

Malé Declaration

**on Control and Prevention of Air Pollution
and its Likely Transboundary Effect for South Asia**



Report of the Inter – Laboratory Comparison of Precipitation Chemistry Analyses among the NIAs of the Malé Declaration

Third attempt Jul. 2011

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National Implementation Agency and National Focal Point

Bangladesh

NFP: Ministry of Environment and Forest

NIA: Department of Environment Dhaka

Bhutan

NFP and NIA: National Environment Commission

India

NFP: Ministry of Environment and Forests

NIA: Central Pollution Control Board, New Delhi

Iran

NFP and NIA: Department of the Environment, Tehran

Maldives

NFP: Ministry of Environment, Energy and Water

NIA: Department of Meteorology

Nepal

NFP: Ministry of Environment Science and Technology

NIA: International Centre for Integrated Mountain Development(ICIMOD) Kathmandu

Pakistan

NFP: Ministry of Environment

NIA: Pakistan Environment Protection Agency, Islamabad

Sri Lanka

NFP: Ministry of Environment and Natural Resources

NIA: Central Environmental Authority, Colombo

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1. INTRODUCTION

Malé Declaration on Control and Prevention of Air Pollution and Its Likely Trans-boundary Effects for South Asia (Malé Declaration) is an intergovernmental agreement to tackle the issue of transboundary air pollution through regional cooperation in South Asia since 1998. Participating countries are Bangladesh, Bhutan, Iran, India, Maldives, Nepal, Pakistan and Sri Lanka with a National Implementing Agency (NIA) established in each country.

The main objective of the Malé Declaration Programme is to promote the establishment of a scientific base for prevention and control of air pollution in South Asia to encourage and facilitate coordinated interventions of all the stakeholders on transboundary and shared air pollution problems at national and regional levels. One monitoring site was established in each participating country and the monitoring network is being implemented based on the common methodologies and standards. The inter-laboratory comparison is a required quality assurance (QA) measure to ensure the harmonization and quality of the data. This inter-laboratory exercises have been practiced by other regional monitoring networks such as Acid Deposition Monitoring Network in East Asia (EANET) for rain water samples or Air Pollution Regional Research Network (AIRPET) for particle composition samples.

This is the third attempt of the inter-laboratory comparison project which involves a round-robin analysis of uniformly prepared artificial rainwater samples by the NIA laboratories of the Malé Declaration project. The overall objective of the inter-laboratory comparison is to recognize the analytical precision and accuracy of the data in each participating NIA laboratory and consequently to provide an opportunity to improve data reliability/quality. The protocol highlighting the methodology of this inter-laboratory comparison has been developed based on Quality Assurance/Quality Control (QA/QC) procedure for Malé Declaration network with reference to the inter-laboratory comparison reports of the EANET project. The sample preparation, distribution and analysis with necessary QA/QC are included in the protocol which was circulated and agreed upon by all NIAs in September 2007, i.e. before the inter-laboratory exercise started.

Artificial rainwater samples contained major ions, were prepared and distributed to NIAs by the reference laboratory at the Asian Institute of Technology (AIT) in July 2011. Seven among eight participating laboratories submitted the analytical data to AIT in time. Obtained data for pH, EC and concentrations of SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} from these 7 laboratories were compared with the prepared values and statistically treated. List of the participating laboratories, individual analytical data, and various statistical parameters are included in this report.

2. INTER – COMPARISON PROCEDURE

2.1 *Participating laboratories*

Seven laboratories of the eight countries of the Malé Declaration Programme (one laboratory per NIA) have participated in this inter-laboratory comparison exercise. The name and the contact addresses of the participating laboratories are included in Appendix 1.

2.2 *Artificial rainwater samples*

Two concentration levels were prepared at the AIT laboratory: the higher concentration sample (No. M31) and the lower concentration sample (No.M32). The ranges of the ten (10) parameters specified in QA/QC of the Malé Declaration including pH, electrical conductivity (EC) and concentrations of ionic species (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}) are presented in Table 1. The broad ranges of each parameter in the prepared samples (Table 1) were informed to NIAs at the time of the sample

distribution. Summary information on the prepared artificial samples is presented in Table 2. These ranges as well as the actual concentration levels for each sample were selected based on the frequency distribution of each parameter obtained from the available data on actual rainwater samples of Malé Declaration Programme that NIA participating laboratories had submitted to the UNEP RRC.AP office.

Table 1 Concentration Ranges in the 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

2.3 Analytical parameters and methods

Participating laboratories were expected to use the analytical methods specified in the “Technical Document for Wet and Dry Deposition Monitoring for Malé Declaration” and closely followed the “Quality Assurance/Quality Control (QA/QC) Programme for Wet and Dry Deposition Monitoring for Malé Declaration” protocol which is summarized in Table 2.

If NIA uses other methods (than the methods specified by the Malé Protocol) for the routine analysis of rainwater samples and if the practice has already been approved by the UNEP RRC.AP then the NIA should use these methods for the artificial rainwater samples.

Thus, the NIA analyzed the artificial rainwater samples following the routine methods they use to get the data that they report to the Malé network. In addition, the NIA were also encouraged to run and report results by other methods if relevant. It was recommended that NIA do at least 3 runs for each parameter and reported the average concentration value and one standard deviation (Average ± STD).

To ensure the accuracy and precision of the data and for proper assessment of the operation conditions, the persons, who were responsible for analyzing wet deposition samples at the NIA, were also required to analyze these artificial rainwater samples of inter-laboratory comparison. An excel data template was provided to the NIA for the data reporting.

Table 2 Analytical methods specified in the Technical Documents for Wet and Dry Deposition monitoring for Malé Declaration

Parameter	Analytical/Instrument method
pH	Glass electrode
Electrical Conductivity	Conductivity Cell
Chloride	Argentometric method
Nitrate	Cadmium reduction method-Spectrophotometry
Sulphate	Spectrophotometry
Sodium	Flame photometry
Potassium	Flame photometry
Calcium	Titrimetry (EDTA method)
Magnesium	Titrimetry
Ammonium	Spectrophotometry (Indophenol)*

*- no biocide of *Thymol* is expected in the prepared samples hence the method can be used
Sources: QA/QC program for wet and dry deposition monitoring for Malé Declaration

2.4 Analytical data checking procedure

The analytical results by NIAs were checked and assessed by AIT using the procedures specified in the “Technical Document for Wet and Dry Deposition Monitoring for Malé Declaration” and closely follow the “Quality Assurance/Quality Control (QA/QC) Programme for Wet and Dry Deposition Monitoring for Malé Declaration” protocol. Thus, the criteria for ion balance (R_1) and for agreement between calculated and measured electrical conductivity (R_2) were used.

The allowable ranges of R_1 and R_2 , according to the Malé QA/QC protocol, are given in Table 3 and 4, respectively. Detailed methods of the calculation of R_1 and R_2 for the high and low artificial rainwater samples are presented in Appendix 2. It is noted that, however, only 5 NIA laboratories submitted the results of all 10 required analytical parameters thus it was possible to calculate these 2 criteria only for these 5 sets of the results.

Table 3 Allowable ranges for R₁ in different concentration ranges

Ceq + Aeq (µeq/L)	R ₁ (%)
<50	±30
50-100	±15
>100	±8

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

Table 4 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 Malé Declaration

2.5 Distributing the artificial samples to NIAs laboratories

The artificial rainwater samples were stored in the 1L polypropylene bottle. Each bottle contains 800 mL of a sample (M31 or M32). Two bottles containing the samples were placed in an ice box with dry ice and sent to the member laboratories through express post (DHL). The samples were departed from AIT on July 13, 2011 to all 8 laboratories. Five among 8 laboratories received the samples within one week others were within two to three weeks. All the Labs reported that samples were delivered in good condition.

It is noted that all the NIAs were requested to analyze the samples within a week after arrival (Protocol for inter-laboratory comparison of precipitation chemistry analyses within the Malé declaration, 2007). Most NIAs analyzed the samples within 2 weeks, except Lab no.4 (Mg²⁺, Ca²⁺) and Lab no.6 where samples were analyzed about 2 months after received. Dates of the events including the sample sending and receiving are included in Appendix 3. Based on the follow-up analysis at AIT during the first attempt, alteration of the concentrations in the samples during the storage and shipment period of 2-3 weeks should not be the main cause of large biases.

Table 5 Outline of artificial rainwater samples

Sample name	Amount of sample	Container	Number of samples	Note
No.M31 (high concentration) No.M32 (low concentration)	~ 800 mL/bottle	Poly-propylene bottle, 1000 mL	1 bottle for each level	Known amount of reagents dissolved in deionized water

3. RESULTS

AIT shipped the artificial rainwater samples to all 8 NIA laboratories of the Malé Declaration Programme and received analytical data reports from 7 out of 8 NIA Labs. The received data are summarized in Table 6 and 7. Note that only 5 NIA laboratories analyzed for all 10 parameters specified in the Malé monitoring protocol. All seven NIAs reported pH and EC data. Beside pH and EC, Lab no.2 measured only four cations Na^+ , K^+ , Ca^{2+} and Mg^{2+} while Lab no.7 did not analyze three cations (e.g. missing data of Na^+ , K^+ and NH_4^+). Lab no.2 did not report the data in the specified units for EC. Only one Lab no.6 reported R1 and R2 values.

According to the Malé Inter-laboratory Comparison Protocol the NIAs would analyze each sample 3 times for all parameters and report results in the provided data template. However, not all NIAs followed this requirement. For those NIAs that reported results of all 3 analyses for each parameter in a sample the standard deviation of the data was calculated and presented in Table 6 and 7. For Lab no.2 that did not report the repeated analysis results, only single values are presented.

