^{2-}) + C(NO_3^-) + C(Cl^-)

  Where, n is electric charge and C_{Ai} = concentration (µmol/L) of anion 'i'.

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

  Ceq (µeq/L) = S n.C_{Ci} (µmol/L) = $10^{(6-pH)}$ + C(NH_4^+) + C(Na^+) + C(K^+) + 2C(Ca^{2+}) +2C(Mg^{2+})

  Where, n is electric charge and C_{Ai} = concentration (µmol/L) of cation 'i'.

- Calculation of ion balance (R_1)

  R_1 (%) = 100 x (**C**eq-**A**eq)/(**C**eq+**A**eq)

According to Male' QA/QC procedure, the allowable ranges of R_1 in different concentrations are given Table 4. Thus, obtained R_1 will be compared with criteria in Table 5. If R_1 is out of range, the data set will be marked with an appropriate flag (I) to indicate unsatisfactory data in term of ion balance and further data analysis will be made to reveal the parameters possibly causing the R_1 to be out of range.

Table 5: Allowable ranges for R_1 in different concentrations

Ceq + Aeq (µeq/L)	R_1 (%)
<50	±30
50-100	±15
>100	±8

Sources: QA/QC program for wet and dry deposition monitoring for Male' Declaration

(2) Comparison between calculated and measured electronic conductivity (R_2)

- Total electric conductivity (Λ calc) will be calculated as follows:

  Λ calc (mS /m) = {349.7 x $10^{(6-pH)}$ + 80.0 x 2C (SO_4^{2-}) + 71.5 C (NO_3^-) +
  76.3 C (Cl^-) + 73.5 C (NH_4^+) + 50.1 C (Na^+) + 73.5 x C (K^+) +
  59.8 x 2C (Ca^{2+}) + 53.3 x 2C (Mg^{2+})} / 10,000

  Where, C denotes the molar concentrations (µmol /L) of ions given in the parenthesis at 25°C. The constant value is ionic equivalent conductance at 25°C for each ion.

- The agreement (ratio of R_2) between calculated (Λ calc) and measured (Λ meas) electric conductivity should be calculated as follows:

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

- The obtained R_2 will be compared with standard values in Table 6. If R_2 is out of range, the data set will be marked with an appropriate flag (C) to indicate unsatisfactory data in term of R_2 criteria and further data analysis will be made to reveal the parameters possibly causing the R_2 to be out of range.

Table 6: Allowable ranges for R_2 for different ranges of EC

Λ measured (mS/m)	**R_2 (%)**
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9

Sources: QA/QC program for wet and dry deposition monitoring for Male' Declaration

2.3 Post – comparison verification: data analysis

Statistical analysis will be conducted for the analytical results received from all participating NIA laboratories. For each analytical parameter of the artificial rainwater samples the statistical estimates to be obtained include the Average, Minimum (Min), Maximum (Max), Standard Deviation (SD), and Number of data point (N). The difference between the averaged analytical values (from all NIA) and the prepared value will be calculated for each analytical parameter and presented in a summary table.

The data obtained from each NIA will be evaluated against the Data Quality Objectives (DQOs) of Malé Declaration which have been specified by the QA/QC program of the Malé Declaration, namely for every parameter the measured value should be within ±15% of deviation from the true value. Thus, the accuracy of the data point (A):

$$A\ (\%) = 100 \times (\text{Prepared value} - \text{Analytical value})/(\text{Prepared value})$$

Accuracy A will be calculated for analytical results of each parameter of the artificial rainwater samples and the data point will be evaluated by the excess of DQOs criteria:

- Flag "E" will be put to the data that exceed DQOs by a factor of 2, i.e between ±15% and ±30%
- Flag "X" will be put to the data that exceed DQOs more than a factor of 2, i.e. beyond ±30% (<-30% or >30%).

(In addition, as mentioned above, the Flag "I" and the flag "C" will be added to the data sets with a poor ion balance and conductivity agreement, respectively.)

