

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

# **Report of the Inter-laboratory Comparison Project 2004 on Wet Deposition**

**7th Attempt**

November 2005

Acid Deposition and Oxidant Research Center

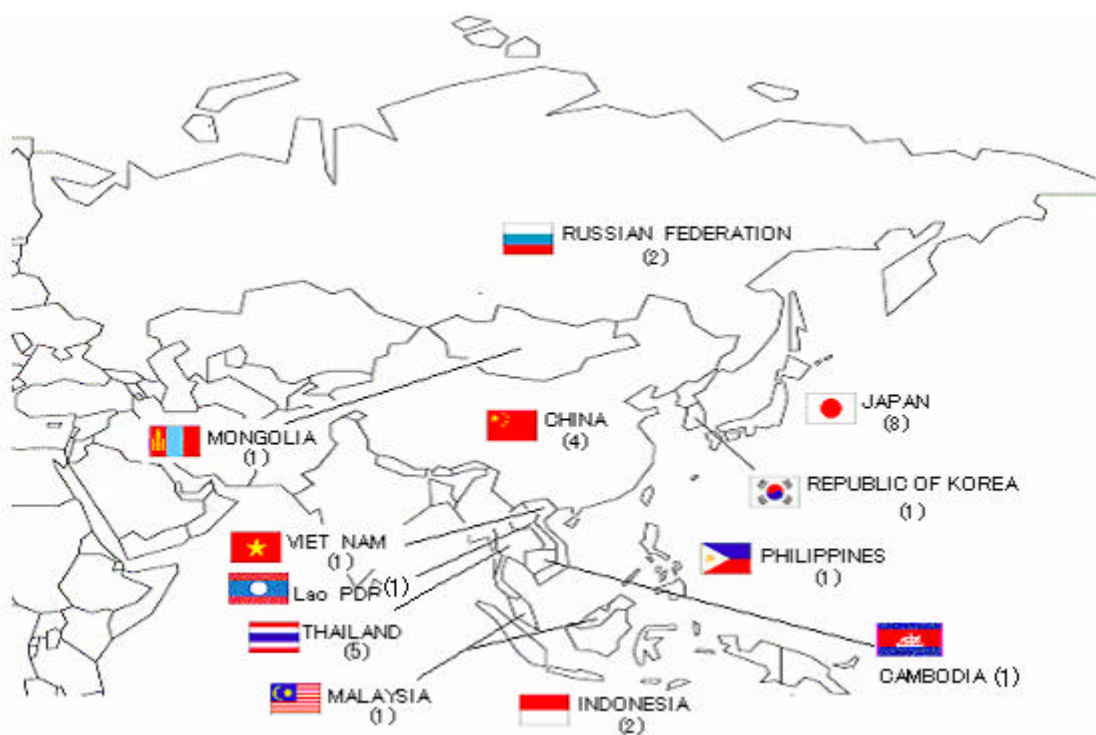
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## 1. INTRODUCTION

This inter-laboratory comparison project (round robin analysis survey of uniformly prepared artificial rainwater samples) was conducted among the analytical laboratories in participating countries 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 practices, (i) to recognize the analytical precision and accuracy of the measurement 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) at the end of 2004. 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 (28 laboratories from 12 countries)

**Fig.1 Laboratories participated in the Inter-comparison project 2004 of the EANET**

## 2. PROCEDURE

### 2.1 Participating Laboratories

Twenty-eight laboratories in charge of chemical analysis in 12 countries of EANET participated in this survey. The Network Center (NC) shipped the artificial rainwater samples to all of these 28 laboratories, and almost 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) were 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**

Artificial rainwater samples	Amount of each sample	Container	Number of samples	Note
No.041 (higher concentration) No.042 (lower concentration )	Approximately 150ml	Poly-propylene bottle 250ml	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 samples 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. The participating laboratories were informed that concentration of each parameter was within range described in Table 3.

**Table 2 Reporting units of analytical parameters**

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>	5 – 100μmol/L	Ca <sup>2+</sup>	1 – 50μmol/L
NO <sub>3</sub> <sup>-</sup>	5 – 100μmol/L	Mg <sup>2+</sup>	1 – 50μmol/L
Cl <sup>-</sup>	5 – 100μmol/L	NH <sub>4</sub> <sup>+</sup>	1 – 50μmol/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 “Quality Assurance/Quality Control (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 ( $\mu\text{eq/L}$ ) is calculated by summing the concentrations of all anions ( $C$ :  $\mu\text{mol/L}$ ).

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

$C_{Ai}$ : electric charge of ion and concentration ( $\mu\text{mol/L}$ ) of anion "i".

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

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

$C_{Ci}$ : electric charge of ion and concentration ( $\mu\text{mol/L}$ ) 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 electrical conductivity (R<sub>2</sub>)**

(1) Total electric conductivity (Λ<sub>calc</sub>) should be calculated as follows;

$$\Lambda_{\text{calc}} (\text{mS/m}) = \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2C (\text{SO}_4^{2-}) + 71.5 \times C (\text{NO}_3^-) \\ + 76.3 \times C (\text{Cl}^-) + 73.5 \times C (\text{NH}_4^+) + 50.1 \times C (\text{Na}^+) + 73.5 \times C (\text{K}^+) \\ + 59.8 \times 2C (\text{Ca}^{2+}) + 53.3 \times 2C (\text{Mg}^{2+}) + 44.5 \times (\text{ALK})\} / 10000$$

C: Molar concentrations (μmol/L) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C. Alkalinity considered to be corresponded to bicarbonate ions (HCO<sub>3</sub><sup>-</sup>).

