

*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 1999**
(Round robin analysis survey)

2nd. Attempt

April 2000

Acid Deposition and Oxidant Research Center

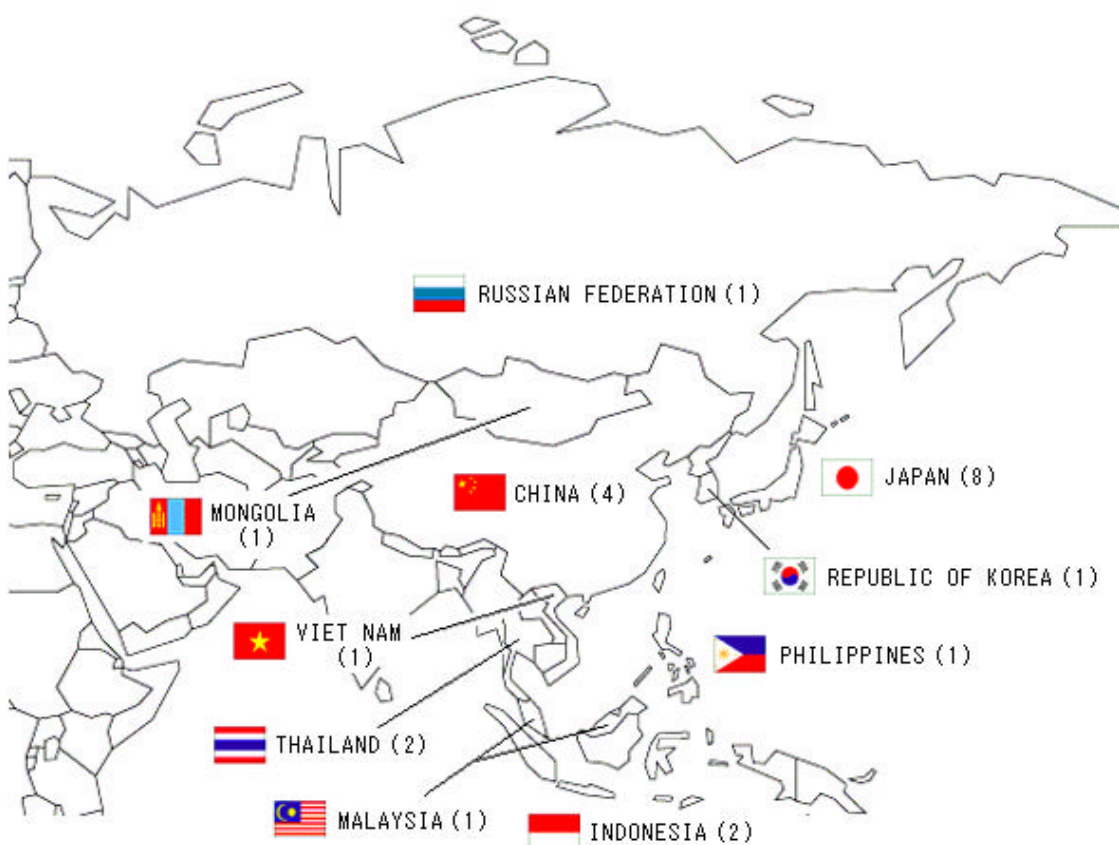
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1. INTRODUCTION

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). All the participating laboratories submitted their analytical data. However, data from one laboratory are not included in this report, because it had an operational problem with its Ion Chromatograph (IC). 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 (22 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 22 laboratories, and data from 21 laboratories were used in this report. 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 dispatched 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	µmol/L
NO ₃ ⁻	micro mole/liter	µmol/L
Cl ⁻	micro mole/liter	µmol/L
Na ⁺	micro mole/liter	µmol/L
K ⁺	micro mole/liter	µmol/L
Ca ²⁺	micro mole/liter	µmol/L
Mg ²⁺	micro mole/liter	µmol/L
NH ₄ ⁺	micro mole/liter	µmol/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

All 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
SO ₄ ²⁻ NO ₃ ⁻ Cl ⁻	Ion Chromatography
Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺	Ion Chromatography or Atomic Absorption /Emission Spectrometry
NH ₄ ⁺	Ion Chromatography or Spectrophotometry (Indophenol blue)

2.5 Data Checking Procedures

a) Calculation of ion balance (R_1)

(1) Total anion (A) equivalent concentration ($\mu\text{eq L}^{-1}$) is calculated by summing the concentrations of all anions (C: $\mu\text{mol L}^{-1}$).

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

n, C_{Ai} : electric charge of ion and concentration ($\mu\text{mol L}^{-1}$) of anion "i".

(2) Total cation (C) equivalent concentration ($\mu\text{eq L}^{-1}$) is calculated by summing the concentrations of all cations (C: $\mu\text{mol L}^{-1}$).

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

n, C_{Ci} : electric charge of ion and concentration ($\mu\text{mol L}^{-1}$) 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) [$\mu\text{eq / L}$]	R_1
< 50	+ 30 ~ - 30
50 ~ 100	+ 15 ~ - 15
> 100	+ 8 ~ - 8

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

<Note>

The pH and EC values are calculated to two decimal places, and other items to one decimal place.

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

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

$$\begin{aligned} \Lambda_{\text{calc}} (\mu\text{S cm}^{-1}) = & 349.7 \times 10^{(6-\text{pH})} + \{80.0 \times 2C (\text{SO}_4^{2-}) + 71.5 C (\text{NO}_3^-) \\ & + 76.3 C (\text{Cl}^-) + 73.5 C (\text{NH}_4^+) + 50.1 C (\text{Na}^+) + 73.5 \times C (\text{K}^+) \\ & + 59.8 \times 2C (\text{Ca}^{2+}) + 53.3 \times 2C (\text{Mg}^{2+})\} / 1000 \end{aligned}$$

C: Molar concentrations (μmol 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

Λ _{meas} [mSm ⁻¹]	R ₂
< 0.5	+ 20 ~ - 20
0.5 ~ 3	+ 13 ~ - 13
> 3	+ 9 ~ - 9

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

<Note>

The pH and EC values are calculated to two decimal places, and other items to one decimal place.

3. RESULTS

The Interim Network Center shipped artificial rainwater samples to 22 laboratories in the participating countries of EANET, and received the data on analytical results from all of them. However, data from one laboratory are not included in this report. Because it had an operational problem with its Ion Chromatograph (IC), and all the ionic constituents were not analyzed. 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	4.14	4.15	0.07	21	3.94	4.22
EC(mS/m)	6.38	6.07	0.22	21	5.68	6.62
SO ₄ ²⁻ (μ mol/L)	67.0	66.6	4.75	20	58.6	80.0
NO ₃ ⁻ (μ mol/L)	75.0	74.6	2.11	19	71.3	79.0
Cl ⁻ (μ mol/L)	104.0	102.4	3.56	21	95.7	106.9
Na ⁺ (μ mol/L)	77.0	77.4	7.19	21	57.4	96.1
K ⁺ (μ mol/L)	8.9	9.3	0.96	20	8.2	11.6
Ca ²⁺ (μ mol/L)	33.0	32.3	3.13	21	23.7	40.2
Mg ²⁺ (μ mol/L)	11.0	10.7	0.73	20	9.5	12.5
NH ₄ ⁺ (μ mol/L)	68.0	69.3	3.22	19	64.7	77.0
[Sample No.2]						
pH	4.59	4.62	0.07	21	4.50	4.75
EC(mS/m)	2.30	2.18	0.13	21	1.82	2.39
SO ₄ ²⁻ (μ mol/L)	24.0	24.3	2.28	20	18.7	30.5
NO ₃ ⁻ (μ mol/L)	27.0	26.8	0.84	19	25.0	28.4
Cl ⁻ (μ mol/L)	38.0	36.8	2.20	21	31.6	42.4
Na ⁺ (μ mol/L)	28.0	28.3	1.93	19	24.1	31.4
K ⁺ (μ mol/L)	3.2	3.3	1.13	21	0.3	6.3
Ca ²⁺ (μ mol/L)	12.0	11.7	1.59	21	7.2	14.3
Mg ²⁺ (μ mol/L)	3.8	3.8	0.50	21	3.0	4.8
NH ₄ ⁺ (μ mol/L)	25.0	24.2	3.44	21	14.7	28.5

(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 ($\pm 15\% \sim \pm 30\%$), 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". Result obtained in this project is compared with the first inter-laboratory comparison in "4 COMPARISON OF 1st AND 2nd INTER-LABORATORY COMPARISON". Finally, proposal to participating laboratories is in "5 PROPOSAL FOR IMPROVEMENT OF MEASUREMENT PRECISIONS."

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	0	1	1	0	2	2	3	0	1	10
X	0	0	1	1	0	0	2	0	1	1	6
Data within DQOs	21	21	19	19	21	19	17	18	20	19	194
Flagged (%)	0.0	0.0	9.5	9.5	0.0	9.5	19.0	14.3	4.8	9.5	7.6

*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), 10 analytical data out of 210 exceeded the DQOs by a factor of 2 and flagged by "E". 6 analytical data out of 210 exceeded the DQOs more than a factor of 2 and flagged by "X".

Flagged by "E" and "X" data were 16 out of 210, it shares 7.6 percents of all reported data of sample No.1.