Table 6 Summary of the analytical results of the high concentration artificial rainwater sample (M31) by NIAs as compared to the prepared levels

Parameter	NIA laboratories								Prepared levels
	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	5.067±0.0115	5.63
EC (mS/m)	2.96±0.3	3.21	2,96±0.01	3.50±0.001		3.77±0,07	2.973±0.032	2.9±0	2.88
SO ₄ ²⁻ (µmol/L)	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 ⁻ (µmol/L)	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 ⁻ (µmol/L)	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 ⁺ (µmol/L)	81±1.2	5.49	87.8±1.50	68.11±2.51		131.22±8.22	na	107.25±0.07	71.03
K ⁺ (µmol/L)	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⁺ (µmol/L)	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⁺ (µmol/L)	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 ⁺ (µmol/L)	37±0.7	na	57.4±1.25	44.13±0.18		40±0.00	na	58.07±0.19	47.40

na: data not available (not analyzed)

BL: Blank

Table 7 Summary of the analytical results of the low concentration artificial rainwater sample (M32) by NIAs as compared to the prepared concentrations

Parameter	NIA laboratory								Prepared levels
	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	na	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	2.184±0.001		0.31±0.01	0.667±0.015	0.6±0	0.62
SO ₄ ²⁻ (µmol/L)	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 ⁻ (µmol/L)	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 ⁻ (µmol/L)	24±5	na	56.42±0	56.04±0		16.43±4.06	8.10±0.13	14.33±0.12	16.05
Na ⁺ (µmol/L)	12±0.7	0.12	15.94±0.5	4.35±0		46.37±9.13	na	6.23±0.19	5.54
K ⁺ (µmol/L)	4±0.5	< BL	7±0.15	8.55±1.48		14.68±2.99	na	4.94±0.04	3.20
Ca ²⁺ (µmol/L)	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⁺ (µmol/L)	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 ⁺ (µmol/L)	7±0.7	na	8.32±0.18	2.7±0.16		13.33±5.77	na	11.73±0.06	9.26

na: data not available(not analyzed)

BL: Blank (<BL can be regarded as not detected)

The statistics were calculated for the obtained data of each parameter such as Average, Minimum (Min.), Maximum (Max.), Standard deviation (S.D.), and Number of data (N) and are presented in Table 8. The relative deviations between the average NIA results for each parameter against the prepared value [$\Delta V/V_p$] are also shown in Table 8. The averages of the submitted data differ from the prepared concentrations, for the low concentration sample (No.M32), within a range of a few percents (~2% for Mg^{2+}) to above 140-156% (Ca^{2+} , K^+ , Na^+). For the high concentration sample (No.M31) the relative deviations are relative smaller, ranging from below 5% (for pH, SO_4^{2-} , Cl^- , Mg^{2+} , NH_4^+) to a maximum of 152% (K^+). Note that no outlier treatment was applied for this small data set and all the received data were included in the analysis.

Table 8 Statistics of the NIA analytical results for the artificial rainwater samples

Parameter	Average (Va)	S.D	N	Min	Max	Prepared (Vp)	$\Delta V/V_p$ (%)
Sample No.M31 (high concentration)							
pH	5.79	0.87	7	5.07	7.66	5.79	2.84
EC (mS/m)	3.18	0.33	7	2.90	3.77	3.18	10.47
SO_4^{2-} ($\mu\text{mol/L}$)	40.6	8.5	6	32.4	50.6	40.60	3.7
NO_3^- ($\mu\text{mol/L}$)	28.7	10.9	6	7.7	40.0	28.70	-26.3
Cl^- ($\mu\text{mol/L}$)	103.4	42.4	6	56.0	178.7	103.40	4.4
Na^+ ($\mu\text{mol/L}$)	80.1	42.7	6	5.5	131.2	80.10	12.8
K^+ ($\mu\text{mol/L}$)	21.9	11.1	6	11.0	36.4	21.90	151.6
Ca^{2+} ($\mu\text{mol/L}$)	42.4	38.3	7	18.3	120.0	42.40	45.9
Mg^{2+} ($\mu\text{mol/L}$)	15.5	8.6	7	2.0	29.6	15.50	0.5
NH_4^+ ($\mu\text{mol/L}$)	47.3	9.8	5	37.0	58.1	47.30	-0.2
Sample No.M32 (low concentration)							
pH	6.04	0.79	7	5.17	7.63	6.04	6.18
EC (mS/m)	0.87	0.61	7	0.31	2.18	0.87	40.74
SO_4^{2-} ($\mu\text{mol/L}$)	11.6	11.5	6	2.9	34.1	11.60	20.2
NO_3^- ($\mu\text{mol/L}$)	5.0	5.2	6	0.1	14.4	5.00	54.7
Cl^- ($\mu\text{mol/L}$)	29.2	21.5	6	8.1	56.4	29.20	82.1
Na^+ ($\mu\text{mol/L}$)	14.2	16.7	6	0.1	46.4	14.20	155.6
K^+ ($\mu\text{mol/L}$)	7.8	4.2	6	4.0	14.7	7.80	144.4
Ca^{2+} ($\mu\text{mol/L}$)	12.7	14.3	7	2.9	40.1	12.70	141.3
Mg^{2+} ($\mu\text{mol/L}$)	5.1	4.5	7	0.5	14.6	5.10	2.0
NH_4^+ ($\mu\text{mol/L}$)	8.6	4.2	5	2.7	13.3	8.60	-7.0

Note: $\Delta V = \text{Average (Va)} - \text{Prepared (Vp)}$

The data obtained from NIAs were evaluated against the Data Quality Objectives (DQOs) of the QA/QC for Malé Declaration Monitoring program, namely for every parameter the measured value should be within $\pm 15\%$ of deviation from the prepared value. The bias (a measure of accuracy) of the data was calculated for analytical results of each parameter of the artificial rainwater samples as below:

$$\text{Bias (\%)} = 100 \times (\text{Analytical value} - \text{Prepared value}) / (\text{Prepared value})$$

Flag "E" was put to the data that exceed DQOs by a factor of 2, i.e between $\pm 15\%$ and $\pm 30\%$.

Flag "X" was put to the data that exceed DQOs more than a factor of 2, i.e. beyond $\pm 30\%$.

The results were evaluated from three aspects:

- i) Sample-wise comparison to gain the concentration dependence assessment: separate analysis for sample No.M31 (higher concentrations) and No.M32 (lower concentrations) and compare the results
- ii) Parameter-wise comparison to assess the data quality for individual parameters, and
- iii) Comparison of circumstances of analysis in each participating laboratory.

Evaluation for each sample is presented in “3.1 Sample-wise comparison”, evaluation for each parameter is presented in “3.2 Parameter-wise comparison” and evaluation of the data against the circumstances in the analytical laboratories such as analytical methods used, number and experiences of the personnel, and other analytical conditions are presented in “3.3 Circumstances of sample analysis”.

3.1 Sample-wise comparison

Sample No.M31 (higher concentrations)

Table 9 presents the evaluation of NIA results for sample No.M31 (higher concentrations), which shows 17 non-reported data points accounting for 21% of total commitment data (10 parameters/NIA x 8 NIA = 80 data points). The non-reported data points were assigned as 999. There were 18 analytical data points out of reported 63 exceeded the DQOs by a factor of ≤ 2 and were flagged by "E". There were 17 analytical data points out of 63 exceeded the DQOs by more than a factor of 2 and were flagged by "X". The total flagged data account for 56% of reported analytical data for this sample, in which flagged "E" and "X" accounted for 29% and 27%, respectively. Two (2) measured data points that were below blank levels were also flagged (Figure 1).

Table 9 Numbers of flagged data for the Sample No.M31 (higher concentrations)

	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
Total available data points	7	7	6	6	6	6	6	7	7	5	63
999 (non-reported data), points	1	1	2	2	2	2	2	1	1	3	17
999 (non-reported data), %	13	13	25	25	25	25	25	13	13	38	21
Flag data (against the number reported data points)											
<i>Flag E</i>	0	1	4	3	2	1	1	0	2	4	18
<i>Flag X</i>	1	1	0	1	2	3	4	2	3	0	17
<i>Below BL</i>							1	1			2
Total flag data (E+X), points	1	2	4	4	4	4	5	2	5	4	35
Flagged data (E+X), %	14	29	67	67	67	67	83	29	71	80	56
Data within the DQOs (against the number of reported data points)											
Data within DQOs, points	6	5	2	2	2	2	0	4	2	1	28
Data within DQOs, %	86	71	33	33	33	33	0	57	29	20	41

Total available data: 63 (including the below blank data)

BL: blank

E: value exceeds the DQO ($\pm 15\%$) by a factor of ≤ 2

X: value exceed the DQO ($\pm 15\%$) more than a factor of 2

Table 10 Analytical results of sample No.M31 (higher concentrations)

	pH	EC (mS/m)	SO ₄ ²⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)	Cl ⁻ (μmol/L)	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	NH ₄ ⁺ (μmol/L)	R1	R2
Lab no.1	5.33	2.96	49 E	30 E	116 E	81	11 E	27	18 E	37 E		
Lab no.2	5.57	3.21	na	na	na	5.49 X	<BL	<BL	2.03 X	na	-	-
Lab no.3	5.29	2.96	32.78 E	33.5	178.7 X	87.8 E	36.4 X	31.5	29.6 X	57.4 E		
Lab no.4	7.66 X	3.5 E	50.63 E	7.7 X	56.04 X	68.11	12.82 X	120 X	15.23	44.13	I	
Lab no.5	na											
Lab no.6	5.95	3.77 X	32.44 E	30.56 E	89.17	131.22 X	30.22 X	18.33 X	8.44 X	40 E	I	C
Lab no.7	5.66	2.97	33.83	30.2 E	76.8 E	na	na	27.24	18.37 E	na	-	-
Lab no.8	5.07	2.9	44.71	40.01	103.59	107.25 X	19.07 X	30.52	16.67	58.07 E	I	

E: value exceeds the DQO ($\pm 15\%$) by a factor of ≤ 2

X: value exceed the DQO ($\pm 15\%$) more than a factor of 2

na: not available (not analyzed)

I: poor ion balance agreement

C: poor electrical conductivity agreement

(-) not enough data to calculate R₁ and R₂

Among 10 measured parameters, pH data had the least flagged data points, i.e. 14%. Most of the others were flagged E or X (29 to 80%). All data points for K^+ were flagged including those flags for data points below BL. The evaluation against the criteria for ion balance (R_1) and electrical conductivity (R_2) was possible only for the data from 5 laboratories (Lab no.1, Lab no.3, Lab no.4, Lab no.6 and Lab no.8) which reported the full composition data sets with 10 parameters. Lab no.6 has both poor “electrical conductivity agreement” and “ion balance”. Only Lab no.1 and Lab no.3 have both R_1 and R_2 within the recommended ranges though many data points of these laboratories were flagged. Thus, due to overall low data quality, meeting the R_1 and R_2 criteria would not guarantee for the good analytical data due to the possible compensation effects of the errors.

