

The Network Center for  
the Acid Deposition Monitoring Network in East Asia

# **Report of the Inter-laboratory Comparison Project 2000 on Wet Deposition**

**3rd. Attempt**

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Acid Deposition and Oxidant Research Center

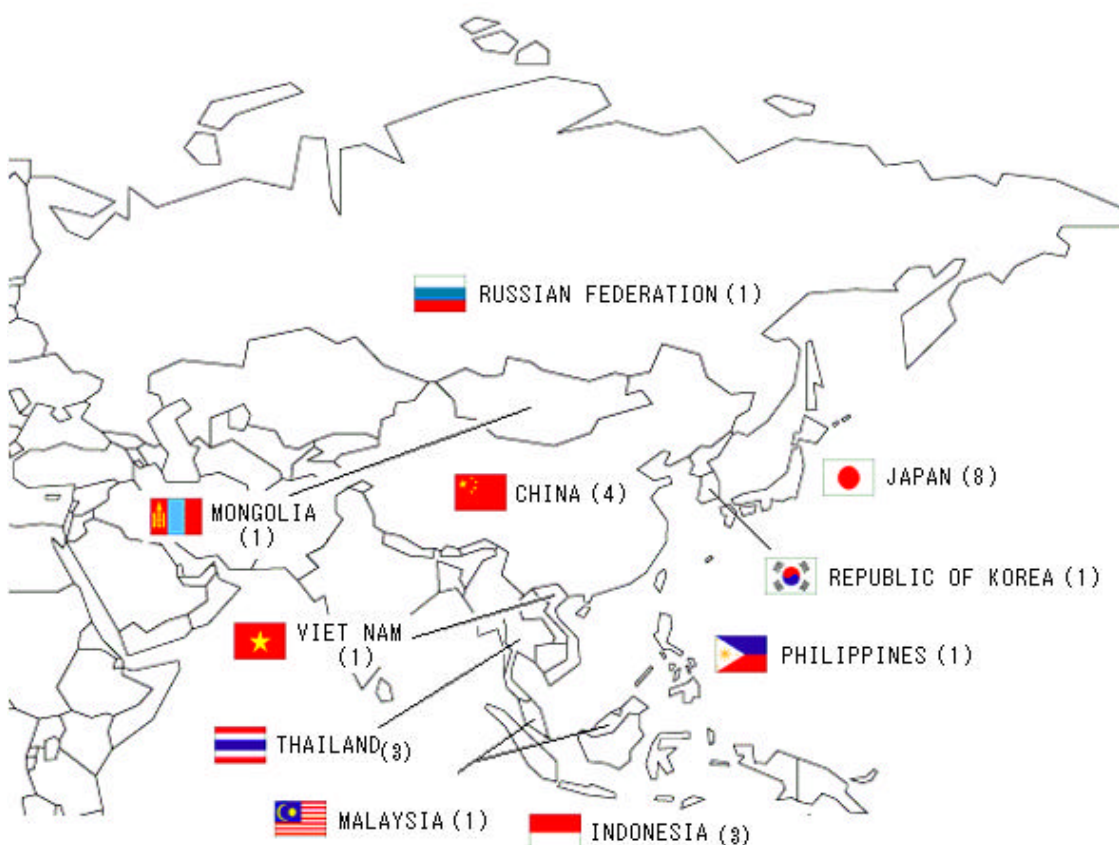
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## 1. INTRODUCTION

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 EANET. The purposes of this project are, 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 Network Center (NC). All of the participating laboratories submitted their analytical data to NC. Obtained data for pH, EC and concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  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

Twenty-four laboratories in charge of chemical analysis of the participating countries of EANET participated in this survey. Four laboratories that have much experience on acid deposition monitoring cooperatively participated in this survey. Network Center (NC) shipped the artificial rainwater samples to all of these 28 laboratories, and all of them submitted their analytical data to NC. The names and contact addresses of the participating laboratories are presented in APPENDIX 1.

### 2.2 Dispatched Rainwater Samples

Two kinds of artificial rainwater samples (higher concentration and lower concentration) are distributed to the laboratories.(See Table 1) 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 sulfate, nitrate, chloride, sodium-ion, potassium-ion, calcium-ion, magnesium-ion and ammonium 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 <sub>4</sub> <sup>2-</sup>	micro mole/liter	μ mol /L
NO <sub>3</sub> <sup>-</sup>	micro mole/liter	μ mol /L
Cl <sup>-</sup>	micro mole/liter	μ mol /L
Na <sup>+</sup>	micro mole/liter	μ mol /L
K <sup>+</sup>	micro mole/liter	μ mol /L
Ca <sup>2+</sup>	micro mole/liter	μ mol /L
Mg <sup>2+</sup>	micro mole/liter	μ mol /L
NH <sub>4</sub> <sup>+</sup>	micro mole/liter	μ mol /L

**Table 3 Concentration range of the artificial rainwater samples\***

Parameter	Range	Parameter	Range
pH	4.0– 5.5	Na <sup>+</sup>	1 – 100 μ mol /L
EC	1.0 – 10.0 mS/m	K <sup>+</sup>	1 – 50 μ mol /L
SO <sub>4</sub> <sup>2-</sup>	10 – 100 μ mol /L	Ca <sup>2+</sup>	1 – 50 μ mol /L
NO <sub>3</sub> <sup>-</sup>	10 – 100 μ mol /L	Mg <sup>2+</sup>	1 – 50 μ mol /L
Cl <sup>-</sup>	10 – 150 μ mol /L	NH <sub>4</sub> <sup>+</sup>	10 – 100 μ mol /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 Wet Deposition Monitoring in East Asia” and “QA/QC Program for Wet Deposition Monitoring in East Asia”. 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 <sub>4</sub> <sup>2-</sup> NO <sub>3</sub> <sup>-</sup> Cl <sup>-</sup>	Ion Chromatography Spectrophotometry
Na <sup>+</sup> K <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup>	Ion Chromatography Atomic Absorption/Emission Spectrometry
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography 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**:  $\mu \text{ mol L}^{-1}$ ).

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

$n$ ,  $C_{\text{Ai}}$ : 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**:  $\mu \text{ mol L}^{-1}$ ).

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

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

(3) Calculation of ion balance ( $R_1$ )

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

(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 Documents for Wet Deposition Monitoring in East Asia (2000)"

**b) Comparison between calculated and measured electrical conductivity (R<sub>2</sub>)**

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

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

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 (R<sub>2</sub>) of calculations ( calc) to measurements( meas) in electric conductivity should be calculated as follows;

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

(3) R<sub>2</sub>, 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 R<sub>2</sub> is not within the range.

**Table 6 Allowable ranges for R<sub>2</sub> in different concentration ranges**

meas (mS/m)	R <sub>2</sub> (%)
< 0.5	+ 20 ~ - 20
0.5 ~ 3	+ 13 ~ - 13
> 3	+ 9 ~ - 9

(Reference) "Technical Documents for Wet Deposition Monitoring in East Asia (2000)"



### 3. RESULTS

The 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  $\pm 10\%$ .  $\text{NH}_4^+$  gave rather varied data than others in both samples.

**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	4.10	4.12	0.04	23	4.06	4.19
EC(mS/m)	6.23	6.05	0.29	24	5.60	6.88
$\text{SO}_4^{2-}$ ( $\mu\text{ mol/L}$ )	59.7	59.7	3.12	21	51.2	65.1
$\text{NO}_3^-$ ( $\mu\text{ mol/L}$ )	63.3	63.9	3.60	23	53.5	73.6
$\text{Cl}^-$ ( $\mu\text{ mol/L}$ )	101.3	100.2	3.97	22	90.9	109.4
$\text{Na}^+$ ( $\mu\text{ mol/L}$ )	51.3	50.0	3.01	22	41.6	56.6
$\text{K}^+$ ( $\mu\text{ mol/L}$ )	9.9	9.8	0.75	22	8.5	11.2
$\text{Ca}^{2+}$ ( $\mu\text{ mol/L}$ )	29.4	29.2	1.69	22	26.3	33.4
$\text{Mg}^{2+}$ ( $\mu\text{ mol/L}$ )	11.7	11.6	0.61	21	10.2	12.8
$\text{NH}_4^+$ ( $\mu\text{ mol/L}$ )	60.5	63.1	7.18	23	51.7	83.0
[Sample No.2] pH	4.85	4.90	0.07	22	4.80	5.09
EC(mS/m)	1.55	1.56	0.09	22	1.35	1.73
$\text{SO}_4^{2-}$ ( $\mu\text{ mol/L}$ )	20.1	20.4	1.72	23	17.7	25.4
$\text{NO}_3^-$ ( $\mu\text{ mol/L}$ )	27.5	27.8	1.04	21	25.8	30.0
$\text{Cl}^-$ ( $\mu\text{ mol/L}$ )	15.5	15.5	1.38	21	12.3	19.1
$\text{Na}^+$ ( $\mu\text{ mol/L}$ )	8.7	8.9	1.04	22	7.1	11.7
$\text{K}^+$ ( $\mu\text{ mol/L}$ )	4.9	4.8	0.47	22	3.7	5.5
$\text{Ca}^{2+}$ ( $\mu\text{ mol/L}$ )	11.0	10.9	0.76	21	9.2	12.6
$\text{Mg}^{2+}$ ( $\mu\text{ mol/L}$ )	7.8	7.5	0.67	23	5.6	8.4
$\text{NH}_4^+$ ( $\mu\text{ mol/L}$ )	18.2	19.2	6.20	24	2.5	36.4

(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 DQOs value: the flag "E" was put to the data that exceed by a factor of 2 of the DQOs ( $\pm 15\% \sim \pm 30\%$ ), and the flag "X" was put to the data that exceed more than a factor of 2 of the DQOs ( $< -30\%$  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”.