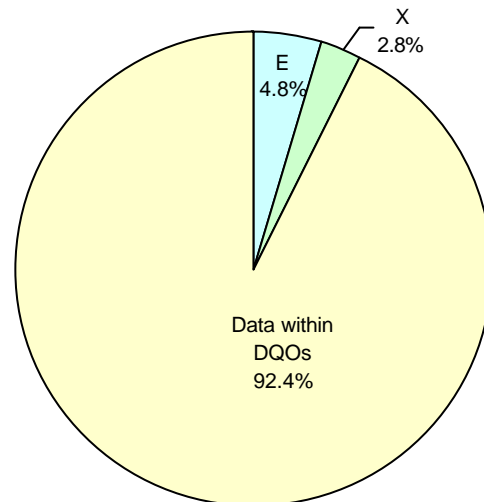


Fig.2 Percentage of flagged data for Sample No.1

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
18CA	4.18	6.02	62.8	71.7	97.4	68.1	8.2	31.8	9.5	66.1	-0.6	-0.7
1F29	4.21	6.14	64.6	74.4	101.0	77.0	E 10.9	31.9	11.5	67.3	-0.2	-1.5
1828	4.21	5.99	67.1	76.0	104.2	84.7	9.5	36.0	11.7	69.5	1.0	1.1
18C8	4.19	6.04	66.0	74.3	103.4	78.6	10.1	33.4	10.5	72.5	0.6	0.9
1B8A	4.18	6.17	61.7	73.2	101.1	77.1	X 4.1	30.9	10.0	66.8	-0.3	-1.6
1829	4.15	6.26	63.9	71.3	98.0	77.2	9.0	33.9	10.1	69.5	2.8	-0.2
1B79	4.18	6.07	65.7	72.6	106.2	76.2	9.3	34.0	10.5	73.5	0.6	1.1
18D8	4.21	6.28	63.7	71.9	100.2	75.6	E 11.1	32.2	10.7	68.4	0.5	-3.0
1878	4.20	6.07	64.7	74.9	96.9	79.6	9.5	32.3	10.6	77.0	2.2	-0.2
17D8	4.17	5.92	E 80.0	76.1	106.9	79.2	9.0	31.5	11.2	68.1	-5.2	4.4
1444	4.20	5.98	64.8	75.2	99.8	75.7	8.9	31.5	9.7	69.1	-0.9	0.0
1788	4.05	5.78	61.9	E 62.8	105.2	73.5	8.5	E 27.5	12.5	66.3	4.2	7.7
1FA9	4.06	6.31	68.2	75.3	103.2	77.0	9.2	32.3	10.8	72.5	2.6	4.8
1648	4.05	6.02	67.7	76.0	103.8	75.5	8.8	32.7	11.1	67.4	2.1	7.4
1EC8	4.18	5.72	58.6	73.0	100.3	76.6	8.5	32.9	9.7	67.4	2.2	2.2
1BC8	4.19	6.08	70.7	77.8	106.6	75.5	8.7	33.4	10.7	66.9	-3.5	1.0
1525	4.12	6.20	71.5	79.0	106.8	81.8	8.8	34.3	10.6	69.4	-0.5	3.8
1748	3.94	6.62	73.4	76.7	105.9	86.6	8.3	29.8	X 7.1	E 51.1	0.8	8.5
1434	4.17	6.30	66.3	72.8	100.8	76.3	8.7	32.8	10.5	64.7	-0.4	-1.3
1D88	4.22	5.68	69.1	75.4	106.1	E 96.1	X 11.6	E 40.2	11.3	74.1	3.8	5.0
1D43	4.16	5.88	X 32.9	X 38.3	95.7	E 57.4	8.4	E 23.7	10.7	X 37.6	I 9.4	-8.4

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	0	2	0	3	2	7	0	18
X	0	0	1	2	0	2	4	1	0	2	12
Data within DQOs	21	20	17	19	19	19	14	18	14	19	180
Flagged (%)	0.0	4.8	19.0	9.5	9.5	9.5	33.3	14.3	33.3	9.5	14.3

*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), 18 analytical data out of 210 exceeded the DQOs by a factor of 2 and flagged by "E". Data from 7 laboratories for Mg²⁺ were flagged by "E". 12 analytical data out of 210 exceeded the DQOs more than a factor of 2 and flagged by "X". More analytical data for cations were flagged by "E" and "X" compared with Sample No.1. 30 analytical data out of 210 were flagged by "E" and "X", it shares 14.3 percents of all reported data of sample No.2.

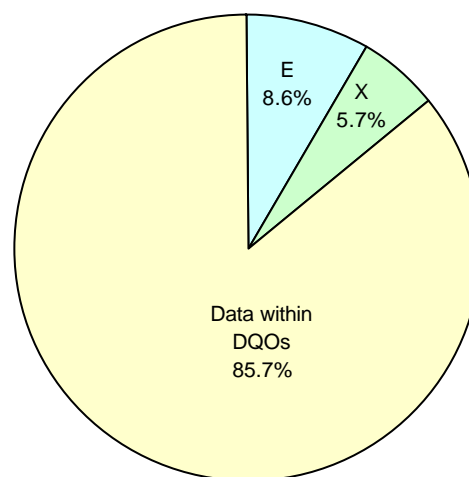


Fig.3 Percentage of flagged data for Sample No.2

Evaluation

More data for Sample No.2 (lower concentrations) were flagged "E" and "X" compared with data for Sample No.1 (higher concentrations). It indicates the difficulty of the analysis of lower concentration samples, particularly cations. Since some data were flagged by "E" or "X", the analytical skill should further be improved.

3.2 ANALYTICAL PARAMETER

pH

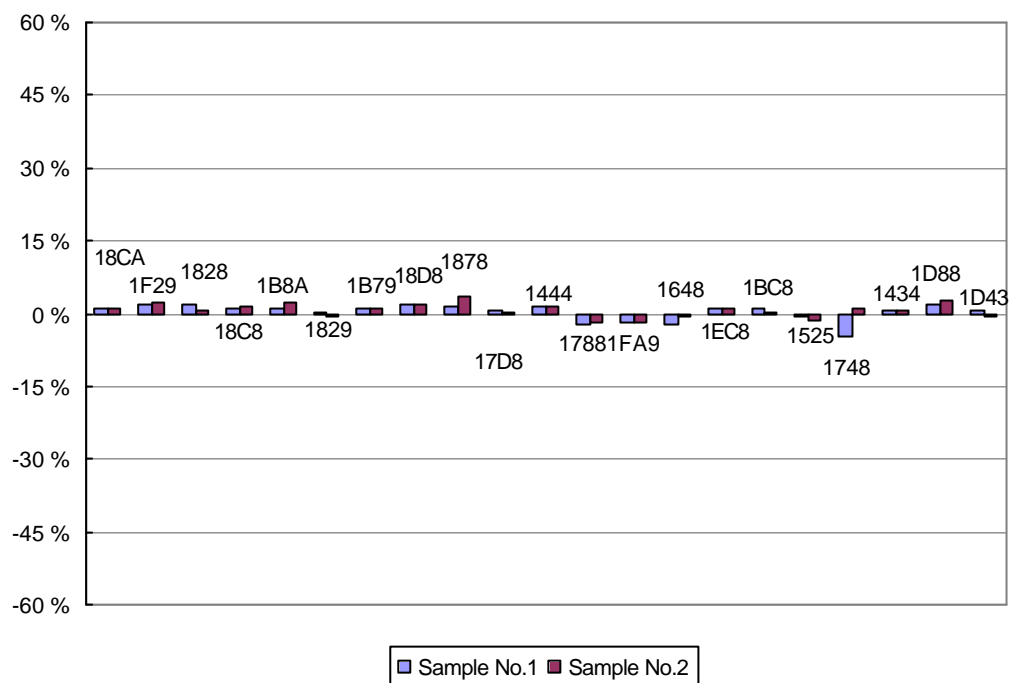


Fig.4 Distribution of pH data normalized by prepared value

Table 12 Analytical method and flagged data of pH

Analytical Method

pH meter and electrode	20/21
No Information	1/21

Flagged data

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

Most participating laboratories used pH meter with glass electrode for measurement of pH. All of obtained data were fairly agreed with prepared value.

EC

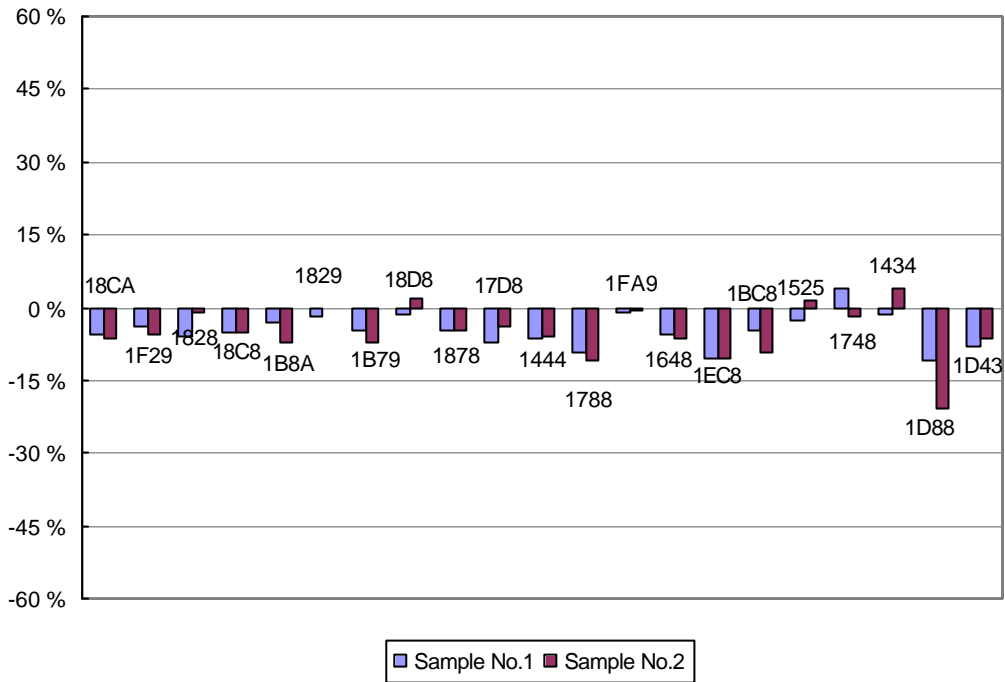


Fig.5 Distribution of EC data normalized by prepared value

Table 13 Analytical method and flagged data of EC

Analytical Method

Conductivity meter and cell	20/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	0	0	0.0
Sample No.2	1	0	4.8

Most participating laboratories used conductivity cell for the measurement of EC. Obtained data were relatively agreed with the prepared value. However, Lab.ID 1D88 submitted rather different values (for sample No.2), and flagged by “E”. Most of the laboratories reported lower data than prepared value.

