

*The Interim Network Center for the Preparatory-Phase Activities of
the Acid Deposition Monitoring Network in East Asia*

**Report of the Inter-laboratory
Comparison Project 1998**

(Round robin analysis survey)

1st. Attempt

November 1999

Acid Deposition and Oxidant Research Center

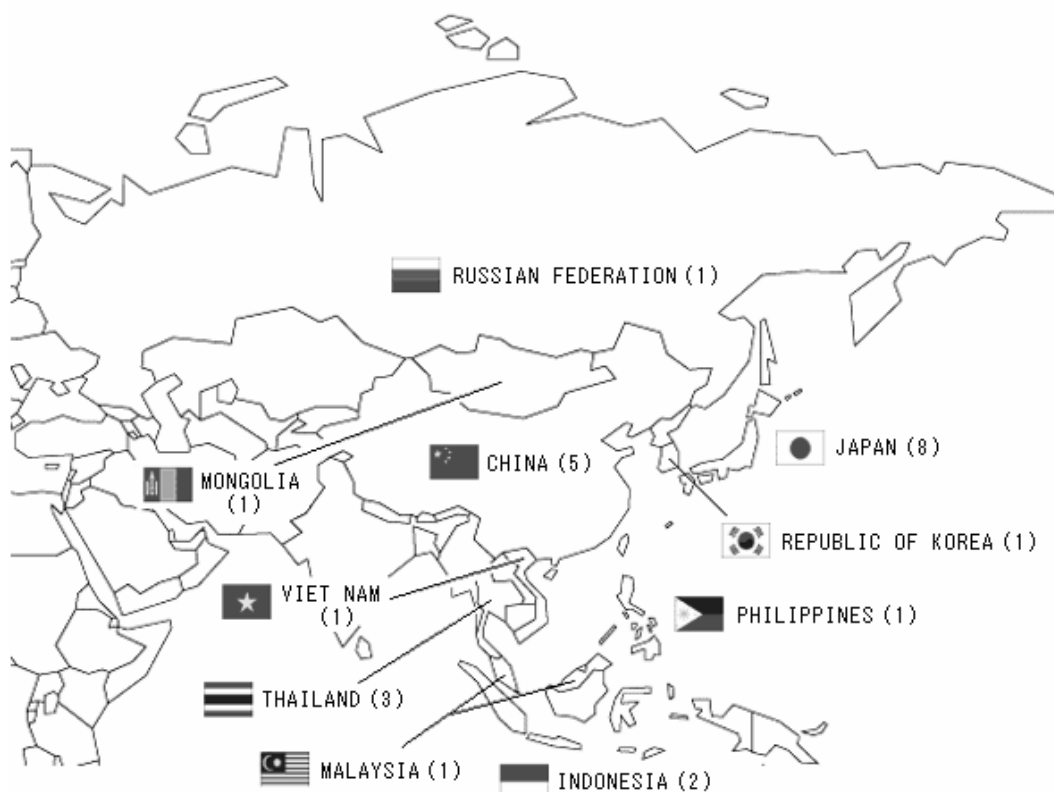
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1. INTRODUCTION

This inter-laboratory comparison project (round robin analysis survey of uniformly prepared artificial rainwater samples) was conducted among the analytical laboratories of the Acid Deposition Monitoring Network in East Asia (EANET), based on the Quality Assurance / Quality Control (QA/QC) Program of the preparatory-phase activities of EANET. The purpose of this project is through the evaluation of analytical results, analytical equipment and its operating condition and other practical problems, (i) to recognize the analytical precision and accuracy of the data in each participating laboratory, and give an opportunity to improve the quality of the analysis on wet deposition monitoring, and (ii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

Artificial rainwater samples which contain major ions were prepared and distributed by the Interim Network Center (INC). Although this is the first trial of the inter-laboratory comparison project in EANET, all the participating laboratories submitted their analytical data. Obtained data for pH, EC, concentrations of SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ were compared with prepared values and statistically treated. List of the participating laboratories, individual analytical data with their Lab.IDs, and various statistical values are included in this report.



* figure in parenthesis shows the numbers of laboratories of each country (24 laboratories from 10 countries)

Fig.1 Laboratories participating in this Inter-comparison project of the EANET

2. PROCEDURE

2.1 Participating Laboratories

Laboratories in charge of chemical analysis of the participating countries of EANET are listed in APPENDIX 1. Interim Network Center (INC) shipped the artificial rainwater samples to all of these 24 laboratories, and all of them submitted their analytical data. The contact addresses of the laboratories are presented in APPENDIX 1.

2.2 Dispatched Rainwater Samples

Two kinds (higher concentrations and lower concentrations) of artificial rainwater samples are distributed to the above mentioned laboratories. The information on the analytical precision and accuracy on individual parameters can be obtained through the statistical treatment of submitted analytical data of 100 times diluted samples.

Table 1 Outline of artificial rainwater samples

Name	Amount of each sample	Container	Number of samples	Note
Artificial rainwater samples No.1 (high concentration) No.2 (low concentration)	Approximately 100ml	Poly-propylene bottle 100ml	One bottle each	Known amount of reagents are solved in deionized water

Before the measurement, each laboratory shall dilute distributed samples 100 times accurately by the specified procedure.

2.3 Analytical Parameters

All participating laboratories were expected to measure and submit the data with the units listed in Table 2 on ten parameters: pH, Electric Conductivity (EC), concentrations of chloride, nitrate, sulfate, ammonium, calcium-ion, magnesium-ion, potassium-ion, and sodium-ion of the samples. It was informed to the participating laboratories that concentration of each parameter was within range described in Table 3.

Table 2 Reporting units of analyte

Analyte	Reporting Units	
pH	pH Unites	–
EC	milli siemens/meter	mS/m
SO ₄ ²⁻	micro mole/liter	umol/L
NO ₃ ⁻	micro mole/liter	umol/L
Cl ⁻	micro mole/liter	umol/L
Na ⁺	micro mole/liter	umol/L
K ⁺	micro mole/liter	umol/L
Ca ²⁺	micro mole/liter	umol/L
Mg ²⁺	micro mole/liter	umol/L
NH ₄ ⁺	micro mole/liter	umol/L

Table 3 Concentration range of the artificial rainwater samples*

Parameter	Range	Parameter	Range
pH	3.9– 4.9	NH ₄ ⁺	0.3 – 3 mg/L
EC	1.5 – 15 mS/m	Ca ²⁺	0.3 – 3 mg/L
Cl ⁻	1 – 10 mg/L	Mg ²⁺	0.05 – 0.5 mg/L
NO ₃ ⁻	1 – 10 mg/L	K ⁺	0.05 – 0.5 mg/L
SO ₄ ²⁻	2 – 20 mg/L	Na ⁺	0.5 – 5.0 mg/L

*100 times diluted samples.

2.4 Analytical Method

Participating laboratories were expected to use analytical methods and data checking procedures that are specified in the “Technical Manual for Monitoring Wet Deposition” and the QA/QC Program for the Preparatory-phase Activities of EANET. Analytical methods specified in the manual are described in Table 4.

Table 4 Analytical methods specified in the manual

Parameter	Analytical method
pH	Glass electrode
EC	Conductivity cell
Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻	Ion Chromatography
NH ₄ ⁺	Ion Chromatography or Spectrophotometry (Indophenol blue)
Ca ²⁺ Mg ²⁺ K ⁺ Na ⁺	Ion Chromatography or Atomic Absorption /Emission Spectrometry

2.5 Data Checking Procedures

a) Calculation of ion balance (R_1)

(1) Total anion (A) equivalent concentration (ueq L^{-1}) is calculated by summing the concentrations of all anions (C: umol L^{-1}).

$$A (\text{ueq L}^{-1}) = \sum n C_{Ai} (\text{umol L}^{-1}) = 2C (\text{SO}_4^{2-}) + C (\text{NO}_3^-) + C (\text{Cl}^-)$$

n, C_{Ai} : electric charge of ion and concentration (umol L^{-1}) of anion "i".

(2) Total cation (C) equivalent concentration (ueq L^{-1}) is calculated by summing the concentrations of all cations (C: umol L^{-1}).

$$C (\text{ueq L}^{-1}) = \sum n C_{Ci} (\text{umol L}^{-1}) = 10^{(6-\text{pH})} + C (\text{NH}_4^+) + C (\text{Na}^+) + C (\text{K}^+) \\ + 2C (\text{Ca}^{2+}) + 2C (\text{Mg}^{2+})$$

n, C_{Ci} : electric charge of ion and concentration (umol L^{-1}) of cation "i".

(3) Calculation of ion balance (R_1)

$$R_1 = 100 \times (C-A) / (C+A)$$

(4) R_1 , which is calculated using the above equation, should be compared with standard values in Table 5. Re-measurement, check with standard solutions, and/or inspection of calibration curves should be undertaken, when R_1 is not within the range.

Table 5 Allowable ranges for R_1 in different concentration ranges

(C+A) [ueq / L]	R_1
< 50	+ 30 ~ - 30
50 ~ 100	+ 15 ~ - 15
> 100	+ 8 ~ - 8

(Reference) Technical Manual for Monitoring Wet Deposition (for EANET)

b) Comparison between calculated and measured electrical conductivity (R₂)

(1) Total electric conductivity (Λ_{calc}) should be calculated as follows;

$$\begin{aligned}\Lambda_{\text{calc}} (\text{uS cm}^{-1}) = & 349.7 \times 10^{(3-\text{pH})} + \{80.0 \times 2C (\text{SO}_4^{2-}) + 71.5 C (\text{NO}_3^-) \\ & + 76.3 C (\text{Cl}^-) + 73.5 C (\text{NH}_4^+) + 50.1 C (\text{Na}^+) + 73.5 \times C (\text{K}^+) \\ & + 59.8 \times 2C (\text{Ca}^{2+}) + 53.3 \times 2C (\text{Mg}^{2+})\} / 1000\end{aligned}$$

C: Molar concentrations ($\mu\text{mol L}^{-1}$) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C.

(2) Ratio (R₂) of calculations to measurements (Λ_{meas}) in electric conductivity should be calculated as follows;

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

(3) R₂, which is calculated using the above equation, should be compared with standard values in Table 6. Re-measurement, check with standard solutions, and/or inspection of calibration curves are necessary, when R₂ is not within the range.

Table 6 Allowable ranges for R₂ in different concentration ranges

$\Lambda_{\text{meas}} [\text{mS m}^{-1}]$	R ₂
< 0.5	+ 20 ~ - 20
0.5 ~ 3	+ 13 ~ - 13
> 3	+ 9 ~ - 9

(Reference) Technical Manual for Monitoring Wet Deposition (for EANET)

3. RESULTS

The Interim Network Center shipped artificial rainwater samples to 24 laboratories in the participating countries of EANET, and received the data on analytical results from all the laboratories. Obtained data are summarized in Table 7. Statistics that were calculated for each constituent of the artificial rainwater samples were: Average, Minimum (Min.), Maximum (Max.), Standard deviation (S.D.), and Number of data (N). For the calculation, outlying data which apart greater than a factor of 3 of S.D. from the Average were not included. As shown in Table.7, average of submitted data were fairly well agreed with the prepared value/concentration within a range of $\pm 10\%$. Cations gave rather varied data both for No.1 and No.2 sample.

