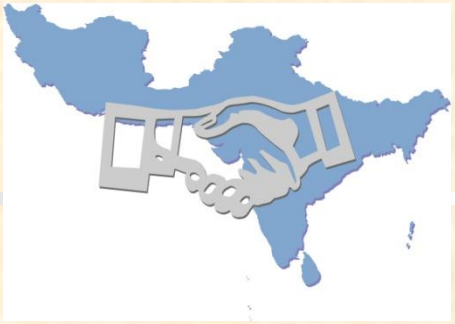
Inter-laboratory calibration of Male' monitoring network: findings of third attempt



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- About the inter-lab calibration for Male' network
- Summary of the protocol
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- 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

- AIT lab.:
  - Prepare reference artificial rainwater samples
  - Distribute the samples
  - Design and deliver QA program to participating labs
- Participating labs analyze sample following the standard operational procedure (Male' QA/QC)
- UNEP & AIT: data acquisition
- AIT: data analysis, reports
- NIA and UNEP: follow-up

Implementation for Male' Network

Activity	Time
Protocol preparation first time	April-Sept.07
First attempt	Nov. 2007 - March 2008
Second attempt	August 2008-Dec. 2008
Third attempt	July 2011-Sept. 2012
Samples sent to laboratories (with the revised protocol)	13 July 2011
Dates of receiving samples	15 July to 1 August 2011
Dates of measurements	15 July to 19 Sept 2011
Final report with recommendations	May 2012
Dissemination	9th refreshment WS

Protocol highlights

- Final version of protocol was sent to all NIAs in July 2011 together with the samples
- QA program has been designed and distributed to NIA with samples
- Two concentration levels: high and low
- The ranges of analyte levels have been given 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	Container	Number of samples sent to NIA
No.M31 (high conc.) No.M32 (low conc.)	~ 800 mL/bottle	Polypropylene bottle, 1L capacity	2 bottles (1 for each level)

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

Sending-receiving samples: principles

- 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: principles

- 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

NIA Lab	Date of receiving sample	Date of measurement									
		pH	EC	SO4	NO3	Cl	Na	K	Ca	Mg	NH4
Bangladesh	27-Jul-11	29 Jul to 4 Aug 2011									
Bhutan	15-Jul-11	15 to 19 Jul 2011									
India	1-Aug-11	1 to 3 Aug 2011									
Iran	23-Jul-11	24-28 Jul 11							11-Sept		28-Jul-11
Maldives	17-Jul-11	NA									
Nepal	18-Jul-11	17 to 19 Sep 11									
Pakistan	20-Jul-11	22 to 29 Jul 11									
Sri-Lanka	20-Jul-11	20 to 23 July 11									

Most NIAs analyzed the samples within 2 weeks, except Lab no.4 (Mg^{2+}, Ca^{2+}) and Lab no.6 where samples were analyzed about 2 months after received.

Data analysis by AIT

- Raw data received: analytical results, operators info, equipment, detection limits, etc.
- Checking for completeness of the analytical data and the information
- Checking the data and compare with criteria and flag if data points are out off the specified ranges
  - Flagged E, flagged X
  - Ion balance: R1 (flagged I)
  - Calculated vs. 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 obtained by each NIA 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% (bias >30%)
- Analysis results for each sample, for individual parameter and based on the circumstance of analysis in NIA labs

QA program for inter-lab comparison (1)

a. Sending samples:

- Samples to be sent to all NIA participating in the same day, icy box, by DHL (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 (2)

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 the analytical results by NIAs for the high concentration sample (M31)