SO₄²⁻

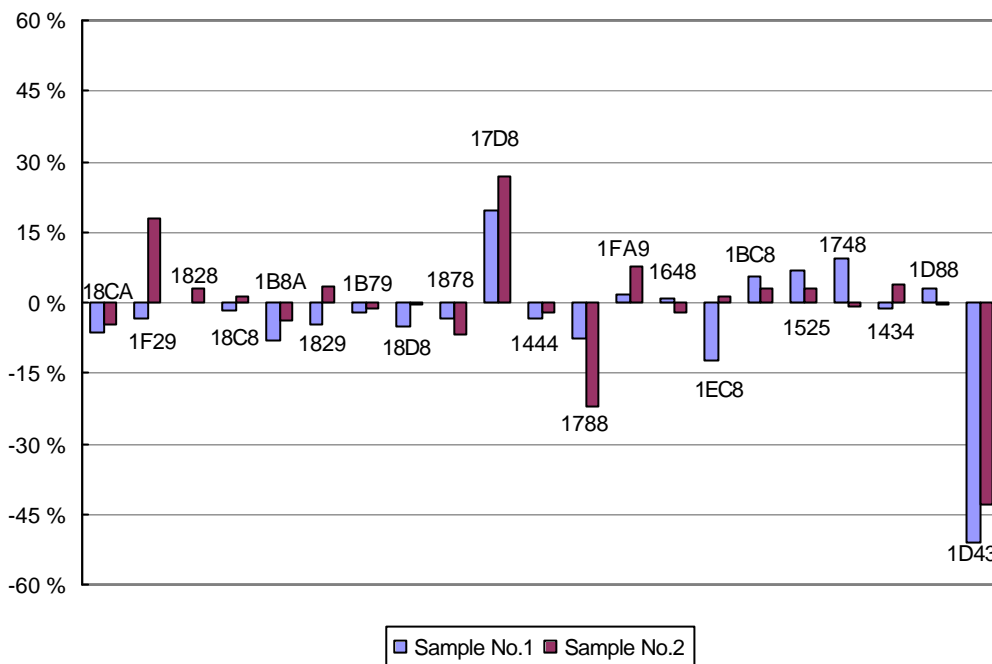


Fig.6 Distribution of SO₄²⁻ data normalized by prepared concentration

Table 14 Analytical method and flagged data of SO₄²⁻

Analytical Method

Ion chromatography	19/21
Spectrophotometry	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	1	1	9.5
Sample No.2	3	1	19.0

Most of participating laboratories employed ion chromatography for the determination of SO₄²⁻ while Lab.ID 1788 used other method (Spectrophotometry). Sample No.1 data of Lab. ID 1D43 were above 30% lower than prepared value and Lab. ID 17D8 (Ion chromatography) were above 15% higher than prepared value. Sample No.2 data of Lab. ID 1D43 were above 30% lower than prepared value and Lab.ID 1F29, 17D8 (Both the method are Ion chromatography) were above 15% higher than prepared value.

NO₃⁻

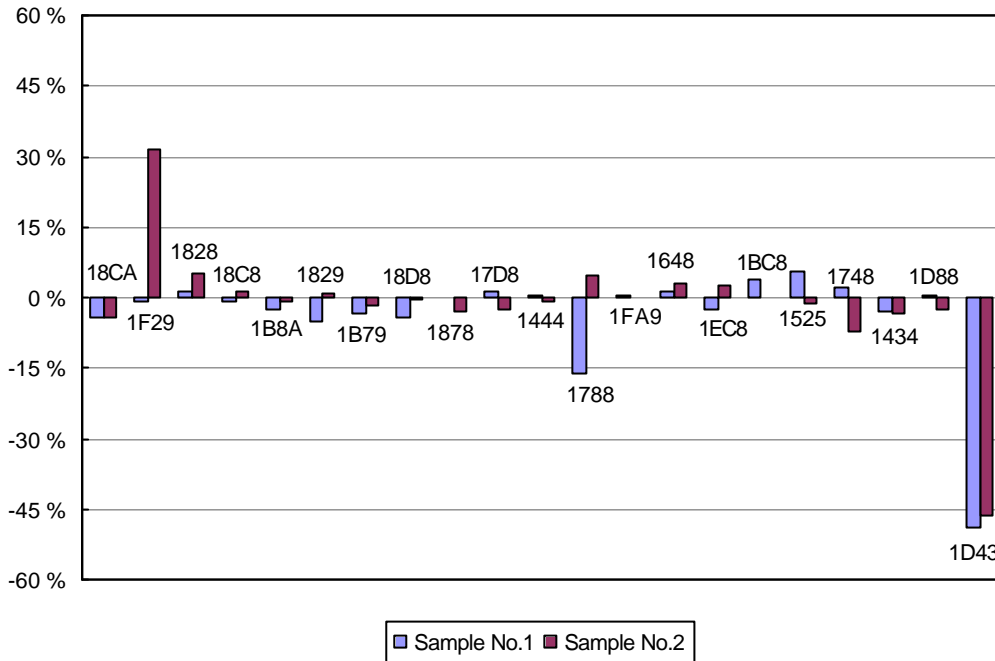


Fig.7 Distribution of NO₃⁻ data normalized by prepared concentration

Table 15 Analytical method and flagged data of NO₃⁻

Analytical Method

Ion chromatography	19/21
Spectrophotometry	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	1	1	9.5
Sample No.2	0	2	9.5

Same as SO₄²⁻, most of participating laboratories employed ion chromatography for the determination of NO₃⁻ while Lab.ID 1788 used other method (Spectrophotometry). Sample No2 data of Lab.ID 1F29 obtained above 30% higher than prepared value, though it used Ion chromatography that is employed by most of participating laboratories. Lab. ID 1D43 obtained above -30% lower than prepared value on sample No.1 and sample No.2. But there is no information on analytical method.

Cl⁻

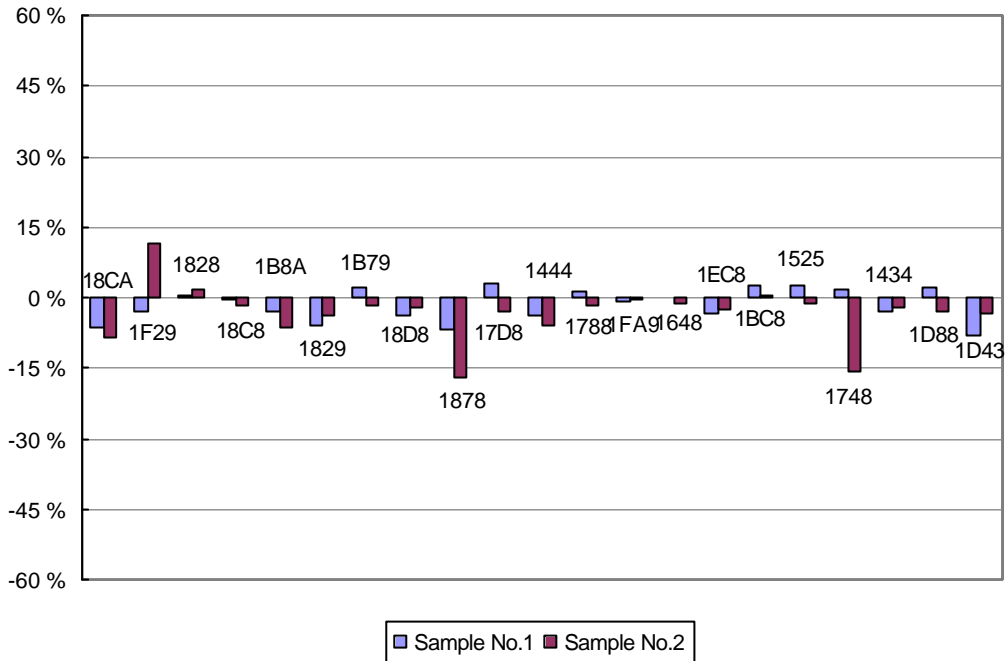


Fig.8 Distribution of Cl⁻ data normalized by prepared concentration

Table 16 Analytical method and flagged data of Cl⁻

Analytical Method

Ion chromatography	19/21
Other method	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	0	0	0.0
Sample No.2	2	0	9.5

Same as SO₄²⁻ and NO₃⁻, most laboratories used ion chromatography for the determination of Cl⁻. Sample No.2 data of Lab.ID 1878 and 1748 (Both the methods are Ion chromatography) are more than -15% lower than prepared value. Data of lab.ID 1788 (Titration by Hg(NO₃)₂) fairly agreed with prepared value.