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

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

(3) 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**

Λ <sub>meas</sub> [mS/m]	R <sub>2</sub>
< 0.5	+20 ~ -20
0.5 ~ 3	+13 ~ -13
> 3	+9 ~ -9

(Reference) "Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)"



### 3. RESULTS

The Network Center shipped artificial rainwater samples to 28 laboratories in the participating countries of EANET, and received the data on analytical results from all 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, averages of submitted data were fairly well agreed with the prepared values/concentrations within a range of  $-5.7\%(K^+)$  to  $1.0\%(Ca^{2+})$  for the sample No.041, and  $-5.3\%(K^+)$  to  $1.1\%(pH)$  for the sample No.042. But there are a few laboratories that submitted measured values of considerable differences with prepared concentrations.

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

Constituents	Prepared (Vp)	Average (Va)	?V/Vp (%)	S.D.	N	Min.	Max.
<b>[Sample No.041]</b>							
pH	4.60	4.64	0.9	0.06	27	4.46	4.82
EC( $\mu$ S/m)	3.94	3.79	-3.9	0.19	27	3.13	4.17
SO <sub>4</sub> <sup>2-</sup> ( $\mu$ mol/L)	58.6	57.0	-2.7	3.03	26	47.3	60.5
NO <sub>3</sub> <sup>-</sup> ( $\mu$ mol/L)	41.4	39.8	-3.8	2.41	26	33.1	43.0
Cl <sup>-</sup> ( $\mu$ mol/L)	76.7	73.7	-4.0	5.96	26	60.1	92.6
Na <sup>+</sup> ( $\mu$ mol/L)	66.7	65.7	-1.5	2.98	26	57.1	69.2
K <sup>+</sup> ( $\mu$ mol/L)	6.9	6.5	-5.7	0.77	25	3.9	8.1
Ca <sup>2+</sup> ( $\mu$ mol/L)	38.9	39.3	1.0	3.46	27	30.8	48.0
Mg <sup>2+</sup> ( $\mu$ mol/L)	9.8	9.4	-3.8	0.99	27	6.7	11.1
NH <sub>4</sub> <sup>+</sup> ( $\mu$ mol/L)	39.4	38.7	-1.7	4.08	27	29.5	48.1
<b>[Sample No.042]</b>							
pH	5.00	5.06	1.1	0.11	28	4.81	5.30
EC(mS/m)	1.33	1.31	-1.2	0.08	28	1.09	1.46
SO <sub>4</sub> <sup>2-</sup> ( $\mu$ mol/L)	17.6	17.2	-2.4	1.02	26	14.4	18.4
NO <sub>3</sub> <sup>-</sup> ( $\mu$ mol/L)	18.4	17.5	-4.9	1.38	27	13.3	19.1
Cl <sup>-</sup> ( $\mu$ mol/L)	22.5	22.3	-1.1	1.51	26	16.8	25.1
Na <sup>+</sup> ( $\mu$ mol/L)	20.5	20.0	-2.3	1.35	26	16.6	22.3
K <sup>+</sup> ( $\mu$ mol/L)	5.0	4.7	-5.3	0.47	25	3.3	5.7
Ca <sup>2+</sup> ( $\mu$ mol/L)	10.0	10.0	0.3	1.42	26	6.9	13.8
Mg <sup>2+</sup> ( $\mu$ mol/L)	2.7	2.6	-4.9	0.38	26	1.7	3.1
NH <sub>4</sub> <sup>+</sup> ( $\mu$ mol/L)	15.1	14.5	-3.8	1.47	26	11.3	16.4

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

?V : Average(Va) - Prepared (Vp)

The Data Quality Objectives (DQOs) 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 in chapter 2.5 .

The flag "I" and the flag "C" show a poor ion balance data sets, and a poor conductivity agreement data sets respectively.

The results were evaluated by the three aspects :

- i) comparison of concentration dependence – sample No.041 (higher concentrations) and No.042 (lower concentrations),
- ii) comparison of individual parameters,
- iii) comparison of circumstances of analysis in each participating laboratory.