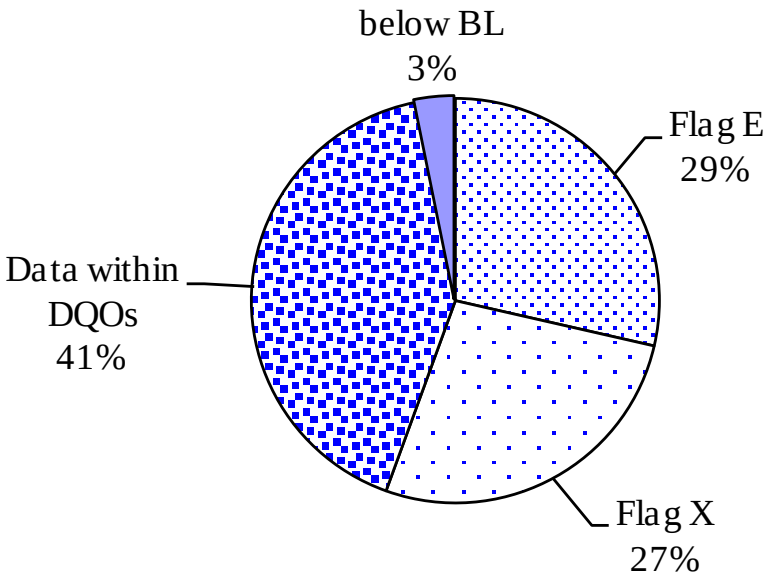
Parameter (μmol/L)	NIA laboratories								Prepared level
	Lab no.1	Lab no.2	Lab no.3	Lab no.4	Lab no.5	Lab no.6	Lab no.7	Lab no.8	
pH	5.33±0.4	5.57	5.29±0.01	7.66±0.01	na	5.95±0.06	5.66±0.05	5.06±0.011	5.63
EC (mS/m)	2.96±0.3	3.21	2,96±0.01	3.50±0.001		3.77±0,07	2.97±0.032	2.9±0	2.88
SO_4^{2-}	49±1	na	32.78±2.6	50.63±0.21		32.44±1.10	33.83±1.63	44.71±0.08	39.10
NO_3^-	30±1	na	33.5±0.6	7.70±0.01		30.56±2.21	30.2±1.98	40.01±0.02	38.87
Cl^-	116±5	na	178.7±8.14	56.04±0.00		89.17±8.13	76.80±0.8	103.59±.03	99.03
Na^+	81±1.2	5.49	87.8±1.50	68.11±2.51		131.2±8.22	na	107.25±0.07	71.03
K^+	11±0.1	< BL	36.4±0.92	12.82±0.00		30.22±2.99	na	19.07±0.10	8.70
Ca^{2+}	27±0.5	< BL	31.5±1.5	120±0.25		18.33±2.89	27.24±1.79	30.52±0.52	29.08
Mg^{2+}	18±0.7	2.03	29.6±0.6	15.23±0.01		8.44±2.93	18.37±1.08	16.67±.06	15.40
NH_4^+	37±0.7	na	57.4±1.25	44.13±0.18		40±0.00	na	58.07±0.19	47.40

Summary of the analytical results by NIAs for the low conc. sample (M32)

