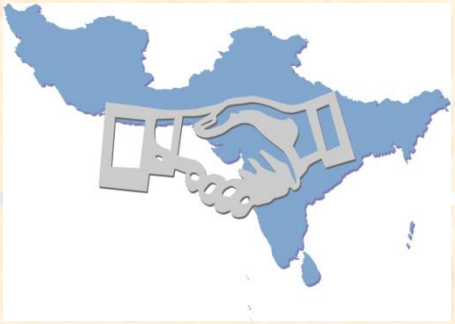
Inter-laboratory calibration of Male's monitoring network: outlook



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Male' Declaration refreshment workshop
Delhi, Nov. 16-18, 2010

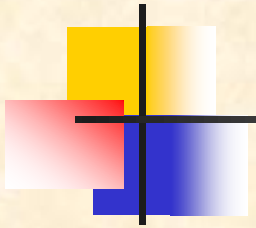
Contents

- About the inter-lab calibration for Male' network
- Summary of the protocol
- Results of first 2 attempts
- Plan for 3rd attempt

Why the inter-lab calibration?

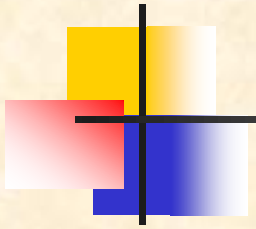
- Data quality is the first concern in any monitoring program
- Consistency/harmonization should be reached for data compilation in a regional network involving different laboratories
- Inter-laboratory calibration is an important element of QA which is specified in Male' protocol

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

Past implementation: 2007-2009

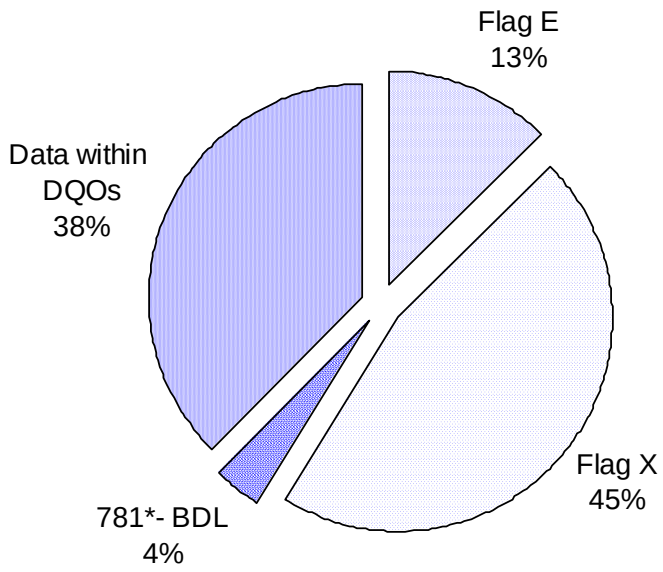
Activity	Time
Protocol preparation	April-Sept.07
Artificial rainwater sample preparation	Nov. 07
First attempt	Nov-2007 - March 2008
Second attempt	August 2008-Dec. 2008
Sent samples to laboratories	August 2008
Data acquisition and handling	Sept- Nov 08
Data analysis	Nov.-Dec. 08
Final report with recommendations	March 2009
Dissemination	Regional refreshment WS

3rd attempt !!!

Protocol highlights

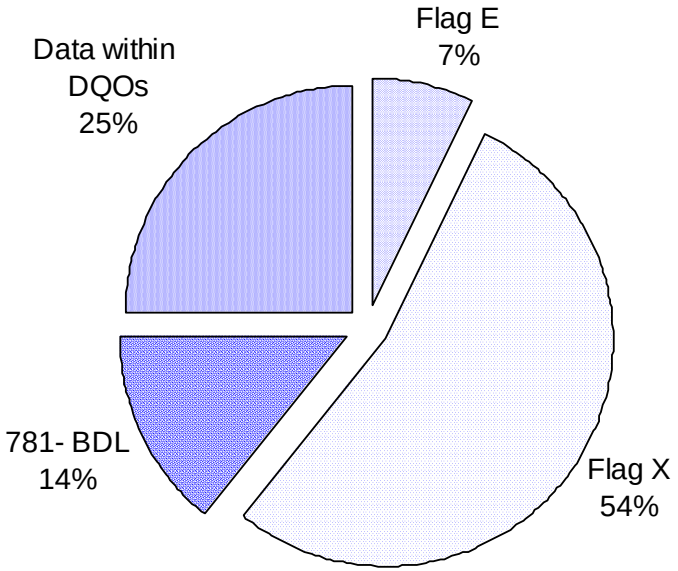
- Final protocol was finalized after communication with NIAs in Sept. 2007
- Samples with two concentration levels: high and low
- QA program has designed and distributed to NIA before the artificial rain sample analysis
- A range containing analyte levels have been included in the final protocol and sent with the samples

