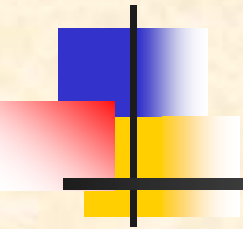


Inter-laboratory calibration of Male's monitoring network: findings of first attempt



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Male' Declaration 5th Regional Stakeholders
Meeting
Colombo, August 19-20, 2008

Contents



- About the inter-lab calibration for Male' network
- Summary of the protocol
- Results of first attempt
- Recommendations for improvement

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

Activity	Time
Protocol preparation	April-Sept.07
Artificial rainwater sample preparation	Nov. 07
First attempt: Nov-2007 - March 2008	
Sent samples to laboratories	Nov. 07
Data acquisition and handling	Nov. 07-March 08
Data analysis	Feb.08-April08
Final report with recommendations	May-June 08
Dissemination	Regional meetings
Second attempt	August 2008

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	NH ₄ ⁺	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 as 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 Lab 4 & 6, March 08

NIA	Receiving sample	Date of measurement										Receiving data
		pH	EC	SO4	NO3	Cl	Na	K	Ca	Mg	NH4	
Lab no.1	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
Lab no.2	21-Nov-07	nr	nr	na	nr	na	nr	nr	na	nr	na	7-Dec-07
Lab no.3	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
Lab no.4	13-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
Lab no.5	15-Nov-07	26-Nov-07	26-Nov-07	na	na	na	na	na	na	na	na	8-Jan-08
Lab no.6	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
Lab no.8	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
Lab no.7	15-Nov-07	data sent after knowing prepared concentrations										

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)

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 $\pm 15\%$ 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 for each sample, for individual parameter and based the circumstance of analysis in NIA labs

Summary of results: Sample M11, high concentration

NIA	pH	EC	SO4	NO3	Cl	Na	K	Ca	Mg	NH4
Lab no.6	5.0±0.08	3.4±0.03	69.7±2.95	26.2±2.37	139.8±46.6	115.9±10.0	49.1±7.4	44.4±9.67	27.8±9.5	66.7±11.5
Lab no.5	4.11±0.06	3.53±0.15	no data							
Lab no.2	7.07	4.1	na	0	na	2.22	23.67	na	1.54	na
Lab no.3	4.46±0.03	3.7±0.0	44±3.86	8.1±0.0	172	77±17.4	33±0.59	40	64	29.3±0.23
Lab no.8	5.27±0.01	3.5±0	55±1	17.3±0.006	8.2±0.001	94.84±0.01	36±1	33±1	22.2±0.55	25.5±0.1
Lab no.4	6.32±0.25	3.22±0.01	67.03±1.37	8.23±0.06	300±0	95±0	33.3±0	200±0	0	27.73±3.42
Lab no.1	5.08±0.02	4.51±0.02	na	na	118.44±1.8	33.42±0.3	36.38±0.18	36.33±0.81	35.49±0.6	69.57±0.49
Lab no.7	no data received in time									
Prepared	4.8	3.5	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

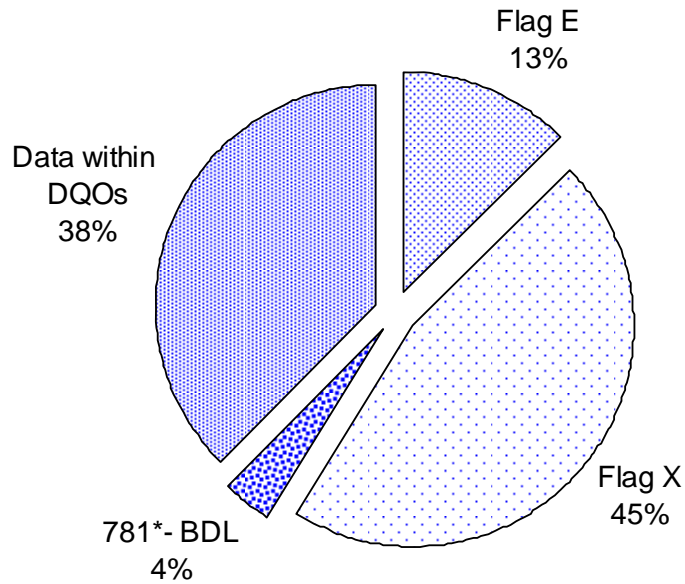
Summary of results: sample M12, low concentration

