

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

# **Report of the Inter-laboratory Comparison Project 2001 on Wet Deposition**

**4th. Attempt**

November 2002  
Acid Deposition and Oxidant Research Center



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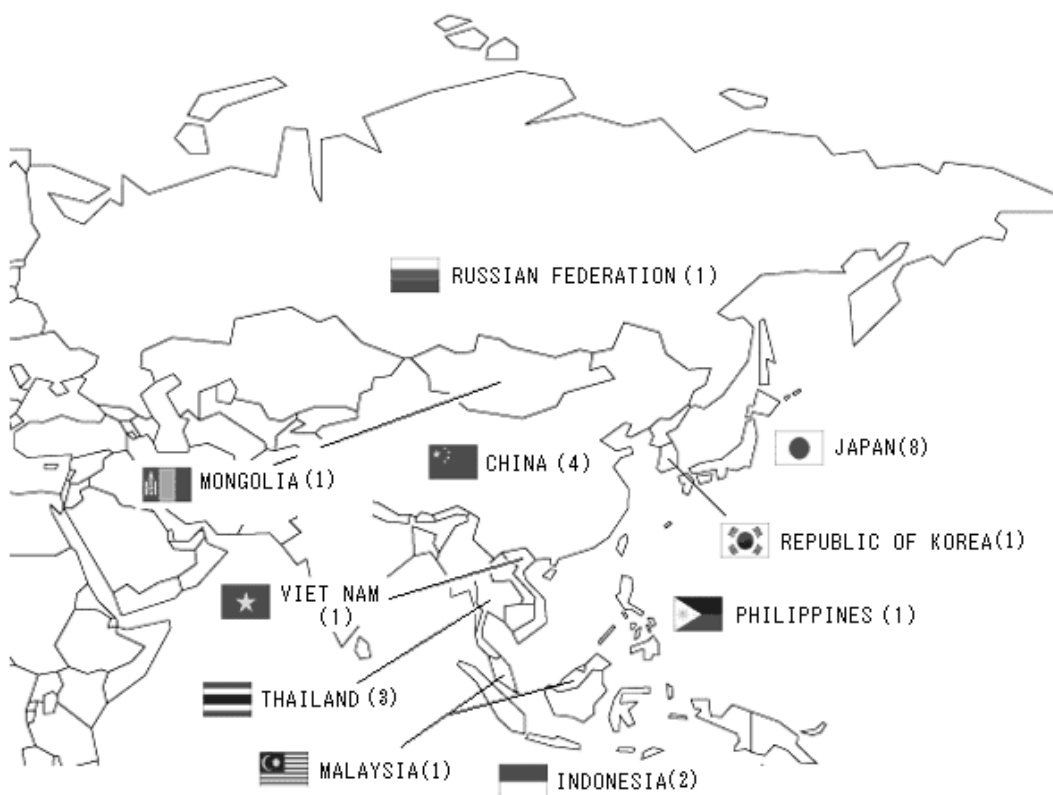
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## 1. INTRODUCTION

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 contained 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 laboratory's short name, and various statistical parameters are included in this report.



\* Figure in parenthesis shows the number of laboratories of each country (23 laboratories from 10 countries)

**Fig.1 Laboratories participated in the Inter-comparison project 2001 of the EANET**

## 2. PROCEDURE

### 2.1 Participating Laboratories

Twenty-three laboratories in charge of chemical analysis in 10 countries of EANET participated in this survey. The Network Center (NC) shipped the artificial rainwater samples to all of these 23 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 (of both 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 (higher concentration) No.2 (lower concentration)	Approximately 100ml	Poly-propyl ene bottle 100ml	One bottle each	Known amount of reagents are dissolved in deionized water

Before the measurement, each laboratory should accurately dilute distributed samples by 100 times under 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. The participating laboratories were informed 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	µmol/L
NO <sub>3</sub> <sup>-</sup>	micro mole/liter	µmol/L
Cl <sup>-</sup>	micro mole/liter	µmol/L
Na <sup>+</sup>	micro mole/liter	µmol/L
K <sup>+</sup>	micro mole/liter	µmol/L
Ca <sup>2+</sup>	micro mole/liter	µmol/L
Mg <sup>2+</sup>	micro mole/liter	µmol/L
NH <sub>4</sub> <sup>+</sup>	micro mole/liter	µmol/L

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

Parameter	Range	Parameter	Range
pH	4.0– 5.5	Na <sup>+</sup>	1 – 100µmol /L
EC	1.0 – 10.0 mS/m	K <sup>+</sup>	1 – 50µmol /L
SO <sub>4</sub> <sup>2-</sup>	10 – 100µmol /L	Ca <sup>2+</sup>	1 – 50µmol /L
NO <sub>3</sub> <sup>-</sup>	10 – 100µmol /L	Mg <sup>2+</sup>	1 – 50µmol /L
Cl <sup>-</sup>	10 – 150µmol /L	NH <sub>4</sub> <sup>+</sup>	10 – 100µmol /L

\* For 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 ( $C$ :  $\mu\text{mol L}^{-1}$ ).

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

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

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

$n$ ,  $C_{\text{Ci}}$ : 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. If  $R_1$  is out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves should be undertaken.

**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 values of electrical conductivity (R<sub>2</sub>)**

(1) Total electric conductivity ( $\Delta_{\text{calc}}$ ) should be calculated as follows;

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

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 ( $\Delta_{\text{calc}}$ ) to measurements ( $\Delta_{\text{meas}}$ ) in electric conductivity should be calculated as follows;

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

(3) R<sub>2</sub>, which is calculated using the above equation, should be compared with standard values in Table 6. If R<sub>1</sub> is out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves are necessary.

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

$\Delta_{\text{meas}}$ (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 23 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 were calculated for each constituent of the artificial rainwater samples such as: Average, Minimum (Min.), Maximum (Max.), Standard deviation (S.D.), and Number of data (N). Outlying data, which are apart from the Average greater than a factor of 3 of S.D. were not included for this calculation. As shown in Table 7, average of submitted data were fairly well agreed with the prepared value/concentration within a range of  $\pm 10\%$ .  $\text{Cl}^-$  and  $\text{NH}_4^+$  gave rather varied data than others for both samples.

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

Constituents	Prepared	Average	S.D.	N	Min.	Max.
[Sample No.1] pH	4.10	4.11	0.04	21	4.03	4.17
EC(mS/m)	7.45	7.14	0.17	21	6.86	7.61
$\text{SO}_4^{2-}$ ( $\mu\text{mol/L}$ )	85.0	84.9	3.53	22	79.3	93.2
$\text{NO}_3^-$ ( $\mu\text{mol/L}$ )	93.3	90.4	4.18	22	78.2	98.1
$\text{Cl}^-$ ( $\mu\text{mol/L}$ )	108.4	105.5	8.17	23	81.4	124.4
$\text{Na}^+$ ( $\mu\text{mol/L}$ )	68.4	67.5	2.21	20	63.5	72.0
$\text{K}^+$ ( $\mu\text{mol/L}$ )	15.8	15.6	0.85	23	13.9	17.5
$\text{Ca}^{2+}$ ( $\mu\text{mol/L}$ )	41.1	39.6	3.27	23	30.5	45.9
$\text{Mg}^{2+}$ ( $\mu\text{mol/L}$ )	18.7	18.8	0.57	21	17.8	20.4
$\text{NH}_4^+$ ( $\mu\text{mol/L}$ )	87.8	89.6	4.05	21	78.5	98.4
[Sample No.2] pH	4.82	4.87	0.09	23	4.67	5.11
EC(mS/m)	1.76	1.68	0.07	22	1.50	1.82
$\text{SO}_4^{2-}$ ( $\mu\text{mol/L}$ )	21.5	21.1	2.23	23	15.6	24.6
$\text{NO}_3^-$ ( $\mu\text{mol/L}$ )	19.4	18.6	0.73	21	16.6	19.7
$\text{Cl}^-$ ( $\mu\text{mol/L}$ )	34.4	33.4	2.57	23	27.0	38.2
$\text{Na}^+$ ( $\mu\text{mol/L}$ )	27.4	26.0	1.72	23	21.7	28.1
$\text{K}^+$ ( $\mu\text{mol/L}$ )	4.0	4.0	0.51	22	2.9	5.2
$\text{Ca}^{2+}$ ( $\mu\text{mol/L}$ )	13.2	12.9	1.77	23	9.4	17.2
$\text{Mg}^{2+}$ ( $\mu\text{mol/L}$ )	3.7	3.7	0.45	22	2.5	4.5
$\text{NH}_4^+$ ( $\mu\text{mol/L}$ )	16.7	16.8	2.94	23	9.1	22.8

(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 during 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 excess of DQOs value: the flag "E" was put to the data that exceed DQOs by a factor of 2 ( $\pm 15\% \sim \pm 30\%$ ), and the flag "X" was put to the data that exceed DQOs more than a factor of 2 ( $< -30\%$  or  $> 30\%$ ). A set of data for each sample was evaluated by the data checking procedures described further 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 circumstances of analysis in each participating laboratory. Evaluation of data on both the sample No.1 and No.2 is presented in "3.1 Comparison by Sample", evaluation of data for each constituent is presented in "3.2 Analytical Parameter", and evaluation of data by the circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is presented in "3.3 Circumstance of Sample Analysis".