First attempt: data quality (flag data points)



M11

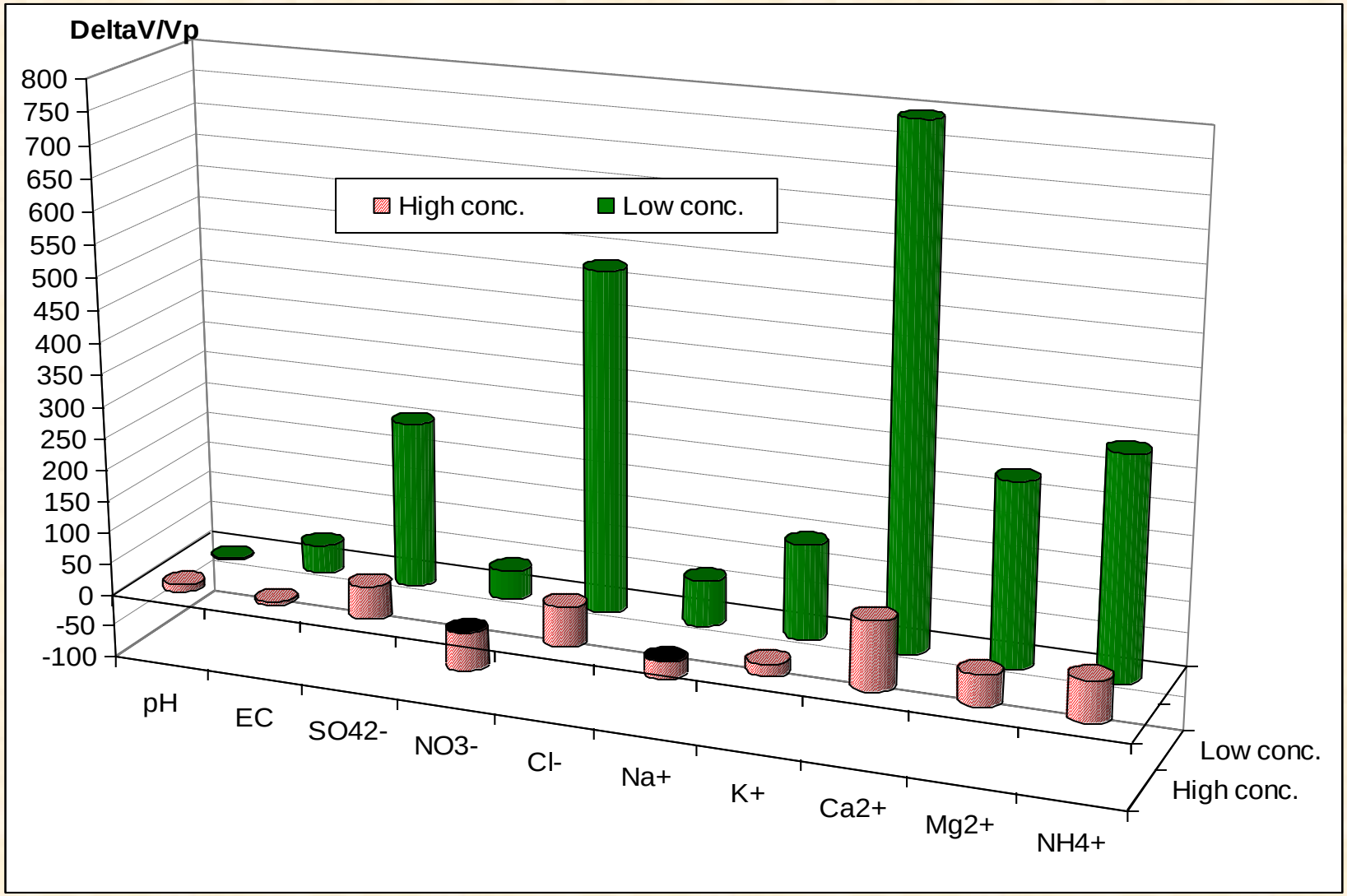
Summary of data quality for high conc



M12

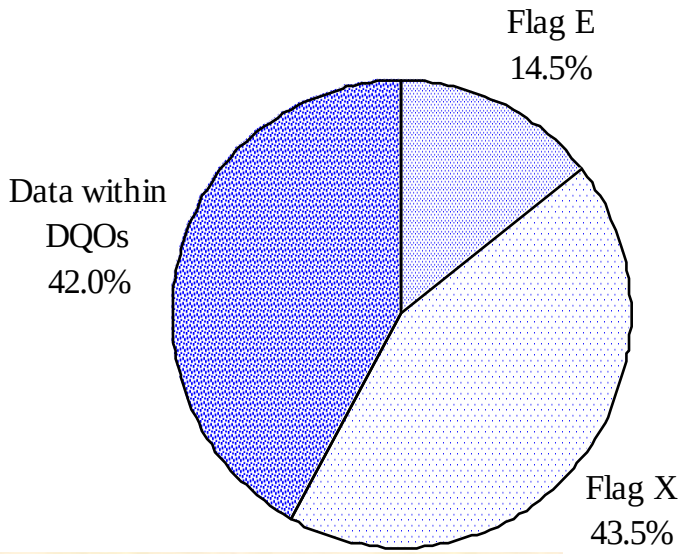