Evaluation of data on both the sample No.041 and No.042 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.041 (higher concentrations)

**Table 8 Numbers of flagged data for the Sample No.041 (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	1	2	1	2	3	0	3	4	2	5	23
X	0	0	1	1	1	0	2	0	1	0	6
Data within DQOs	27	26	25	24	23	26	21	23	24	22	241
Flagged(%)	3.6	7.1	7.4	11.1	14.8	0.0	19.2	14.8	11.1	18.5	10.7

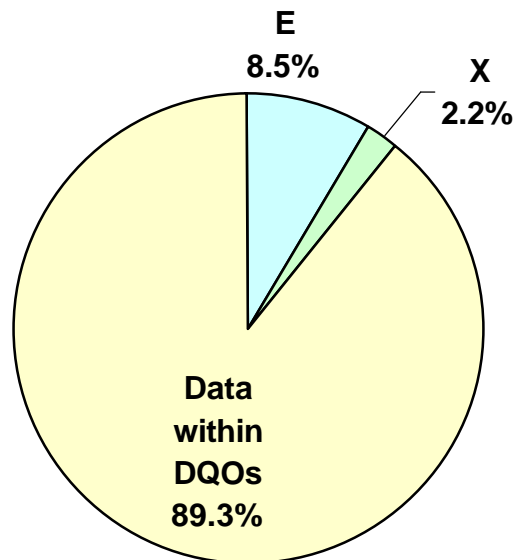
(Total data=270)

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

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

For sample No.041 (higher concentrations), 23 analytical data out of 270 exceeded the DQOs by a factor of 2 and flagged by "E". 6 analytical data out of 270 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" were 29 out of 270, shared about 10.7 percents of all reported data for sample No.041 (Fig.2). Especially measured values of K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> have many results with flags. (Table9)

Comparing the results in 2004 with that in 2003, especially the ratio of flagged data in Na<sup>+</sup> decreased. On the other hand, the ratio of flagged data in K<sup>+</sup> increased.



**Fig.2 Percentage of flagged data for Sample No.041**

Table 9 Analytical Results of Sample No.041

Lab.ID	pH	EC (mS/m)	SO <sub>4</sub> <sup>2-</sup> (μmol/L)	NO <sub>3</sub> <sup>-</sup> (μmol/L)	Cl <sup>-</sup> (μmol/L)	Na <sup>+</sup> (μmol/L)	K <sup>+</sup> (μmol/L)	Ca <sup>2+</sup> (μmol/L)	Mg <sup>2+</sup> (μmol/L)	NH <sub>4</sub> <sup>+</sup> (μmol/L)	R1	R2
CN01	4.63	3.75	60.5	40.7	69.8	69.2	6.9	40.4	10.6	37.3	1.6	1.7
CN02	4.64	3.58	59.1	40.7	74.1	65.7	6.4	38.3	10.5	33.6	-1.5	2.9
CN03	4.61	4.01	58.9	40.3	72.8	67.5	6.2	40.0	10.0	38.5	1.2	-1.4
CN04	4.60	3.71	60.3	40.2	71.5	68.5	7.1	40.7	10.4	39.2	2.1	3.2
ID01	4.61	4.17	58.3	39.3	72.2	66.7	6.3	37.8	8.9	42.4	1.1	-3.8
ID02	4.66	3.71	52.6	40.7	80.7	66.5	6.4	42.3	9.7	29.5	0.4	0.1
JP01	4.66	3.91	56.0	39.9	70.7	66.0	6.6	36.3	9.0	39.9	0.5	-2.9
JP02	4.67	3.76	57.4	40.4	74.9	66.8	6.8	37.8	9.8	33.3	-1.5	-0.6
JP03	4.65	3.79	57.7	39.4	74.0	66.9	6.5	48.0	10.0	40.4	4.9	1.6
JP04	4.70	3.83	58.9	41.3	74.9	66.4	6.7	37.7	9.4	38.9	-1.7	-1.4
JP05	4.66	3.79	56.6	41.4	76.6	65.3	6.6	38.8	9.4	37.9	-0.7	-0.3
JP06	4.69	3.71	54.0	39.3	65.8	69.2	7.3	38.5	9.9	39.7	4.6	-1.2
JP07	4.64	3.72	59.6	41.1	74.6	65.1	6.4	39.3	9.5	40.4	-0.5	1.8
JP08	4.69	3.75	57.7	40.4	75.3	67.1	7.1	40.1	9.6	40.9	0.8	0.3
KR01	4.46	3.78	59.3	33.1	80.3	57.3	10.5	30.8	9.8	41.0	-1.6	4.7
MY01	4.69	3.91	58.6	40.9	75.2	66.8	6.4	38.0	9.3	40.1	-1.1	-2.1
MN01	4.66	3.80	57.4	40.8	63.8	68.6	8.1	39.0	10.4	40.7	4.1	-0.8
PH01	4.56	3.84	58.3	42.7	71.5	62.4	7.4	37.0	9.6	31.9	-1.8	0.7
RU01	4.61	4.01	59.1	41.2	77.3	67.7	7.1	39.4	9.3	47.2	1.5	-0.2
RU02	4.62	3.99	54.2	40.7	67.0	57.1	6.8	39.7	9.6	48.1	4.1	-2.8
TH01	4.65	3.83	59.2	40.4	74.5	65.0	6.4	39.4	9.5	38.6	-0.7	-0.2
TH02	4.71	3.94	54.9	36.2	75.5	66.6	6.7	46.3	11.1	37.8	5.1	-2.8
TH03	4.56	3.75	57.4	35.9	77.1	64.4	3.9	38.7	6.7	33.7	-1.7	1.4
TH04	4.82	3.13	50.9	33.5	60.1	68.1	6.0	31.9	7.0	36.9	2.1	0.4
TH05	4.59	3.61	47.3	41.8	47.3	63.2	5.4	42.1	9.1	35.7	11.7	-1.1
VN01	4.66	3.86	58.7	43.0	72.3	63.8	5.7	44.1	8.8	38.8	0.7	-0.4
CA01	5.75	2.90	19.7	23.5	92.6			38.2	7.6	43.5		
LO01	4.58	3.58										