Na⁺

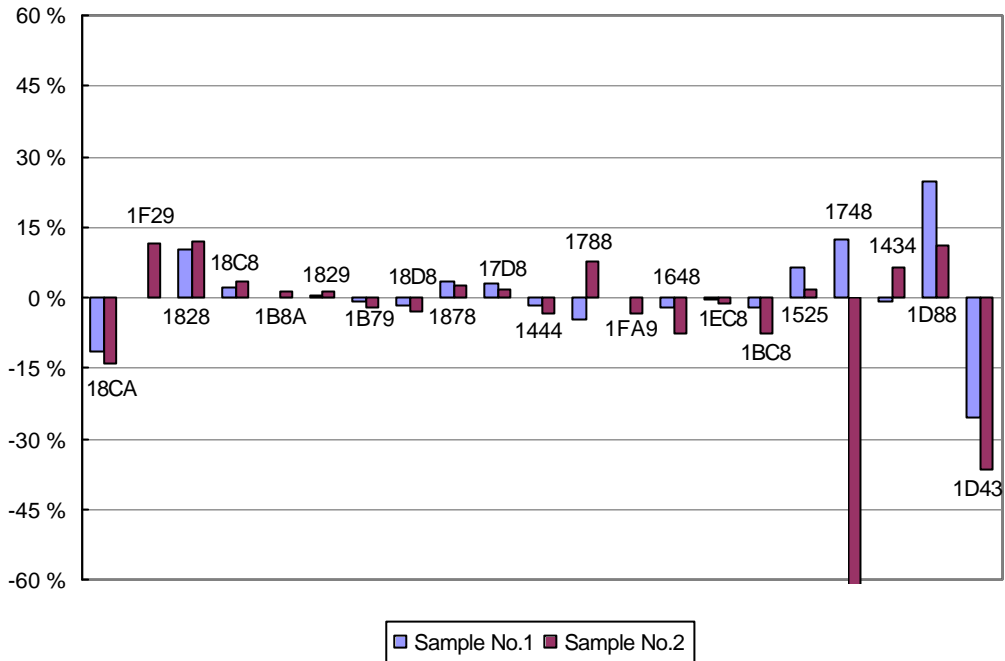


Fig.9 Distribution of Na⁺ data normalized by prepared concentration

Table 17 Analytical method and flagged data of Na⁺

Analytical Method

Ion chromatography	13/21
Atomic absorption / Flame (emission) photometry	6/21
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	2	0	9.5
Sample No.2	0	2	9.5

Among 21 participating laboratories, 13 laboratories employed ion chromatography, 6 laboratories employed atomic absorption / flame (emission) photometry, and 1 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. Sample No.2 data of Lab.ID 1748 (Atomic absorption) is quite a different value in comparison with the others.

K⁺

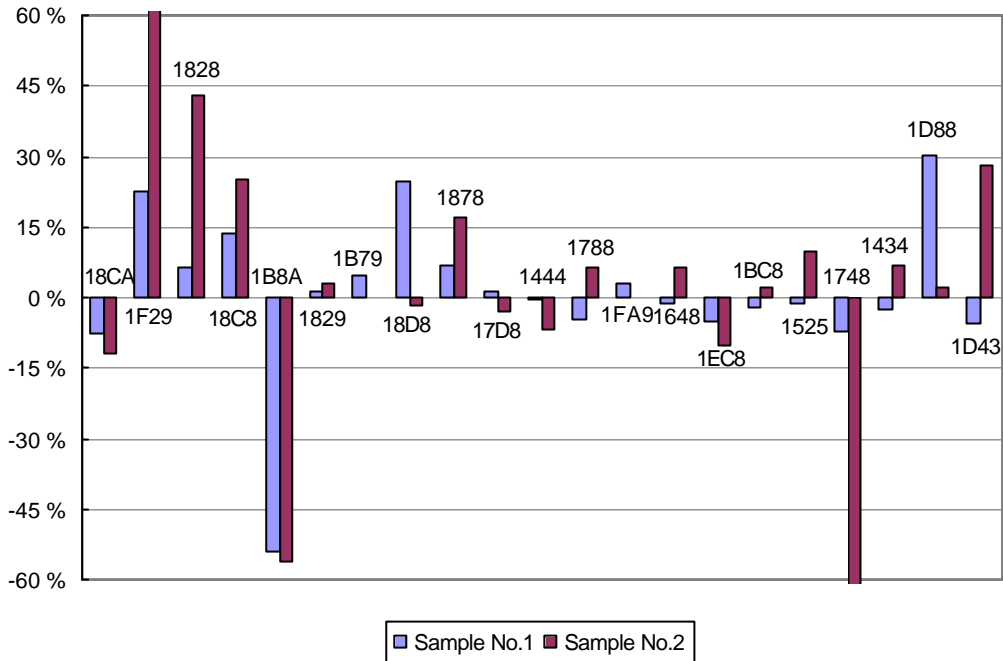


Fig.10 Distribution of K⁺ data normalized by prepared concentration

Table 18 Analytical method and flagged data of K⁺

Analytical Method

Ion chromatography	13/21
Atomic absorption / Flame (emission) photometry	6/21
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	2	2	19.0
Sample No.2	3	4	33.3

Same as Na⁺, 13 laboratories employed ion chromatography, 6 laboratories employed atomic absorption / flame (emission) photometry, and 1 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 number of flagged data were larger in comparison with the other analytical data. Sample No.2 data of lab.ID 1F29 and 1748 were far from prepared value.

Ca²⁺

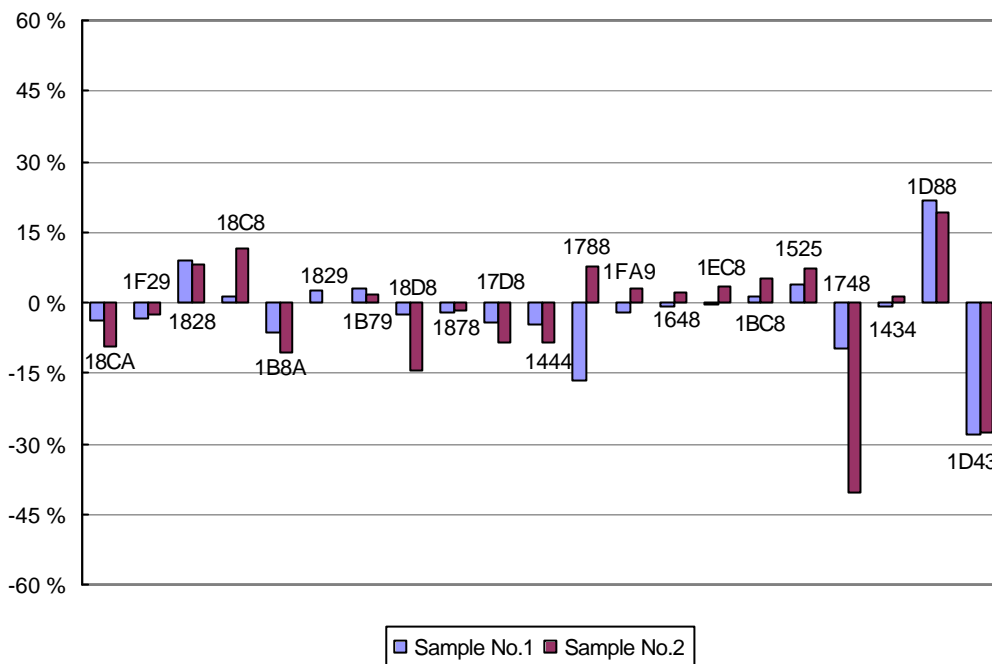


Fig.11 Distribution of Ca²⁺ data normalized by prepared concentration

Table 19 Analytical method and flagged data of Ca²⁺

Analytical Method

Ion chromatography	13/21
Atomic absorption / Flame (emission) photometry	5/21
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/21
Other method	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	3	0	14.3
Sample No.2	2	1	14.3

For the analysis of Ca²⁺, 13 laboratories employed ion chromatography, and 5 laboratories employed atomic absorption/flame (emission) photometry. The others employed inductively coupled plasma mass spectrometry (ICP-MS, Lab.ID 17D8) and Titration (Lab.ID 1788) for the determination of Ca²⁺. Lab. ID 1748 that used Atomic absorption submitted much lower data.

Mg²⁺

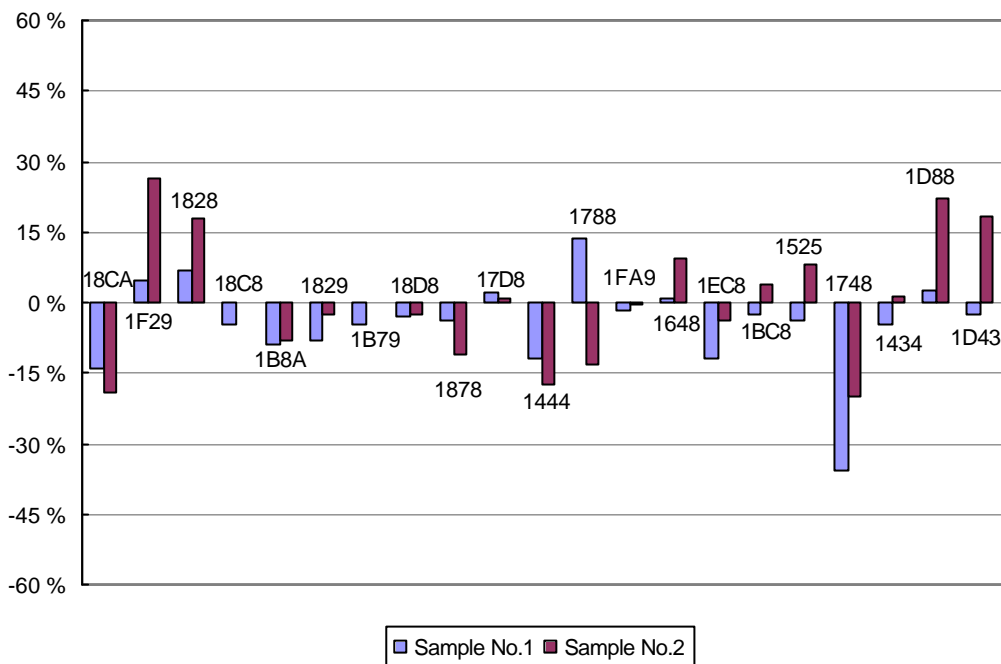


Fig.12 Distribution of Mg²⁺ data normalized by prepared concentration

Table 20 Analytical method and flagged data of Mg²⁺

Analytical Method

Ion chromatography	13/21
Atomic absorption / Flame (emission) photometry	5/21
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/21
Calculation	1/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	0	1	4.8
Sample No.2	7	0	33.3

Among 21 participating laboratories, 13 laboratories employed ion chromatography, 5 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 one laboratory determined the concentration of Mg²⁺ by calculation (Lab.ID 1788). Lab.ID 1748 that used Atomic absorption submitted rather low data.