**Table 7 Summary of analytical results of the artificial rainwater samples
(Reported data after outliers were removed)**

Constituents	Prepared	Average	S.D.	N	Min.	Max.
[Sample No.1]						
pH	4.05	4.06	0.04	22	3.97	4.12
EC(mS/m)	7.94	7.27	0.71	24	5.16	7.86
SO ₄ ²⁻ (umol/L)	83.5	82.1	7.80	23	64.0	99.0
NO ₃ ⁻ (umol/L)	93.3	90.7	9.08	22	66.0	109.0
Cl ⁻ (umol/L)	129.0	126.9	9.02	22	110.0	149.0
Na ⁺ (umol/L)	95.8	93.2	7.87	21	71.6	107.0
K ⁺ (umol/L)	11.1	10.6	1.75	23	7.9	14.0
Ca ²⁺ (umol/L)	41.1	39.0	8.08	23	18.6	60.3
Mg ²⁺ (umol/L)	13.1	12.3	3.41	22	0.8	18.2
NH ₄ ⁺ (umol/L)	84.8	77.3	22.8	24	15.8	122.0
[Sample No.2]						
pH	4.51	4.53	0.06	22	4.41	4.69
EC(mS/m)	2.82	2.68	0.15	23	2.22	2.85
SO ₄ ²⁻ (umol/L)	29.1	28.1	3.34	22	19.3	36.0
NO ₃ ⁻ (umol/L)	36.1	35.6	3.78	23	27.0	43.6
Cl ⁻ (umol/L)	45.1	42.1	6.66	23	25.3	57.4
Na ⁺ (umol/L)	33.5	32.9	3.55	22	26.7	39.6
K ⁺ (umol/L)	7.4	7.0	1.56	23	3.3	10.1
Ca ²⁺ (umol/L)	14.3	14.5	2.93	23	7.5	20.7
Mg ²⁺ (umol/L)	4.6	4.5	1.20	22	0.4	6.2
NH ₄ ⁺ (umol/L)	29.5	27.2	8.70	24	3.2	43.2

(note) Prepared : Value or concentration which was calculated from the amount of chemicals used for the preparation of samples.

The Data Quality Objectives (DQOs) of data obtained by the preparatory-phase activities of EANET was specified for every constituent as $\pm 15\%$ by the QA/QC program of the EANET. In this report, analytical data on the artificial rainwater samples were compared with the prepared value/concentration and evaluated by the DQO value: the flag "E" was put to the data that exceed by a factor of 2 of the DQO ($\pm 15\%$ - $\pm 30\%$), and the flag "X" was put to the data that exceed more than a factor of 2 of the DQO ($< -30\%$ or $> 30\%$). A set of data for each sample were evaluated by the data checking procedures described in chapter 2.5 of this report. The flag "I" was put to poor ion balance data sets, and the flag "C" was put to poor conductivity agreement data sets.

The results were evaluated from the three aspects: i) comparison of concentration dependence – sample No.1 (higher concentrations) and No.2 (lower concentrations), ii) comparison of individual parameters, and iii) comparison of circumstance of analysis in each participating laboratory. Evaluation of data between the sample No.1 and No.2 is shown in "3.1 COMPARISON BY SAMPLE", evaluation of data for each constituent is shown in "3.2 ANALYTICAL PARAMETER", and evaluation of data by circumstance of analysis such as analytical method used, experience of personnel, and other analytical condition is described in "3.3 CIRCUMSTANCE OF SAMPLE ANALYSIS".

For a reference, the inter-laboratory comparison results using the same artificial rainwater sample obtained by 35 laboratories which belong to Japanese National Monitoring Network of Acid Deposition is shown in APPENDIX 5.

3.1 COMPARISON BY SAMPLE

Sample No.1 (higher concentrations)

Table 8 Number of flagged data for the Sample No.1 (higher concentrations)

Flag*	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
E	0	2	4	3	1	1	10	2	1	4	28
X	0	1	1	2	2	3	1	4	6	4	24
Data within DQOs	24	21	19	19	21	20	13	18	17	16	188
Flagged (%)	0.0	12.5	20.8	20.8	12.5	16.7	45.8	25.0	29.2	33.3	21.7

*E : Value Exceeded the DQO by a factor of 2

*X : Value Exceeded the DQO more than a factor of 2

For sample No.1 (higher concentrations), 28 analytical data out of 240 exceeded the DQOs by a factor of 2 and flagged by "E". Data from 10 laboratories for K⁺ were flagged by "E". 24 analytical data out of 240 exceeded the DQOs more than a factor of 2 and flagged by "X". Data from 6 laboratories for Mg²⁺ were flagged by "X".

Flagged by "E" and "X" data were 52 out of 240, it shares about 22 percents of all reported data of sample No.1.

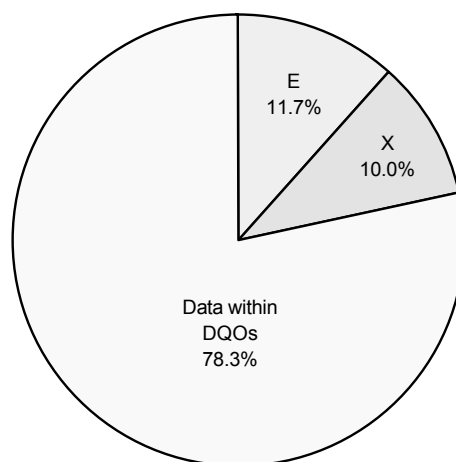


Fig.2 Percentage of flagged data for Sample No.1

Table 9 Analytical Results of Sample No.1

Lab. ID	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 -
1AB9	4.12	7.57	82.6	90.6	127.0	87.5	E 8.5	38.6	12.3	80.2	-3.9	-2.0
1F29	4.05	7.01	75.7	88.5	126.0	107.0	E 12.8	38.2	12.6	84.3	3.8	5.1
1878	4.10	7.41	77.0	92.9	123.0	91.6	11.7	38.4	13.7	92.8	1.3	0.2
1B79	4.06	7.86	82.1	90.0	131.0	99.6	E 13.2	42.1	13.4	91.1	2.1	0.3
18CA	4.10	7.42	82.1	93.2	130.0	89.0	10.1	37.3	11.8	84.1	-3.6	0.3
1829	4.08	7.53	78.2	88.4	122.0	98.5	10.9	40.0	13.6	87.0	2.7	0.2
17D8	4.08	7.51	E 96.8	98.9	131.0	99.3	11.7	42.9	E 15.5	82.0	-3.7	3.3
18D8	4.03	7.51	74.8	99.0	130.0	98.2	12.4	37.6	14.5	88.0	2.3	3.1
14D4	4.04	7.28	87.8	101.0	142.0	E 71.6	E 8.3	46.4	X 7.9	E 71.6	I -8.7	4.6
1788	3.97	7.73	89.5	79.9	111.3	98.0	11.0	41.6	X 29.0	86.4	I 9.0	5.4
1444	4.08	7.66	80.0	90.9	123.0	99.0	10.9	38.9	12.4	86.0	1.0	-0.5
1434	4.09	7.58	E 99.0	E 109.0	E 149.0	105.0	12.7	X 60.3	X 18.2	X 122.0	2.4	7.3
1525	4.02	7.47	79.9	89.1	131.0	91.7	E 8.4	E 34.8	X 0.0	83.3	-4.3	2.2
1442	4.11	7.39	E 69.8	91.4	115.0	X 15.9	X 1.2	X 6.2	X 0.8	X 18.6	I -46.2	C -13.2
1828	4.05	7.73	80.4	93.6	115.0	89.2	E 9.0	38.8	12.5	88.2	1.2	-0.1
1D88	4.22	X 5.16	E 64.0	E 71.8	X 81.5	X 50.3	E 8.0	X 20.7	X 6.8	X 43.8	I -12.8	0.6
1748	4.65	E 5.64	90.1	X 21.7	X 275.0	X 163.0	E 9.0	X 18.6	11.9	E 67.0	I -19.3	4.7
1CF9	4.04	7.78	83.9	92.4	128.0	90.9	10.7	39.1	13.0	85.1	-0.8	1.0
1648	4.05	E 5.85	80.0	93.7	133.0	94.9	10.2	39.0	12.0	89.8	-0.1	C 14.8
1FA9	4.00	7.77	83.5	92.0	127.0	91.6	11.1	39.7	13.2	84.9	0.9	2.9
1BC8	4.08	7.70	88.3	94.7	128.0	89.8	10.6	40.4	13.0	E 71.5	-4.9	-0.3
1D43	4.10	6.81	X 380.0	X 212.0	130.0	82.5	E 7.9	35.4	13.3	X 15.8	I -59.1	C 29.5
18C8	4.00	7.57	83.0	E 66.0	110.0	87.0	E 14.0	40.0	14.0	E 72.0	5.4	1.7
1EC8	4.07	7.51	79.2	88.1	129.3	96.0	10.7	E 49.2	13.7	80.9	2.9	1.6

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

I:Poor ion balance (R1)

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

C:Poor conductivity agreement (R2)

Sample No.2 (lower concentrations)

Table 10 Number of flagged data for the Sample No.2 (lower concentrations)

Flag*	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
E	0	1	3	3	3	4	8	1	3	2	28
X	1	1	3	1	3	2	4	6	6	5	32
Data within DQOs	23	22	18	20	18	18	12	17	15	17	180
Flagged (%)	4.2	8.3	25.0	16.7	25.0	25.0	50.0	29.2	37.5	29.2	25.0

*E : Value Exceeded the DQO by a factor of 2

*X : Value Exceeded the DQO more than a factor of 2

For sample No.2 (lower concentrations), 28 analytical data out of 240 exceeded the DQOs by a factor of 2 and flagged by "E". Data from 8 laboratories for K⁺ were flagged by "E". 32 analytical data out of 240 exceeded the DQOs more than a factor of 2 and flagged by "X". More analytical data for cations were flagged by "X" compared with Sample No.1. 60 analytical data out of 240 were flagged by "E" and "X", it shares 25 percents of all reported data of sample No.2.

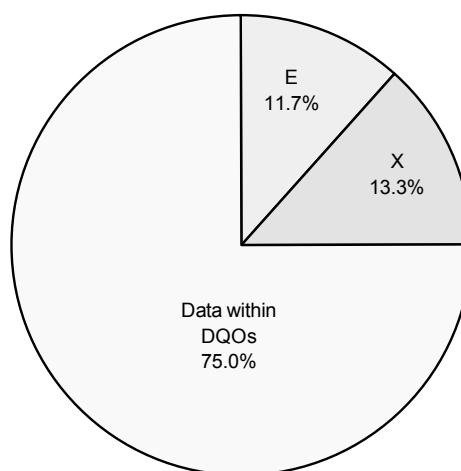


Fig.3 Percentage of flagged data for Sample No.2

Evaluation

Number of flagged data "E" for Sample No.1 and Sample No.2 were almost similar. However, more data for Sample No.2 (lower concentrations) were flagged "X" compared with data for Sample No.1 (higher concentrations). It indicates the difficulty of the analysis of lower concentration sample, particularly cations. Since so many data were flagged by "E" or "X", the analytical skill should be improved.