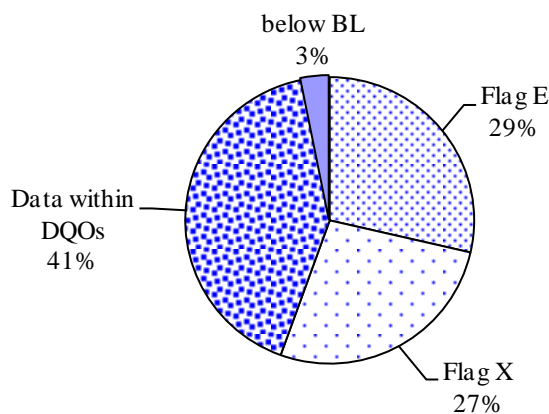


Fig.1 Percentage of data meeting DQOs and flagged data for Sample No.M31 (higher concentrations)

Sample M32 (lower concentrations)

Table 11 presents the evaluation of NIA results for sample No.M32 (lower concentrations), which shows 17 non-reported data points accounting for 21% of total 80 committed data points. These non-reported data points were assigned to as 999. There were 8 analytical data points out of 63 exceeded the DQOs by a factor of ≤ 2 and were flagged "E", 36 analytical data points exceeded the DQOs by more than a factor of 2 and were flagged "X". Two (2) data points reported below blank were also flagged. Total flagged data account for 70% of analytical data points for this sample, in which E and X flag accounted for 13% and 57%, respectively (Figure 2).

As presented in Tables 12, measured pH had less flagged data points (14%). Above 68% of analytical results of every ion were flagged and 100% of NO_3^- and K^+ (including the flags for the below blank data points) results were flagged. The evaluation against the criteria for ion balance (R_1) and electrical conductivity (R_2) was possible only for the data from 5 laboratories (Lab no.1, Lab no.3, Lab no.4, Lab no.6 and Lab no.8). Most of NIAs had poor agreement for both electrical conductivity and ion balance except for Lab no.1 and Lab no.8 which had the R_1 within the DQOs although most of its reported data were flagged. Similarly to the discussion for sample M31 presented above, meeting the R_1 and R_2 criteria would not guarantee for the good analytical data.

Table 11 Numbers of flagged data for the Sample No.M32 (lower concentrations)

	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
Total available data points	7	7	6	6	6	6	6	7	7	5	63
999 (non-reported data), points	1	1	2	2	2	2	2	1	1	3	17
999 (non-reported data), %	13	13	25	25	25	25	25	13	13	38	21
Flag data (against the number reported data points)											
<i>Flag E</i>	0	1	1	1	0	1	1	0	1	2	8
<i>Flag X</i>	1	3	3	5	4	4	4	5	5	2	36
<i>Below BL</i>							1	1			2
Total flag data (E+X), points	1	4	4	6	4	5	5	5	5	4	44
Flagged data (E+X), %	14	57	67	100	67	83	83	71	71	80	70
Data within the DQOs (against the number of reported data points)											
Data within DQOs, points	6	3	2	0	2	1	0	1	2	1	17
Data within DQOs, %	86	43	33	0	39	17	0	14	29	20	27

Total available data: 63 (including the below blank data)

BL: blank

E: value exceeds the DQO ($\pm 15\%$) by a factor of ≤ 2

X: value exceed the DQO ($\pm 15\%$) more than a factor of 2

Table 12 Analytical results of sample No.M32 (lower concentrations)

	pH	EC (mS/m)	SO ₄ ²⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)	Cl ⁻ (μmol/L)	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	NH ₄ ⁺ (μmol/L)	R1	R2
Lab no.1	5.8	0.8 E	11.0	7.0 X	24.0 X	12.0 X	4.0 E	3.5 X	6.0 X	7.0 E		
Lab no.2	6.0	0.9 X	na	na	na	0.1 X	< BL	< BL	0.5 X	na	-	-
Lab no.3	5.4	0.7	8.1 E	2.2 X	56.4 X	15.9 X	7.0 X	16.0 X	14.6 X	8.3	I	
Lab no.4	7.6 X	2.2 X	34.1 X	0.1 X	56.0 X	4.4 E	8.6 X	40.1 X	3.9 E	2.7 X	I	C
Lab no.5	na											
Lab no.6	6.3	0.3 X	3.4 X	14.4 X	16.4	46.4 X	14.7 X	8.3 X	3.4 X	13.3 X	I	C
Lab no.7	6.0	0.7	2.9 X	2.0 X	8.1 X	na	na	2.9 X	2.4 X	na	-	-
Lab no.8	5.2	0.6	10.3	4.1 E	14.3	6.2	4.9 X	5.2	5.3	11.7 E		

E: value exceeds the DQO (±15%) by a factor of ≤2

X: value exceed the DQO (±15%) more than a factor of 2

I: poor ion balance agreement

C: poor electrical conductivity agreement

(-) not enough data to calculate R₁ and R₂

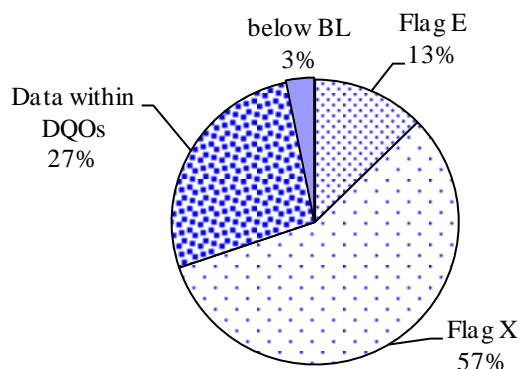


Fig.2 Percentage of data meeting DQOs and flagged data for Sample No.M32 (lower concentrations)

Summary remarks

There is a larger number of non-reported data in the third attempt as compared to second attempt (18-19 vs. 11) but lower than the first attempt (24 missing data points per sample). Overall, only pH, EC and Mg^{2+} were analyzed by all 7 NIA laboratories which submitted the results. The complete sets data of required 10 parameters, specified in the Malé declaration monitoring protocol, were submitted only by 5 NIA laboratories (Lab no.1, Lab no.3, Lab no.4, Lab no.6 and Lab no.8) which were used for the evaluation against the criteria R_1 and R_2 . Only one data set satisfied both R_1 and R_2 criteria for both samples (Lab no.1, M31 and M32). Lab no. 3 had both R_1 and R_2 criteria satisfied for sample M31 and also quite closely meet the criteria for sample M32. However, many data points reported by these laboratories were flagged. Thus, because of the overall low data quality, meeting the R_1 and R_2 criteria would not guarantee for the good analytical results due to the possible compensation errors. However, if these criteria are not satisfied then the overall data quality is questionable. Thus, checking these criteria would help the NIAs to quickly assess the overall data quality. Nevertheless, only 1 NIAs (lab no. 6) submitted R_1 and R_2 calculation results though these values are required in the protocol for all laboratories.

Overall, the percentages of flagged data points are high for both samples. The total data points satisfying the DQOs for sample M31 (higher concentrations) account for 41% which is higher than that (27%) for sample M32. Total number of flagged data by “E” as well as flagged data by “X” for sample M32 was higher than that for sample No.M31 (56 and 70%, respectively). It indicates the difficulty of the analysis of the lower concentration sample. One lab reported a value “below blank” (regarded as below the detection limit) for K^+ and Ca^{2+} in both samples which suggests the need for improvement the analysis method, specifically the preparation of the laboratory blanks used in this laboratory.

3.2 Parameter-wise evaluation

The results are analyzed and discussed for each analytical parameter separately as presented below.

1) pH

Most of the participating laboratories reported pH results. There is no consistency in reporting the equipment names thus it is assumed that the glass electrode was used as recommended by the Malé monitoring protocol (Table 13). The pH measurement was carried out at the temperature close to the recommended condition (~25°C) except for Lab no.2 which measured pH at 20.9°C and Lab no.6 at 17-18°C. Among all the parameters, pH data set has the smallest flagged data points. The relative deviation of the average submitted pH data as compared to the prepared was 3% for sample M31 and 6% for sample M32 (Table 8). Most of the data satisfied the DQOs of the Malé declaration QA/QC program (Fig.3). There was “X” flagged data points for pH by the Lab no.4. The different (lower measurement temperatures) by the Lab no.2 (at 20.9°C) and no.6 (at 17-18°C), as compared to the recommended, did not seem to affect on the final results which, however, this may also be caused by compensating errors. Lab no.4 reported pH value of 7.6 for both high and low concentration samples which are abnormally high (for acid rain samples, pH should be below 6.5). It is expected that this type of error should be noticed and double-checked, and the samples should be re-analyzed by NIA before sending the data for this inter-laboratory comparison exercise.

