# Inter-laboratory calibration of Male's monitoring network: preliminary findings

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# Contents

- About the inter-lab calibration for Male’ network
- Summary of the protocol
- Results of first attempt

# 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

# 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

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

# Implementation for Male' Network: First Attempt

| Activity | Time |
|---|---|
| Protocol preparation | April-Sept.07 |
| Artificial rainwater sample preparation | Nov. 07 |
| Sent samples to laboratories | Nov. 07 |
| Data acquisition and handling | Nov. 07-March 08 |
| Data analysis | Feb.08-April08 |
| Final report with recommendations | April-May 08 |
| Dissemination | Male' regional meetings |
| Next attempt | ??? |

# Protocol highlights

- Final protocol was sent to all NIAs in Nov. 2007 together with the samples
- Two concentration levels: high and low
- QA program has designed and distributed to NIA before the sample analysis
- A range containing analyte levels have been included in the final protocol and sent with samples

# Concentration ranges in Male' artificial rain water samples

| Parameter | Range | Parameter | Range |
|---|---|---|---|
| pH | 4-6.5 | $Na^+$ | 1 – 150 µmol/L |
| EC | 0.2-10 mS/m | $K^+$ | 1 – 50 µmol/L |
| $SO_4^{2-}$ | 1 – 100 µmol/L | $Ca^{2+}$ | 1 – 50 µmol/L |
| $NO_3^-$ | 1 – 100 µmol/L | $Mg^{2+}$ | 1 – 50 µmol/L |
| $Cl^-$ | 5 – 150 µmol/L | $NH4^+$ | 1 – 100 µmol/L |

# Outline of artificial rainwater samples

| Sample name | Amount of sample in a container | Bottle | Number of bottle per sample |
|---|---|---|---|
| No. M11 (high concentration) | Approximately 800 mL | Poly-propylene of 1 L capacity | 1 bottle for each sample |
| No. M12 (low concentration) | | | |

M11 and M12 contain known amount of reagents dissolved in de-ionized water

# Sending-receiving samples

- Samples were sent to NRIs by fast delivery services
- Samples were sent in dry ice boxes
- Dates of sending samples recorded
- Laboratories were requested to 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 UNEP/AIT so that measures to be taken

# Data acquisition

- Data excel template was sent to laboratories by email and a hard copy with each sample box
- Laboratories were requested to analyze the samples as soon as possible and should be within 1 week
- NIAs were requested to send analytical results to UNEP and AIT by email and a hard copy to UNEP by fax within 7 days after the analysis completed
- Laboratories were requested to check the data quality and R1 and R2 before submitting
- AIT and UNEP follow up to get the data from NIAs

# Sending and receiving dates

Date of sending samples (batch 1, main) to all countries: 13-Nov.07
Date of sending additional samples to Nepal & Iran: first week, March 08

| Country | Date of receiving samples | Date of measurement | | | | | | | | | | Date of data received at AIT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | EC | SO4= | NO3- | Cl- | Na+ | K+ | Ca2+ | Mg2+ | NH4+ | |
| Nepal | 9-Mar-08 | 11-Mar-08 | 11-Mar-08 | 12-Mar-08 | 12-Mar-08 | 11-Mar-08 | 13-Mar-08 | 13-Mar-08 | 11-Mar-08 | 11-Mar-08 | 12-Mar-08 | 20-Mar-08 |
| India | 15-Nov-07 | 16-Nov-07 | 16-Nov-07 | 16-Nov-07 | 17-Nov-07 | 16-Nov-07 | 19-Nov-07 | 19-Nov-07 | 16-Nov-07 | 16-Nov-07 | 20-Nov-07 | 13-Dec-07 |
| Bangladesh | 15-Nov-07 | 19-Nov-07 | 19-Nov-07 | na | na | 19-Nov-07 | 21-Nov-07 | 21-Nov-07 | 20-Nov-07 | 20-Nov-07 | 27-Nov-07 | 7-Feb-08 |
| Srilanka | 15-Nov-07 | 14-Nov-07 | 14-Nov-07 | 16-Nov-07 | 16-Nov-07 | 16-Nov-07 | 17-Nov-07 | nr | 17-Nov-07 | 17-Nov-07 | 14-Nov-07 | 12-Dec-07 |
| Maldives | 15-Nov-07 | 26-Nov-07 | 26-Nov-07 | na | na | na | na | na | na | na | na | 8-Jan-08 |
| Bhutan | 21-Nov-07 | nr | nr | na | nr | na | nr | nr | na | nr | na | 7-Dec-07 |
| Iran | 11-Mar-08 | 9-Mar-08 | 9-Mar-08 | 15-Mar-08 | 10-Mar-08 | 12-Mar-08 | 13-Mar-08 | 13-Mar-08 | 16-Mar-08 | 16-Mar-08 | 11-Mar-08 | 25-Mar-08 |
| Pakistan | 15-Nov-07 | no data recieved | | | | | | | | | | |