Table 11 Analytical Results of Sample No.2

Lab. ID	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
	-										-	-
1AB9	4.56	2.62	28.4	35.2	42.4	E 26.7	E 5.7	13.0	4.0	26.4	-5.5	-1.1
1F29	4.53	2.57	25.4	33.1	40.8	38.5	E 8.7	13.0	4.4	29.2	6.0	1.7
1878	4.59	2.68	26.4	35.4	41.3	32.1	7.5	13.9	4.8	33.3	2.4	-2.1
1B79	4.53	2.85	28.2	35.1	47.0	33.4	7.1	14.3	4.5	32.2	0.5	-1.5
18CA	4.56	2.71	28.9	36.1	44.2	E 27.4	E 5.8	12.3	E 3.8	29.7	-5.9	-1.9
1829	4.51	2.73	28.3	34.1	38.8	33.3	7.1	13.9	4.5	30.2	3.3	0.0
17D8	4.52	2.69	E 36.0	37.3	44.5	34.8	8.0	14.0	5.1	27.0	-5.3	3.6
18D8	4.49	2.70	E 24.5	36.6	46.2	34.0	7.0	14.5	4.9	32.5	4.7	2.3
14D4	4.69	2.41	E 24.1	35.3	44.6	32.6	E 5.5	16.4	X 2.3	31.3	-0.3	-1.3
1788	4.51	2.76	27.1	41.3	44.9	E 39.6	7.4	X 20.7	X 13.5	32.3	I 12.0	4.7
1444	4.55	2.76	28.2	35.6	45.3	33.5	7.0	13.1	4.3	30.5	-1.2	-1.4
1434	4.63	2.60	33.4	39.6	47.3	36.8	E 8.8	X 20.4	X 6.2	X 43.2	3.7	5.0
1525	4.44	2.73	31.3	E 43.6	E 57.4	E 27.5	X 3.3	X 9.9	X 0.0	E 23.2	I -19.6	4.2
1442	4.60	2.79	X 13.9	E 27.9	X 25.3	X 3.8	X 0.5	X 1.9	X 0.4	X 3.2	I -37.0	C -28.1
1828	4.53	2.74	30.2	38.5	38.9	29.0	E 5.3	15.3	5.0	X 19.9	-5.1	-1.6
1D88	4.84	X 1.42	25.8	32.9	E 32.5	29.7	7.5	12.8	4.0	X 18.6	-6.0	C 15.4
1748	X 6.07	2.43	X 19.3	X 7.6	X 98.6	X 98.7	6.9	X 7.5	X 6.1	E 21.6	3.5	-9.6
1CF9	4.48	2.83	29.0	35.1	42.8	31.7	6.9	14.6	4.5	31.8	2.1	0.6
1648	4.50	E 2.22	28.0	35.8	43.0	32.6	6.8	14.4	4.7	32.5	2.5	11.8
1FA9	4.45	2.81	29.9	35.6	45.7	33.4	X 10.1	13.7	4.5	32.7	2.4	3.5
1BC8	4.53	2.85	27.6	34.1	43.1	30.4	7.0	14.3	4.5	28.5	0.2	-3.1
1D43	4.56	2.60	X 78.3	41.0	X 28.6	33.8	X 4.5	15.2	E 5.5	X 5.2	I -33.6	C 10.5
18C8	4.41	2.80	29.0	E 27.0	E 37.0	38.0	E 8.7	X 19.0	E 5.3	28.0	I 14.1	4.2
1EC8	4.58	2.67	28.9	32.8	46.2	35.8	E 9.2	E 16.6	4.7	29.7	2.5	0.2

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

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

I:Poor ion balance (R1)

C:Poor conductivity agreement (R2)

3.2 ANALYTICAL PARAMETERS

pH

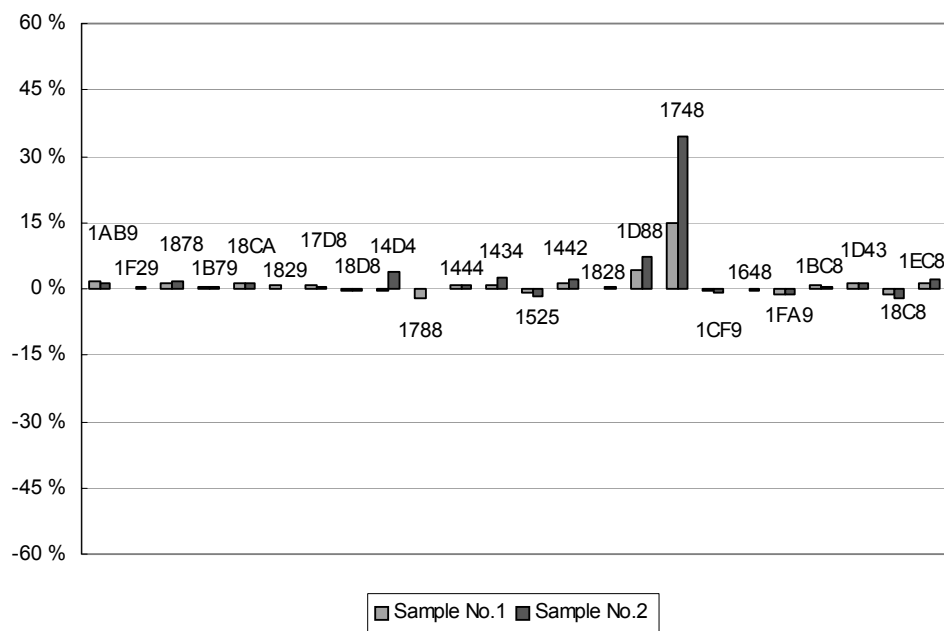


Fig.4 Distribution of pH data normalized by prepared value

Table 12 Analytical method and flagged data of pH

Analytical Method

pH meter and electrode	22 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	0	0	0.0
Sample No.2	0	1	4.2

All participating laboratories used pH meter with glass electrode for measurement of pH. Most of obtained data were fairly agreed with prepared value. But in the case of Sample No.2, the data from Lab.ID 1748 exceeded the DQO by more than a factor of 2 and flagged by "X". Many laboratories submitted slightly higher data than expected. We should carefully treat the sample particularly at dilution and during the storage of samples.

EC

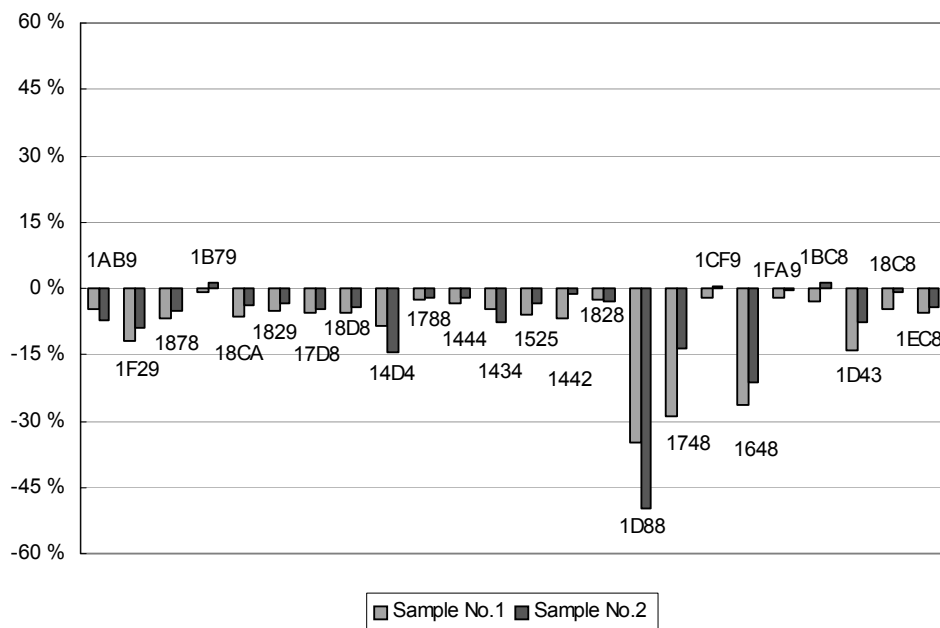


Fig.5 Distribution of EC data normalized by prepared value

Table 13 Analytical method and flagged data of EC

Analytical Method

Conductivity meter and cell	22 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	2	1	12.5
Sample No.2	1	1	8.3

All participating laboratories used conductivity cell for the measurement of EC. Obtained data were relatively agreed with the prepared value. However, Lab.ID 1D88, 1748 and 1648 submitted very different values, and flagged by “E” or “X”. Most of the laboratories reported lower data than prepared value. We should carefully treat the sample particularly at dilution and during the storage of samples.

SO₄²⁻

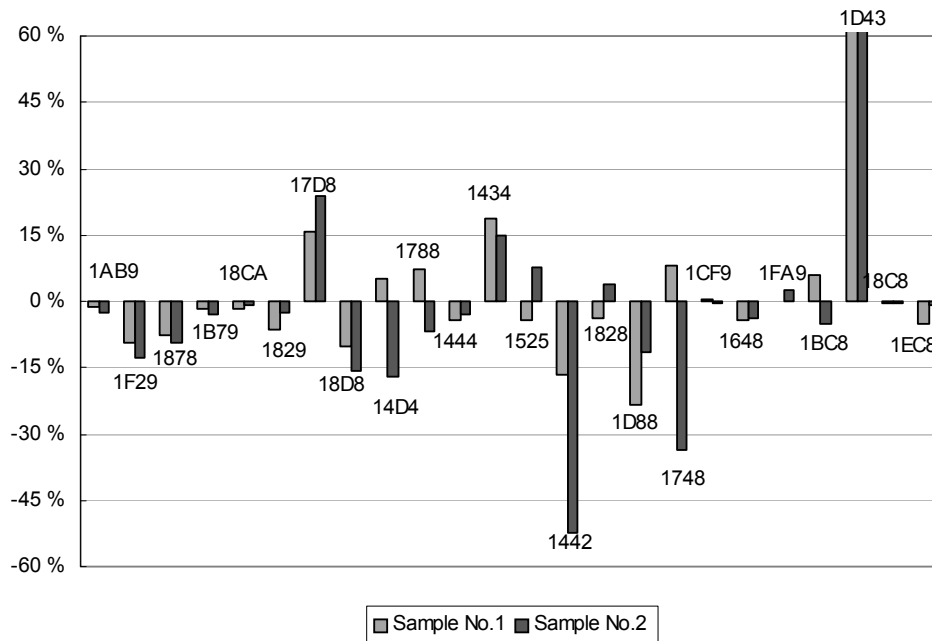


Fig.6 Distribution of SO₄²⁻ data normalized by prepared concentration

Table 14 Analytical method and flagged data of SO₄²⁻

Analytical Method

Ion chromatography	20 / 24
Spectrophotometry	1 / 24
Other method	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	4	1	20.8
Sample No.2	3	3	25.0

Most of participating laboratories employed ion chromatography for the determination of SO₄²⁻ except two laboratories which used spectrophotometry and other method (liquid chromatography) respectively. Lab.ID 1788 used spectrophotometry, and Lab.ID 18D8 used other method. But, much difference of the data was not observed by these analytical methods. Among other ionic constituents, data on SO₄²⁻ agreed with prepared concentration, though Lab.ID 1D43 data were significantly different.

