

Protocol for inter-laboratory calibration of Male's monitoring network



Nguyen Thi **Kim Oanh**
EEM/SERD, AIT

Male' Declaration 4th Regional Stakeholders-cum-
Regional Coordination Meeting
October 2-3, 2007

Contents



- Why inter-lab comparison?
- What planned for Male' network?
- How to implement?
- What is the follow-up to improve the data quality?



Why the inter-lab calibration?

- Data quality is the first concern in any monitoring program
- Consistency/harmonization should be reached for data compilation in a regional network involving different laboratories
- Inter-laboratory calibration is an important element of QA which is specified in Male' protocol

Common elements of a QA program of environmental monitoring



Objectives of inter-lab comparison



- To recognize the analytical precision and accuracy of the data by the participating laboratories (NIA)
- To provide an opportunity to improve data reliability/quality

Main Activities of Inter-lab Comparison



- Design and deliver a QA program to participating labs
- Prepare reference samples
- Distribute the samples
- Participating labs analyze sample following the standard operational procedure (Male's QA/QC Protocol)
- Data acquisition and data analysis
- Reporting and follow-up

What are Planned for Male' Network?



- Protocol preparation
- Artificial rainwater sample preparation
- Sending samples to laboratories
- Data acquisition and handling
- Data analysis
- Reporting and dissemination
- Recommendations to improve the data quality
- ➔ Needs active participation and responsibility of involved laboratories for the success

The Protocol highlights



- First draft was prepared and presented, discussed at the “Refresher training” at AIT in March 07
- The revised version was sent for comments (to IVL and NIA) in April-May 2007
- The finalized version available (August 2007)
 - Proposed concentrations: 2 levels (high and low)
 - A brief QA program has been designed and will be distributed to NIA before the sample analysis
 - A range containing levels of analytes in samples will be informed to labs in the document enclosed with samples

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

Actual ranges are based on the monitoring results from NIAs

Ranges of data from NIA (cont.)

		EC	pH	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
Maldives	Min-Max	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	5 - 95%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Method										
Nepal	Min-Max	4.5-6.0	5.8-6.2	32	N/A	8-13	N/A	N/A	N/A	N/A	N/A
	5 - 95%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Method	0	1	2	3	5	8	8	5	5	2
Pakistan	Min-Max	1.6-39	6.2-8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	5 - 95%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Method	0	1	6	6	6	6	6	6	6	6
Overall	Min-Max	0 - 37.5	0 - 8	4-71	1.8-38	7-224	0.6-203	0.3-252	0-56	1-29	0-45
	5 - 95%	0.1-12	4.6-7.6	4.5-62	1.9-38	9.6-119	1-134	0.5-26	1.6-44	1.4-22	0-35

Code	Methods	Code	Methods
0	pH meter with electrode	5	Titrimetry method
1	Conductivity cell	6	Ion Chromatography
2	Spectrophotometry	7	Flame photometry
3	Cadmium reduction method-Spectrophotometry	8	Atomic Absorption Spectrometry
4	Argentometric method	9	Flame photometry

Sending-receiving samples



- Samples to be sent to NRIs by fast delivery services
- Samples to be sent in dry ice boxes
- Dates of sending samples will be recorded
- Laboratories will note the dates and the conditions of samples as received and communicate immediately to UNEP and AIT at soon as the samples received
- if abnormal conditions of samples occurred when received the lab should notify AIT so that measures to be taken

Data acquisition



- Data template (excel) will be sent to laboratories by email and a hard copy in each sample box
- Laboratories to analyze the samples as soon as possible and should be within 1 week after received
- Data to be sent to UNEP and AIT by email and a hard copy to be sent by fax not later than 7 days after the analysis completed
- Laboratories are responsible to check the data quality and R1 and R2 before sending to AIT and UNEP
- AIT and UNEP will work together to get the data from NIAs as scheduled

Data Checking by AIT



- Raw data: analytical results, operators info, equipment, detection limits, etc.
- Checking for completeness of the analytical data and the information
- Check the data and compare with criteria (Male's Protocol) and flag if is out of the ranges
 - Ion balance: R1 (flagged I)
 - Calculated and measured conductivity: R2 (flagged C)

Allowable Ranges for R1 in Different Concentrations

C_{eq} + A_{eq} (μeq/L)	R₁ (%)
<50	± 30
50-100	± 15
>100	± 8

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

Allowable Ranges for R2 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

Data analysis (1)



Compile data and perform statistical analysis:

- Average, Max, Min, STD of data from all NIA for each parameter
- Estimate the bias: difference between the actual concentration and the results sent by each laboratory
- Precision: compile the data for precision estimation based on the repeated analysis results sent by NIAs (>3 data points per level)

Data analysis (2)

- Flag the data points against the DQO:
 - Flag "E" will be put to the data that exceed DQOs by a factor of 2, i.e. between $\pm 15\%$ and $\pm 30\%$
 - Flag "X" will be put to the data that exceed DQOs more than a factor of 2, i.e. beyond $\pm 30\%$ ($< -30\%$ or $> 30\%$).
- Analysis results: (1) for each level, (2) for individual parameter, and (3) based the circumstance of analysis in NIA labs

QA program for the inter-lab comparison

a. Sending samples:

- Samples to be sent to all NIA participating in the same day
- Samples to be sent in icy (dry ice) box by Express

b. Guideline for handling samples

- De-ionized water used for rinsing glassware and equipment (in contact with samples) should have EC of < 0.15 mS/m
- Samples to be analyzed within a week after arrival
- Samples to be refrigerated and necessary measures to be taken (tightly capped, keep in clean refrigerators) if stored
- NIA to analyze each sample for a few times (at least 3 times) and report results of each analysis

c. Data template to be used to enter the results

QA program for the inter-lab comparison (Cont.)



d. Analytical procedure:

- Temperature (25°C) of water for measuring EC, pH
- Analytical methods for ions follow the methods currently used by NIA for routine rain samples (already approved by UNEP)

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

- Refrigerated samples (4°C) and stored in icy box in room temperature;
- Both types of samples to analyzed at interval 1-2 days after departing samples to NIA in order to detect any change of concentrations in samples with storage time and storage methods.



Time schedule: 2 attempts

- First attempt: June-Nov. 2007
 - Samples sent to labs: September 2007
 - Results received: 1 weeks after samples arrived labs (approximately 2 weeks after sending)
 - Data analysis communication to labs: Oct. 2007
 - Data reporting and follow up: Nov. 2007
- Second attempt: March-April 2008
- Updated protocol for further use in the network

Thank you!