na: sample not analyzed

nr: measurement results reported but not but date of measurement

# Data Analysis by AIT

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

# Allowable Ranges for Ion Balance (R1) 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

# 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 NIAs for each parameter
  - Estimate the bias: difference between the actual concentration and the results sent by each lab

# 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 (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%)
- Analysis results for each sample, for individual parameter and based the circumstance of analysis in NIA labs

# QA program for 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)

c. Data template to be used

# QA program for the inter-lab comparison *(cont.)*

d. Analytical procedure:

- Temperature (25$^{o}$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$^{o}$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.

# Summary of results:
# Sample M11, high concentration

| Country | pH | EC | SO4= | NO3- | Cl- | Na+ | K+ | Ca2+ | Mg2+ | NH4+ |
|---|---|---|---|---|---|---|---|---|---|---|
| Nepal | 5.0±0.08 | 3.4±0.03 | 69.7±2.9 | 26.2±2.4 | 140±46.6 | 116±10 | 49.1±7.4 | 44.4±9.67 | 27.8±9.5 | 66.7±11.5 |
| Maldive | 4.11±0.06 | 3.53±0.15 | no data | | | | | | | |
| Bhutan | 7.07 | 4.1 | na | 0 | na | 2.2 | 23.7 | na | 1.5 | na |
| India | 4.46 | 3.7 | 44 | 8.1 | 172 | 77 | 33 | 40 | 64 | 29.3 |
| Srilanka | 5.27 | 3.5 | 55 | 17.29 | 8.2 | 94.8 | 36 | 33 | 22.2 | 25.5 |
| Iran | 6.32±0.25 | 3.22±0.01 | 67.0±1.4 | 8.2±0.06 | 300±0 | 95±0 | 33.3±0 | 200±0 | 0 | 27.7±3.4 |
| Bangladesh | 5.09 | 4.50 | na | na | 117.59 | 33.40 | 36.39 | 36.33 | 35.5 | 69.57 |
| Pakistan | No data received | | | | | | | | | |
| Prepared conc (cal) | 4.8 | 3.45 | 39.0 | 37.5 | 90.9 | 95.6 | 29.7 | 34.0 | 20.3 | 26.7 |

Problem of reporting Zero: Not detected?