### 3.1 Comparison by Sample

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

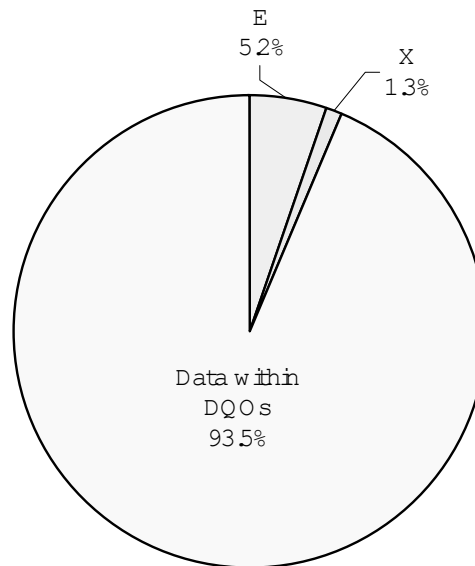
**Table 8 Number of flagged data for the Sample No.1 (higher concentrations)**

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	1	1	2	2	2	0	3	1	0	12
X	0	0	0	0	0	0	0	0	1	2	3
Data within DQOs	23	22	22	21	21	21	23	20	21	21	215
Flagged(%)	0.0	4.3	4.3	8.7	8.7	8.7	0.0	13.0	8.7	8.7	6.5

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

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

For sample No.1 (higher concentrations), 12 analytical data out of 230 exceeded the DQOs by a factor of 2 and flagged by "E". 3 analytical data out of 230 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" were 15 out of 230, shared about 6.5 percents of all reported data for sample No.1 (Fig.2).



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

**Table 9 Analytical Results of Sample No.1 (higher concentrations)**

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)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	(µmol/L)	-	-							
CN01	4.11	7.20	81.7	81.7	111.4	E	55.4	16.2	E	34.9	X	12.6	91.6	-3.0	-0.9				
CN02	4.07	7.36	84.8	92.6	102.0		67.4	15.2		39.3		18.6	90.7	1.4	1.3				
CN03	4.08	7.01	81.2	91.0	101.9		64.7	15.7		39.1		18.2	91.9	2.0	2.8				
CN04	4.09	7.00	82.7	91.7	104.7		65.2	15.7		40.8		18.8	91.8	1.5	2.9				
ID01	4.57	E	5.78	87.4	E	73.1	E	81.4	64.5	15.8	E	30.5	19.8	X	55.1	I	-11.2	-8.2	
ID02	4.12		6.86	86.8		84.1		124.4	66.4	16.4		40.0	18.9		88.5		-2.3	3.6	
JP01	4.15		7.30	84.5		92.6		102.2	69.9	14.0		39.7	18.6		89.9		-0.4	-1.7	
JP02	4.12		7.06	84.2		93.1		107.0	68.9	14.4		41.3	18.6		84.0		-0.8	1.3	
JP03	4.15		6.99	83.2		89.3		112.0	66.8	15.1		39.8	18.4	X	47.3		-7.5	-1.6	
JP04	4.15		7.02	82.6		91.6		109.0	76.7	15.7		45.9	20.4		90.1		2.7	1.4	
JP05	4.06		7.19	80.9		89.0		101.0	69.2	15.6		42.9	19.0		78.5		3.1	2.1	
JP06	4.15		7.02	79.3		91.4		98.5	70.5	16.7		40.1	18.9		98.4		3.6	0.1	
JP07	4.14		7.38	E	69.0	93.3		108.0	68.2	15.5		41.2	18.7		87.2		3.4	-3.2	
JP08	4.17		7.03	83.7		92.0		108.0	68.6	15.5		40.7	18.5		87.3		-1.4	-0.4	
KR01	4.12		7.26	92.3		89.2		108.5	67.1	15.2		36.1	19.2		96.3		-2.3	0.9	
MY01	4.03		7.03	93.2		88.9	E	91.1	72.0	16.7		40.6	19.4		89.6		3.3	6.0	
MN01	4.11		7.17	90.9		98.1		111.1	68.2	15.3		41.4	17.8		93.6		-2.3	2.6	
PH01	4.15		6.42	84.4		91.3		102.6	66.5	15.0	E	33.0	18.6		91.1		-2.3	4.1	
RU01	4.09		7.18	82.0		93.5		111.0	64.9	17.5		37.1	18.1		89.8		-0.6	1.6	
TH01	4.16		7.17	86.4		93.3		109.3	63.5	15.8		42.4	19.4		88.8		-2.0	-0.5	
TH02	4.10		7.02	87.5		92.0		107.7	70.1	16.2		41.4	18.7		88.9		0.0	3.1	
TH03	3.96		7.12	84.1		90.8		101.2	67.2	13.9		40.4	18.8		86.8		4.7	8.0	
VN01	4.09		7.61	85.0	E	78.2		113.4	E	48.1		14.5	41.6	E	22.0		86.2	-0.6	-1.8

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

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

I:Poor ion balance (R1)

C:Poor conductivity agreement (R2)

**Sample No.2 (lower concentrations)**

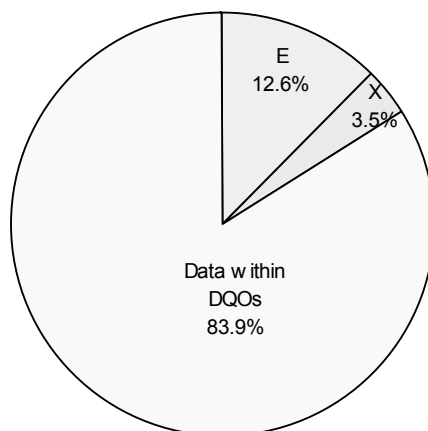
**Table 10 Number of flagged data for the Sample No.2 (lower concentrations)**

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	1	3	1	3	2	5	7	5	2	29
X	0	0	0	1	0	0	1	1	2	3	8
Data within DQOs	23	22	20	21	20	21	17	15	16	18	193
Flagged(%)	0.0	4.3	13.0	8.7	13.0	8.7	26.1	34.8	30.4	21.7	16.1

\*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), 29 analytical data out of 230 exceeded the DQOs by a factor of 2 and flagged by "E". For Ca<sup>2+</sup>, data from 7 laboratories were flagged by "E". 8 analytical data out of 230 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" were 37 analytical data out of 230, shared up to 16.1 percents of all reported data for sample No.2 (Fig.3).



**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 SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>. The data on Ca<sup>2+</sup> included a high rate(>10%) of the flagged data for the both concentration samples .



**Table 11 Analytical Results of Sample No.2 (lower concentrations)**

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)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	-	-
CN01	4.87	1.66	E 15.6	16.6	33.7	E 22.8	3.8	13.0	X 2.5	X 22.8	7.1	-2.2
CN02	4.79	1.78	23.3	19.3	33.7	25.9	4.0	13.3	3.6	17.1	-1.3	1.0
CN03	4.83	1.66	23.3	18.9	35.3	23.4	3.7	13.9	3.9	17.0	-3.2	3.3
CN04	4.81	1.66	22.0	18.8	35.3	25.2	4.4	14.2	3.7	17.3	0.0	3.8
ID01	5.02	E 1.36	E 17.5	X 13.6	E 29.1	24.6	E 3.3	E 9.4	3.7	E 12.4	-1.0	-1.2
ID02	4.93	1.50	18.5	18.2	34.3	25.8	4.1	12.8	3.6	X 9.1	-3.5	0.5
JP01	4.88	1.75	21.2	18.5	30.8	27.8	4.0	12.3	3.6	17.5	1.4	-2.9
JP02	4.84	1.72	21.5	19.1	34.1	27.6	3.5	E 15.2	3.7	15.5	1.4	0.7
JP03	4.89	1.66	21.1	19.4	34.4	26.6	3.7	12.9	3.6	18.2	-0.8	0.5
JP04	4.92	1.67	22.0	19.0	35.1	27.7	4.3	13.0	3.6	19.0	-1.0	0.3
JP05	4.87	1.75	20.5	18.5	33.1	26.9	3.7	14.8	E 4.3	17.1	3.5	-1.6
JP06	4.90	1.69	18.3	17.4	E 27.0	24.5	3.7	12.9	E 2.9	17.2	5.1	-5.1
JP07	4.86	1.69	21.3	18.6	33.4	27.2	E 2.9	E 10.3	E 2.9	17.8	-3.6	-1.1
JP08	4.91	1.68	21.8	18.7	34.2	27.7	3.8	13.1	3.6	16.6	-1.4	-0.7
KR01	4.88	1.63	24.6	18.6	31.9	27.3	E 5.2	12.7	4.0	X 10.1	-5.6	1.4
MY01	4.67	1.73	23.6	17.3	E 27.9	28.1	4.0	E 11.2	3.6	16.8	3.9	5.4
MN01	4.83	1.75	22.6	19.4	36.0	27.5	4.0	12.9	3.9	18.9	-0.8	1.3
PH01	5.11	1.56	21.8	18.7	32.4	24.9	4.6	E 10.4	3.9	E 20.3	-4.7	-2.8
RU01	4.80	1.74	21.7	19.1	33.1	25.6	E 4.6	E 11.0	3.7	18.7	-0.8	0.6
TH01	4.89	1.67	21.7	18.9	34.1	26.3	4.3	E 15.7	E 4.5	15.5	1.5	0.9
TH02	4.75	1.57	22.7	18.6	35.3	27.9	4.2	12.6	3.8	18.9	1.1	9.2
TH03	4.80	1.63	21.3	19.7	35.8	26.0	E 5.0	X 17.2	E 4.4	17.3	4.5	6.5
VN01	4.85	1.82	E 16.6	E 23.7	38.2	E 21.7	X 7.5	11.5	X 8.7	15.2	2.0	-2.6

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

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

I:Poor ion balance (R1)

C:Poor conductivity agreement (R2)

### 3.2 Analytical Parameter

The general overviews of data were presented below in Figures and Tables for each analytical parameter. The results received from each laboratory were normalized by prepared values to evaluate a deviation. The numbers of flagged data were shown in table for each analytical parameter.