NH₄⁺

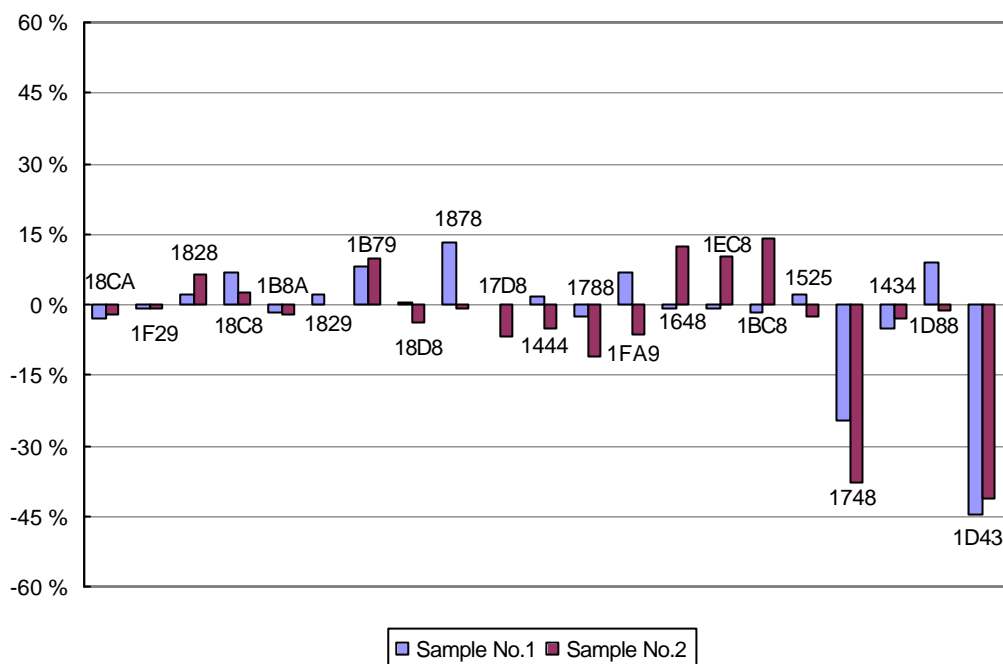


Fig.13 Distribution of NH₄⁺ data normalized by prepared concentration

Table 21 Analytical method and flagged data of NH₄⁺

Analytical Method

Ion chromatography	14/21
Spectrophotometry (Indophenol)	4/21
Spectrophotometry (Other method)	2/21
No Information	1/21

Flagged data

	E	X	Flagged (%)
Sample No.1	1	1	9.5
Sample No.2	0	2	9.5

Most of participating laboratories used recommended analytical method of EANET for the determination of NH₄⁺: 14 laboratories employed ion chromatography and 4 laboratories employed spectrophotometry(Indophenol). The data of Lab.ID 1748 (spectrophotometry) and 1D43 were flagged.

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.

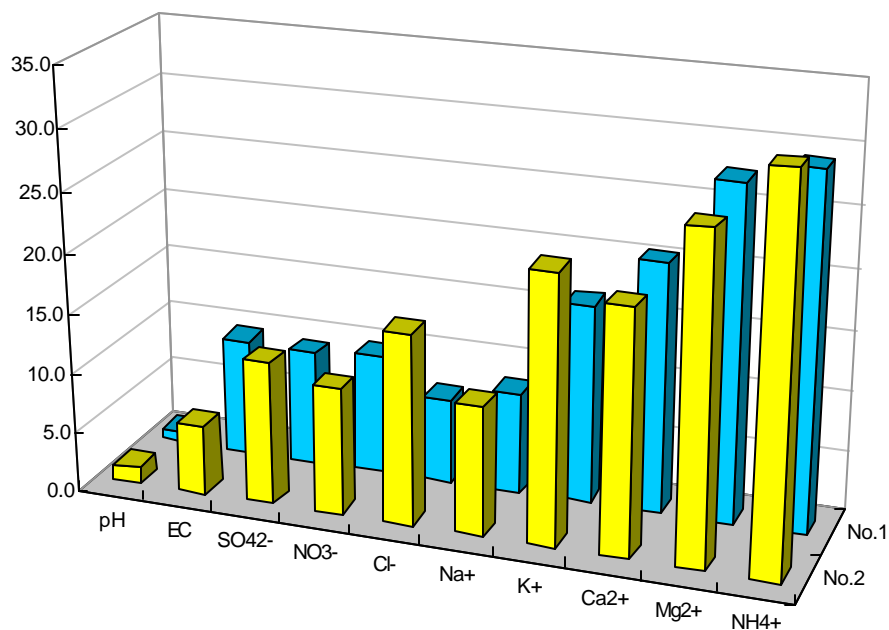


Fig.14 Relative standard deviation of each constituents

(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. In general, much difference of data was not found among different analytical methods.

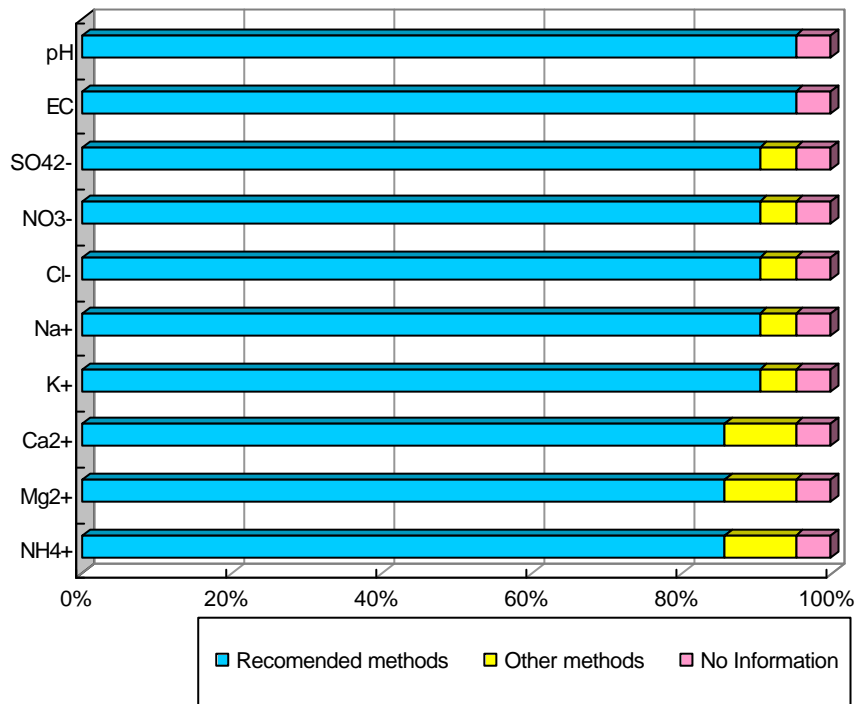


Fig.15 Ratio of recommended method used in the project

Table 22 List of methods

Code	Method
0	pH meter with electrode
1	Conductivity meter and cell
2	Acid / base titration
3	Atomic absorption / Flame photometry
4	Emission spectrography
5	Ion chromatography
6	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
7	Calculation
8	Indophenol Spectrophotometric
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	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	20									
1		20								
2										
3						6	6(1)	5	5(1)	
4										
5			19(1)	19	19	13(1)	13(3)	13(1)	13	14
6										
7										
8										4(1)
9						1	1	1	1	
10										
X			1	1(1)	1			1(1)	1	2
?	1	1	1(1)	1(1)	1	1(1)	1	1(1)	1	1(1)

Sample No.2

Method	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
0	20									
1		20(1)								
2										
3						6(1)	6(1)	5(1)	5(1)	
4										
5			19(2)	19(1)	19(2)	13	13(5)	13(1)	13(5)	14
6										
7										
8										4(1)
9						1	1	1	1	
10										
X			1(1)	1	1			1	1	2
?	1	1	1(1)	1(1)	1	1(1)	1(1)	1(1)	1(1)	1(1)

Reverse mesh is recommended method of EANET

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

Number of Staff in 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 nine 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 or pH, EC and ionic items. In most cases that more than one staff carried out the analysis of the round robin samples, anions and cations were analyzed separately by different staffs (6 laboratories out of 9 laboratories). In one laboratory, three staffs collaborated 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 ⁺
18CA	1	A	A	A	A	A	A	A	A	A	A
1F29	1	A	A	A	A	A	A	A	A	A	A
1828	2	A	A	B	B	B	B	B	B	B	B
18C8	1(?)	A	A	A	A	A	A	A	A	A	+
1B8A	1	A	A	A	A	A	A	A	A	A	A
1829	1	A	A	A	A	A	A	A	A	A	A
1B79	1	A	A	A	A	A	A	A	A	A	A
18D8	3	A	A	B	B	B	C	C	C	C	A
1878	1	A	A	A	A	A	A	A	A	A	A
17D8	4	A	A	B	B	B	C	C	C	C	D
1444	1	A	A	A	A	A	A	A	A	A	A
1788	2	A	A	B	B	B	A	A	A	A	A
1FA9	4	A	A	B	B	B	C	C	C	C	D
1648	3	A	A	A, B	A, B	A, B	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C
1EC8	2	A	B	A	A	A	A	A	A	A	A
1BC8	2	A	A	A	A	A	B	B	B	B	A
1525	1	A	A	A	A	A	A	A	A	A	A
1748	4	A	B	C	C	C	D	D	D	D	B
1434	1	A	A	A	A	A	A	A	A	A	A
1D88	+	+	+	+	+	+	+	+	+	+	+
1D43	+	+	+	+	+	+	+	+	+	+	+

“+”: 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” on analysis / measurement.