NO₃⁻

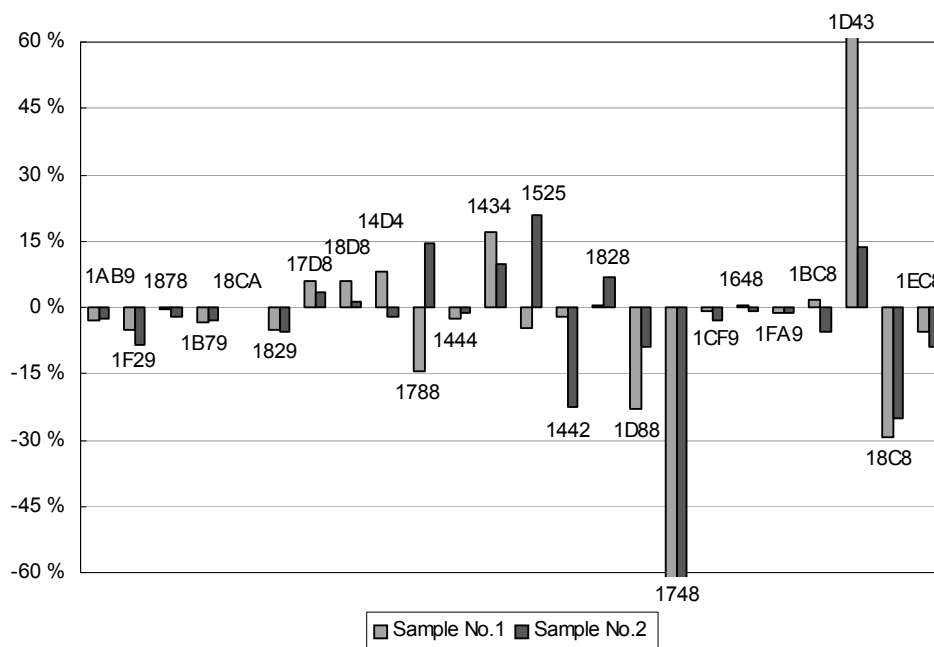


Fig.7 Distribution of NO₃⁻ data normalized by prepared concentration

Table 15 Analytical method and flagged data of NO₃⁻

Analytical Method

Ion chromatography	20 / 24
Spectrophotometry	1 / 24
Other method	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	3	2	20.8
Sample No.2	3	1	16.7

Same as SO₄²⁻, most of participating laboratories employed ion chromatography for the determination of NO₃⁻ except two laboratories which used spectrophotometry and other method (liquid chromatography) respectively. Lab.ID 1788 used spectrophotometry, and obtained data were different tendency for the Sample No.1 and the Sample No.2. On the other hand, Lab.ID 18D8 used other method (liquid chromatography) and obtained fairly good data. Among other ionic constituents, data on NO₃⁻ relatively agreed with prepared concentration, though Lab.ID 1748 and 1D43 data were significantly different.

Cl⁻

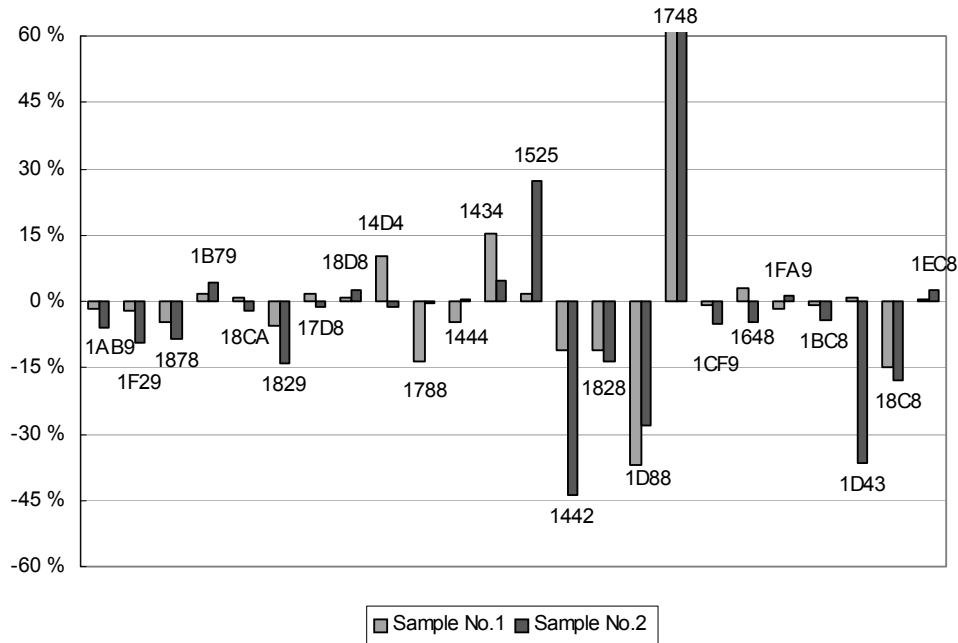


Fig.8 Distribution of Cl⁻ data normalized by prepared concentration

Table 16 Analytical method and flagged data of Cl⁻

Analytical Method

Ion chromatography	20 / 24
Titration	1 / 24
Other method	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	1	2	12.5
Sample No.2	3	3	25.0

Same as SO₄²⁻ and NO₃⁻, most laboratories used ion chromatography for the determination of Cl⁻. Data of Lab.ID 1788 (titration method) and Lab.ID 18D8 (other method (liquid chromatography)) seemed similar to the data obtained by ion chromatography. Lab.ID 1748 submitted significantly different values same as the data on NO₃⁻.

Na⁺

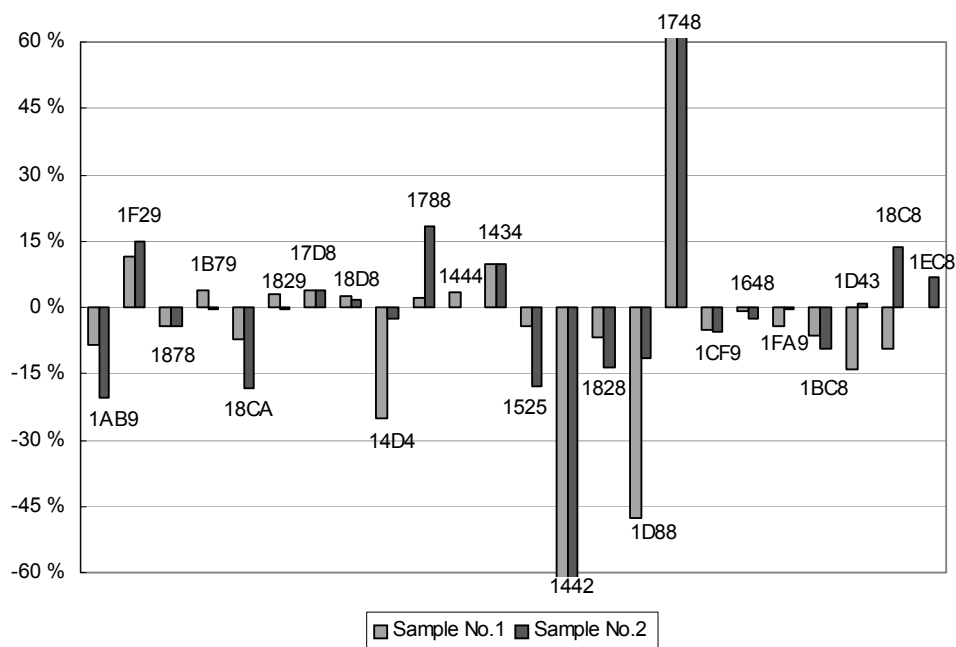


Fig.9 Distribution of Na⁺ data normalized by prepared concentration

Table 17 Analytical method and flagged data of Na⁺

Analytical Method

Ion chromatography	14 / 24
Atomic absorption / Flame (emission) photometry	7 / 24
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	1	3	16.7
Sample No.2	4	2	25.0

Among 24 participating laboratories, 14 laboratories employed ion chromatography, 7 laboratories employed atomic absorption/flame (emission) photometry, and the other one laboratory (Lab.ID 17D8) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Na⁺. There was no clear difference of data obtained by these three analytical methods. Compared with other cations, analytical data for Na⁺ did not differ significantly from prepared value, except two laboratories (Lab.ID 1442 and 1748).

K⁺

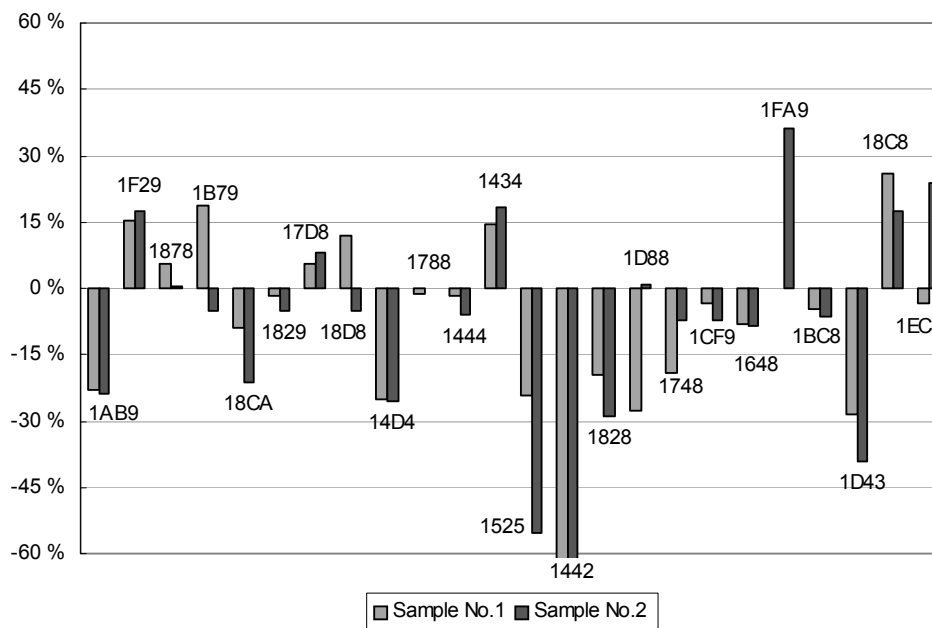


Fig.10 Distribution of K⁺ data normalized by prepared concentration

Table 18 Analytical method and flagged data of K⁺

Analytical Method

Ion chromatography	14 / 24
Atomic absorption / Flame (emission) photometry	7 / 24
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	10	1	45.8
Sample No.2	8	4	50.0

Same as Na⁺, 14 laboratories employed ion chromatography, 7 laboratories employed atomic absorption/flame (emission) photometry, and the other one laboratory (Lab.ID 17D8) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of K⁺. There was no clear difference of data obtained by these three analytical methods. Most laboratories submitted relatively different data from the prepared concentration, and nearly half of the data were flagged by "E" or "X". The data from Lab.ID 1442 differed significantly.