#### pH

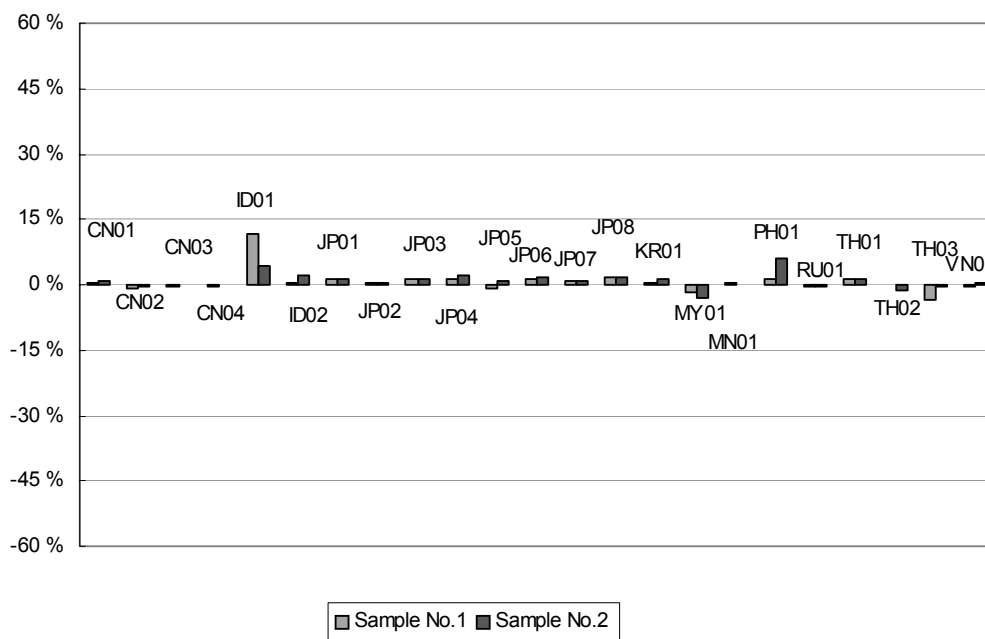


Fig.4 Distribution of pH data normalized by prepared value

Table 12 Analytical method and flagged data of pH

#### Analytical Method

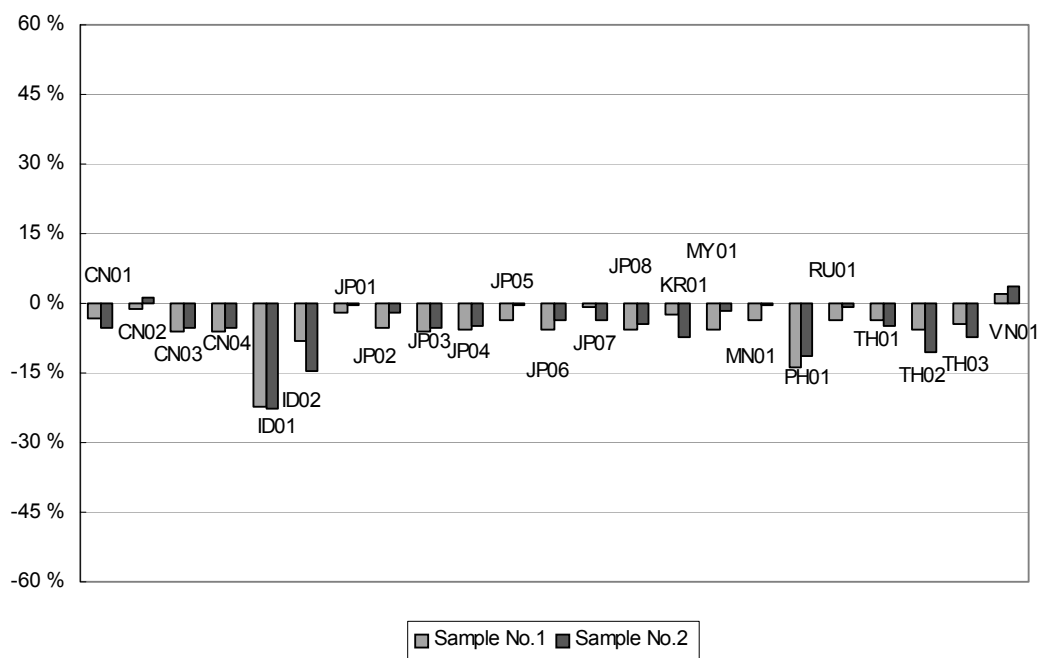
pH meter and electrode	23/23
------------------------	-------

#### Flagged data

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

All participating laboratories used pH meter with glass electrode for measurement of pH. Most of obtained data were agreed with prepared value. Many laboratories submitted slightly higher pH values than prepared value. The relative standard deviations of the pH values for sample No.1 and No.2 were good as a result of 0.9% □1.8% after rejecting the data which exceeds 3 times of standard deviation from average 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	23/23
-----------------------------	-------

### Flagged data

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

All participating laboratories used conductivity cell for the measurement of EC. Obtained data were almost agreed with the prepared value. However, Lab.ID01 submitted flagged data by "E" for sample No.1 and No.2. Most of the laboratories reported lower data than prepared value.

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

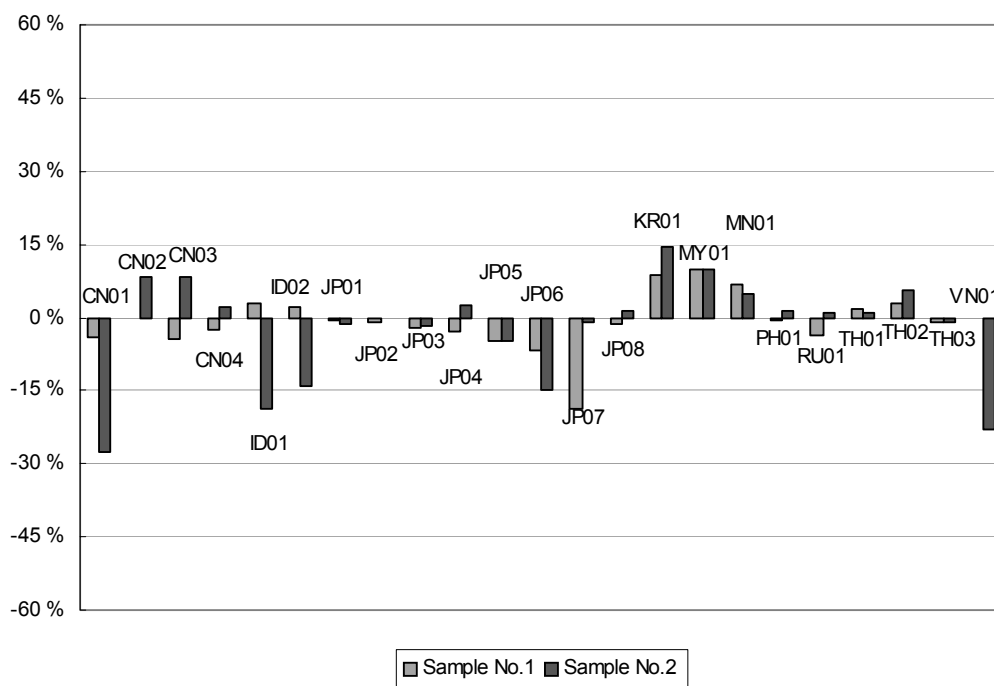


Fig.6 Distribution of SO<sub>4</sub><sup>2-</sup> data normalized by prepared concentration

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

**Analytical Method**

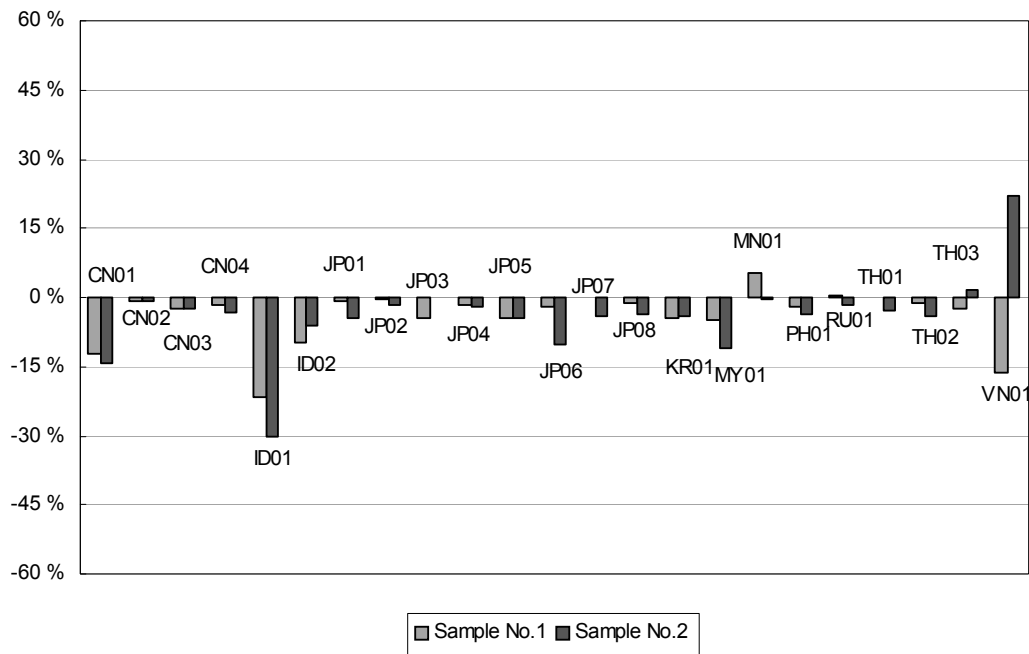
Ion chromatography	22/23
Spectrophotometry	1/23

**Flagged data**

	E	X	Flagged (%)
Sample No.1	1	0	4.3
Sample No.2	3	0	13.0

All of the participating laboratories used ion chromatography for the determination of SO<sub>4</sub><sup>2-</sup> except for one laboratory (Lab.VN01), which used spectrophotometry. Sample No1 or No2 data of Lab.CN01, ID01, JP07, VN01 were about 15% lower than prepared value.