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.042 (lower concentrations)

**Table 10 Number of flagged data for the Sample No.042 (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	2	3	1	3	1	5	4	5	25
X	0	0	1	0	1	0	2	3	2	1	10
Data within DQOs	28	26	24	24	25	23	23	19	21	21	235
Flagged(%)	0.0	3.6	11.1	11.1	7.4	11.5	11.5	29.6	22.2	22.2	13.0

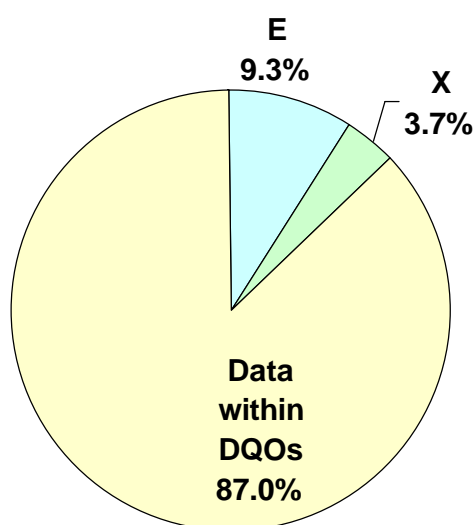
(Total data=270)

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

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

For sample No.042 (lower concentrations), 25 analytical data out of 270 exceeded the DQOs by a factor of 2 and flagged by "E". 10 analytical data out of 270 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" were 35 analytical data out of 270, shared up to 13.0 percents of all reported data for sample No.042 (Fig.3). Many data on Ca<sup>2+</sup>, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> were marked with flags E or flags X (Table 11).

Comparing the results in 2004 with that in 2003, the ratio of flagged data of 8 constituents decreased. Especially the ratio of K<sup>+</sup> decreased significantly. On the other hand, the ratio of Ca<sup>2+</sup> increased.



**Fig.3 Percentage of flagged data for Sample No.042**

### Evaluation

The ratio of the flagged data for sample No.041 was 10.7 percent, and the No.031 (2003) was 14.3 percent. Both of them had almost same concentration for each ion. For the sample with low concentration, the ratio of flagged data in the sample No.042 was 13.0 percent and the No.032 (2003) was 18.2 percent.

In general terms, this indicates the difficulty of the analysis would depend on the concentration in the sample especially on the trace analysis.



Table 11 Analytical Results of Sample No.042

Lab.ID	pH	EC (mS/m)	SO <sub>4</sub> <sup>2-</sup> (μmol/L)	NO <sub>3</sub> <sup>-</sup> (μmol/L)	Cl <sup>-</sup> (μmol/L)	Na <sup>+</sup> (μmol/L)	K <sup>+</sup> (μmol/L)	Ca <sup>2+</sup> (μmol/L)	Mg <sup>2+</sup> (μmol/L)	NH <sub>4</sub> <sup>+</sup> (μmol/L)	R1	R2
CN01	5.02	1.26	18.2	18.3	22.6	20.5	4.7	11.0	3.1	14.0	-0.2	2.8
CN02	5.03	1.27	17.7	18.0	22.3	19.9	4.6	9.3	3.1	13.5	-2.4	0.6
CN03	5.01	1.40	17.9	18.6	23.2	20.6	4.6	11.3	3.0	14.2	0.1	-1.9
CN04	5.02	1.28	18.1	18.4	23.1	20.6	4.9	11.5	3.0	14.3	0.4	2.5
ID01	5.30	1.41	17.8	18.3	22.8	19.4	4.3	9.6	2.3	16.4	-5.3	-10.0
ID02	4.98	1.32	17.4	15.7	25.1	20.6	4.6	11.8	X 5.3	X 6.1	0.2	0.3
JP01	5.11	1.35	16.7	18.0	20.9	21.1	5.1	8.4	2.4	16.4	-0.2	-5.2
JP02	5.01	1.33	17.4	17.1	21.5	20.8	4.9	8.2	2.7	E 12.5	-2.5	-2.5
JP03	5.02	1.34	16.7	17.4	20.8	20.5	4.6	9.8	2.4	15.7	2.2	-2.3
JP04	5.11	1.31	17.5	18.1	21.8	20.6	4.7	9.9	2.7	14.9	-1.2	-2.7
JP05	5.05	1.33	17.0	17.9	21.9	19.8	4.7	9.9	2.5	15.0	-0.4	-2.4
JP06	5.06	1.31	17.3	17.2	21.9	18.9	4.8	9.3	E 2.1	15.3	-2.2	-2.4
JP07	5.04	1.32	17.4	18.3	21.7	21.4	5.7	9.4	2.6	14.6	0.0	-1.1
JP08	5.09	1.31	17.0	17.8	22.0	20.8	4.9	9.8	2.7	15.9	0.6	-2.2
KR01	4.94	1.27	18.1	17.8	25.0	E 17.2	X 3.3	6.9	3.0	E 12.0	-10.7	2.0
MY01	5.12	1.46	17.7	18.3	22.4	19.7	4.3	10.2	2.3	15.8	-2.5	-8.0
MN01	5.04	1.34	17.1	18.0	23.8	21.7	5.4	10.7	3.0	15.8	2.2	-0.5
PH01	4.99	1.33	17.6	18.6	22.1	E 17.2	5.2	10.8	E 2.1	E 12.5	-3.4	-0.8
RU01	5.01	1.40	18.4	19.1	23.4	21.1	4.8	9.8	2.6	15.4	-2.2	-1.8
RU02	5.04	1.42	18.2	18.5	21.8	E 16.6	4.4	9.3	2.9	15.9	-4.3	-5.1
TH01	5.04	1.35	17.6	18.2	21.8	20.5	4.7	11.0	2.7	15.2	1.1	-1.6
TH02	5.08	1.28	15.4	16.0	21.6	19.9	4.5	10.3	2.7	15.9	4.3	-2.5
TH03	4.86	1.38	16.1	E 14.8	22.9	18.8	X 2.3	10.0	E 1.9	E 11.5	0.2	-0.9
TH04	5.22	E 1.09	E 14.5	E 14.6	E 16.8	22.3	5.2	7.3	X 1.7	15.2	5.0	-2.2
TH05	5.29	1.28	E 14.4	17.7	X 15.2	19.5	4.2	11.6	2.7	14.4	7.6	-9.7
VN01	5.02	1.36	17.4	18.5	23.6	20.7	E 4.0	X 13.8	E 1.9	13.9	1.7	-0.5
CA01	5.24	1.13	X < 10	E 13.3	22.0			X 15.9	2.7	E 11.3		
LO01	4.81	1.18										