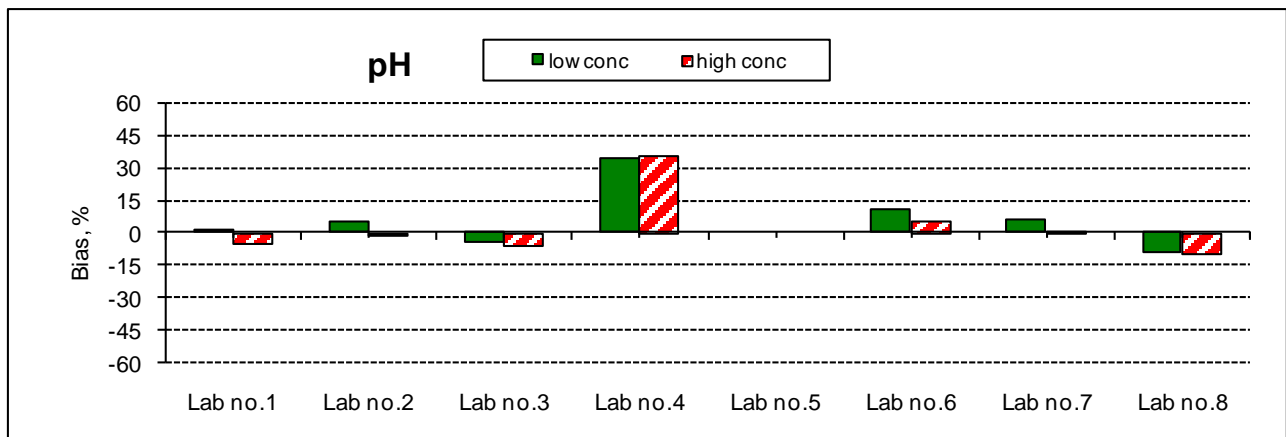


Fig.3 Distribution of pH data normalized by prepared value

Table 13 Analytical methods and flagged data of pH

Analytical methods	
pH meters (glass electrode)	7/8
Non-reported data	1/8

Flagged data	E	X	Flagged %
Sample No.M31	0	1	14
Sample No.M32	0	1	14

2) EC

All participating laboratories used conductivity meters to measure EC. There is inconsistency in reporting the equipment names. It is assumed that the conductivity cell was used as recommended by the Malé monitoring protocol (Table 14). The relative deviations of the average reported data and the prepared value were 41% and 10% for sample M32 and M31, respectively (Table 8). As presented in Fig.4, there were one “E” (Lab no.6) and one “X” (Lab no. 4) flagged data points for the EC values for the higher concentration sample (M31). For lower concentration sample (M32), there was one data flagged “E” (Lab no.1) and 3 data points flagged “X” (Lab no.2, Lab no.4 and Lab no.6). Most of laboratories carried out the EC measurement at the temperatures close to the recommended condition (~25°C) except for Lab no.2 which measured EC at 21°C. This may effect on the measured data for the lower concentration sample.

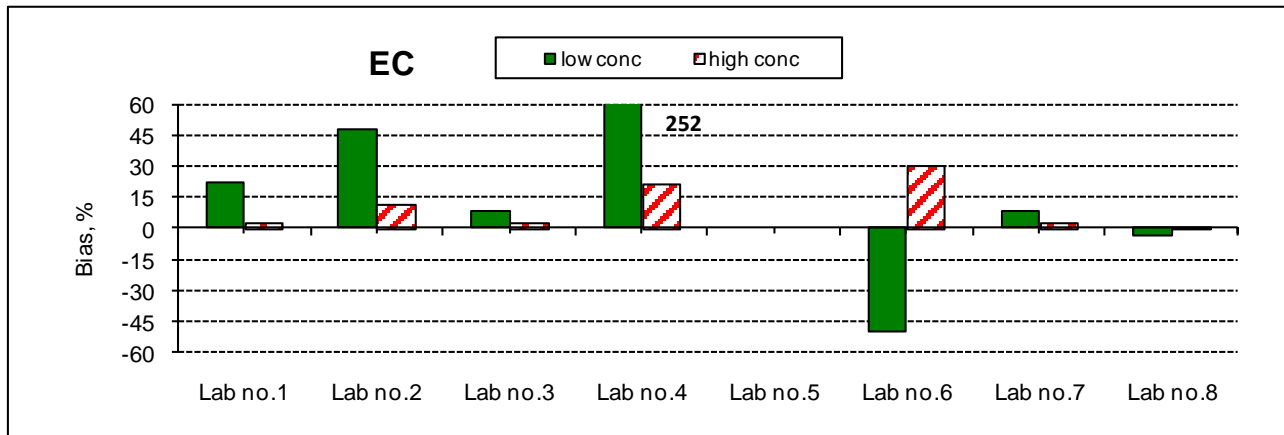


Fig.4 Distribution of EC data normalized by prepared value (off-scale values are indicated, %)

Table 14 Analytical methods and flagged data of EC

Analytical methods	
Conductivity Cell	7/8
Non-reported data	1/8

Flagged data	E	X	Flagged %
Sample No.M31	1	1	29
Sample No.M32	1	3	57

3) SO_4^{2-}

Six countries submitted SO_4^{2-} analytical data, five of them used spectrophotometry, one laboratory (Lab no.8) employed an ion chromatograph (IC) for the determination (Table 15).

There was no “X” flagged data but four flagged “E” for the higher concentration sample (M31, Fig.5) while it was 3 and 1, respectively, for the lower concentration sample (M32). A concentration below blank for both concentration samples by Lab no.2 was reported. However, the detection limit of the equipment and method (for $BaSO_4$ precipitation) were not reported. Two data points were within the DQOs for higher concentration sample (Lab no.7 and Lab no.8) and two data points for the lower concentration sample (Lab. no 1 and Lab no. 8). Though five laboratories used the spectrophotometry but the biases were different. Lab no.8, which used the ion chromatography, produced no flagged results for both samples M31 and M32. The largest bias was for Lab no. 2 results for the lower concentration sample (2.5 times higher than the prepared).

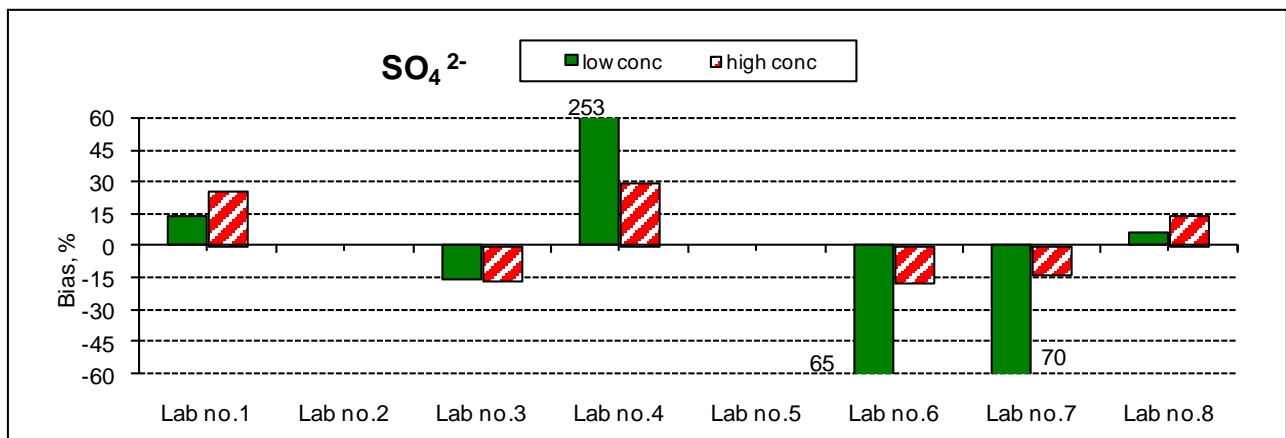


Fig.5 Distribution of SO_4^{2-} data normalized by prepared value (off-scale values are indicated, %)

Table 15 Analytical methods and flagged data of SO_4^{2-}

Analytical methods	
Spectrophotometry	5/8
Ion Chromatography	1/8
Non-reported data	2/8

Flagged data	E	X	Flagged %
Sample No.M31	4	0	57
Sample No.M32	1	3	57

4) NO_3^-

Six countries submitted NO_3^- analytical data. Lab no.8 laboratory employed an IC whereas others used spectrophotometers for the determination of NO_3^- (Table 16).

Most data submitted by the six NIAs were flagged “E” or “X” for both high and low concentration samples. Only 2 data points were within the DQOs for Lab no.3 and Lab no.8 for M32 (Fig.6). The data produced by Lab no.8 using IC also appear to be less biased for the lower concentration sample (M32).

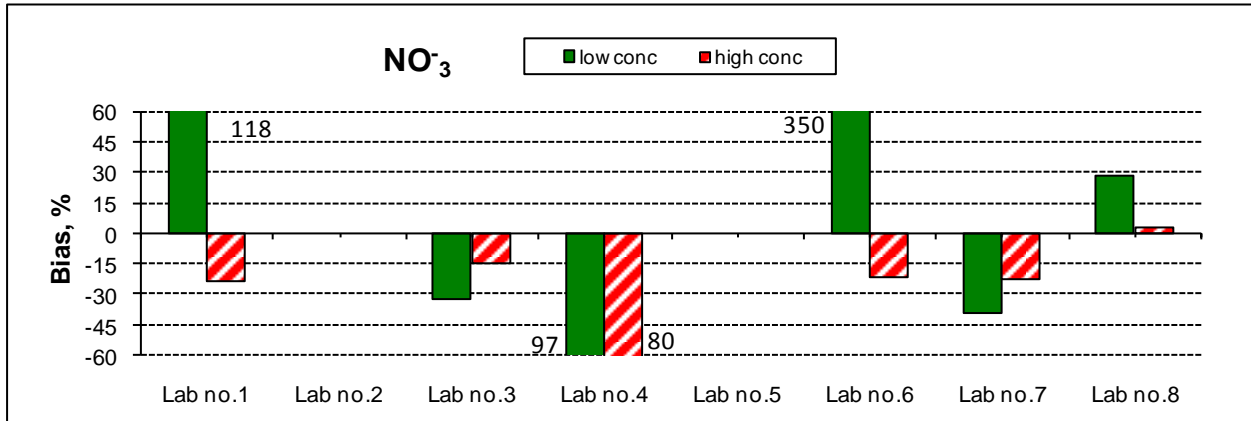


Fig.6 Distribution of NO_3^- data normalized by prepared value (off-scale values are indicated)

Table 16 Analytical methods and flagged data of NO_3^-

Analytical methods	
Spectrophotometry	5/8
Ion Chromatography	1/8
Non-reported data	2/8

Flagged data	E	X	Flagged %
Sample No.M31	3	1	67
Sample No.M32	1	5	100

5) Cl^-

Among six NIAs submitted Cl^- analytical data, only Lab no.8 employed an IC while others used the recommended Argentometric method by the Male’ protocol for the Cl^- determination (Table 17). Results for M31 and M32 reported by Lab no.6 and Lab no.8 were within DQOs (Fig.7). There were 2 data points flagged “E” and 2 flagged “X” for the higher concentration sample, while 4 data points flagged “X” flagged for the lower concentration sample. The bias for Cl^- was the largest by Lab no.3 and Lab no.4, around 2.5 times higher than the prepared concentration biases for the lower concentration sample (M32).