### 3.1 Comparison by Sample

#### Sample No.1 (higher concentrations)

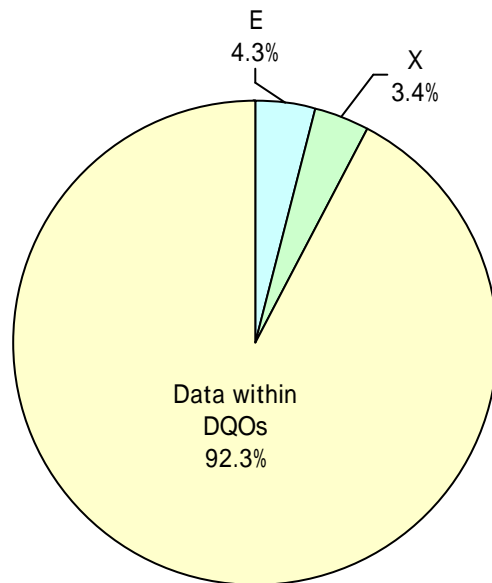
**Table 8 Number of flagged data for the Sample No.1 (higher concentrations)**

Flag*	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Total
E	0	0	2	2	1	2	0	0	1	2	10
X	1	0	1	1	0	0	0	1	1	3	8
Data within DQOs	23	24	21	21	23	21	22	22	21	19	217
Flagged (%)	4.2	0.0	12.5	12.5	4.2	8.7	0.0	4.3	8.7	20.8	7.7

\*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), 10 analytical data out of 235 exceeded the DQOs by a factor of 2 and flagged by "E". 8 analytical data out of 235 exceeded the DQOs more than a factor of 2 and flagged by "X". Flagged by "E" and "X" data were 18 out of 235, it shares about 7.7 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 <sub>4</sub> <sup>2-</sup> (μ mol/L)	NO <sub>3</sub> <sup>-</sup> (μ mol/L)	Cl <sup>-</sup> (μ mol/L)	Na <sup>+</sup> (μ mol/L)	K <sup>+</sup> (μ mol/L)	Ca <sup>2+</sup> (μ mol/L)	Mg <sup>2+</sup> (μ mol/L)	NH <sub>4</sub> <sup>+</sup> (μ mol/L)	R1	R2
	-										-	-
1B8A	4.11	6.11	57.2	63.7	93.4	48.7	9.8	26.3	10.2	60.0	-0.4	-1.1
18C8	4.12	6.01	58.9	63.9	102.1	48.1	8.5	29.7	11.7	63.8	-0.8	0.6
1B79	4.13	5.86	57.4	61.2	101.3	46.6	9.4	29.7	11.5	63.2	-0.3	0.9
1F29	4.19	6.01	57.0	62.6	100.0	53.3	10.0	27.8	11.3	59.4	-2.1	-3.4
1829	4.11	6.10	60.3	64.0	101.0	50.9	9.0	28.7	12.8	56.1	-1.6	0.2
1878	4.14	5.96	59.0	63.6	100.0	52.9	10.2	28.7	11.8	E 70.1	0.9	0.5
1AB9	4.09	6.07	E 44.1	61.9	98.9	51.2	9.2	29.6	11.6	59.3	6.4	-0.7
1444	4.14	5.88	59.9	63.0	96.9	49.7	10.0	29.2	11.6	63.2	-0.5	0.5
1828	4.16	6.03	58.5	64.1	97.6	51.8	10.1	29.3	11.7	59.6	-1.1	-1.9
14D4	4.17	6.72	51.2	E 53.5	105.8	50.8	no data	33.4	E 15.1	X 83.0	no data	no data
1D43	4.19	5.94	57.2	59.7	97.4	51.2	10.5	31.3	11.5	55.8	-0.7	-3.1
1929	X 2.70	5.60	63.2	E 73.6	217.5	no data	no data	no data	no data	X 97.0	no data	no data
1788	4.09	6.73	X 91.6	X 27.8	E 72.0	E 37.4	8.5	X 40.1	X 18.0	51.7	2.1	-2.8
1525	4.14	5.80	64.9	67.6	90.9	52.2	9.7	31.0	11.1	63.9	-1.0	2.0
17D8	4.09	5.85	E 77.5	67.4	106.2	56.6	10.9	30.2	12.6	59.6	-5.6	6.6
18D8	4.10	6.10	61.7	66.7	103.6	49.6	9.8	27.0	12.5	63.4	-2.2	1.4
1EC8	4.13	6.00	58.1	64.1	100.6	50.3	10.6	31.3	11.7	60.9	0.2	0.2
1FA9	4.08	5.98	65.1	66.1	109.4	E 41.6	10.8	27.1	11.1	57.5	-6.3	3.5
1BC8	4.12	5.90	58.6	62.6	100.7	46.1	10.1	29.3	11.6	64.3	-0.4	1.3
1648	4.12	5.99	59.9	64.1	103.1	46.5	9.5	31.1	12.2	64.0	-0.8	1.2
1748	4.19	6.00	60.4	63.5	98.9	51.0	9.6	27.9	10.8	X 80.4	0.0	-1.7
1D88	4.13	5.86	60.4	61.9	98.7	51.7	11.2	29.0	12.1	62.2	0.0	1.4
1434	4.06	5.93	60.4	62.5	100.0	51.3	8.6	28.3	10.9	58.7	0.1	4.0
1442	4.06	6.88	64.8	67.9	98.0	48.3	9.1	27.0	11.5	E 72.4	-0.3	-2.1

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)**

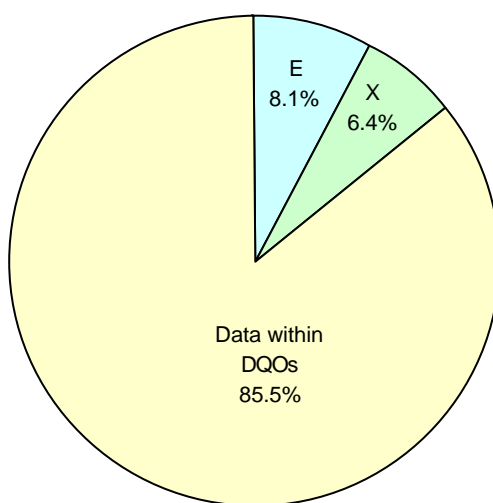
**Table 10 Number of flagged data for the Sample No.2 (lower concentrations)**

Flag*	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Total
E	0	2	2	1	2	5	1	1	3	2	19
X	1	0	1	2	3	2	0	2	0	4	15
Data within DQOs	23	22	21	21	19	16	21	20	20	18	201
Flagged (%)	4.2	8.3	12.5	12.5	20.8	30.4	4.5	13.0	13.0	25.0	14.5

\*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), 19 analytical data out of 235 exceeded the DQOs by a factor of 2 and flagged by "E". For Na<sup>+</sup>, data from 5 laboratories were flagged by "E". 15 analytical data out of 235 exceeded the DQOs more than a factor of 2 and flagged by "X". "E" and "X" were flagged to 34 analytical data out of 235, it shares 14.5 percents of all reported data of sample No.2.



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

**Evaluation**

Number of flagged data for Sample No.2 was about twice in the rate of flagged data as compared with Sample No.1. It indicates the difficulty of the analysis of lower concentration sample, particularly for Cl<sup>-</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>. The data of NH<sub>4</sub><sup>+</sup> included a high rate(>20%) of the flagged data for the both concentration samples .

**Table 11 Analytical Results of Sample No.2**

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	R1	R2
	-	(mS/m)	(μ mol/L)	(μ mol/L)	(μ mol/L)	(μ mol/L)	(μ mol/L)	(μ mol/L)	(μ mol/L)	(μ mol/L)	-	-
1B8A	4.83	1.56	19.2	27.4	14.0	8.7	4.2	10.5	7.4	20.2	2.4	-0.2
18C8	4.87	1.56	19.9	28.0	16.0	8.4	4.3	12.5	8.2	18.6	1.4	0.0
1B79	4.88	1.35	19.3	26.5	15.2	7.8	4.2	11.0	7.7	19.0	0.7	5.2
1F29	4.96	1.51	20.3	28.9	17.3	X 11.7	4.9	E 9.2	7.4	19.0	-4.2	-1.3
1829	4.82	1.60	19.7	27.1	15.2	9.2	4.3	11.4	7.8	17.7	1.8	-0.6
1878	4.95	1.51	20.1	27.1	15.7	8.4	5.0	10.9	7.8	18.5	-1.5	-1.8
1AB9	4.83	1.56	20.3	27.7	16.1	8.3	4.4	11.5	7.7	17.3	-0.8	0.7
1444	4.91	1.49	19.9	27.4	14.7	8.5	4.9	11.2	7.8	18.3	0.1	-0.1
1828	4.94	1.53	19.7	27.4	16.0	8.8	5.5	11.3	8.4	18.6	0.5	-1.8
14D4	5.22	1.69	17.7	E 22.2	X 23.5	E 10.2	no data	X 14.9	E 6.4	X 36.4	no data	no data
1D43	5.01	1.55	19.7	26.7	E 19.1	9.4	5.4	10.6	E 5.6	15.9	-7.8	-5.7
1929	X 3.18	E 2.00	X 27.9	X 44.4	X 89.1	no data	no data	no data	no data	X 28.7	no data	no data
1788	4.98	1.66	E 25.4	X 12.8	X 26.9	X 21.7	4.3	X 23.2	E 6.3	X 2.5	4.0	-2.7
1525	4.94	1.56	21.9	29.6	16.1	9.2	5.3	12.6	8.2	18.4	-2.1	-0.5
17D8	4.86	1.53	E 25.2	28.7	14.8	8.9	5.2	10.7	8.0	16.5	-6.9	2.9
18D8	4.83	1.57	21.0	30.0	15.7	E 7.1	4.5	11.0	8.4	19.3	-1.9	1.6
1EC8	4.92	1.53	19.6	28.6	15.4	8.3	4.9	9.9	7.5	16.6	-4.1	-2.5
1FA9	4.81	1.50	21.5	29.4	17.6	E 7.3	5.4	10.2	7.2	16.8	-6.1	4.1
1BC8	4.86	1.40	19.3	27.9	15.2	E 10.3	5.1	10.5	7.7	E 14.3	-1.1	3.7
1648	4.86	1.51	19.3	27.9	15.1	E 10.4	4.8	10.4	7.9	18.6	1.6	1.0
1748	5.09	1.70	19.9	27.8	E 12.3	8.8	4.8	10.1	7.0	X 32.4	5.0	-9.4
1D88	4.91	E 1.18	19.7	27.0	14.1	9.8	5.3	11.2	7.9	20.3	3.2	12.0
1434	4.85	1.64	20.7	25.8	15.6	8.3	E 3.7	10.8	7.4	15.6	-2.8	-3.8
1442	4.80	1.73	19.8	27.1	14.2	9.0	4.7	10.7	7.4	E 21.8	3.9	-3.4

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)