NIA	pH	EC	SO4	NO3	Cl	Na	K	Ca	Mg	NH4
Lab no.6	5.58±0.17	0.34±0.01	13.6±2.94	6.95±1.82	54.3±13.5	26±7.5	13.9±1.85	22.3±9.5	16.6±0.2	26.7±5.8
Lab no.5	5.73± 0.05	0.35±0.01	no data							
Lab no.2	7.07	0.4	na	0	na	1.99	1.94	na	0.10	na
Lab no.3	5.43±0.02	0.4±0.0	<40	<0.8	110	<30	<18	<40	<40	6.9
Lab no.8	6.5±0.0	0.4±0.0	2.9±0.1	1.58±0.006	5.6±0.1	7.4±0.1	2.63±0.01	3.52±0.01	2±0.1	2±0.1
Lab no.4	6.00±0.12	0.55±0.01	17.37±0.8	0.2±0.1	100±0	4±0	0.8±0	41.67±2.89	0	19.1±1.28
Lab no.1	5.5±0.05	1.3±0.016	na	na	24±1.03	4.59±0.08	5.74±0.18	7±0.6	6.33±0.5	12.92±0.18
Lab no.7	no data received in time									
Prepared	5.8	0.37	3.1	2.0	9.3	5.2	2.0	2.1	1.6	3.0

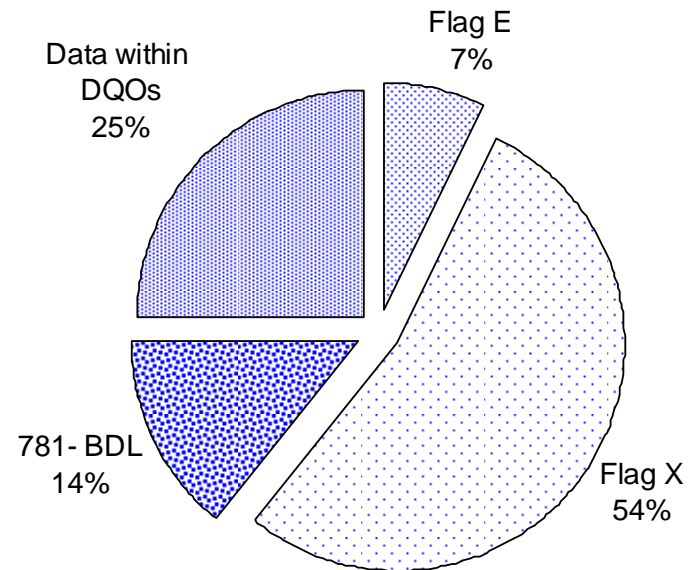
Problem of reporting Zero: Not detected?

➔ Detection limit to be reported

Data quality: flag data points



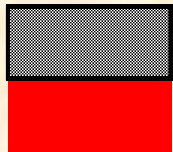
Summary of data quality for high conc



Summary of the data quality for low conc.

Data quality for different parameters

NIA	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
Lab no.1			NA	NA						
Lab no.2			NA		NA			NA		NA
Lab no.3										
Lab no.4										
Lab no.5			NA	NA	NA	NA	NA	NA	NA	NA
Lab no.6										
Lab no.8										