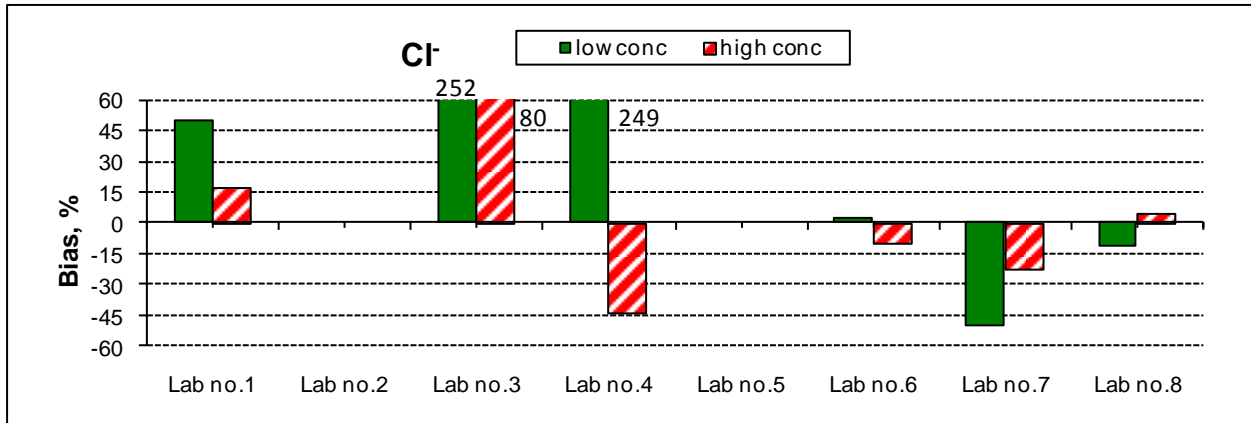


Fig.7 Distribution of Cl⁻ data normalized by prepared value (off-scale values are indicated, %)

Table 17 Analytical methods and flagged data of Cl⁻

Analytical methods	
Argentometric - Titrimetry	5/8
Ion Chromatography	1/8
Non-reported data	2/8

Flagged data	E	X	Flagged %
Sample No.M31	2	2	67
Sample No.M32	0	4	67

6) Na⁺

Among six laboratories submitted Na⁺ analytical results (Lab no.5 and 7 did not report the data). Lab no.1, 2 and 6 used Atomic Absorption Spectrophotometer (AAS), Lab no. 3 and 4 used the flame emission spectrometry while Lab no. 8 used IC (Table 18). Two reported data points by Lab no. 1 and 4 were within DQOs; one by Lab no.3 was flagged “E” and three by Lab no. 2, 6 and 8 were flagged “X” for the higher concentration sample (Fig.8). For the lower concentration sample, only one data by Lab no.8 was within DQOs, the other 5 data points were flagged “E” or “X”.

The bias for Cl⁻ was the most significant among all analyzed parameters and the largest biases were for results of Lab no.6, around 7 times higher than the prepared level in the lower concentration sample.

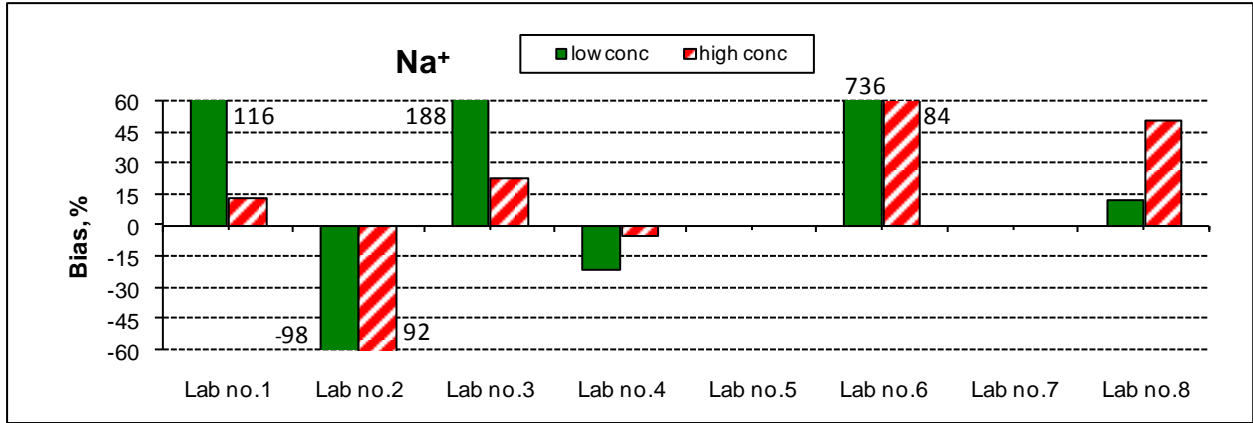


Fig.8 Distribution of Na⁺ data normalized by prepared value (off-scale values are indicated)

Table 18 Analytical methods and flagged data of Na⁺

Analytical methods	
Atomic absorption spectrophotometry	3/8
Flame emission spectrometry	2/8
Ion Chromatography	1/8
Non-reported data	2/8

Flagged data	E	X	Flagged %
Sample No.M31	1	3	67
Sample No.M32	1	4	83

7) K⁺

The number of NIA laboratories, the analytical methods and number of reported results for K⁺ were similar as for the Na⁺ analysis (Table 19). All of data points were flagged for both higher (M31) and lower (M32) concentration samples which did not depend on analytical instruments used (Fig.9). One result by Lab no. 2 was negative value and was considered as below blank concentration.

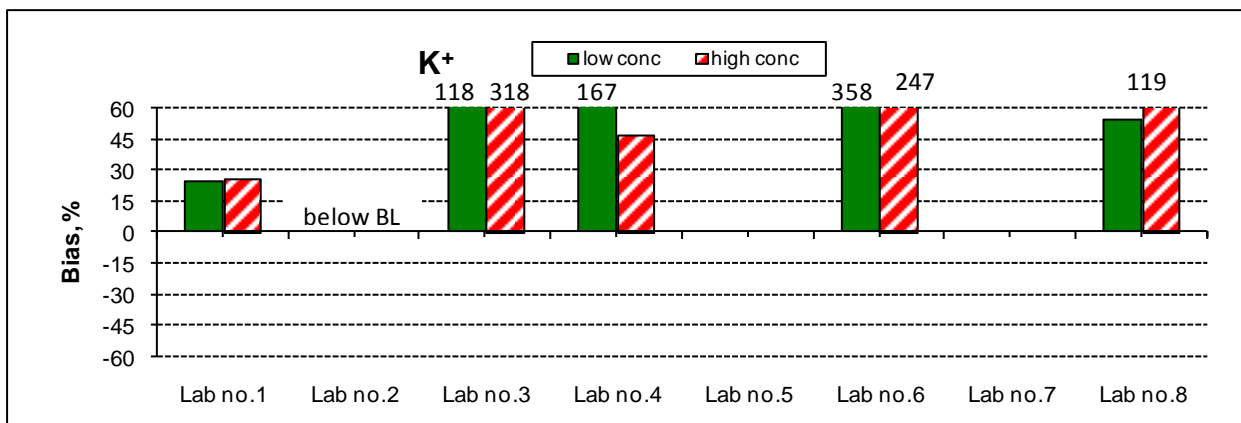


Fig.9 Distribution of K⁺ data normalized by prepared value (off-scale values are indicated, %)

Table 19 Analytical methods and flagged data of K⁺

Analytical methods	
Atomic absorption spectrophotometry	3/8
Flame emission spectrometry	2/8
Ion Chromatography	1/8
Non-reported data	2/8

Flagged data	E	X	< blank	Flagged %
Sample No.M31	1	4	1	100
Sample No.M32	1	4	1	100

*% flag includes below blank (negative) data points

8) Ca²⁺

Seven laboratories submitted the analytical data for Ca²⁺. Three laboratories (Lab no.3, 4 and 6) used the titrimetry method, two laboratories (Lab no.1 and 2) used AAS, Lab no. 7 used spectrophotometry and Lab no.8 used IC (Table 20).

Lab no. 1, 3, 7 and 8 used different analysis methods but obtained results were within DQOs for the higher concentration sample. Lab no. 4 and 6 used the same analysis method as Lab no. 3 but reported data flagged "X". Result for Lab no. 2, which used the same analysis method as Lab no. 1, was negative (below blank). Only data points by Lab no.8, where IC was used, were within DQOs, other data were flagged "X" for the lower concentration sample.