### 3.2 Analytical Parameter

#### pH

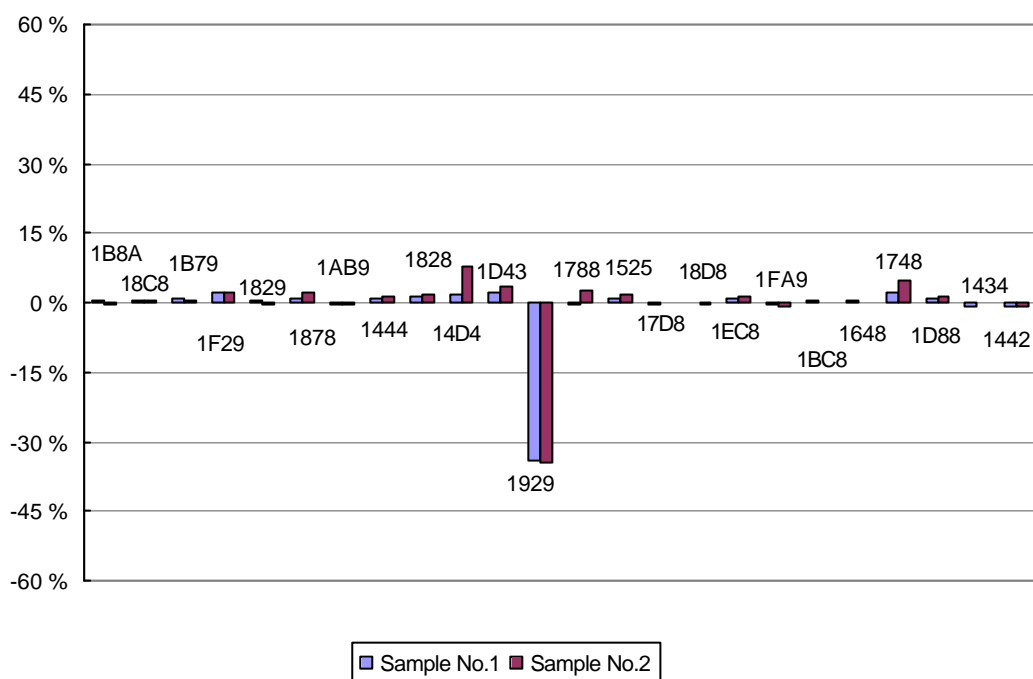


Fig.4 Distribution of pH data normalized by prepared value

Table 12 Analytical method and flagged data of pH

#### Analytical Method

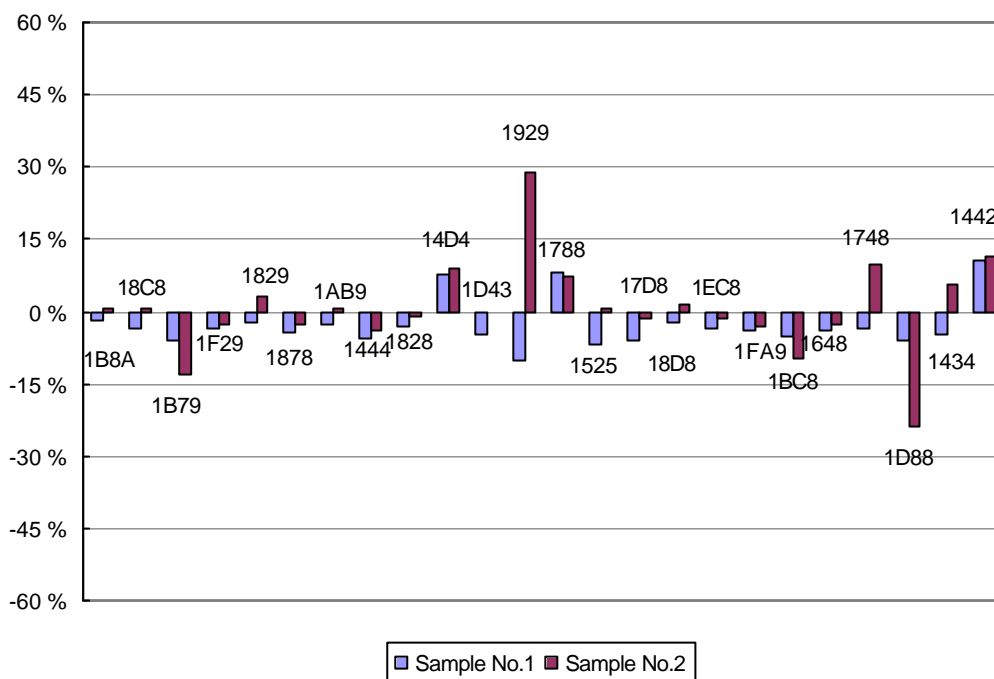
pH meter and electrode	24/24
------------------------	-------

#### Flagged data

	E	X	Flagged (%)
Sample No.1	0	1	4.2
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 agreed with prepared value. But the data of Lab.ID 1929 were out of the DQOs in the both samples and flagged by "X". Many laboratories submitted slightly higher pH values than prepared value. The relative standard deviations of the pH values for sample No1. and No.2 after rejecting the data which exceeds 3 times of standard deviation from average value were good as a result of 0.9% ~ 1.5%.

**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	24/24
-----------------------------	-------

**Flagged data**

	E	X	Flagged (%)
Sample No.1	0	0	0
Sample No.2	2	0	8.3

All participating laboratories used conductivity cell for the measurement of EC. Obtained data were almost agreed with the prepared value. However, Lab.ID 1929 and 1D88 submitted flagged data by "E". Most of the laboratories reported lower data value than prepared value.

SO<sub>4</sub><sup>2-</sup>

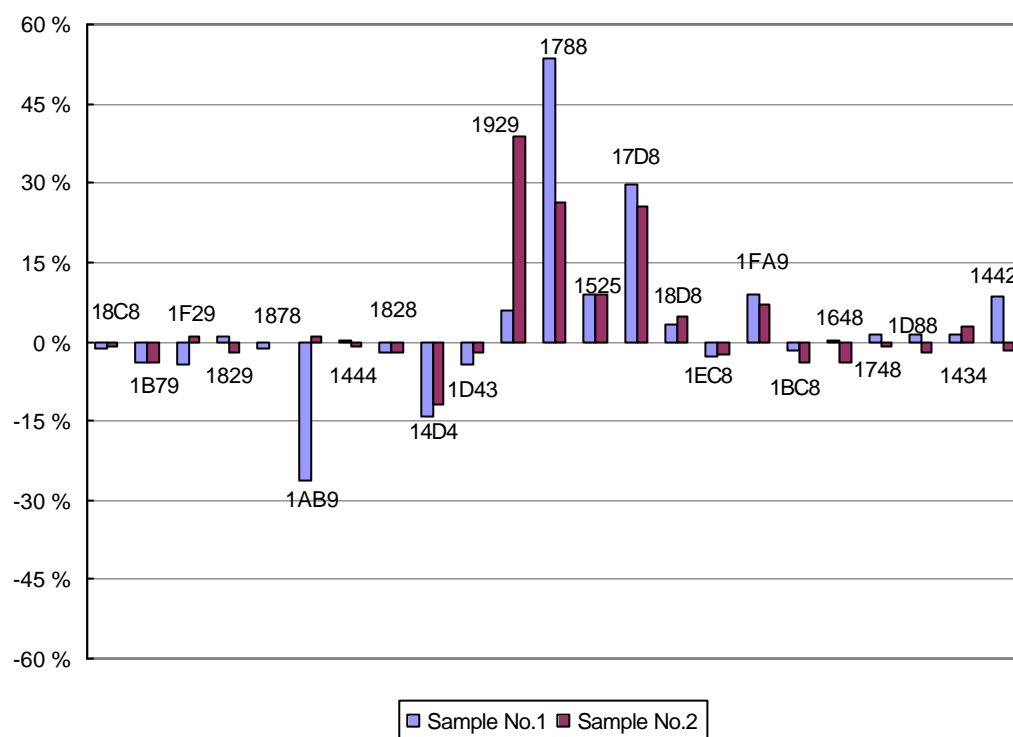


Fig.6 Distribution of SO<sub>4</sub><sup>2-</sup> data normalized by prepared concentration

Table 14 Analytical method and flagged data of SO<sub>4</sub><sup>2-</sup>

**Analytical Method**

Ion chromatography	22/24
Spectrophotometry	2/24

**Flagged data**

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

All of the participating laboratories used ion chromatography for the determination of SO<sub>4</sub><sup>2-</sup> except for 2 laboratories (Lab.ID 1788 and 1929), which used spectrophotometry. Sample No1 and No2 data of Lab.ID 17D8 were about 20% higher than prepare value. This laboratory has submitted flagged data in 1<sup>st</sup> and 2<sup>nd</sup> attempt. It seemed to be a system error in the analysis. (As the concentration of standard sample was not correct)

NO<sub>3</sub><sup>-</sup>

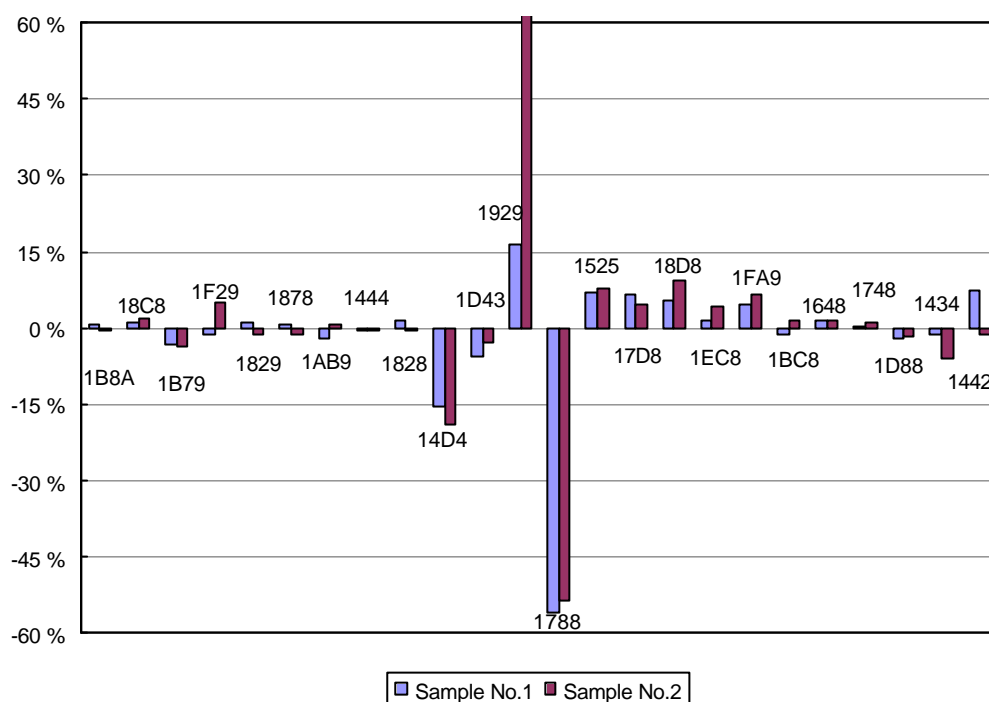


Fig.7 Distribution of NO<sub>3</sub><sup>-</sup> data normalized by prepared concentration

Table 15 Analytical method and flagged data of NO<sub>3</sub><sup>-</sup>

**Analytical Method**

Ion chromatography	22/24
Spectrophotometry	2/24

**Flagged data**

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

The both data of Lab.ID 1929 and 1788 (obtained by spectrophotometry) were all flagged. It seemed to be a problem in the analytical procedure with titration method. The results of Lab.ID 14D4 (obtained by ion chromatography) were about 15% lower value than the prepared value. It seemed to be the calibration error in the analysis.