**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	22/23
Spectrophotometry	1/23

**Flagged data**

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

The both data of Lab.ID01 (obtained by ion chromatography ) and Lab.VN01 (obtained by spectrophotometry) were all flagged. The results of Lab.ID01 (obtained by ion chromatography) were about 15-30% lower than the prepared value. It seemed to be the calibration error in the analysis. The results of Lab.VN01 were about 15% lower or higher value than the prepared value. It seemed to be a problem in the analytical procedure with spectrophotometry method.

Cl<sup>-</sup>

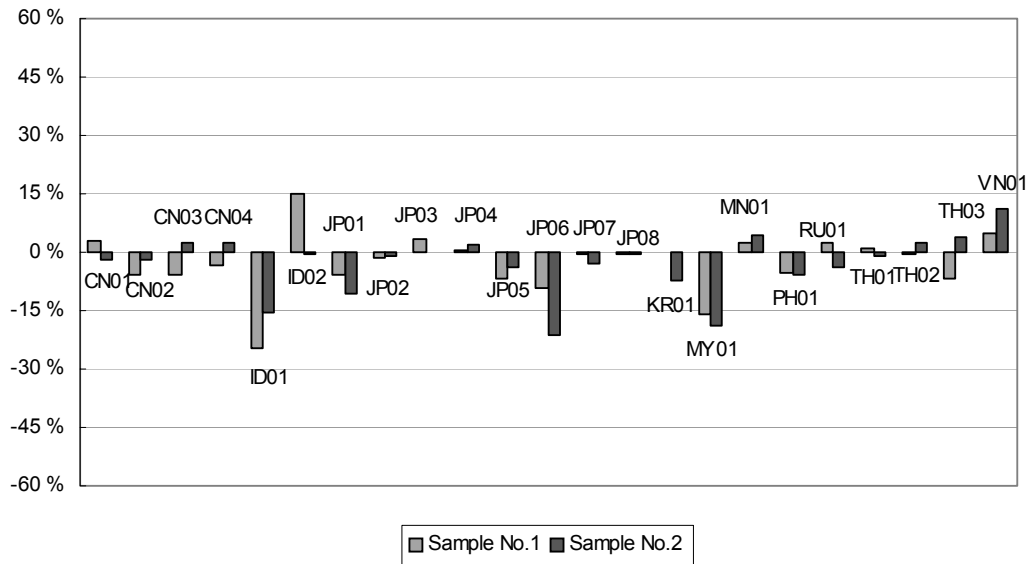


Fig.8 Distribution of Cl<sup>-</sup> data normalized by prepared concentration

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

**Analytical Method**

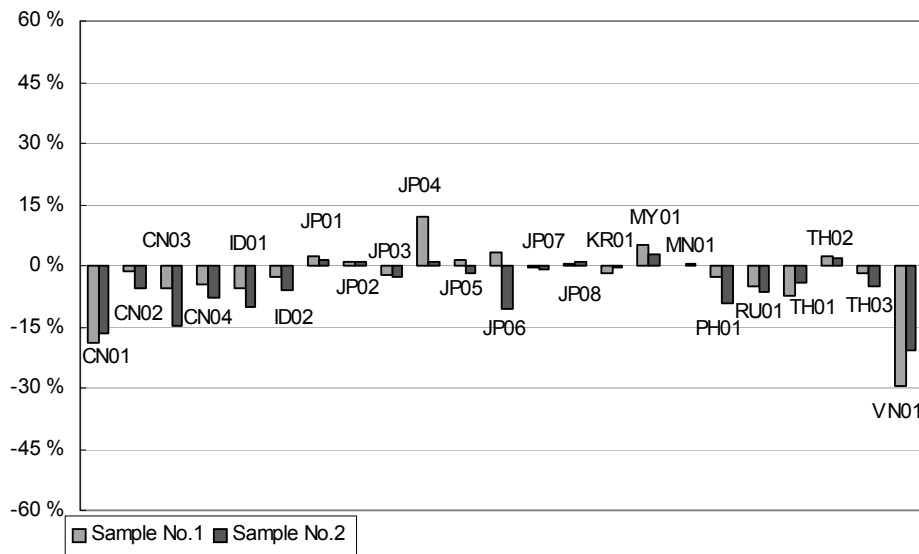
Ion chromatography	22/23
Titration/Spectrophotometry	1/23

**Flagged data**

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

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>. One laboratory (Lab.VN01) used titration method for the determination of Cl<sup>-</sup>. Data on sample No1 and No2 of Lab.ID01, JP06, MY01 were about 15% lower than prepared value. It seemed to be the calibration error in the analysis.

## 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>**

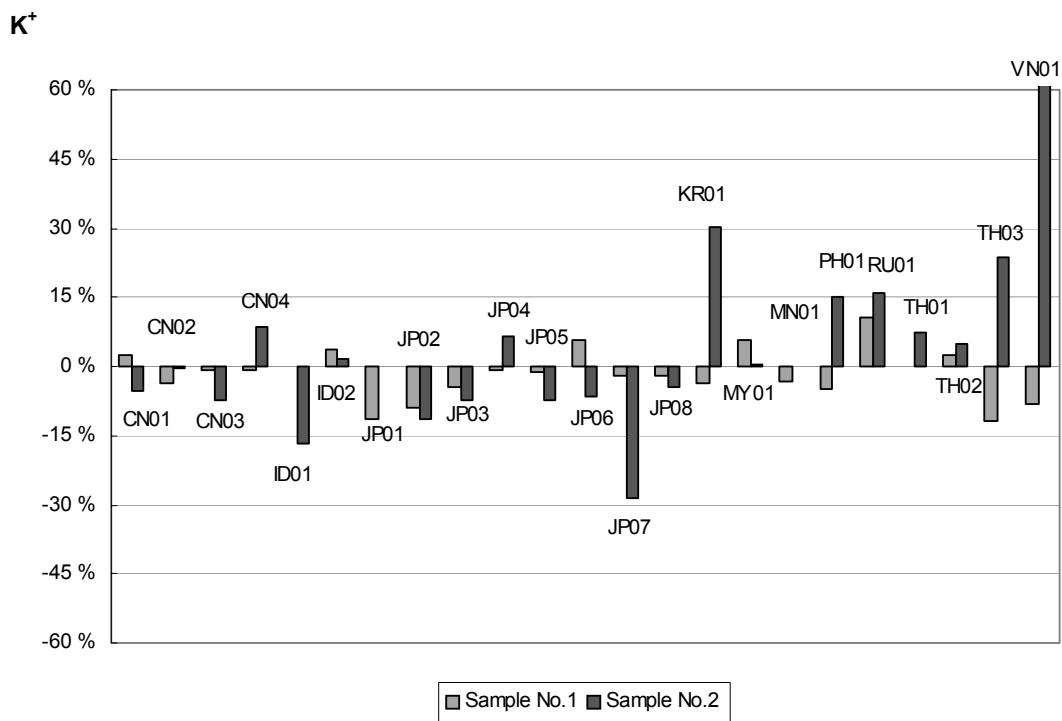
### Analytical Method

Ion chromatography	15/23
Atomic absorption / Flame (emission) photometry	7/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23

### Flagged data

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

15 laboratories used ion chromatography, 7 laboratories used atomic absorption/flame (emission) photometry, and the other one laboratory (Lab.MY01) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Na<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 a few flagged data in this survey.