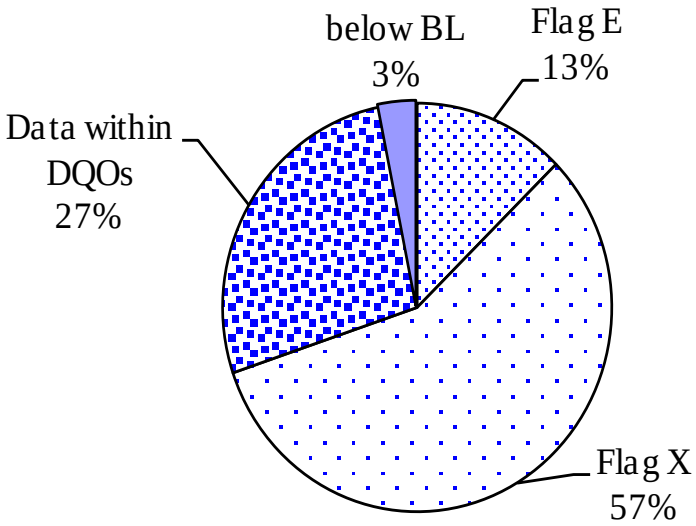
Parameter (μmol/L)	NIA laboratory								Prepared
	Lab no.1	Lab no.2	Lab no.3	Lab no.4	Lab no.5	Lab no.6	Lab no.7	Lab no.8	
pH	5.76±0.4	5.97	5.44±0.02	7.63±0.01		6.29±0.19	6.03±0.05	5.17±.01	5.69
EC (mS/m)	0.76±0.3	0.92	0.667±0.002	2.18±0.001		0.31±0.01	0.67±0.015	0.6±0	0.62
SO_4^{2-}	11±1	na	8.09±0.21	34.14±0.31		3.4±1.9	2.91±0.38	10.29±0.03	9.68
NO_3^-	7±1	na	2.17±0.13	0.07±0		14.43±3.73	1.95±0.15	4.12±0.09	3.20
Cl^-	24±5	na	56.42±0	56.04±0		16.43±4.06	8.10±0.13	14.33±0.12	16.05