Cl<sup>-</sup>

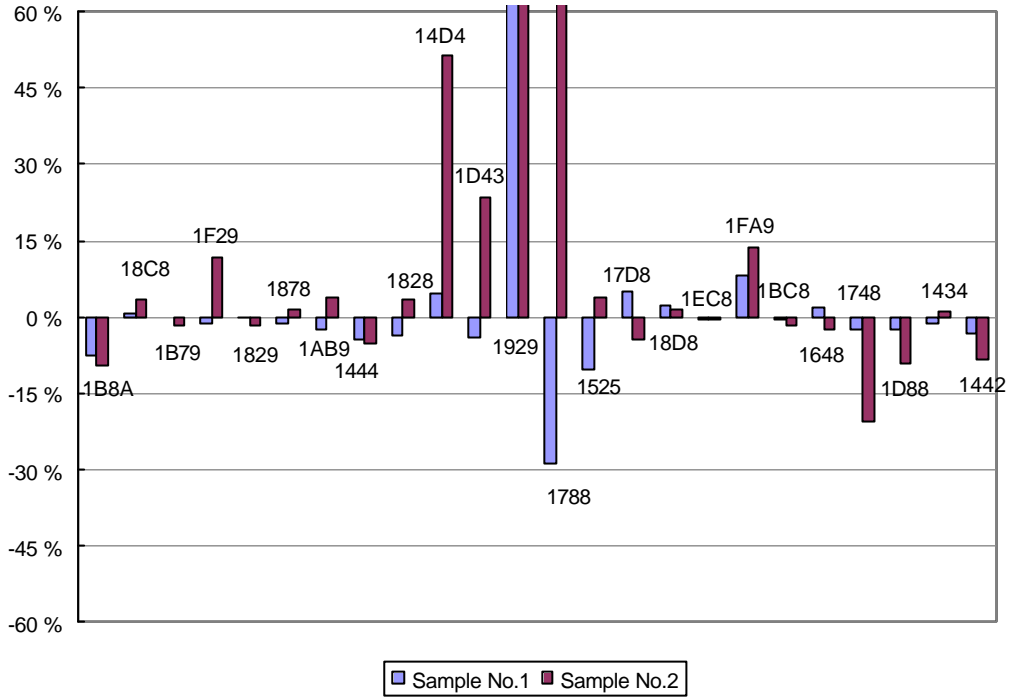


Fig.8 Distribution of Cl<sup>-</sup> data normalized by prepared concentration

Table 16 Analytical method and flagged data of Cl<sup>-</sup>

**Analytical Method**

Ion chromatography	22/24
Titration/Spectrophotometry	2/24

**Flagged data**

	E	X	Flagged (%)
Sample No.1	1	0	4.2
Sample No.2	2	3	20.8

Same as SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, most laboratories used ion chromatography for the determination of Cl<sup>-</sup>. Data of Lab.ID 1929(spectrophotometry) and Lab.ID 1788 (titration method) submitted significantly different values same as the data on NO<sub>3</sub><sup>-</sup>. Sample No.2' data obtained by Lab.ID 14D4 and 1D43 were higher than prepared value more than 20%. In this case, a contamination from the circumstance could be considered as one of the causes because Sample No.1 data were good.

Na<sup>+</sup>

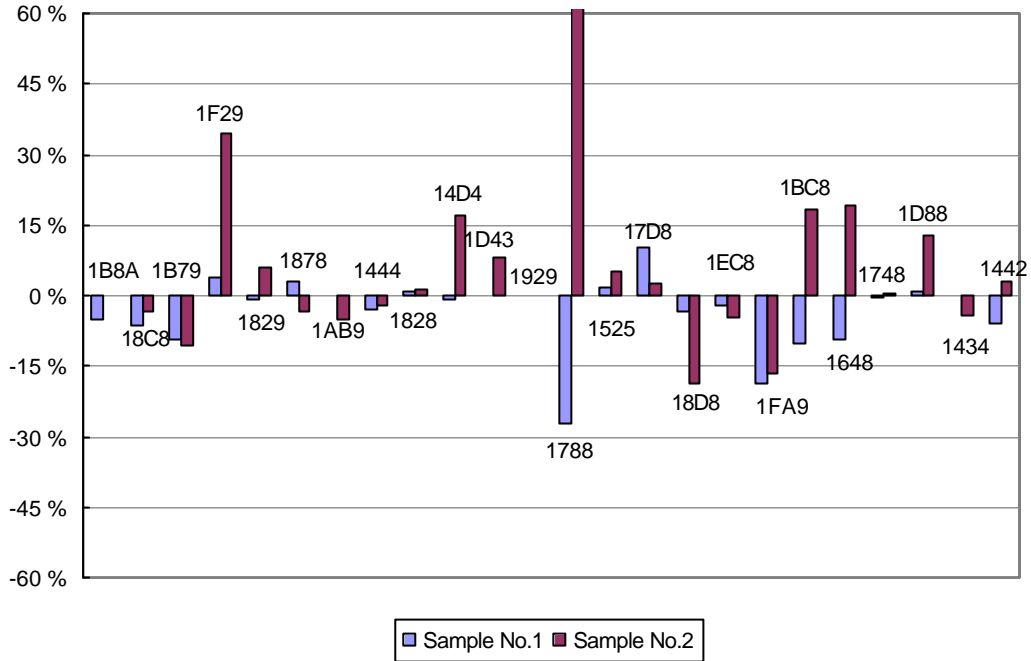


Fig.9 Distribution of Na<sup>+</sup> data normalized by prepared concentration

Table 17 Analytical method and flagged data of Na<sup>+</sup>

**Analytical Method**

Ion chromatography	14/23
Atomic absorption / Flame (emission) photometry	8/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23

**Flagged data**

	E	X	Flagged (%)
Sample No.1	2	0	8.7
Sample No.2	5	2	30.4

14 laboratories used ion chromatography, 8 laboratories used 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<sup>+</sup>.

There was clearly difference of data obtained by different analytical methods in Sample No.2. Most of the data by ion chromatography were satisfied of the DQOs. But almost of the data by atomic absorption/flame (emission) spectrometry was flagged out of the DQOs.(Lad.ID 14D4,1788,18D8,1FA9,1BC8,1648)

K<sup>+</sup>

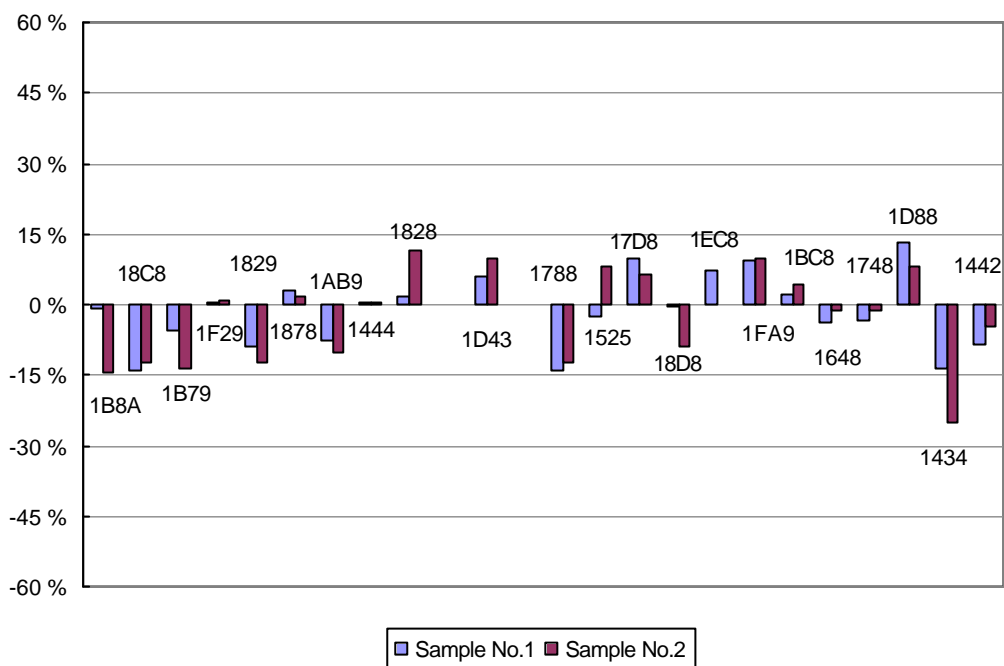


Fig.10 Distribution of K<sup>+</sup> data normalized by prepared concentration

Table 18 Analytical method and flagged data of K<sup>+</sup>

**Analytical Method**

Ion chromatography	14/22
Atomic absorption / Flame (emission) photometry	7/22
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/22

**Flagged data**

	E	X	Flagged (%)
Sample No.1	0	0	0
Sample No.2	1	0	4.5

Same as Na<sup>+</sup>, 14 laboratories used ion chromatography, 7 laboratories used 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<sup>+</sup>. There was no clear difference of data obtained by these three analytical methods. Most laboratories submitted adequate data for the prepared concentration, and there was least flagged data in this survey.

Ca<sup>2+</sup>

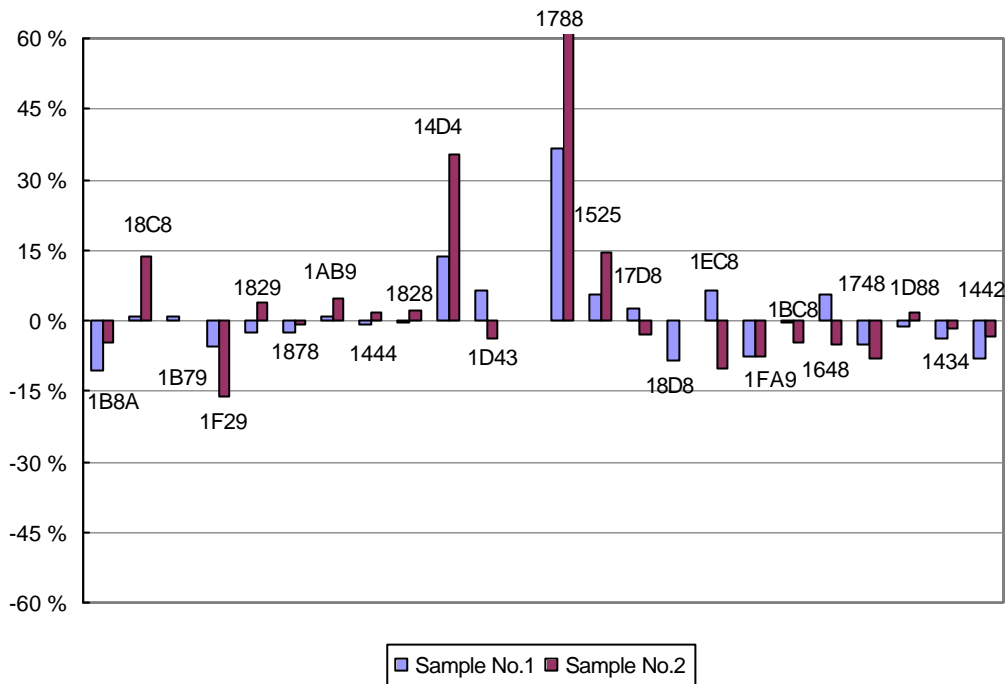


Fig.11 Distribution of Ca<sup>2+</sup> data normalized by prepared concentration

Table 19 Analytical method and flagged data of Ca<sup>2+</sup>

**Analytical Method**

Ion chromatography	13/23
Atomic absorption / Flame (emission) photometry	8/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23
Other method(Titration)	1/23

**Flagged data**

	E	X	Flagged (%)
Sample No.1	0	1	4.3
Sample No.2	1	2	13

Same as Na<sup>+</sup> and K<sup>+</sup>, ion chromatography, atomic absorption /flame (emission) photometry, ICP-MS and titration were used for the analysis of Ca<sup>2+</sup>.