**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	15/23
Atomic absorption / Flame (emission) photometry	7/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23

**Flagged data**

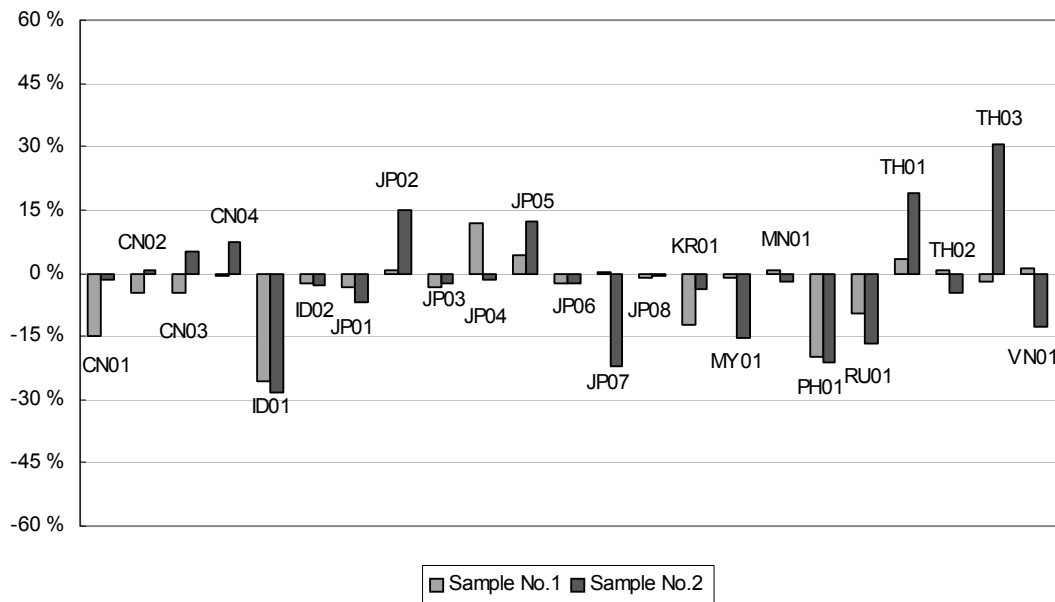
	E	X	Flagged (%)
Sample No.1	0	0	0
Sample No.2	5	1	26.0

Same as Na<sup>+</sup>, 15 laboratories used ion chromatography, 7 laboratories used atomic absorption/flame (emission) photometry, and the other one laboratory (Lab.MY01) used inductively coupled plasma mass spectrometry (ICP-MS) for the determination of K<sup>+</sup>.

There was clearly difference of data obtained by different analytical methods for Sample No.2. Most of the data by ion chromatography were satisfied with the DQOs. But over half of the data by atomic absorption/flame (emission) spectrometry was flagged out of the DQOs.(Lab.ID01, KR01, RU01, VN01)



## 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

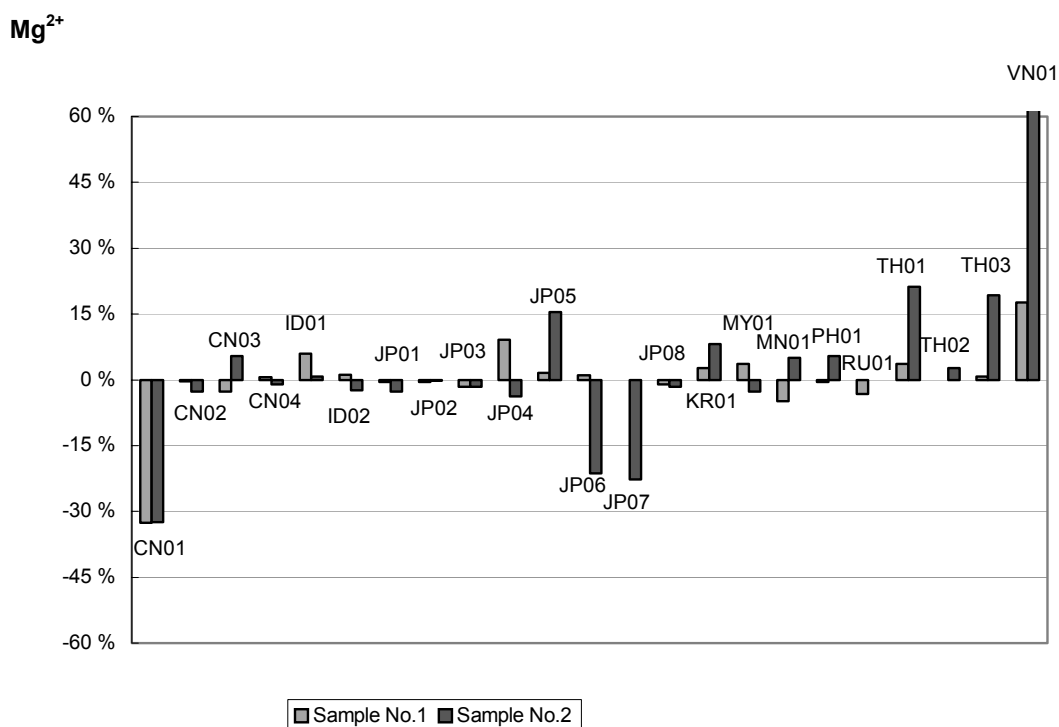
Ion chromatography	15/23
Atomic absorption / Flame (emission) photometry	6/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23
Other method(Titration)	1/23

### Flagged data

	E	X	Flagged (%)
Sample No.1	2	0	13.0
Sample No.2	7	1	13.0

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.ID01, PH01 (atomic absorption photometry) submitted significantly deviated data for both Sample No.1 and Sample No.2.



**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**

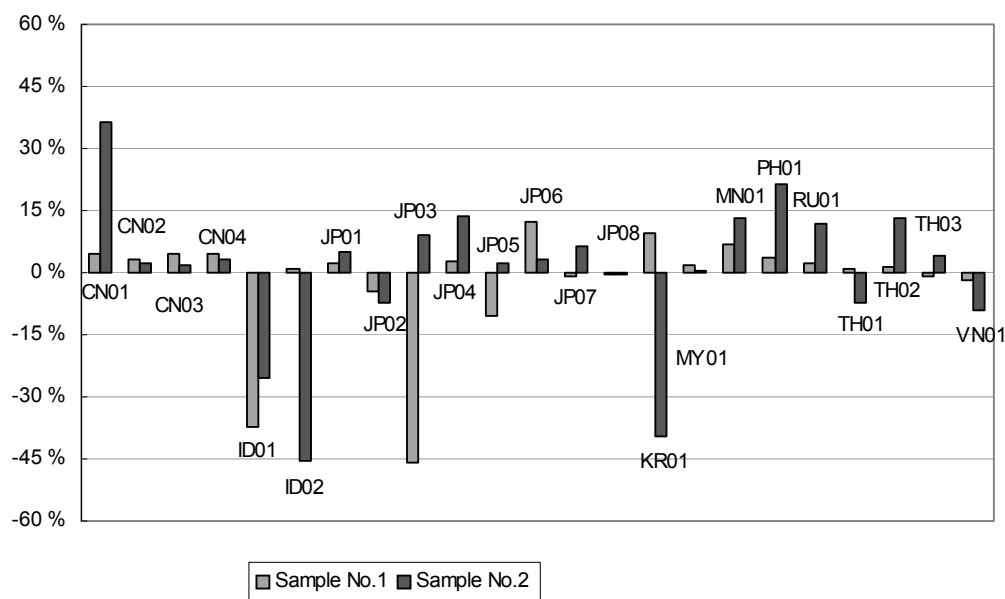
Ion chromatography	15/23
Atomic absorption / Flame (emission) photometry	6/23
Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)	1/23
Other method	1/23

**Flagged data**

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

15 laboratories used ion chromatography, 6 laboratories used atomic absorption/flame (emission) photometry, and one laboratory (Lab.MY01) used inductively coupled plasma mass spectrometry (ICP-MS) as analytical instruments for the determination of Mg<sup>2+</sup>. 1 laboratory (Lab.VN01) 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 are significantly outstanding from prepared concentration (Lab.VN01).

**NH<sub>4</sub><sup>+</sup>**



**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	16/23
Spectrophotometry (Indophenol blue)	3/23
Other method (Spectrophotometry)	4/23

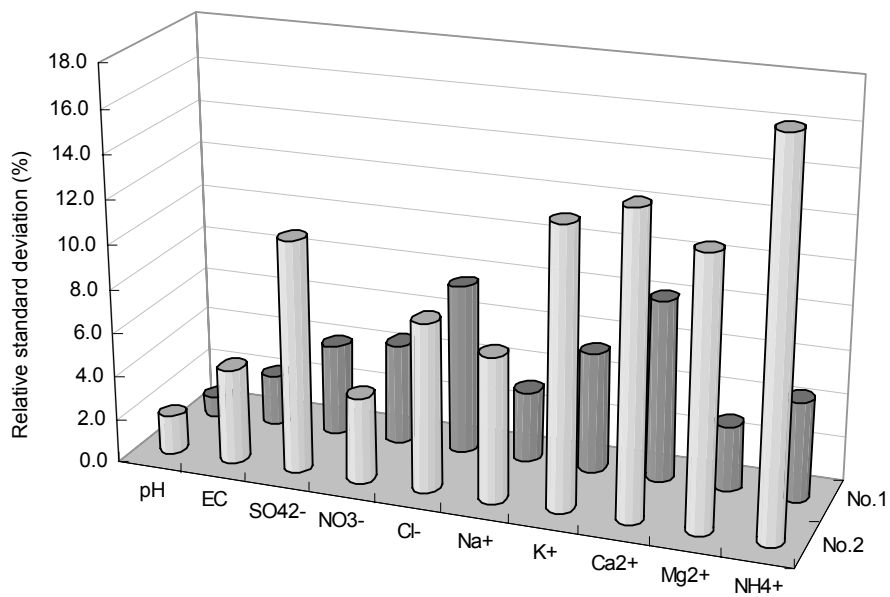
**Flagged data**

	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>: 16 laboratories used ion chromatography. 3 laboratories used spectrometry (Indophenol blue). Five laboratories (Lab.CN01, ID01, ID02, JP03, KR01) submitted significantly different data. Lab.CN01, ID02 and JP03 used ion chromatography and their data were deviated from prepared concentration. Lab.ID01 and Lab.KR01 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. And, data on other cations such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were varied over 10%. It is expected to improve the quality of data that has large deviation through the QA/QC activities in each laboratory.