Na^+	12±0.7	0.12	15.94±0.5	4.35±0	na	46.37±9.13	na	6.23±0,19	5.54
K^+	4±0.5	< BL	7±0.15	8.55±1.48		14.68±2.99	na	4.94±0.04	3.20
Ca^{2+}	3.5±0.5	< BL	16±1.2	40.13±0.34		8.33±2.89	2.85±0.10	5.22±0.13	5.25
Mg^{2+}	6±0.3	0.49	14.6±0.7	3.89±0.01		3.37±2.92	2.42±0.49	5.27±0.01	5.05
NH_4^+	7±0.7	na	8.32±0.18	2.7±0.16		13.33±5.77	na	11.73±0.06	9.26

Data quality: flag data points

M31 (high conc.)



M32 (low conc.)



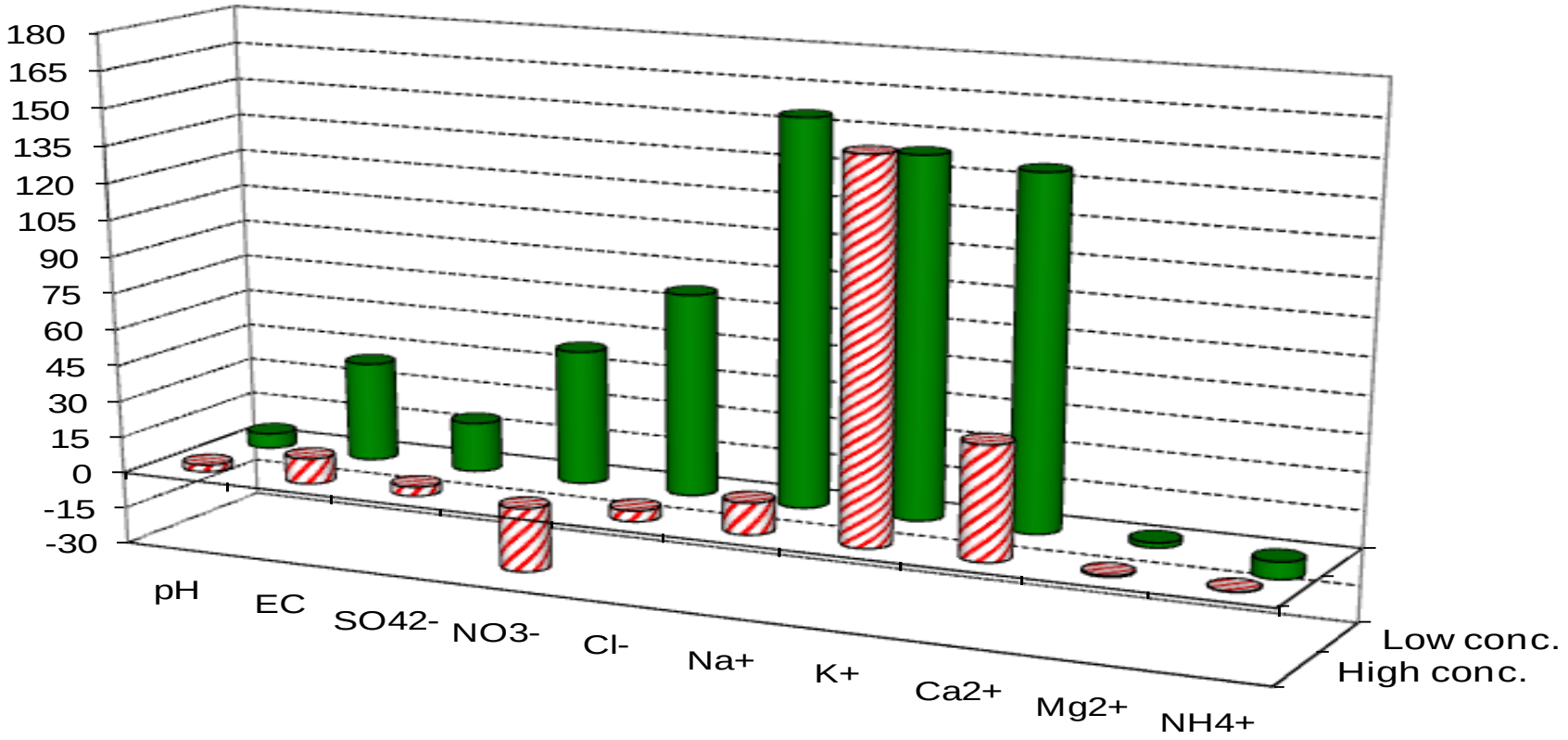
Data quality for different parameters and staff experience