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 ⁺
18CA	1	1	1	1	1	1	1	1	1	1
1F29	11	11	11	11	11	11	11	11	11	11
1828	6	6	2	2	2	2	2	2	2	2
18C8	2	2	2	2	2	2	2	2	2	2
1B8A	15	15	15	15	15	15	15	15	15	15
1829	3	3	3	3	3	3	3	3	1	1
1B79	2	2	2	2	2	2	2	2	2	2
18D8	2	2	2	2	2	2	2	2	2	2
1878	5	5	5	5	5	5	5	5	5	5
17D8	1	1	1	1	1	1	1	1	1	1
1444	2	2	2	2	2	2	2	2	2	2
1788	15	15	5	1	5	15	15	15	15	15
1FA9	4	4	9	9	9	4	4	4	4	4
1648	8	8	8	8	8	8	8	8		8
1EC8	7	8	7	7	7	7	7	7	7	7
1BC8	5	5	5	5	5	1	1	1	1	5
1525	3	3	4	3	3	3	3	3	3	3
1748	5	5	1	1	1	1	1	1	1	5
1434	4	4	4	4	4	4	4	4	4	4
1D88	+	+	+	+	+	+	+	+	+	+
1D43	+	+	+	+	+	+	+	+	+	+

“+”: No information.

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

1 year means experienced with one year or less.

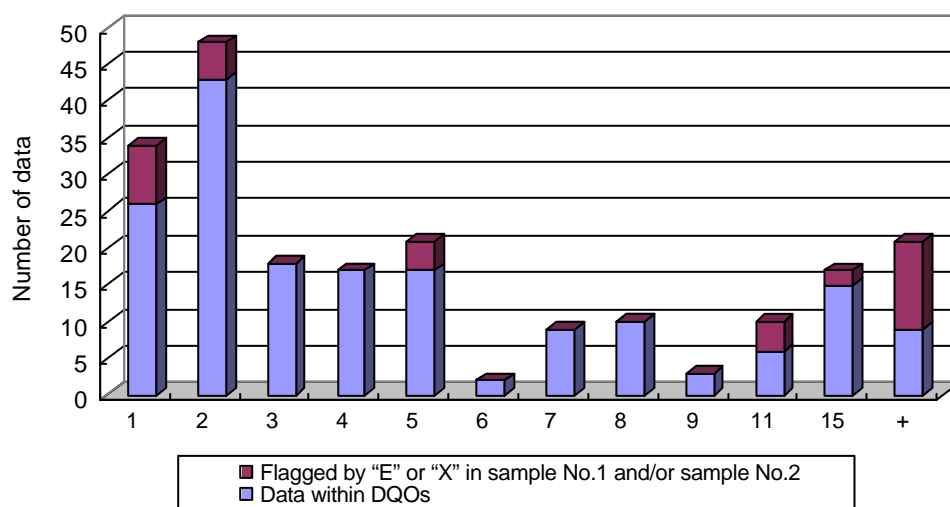


Fig.16 Relationship between flagged data and the years of experience

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 is the recommended condition by EANET. Water temperature was equal or lower than 20 degrees centigrade for four laboratories. 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
18CA	25.0	25.0	25.0	25.0
1F29	25.5	25.6	25.5	25.6
1828	25.0	25.0	25.0	25.0
18C8	24.9	24.9	25.1	25.1
1B8A	25.1-25.4	25.0-25.1	25.1-25.4	25.0-25.1
1829	22.8	22.8	22.8	22.8
1B79	24.8	24.8	24.8	24.8
18D8	25.0	25.0	25.0	25.0
1878	25.0	25.0	25.0	25.0
17D8	25.0	25.0	24.8	24.8
1444	25.0	25.0	25.0	25.0
1788	25.5	25.5	25.5	25.5
1FA9	17.0	17.0	17.0	17.0
1648	17.2	17.9	17.2	17.9
1EC8	18.0	18.0	25.0	25.0
1BC8	10.9	10.9	13.0	13.0
1525	24.3	24.3	24.3	24.3
1748	25.0	25.0	25.0	25.0
1434	25.0	25.0	25.0	25.0
1D88	25.0	25.0	25.0	E 25.0
1D43	+	+	+	+

“+”: No information.

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

Start Date of Measurement

INC sent artificial rainwater samples to participating laboratories in the end of November, 1999. Most the laboratories started measurement of samples within about three months. Fig. 17 shows number of laboratories in terms of start date and the percentage of flag “E” and “X”. Clear relationship was not found between start date and the percentage of flag “E” and “X”.

Table 27 Number of start date and flags

Start date of measurement	Number of Laboratories	Count of E	Count of X
Nov. 1999	1	1	0
Dec. 1999	3	4	4
Jan. 2000	6	1	1
Feb. 2000	8	12	5
Mar. 2000	1	0	0
Apr. 2000	1	5	1
No Information	1	5	7

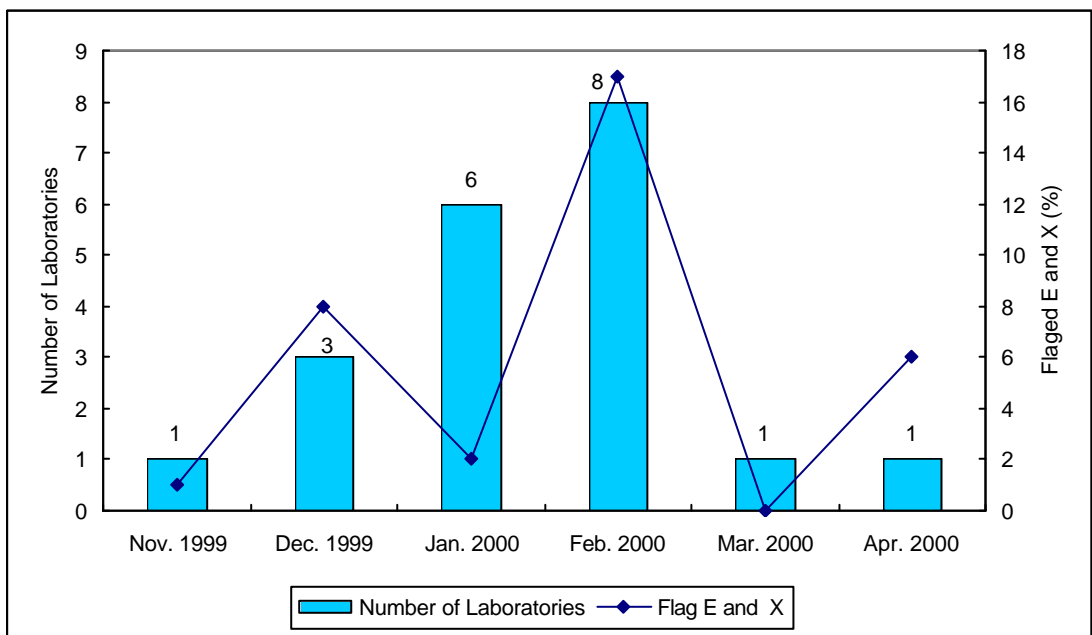


Fig.17 Start date of measurement & flag “E” and “X”

4 COMPARISON OF 1st AND 2nd INTER-LABORATORY COMPARISON

As described in Fig. 18 in the first inter-laboratory comparison project, data meeting DQOs were between 75 percents to 80 percents of whole data both for the sample No.1 and the sample No.2. Data meeting DQOs increased in the second inter-laboratory comparison project. Between 85 percents to 90 percents of whole data for the sample No.1 and the sample No.2 met DQOs, though the data submitted only from 21 laboratories. Concentration of constituents was almost same or rather lower in the second one for some ions. This remarkable improvement of results of the inter-laboratory comparison indicates the effort of each participating laboratory.

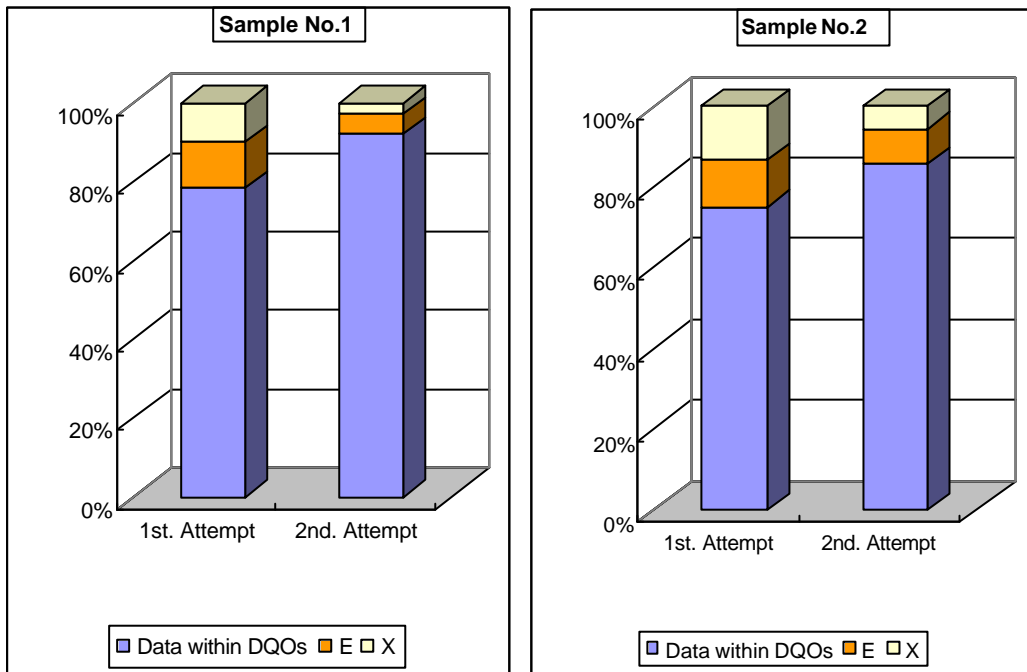


Fig.18 Comparison of 1st and 2nd inter-laboratory comparison

5. PROPOSAL FOR IMPROVEMENT OF MEASUREMENT PRECISIONS

1. Water temperature at measurement of pH and EC

Clear relationship was not found between water temperature and result of measurements. But, since measurements of pH and EC are generally influenced by water temperature, it is desirable to measure pH and EC at 25 degrees centigrade, if water bath is available.