The results will be evaluated by the three aspects: sample wise, parameter wise and the circumstance of analysis in NIA, as presented below.

2.3.1 Evaluation of data quality by sample (sample wise)

Evaluation will be made for each concentration level separately (high and low) to assess the performance of NIA related to the concentration levels of constituents in the samples.

2.3.2 Evaluation of data quality by individual parameters (parameter wise)

The analytical results by each NIA will be normalized (subtracted) by the prepared values and the results will be tabulated and graphically presented to assess the deviation for each parameter (of 10 parameters) in both samples. Evaluation against analytical methods and the flagged data will also be made.

2.3.3 Evaluation against circumstances of analysis in each participating laboratory

- Methods used for chemical analysis: recommended methods by Technical documents for Wet and Dry Deposition Monitoring for Malé Declaration and other methods. The quality of data (flagged data) vs. analytical methods will be presented.
- Number of staff in charge with the measurement in each NIA: number of flagged data points vs. the operator(s) in each NIA. *(The operators will be presented in letters such as A and B, no name will be mentioned).*
- Years of experiences of operators vs. the data quality (the number of flagged data points)
- Water temperature of measurement of pH and EC. The flagged data points will be highlighted.

2.3.4 Comparison between the first and second inter-lab comparison attempt

This exercise will be done only after the second attempt.

2.3.4 Suggestions/recommendations to improve the data quality

A set of suggestions/recommendations will be made and communicated to NIA in order to possibly improve the data quality.

2.4 Results dissemination

Results of each the inter-laboratory comparison QA exercise will be compiled in a report and submitted to the UNEP RRC.AP. Presentations will be made at the Male' Declaration training-refresher in 2007 and 2008.

References

1. UNEP RRCAP, 2004: Technical Documents for Wet and Dry Deposition monitoring for Malé Declaration. March 2004. Adopted from: http://www.rrcap.unep.org/ew/air/male/manual/wetDry/03-chapter3.pdf.
2. Quality Assurance/Quality Control (QA/QC) Programme for Wet and Dry Deposition Monitoring for Malé Declaration. March 2004. Adopted from: http://www.rrcap.unep.org/ew/air/male/manual/wetDry/12-QAQC.pdf
3. Reports of the EANET Inter – laboratory comparison Project 2003 (Round robin analysis survey 6^{th} – 7^{th} – 8^{th} Attempts) 2004, 2005, and 2006.

Appendix A1: QA program for the inter-lab comparison

(will be completed)

a. Design a data template for participating labs to enter results

b. Guideline for dilution of samples

- Deionized water to be used should have EC <0.15 mS/m
- Use 10 mL concentrated sample and add 90 mL of deionized water to make 100 mL of diluted samples for analysis

c. Analytical procedure:

- Temperature (25ºC) of water for measuring EC, pH
- Samples to be analyzed within a week after arrival
- If storage is required before analysis (not more than a week) samples to be refrigerated and necessary measures to be taken (tightly capped, keep in clean refrigerators) to prevent cross-contamination from other samples, etc.
- NIA is expected to analyze each sample for a few times (at least 3 times) to ensure the precision.

d. AIT follow-up analysis after departing the samples:

- AIT laboratory will storage the same samples in cool temperature (4^0C) and in room temperature
- The samples will be diluted and to analyzed day by day or every 2 days after departing samples to NIA in order to detect any change of concentrations in samples with storage time and storage methods.

Table A1: Reporting units of analytical parameters

Analyte	Reporting Units	
pH	pH Unites	-
EC	milli siemens/meter	mS/m
SO_4^{2-}	micro mole/liter	µmol/L
NO_3^-	micro mole/liter	µmol/L
Cl^-	micro mole/liter	µmol/L
NH_4^+	micro mole/liter	µmol/L
Na^+	micro mole/liter	µmol/L
K^+	micro mole/liter	µmol/L
Ca^{2+}	micro mole/liter	µmol/L
Mg^{2+}	micro mole/liter	µmol/L