There was no clear difference of data obtained by these analytical methods. Lab.ID 1788(titration) submitted significantly different data for both Sample No.1 and Sample No.2.

Mg<sup>2+</sup>

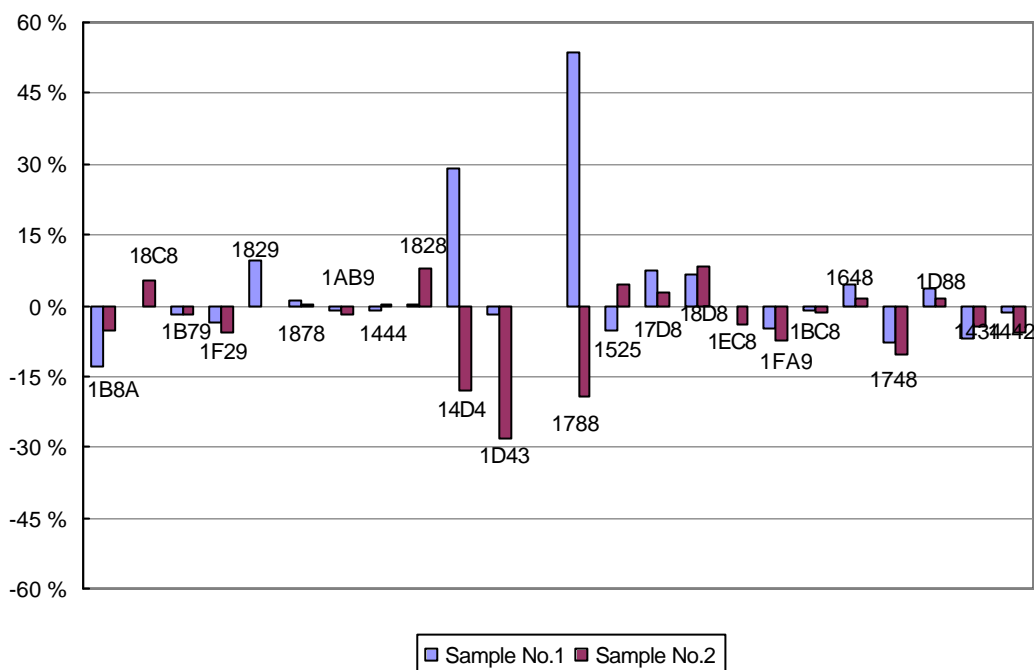


Fig.12 Distribution of Mg<sup>2+</sup> data normalized by prepared concentration

Table 20 Analytical method and flagged data of Mg<sup>2+</sup>

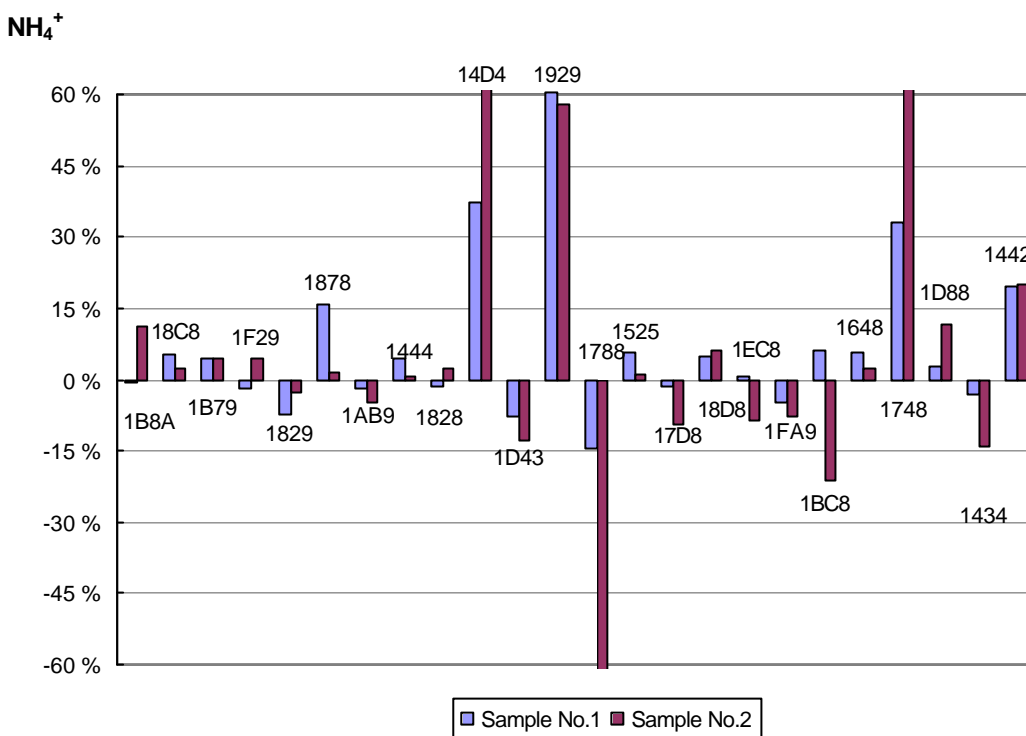
**Analytical Method**

Ion chromatography	13/23
Atomic absorption / Flame (emission) photometry	7/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23
Other method	2/23

**Flagged data**

	E	X	Flagged (%)
Sample No.1	1	1	8.7
Sample No.2	3	0	13.0

13 laboratories used ion chromatography, 7 laboratories used atomic absorption/flame (emission) photometry, and one laboratory (Lab.ID 17D8) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Mg<sup>2+</sup> as analytical instruments. 2 laboratories (Lab.ID 1D43, 1788) determined the concentration of Mg<sup>2+</sup> by calculation, subtracting the concentration of Ca<sup>2+</sup> from concentration obtained by EDTA titration method. The data obtained by the calculation significantly differed from prepared concentration (Lab.ID 1D43, 1788)



**Fig.13 Distribution of NH<sub>4</sub><sup>+</sup> data normalized by prepared concentration**

**Table 21 Analytical method and flagged data of NH<sub>4</sub><sup>+</sup>**

**Analytical Method**

Ion chromatography	15/24
Spectrophotometry (Indophenol blue)	3/24
Other method (Spectrophotometry)	6/24

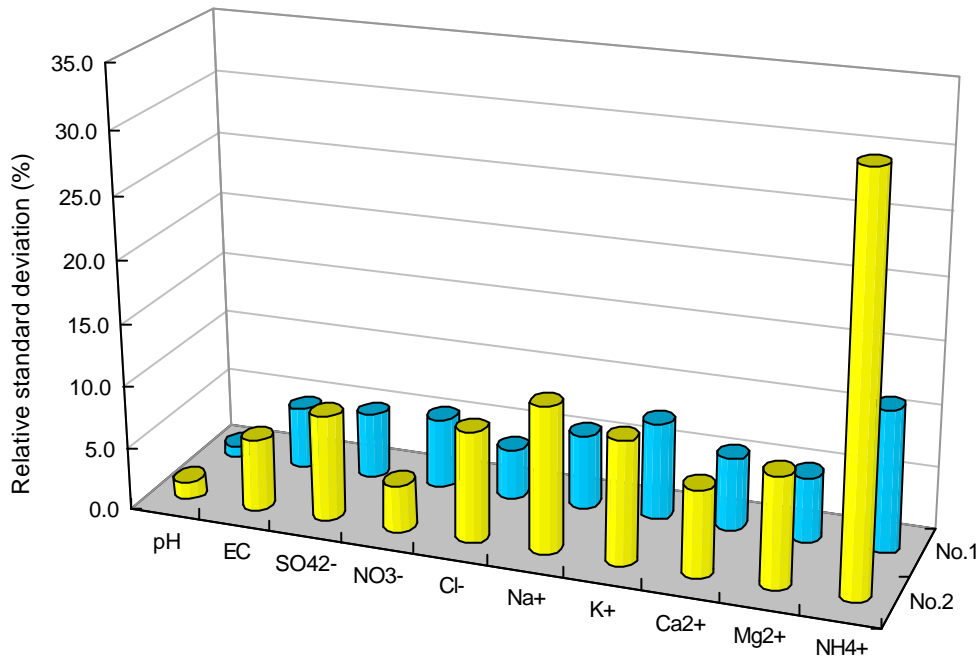
**Flagged data**

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

19 laboratories used recommended analytical method of EANET for the determination of NH<sub>4</sub><sup>+</sup>: 15 laboratories used ion chromatography. 3 laboratories used spectrometry (Indophenol blue). Four laboratories (Lab.ID 14D4, 1929,1788 and 1748) submitted significantly different data. Lab.ID 14D4 and 1748 used ion chromatography and the both data deviated in the same way. Lab.ID1929 and 1788 used other method (Spectrophotometry).

## 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. However, this discrepancy seems to be less than previous round robin project. Analytical data of  $\text{NH}_4^+$  were varied particularly in this project. However, other cation's data, such as  $\text{K}^+$  and  $\text{Mg}^{2+}$  were improved, though concentrations of these constituents are still lower than others. It is expected to improve the quality of data that has large deviation through the QA/QC activities in each laboratory.



**Fig.14 Relative standard deviation of each constituent**

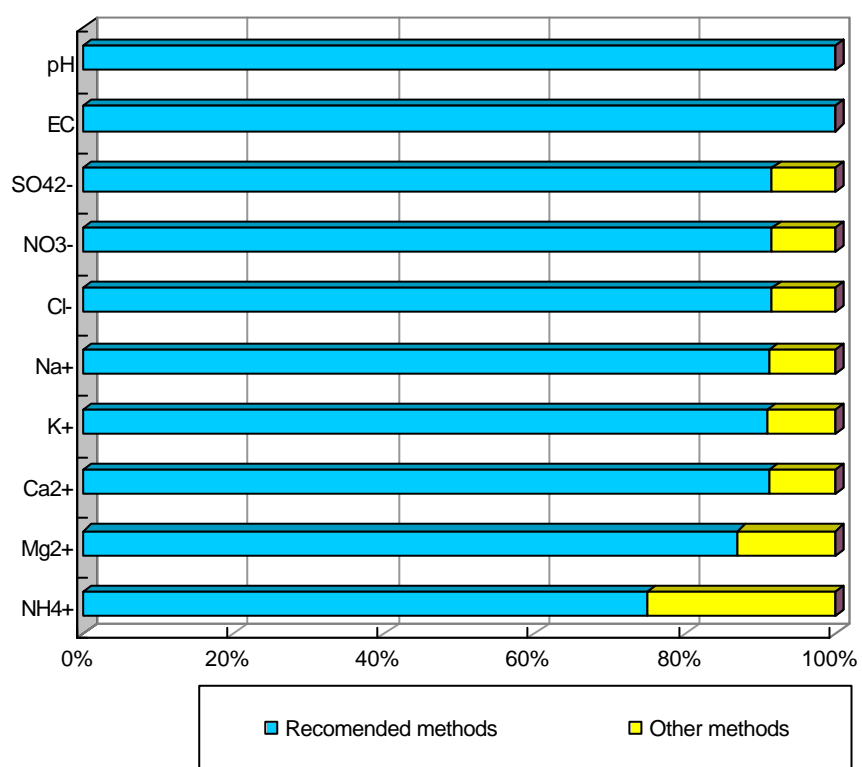
(Relative standard deviation (%) = Standard deviation / Average x100, Reported data after outliers were removed)