2. Contamination of samples

Staff in charge of measurement must pay due attention to contamination of samples (a way to adequately store samples, deionized water in use, etc.). Especially, in case of low concentration samples, contamination could significantly influence results of measurement.

3. Experience of measurement

Results of measurement do not always depend on experience of measurement. But experience is very important in terms of evaluation of analyzed data, troubleshooting for equipment and so on.

4. Availability of manual and other technical documents

Manual and other technical documents must be always kept available for staff in charge of measurement. Manual and other technical documents supplement your experience of measurement. The documents that must be available include technical documents for measurement, Operation manual for equipments, Standard Operating Procedures (SOPs) for your laboratories and so on.

5. System to reduce mistakes

In order to reduce mistakes, it would be useful to establish a procedure to record and calculate the measured data, including a checking system to avoid mistakes. All the staff to work for the monitoring activities are recommended to comply with such a procedure.

6. REFERENCES

- 1) Guideline 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
- 3) Guidelines for Acid Deposition Monitoring in East Asia: The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.
- 4) Technical Documents for Wet Deposition Monitoring in East Asia: The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.
- 5) Report of the Inter-laboratory Comparison Project 1998 (Round robin analysis survey) [†] Attempt: Acid Deposition and Oxidant Research Center, November 1999.

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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	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
18CA	4.18	6.02	62.8	71.7	97.4	68.1	8.2	31.8	9.5	66.1
1F29	4.21	6.14	64.6	74.4	101.0	77.0	10.9	31.9	11.5	67.3
1828	4.21	5.99	67.1	76.0	104.2	84.7	9.5	36.0	11.7	69.5
18C8	4.19	6.04	66.0	74.3	103.4	78.6	10.1	33.4	10.5	72.5
1B8A	4.18	6.17	61.7	73.2	101.1	77.1	4.1	30.9	10.0	66.8
1829	4.15	6.26	63.9	71.3	98.0	77.2	9.0	33.9	10.1	69.5
1B79	4.18	6.07	65.7	72.6	106.2	76.2	9.3	34.0	10.5	73.5
18D8	4.21	6.28	63.7	71.9	100.2	75.6	11.1	32.2	10.7	68.4
1878	4.20	6.07	64.7	74.9	96.9	79.6	9.5	32.3	10.6	77.0
17D8	4.17	5.92	80.0	76.1	106.9	79.2	9.0	31.5	11.2	68.1
1444	4.20	5.98	64.8	75.2	99.8	75.7	8.9	31.5	9.7	69.1
1788	4.05	5.78	61.9	62.8	105.2	73.5	8.5	27.5	12.5	66.3
1FA9	4.06	6.31	68.2	75.3	103.2	77.0	9.2	32.3	10.8	72.5
1648	4.05	6.02	67.7	76.0	103.8	75.5	8.8	32.7	11.1	67.4
1EC8	4.18	5.72	58.6	73.0	100.3	76.6	8.5	32.9	9.7	67.4
1BC8	4.19	6.08	70.7	77.8	106.6	75.5	8.7	33.4	10.7	66.9
1525	4.12	6.20	71.5	79.0	106.8	81.8	8.8	34.3	10.6	69.4
1748	3.94	6.62	73.4	76.7	105.9	86.6	8.3	29.8	7.1	51.1
1434	4.17	6.30	66.2	72.8	100.8	76.3	8.7	32.8	10.5	64.7
1D88	4.22	5.68	69.1	75.4	106.1	96.1	11.6	40.2	11.3	74.1
1D43	4.16	5.88	32.9	38.3	95.7	57.4	8.4	23.7	10.7	37.6
Prepared value	4.14	6.38	67.0	75.0	104.0	77.0	8.9	33.0	11.0	68.0
Number of data	21	21	21	21	21	21	21	21	21	21
Average	4.15	6.07	65.0	72.3	102.4	77.4	9.0	32.3	10.5	66.9
Minimum	3.94	5.68	32.9	38.3	95.7	57.4	4.1	23.7	7.1	37.6
Maximum	4.22	6.62	80.0	79.0	106.9	96.1	11.6	40.2	12.5	77.0
Standard deviation	0.07	0.22	8.70	8.45	3.57	7.19	1.47	3.13	1.07	8.37

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	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
18CA	4.64	2.15	22.9	25.9	34.8	24.1	2.8	10.9	3.1	24.5
1F29	4.69	2.17	28.3	35.5	42.4	31.2	6.3	11.7	4.8	24.8
1828	4.61	2.28	24.7	28.4	38.7	31.4	4.6	12.9	4.5	26.5
18C8	4.65	2.18	24.3	27.3	37.3	28.9	4.0	13.4	3.8	25.6
1B8A	4.70	2.13	23.1	26.8	35.6	28.3	1.4	10.7	3.5	24.5
1829	4.57	2.30	24.8	27.2	36.6	28.3	3.3	12.0	3.7	25.0
1B79	4.63	2.13	23.7	26.5	37.4	27.4	3.2	12.2	3.8	27.4
18D8	4.67	2.34	23.9	26.9	37.2	27.2	3.2	10.3	3.7	24.1
1878	4.75	2.19	22.4	26.2	31.6	28.7	3.8	11.8	3.4	24.8
17D8	4.60	2.21	30.5	26.3	36.8	28.5	3.1	11.0	3.8	23.3
1444	4.66	2.16	23.5	26.8	35.7	27.1	3.0	11.0	3.1	23.7
1788	4.51	2.05	18.7	28.3	37.4	30.1	3.4	12.9	3.3	22.2
1FA9	4.50	2.29	25.8	27.0	37.8	27.1	3.2	12.4	3.8	23.4
1648	4.56	2.15	23.5	27.8	37.6	25.8	3.4	12.2	4.2	28.1
1EC8	4.63	2.06	24.3	27.7	37.0	27.7	2.9	12.4	3.7	27.6
1BC8	4.60	2.09	24.7	27.0	38.1	25.8	3.3	12.6	4.0	28.5
1525	4.53	2.33	24.7	26.7	37.6	28.4	3.5	12.9	4.1	24.4
1748	4.64	2.26	23.8	25.0	32.0	2.3	0.3	7.2	3.0	15.5
1434	4.61	2.39	24.9	26.0	37.3	29.7	3.4	12.1	3.8	24.2
1D88	4.71	1.82	23.9	26.3	36.8	31.1	3.3	14.3	4.6	24.7
1D43	4.57	2.15	13.7	14.5	36.7	17.8	4.1	8.7	4.5	14.7
Prepared value	4.59	2.30	24.0	27.0	38.0	28.0	3.2	12.0	3.8	25.0
Number of data	21	21	21	21	21	21	21	21	21	21
Average	4.62	2.18	23.8	26.7	36.8	26.5	3.3	11.7	3.8	24.2
Minimum	4.50	1.82	13.7	14.5	31.6	2.3	0.3	7.2	3.0	14.7
Maximum	4.75	2.39	30.5	35.5	42.4	31.4	6.3	14.3	4.8	28.5
Standard deviation	0.07	0.13	3.21	3.46	2.20	6.28	1.13	1.60	0.50	3.44

APPENDIX 3 Normalized value 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 ⁺ (%)
18CA	101.0	94.4	93.7	95.6	93.7	88.4	92.1	96.4	85.9	97.2
1F29	101.7	96.2	96.4	99.2	97.1	100.0	122.5	96.7	104.5	99.0
1828	101.7	93.9	100.1	101.3	100.2	110.0	106.3	109.0	106.7	102.2
18C8	101.2	94.7	98.5	99.1	99.4	102.1	113.5	101.2	95.5	106.6
1B8A	101.0	96.7	92.1	97.6	97.2	100.1	46.1	93.6	90.9	98.2
1829	100.2	98.1	95.4	95.1	94.2	100.3	101.1	102.7	91.8	102.2
1B79	101.0	95.1	98.1	96.8	102.1	99.0	104.5	103.0	95.5	108.1
18D8	101.7	98.4	95.0	95.9	96.3	98.2	124.8	97.5	96.8	100.5
1878	101.4	95.1	96.6	99.9	93.2	103.4	107.0	97.9	96.4	113.2
17D8	100.7	92.8	119.4	101.4	102.8	102.9	101.1	95.5	102.1	100.1
1444	101.4	93.7	96.7	100.3	96.0	98.3	99.6	95.5	88.2	101.6
1788	97.8	90.6	92.4	83.7	101.2	95.5	95.5	83.3	113.6	97.5
1FA9	98.1	98.9	101.8	100.4	99.3	100.0	102.9	97.8	98.2	106.6
1648	97.8	94.4	101.0	101.3	99.8	98.0	98.7	99.0	100.9	99.1
1EC8	101.0	89.7	87.5	97.3	96.4	99.5	94.9	99.6	88.1	99.1
1BC8	101.2	95.3	105.5	103.7	102.5	98.1	97.8	101.2	97.6	98.4
1525	99.5	97.1	106.8	105.4	102.7	106.3	98.7	104.0	96.4	102.1
1748	95.2	103.8	109.6	102.3	101.8	112.4	92.7	90.3	64.4	75.2
1434	100.7	98.7	98.9	97.0	96.9	99.1	97.6	99.3	95.2	95.1
1D88	101.9	89.0	103.1	100.5	102.0	124.8	130.3	121.8	102.4	109.0
1D43	100.5	92.2	49.1	51.1	92.0	74.5	94.4	71.8	97.3	55.3
Minimum	95.2	89.0	49.1	51.1	92.0	74.5	46.1	71.8	64.4	55.3
Maximum	101.9	103.8	119.4	105.4	102.8	124.8	130.3	121.8	113.6	113.2
Average	100.3	95.2	97.0	96.4	98.4	100.5	101.0	98.0	95.6	98.4