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

I:\Poor ion balance (R1)

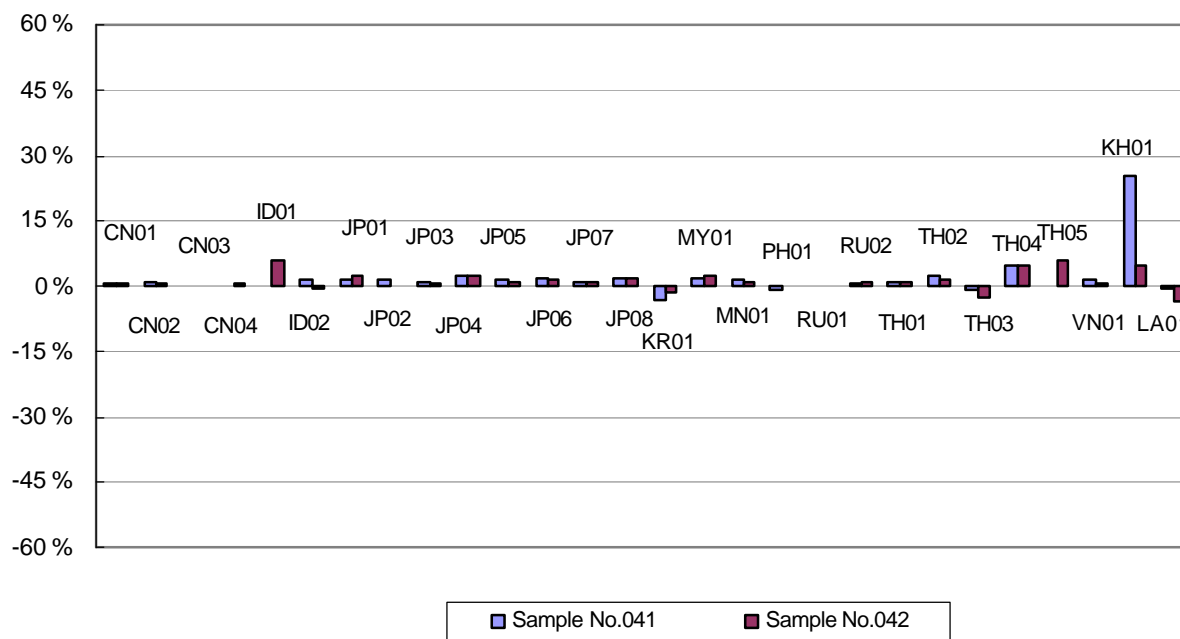
X:\Value exceeded the DQO(±15) more than a factor of 2

C:\Poor conductivity agreement (R2)

### 3.2 Analytical Parameter

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 their deviation. The numbers of flagged data were indicated 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