### 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.



**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 Spectrometry
4	Emission Spectrometry
5	Ion chromatography
6	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
7	Calculation
8	Indophenol Spectrophotometry
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
X	Other method
?	No information

**Table 23 Analytical Method**

SampleNo.1

Method	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
0	24(1)									
1		24								
2					1(1)			1(1)	2(2)	
3						8(2)	7	8	7	
4										
5			22(2)	22(1)	22	14	14	13	13	15(3)
6										
7										
8			2(1)	2(2)	1					3(1)
9						1	1	1	1	
10										
X										6(1)
Flagged E	1		2	2	1	2	0	1	1	2
Flagged X			1	1					1	3

Sample No.2

Method	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
0	24(1)									
1		24(2)								
2					1(1)			1(1)	2(2)	
3						8(6)	7	8(1)	7(1)	
4										
5			22(1)	22(1)	22(3)	14(1)	14(1)	13(1)	13	15(3)
6										
7										
8			2(2)	2(2)	1(1)					3(1)
9						1	1	1	1	
10										
X										6(2)
Flagged E	1	2	2	1	2	5	1	1	3	2
Flagged X			1	2	3	2		2		4

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. In twelve laboratories, only one person carried out measurement of rainwater samples in each Lab.. In other laboratories, 2 to 4 persons carried out measurement, and usually their responsibilities were separated by the methods 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 one laboratory, three staffs collaborate to analyze same constituents.

**Table 24 Staff in charge of measurement**

Lab.ID	Total	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
1B8A	1	A	A	A	A	A	A	A	A	A	A
18C8	1	A	A	A	A	A	A	A	A	A	A
1B79	1	A	A	A	A	A	A	A	A	A	A
1F29	1	A	A	A	A	A	A	A	A	A	A
1829	1	A	A	A	A	A	A	A	A	A	A
1878	1	A	A	A	A	A	A	A	A	A	A
1AB9	1	A	A	A	A	A	A	A	A	A	A
1444	1	A	A	A	A	A	A	A	A	A	A
1828	2	A	A	B	B	B	A	A	A	A	A
14D4	3	A	B	B	B	B	C		C	C	C
1D43	2	A	A	A	A	A	A	A	B	B	A
1929	1	A	A	A	A	A					A
1788	3	A	A	B	C	B	A	A	B	B	A
1525	2	+	+	+	+	+	+	+	+	+	+
17D8	3	A	A	B	B	B	C	C	C	C	C
18D8	3	A	A	B	B	B	C	C	C	C	A
1EC8	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
1648	3	A	A	B	B	B	C	C	C	C	A
1748	3	A	A	B	B	B	C	C	C	C	A
1D88	1	A	A	A	A	A	A	A	A	A	A
1434	1	A	A	A	A	A	A	A	A	A	A
1442	3	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C

“+”: No information, “A”, “B”, “C”, and “D” represent individuals of staff in each laboratory who are in charge of measurement. Reverse mesh: “E” or “X” in sample No.1 and/or sample No.2 flagged Data.

## 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”, same as previous surveys.

**Table 25 Years of experience**

Unit: year

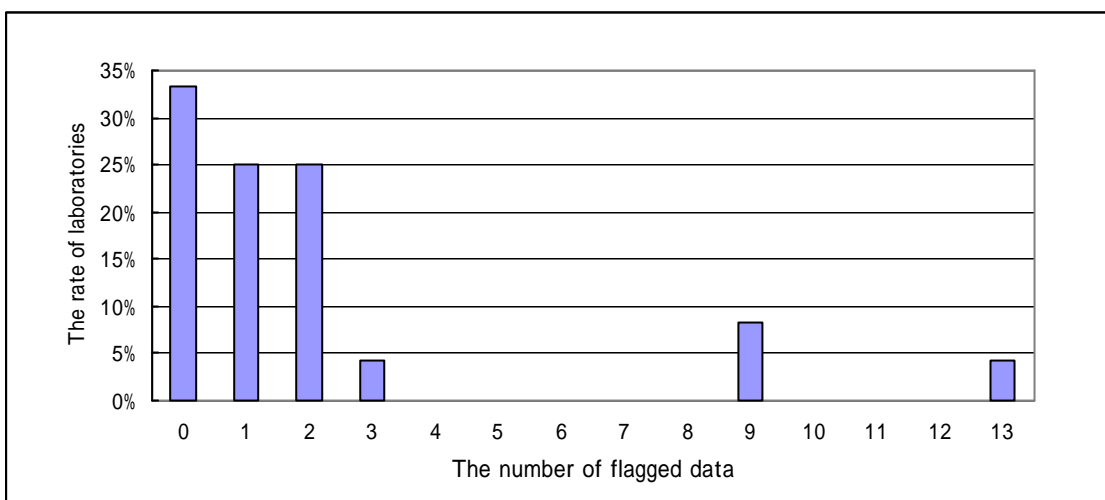
Lab.ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
1B8A	16	16	16	16	16	16	16	16	16	16
18C8	3	3	3	3	3	3	3	3	3	3
1B79	3	3	3	3	3	3	3	3	3	3
1F29	12	12	12	12	12	12	12	12	12	12
1829	4	4	4	4	4	4	4	4	4	4
1878	6	6	6	6	6	6	6	6	6	6
1AB9	4	4	4	4	4	4	4	4	4	4
1444	3	3	3	3	3	3	3	3	3	3
1828	3	3	3	3	3	3	3	3	3	3
14D4	1	11	11	11	11	3		3	3	3
1D43	3	3	3	3	3	3	3	3	3	3
1929	10	10	10	10	10					10
1788	16	16	6	2	6	16	16	6	6	16
1525	+	+	+	+	+	+	+	+	+	+
17D8	3	3	1	1	1	2	2	2	2	2
18D8	2	2	3	3	3	1	1	1	1	2
1EC8	8	8	8	8	8	8	8	8	8	8
1FA9	3	3	9	9	9	6	6	6	6	5
1BC8	1	1	6	6	6	1	1	1	1	6
1648	5	5	16	16	16	12	12	12	12	5
1748	5	5	2	2	2	2	2	2	2	5
1D88	2	2	2	2	2	2	2	2	2	2
1434	6	6	6	6	6	6	6	6	6	6
1442	1	1	1	1	1	1	1	1	1	1

“+”: No information.

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

1 year means experience with one year or less

**The number of flagged data in laboratories**



**Fig.16 The distribution of laboratories with the number of flagged data**

**Table 26 Number of flagged data in each laboratory.**

Number of flagged data	Number of laboratories	Share
0	8	33.3%
1	6	25.0%
2	6	25.0%
3	1	4.2%
4~8	0	0%
9	2	8.3%
10~12	0	0%
13	1	4.2%

In this project, the number of flagged data was 52 among a total of 470 data. The attribution of flagged data in each laboratory was as shown in Table 26.

Number of excellent laboratories without flagged data was 8, which was equivalent to 1/3 of the whole participating laboratories. Moreover, laboratories that submitted less than 2 flagged data, which seemed to be managed comparatively well, were 20 (83.3% of whole). On the other hand, 2 laboratories with 9 flagged data and 1 laboratory with 13 flagged data need some improvement. Two of these laboratories could use neither ion chromatography nor atomic absorption spectrometry, though they had individual equipment. Therefore, these laboratories should make an effort for implement of analytical procedure.

### Water Temperature at measurement (pH and EC)

As described in Table 27, most of the participating laboratories measured pH and EC around 25 degrees centigrade, which is the recommended condition by EANET. There were three laboratories that water temperature was equal or lower than 20 degrees centigrade. However, these laboratories reported adequate data.

**Table 27 Water temperature at measurement (pH and EC)** Unit: degrees centigrade

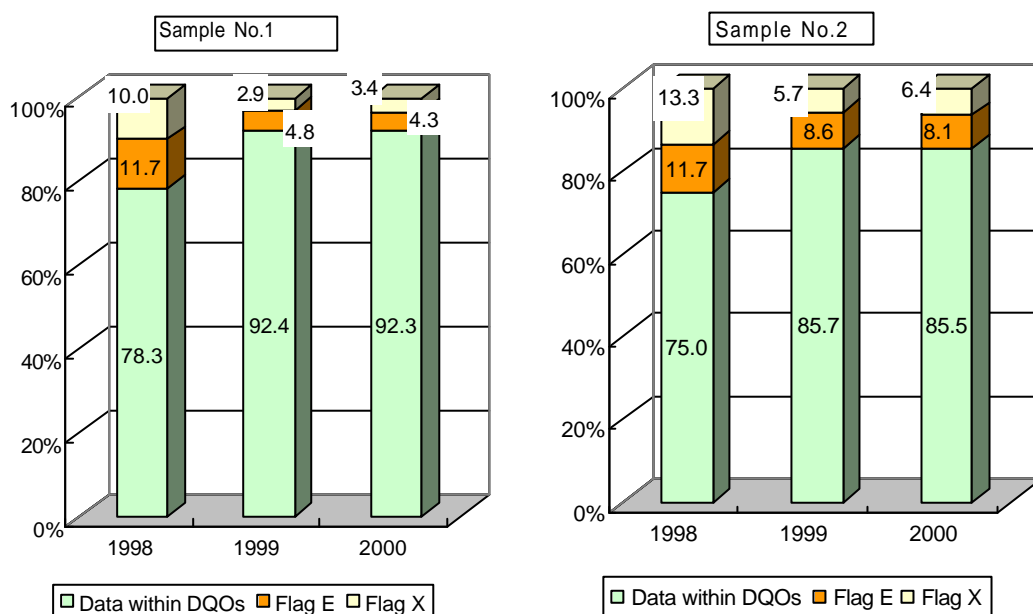
Lab.ID	pH Sample o.1	pH SampleNo.2	EC SampleNo.1	EC Sample No.2
1B8A	22.9~23.5	22.9~23.5	22.4~23.7	22.4~23.7
18C8	25.0	25.0	25.0	25.0
1B79	24.9	24.9	24.7	24.7
1F29	24.6	24.6	24.5	24.5
1829	22.7	22.7	22.7	22.7
1878	25.0	25.0	25.0	25.0
1AB9	25.0	25.0	25.0	25.0
1444	25.0	25.0	25.0	25.0
1828	25.0	25.0	25.0	25.0
14D4	25.6	25.6	25.6	25.6
1D43	25.0	25.0	25.0	25.0
1929	X 25.0	X 25.0	25.0	E 25.0
1788	25.0	25.0	25.0	25.0
1525	26.2	26.2	26.2	26.2
17D8	23.2	23.2	23.2	23.2
18D8	25.0	25.0	25.0	25.0
1EC8	25.0	25.0	25.0	25.0
1FA9	19.0	19.0	19.0	19.0
1BC8	11.3	11,3	11.4	11,4
1648	15.1	15.2	14.1	14.3
1748	25.4	25.4	25.4	25.4
1D88	25.0	25.0	25.0	E 25.0
1434	25.0	25.0	25.0	25.0
1442	25.0	25.0	25.0	25.0

E: E flagged the data (Value exceeded the DQO( ± 15%))

X: X flagged the data (Value exceeded the DQO( ± 30%))

#### 4 COMPARISON OF 1<sup>st</sup>, 2<sup>nd</sup> AND 3<sup>rd</sup> INTER-LABORATORY COMPARISON

The result of surveys carried out 3 times so far, on the number of flag data is shown in Fig. 17. For the first survey (1998), the rate of data that satisfied the required data quality objectives (DQOs) was about 75-78%. On the 2<sup>nd</sup> (1999) and 3<sup>rd</sup> (2000) survey, the rates of DQOs were 85-93%. The data quality seemed to be improved by accumulating experiences. However, the results of the 2<sup>nd</sup> and 3<sup>rd</sup> survey remain almost same. There seem to be room to be improved taking account the laboratories, which have inadequate using condition of equipment or apparatus. Especially, for the low concentration sample (Sample No.2), which contains about 15% fagged data, contamination from used instrument, measurement apparatus and so on might be considered and should be reduced to improve the data quality. It is also important to secure the reduction of background noise and to keep the linearity of calibration curve in analytical process.