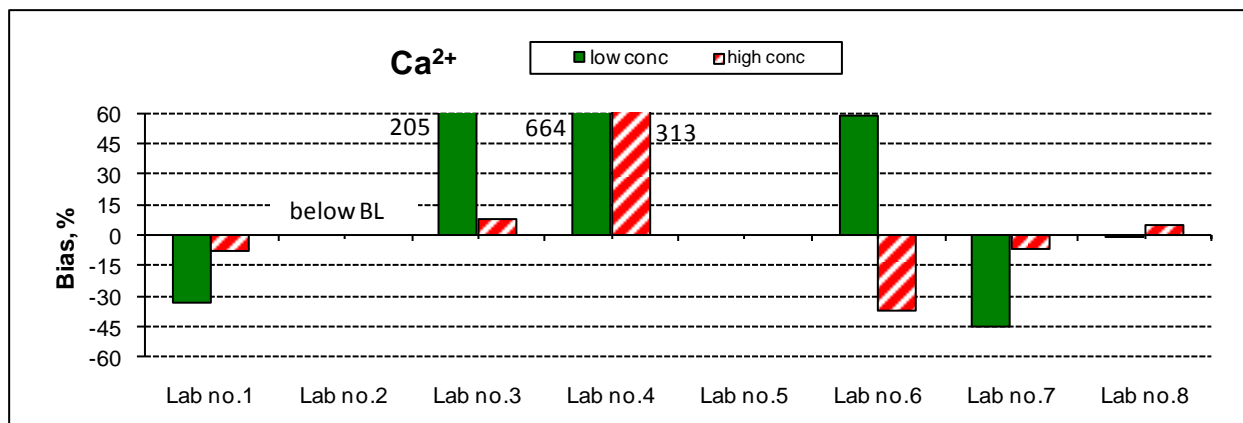


Fig.10 Distribution of Ca²⁺ data normalized by prepared value (off-scale values are indicated, %)

Table 20 Analytical methods and flagged data of Ca²⁺

Analytical method	
Titrimetry	3/8
Atomic Absorption Spectrophotometry	2/8
Spectrophotometry	1/8
Ion Chromatography	1/8
Non-reported data	1/8

Flagged data	E	X	< blank	Flagged %
Sample No.M31	0	2	1	43
Sample No.M32	0	5	1	86

**%flag includes below data*

9) Mg²⁺

The number of NIA laboratories, the analytical methods and number of reported results for Mg²⁺ were similar as for Ca²⁺ analysis (Table 21).

Six among seven data points for the lower concentration sample (M32) were flagged “X”, only data by the Lab no.8 was within DQOs. For the higher concentration sample, three data points for sample M31 were flagged “X”, two were flagged “E”, the results from lab no.4 and 8 was within DQOs (Fig.11). Again, the laboratories, which applied the same analytical method, produced different biases. Similar to the Ca²⁺ analysis, the laboratory used IC method was the one that showed the lowest bias of all.

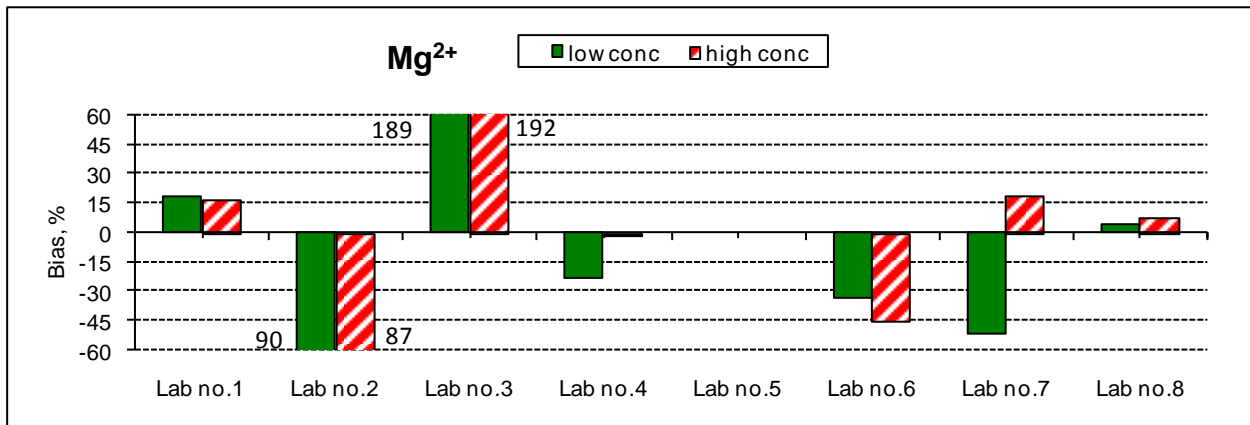


Fig.11 Distribution of Mg²⁺ data normalized by prepared value (off-scale values are indicated)

Table 21 Analytical methods and flagged data of Mg²⁺

Analytical method	
Titrimetry	3/8
Atomic Absorption Spectrophotometry	2/8
Spectrophotometry	1/8
Ion Chromatography	1/8
Non-reported data	1/8

Flagged data	E	X	Flagged %
Sample No.M31	2	3	71
Sample No.M32	1	5	86

10) NH_4^+

Five NIAs submitted the analytical results. Lab no.1, 3 and 4 used spectrophotometry method as recommended by the Malé declaration. Lab no.6 applied the Nessler method, Lab no.8 used the IC (Table 22). Only one data for the higher concentration sample (M31) and one data for the lower concentration sample (M32) was within DQOs. The other four data points for the higher concentration sample were flagged “E” while for the lower concentration sample there was two flagged “E” and two flagged “X” (Fig.12).

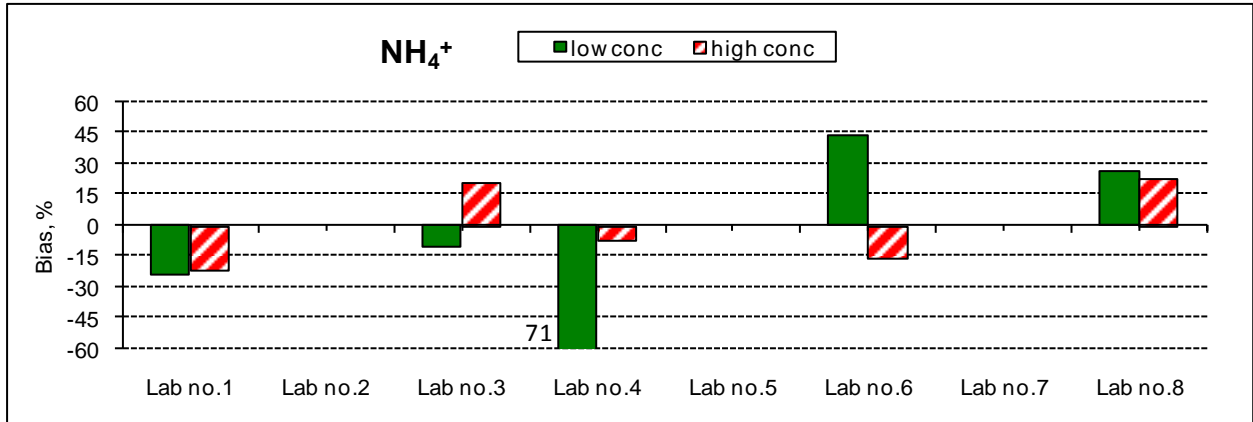


Fig.12 Distribution of NH_4^+ data normalized by prepared value (off-scale values are indicated, %)

Table 22 Analytical methods and flagged data of NH_4^+

Analytical method	
Spectrophotometry	3/8
Titration (Distillation)	1/8
Ion Chromatography	1/8
Non-reported data	3/8

Flagged data	E	X	Flagged %
Sample No.M31	4	0	80
Sample No.M32	2	2	80

Summary remarks

Among the analytical parameters, pH and EC results appeared to be more accurate with lower bias by most of NIAs. Results by some NIAs were higher while others were lower than the prepared values. The submitted analytical results for all specified anions and cations are in general highly biased. K^+ has 100% data points flagged for both samples while NO_3^- has 100% flagged data for lower concentration sample.

Other ions have large portions (above 65%) of the flagged results for both samples M31 and M32. It appeared that the methods that involve intensive sample treatment would result in more biases (ions) while simple measurements for pH and EC produced better results.

The bias for Na^+ , K^+ and Mg^{2+} were generally the highest. The relative deviation between the average submitted data and the prepared value of each parameter (%) is presented in Figure 13 which shows high positive biases for Cl^- , Na^+ , K^+ , Ca^{2+} for the lower concentration sample (M32). For the higher concentration sample less number of biased parameters but still show positive biases for K^+ though in general the biases are lower than for M32. This again indicates the lower accuracy in analyzing low levels of constituents in the sample. Further improvement is still required in the sample analysis in the network. Strict implementation of the Malé Declaration QA/QC program in each NIA laboratory is expected to improve the accuracy of the analysis.