Summary of the data quality for low conc.

1st attempt: relative deviation between average submitted data and prepared value (%)

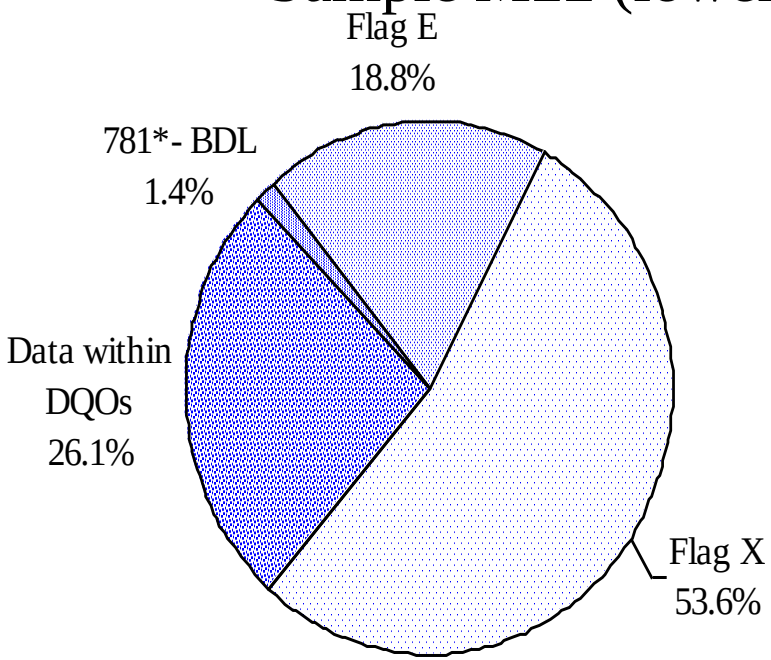


2nd attempt: data quality (flag data points)