➔ Detection limit to be reported

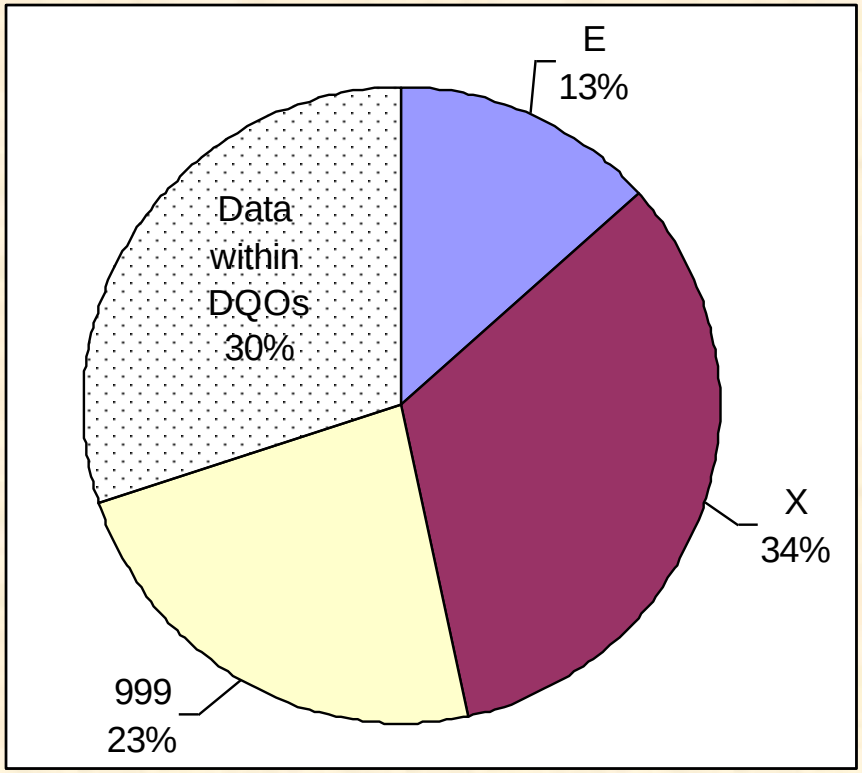
# Summary of results: sample M12, low concentration

| Country | pH | EC | SO4= | NO3- | Cl- | Na+ | K+ | Ca2+ | Mg2+ | NH4+ |
|---|---|---|---|---|---|---|---|---|---|---|
| Nepal | 5.58±0.17 | 0.34±0.01 | 13.6±2.9 | 6.95±1.8 | 54.3±13.5 | 26±7.5 | 13.9±1.85 | 22.3±9.5 | 16.6±0.2 | 26.7±5.8 |
| Maldive | 5.73± 0.05 | 0.35±0.01 | no data | | | | | | | |
| Bhutan | 7.07 | 0.4 | na | 0 | na | 2.0 | 1.9 | na | 0.10 | na |
| India | 5.43 | 0.4 | <30 | <0.5 | 110 | <20 | <11 | <40 | <40 | 6.9 |
| Srilanka | 6.5 | 0.4 | 2.9 | 1.58 | 5.6 | 7.4 | 2.6 | 3.52 | 2 | 2 |
| Iran | 6.0±0.12 | 0.55±0.01 | 17.4±0.8 | 0.2±0.1 | 100 | 4 | 0.8 | 42±2.9 | 0 | 19.1±1.3 |
| Bangladesh | 5.51 | 1.30 | na | na | 24.0 | 4.6 | 5.7 | 7.00 | 6.3 | 12.9 |
| Pakistan | No data received | | | | | | | | | |
| Prepared conc (cal) | 5.8 | 0.37 | 3.1 | 2.0 | 9.3 | 5.2 | 2.0 | 2.1 | 1.6 | 3.0 |