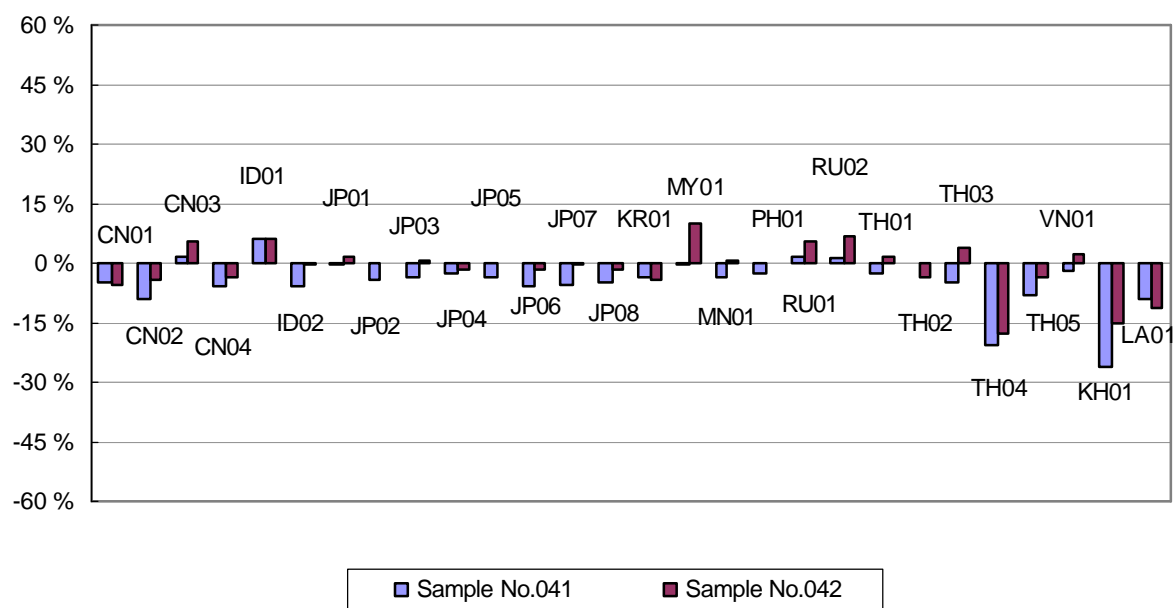
pH meter and electrode	28/28
------------------------	-------

#### Flagged data

	E	X	Flagged (%)
Sample No.041	1	0	3.6
Sample No.042	0	0	0.0

All participating laboratories used pH meter with glass electrode for measurement of pH. Most of the obtained data satisfied the DQOs of the QA/QC program of the EANET. Many laboratories submitted slightly higher pH values than prepared value. The relative standard deviations of the pH values for sample No.041 and No.042 were good to be 1.4% and 2.1%.

## 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	28/28
-----------------------------	-------

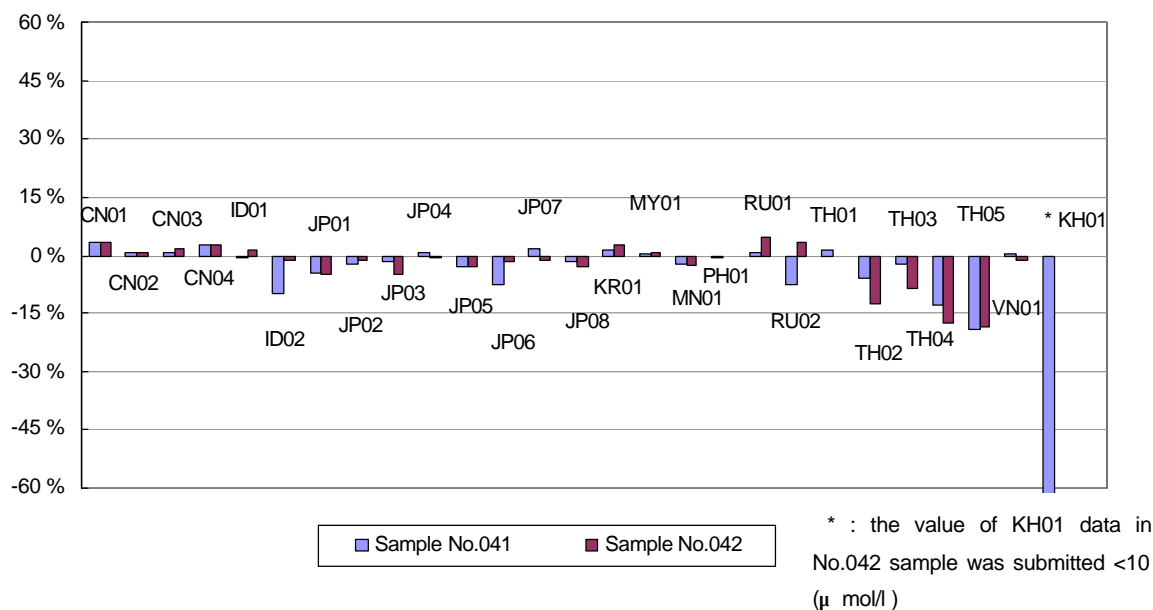
### Flagged data

	E	X	Flagged (%)
Sample No.041	2	0	7.1
Sample No.042	1	0	3.6

All participating laboratories used conductivity cell for the measurement of EC. Obtained data almost satisfied the DQOs of the QA/QC program of the EANET. However, Lab.TH04 reported the data flagged by “E” in both sample. It had some problem in a calibration for the measurement. 13 of 28 laboratories reported lower data than prepared value for both sample No.041 and No.042.