Country	Total staff	Year of experience	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Bangladesh	2	~5 year										
Bhutan	2	~7 years			NA	NA	NA		high BL	high BL		NA
India	3	>11 years										
Iran	2	>8 years										
Maldives			NA		NA	NA	NA	NA	NA	NA	NA	NA
Nepal	1	7 years										
Pakistan	1	> 11 years						NA	NA			NA
Sri-Lanka	2	> 8 years										

Dark mesh: flagged (E or X) in sample No.M31 or sample M32.
Red colored: flagged (E or X) data of both sample.M31 and.M32
NA: No data (not analyzed)

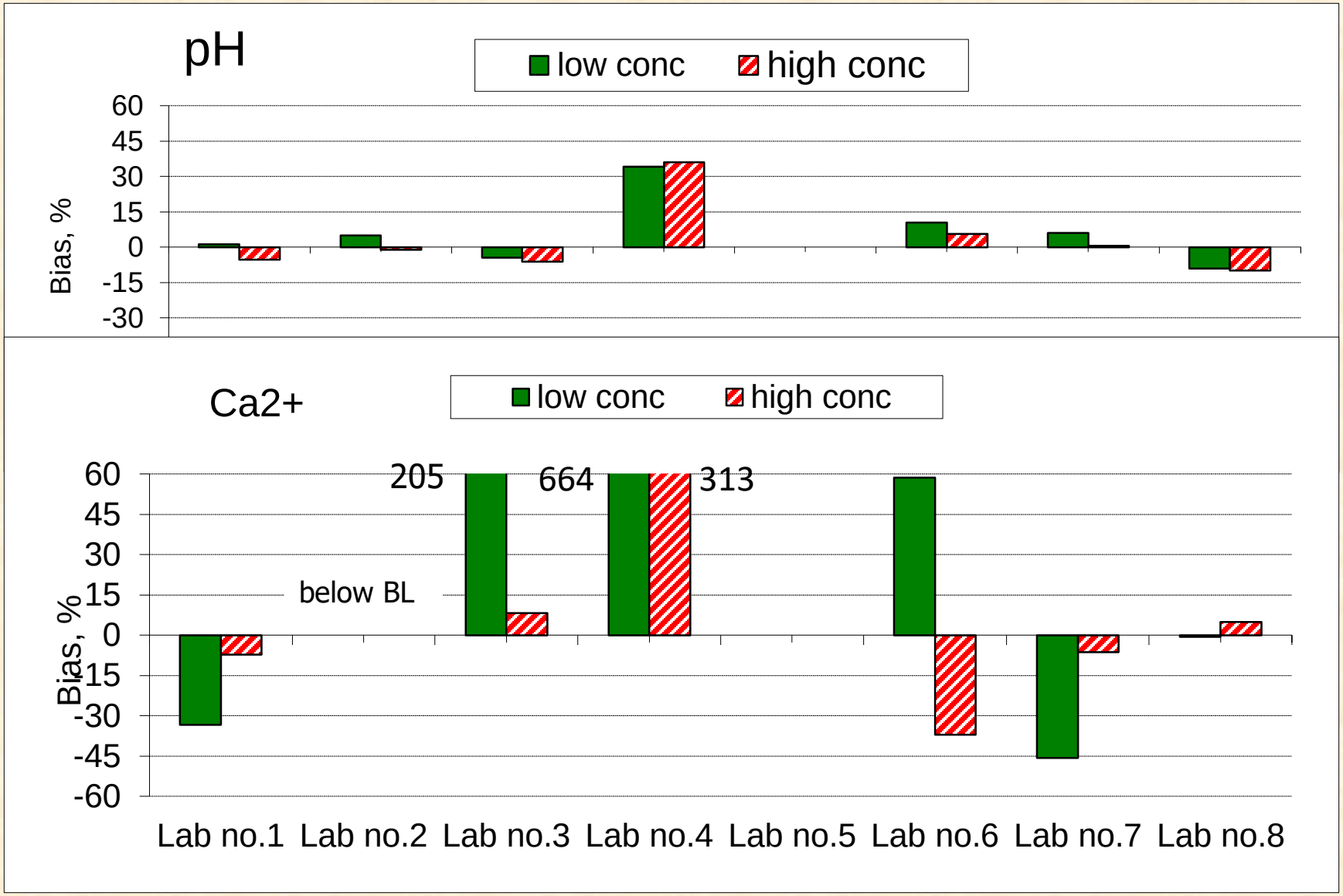
Relative deviation between average submitted data and prepared value

High conc: M31; Low conc.: M32



[ΔV = Average (Va) – Prepared (Vp)]