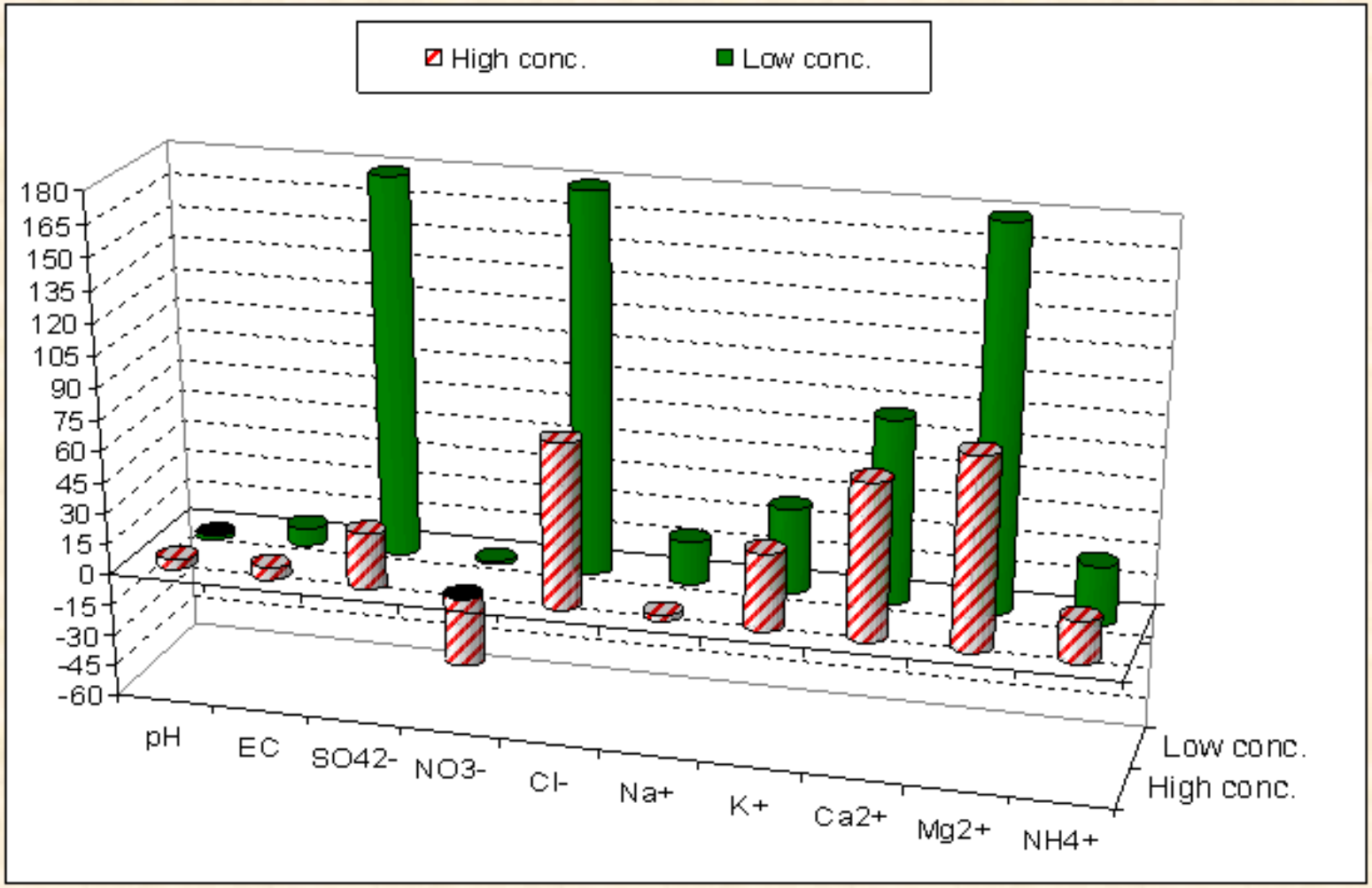
Sample M21 (higher conc.)



Sample M22 (lower conc.)