$\text{SO}_4^{2-}$



**Fig.6 Distribution of  $\text{SO}_4^{2-}$  data normalized by prepared concentration**

**Table 14 Analytical method and flagged data of  $\text{SO}_4^{2-}$**

**Analytical Method**

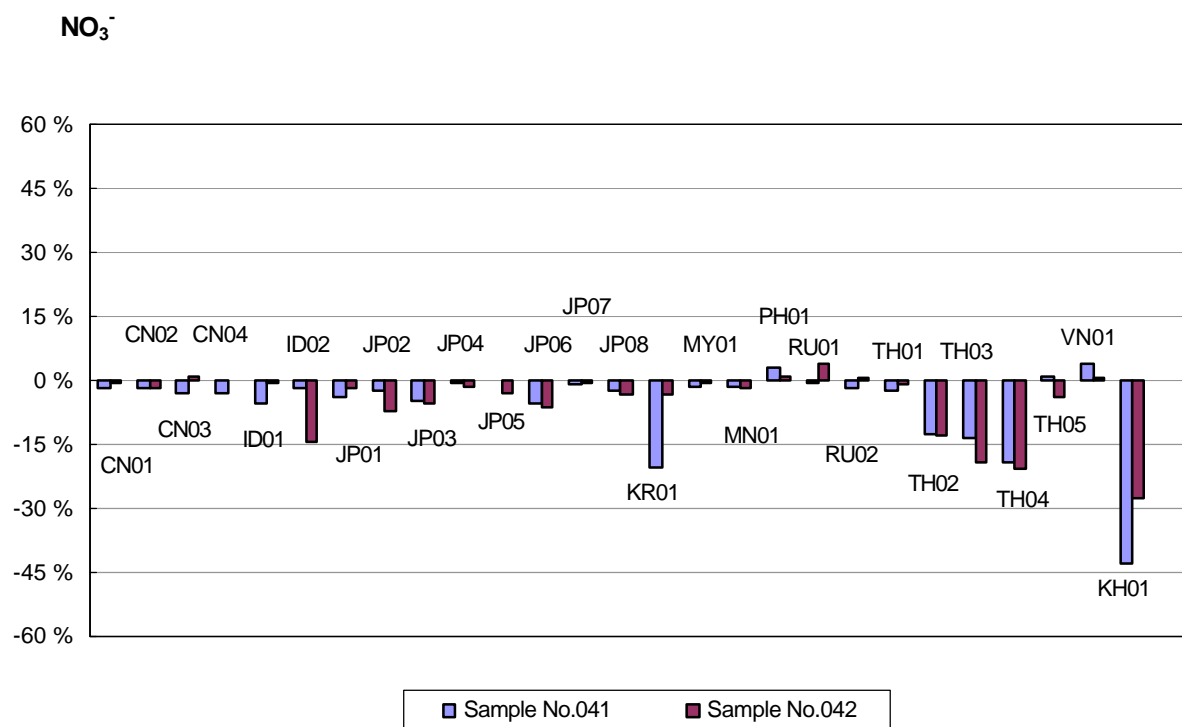
Ion chromatography	25/27
Spectrophotometry	1/27
Nephelometry	1/27

**Flagged data**

	E	X	Flagged (%)
Sample No.041	1	1	7.4
Sample No.042	2	1	11.1

All of the participating laboratories used ion chromatography for the determination of  $\text{SO}_4^{2-}$  except for two laboratories. One laboratory (RU02) used Nephelometry and another laboratory (KH01) used Spectrophotometry.

Results of TH05 had "E" flag for both of samples and one's from TH04 flagged in the sample No.042. Both laboratories reported lower data than the prepared value.



**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	25/27
Spectrophotometry	1/27
Colorimetry	1/27

**Flagged data**

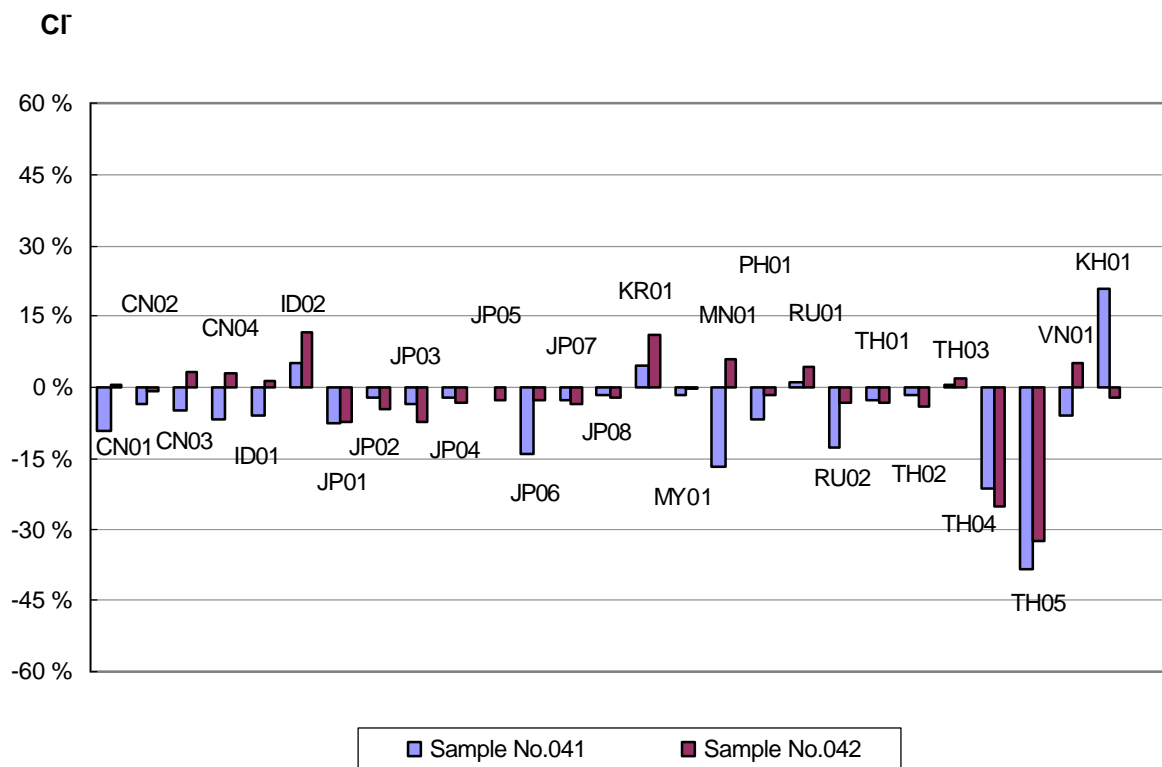
	E	X	Flagged (%)
Sample No.041	2	1	11.1
Sample No.042	3	0	11.1