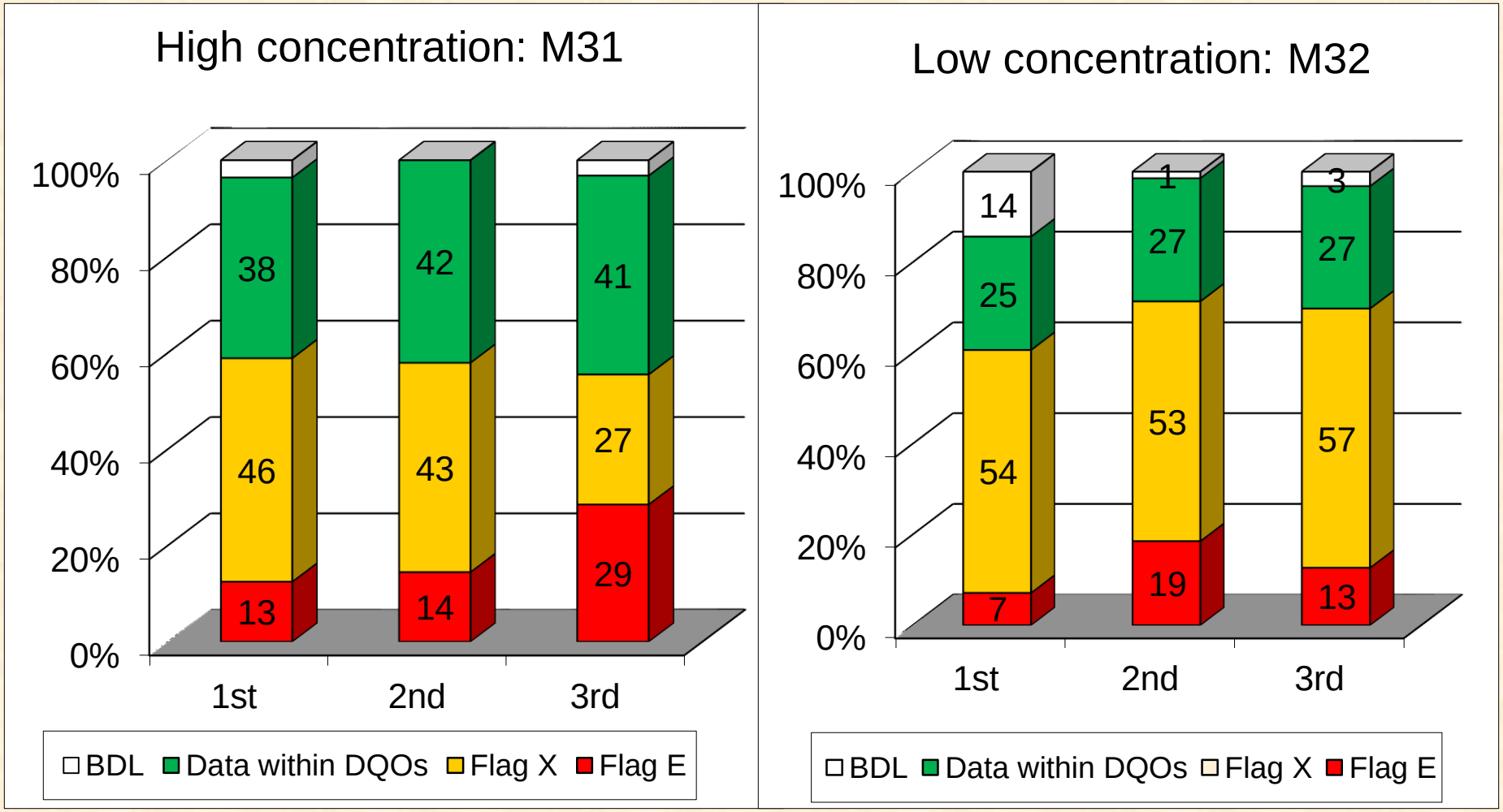
Bias by different labs for pH (low bias) and Ca^{2+} (high bias)



Parameter-wise analysis

- pH, EC, SO_4^{2-}, NH_4^+ results are relatively more accurate with lower bias
- Low conc. sample: high bias of Na^+, K^+, Ca^{2+}
- Average bias was <150% for all parameters but the ranges are wide
- One lab did not report data
- Some labs have results with high bias for many parameters

Comparison between 1st, 2nd, 3rd attempts



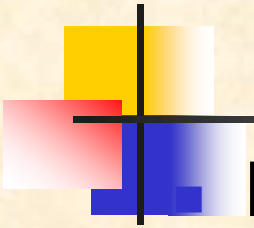
Summary remarks

- Strong bias for most of parameters, especially for low conc. sample M32
- Large number of non-reported data (63/80)
- Results for parameters requiring less sample treatment are more accurate (pH, EC)
- Intensive treatment of samples may introduce errors from dosing and glassware contamination and the impurity of chemicals/reagents used for the treatment
- More advanced equipment (IC) would readily allow NIA labs to repeat analyses to check the precision
- Only 5 NIAs have enough results for R1 and R2 calculation, only one NIA calculated R1 and R2 values

General recommendations for improvement

- Strictly follow the Malé QA/QC Monitoring Protocol
- SOPs must be prepared and adopted by NIAs for the management of apparatus, reagents, and procedure of operation
- Consider using methods requiring less sample treatment
- Repeated analyses to evaluate the precision (~3 times)

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, and data quality check
- Commitment to produce good data quality, e.g. request the staff to strictly follow SOPs
- A log book should be kept for the sampling and analysis in each NIA laboratory

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 (SRM) to evaluate the measurement methods periodically (~ once/year)
- 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 lab.: discard obvious erroneous data, calculate precision, calculate R1 and R2, etc.

Wrong data provide wrong information and it is a big waste of resources!

Thank you!