Ca²⁺

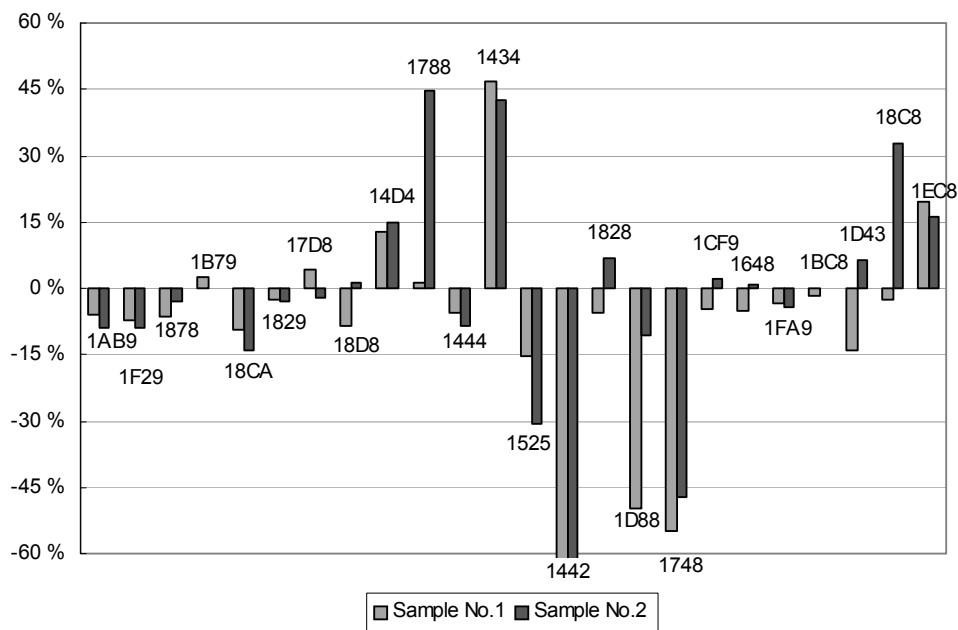


Fig.11 Distribution of Ca²⁺ data normalized by prepared concentration

Table 19 Analytical method and flagged data of Ca²⁺

Analytical Method

Ion chromatography	14 / 24
Atomic absorption / Flame (emission) photometry	7 / 24
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	2	4	25.0
Sample No.2	1	6	29.2

Same as Na⁺ and K⁺, 14 laboratories employed ion chromatography, 7 laboratories employed atomic absorption/flame (emission) photometry, and the other one laboratory (Lab.ID 17D8) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Ca²⁺. There was no clear difference of data obtained by these three analytical methods. Lab.ID 1442 submitted significantly different data for both Sample No.1 and Sample No.2.

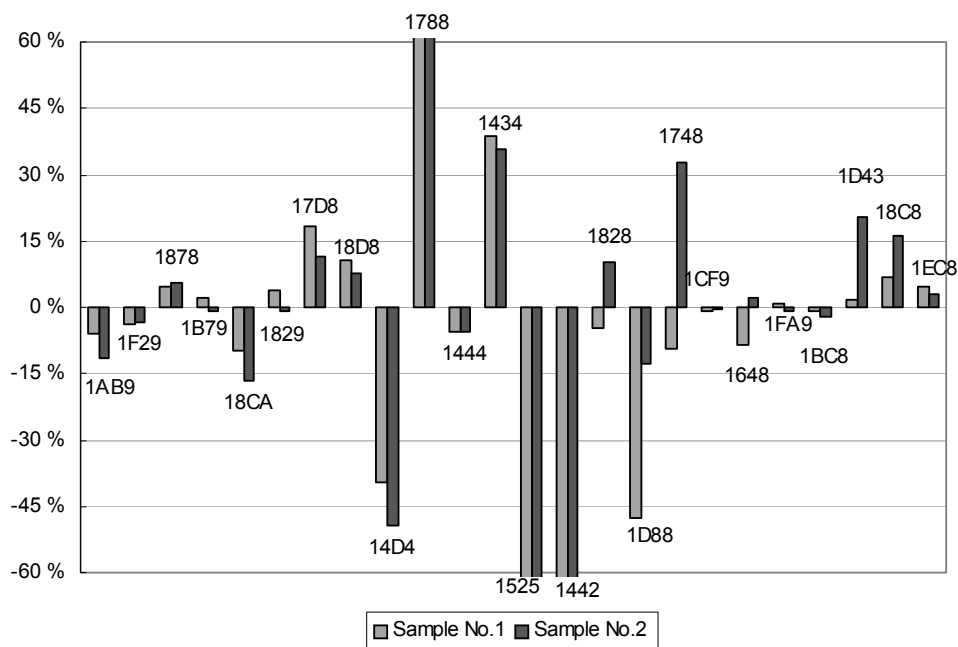
Mg²⁺

Fig.12 Distribution of Mg²⁺ data normalized by prepared concentration

Table 20 Analytical method and flagged data of Mg²⁺

Analytical Method

Ion chromatography	14 / 24
Atomic absorption / Flame (emission) photometry	6 / 24
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1 / 24
Calculation	1 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	1	6	29.2
Sample No.2	3	6	37.5

Among 24 participating laboratories, 14 laboratories employed ion chromatography, 6 laboratories employed atomic absorption/flame (emission) photometry, and one laboratory (Lab.ID 17D8) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Mg²⁺. The other one laboratory calculated the concentration of Mg²⁺ by calculation, subtracting the concentration of Ca²⁺ from concentration obtained by EDTA titration method (Lab.ID 1788). The data obtained by the calculation significantly differed from prepared concentration (Lab.ID 1788). Other laboratories that submitted significantly different data were Lab.ID 1525 and 1442. Lab.ID 1525 submitted the data of Mg²⁺ lower than detection limit.

NH₄⁺

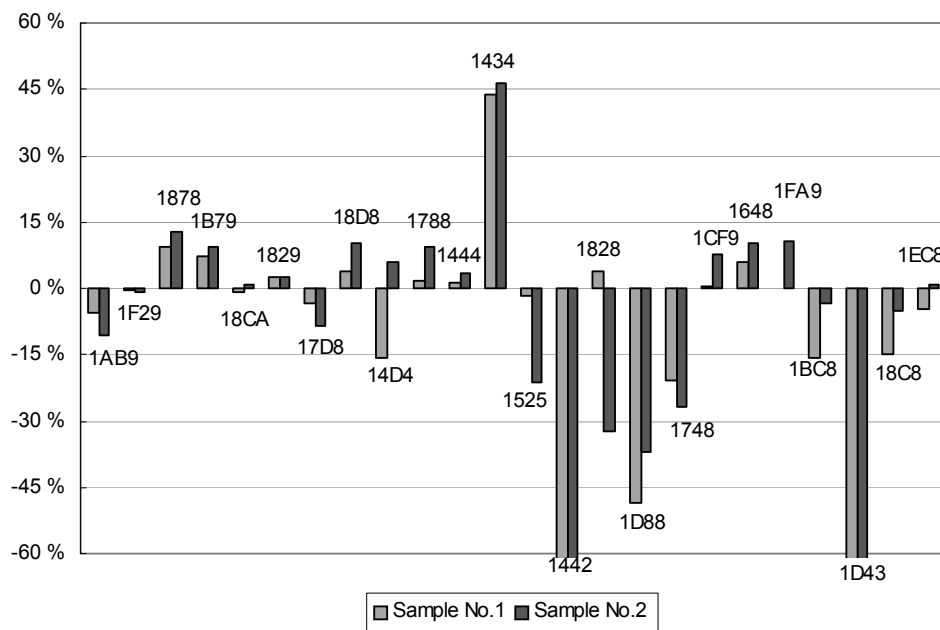


Fig.13 Distribution of NH₄⁺ data normalized by prepared concentration

Table 21 Analytical method and flagged data of NH₄⁺

Analytical Method

Ion chromatography	15 / 24
Spectrophotometry	5 / 24
Other method	2 / 24
No information	2 / 24

Flagged data

	E	X	Flagged (%)
Sample No.1	4	4	33.3
Sample No.2	2	5	29.2

Most participating laboratories used recommended analytical method of EANET for the determination of NH₄⁺: 15 laboratories employed ion chromatography and 7 laboratories employed spectrophotometry. Obtained data for NH₄⁺ varied. Two laboratories (Lab.ID 1442 and 1D43) submitted significantly different data.

Overall Evaluation

Data on pH and EC were less varied compared with other ionic constituents. Measured data on pH were slightly higher than the prepared value. On the other hand, measured data on EC were slightly lower than the prepared value. Cause of this discrepancy is not clear by the results of this round robin project. Analytical data of ionic constituents were varied particularly for cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+) as described in Fig.14. The cause of large deviation of analytical data for some cations (K^+ , Ca^{2+} , and Mg^{2+}) was supposed to be the difficulty of analysis on lower concentration constituents. However, analytical data on other cations (Na^+ and NH_4^+) also showed large deviation in this project. Possible causes of these deviations were not clear by limited information obtained by this project. Quality of data is expected to be improved in the future by accumulation of experience on round robin samples and QA/QC activities in each laboratory.

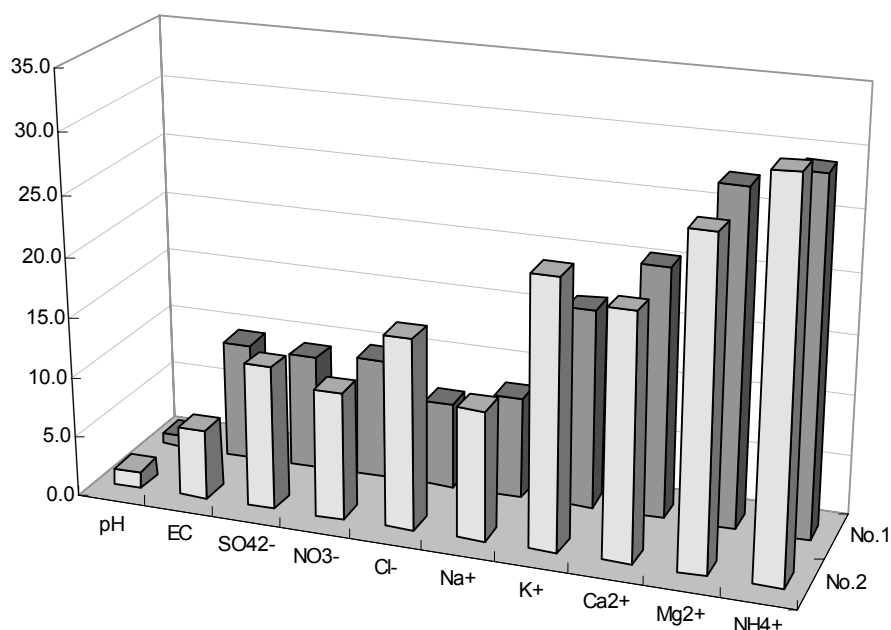


Fig.14 Relative standard deviation of each constituents

(Relative standard deviation (%) = Standard deviation / Average * 100, Reported data after outliers were removed)

3.3 CIRCUMSTANCE OF SAMPLE ANALYSIS

Methods Used

As shown in Fig.15, most of participating laboratories employed recommended methods of EANET, particularly for pH and EC measurements. The codes for the various analytical methods used in this project are shown in Table 22. One laboratory used liquid chromatograph method which is other than those listed. This method was grouped under the "X" code. For NH_4^+ analysis, present questionnaire could not distinguish recommended "indophenol blue spectrophotometry" and "other spectrophotometric methods", though most laboratories seem to use "indophenol blue spectrophotometry". In general, much difference of data was not found among different analytical methods. In future projects, the questionnaire should be improved to obtain more correct and detailed information such as history of the equipment and frequency of usage and so on.