(Relative standard deviation (%) = (Standard deviation / Average) x100; Reported data after removing the outliers)

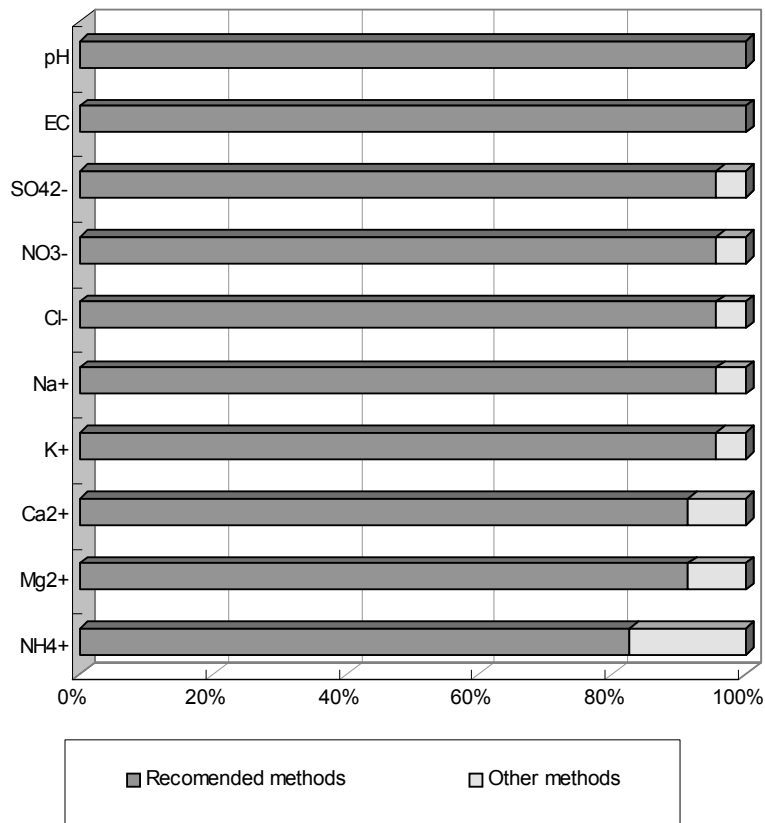
**Fig.14** Relative standard deviation of each constituent



### 3.3 Circumstance of Sample Analysis

#### Methods Used

As shown in Fig.15, most of participating laboratories made use of 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. Not recommended methods of EANET were used in some laboratories for anion & cation analysis.



**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	Spectrophotometry
8	Indophenol Spectrophotometry
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
X	Other method

**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	23									
1		23(1)								
2					1			1	1(1)	
3						7(1)	7	6(2)	6	
4										
5			22(1)	22(1)	22(2)	15(1)	15	15(1)	15(1)	16(1)
6										
7			1	1(1)						4(1)
8										3
9						1	1	1	1	
10										
X										
Flagged E	0	1	1	2	2	2	0	3	1	0
Flagged X	0	0	0	0	0	0	0	0	1	2

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	23									
1		23(1)								
2					1			1	1(1)	
3						7(1)	7(4)	6(3)	6	
4										
5			22(2)	22(1)	22(3)	15(1)	15(2)	15(4)	15(6)	16(2)
6										
7			1(1)	1(1)						4(1)
8										3(2)
9						1	1	1(1)	1	
10										
X										
Flagged E	0	1	3	1	3	2	5	7	5	2
Flagged X	0	0	0	1	0	0	1	1	2	3

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 thirteen laboratories, only one person carried out measurement of rainwater samples in each Lab. In other laboratories, from 2 to 5 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 10 laboratories). In one laboratory, two 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>
CN01	1	A	A	A	A	A	A	A	A	A	A
CN02	4	A	A	B	B	B	C	C	C	C	D
CN03	1	A	A	A	A	A	A	A	A	A	A
CN04	1	A	A	A	A	A	A	A	A	A	A
ID01	3	A	B	, b	, b	, b	, a	, a	A	B	A
ID02	3	A	A	B	B	B	A	A	C	C	B
JP01	1	A	A	A	A	A	A	A	A	A	A
JP02	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A
JP05	1	A	A	A	A	A	A	A	A	A	A
JP06	1	A	A	A	A	A	A	A	A	A	A
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
KR01	1	A	A	A	A	A	A	A	A	A	A
MY01	4	A	A	B	B	B	C	C	C	C	D
MN01	2	A	B	B	B	B	,	,	,	,	,
PH01	5	A	A	B	B	B	C,D	C,D	C,D	C,D	E
RU01	3	A	A	B	B	B	C	C	C	C	A
TH01	2	A	A	B	B	B	A	A	A	A	A
TH02	2	A	A	B	B	B	B	B	B	B	B
TH03	1	A	A	A	A	A	A	A	A	A	A
VN01	2	A	A	B	B	B	A	A	B	B	A

"A", "B", "C", and "D" represent individuals of staff in each laboratory who are in charge of measurement.

Reverse mesh: Flagged data of "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”, same as previous surveys.

**Table 25 Years of experience**

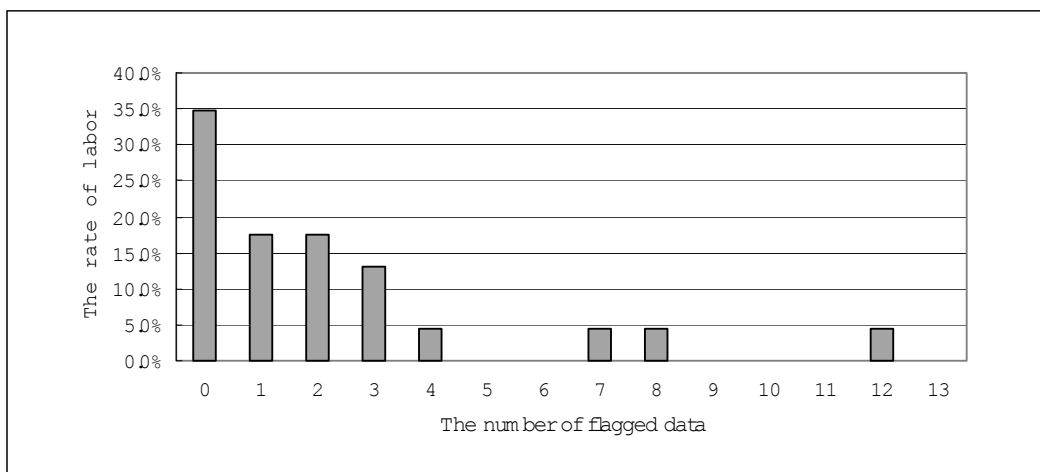
Unit: year

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>
CN01	10	10	10	10	10	10	10	10	10	10
CN02	5	5	10	10	10	2	2	2	2	6
CN03	2	2	2	2	2	2	2	2	2	2
CN04	6	6	6	6	6	6	6	6	6	6
ID01	2	2	12	12	12	2	2	2	2	2
ID02	1	1	3	3	3	1	1	1	1	3
JP01	17	17	17	17	17	17	17	17	17	17
JP02	2	2	2	2	2	2	2	2	2	2
JP03	4	4	4	4	4	4	4	4	4	4
JP04	13	13	13	13	13	13	13	13	13	13
JP05	5	5	5	5	5	5	5	5	5	5
JP06	1	1	1	1	1	1	1	1	1	1
JP07	5	5	5	5	5	5	5	5	5	5
JP08	1	1	1	1	1	1	1	1	1	1
KR01	3	3	3	3	3	3	3	3	3	3
MY01	4	4	4	4	4	1	1	1	1	3
MN01	4	4	4	4	4	4	4	4	4	4
PH01	2	2	3	3	3	5	5	5	5	4
RU01	4	4	4	4	4	2	2	2	2	4
TH01	1	1	3	3	3	1	1	1	1	1
TH02	1	1	1	1	1	1	1	1	1	1
TH03	1	1	1	1	1	1	1	1	1	1
VN01	16	16	7	7	6	16	16	7	7	16

Reverse mesh: Flagged data of “E” or “X” in sample No.1 and/or sample No.2

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	34.8%
1	4	17.4%
2	4	17.4%
3	3	13.0%
4	1	4.3%
5~6	0	0.0%
7	1	4.3%
8	1	4.3%
9~11	0	0.0%
12	1	4.3%