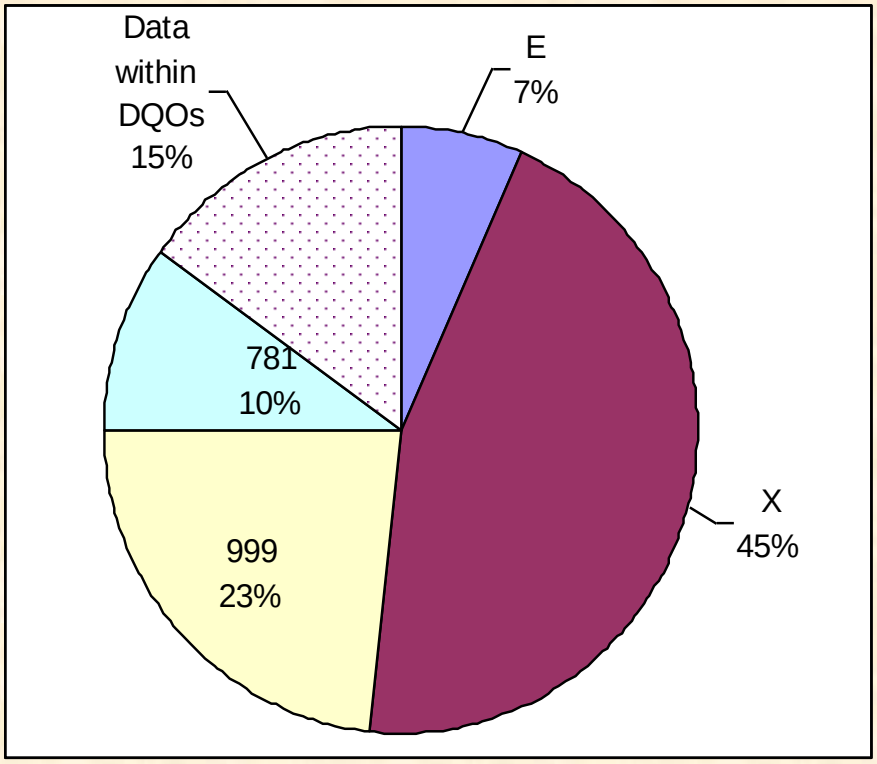
Problem of reporting Zero: Not detected?

➔ Detection limit to be reported

# Data quality: flag data points




M11: high conc.
Total data points: 60




M12: low conc.
Total data points: 60

(Iran data not yet included)

# Numbers of flagged data for sample M11 (high concentrations)

| Flag | pH | EC | $SO_4^{2-}$ | $NO_3^-$ | $Cl^-$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $NH_4^+$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E | 0 | 1 | 0 | 0 | 0 | 3 | 3 | 1 | 0 | 0 | 8 |
| X | 1 | 0 | 2 | 4 | 3 | 2 | 1 | 1 | 4 | 2 | 20 |
| 999 | 0 | 0 | 3 | 2 | 2 | 1 | 1 | 2 | 1 | 2 | 14 |
| 781 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Within DQOs | 5 | 5 | 1 | 0 | 1 | 0 | 1 | 2 | 1 | 2 | 18 |
| Flagged (%) | 17 | 17 | 83 | 100 | 83 | 100 | 83 | 67 | 83 | 67 | 70 |

E: Value exceeded the DQO (±15%) by a factor of 2

X: Value exceeded the DQO (±15%) more than a factor of 2

999: Missing measurement, reason not specified.

781: Below detection limit.

# Numbers of flagged data for sample M12 (lower concentrations)

| Flag | pH | EC | $SO_4^{2-}$ | $NO_3^-$ | $Cl^-$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $NH_4^+$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 4 |
| X | 0 | 4 | 1 | 2 | 4 | 3 | 3 | 3 | 3 | 4 | 27 |
| 999 | 0 | 0 | 3 | 2 | 2 | 1 | 1 | 2 | 1 | 2 | 14 |
| 781 | 0 | 0 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 6 |
| Within DQOs | 5 | 1 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 9 |
| Flagged (%) | 17 | 83 | 83 | 100 | 100 | 83 | 83 | 100 | 100 | 100 | 85 |