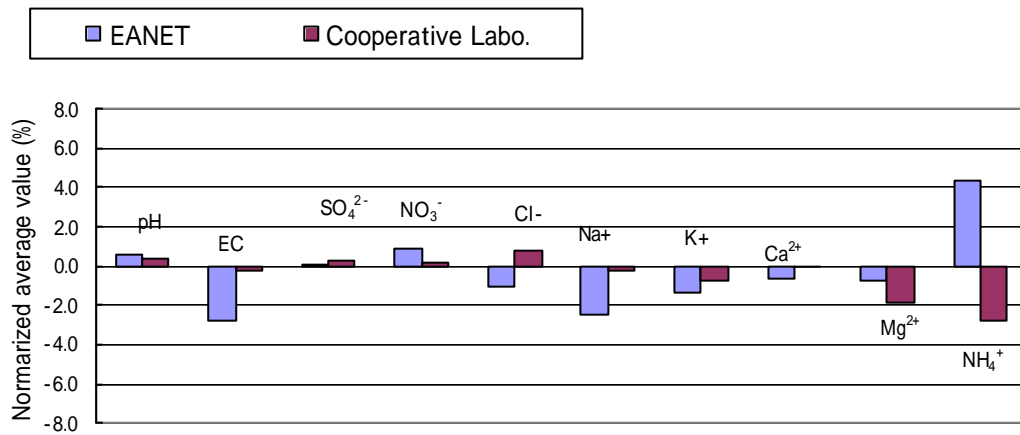


Fig, 17 Comparison of 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> inter-laboratory comparison project

## 5 COMPARISON OF EANET AND COOPERATIVE LABORATORIES

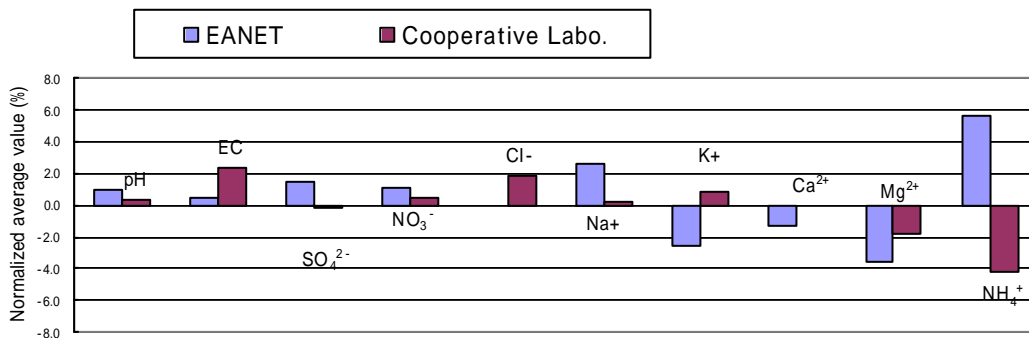
4 laboratories that have long time experiences on acid deposition monitoring cooperatively participated in this survey, and the result of the same sample submitted from these laboratories were comparing with that of EANET laboratories.

The normalized average values (%) of these cooperative laboratories and EANET laboratories compared. As described in Fig.18, for high concentration sample, more differences from prepared values were seen in EANET laboratories' data than that of cooperative laboratories data on EC and Na<sup>+</sup> measurements. However, for low concentration sample (Fig.19), this tendency is not so clear, and some constituents (EC and Cl<sup>-</sup>), cooperative laboratories gave much difference from prepared value. For both samples, average data of EANET and cooperative laboratories on NH<sub>4</sub><sup>+</sup> were mostly differed from the prepared value. As described in Fig.20 and Fig.21, in the comparison of relative standard deviation of data among laboratories of EANET and cooperative laboratories, cooperative laboratories' data had less deviation for all constituents than that of EANET laboratories.



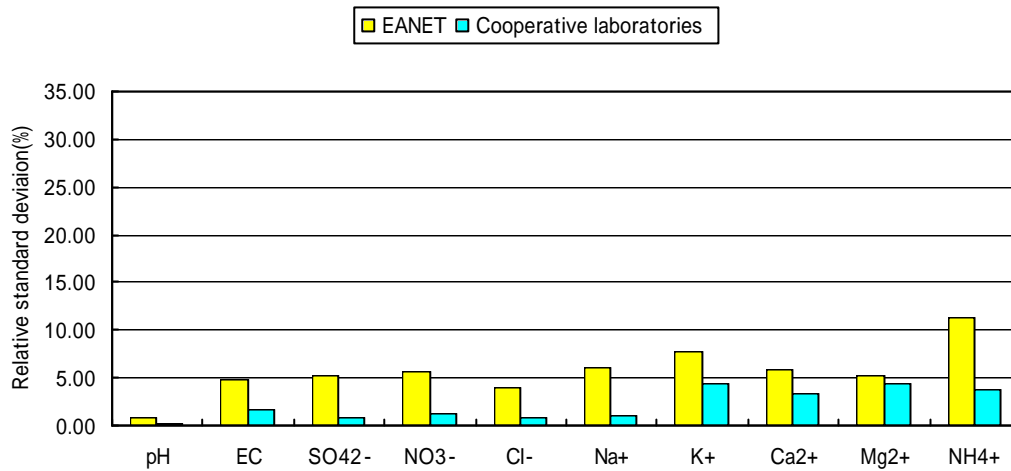
**Fig.18 Comparison of EANET and cooperative laboratories in the normalized average values for Sample No.1**

\* Normalized average values(%)=(averagex100/prepared value) – 100

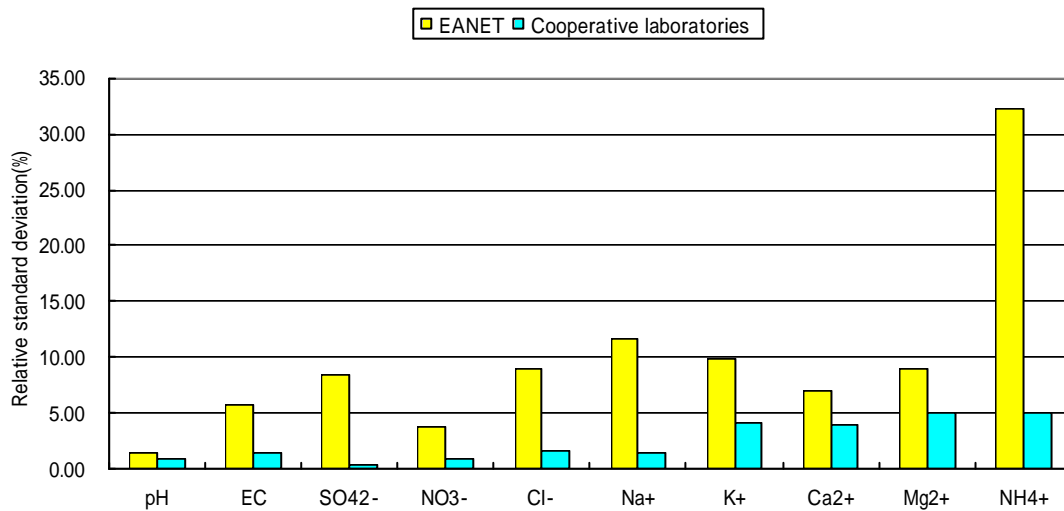


**Fig.19 Comparison of EANET and cooperative laboratories in the normalized average values for Sample No.2**

\* Normalized average values(%)=(averagex100/prepared value) – 100



**Fig.20 Comparison of EANET and cooperative laboratories in relative standard deviation of each constituent for Sample No.1**



**Fig.21 Comparison of EANET and cooperative laboratories in relative standard deviation of each constituent for Sample No.2**

## 6. PROPOSAL FOR IMPROVEMENT OF MEASUREMENT PRECISIONS

- 1 . Items to be taken care of in the measurement of pH and EC.
  - Deviation of temperature causes large error in the measurement of low electric conductivity. It is recommended to use a 25 °C water bath in measurement of pH and EC. Although there is no clear evidence in the results of this survey, the error seemed to be induced by this reason. It is recommended to make sure that there is no difference between the temperatures of individual samples and that of the reference materials.
  - As for an immersed type cell, since it is known that a sample easily absorbs gases in the air and it causes electrical conductivity changes, handling of a sample should be careful, and stirring for dilution should be performed slowly.
- 2 . Reduction of contamination.
  - In the analysis of low concentration ion compounds, a contamination from circumstances causes a large error. It seems that a lot of flagged data are caused by contamination of samples. Contamination comes from an instrument, solvent, apparatus in use, air, etc. So, you should take care of the undermentioned items.
    - 1) Using deionized water (<1.5µS/cm) for measurements, analyses, dilution and cleaning
    - 2) Using high quality substance (certified materials) for reagent and standard sample.
    - 3) The sample should be stored in a dark and cold place.
    - 4) Sample vials should be selected the polyester for cation.
- 3 . Items to be taken care of in the analysis of Na<sup>+</sup> by atomic absorption spectrometry.
  - In this project, most of Na<sup>+</sup> data obtained by atomic absorption spectrometry (AA) were flagged in the analysis of sample No.2 (low concentration). It is well known that AA is influenced by the analytical environment (ambient air, operator, coexistent substitutes etc), and other error is induced by chemical interference in AA. So, a field blank test should be undertaken to confirm contamination and background level of Na<sup>+</sup>.
  - Addition of lanthanum nitrate solution is effective to eliminate the interference of coexisting anions, and unequal ionization ratio in the flame between the sample and standard solutions. (Reference 2 Technical Document for Wet Deposition Monitoring)
- 4 . How to improve the precision of NH<sub>4</sub><sup>+</sup> determination.
  - In this project, relative standard deviation of NH<sub>4</sub><sup>+</sup> among laboratories was the largest. It is known that NH<sub>4</sub><sup>+</sup> is one of the difficult constituents for determination, because the contamination from ambient air, there are the loss of the constituents due to adsorption etc., and the difficulties of getting linearity of calibration in using suppressor type ion chromatography. So, you should check the calibration curve and use fresh deionized water and reagent solution. It is highly recommended to wash sample cups with deionized water immediately prior to use, and rinse cups again with portion of the standard or sample to be analyzed by spectrophotometry, as well as checking the calibration curve.