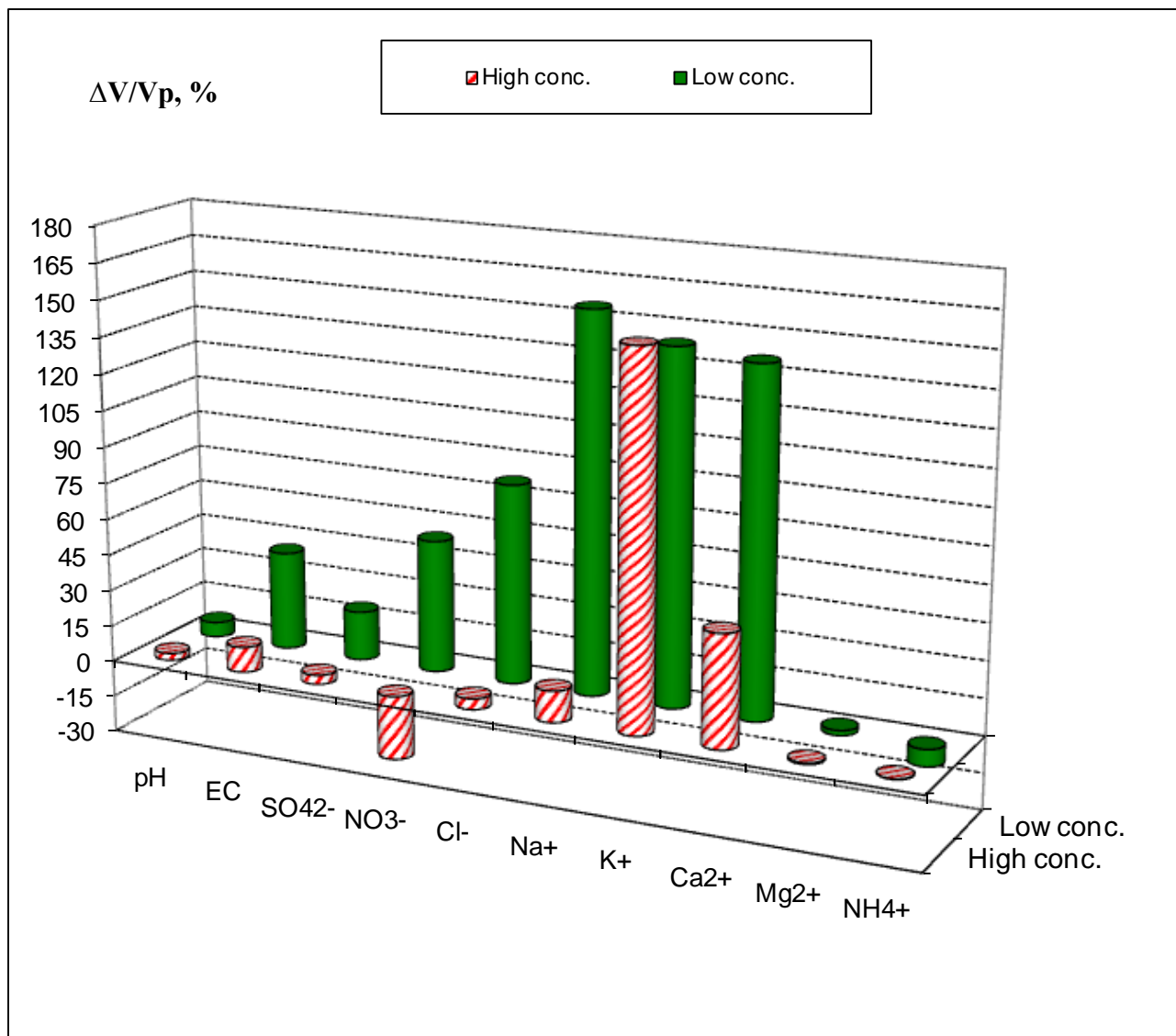


Fig.13 Relative deviation between average submitted data and prepared value
 $[\Delta V = \text{Average } (V_a) - \text{Prepared } (V_p)]$

Other remarks:

- An excel data template was provided to the NIA for the data reporting but not all NIAs followed
- Lab no.2 reported data not following the standard unit as required on the Male Manual for EC
- Lab no. 4 analyzed Ca^{2+} and Mg^{2+} in September, i.e. almost two months after receiving the samples.
- Lab no. 6 reported wrong receiving date of the samples, i.e. September instead of July (confirmed by the DHL track chain) and submitted highly fluctuating triple measurements of several ions (SO_4^{2-} , Ca^{2+} , Mg^{2+} and NH_4^+ for the low concentration sample, and Mg^{2+} for the high concentration sample.
- Some NIAs reported detection limits which are higher than the concentrations prepared for the lower concentration sample
- Only one NIA reported R1 and R2 values

3.3 *Circumstance of Sample Analysis*

1) Measurement methods used

Not all NIAs used the recommended methods by the Malé Declaration Monitoring Protocol. A summary of the methods used for each parameter is presented in Table 23. It is noted that some NIAs did not report the specific name of the methods following the Malé protocol. Thus, the name of the same methods may be reported differently and also not precisely. For example, some NIAs simply reported the spectrophotometer without mentioning other information such as reaction agents used, etc.

Table 23 Recommended methods and methods used by NIAs

Para.	Recommended method	Bangladesh	Maldives	Bhutan	India	Iran	Nepal	Pakistan	Sri-Lanka
pH	Glass electrode	Electrode	NA	Multi para test kit	WTW	Glass electrode	pH meter	Glass electrode	Electrode
EC	Conductivity Cell	Electrode	NA	Multi para test kit	WTW	conductivity cell	conductivity cell	Conductivity cell	Electrode
SO ₄ ²⁻	Spectrophotometry	Spectrophotometry	NA	NA	Elico	Spectrophotometry	Spectrophotometry	Spectrophotometry	IC
NO ₃ ⁻	Cadmium reduction method-Spectrophotometry	Spectrophotometry	NA	NA	Elico	Spectrophotometry	Spectrophotometry	Spectrophotometry	IC
Cl ⁻	Argentometric method	Argentometric	NA	NA	Titration	Argentometric	Titrimetry	Argentometric	IC
Na ⁺	Flame photometry	AAS	NA	AAS	Flame photometry	Flame photometer	AAS	NA	IC
K ⁺	Flame photometry	AAS	NA	AAS	Flame photometry	Flame photometer	AAS	NA	IC
Ca ²⁺	Titrimetry (EDTA method)	AAS	NA	AAS	Titrimetry	Titrimetry	Titrimetry	Spectrophotometry	IC
Mg ²⁺	Titrimetry	AAS	NA	AAS	By difference	Titrimetry	Titrimetry	Spectrophotometry	IC
NH ₄ ⁺	Spectrophotometry (Indophenol)	same	NA	NA	Elico	Spectrophotometry	distillation	na	IC

na: data not available (not analyzed)

IC: Ion Chromatograph

AAS: Atomic Absorption Spectrophotometry

AES: Flame Atomic Emission Spectrometry

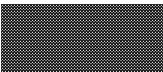

same: applied the same method as recommended method

2) Number of staff in charge of measurement and year of experience

The numbers of staff in charge of measurement and year of experience on rainwater samples are shown in Table 24. Given the overall low accuracy of the data, there is no strong association between the data quality and the number of years of experience or number of staff involved in the sample analysis.

Table 24. Staff in charge of measurement and year of 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	more than 11 years										
Iran	2	more than 8 years										
Maldives			NA		NA	NA	NA	NA	NA	NA	NA	NA
Nepal	1	7 years										
Pakistan	1	more than 11 years						NA	NA			NA
Sri-Lanka	2	more than 8 years										

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

3) Water temperature at measurement (pH and EC)

Most of the NIA laboratories measured pH and EC at the recommended temperature (25⁰C). However, Lab no.2 and 6 measured these two parameters at temperature lower than 25⁰C (Table 14). However, this did not seem to significantly affect the measurement results.

Table 14 Water temperature at measurement for pH and EC (°C)

Country	pH		EC	
	No. M31	No. M32	No. M31	No. M32
Bangladesh	24.8	24.8	24.8	24.8
Bhutan	20.9	20.9	20.9	20.9
India	25.0	25.0	25.0	25.0
Iran	25.0	25.0	25.0	25.0
Maldives	NA	NA	NA	NA
Nepal	17-18	17-18	25.0	25.0
Pakistan	25 - 26	25 - 26	25 - 26	25 - 26
Sri-Lanka	27.0	27.0	27.0	27.0

Blue (dark) background: difference of more than 2°C of the recommended value (25°C)

4. Comparison between the first and the second attempts

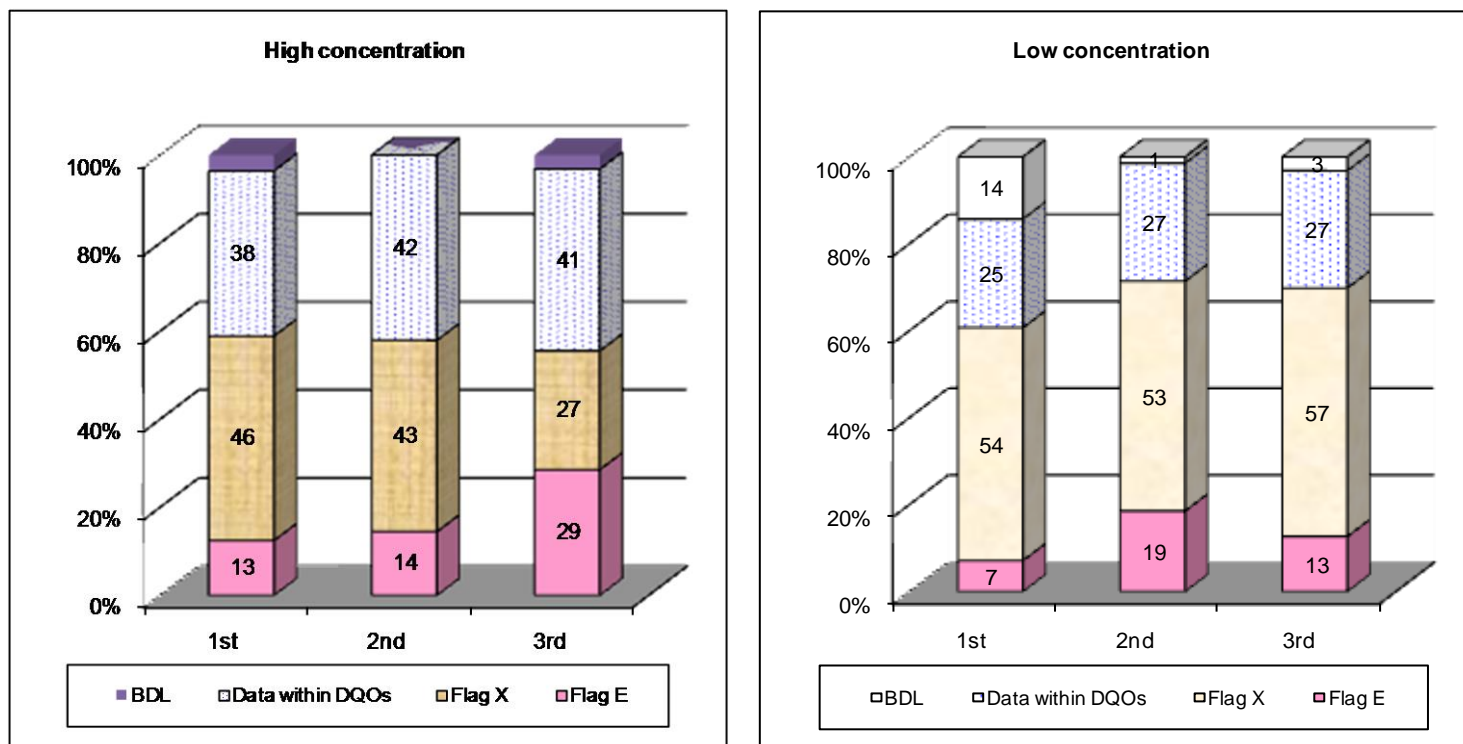


Fig. 14 Comparison of 1st, 2nd and 3rd attempts

The data quality still remains the major issue. The percentage of the data within the DQOs is more or less still the same as previous attempts. The flagged “E” data points in the third attempt increased while those with flags “X” (lower quality) reduced for the higher concentration sample (Figure 14). The 3rd attempt also shows certain improvement in term of the number of NIA laboratories submitted the analytical results: one NIA that did not report any analytical results and 7 NIAs submitted most of the requirement parameters. Most NIA laboratories submitted triple or duplicate measurements (except for Lab no. 2).