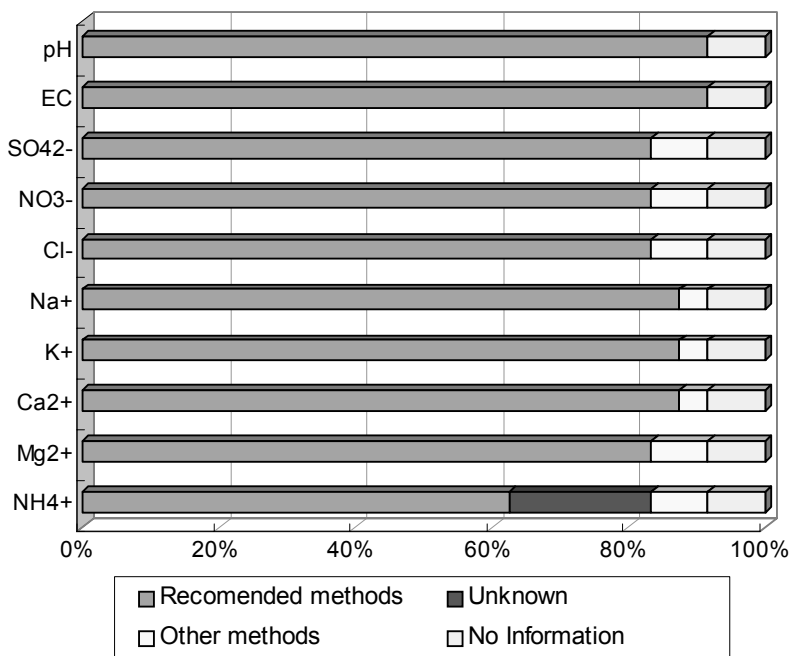


Fig.15 Ratio of recommended method used in the project

Table 22 List of methods

Code	Method
0	pH meter with electrode
1	Conductivity cell
2	Titration
3	Atomic absorption / Flame (emission) photometry
4	Ion chromatography
5	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
6	Calculation
7	Spectrophotometry
8	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
9	Graphite Furnace Atomic Absorption spectrometry (GFAA)
X	Other method
?	No information

Table 23 Analytical Method

Sample No.1

Method	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
0	22									
1		22(3)								
2					1					
3						7(1)	7(2)	7(1)	6	
4			20(4)	20(3)	20(3)	14(3)	14(7)	14(5)	14(5)	15(5)
5										
6									1(1)	
7			1	1						5(1)*
8						1	1	1	1(1)	
9										
X			1	1	1					2
?	2	2	2(1)	2(2)	2	2	2(2)	2	2	2(2)

Sample No.2

Method	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
0	22(1)									
1		22(2)								
2					1					
3						7(2)	7(2)	7(2)	6(1)	
4			20(4)	20(3)	20(4)	14(4)	14(8)	14(4)	14(5)	15(5)
5										
6									1(1)	
7			1	1						5(1)*
8						1	1	1	1	
9										
X			1(1)	1	1					2
?	2	2	2(1)	2(1)	2(2)	2	2(2)	2(1)	2(2)	2(1)

Reverse mesh is recommended method of EANET

() : Number of data which flagged by "E" or "X"

* : unknown

Charge of Measurement

Number of staff in charge of measurement on rainwater samples is described in Table 24. Measurement of rainwater samples was carried out by only one staff in twelve laboratories. In other laboratories, measurement was carried out by 2 to 4 staffs, and usually their responsibility was separated by the method used for analysis such as anions and cations. In most cases that plural staffs carried out the analysis of the round robin samples, anions and cations were analyzed separately by different staffs (7 laboratories out of 9 laboratories). In two laboratories, two staffs collaborate to analyze same constituents.

Table 24 Staff in charge of measurement

Lab.ID	Total	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
1AB9	1	A	A	A	A	A	A	A	A	A	A
1F29	1	A	A	A	A	A	A	A	A	A	A
1878	1	A	A	A	A	A	A	A	A	A	A
1B79	1	A	A	A	A	A	A	A	A	A	A
18CA	1	A	A	A	A	A	A	A	A	A	A
1829	1	A	A	A	A	A	A	A	A	A	A
17D8	2	A	A	A	A	A	B	B	B	B	B
18D8	3	A	A	A,B	A,B	A,B	A,C	A,C	A,C	A,C	A
14D4	2	A	B	B	B	B	B	B	B	B	B
1788	2	A	A	B	B	B	A	A	A	A	A
1444	1	A	A	A	A	A	A	A	A	A	A
1434	1	A	A	A	A	A	A	A	A	A	A
1525	1	A	A	A	A	A	A	A	A	A	A
1442	2	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B
1828	2	A	A	A	A	A	B	B	B	B	B
1D88	1	A	A	A	A	A	A	A	A	A	A
1748	2	A	A	A	A	A	B	B	B	B	B
1CF9	1	A	A	A	A	A	A	A	A	A	A
1648	1	A	A	A	A	A	A	A	A	A	A
1FA9	4	A	A	B	B	B	C	C	C	C	D
1BC8	2	A	A	B	B	B	A	A	A	A	B
1D43	?	+	+	+	+	+	+	+	+	+	+
18C8	?	+	+	+	+	+	+	+	+	+	+
1EC8	3	A	B	C	C	C	C	C	C	C	C

"+": No information, "A", "B", "C", and "D" represents individual staffs in each laboratory who are in charge of measurement. Reverse mesh: Data were flagged by "E" or "X" in sample No.1 and/or sample No.2.

Years of experience

By information obtained through this project, clear evidence of data quality improvement was not found in terms of “years of experience of the staff”.

Table 25 Years of experience

Unit: year

Lab.ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
1AB9	3	3	3	3	3	3	3	3	3	3
1F29	25	25	25	25	25	25	25	25	25	25
1878	4	4	4	4	4	4	4	4	4	4
1B79	1	1	1	1	1	1	1	1	1	1
18CA	5	5	5	5	5	5	5	5	5	5
1829	2	2	2	2	2	2	2	2	2	2
17D8	3	3	3	3	3	1	1	1	1	1
18D8	1	1	1	1	1	1	1	1	1	1
14D4	10	10	10	10	10	10	10	10	10	10
1788	15	15	5	5	5	15	15	15	15	15
1444	1	1	1	1	1	1	1	1	1	1
1434	3	3	3	3	3	3	3	3	3	3
1525	2	2	2	2	2	2	2	2	2	2
1442	1	1	1	1	1	1	1	1	1	1
1828	2	2	2	2	2	2	2	2	2	2
1D88	3	3	3	3	3	3	3	3	3	3
1748	3	3	3	3	3	3	3	3	3	3
1CF9	8	8	8	8	8	8	8	8	8	8
1648	8	8	8	8	8	8	8	8	8	8
1FA9	3	3	8	8	8	6	6	6	6	4
1BC8	4	4	4	4	4	4	4	4	4	4
1D43	+	+	+	+	+	+	+	+	+	+
18C8	+	+	+	+	+	+	+	+	+	+
1EC8	10	7	6	6	6	6	6	6	6	6

“+”: No information.

Reverse mesh: Data were flagged by “E” or “X” in sample No.1 and/or sample No.2.

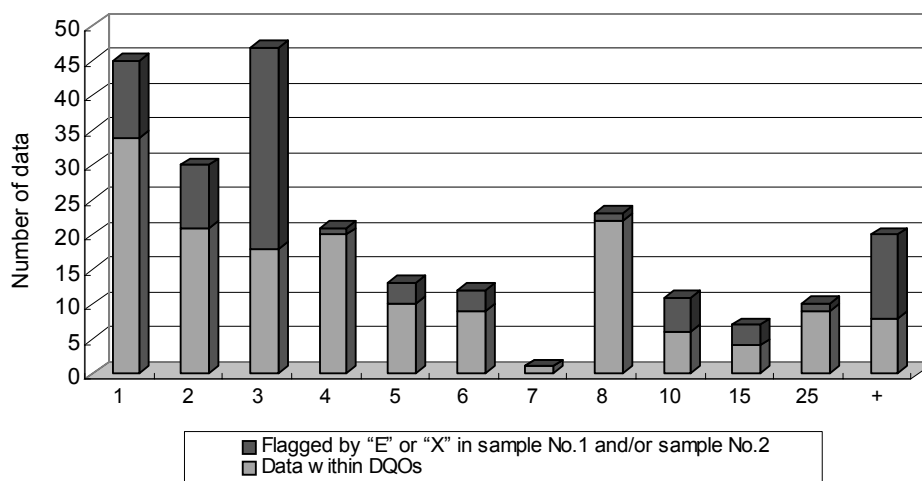


Fig.16 Relationship between flagged data and the years of experience

Water Temperature at measurement (pH and EC)

As described in Table 26, most of the participating laboratories measured pH and EC around 25 degrees centigrade, which the recommended condition by EANET. Water temperature was equal or lower than 20 degrees centigrade for 4 data out of 6 which were flagged by “E” or “X”. However, several laboratories reported adequate data though the temperature is lower than 20 degrees centigrade.

Table 26 Water temperature at measurement (pH and EC) Unit: degrees centigrade

Lab.ID	pH Sample No.1	pH Sample No.2	EC Sample No.1	EC Sample No.2
1AB9	25.0	25.0	25.0	25.0
1F29	25.0	25.0	25.0	25.0
1878	24.8 - 25.2	24.7 - 25.0	24.8 - 25.3	24.8 - 25.2
1B79	25.0	25.0	+	25.0
18CA	24.6	24.7	24.5	24.3
1829	23.5	23.5	23.5	23.5
17D8	24.6	24.6	25.6	25.6
18D8	22.6	22.6	26.6	26.6
14D4	25.0	25.0	25.0	25.0
1788	23.4	23.4	23.4	23.4
1444	25.0	25.0	25.0	25.0
1434	24.5	24.5	24.5	24.5
1525	24.3	24.3	25.2	26.0
1442	25.0	25.0	22.5	22.6
1828	25.0	25.0	25.0	25.0
1D88	20.4	20.4	X 20.4	X 20.4
1748	25.0	X 25.0	E 25.0	25.0
1CF9	16.0	16.0	15.0	15.0
1648	15.7	16.0	E 15.7	E 16.0
1FA9	15.0	15.0	15.0	15.0
1BC8	13.0	13.0	13.0	14.0
1D43	+	+	+	+
18C8	+	+	+	+
1EC8	+	23.0	+	25.5

“+”: No information.