In this project, the number of flagged data was 52 among a total of 460 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 about 1/3 of the all-participating laboratories. Moreover, 16 laboratories (70% of all) submitted less than 2 flagged data, which seemed to be managed comparatively well. On the other hand, 2 laboratories with 7~8 flagged data and 1 laboratory with 12 flagged data need some improvement. One of these laboratories could use neither ion chromatography nor atomic absorption spectrometry, although they had this kind of individual equipment. Therefore, these laboratories should make an effort for implementation 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 two laboratories that water temperature was 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 No.1	pH Sample No.2	EC Sample No.1	EC Sample No.2
CN01	25	25	25	25
CN02	19	19	19	19
CN03	11	11	11	11
CN04	25	25	25	25
ID01	25.6	25.6	E 25.6	E 25.6
ID02	25	25	25	25
JP01	23.1□ 23.6	22.8□ 23.7	22.3□ 23.0	22.3□ 22.9
JP02	25	25	25	25
JP03	24.8	24.8	24.8	24.8
JP04	24.5	24.6	24.9	25
JP05	22.5	22.5	22.5	22.5
JP06	25	25	25	25
JP07	25	25	25	25
JP08	25	25	25	25
KR01	25	25	25	25
MY01	23.7	22.7	25.1	24.1
MN01	25	25	25	25
PH01	25	25	25	25
RU01	25	25	25	25
TH01	24.5	25	24.5	25.5
TH02	25	25	25	25
TH03	25	25	25	25
VN01	25	25	25	25

E: E flagged the data (Value exceeded the DQO( $\pm 15\%$ ))

X: X flagged the data (Value exceeded the DQO( $\pm 30\%$ ))

#### 4. COMPARISON OF 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> AND 4<sup>th</sup> SURVEY

The inter-comparison surveys were carried out 4 times, so far their results of the number of flagged data are 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), 3<sup>rd</sup> (2000), and 4<sup>th</sup> (2001) survey, the rates of DQOs were up to 84-93%. The data quality seemed to be improved by accumulating experiences. However, the results of the 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> survey remain at almost same levels. This seems to be a room to be improved taking into account the laboratories, which have inadequate using condition of equipment or apparatus. Contamination from used instrument, measurement apparatus and so on might be considered, especially, for the low concentration sample (Sample No.2), which contains about 16% flagged data, all above 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.

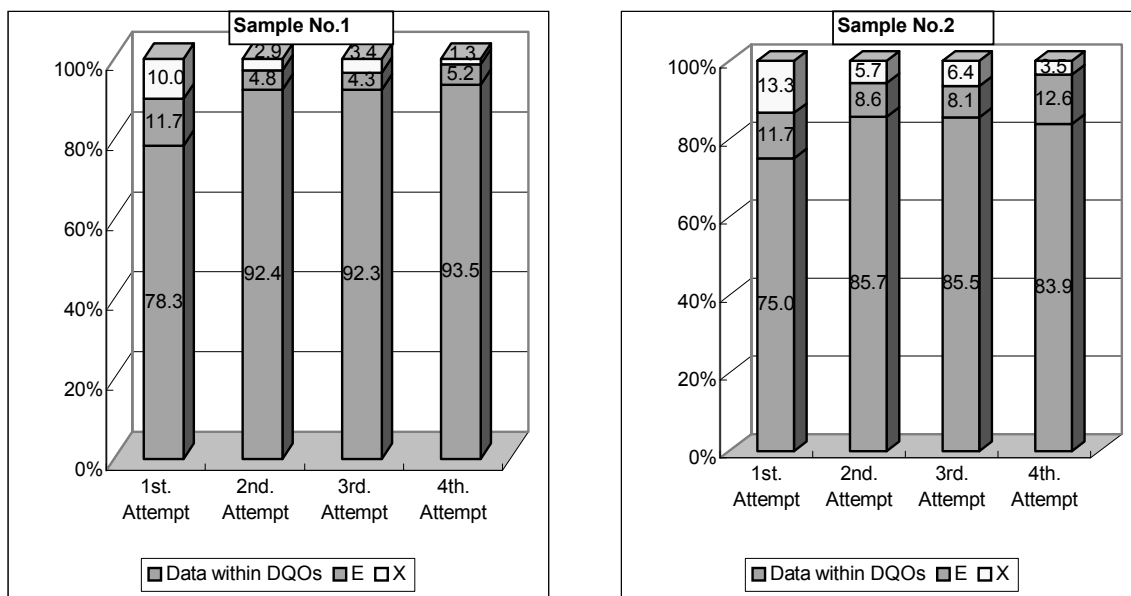


Fig. 17 Comparison of 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> inter-laboratory comparison project

## **5. FOR IMPROVEMENT OF MEASUREMENT PRECISIONS**

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

### **5.1 Fundamental measurement and analysis matters**

Clearance from contamination of the apparatus, materials and reagents used for measurement and analysis must be confirmed beforehand; blank values of target substances should be as low as possible. Measurement and analysis should be conducted by persons who are well trained.

To maintain high analytical quality, SOPs must be prepared for the management of apparatus, materials and reagents.

Other details on measurement and analysis of samples are as follows.

#### **1) Deionized water**

Water with a conductivity less than 0.15mS/m is acceptable for measurements, analyses, dilution of precipitation samples and cleaning.

#### **2) Certified materials and certified samples**

The measurements are evaluated by comparison of measured results of samples and certified materials. In order to assure the reliability of measurements, the certified solutions and certified materials that were certified for traceability should be used as much as possible.

#### **3) Pretreatment of samples at analytical laboratory**

Conductivity and pH should be measured as soon as possible after sample receiving, and checking agreement of samples and sample list.

Effort should be made to start analysis of the other parameters within a week of sample arrival in the laboratory and to complete the data sets by measuring EC, pH and all other chemical parameters.

#### **4) Adjustment of analytical instruments**

Each of the analytical instruments must be calibrated when they are used, and they should be adjusted as appropriate.

### **5.2 Evaluation of reliability**

#### **1) Sensitivity fluctuation of analytical instruments**

While numerous samples are measured, measurements should be continued after confirming that the sensitivity fluctuation is within the prescribed range.

##### **a) For example, Ion chromatography**

A new calibration should be performed not more than 30-sample measurements. Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration. Control charts should be applied for the measurement of the reference materials. Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent. If the results of the control solutions are outside of 3 standard deviations, or out of 15 % from the expected value, the reasons should be found and corrections will be made, and reference solution will be measured again.

If the retention time changes slowly while the separator column is deteriorating, then adequate actions could be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.

### **5.3 Data control**

#### **1) Data check in analysis organizations**

When the sensitivity of instruments is not stable, when the results of duplicate analyses or

re-measurements are significantly different, or when the ratio of a theoretical value to that for determined data in ion balances and electrical conductivity is significantly different from 1.0, measurement should be repeated since reliability is low. When samples seem to be obviously contaminated, these data should be treated as unrecorded data.

Abnormal or unrecorded data can corrupt research results. So, careful checks are needed to avoid data of inadequate quality. When abnormal or unrecorded data appear, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

## 6. 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
- 5) Report of the Inter-laboratory Comparison Project 2000  
(Round robin analysis survey 3<sup>rd</sup>. Attempt) October 2001

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## APPENDIX 2 Original data

Sample No.1(higher concentrations)

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
CN01	4.11	7.20	81.7	81.7	111.4	55.4	16.2	34.9	12.6	91.6
CN02	4.07	7.36	84.8	92.6	102.0	67.4	15.2	39.3	18.6	90.7
CN03	4.08	7.01	81.2	91.0	101.9	64.7	15.7	39.1	18.2	91.9
CN04	4.09	7.00	82.7	91.7	104.7	65.2	15.7	40.8	18.8	91.8
ID01	4.57	5.78	87.4	73.1	81.4	64.5	15.8	30.5	19.8	55.1
ID02	4.12	6.86	86.8	84.1	124.4	66.4	16.4	40.0	18.9	88.5
JP01	4.15	7.30	84.5	92.6	102.2	69.9	14.0	39.7	18.6	89.9
JP02	4.12	7.06	84.2	93.1	107.0	68.9	14.4	41.3	18.6	84.0
JP03	4.15	6.99	83.2	89.3	112.0	66.8	15.1	39.8	18.4	47.3
JP04	4.15	7.02	82.6	91.6	109.0	76.7	15.7	45.9	20.4	90.1
JP05	4.06	7.19	80.9	89.0	101.0	69.2	15.6	42.9	19.0	78.5
JP06	4.15	7.02	79.3	91.4	98.5	70.5	16.7	40.1	18.9	98.4
JP07	4.14	7.38	69.0	93.3	108.0	68.2	15.5	41.2	18.7	87.2
JP08	4.12	7.26	92.3	89.2	108.5	67.1	15.2	36.1	19.2	96.3
KR01	4.17	7.03	83.7	92.0	108.0	68.6	15.5	40.7	18.5	87.3
MY01	4.03	7.03	93.2	88.9	91.1	72.0	16.7	40.6	19.4	89.6
MN01	4.11	7.17	90.9	98.1	111.1	68.2	15.3	41.4	17.8	93.6
PH01	4.15	6.42	84.4	91.3	102.6	66.5	15.0	33.0	18.6	91.1
RU01	4.09	7.18	82.0	93.5	111.0	64.9	17.5	37.1	18.1	89.8
TH01	4.16	7.17	86.4	93.3	109.3	63.5	15.8	42.4	19.4	88.8
TH02	4.10	7.02	87.5	92.0	107.7	70.1	16.2	41.4	18.7	88.9
TH03	3.96	7.12	84.1	90.8	101.2	67.2	13.9	40.4	18.8	86.8
VN01	4.09	7.61	85.0	78.2	113.4	48.1	14.5	41.6	22.0	86.2
Prepared value	4.10	7.45	85.0	93.3	108.4	68.4	15.8	41.1	18.7	87.8
Data count	23	23	23	23	23	23	23	23	23	23
Average	4.13	7.05	84.2	89.6	105.5	66.5	15.6	39.6	18.7	86.2
Minimum	3.96	5.78	69.0	73.1	81.4	48.1	13.9	30.5	12.6	47.3
Maximum	4.57	7.61	93.2	98.1	124.4	76.7	17.5	45.9	22.0	98.4
Standard deviation	0.11	0.35	4.74	5.40	8.17	5.45	0.85	3.27	1.55	11.54