## 7. REFERENCES

- 1) Guidelines for Acid Deposition Monitoring in East Asia  
March 2000 adopted at:  
The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.
- 2) Technical Documents for Wet Deposition Monitoring in East Asia
  - Technical Manual for Wet Deposition Monitoring in East Asia
  - Quality Assurance / Quality Control (QA/QC) Program for the Preparatory-Phase Wet Deposition Monitoring in East Asia,  
March 2000 adopted at:  
The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.
- 3) Report of the Inter-laboratory Comparison Project 1998  
(Round robin analysis survey 1<sup>st</sup>. Attempt) November 1999.
- 4) Report of the Inter-laboratory Comparison Project 1999  
(Round robin analysis survey 2<sup>nd</sup>. Attempt) October 2000

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## APPENDIX 2 Original data

Sample No.1

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
	-	mS/m	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
1B8A	4.11	6.11	57.2	63.7	93.4	48.7	9.8	26.3	10.2	60.0
18C8	4.12	6.01	58.9	63.9	102.1	48.1	8.5	29.7	11.7	63.8
1B79	4.13	5.86	57.4	61.2	101.3	46.6	9.4	29.7	11.5	63.2
1F29	4.19	6.01	57.0	62.6	100.0	53.3	10.0	27.8	11.3	59.4
1829	4.11	6.10	60.3	64.0	101.0	50.9	9.0	28.7	12.8	56.1
1878	4.14	5.96	59.0	63.6	100.0	52.9	10.2	28.7	11.8	70.1
1AB9	4.09	6.07	44.1	61.9	98.9	51.2	9.2	29.6	11.6	59.3
1444	4.14	5.88	59.9	63.0	96.9	49.7	10.0	29.2	11.6	63.2
1828	4.16	6.03	58.5	64.1	97.6	51.8	10.1	29.3	11.7	59.6
14D4	4.17	6.72	51.2	53.5	105.8	50.8	-	33.4	15.1	83.0
1D43	4.19	5.94	57.2	59.7	97.4	51.2	10.5	31.3	11.5	55.8
1929	2.70	5.60	63.2	73.6	217.5	--	--	--	--	97.0
1788	4.09	6.73	91.6	27.8	72.0	37.4	8.5	40.1	18.0	51.7
1525	4.14	5.80	64.9	67.6	90.9	52.2	9.7	31.0	11.1	63.9
17D8	4.09	5.85	77.5	67.4	106.2	56.6	10.9	30.2	12.6	59.6
18D8	4.10	6.10	61.7	66.7	103.6	49.6	9.8	27.0	12.5	63.4
1EC8	4.13	6.00	58.1	64.1	100.6	50.3	10.6	31.3	11.7	60.9
1FA9	4.08	5.98	65.1	66.1	109.4	41.6	10.8	27.1	11.1	57.5
1BC8	4.12	5.90	58.6	62.6	100.7	46.1	10.1	29.3	11.6	64.3
1648	4.12	5.99	59.9	64.1	103.1	46.5	9.5	31.1	12.2	64.0
1748	4.19	6.00	60.4	63.5	98.9	51.0	9.6	27.9	10.8	80.4
1D88	4.13	5.86	60.4	61.9	98.7	51.7	11.2	29.0	12.1	62.2
1434	4.06	5.93	60.4	62.5	100.0	51.3	8.6	28.3	10.9	58.7
1442	4.06	6.88	64.8	67.9	98.0	48.3	9.1	27.0	11.5	72.4
Prepared value	4.10	6.23	59.7	63.3	101.3	51.3	9.9	29.4	11.7	60.5
Data count	24	24	24	24	24	23	22	23	23	24
Average	4.07	6.05	61.1	62.4	103.9	49.5	9.8	29.7	12.0	64.6
Minimum	2.70	5.60	44.1	27.8	72.0	37.4	8.5	26.3	10.2	51.7
Maximum	4.19	6.88	91.6	73.6	217.5	56.6	11.2	40.1	18.0	97.0
Standard deviation	0.29	0.29	8.50	8.02	24.64	3.91	0.75	2.77	1.56	9.76

Sample No.2

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
	-	mS/m	µmol/L	µmol/L	µmol/L	µmol/L	µmol/L	µmol/L	µmol/L	µmol/L
1B8A	4.83	1.56	19.2	27.4	14.0	8.7	4.2	10.5	7.4	20.2
18C8	4.87	1.56	19.9	28.0	16.0	8.4	4.3	12.5	8.2	18.6
1B79	4.88	1.35	19.3	26.5	15.2	7.8	4.2	11.0	7.7	19.0
1F29	4.96	1.51	20.3	28.9	17.3	11.7	4.9	9.2	7.4	19.0
1829	4.82	1.60	19.7	27.1	15.2	9.2	4.3	11.4	7.8	17.7
1878	4.95	1.51	20.1	27.1	15.7	8.4	5.0	10.9	7.8	18.5
1AB9	4.83	1.56	20.3	27.7	16.1	8.3	4.4	11.5	7.7	17.3
1444	4.91	1.49	19.9	27.4	14.7	8.5	4.9	11.2	7.8	18.3
1828	4.94	1.53	19.7	27.4	16.0	8.8	5.5	11.3	8.4	18.6
14D4	5.22	1.69	17.7	22.2	23.5	10.2	-	14.9	6.4	36.4
1D43	5.01	1.55	19.7	26.7	19.1	9.4	5.4	10.6	5.6	15.9
1929	3.18	2.00	27.9	44.4	89.1	-	-	-	-	28.7
1788	4.98	1.66	25.4	12.8	26.9	21.7	4.3	23.2	6.3	2.5
1525	4.94	1.56	21.9	29.6	16.1	9.2	5.3	12.6	8.2	18.4
17D8	4.86	1.53	25.2	28.7	14.8	8.9	5.2	10.7	8.0	16.5
18D8	4.83	1.57	21.0	30.0	15.7	7.1	4.5	11.0	8.4	19.3
1EC8	4.92	1.53	19.6	28.6	15.4	8.3	4.9	9.9	7.5	16.6
1FA9	4.81	1.50	21.5	29.4	17.6	7.3	5.4	10.2	7.2	16.8
1BC8	4.86	1.40	19.3	27.9	15.2	10.3	5.1	10.5	7.7	14.3
1648	4.86	1.51	19.3	27.9	15.1	10.4	4.8	10.4	7.9	18.6
1748	5.09	1.70	19.9	27.8	12.3	8.8	4.8	10.1	7.0	32.4
1D88	4.91	1.18	19.7	27.0	14.1	9.8	5.3	11.2	7.9	20.3
1434	4.85	1.64	20.7	25.8	15.6	8.3	3.7	10.8	7.4	15.6
1442	4.80	1.73	19.8	27.1	14.2	9.0	4.7	10.6	7.4	21.8
Prepared value	4.85	1.55	20.1	27.5	15.5	8.7	4.9	11.0	7.8	18.2
Data count	24	24	24	24	24	23	22	23	23	24
Average	4.84	1.56	20.7	27.6	19.4	9.5	4.8	11.6	7.5	19.2
Minimum	3.18	1.18	17.7	12.8	12.3	7.1	3.7	9.2	5.6	2.5
Maximum	5.22	2.00	27.9	44.4	89.1	21.7	5.5	23.2	8.4	36.4
Standard deviation	0.36	0.15	2.26	4.80	14.85	2.80	0.47	2.71	0.67	6.20



## Original data/Prepared value x100--- Sample No.2

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
	-	mS/m	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
1B8A	99.6	100.6	95.5	99.6	90.3	100.0	85.7	95.5	94.9	111.0
18C8	100.4	100.6	99.0	101.8	103.2	96.6	87.8	113.6	105.1	102.2
1B79	100.6	87.1	96.0	96.4	98.1	89.2	86.3	100.0	98.2	104.4
1F29	102.3	97.4	101.0	105.1	111.6	134.5	100.8	83.9	94.2	104.4
1829	99.4	103.2	98.0	98.5	98.1	105.7	87.8	103.6	100.0	97.3
1878	102.1	97.4	100.0	98.5	101.3	96.7	101.8	99.1	100.4	101.6
1AB9	99.6	100.6	101.0	100.7	103.9	94.8	90.0	104.5	98.2	95.1
1444	101.2	96.1	99.0	99.6	94.8	97.8	100.6	101.8	100.1	100.5
1828	101.9	98.9	98.0	99.6	103.5	101.1	111.3	102.3	107.8	102.2
14D4	107.6	108.8	88.1	80.9	151.5	117.2	-	135.5	81.8	199.8
1D43	103.3	100.0	98.0	97.1	123.2	108.0	109.6	96.4	71.8	87.4
1929	65.6	129.0	138.8	161.5	574.8	-	-	-	-	157.7
1788	102.7	107.1	126.4	46.5	173.5	249.4	87.8	210.9	80.8	13.7
1525	101.9	100.6	109.0	107.6	103.9	105.2	108.0	114.5	104.6	101.1
17D8	100.2	98.7	125.4	104.4	95.6	102.6	106.5	97.0	102.9	90.4
18D8	99.6	101.3	104.6	109.2	101.3	81.1	91.0	99.8	108.1	106.2
1EC8	101.4	98.7	97.5	104.0	99.4	95.4	100.0	90.0	96.2	91.2
1FA9	99.2	96.8	107.2	106.7	113.7	83.3	109.8	92.3	92.4	92.3
1BC8	100.2	90.3	96.0	101.5	98.1	118.4	104.1	95.5	98.7	78.6
1648	100.2	97.4	96.0	101.5	97.4	119.0	98.6	94.9	101.7	102.2
1748	104.9	109.7	99.0	101.1	79.4	100.6	98.8	91.8	89.7	178.0
1D88	101.2	76.1	98.0	98.2	91.0	112.6	108.2	101.8	101.3	111.5
1434	100.0	105.8	102.8	93.8	100.9	95.7	75.1	98.1	95.4	85.8
1442	98.97	111.61	98.3	98.5	91.6	103.0	95.2	96.8	94.3	119.9
Minimum	65.6	76.1	88.1	46.5	79.4	81.1	75.1	83.9	71.8	13.7
Maximum	107.6	129.0	138.8	161.5	574.8	249.4	111.3	210.9	108.1	199.8
Average	99.75	100.59	103.0	100.5	125.0	109.0	97.5	105.2	96.5	105.6