Note that, the concentration levels prepared in the higher concentration samples were similar for three attempts while those in the lower concentration sample in the 2nd and 3rd attempt were increased 2 to 5 times. This may be the reason for the substantial reduction of the below detection limit data points in these later attempts.

5. Implementation for improvement of measurement accuracy and precisions

The analytical results submitted by NIAs show strong bias from the prepared values for most of the parameters, especially for the low concentrations in sample M32. Various factors may lead to the low accuracy of the data. It is observed that not all NIAs follow the Malé QA/QC Monitoring Protocol strictly in term of the equipment and methods. If NIAs have more advanced equipment (IC) in place it would be easier to do the repeated analyses hence to check the precision of the data themselves. In general, the methods require intensive sample treatment provide lower accuracy. The parameters that can be measured directly such as pH and EC produced much better accuracy than the ions. The intensive treatment of samples may introduce errors from various dosing and glassware contamination as well as the purity of the chemicals used

for the sample treatment. In this case, the NIAs have to observe the standard operating procedures (SOP) of the analytical methods and the QA/QC elements required by the Malé monitoring protocol.

The following fundamental recommendations matters should be taken into account in measurement, analysis, and data control processes.

Fundamental factors to improve data quality

- Properly clean the apparatus/glassware
- Use the materials and reagents of required purity with as low as possible blank values of target analytical substances.
- Measurement and analysis should be conducted by persons who are well trained and are committed to produce high quality data. In-house expertise within each NIA laboratory should be developed for this purpose. If NIAs have the samples analyzed by other institutions, the data control and data quality check should be in place and should be done by in-house experts of the NIAs.
- SOPs must be prepared for the management of apparatus, reagents, and procedure of operation. The SOPs have to be followed strictly.
- A log book should be kept for the sampling and analysis in each NIA laboratory
- Details on measurement and analysis of samples are presented below.

1) Deionized water

Use only water with conductivity less than 0.15mS/m for dilution of samples and cleaning the glassware for measurements and analyses. It was reported by one NIA that the water used was not pure enough (high EC) while other NIAs did not mention about the EC of the water used. This is a simple check that may help much to improve data quality.

2) Use certified materials and certified samples (SRM) to standardize the used methods

- NIA laboratories should use the standard reference materials to evaluate their measurement methods. These are samples with known concentrations to NIAs and they can compare the measurement results with the certified values. Thus, repeated analyses can be made and the NIA measurement procedures can be calibrated samples until the results are within the ranges of the certified values.
- The certified/standard reference materials (certified solutions and certified materials) should be used periodically in each NIA laboratory as a QC element for their routine analysis. The Malé Declaration Programmes can consider to purchase the SRM and distribute to NIAs at least once per year.

3) Pretreatment of samples, storage and analysis time

- Conductivity and pH should be measured as soon as possible after sample receiving at the temperature recommended by Malé QA/QC monitoring protocol of 25°C. Temperature of the measurements should be recorded. In this inter-laboratory exercise 2 NIAs did not follow this requirement (deviation of more than 2°C).
- Other parameters should be analyzed within a week of sample receiving. The samples should be capped and stored properly in refrigerators all the time before analysis. Care should be taken to avoid the cross-contamination during sample transport and storage.
- It is noted in this exercise that the parameters that were analyzed by methods requiring intensive sample treatment had the analytical results with strong biases. SOPs need to be followed closely in this case. Hands-on trainings for the staff can be offered within each NIA by more experienced staff or by Malé Declaration Programme.
- Repeated analyses should be made to ensure the data quality (precision). In this inter-laboratory exercise, 3 analyses are required for each parameter. However, not all NIAs submitted the results.

- A log book should be kept to record the timing (arrival in the laboratory, analysis etc.) and the conditions of the samples, personnel involved, conditions of the equipment etc.

4) Calibration of analytical instruments

- Each analytical instrument must be calibrated when it is used. The appropriate adjustments should be made. For sophisticated equipments, the calibration curves must be checked regularly by a standard solution.
- Standard solutions and reference solutions must be prepared from different stock solutions to ensure the independence (to eliminate the same systematic error in these solutions)
- New calibration and standard curves should be prepared if a new reagent bottle is used.
- Calibration should be done regularly, after 20-30 measurements, even though the same reagent bottles are still used.
- The calibration curves have to be checked before each analysis by injecting a standard solution (with known concentration)

5) Data quality checking and control by NIA laboratory

- When samples seem to be obviously contaminated, these data should be marked and treated as unrecorded data. A log book record may be very useful for this track.
- In house experts should check for abnormal data points in the data series. A simple time series plot may help to detect the abnormality. Appropriate reasons should be specified to explain the situation.
- Incorrect data can corrupt the overall research results. Careful checks are needed to avoid producing data of inadequate quality. When abnormal or unrecorded data appear, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.
- The standard deviation of the repeated analyses should be as small as possible to ensure the data precision. Highly precise data ensure that there are no random errors. The random errors can be caused by human mistakes, ambient conditions (including contamination) as well as the unstable instrument sensitivity. The random errors cause the results of repeated analyses or re-measurements to be significantly different. If the standard deviation of the repeated analyses is small and the analytical methods are made following the SOP then the data quality is ensured.
- Calculating the criteria for ion balance (R_1) and for agreement between calculated and measured electronic conductivity (R_2) following the Male Protocol. Once these criteria are not met then the measurement data quality should be reexamined. It is note that, however, meeting these criteria is the necessary condition but not the enough condition.

Overall comment: “It’s better to have no data than to have wrong data. Wrong data will give wrong information hence may be quite expensive if the actions are taken in the wrong direction”.

5. REFERENCES

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APPENDIX 1: Participating laboratories

Countries/Laboratories

1. Bangladesh

Khulna Divisional Laboratory, Department of Environment, Govt. of the People's Republic of Bangladesh

2. Bhutan

National Environment Commission (NEC), Royal Government of Bhutan

3. Iran

Environmental Research Center, Air Pollution Research Office, Station directorate environment

4. India

Central Pollution Control Board, Ministry of Environment & Forests, Government of India

5. Maldives

Maldives Climate Observatory, Department of Meteorology

6. Nepal

Central Soil & Plant Analysis Laboratory, Institute of agriculture and Animal Science, Chitwan

7. Pakistan

Pakistan Environmental Protection Agency

8. Sri Lanka

Central Environmental Authority

Appendix 2: Calculation of R1 and R2 for artificial rain water sample

(1) Calculation of ion balance (R₁)

- Total anion (A_{eq}) of equivalent concentration (μeq/L) is calculated by summing the concentration of all anions (C: μmol/L).

$$A_{eq} (\mu\text{eq/L}) = \sum n \cdot C_{Ai} (\mu\text{mol/L}) = 2C(\text{SO}_4^{2-}) + C(\text{NO}_3^-) + C(\text{Cl}^-)$$

Where, n is electric charge and C_{Ai} = concentration (μmol/L) of anion 'i'.

- Total cation (C_{eq}) equivalent concentration (μeq/L) is calculated by summing the concentration of all cations (C: μmol/L).

$$C_{eq} (\mu\text{eq/L}) = \sum n \cdot C_{Ci} (\mu\text{mol/L}) = 10^{(6-\text{pH})} + C(\text{NH}_4^+) + C(\text{Na}^+) + C(\text{K}^+) + 2C(\text{Ca}^{2+}) + 2C(\text{Mg}^{2+})$$

Where, n is electric charge and C_{Ci} = concentration (μmol/L) of cation 'i'.

- Calculation of ion balance (R₁)

$$R_1 (\%) = 100 \times (C_{eq} - A_{eq}) / (C_{eq} + A_{eq})$$

(2) Calculation of R₂ (calculated vs. measured EC)

- Total electric conductivity (Λ_{calc}) is calculated as follows:

$$\Lambda_{\text{calc}} (\text{mS/m}) = \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2C(\text{SO}_4^{2-}) + 71.5 \times C(\text{NO}_3^-) + 76.3 \times C(\text{Cl}^-) + 73.5 \times C(\text{NH}_4^+) + 50.1 \times C(\text{Na}^+) + 73.5 \times C(\text{K}^+) + 59.8 \times 2C(\text{Ca}^{2+}) + 53.3 \times 2C(\text{Mg}^{2+})\} / 10,000$$

Where, C denotes the molar concentrations (μmol/L) of ions given in the parenthesis at 25°C. The constant value is ionic equivalent conductance at 25°C for each ion.

- The agreement (ratio of R₂) between calculated (Λ_{calc}) and measured (Λ_{meas}) electric conductivity should be calculated as follows:

$$R_2 = 100 \times (\Lambda_{\text{calc}} - \Lambda_{\text{meas}}) / (\Lambda_{\text{calc}} + \Lambda_{\text{meas}})$$

Appendix 3: Dates of Events

Date of sending samples 13-Jul-11

Country	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-Sep-11		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									

na: sample not analyzed