Reverse mesh: Data were flagged by “E” or “X”.

4. REFERENCES

- 1) Guidelines and Technical Manuals for Acid Deposition Monitoring Network in East Asia, adopted by the Expert Meeting on Acid Deposition Monitoring Network in East Asia: Environment Agency, Government of Japan, March 1997.
- 2) Quality Assurance / Quality Control (QA/QC) Program for the Preparatory-Phase Wet Deposition Monitoring in East Asia, The First Meeting of the Interim Scientific Advisory Group for the Preparatory-Phase Activities of EANET, 12-14 October 1998, Yokohama, Japan.

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APPENDIX 2 Original data

Original Data --- Sample No.1

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
-	mS/m	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L
1AB9	4.12	7.57	82.6	90.6	127.0	87.5	8.5	38.6	12.3	80.2
1F29	4.05	7.01	75.7	88.5	126.0	107.0	12.8	38.2	12.6	84.3
1878	4.10	7.41	77.0	92.9	123.0	91.6	11.7	38.4	13.7	92.8
1B79	4.06	7.86	82.1	90.0	131.0	99.6	13.2	42.1	13.4	91.1
18CA	4.10	7.42	82.1	93.2	130.0	89.0	10.1	37.3	11.8	84.1
1829	4.08	7.53	78.2	88.4	122.0	98.5	10.9	40.0	13.6	87.0
17D8	4.08	7.51	96.8	98.9	131.0	99.3	11.7	42.9	15.5	82.0
18D8	4.03	7.51	74.8	99.0	130.0	98.2	12.4	37.6	14.5	88.0
14D4	4.04	7.28	87.8	101.0	142.0	71.6	8.3	46.4	7.9	71.6
1788	3.97	7.73	89.5	79.9	111.3	98.0	11.0	41.6	29.0	86.4
1444	4.08	7.66	80.0	90.9	123.0	99.0	10.9	38.9	12.4	86.0
1434	4.09	7.58	99.0	109.0	149.0	105.0	12.7	60.3	18.2	122.0
1525	4.02	7.47	79.9	89.1	131.0	91.7	8.4	34.8	0.0	83.3
1442	4.11	7.39	69.8	91.4	115.0	15.9	1.2	6.2	0.8	18.6
1828	4.05	7.73	80.4	93.6	115.0	89.2	9.0	38.8	12.5	88.2
1D88	4.22	5.16	64.0	71.8	81.5	50.3	8.0	20.7	6.8	43.8
1748	4.65	5.64	90.1	21.7	275.0	163.0	9.0	18.6	11.9	67.0
1CF9	4.04	7.78	83.9	92.4	128.0	90.9	10.7	39.1	13.0	85.1
1648	4.05	5.85	80.0	93.7	133.0	94.9	10.2	39.0	12.0	89.8
1FA9	4.00	7.77	83.5	92.0	127.0	91.6	11.1	39.7	13.2	84.9
1BC8	4.08	7.70	88.3	94.7	128.0	89.8	10.6	40.4	13.0	71.5
1D43	4.10	6.81	380.0	212.0	130.0	82.5	7.9	35.4	13.3	15.8
18C8	4.00	7.57	83.0	66.0	110.0	87.0	14.0	40.0	14.0	72.0
1EC8	4.10	7.50	79.2	88.1	129.3	96.0	10.7	49.2	13.7	80.9
Prepared value	4.05	7.94	83.5	93.3	129.0	95.8	11.1	41.1	13.1	84.8
Number of data	24	24	24	24	24	24	24	24	24	24
Average	4.09	7.27	94.5	92.9	131.2	91.1	10.2	37.7	12.5	77.3
Minimum	3.97	5.16	64.0	21.7	81.5	15.9	1.2	6.2	0.0	15.8
Maximum	4.65	7.86	380.0	212.0	275.0	163.0	14.0	60.3	29.0	122.0
Standard deviation	0.1	0.7	61.3	30.3	33.1	24.5	2.6	10.4	5.4	22.8

Original Data --- Sample No.2

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
-	mS/m	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L	umol/L
1AB9	4.56	2.62	28.4	35.2	42.4	26.7	5.7	13.0	4.0	26.4
1F29	4.53	2.57	25.4	33.1	40.8	38.5	8.7	13.0	4.4	29.2
1878	4.59	2.68	26.4	35.4	41.3	32.1	7.5	13.9	4.8	33.3
1B79	4.53	2.85	28.2	35.1	47.0	33.4	7.1	14.3	4.5	32.2
18CA	4.56	2.71	28.9	36.1	44.2	27.4	5.8	12.3	3.8	29.7
1829	4.51	2.73	28.3	34.1	38.8	33.3	7.1	13.9	4.5	30.2
17D8	4.52	2.69	36.0	37.3	44.5	34.8	8.0	14.0	5.1	27.0
18D8	4.49	2.70	24.5	36.6	46.2	34.0	7.0	14.5	4.9	32.5
14D4	4.69	2.41	24.1	35.3	44.6	32.6	5.5	16.4	2.3	31.3
1788	4.51	2.76	27.1	41.3	44.9	39.6	7.4	20.7	13.5	32.3
1444	4.55	2.76	28.2	35.6	45.3	33.5	7.0	13.1	4.3	30.5
1434	4.63	2.60	33.4	39.6	47.3	36.8	8.8	20.4	6.2	43.2
1525	4.44	2.73	31.3	43.6	57.4	27.5	3.3	9.9	0.0	23.2
1442	4.60	2.79	13.9	27.9	25.3	3.8	0.5	1.9	0.4	3.2
1828	4.53	2.74	30.2	38.5	38.9	29.0	5.3	15.3	5.0	19.9
1D88	4.84	1.42	25.8	32.9	32.5	29.7	7.5	12.8	4.0	18.6
1748	6.07	2.43	19.3	7.6	98.6	98.7	6.9	7.5	6.1	21.6
1CF9	4.48	2.83	29.0	35.1	42.8	31.7	6.9	14.6	4.5	31.8
1648	4.50	2.22	28.0	35.8	43.0	32.6	6.8	14.4	4.7	32.5
1FA9	4.45	2.81	29.9	35.6	45.7	33.4	10.1	13.7	4.5	32.7
1BC8	4.53	2.85	27.6	34.1	43.1	30.4	7.0	14.3	4.5	28.5
1D43	4.56	2.60	78.3	41.0	28.6	33.8	4.5	15.2	5.5	5.2
18C8	4.41	2.80	29.0	27.0	37.0	38.0	8.7	19.0	5.3	28.0
1EC8	4.60	2.70	28.9	32.8	46.2	35.8	9.2	16.6	4.7	29.7
Prepared value	4.51	2.82	29.1	36.1	45.1	33.5	7.4	14.3	4.6	29.5
Number of data	24	24	24	24	24	24	24	24	24	24
Average	4.61	2.63	29.6	34.4	44.4	34.5	6.8	13.9	4.6	27.2
Minimum	4.41	1.42	13.9	7.6	25.3	3.8	0.5	1.9	0.0	3.2
Maximum	6.07	2.85	78.3	43.6	98.6	98.7	10.1	20.7	13.5	43.2
Standard deviation	0.3	0.3	11.2	6.8	13.2	15.3	2.0	3.8	2.4	8.7

APPENDIX 3 Normalized by prepared value

Original data / Prepared Value x 100 (%) --- Sample No.1

Lab. ID	pH (%)	EC (%)	SO ₄ ²⁻ (%)	NO ₃ ⁻ (%)	Cl ⁻ (%)	Na ⁺ (%)	K ⁺ (%)	Ca ²⁺ (%)	Mg ²⁺ (%)	NH ₄ ⁺ (%)
1AB9	101.7	95.3	98.9	97.1	98.4	91.3	76.9	93.9	93.9	94.6
1F29	100.0	88.3	90.7	94.9	97.7	111.7	115.3	92.9	96.2	99.4
1878	101.2	93.3	92.2	99.6	95.3	95.6	105.4	93.4	104.6	109.4
1B79	100.2	99.0	98.3	96.5	101.6	104.0	118.9	102.4	102.3	107.4
18CA	101.2	93.5	98.3	99.9	100.8	92.9	91.0	90.8	90.1	99.2
1829	100.7	94.8	93.7	94.7	94.6	102.8	98.2	97.3	103.8	102.6
17D8	100.7	94.6	115.9	106.0	101.6	103.7	105.4	104.4	118.3	96.7
18D8	99.5	94.6	89.6	106.1	100.8	102.5	111.7	91.5	110.7	103.8
14D4	99.8	91.7	105.1	108.3	110.1	74.7	74.8	112.9	60.2	84.4
1788	98.0	97.4	107.2	85.6	86.3	102.3	98.8	101.3	221.1	101.9
1444	100.7	96.5	95.8	97.4	95.3	103.3	98.2	94.6	94.7	101.4
1434	101.0	95.5	118.6	116.8	115.5	109.6	114.4	146.7	138.9	143.9
1525	99.3	94.1	95.7	95.5	101.6	95.7	75.9	84.7	0.0	98.2
1442	101.5	93.1	83.6	98.0	89.1	16.6	11.0	15.1	6.3	21.9
1828	100.0	97.4	96.3	100.3	89.1	93.1	80.6	94.4	95.4	104.0
1D88	104.2	65.0	76.6	77.0	63.2	52.5	72.4	50.4	52.1	51.7
1748	114.8	71.0	107.9	23.3	213.2	170.1	81.0	45.3	90.8	79.0
1CF9	99.8	98.0	100.5	99.0	99.2	94.9	96.4	95.1	99.2	100.4
1648	100.0	73.7	95.8	100.4	103.1	99.1	91.9	94.9	91.6	105.9
1FA9	98.8	97.9	100.0	98.6	98.4	95.6	100.0	96.6	100.8	100.1
1BC8	100.7	97.0	105.7	101.5	99.2	93.7	95.5	98.3	99.2	84.3
1D43	101.2	85.8	455.1	227.2	100.8	86.1	71.4	86.1	101.5	18.6
18C8	98.8	95.3	99.4	70.7	85.3	90.8	126.1	97.3	106.9	84.9
1EC8	100.5	94.6	94.9	94.4	100.3	100.2	96.1	119.7	104.6	95.4
Minimum	98.0	65.0	76.6	23.3	63.2	16.6	11.0	15.1	0.0	18.6
Maximum	114.8	99.0	455.1	227.2	213.2	170.1	126.1	146.7	221.1	143.9
Average	101.0	91.5	113.2	99.5	101.7	95.1	92.0	91.7	95.1	91.2