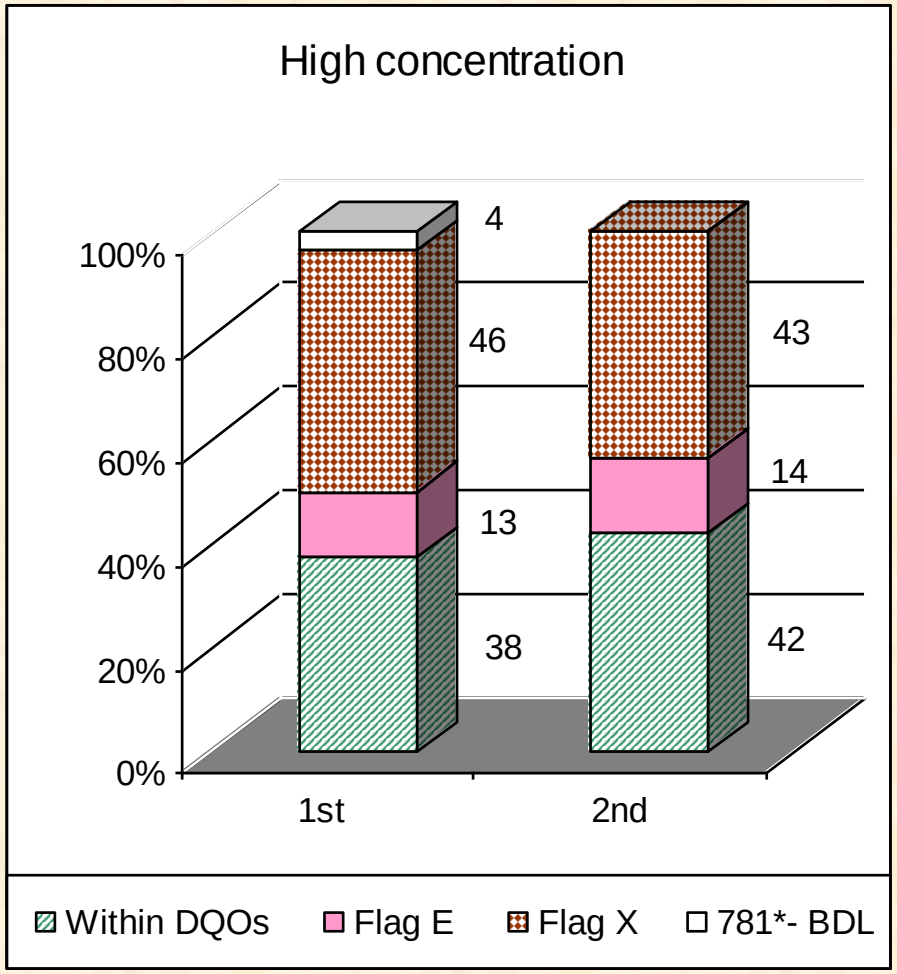


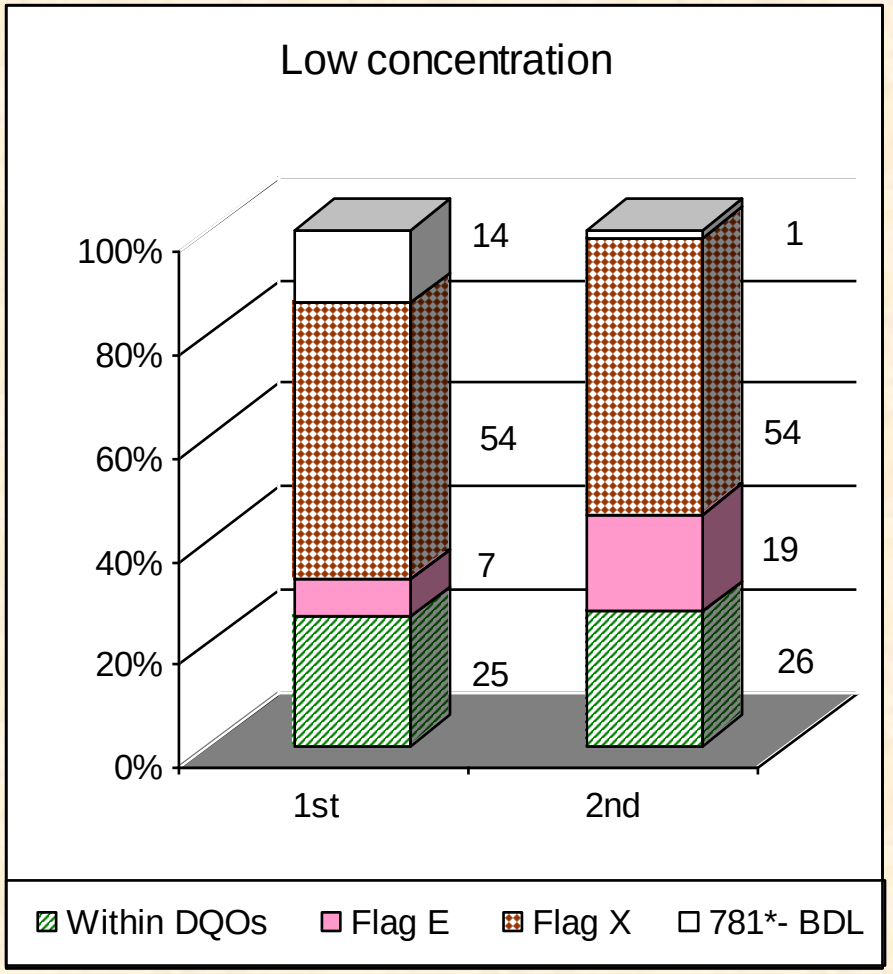
2nd attempt: Relative deviation between average submitted data and prepared value