Sample No.2(lower concentrations)

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
CN01	4.87	1.66	15.6	16.6	33.7	22.8	3.8	13.0	2.5	22.8
CN02	4.79	1.78	23.3	19.3	33.7	25.9	4.0	13.3	3.6	17.1
CN03	4.83	1.66	23.3	18.9	35.3	23.4	3.7	13.9	3.9	17.0
CN04	4.81	1.66	22.0	18.8	35.3	25.2	4.4	14.2	3.7	17.3
ID01	5.02	1.36	17.5	13.6	29.1	24.6	3.3	9.4	3.7	12.4
ID02	4.93	1.50	18.5	18.2	34.3	25.8	4.1	12.8	3.6	9.1
JP01	4.88	1.75	21.2	18.5	30.8	27.8	4.0	12.3	3.6	17.5
JP02	4.84	1.72	21.5	19.1	34.1	27.6	3.5	15.2	3.7	15.5
JP03	4.89	1.66	21.1	19.4	34.4	26.6	3.7	12.9	3.6	18.2
JP04	4.92	1.67	22.0	19.0	35.1	27.7	4.3	13.0	3.6	19.0
JP05	4.87	1.75	20.5	18.5	33.1	26.9	3.7	14.8	4.3	17.1
JP06	4.90	1.69	18.3	17.4	27.0	24.5	3.7	12.9	2.9	17.2
JP07	4.86	1.69	21.3	18.6	33.4	27.2	2.9	10.3	2.9	17.8
JP08	4.91	1.68	21.8	18.7	34.2	27.7	3.8	13.1	3.6	16.6
KR01	4.88	1.63	24.6	18.6	31.9	27.3	5.2	12.7	4.0	10.1
MY01	4.67	1.73	23.6	17.3	27.9	28.1	4.0	11.2	3.6	16.8
MN01	4.83	1.75	22.6	19.4	36.0	27.5	4.0	12.9	3.9	18.9
PH01	5.11	1.56	21.8	18.7	32.4	24.9	4.6	10.4	3.9	20.3
RU01	4.80	1.74	21.7	19.1	33.1	25.6	4.6	11.0	3.7	18.7
TH01	4.89	1.67	21.7	18.9	34.1	26.3	4.3	15.7	4.5	15.5
TH02	4.75	1.57	22.7	18.6	35.3	27.9	4.2	12.6	3.8	18.9
TH03	4.80	1.63	21.3	19.7	35.8	26.0	5.0	17.2	4.4	17.3
VN01	4.85	1.82	16.6	23.7	38.2	21.7	7.5	11.5	8.7	15.2
Prepared value	4.82	1.76	21.5	19.4	34.4	27.4	4.0	13.2	3.7	16.7
Data count	23	23	23	23	23	23	23	23	23	23
Average	4.87	1.67	21.1	18.6	33.4	26.0	4.2	12.9	3.9	16.8
Minimum	4.67	1.36	15.6	13.6	27.0	21.7	2.9	9.4	2.5	9.1
Maximum	5.11	1.82	24.6	23.7	38.2	28.1	7.5	17.2	8.7	22.8
Standard deviation	0.09	0.10	2.23	1.65	2.57	1.72	0.87	1.77	1.12	2.94

### APPENDIX 3 Normalized values by prepared value

Normalized values by prepared value Sample No.1

	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>
CN01	100.2	96.6	96.1	87.6	102.8	81.0	102.5	84.9	67.4	104.3
CN02	99.3	98.8	99.7	99.3	94.1	98.6	96.5	95.5	99.7	103.3
CN03	99.5	94.1	95.5	97.5	94.0	94.6	99.4	95.1	97.3	104.7
CN04	99.8	94.0	97.3	98.2	96.5	95.2	99.1	99.2	100.6	104.6
ID01	111.5	77.6	102.8	78.4	75.1	94.3	100.1	74.2	105.9	62.8
ID02	100.5	92.1	102.1	90.1	114.8	97.1	103.8	97.4	101.2	100.8
JP01	101.2	98.0	99.4	99.2	94.3	102.2	88.6	96.6	99.5	102.4
JP02	100.5	94.8	99.1	99.8	98.7	100.7	91.1	100.5	99.5	95.7
JP03	101.2	93.8	97.9	95.7	103.3	97.7	95.6	96.8	98.4	53.9
JP04	101.2	94.2	97.2	98.2	100.6	112.1	99.4	111.7	109.1	102.6
JP05	99.0	96.5	95.2	95.4	93.2	101.2	98.9	104.4	101.6	89.4
JP06	101.2	94.2	93.3	98.0	90.9	103.1	105.7	97.6	101.1	112.1
JP07	101.0	99.1	81.2	100.0	99.6	99.7	98.1	100.2	100.0	99.3
JP08	101.7	94.4	98.5	98.6	99.6	100.3	98.1	99.0	98.9	99.4
KR01	100.5	97.4	108.6	95.6	100.1	98.1	96.2	87.8	102.7	109.7
MY01	98.3	94.4	109.6	95.2	84.1	105.3	105.9	98.9	103.7	102.0
MN01	100.2	96.2	106.9	105.2	102.5	99.8	96.8	100.8	95.1	106.6
PH01	101.2	86.2	99.3	97.9	94.6	97.2	94.9	80.3	99.5	103.8
RU01	99.8	96.4	96.5	100.2	102.4	94.9	110.6	90.3	96.7	102.3
TH01	101.5	96.2	101.6	100.0	100.9	92.8	99.9	103.2	103.6	101.1
TH02	100.0	94.2	102.9	98.6	99.4	102.5	102.5	100.7	100.0	101.3
TH03	96.6	95.6	99.0	97.4	93.4	98.3	88.1	98.2	100.7	98.9
VN01	99.8	102.1	100.0	83.8	104.6	70.3	91.8	101.2	117.6	98.2
Minimum	96.6	77.6	81.2	78.4	75.1	70.3	88.1	74.2	67.4	53.9
Maximum	111.5	102.1	109.6	105.2	114.8	112.1	110.6	111.7	117.6	112.1
Average	100.7	94.6	99.1	96.1	97.4	97.3	98.4	96.3	100.0	98.2

Normalized values by prepared value 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>
CN01	101.0	94.5	72.6	85.6	98.0	83.2	94.8	98.5	67.6	136.5
CN02	99.4	101.4	108.1	99.4	97.9	94.6	99.8	100.5	97.3	102.4
CN03	100.2	94.5	108.4	97.4	102.6	85.4	92.5	105.3	105.4	101.8
CN04	99.8	94.5	102.1	96.9	102.5	91.9	108.8	107.3	98.9	103.4
ID01	104.1	77.3	81.4	69.9	84.7	89.7	83.3	71.5	100.8	74.4
ID02	102.3	85.4	86.0	94.0	99.7	94.1	101.8	96.9	97.6	54.5
JP01	101.2	99.7	98.6	95.4	89.5	101.5	100.0	93.2	97.3	104.8
JP02	100.4	97.9	100.0	98.5	99.1	100.7	88.5	115.2	99.7	92.8
JP03	101.5	94.5	98.1	100.0	100.0	97.1	92.8	97.7	98.4	109.0
JP04	102.1	95.1	102.3	97.9	102.0	101.1	106.5	98.5	96.2	113.8
JP05	101.0	99.7	95.3	95.4	96.2	98.1	92.5	112.1	115.4	102.4
JP06	101.7	96.2	85.1	89.7	78.5	89.4	93.5	97.7	78.6	103.0
JP07	100.8	96.2	99.1	95.9	97.1	99.3	71.3	78.0	77.3	106.6
JP08	101.9	95.7	101.4	96.4	99.4	101.1	95.5	99.2	98.4	99.4
KR01	101.2	92.8	114.4	95.9	92.7	99.6	130.0	96.2	108.1	60.5
MY01	96.9	98.5	109.7	89.1	81.0	102.6	100.3	84.5	97.3	100.4
MN01	100.2	99.5	104.9	99.8	104.5	100.5	100.2	97.9	105.0	113.2
PH01	106.0	88.8	101.4	96.4	94.2	90.9	115.0	78.8	105.4	121.6
RU01	99.6	99.1	100.9	98.4	96.3	93.3	115.8	83.3	100.0	111.8
TH01	101.5	95.3	101.0	97.2	99.2	95.8	107.2	118.9	121.1	92.8
TH02	98.5	89.4	105.6	95.9	102.6	101.8	105.0	95.5	102.7	113.2
TH03	99.6	92.8	99.2	101.6	103.9	95.0	123.8	130.4	119.3	103.9
VN01	100.6	103.6	77.2	122.2	111.0	79.2	187.5	87.1	235.1	91.0
Minimum	96.9	77.3	72.6	69.9	78.5	79.2	71.3	71.5	67.6	54.5
Maximum	106.0	103.6	114.4	122.2	111.0	102.6	187.5	130.4	235.1	136.5
Average	100.94	94.90	97.9	96.0	97.1	95.0	104.6	97.6	105.3	100.6