Original data / Prepared Value x 100 (%) --- Sample No.2

Lab. ID	pH (%)	EC (%)	SO ₄ ²⁻ (%)	NO ₃ ⁻ (%)	Cl ⁻ (%)	Na ⁺ (%)	K ⁺ (%)	Ca ²⁺ (%)	Mg ²⁺ (%)	NH ₄ ⁺ (%)
1AB9	101.1	92.9	97.6	97.5	94.0	79.7	76.1	90.9	88.6	89.5
1F29	100.4	91.1	87.3	91.7	90.5	114.9	117.7	90.9	96.5	99.0
1878	101.8	95.0	90.7	98.1	91.6	95.8	100.4	97.2	105.5	112.9
1B79	100.4	101.1	96.9	97.2	104.2	99.7	95.0	100.0	99.1	109.2
18CA	101.1	96.1	99.3	100.0	98.0	81.8	78.6	86.0	83.3	100.7
1829	100.0	96.8	97.3	94.5	86.0	99.4	95.0	97.2	99.3	102.4
17D8	100.2	95.4	123.7	103.3	98.7	103.9	108.1	97.9	111.6	91.5
18D8	99.6	95.7	84.2	101.4	102.4	101.5	94.7	101.4	107.5	110.2
14D4	104.0	85.5	82.8	97.8	98.9	97.3	74.3	114.7	50.4	106.1
1788	100.0	97.9	93.1	114.4	99.6	118.2	100.1	144.8	296.1	109.5
1444	100.9	97.9	96.9	98.6	100.4	100.0	94.1	91.6	94.5	103.4
1434	102.7	92.2	114.8	109.7	104.9	109.9	118.5	142.7	135.7	146.4
1525	98.4	96.8	107.6	120.8	127.3	82.1	44.5	69.2	0.0	78.6
1442	102.0	98.9	47.8	77.3	56.1	11.4	7.3	13.1	9.0	10.9
1828	100.4	97.2	103.8	106.6	86.3	86.6	70.9	107.0	110.3	67.5
1D88	107.3	50.4	88.7	91.1	72.1	88.7	100.8	89.5	87.3	63.1
1748	134.6	86.2	66.3	21.2	218.6	294.6	92.9	52.7	132.7	73.2
1CF9	99.3	100.4	99.7	97.2	94.9	94.6	92.7	102.1	99.6	107.8
1648	99.8	78.7	96.2	99.2	95.3	97.3	91.4	100.7	102.0	110.2
1FA9	98.7	99.6	102.7	98.6	101.3	99.7	136.1	95.8	99.1	110.8
1BC8	100.4	101.1	94.8	94.5	95.6	90.7	93.7	100.0	98.0	96.6
1D43	101.1	92.2	269.1	113.6	63.4	100.9	60.9	106.3	120.4	17.6
18C8	97.8	99.3	99.7	74.8	82.0	113.4	117.3	132.9	116.2	94.9
1EC8	101.6	94.7	99.2	90.8	102.4	106.8	124.5	116.3	103.9	100.6
Minimum	97.8	50.4	47.8	21.2	56.1	11.4	7.3	13.1	0.0	10.9
Maximum	134.6	101.1	269.1	120.8	218.6	294.6	136.1	144.8	296.1	146.4
Average	102.2	93.0	101.7	95.4	98.5	102.9	91.1	97.5	101.9	92.2

APPENDIX 4 Manufacturer's name of instruments and model

Lab.ID	pH meter / electrode	
1AB9	HORIBA	M-13 / 6377-10D
1F29	HORIBA	F-13 / 6350-10D
1878	TOA	HM-60V / GST-5422S
1B79	TOA	HM-30S / GSV-201
18CA	HORIBA	F-8E / S815-1
1829	HORIBA	L7 / 6300
17D8	TOA	HM-30S / GST-5311C
18D8	HORIBA	F21 / S8721
14D4	Corning	model 125 USA
1788	HACH	CO150 USA / CO 80537 USA
1444	HORIBA	F24 / 6367-10D
1434	HORIBA	F21 / S8721
1525	TOA	HM-30V / GST-5421C
1442	HORIBA	D-24, D-20
1828	TOA	HM-30V / GST-5421C
1D88	Fisher Scientific	pH / Ion / Conductivity meter
1748	METROOHM	744 pH Meter
1CF9	No Information	No Information
1648	No Information	No Information
1FA9	Xiamen Analytical Instrument	PHS-301
1BC8	No Information	PHS-301 / 231C
1D43	No Information	No Information
18C8	No Information	No Information
1EC8	Dengfeng Analytical Instrument	DF808A / 231

Lab.ID	EC meter / cell	
1AB9	HORIBA	DS-14 / 3552-10D
1F29	DKK	A0-6 / 2071
1878	TOA	CM-60V / CT-54101C
1B79	TOA	CM-40S / CGT-511C
18CA	HORIBA	DS-12 / 3551-10D
1829	TOA	CM-20S / CG-511B
17D8	CYBERSCAN	CON200
18D8	TOA	CM-14P / CVP-101P
14D4	TOA	CM-203 / C8
1788	HACH	EC10 USA / 50160
1444	HORIBA	DS-15 / 3551-10D
1434	HORIBA	ES-12 / 3582-10D
1525	TOA	CM-40S / 511B
1442	HORIBA	D-24, D-20
1828	TOA	CM-11P
1D88	Fisher Scientific	pH / Ion / Conductivity meter
1748	HACH	44600-00
1CF9	HORIBA	D-515
1648	No Information	No Information
1FA9	Shanghai Rex Instrument / Shanghai Dian Guang Parts	DDS-301 / DJS-1
1BC8	Shanghai Lei-Ci Instrument	DDS-11C / DJS-1
1D43	No Information	No Information
18C8	No Information	No Information
1EC8	Shanghai Lei-Ci Instrument	DDS-11A / DJS-1

Lab.ID	SO ₄ ²⁻ NO ₃ ⁻ Cl ⁻		
1AB9	IC	DIONEX	DX-AQ 1110
1F29	IC	YOKOGAWA	IC-7000
1878	IC	DIONEX	DX-AQ
1B79	IC	DIONEX	DX-3000
18CA	IC	YOKOGAWA	IC-7000
1829	IC	DIONEX	2000i / SP
17D8	IC	DIONEX	DX-500
18D8	Others	EKONOVA	Milikhrom A-02
14D4	IC	DIONEX	DX-500
1788	Others	No Information	SO ₄ ²⁻ NO ₃ ⁻ :UV-VIS system, (Cl ⁻ :Titration by Hg(NO ₃) ₂)
1444	IC	YOKOGAWA	IC-7000
1434	IC	WATERS	432,717,626
1525	IC	DIONEX	DX-100
1442	IC	DIONEX	DX-120
1828	IC	DIONEX	DX-120
1D88	IC	DIONEX	DX-500
1748	IC	DIONEX	DX-5000
1CF9	IC	DIONEX	100
1648	IC	DIONEX	2120i
1FA9	IC	DIONEX	DX-300
1BC8	IC	DIONEX	16
1D43		No Information	No Information
18C8		No Information	No Information
1EC8	IC	SHIMADZU	CDD-6A

Lab.ID	Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺		
1AB9	IC	SHIMADZU	HIC-6A
1F29	AAS	HITACHI	Z-6100
1878	IC	DIONEX	DX-AQ
1B79	IC	DIONEX	DX-120
18CA	IC	DIONEX	DX-500
1829	AAS	HITACHI	180-80
17D8	ICP-MS	Parkin Elmer	ELAN 6000 ICPMS
18D8	Others	CARL ZEISS JENA	AAS-30
14D4	IC	DIONEX	DX-500
1788	Others	No Information	(Flame Photometry)
1444	IC	DIONEX	DX-500 / EG40
1434	IC	WATERS	432, 717, 626
1525	IC	DIONEX	DX-100
1442	IC	DIONEX	DX-120
1828	IC	DIONEX	DX-120
1D88	IC	DIONEX	DX-500
1748	AAS	GBC	Avanta
1CF9	IC	DIONEX	100
1648	IC	DIONEX	2120i
1FA9	AAS	HITACHI	Z-8000
1BC8	AAS	No Information	AA-680
1D43		No Information	No Information
18C8		No Information	No Information
1EC8	IC	SHIMADZU	CDD-6A

Lab.ID	NH ₄ ⁺		
1AB9	IC	SHIMADZU	HIC-6A
1F29	SP	HITACHI	U-1000
1878	IC	DIONEX	DX-AQ
1B79	IC	DIONEX	DX-120
18CA	IC	DIONEX	DX-500
1829	SP	SHIMADZU	UV-150-02
17D8	Others	BRAN & LUEBBE	TRAACS model 800
18D8	SP	PHILIPS	PV-8700
14D4	IC	DIONEX	DX-500
1788	SP	No Information	(UV-VIS system)
1444	IC	DIONEX	DX-500 / EG40
1434	IC	WATERS	432, 717, 626
1525	IC	DIONEX	DX-100
1442	IC	DIONEX	DX-120
1828	IC	DIONEX	DX-120
1D88	IC	DIONEX	DX-500
1748	SP	SHIMADZU	UV-VIS 120-02
1CF9	IC	DIONEX	100
1648	IC	DIONEX	2120i
1FA9	Others	Xiamen Analitical Instrument	7230
1BC8	IC	DIONEX	16
1D43		No Information	No Information
18C8		No Information	No Information
1EC8	IC	SHIMADZU	CDD-6A

SP : Spectrophotometry

APPENDIX 5 Results of inter-laboratory comparison project obtained by the laboratories of Japanese National Acid Deposition Monitoring Network

(Reported data after outliers were removed)

Constituents	Prepared	Average	S.D.	N	Min.	Max.
[Sample No.1]						
pH	4.05	4.08	0.04	35	3.98	4.14
EC(mS/m)	7.94	7.49	0.26	35	6.84	7.99
SO ₄ ²⁻ (umol/L)	83.5	78.9	6.32	35	60.3	92.1
NO ₃ ⁻ (umol/L)	93.3	92.4	3.76	34	86.4	103.0
Cl ⁻ (umol/L)	129.0	127.0	5.10	35	116.0	138.0
Na ⁺ (umol/L)	95.8	94.9	5.86	35	83.0	112.0
K ⁺ (umol/L)	11.1	11.0	1.53	35	7.1	14.1
Ca ²⁺ (umol/L)	41.1	39.5	1.72	34	34.6	42.1
Mg ²⁺ (umol/L)	13.1	13.1	0.78	34	11.5	14.8
NH ₄ ⁺ (umol/L)	84.8	86.0	3.09	34	77.2	92.8
[Sample No.2]						
pH	4.51	4.53	0.04	35	4.42	4.62
EC(mS/m)	2.82	2.70	0.12	35	2.41	2.98
SO ₄ ²⁻ (umol/L)	29.1	28.3	2.28	35	23.2	33.5
NO ₃ ⁻ (umol/L)	36.1	35.8	1.55	33	33.1	40.3
Cl ⁻ (umol/L)	45.1	43.8	3.20	35	36.8	53.1
Na ⁺ (umol/L)	33.5	32.7	2.68	35	26.7	38.5
K ⁺ (umol/L)	7.4	7.0	0.93	35	4.7	9.0
Ca ²⁺ (umol/L)	14.3	13.7	1.41	35	9.9	16.0
Mg ²⁺ (umol/L)	4.6	4.4	0.62	35	3.2	6.2
NH ₄ ⁺ (umol/L)	29.5	30.1	1.94	34	24.8	34.3