High conc: M21; Low conc.: M22

Overview of 1st and 2nd attempts





Summary remarks

- Strong bias for most of the parameters, especially for low concentration sample
- Results of parameters requiring less sample treatment are more accurate
- Large number of non-reported data
- Reported zero values not providing detection limits
- Low sensitivity of equipment in some labs
- A few NRIs have enough results for R1 and R2 calculation, most not submitted the R1 and R2

Recommendations for improvement

- General:
  - Strictly follow the Malé QA/QC Monitoring Protocol: standard operating procedures (management of apparatus, reagents, and procedure of operation)
  - Consider using methods requiring less sample treatment
  - Repeated analyses for precision estimate
- Fundamental factors to improve data quality
  - Properly clean the apparatus/glassware
  - Use materials/reagents of required purity with low blank
  - In house-expertise within each lab for sampling and analysis
  - In-house expertise for the data quality check especially if samples are analyzed by other institutions
  - A log book should be kept, etc.

Specific recommendations for sample analysis

- Use deionized water with conductivity <0.15mS/m for dilution of samples and cleaning glassware
- Use the standard reference materials to evaluate the measurement methods
- Pretreatment of samples, storage and analysis time: pH and EC measurement at 25^{o}C and as soon as possible; other parameters to be analyzed within 1 week
- Calibrate analytical instrument, develop new calibration curves for new reagent bottles, etc.
- Data quality checking and control by NIA laboratory: discard obvious erroneous data, calculate precision, Calculate R1 and R2, etc.

Plan for third attempt

- Follow the protocol
- Time to be decided: in 2011
- NIA: to check the reports of 2 past attempts and consider the recommendations to improve the results

Outline of artificial rainwater samples

Sample name	Amount of sample in a container	Bottle	Number of bottle per sample
No. M31 (high concentration)	Approximately 800 mL	Poly-propylene of 1 L capacity	1 bottle for each sample
No. M32 (low concentration)			

M31 and M32 contain known amount of reagents dissolved in de-ionized water

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

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 recorded
- Laboratories are 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 will be sent to laboratories by email and a hard copy with each sample box
- Laboratories are requested to analyze the samples as soon as possible and should be within 1 week
- NIAs are 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 are requested to check the data quality and R1 and R2 before submitting
- AIT and UNEP follow up to get the data from NIAs

Data Analysis

- 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

Flag I for a sample: poor ion balance agreement

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

Flag C for a sample: poor electrical cond. agreement

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

Data flagging for analytical parameters

- Flag the data points against the DQO:

Bias (%) =100 x (Analytical val – Prepared val)/(Prepared val)

  - Meeting DQOs: bias within ±15%
  - Flag "E“: bias exceeds DQOs by a factor of 2 (±15% to ±30%)
  - Flag "X”: bias exceeds DQOs more than a factor of 2, i.e. beyond ±30%

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

WE'd better to have no data than to have wrong data!

Thank you!