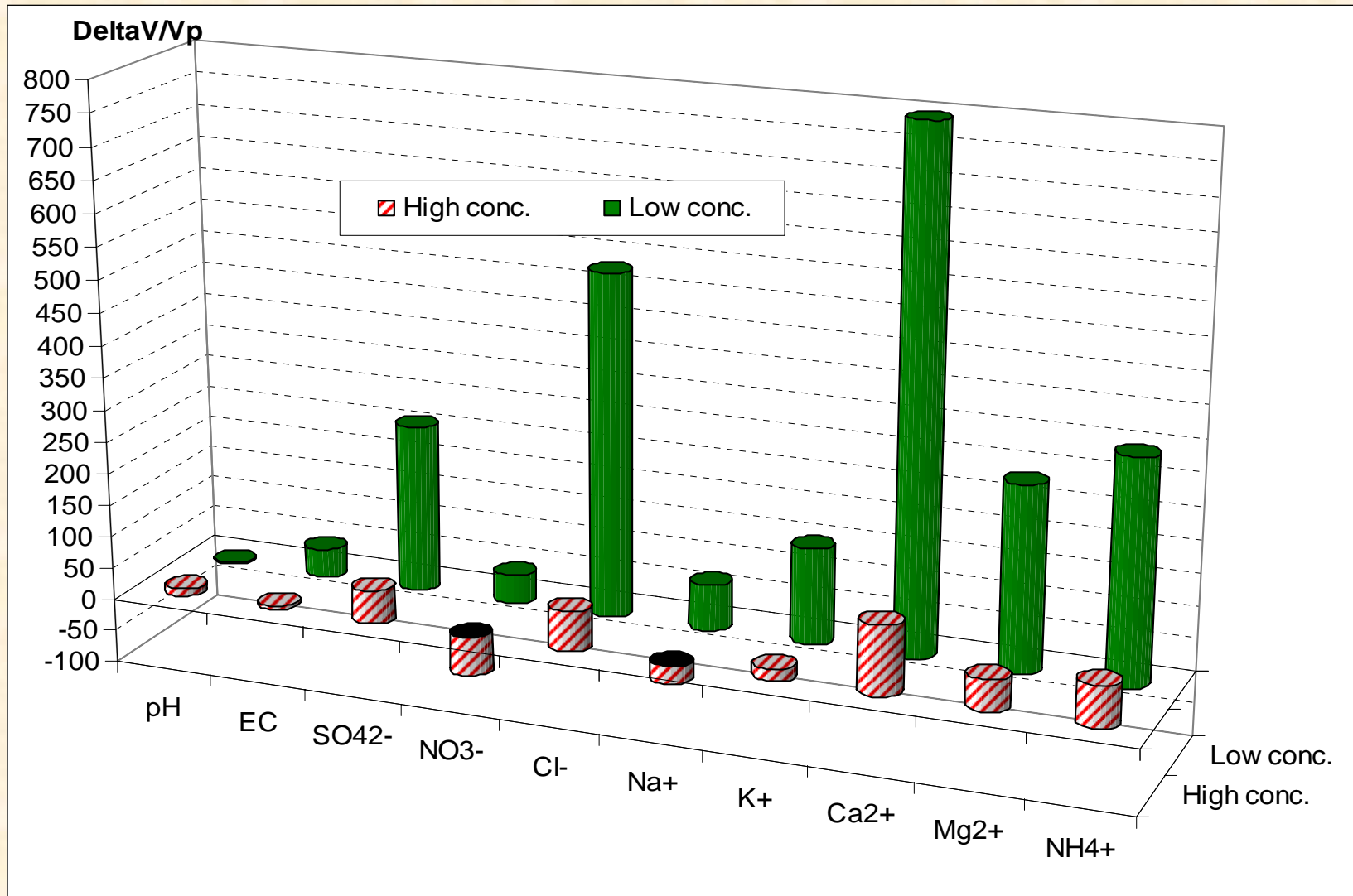


Dotted mesh: flagged data (E or X) in either sample No.M11 or sample No.M12.

Darked mesh: flagged (E or X) data of both sample No.M11 and No.M12

NA: not analyzed (no data)