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 ⁺ (%)
18CA	101.1	93.5	95.4	95.9	91.6	86.1	88.1	90.8	80.8	98.0
1F29	102.2	94.3	117.9	131.5	111.6	111.4	196.9	97.5	126.3	99.2
1828	100.4	99.1	103.0	105.2	101.9	112.0	142.9	107.9	117.8	106.2
18C8	101.3	94.8	101.3	101.1	98.2	103.2	125.0	111.7	100.0	102.4
1B8A	102.4	92.6	96.3	99.3	93.7	101.1	43.8	89.2	92.1	98.0
1829	99.6	100.0	103.3	100.7	96.3	101.1	103.1	100.0	97.4	100.0
1B79	100.9	92.6	98.8	98.1	98.4	97.9	100.0	101.7	100.0	109.6
18D8	101.7	101.7	99.8	99.8	97.9	97.0	98.4	85.5	97.4	96.3
1878	103.5	95.2	93.3	97.0	83.2	102.5	117.2	98.3	88.9	99.2
17D8	100.2	96.1	127.0	97.4	96.9	101.7	97.2	91.4	101.1	93.3
1444	101.5	93.9	97.9	99.3	93.9	96.8	93.1	91.7	82.6	94.8
1788	98.3	89.1	77.9	104.8	98.4	107.5	106.3	107.5	86.8	88.8
1FA9	98.0	99.6	107.5	99.9	99.5	96.8	100.0	103.2	99.5	93.6
1648	99.3	93.5	97.7	103.1	98.8	92.2	106.6	101.9	109.2	112.3
1EC8	100.9	89.6	101.2	102.6	97.2	98.9	89.7	103.3	96.1	110.3
1BC8	100.2	90.9	102.9	100.0	100.3	92.3	102.2	105.2	103.9	114.0
1525	98.7	101.4	103.0	98.9	98.8	101.5	110.0	107.3	108.2	97.6
1748	101.1	98.3	99.2	92.6	84.2	8.1	8.4	59.7	80.0	62.0
1434	100.4	104.0	103.8	96.4	98.0	106.2	106.8	101.2	101.2	97.0
1D88	102.6	79.1	99.6	97.4	96.8	111.1	102.2	119.2	122.1	98.6
1D43	99.6	93.5	57.1	53.7	96.6	63.6	128.1	72.5	118.4	58.8
Minimum	98.0	79.1	57.1	53.7	83.2	8.1	8.4	59.7	80.0	58.8
Maximum	103.5	104.0	127.0	131.5	111.6	112.0	196.9	119.2	126.3	114.0
Average	100.7	94.9	99.0	98.8	96.8	94.7	103.1	97.5	100.5	96.7

APPENDIX 4 Manufacturer's name and model of instruments

Lab.ID	pH meter	
18CA	HORIBA	F-8E
1F29	HORIBA	F-13
1828	TOA	HM-30V
18C8	TOA	HM-30G
1B8A	TOA	HM-30S
1829	HORIBA	L-7LC
1B79	TOA	HM-30S
18D8	HORIBA	F-21
1878	TOA	HM-60G
17D8	JADAU	HM-305
1444	HORIBA	F-24
1788	HACH	CO 150 USA
1FA9	XIMEN Analytical Instrument Factory	PHS-301
1648	Mettler-Toledo Instruments (Shanghai) Ltd.	320
1EC8	Dengfeng Analytical instrument	DF808A
1BC8	Shanghai Second Analytical Instrument Inc.	PHS-3
1525	TOA	HM-30V
1748	ORION	250A
1434	HORIBA	F21
1D88	Fisher Scinentific	accumet medol 50
1D43	No Information	No Information

Lab.ID	EC meter	
18CA	HORIBA	DS-12
1F29	DKK	AOL-40
1828	TOA	CM-11P
18C8	TOA	CM-30G
1B8A	TOA	CM-30V
1829	TOA	CM-20S
1B79	TOA	CM-40S
18D8	TOA	CM-14D
1878	TOA	CM-60G
17D8	HANNA	H1 9032
1444	HOIRBA	DS-15
1788	HACH	EC10 USA
1FA9	Shanghai LeiCi Instrument	DDS-307
1648	TOA	CM-60S
1EC8	Shanghai LeiCi Instrument	DDS-307
1BC8	Shanghai LeiCi Instrument	DDS-11C
1525	TOA	CM-40S
1748	HACH	44600-00
1434	HORIBA	ES-12
1D88	ORION	Model 150
1D43	No Information	No Information

Lab.ID	SO ₄ ²⁻ NO ₃ ⁻		
18CA	IC	YOKOGAWA	IC-7000
1F29	IC	YOKOGAWA	IC-7000
1828	IC	DIONEX	DX-120
18C8	IC	SHIMADZU	LC-10AD, CTO-10A, CDD-6A
1B8A	IC	DIONEX	DX-500
1829	IC	DIONEX	2000i/ sp
1B79	IC	DIONEX	4000i
18D8	IC	ECONOVA	Milihrom A-02
1878	IC	DIONEX	DX-500
17D8	IC	DIONEX	DX-500
1444	IC	YOKOGAWA	IC7000
1788	Others	HEWLETT PACKARD	HP 8453
1FA9	IC	DIONEX	DX-300
1648	IC	DIONEX	DIONEX-2120i
1EC8	IC	SHIMADZU	CDD-6A
1BC8	IC	DIONEX	DIONEX 16
1525	IC	DIONEX	DX-100
1748	IC	DIONEX	DX-5000
1434	IC	WATERS	432/ 717/ 626
1D88	IC	DIONEX	500
1D43		No Information	No Information

Lab.ID	Cl ⁻		
18CA	IC	YOKOGAWA	IC-7000
1F29	IC	YOKOGAWA	IC-7000
1828	IC	DIONEX	DX-120
18C8	IC	SHIMADZU	LC-10AD, CTO-10A, CDD-6A
1B8A	IC	DIONEX	DX-500
1829	IC	DIONEX	2000i/ sp
1B79	IC	DIONEX	4000i
18D8	IC	ECONOVA	Milihrom A-02
1878	IC	DIONEX	DX-500
17D8	IC	DIONEX	DX-500
1444	IC	YOKOGAWA	IC7000
1788	Others	Titration by Hg (NO3)2	No Information
1FA9	IC	DIONEX	DX-300
1648	IC	DIONEX	DIONEX-2120i
1EC8	IC	SHIMADZU	CDD-6A
1BC8	IC	DIONEX	DIONEX 16
1525	IC	DIONEX	DX-100
1748	IC	DIONEX	DX-5000
1434	IC	WATERS	432/ 717/ 626
1D88	IC	DIONEX	500
1D43		No Information	No Information

Lab.ID	Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺		
18CA	IC	DIONEX	DX500
1F29	IC	YOKOGAWA	IC7000
1828	IC	DIONEX	DX-120
18C8	IC	SHIMADZU	LC-10ADvp, CTO-10Avp, CDD-6A
1B8A	IC	DIONEX	DX-500
1829	AA	PERKIN ELMER	Aanalyst 800
1B79	IC	DIONEX	DX-120
18D8	Flam	CARL ZEISS JENA	AAS-30
1878	IC	DIONEX	DX-500
17D8	Others	PERKIN ELMER	ELAN 6000
1444	IC	DIONEX	DX-500
1788	Others	JENWAY	PFP 7
1FA9	IC	HITACHI	Z-8000
1648	IC	DIONEX	DIONEX-2120i
1EC8	IC	SHIMADZU	CDD-6A
1BC8	AA	SHIMADZU	AA-680G
1525	IC	DIONEX	DX-100
1748	AA	No Information	No Information
1434	IC	WATERS	432/ 717/ 626
1D88	IC	DIONEX	500
1D43		No Information	No Information

Lab.ID	NH ₄ ⁺		
18CA	IC	DIONEX	DX500
1F29	IC	YOKOGAWA	IC7000
1828	IC	DIONEX	DX-120
18C8	IC	SHIMADZU	LC-10ADvp, CTO-10Avp, CDD-6A
1B8A	IC	DIONEX	DX-500
1829	SP	SHIMADZU	UV-150-02
1B79	IC	DIONEX	DX-120
18D8	SP	Philips	UV / Visible Spectrophotometry PV8700
1878	IC	DIONEX	DX-500
17D8	SP	BRAN & LUEBBE	TRAACS MODEL 800 AUTOANALYSER
1444	IC	DIONEX	DX500
1788	Others	HEWLETT PACKARD	HP 8453
1FA9	SP	Xiamen Analitical Instrument	7230
1648	IC	DIONEX	DIONEX-2120i
1EC8	IC	SHIMADZU	CDD-6A
1BC8	IC	DIONEX	DIONEX 16
1525	IC	DIONEX	DX-100
1748	SP	SHIMADZU	UV-120-02
1434	IC	WATERS	432/ 717/ 626
1D88	IC	DIONEX	500
1D43		No Information	No Information

SP : Spectrophotometry