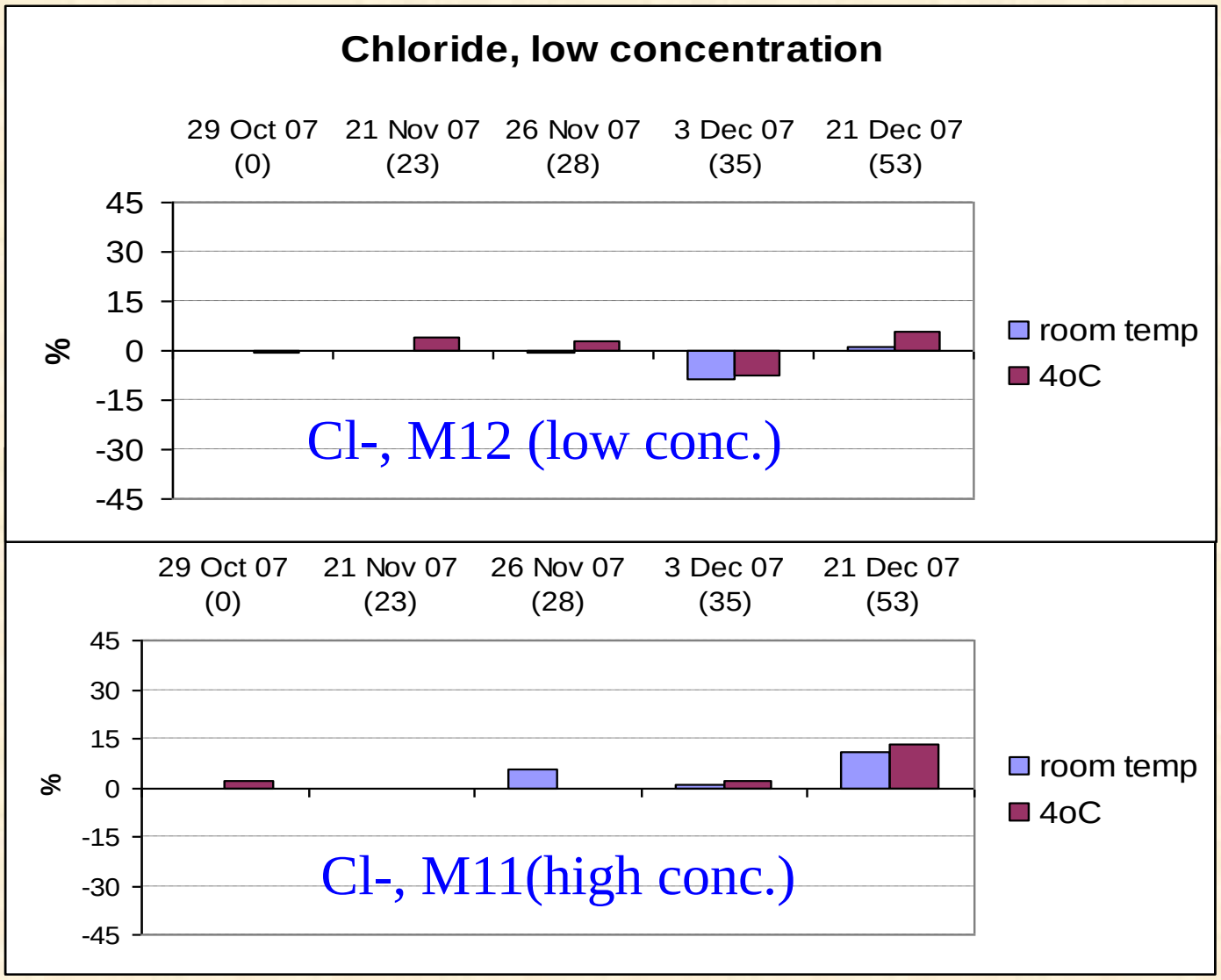
E: Value exceeded the DQO (±15%) by a factor of 2

X: Value exceeded the DQO (±15%) more than a factor of 2

999: Missing measurement, reason not specified.

781: Below detection limit.

# AIT follow-up analysis



# Next steps

- Final report in April-May 2008
- Second attempt ?
- Updated protocol for further use in the network

*Thank you!*