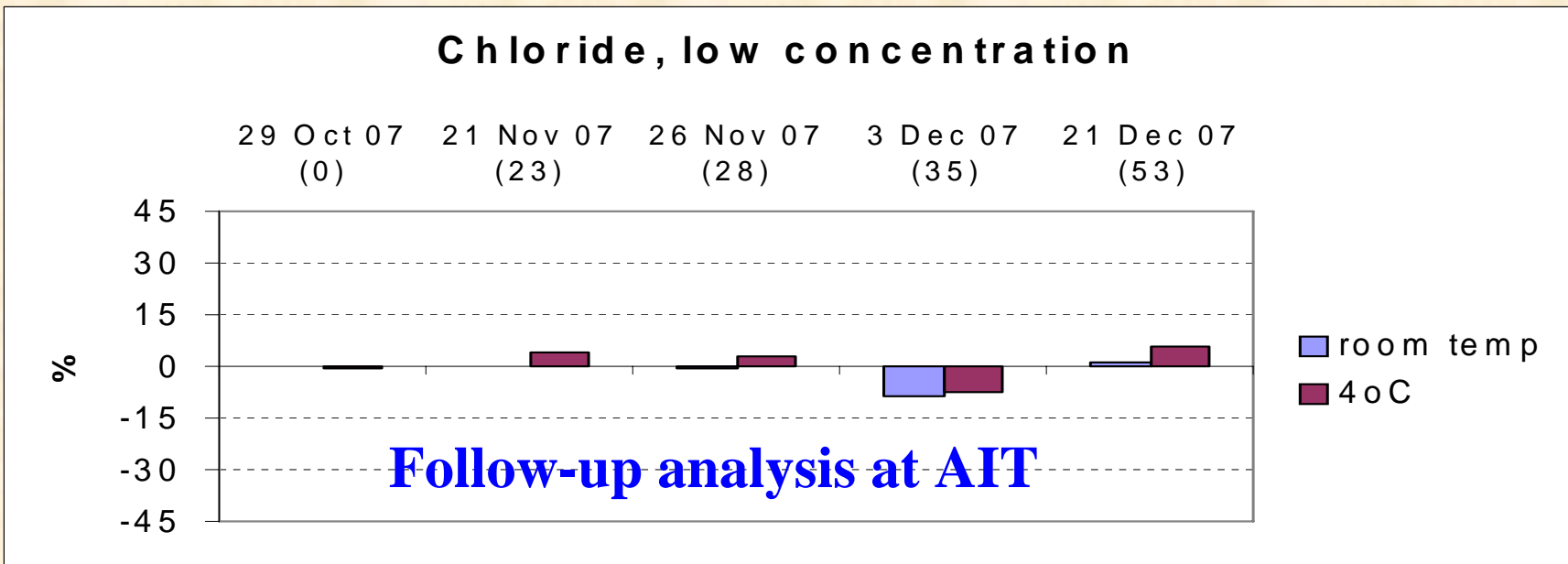
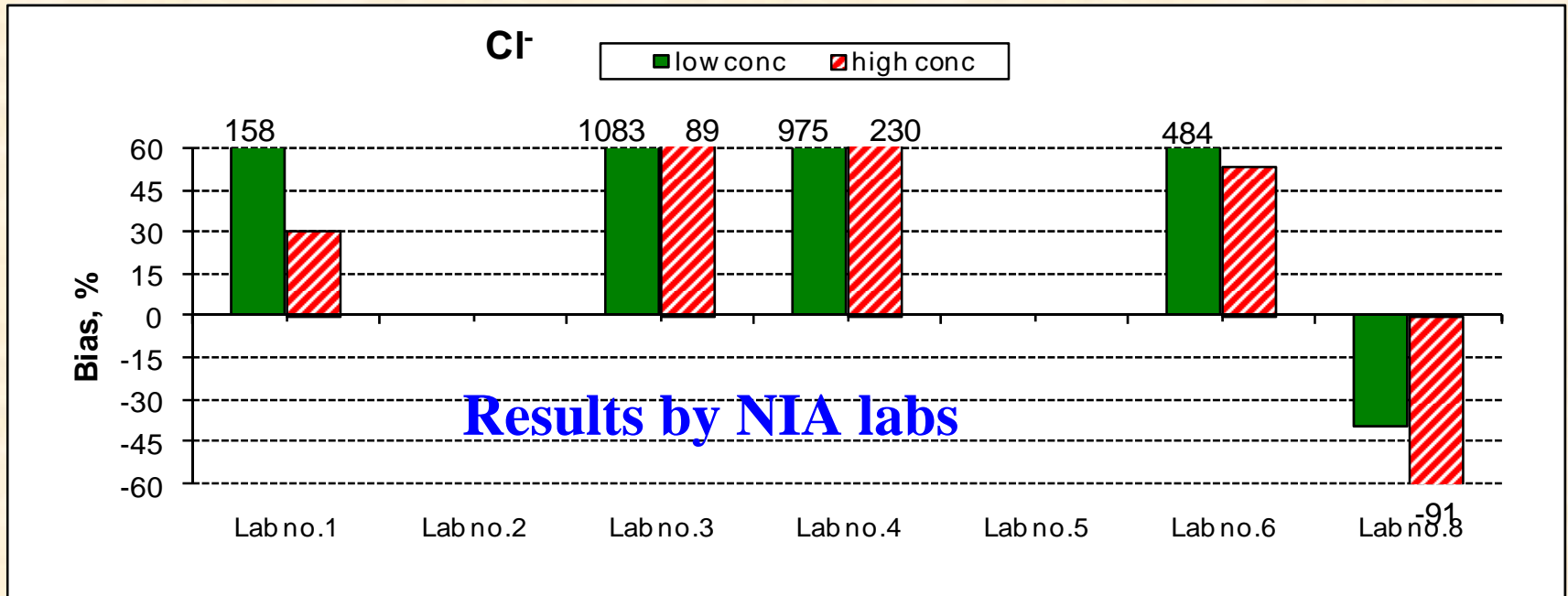
Relative deviation between average submitted data and prepared value



Parameter-wise analysis



- pH and EC results are more accurate with lower bias
- Cl⁻ and NO₃⁻ have 100% data points flagged for both samples
- For all ions the bias >500% is common
- Overall, bias for Cl⁻ is highest but the max. bias is for Ca²⁺



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, none 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 if samples are analyzed by other institutions
 - A log book should be kept, etc.

Specific recommendations for sample analysis



- Use deionized water with conductivity $<0.15\text{mS/m}$ 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°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.

**It'd better to have no data than to have
wrong data!**

Thank you!