All of the participating laboratories used ion chromatography for the determination of NO<sub>3</sub><sup>-</sup> except for two laboratories. One laboratory (RU02) used Colorimetry and another laboratory (KH01) used Spectrophotometry.

Almost all of the laboratories reported lower data than prepared value for both sample No.041 and No.042.

The ratio of flagged data was decreased approximately twice as much as the project 2003 for the sample with higher concentration.

The data of the Lab.TH04 (obtained with ion chromatography) were flagged in sample No.041 and No.042.



**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	25/27
Titration	2/27

**Flagged data**

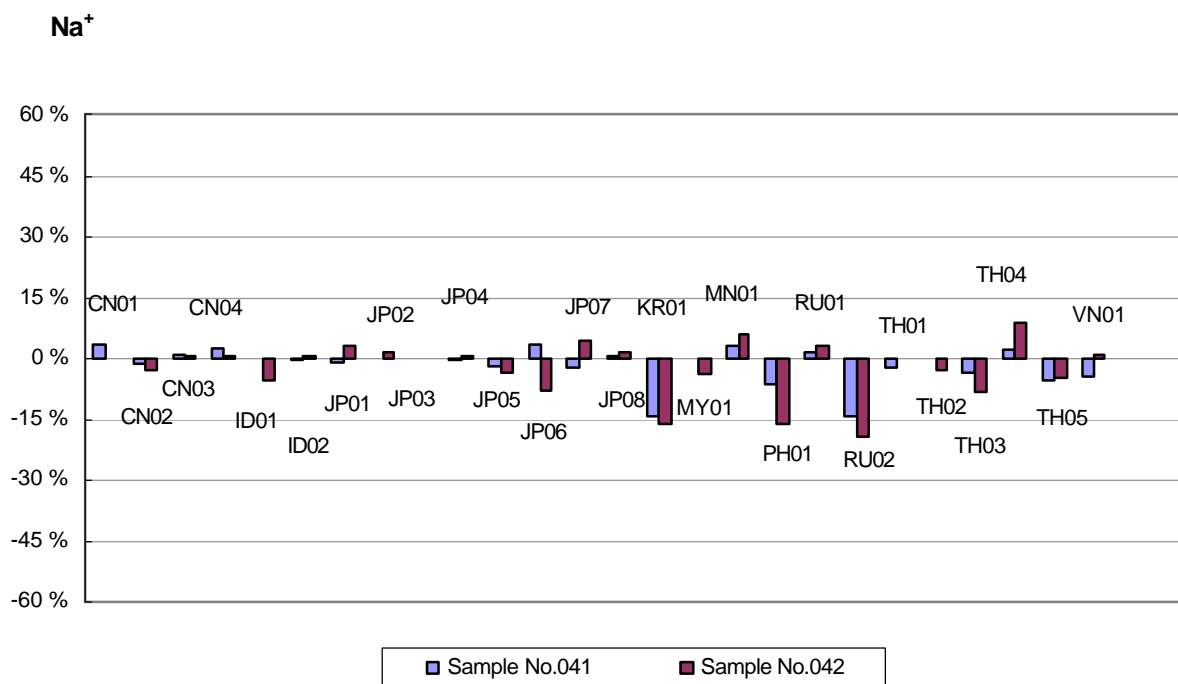
	E	X	Flagged (%)
Sample No.041	3	1	14.8
Sample No.042	1	1	7.4

Same as for analysis of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, 25 laboratories used ion chromatography for the determination of Cl<sup>-</sup>. The Lab.RU02 and KH01 used titration method.

Lab.TH05 reported the data flagged by "X".

The ratio of the flagged data in the higher concentration sample is higher than that in the lower concentration as same as the data in last year.

The data of Lab.TH05 exceeded 30% for both sample No.041 and No.042. Inappropriate analytical condition seemed to be one of the possible causes on checking IC chromatogram.



**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**

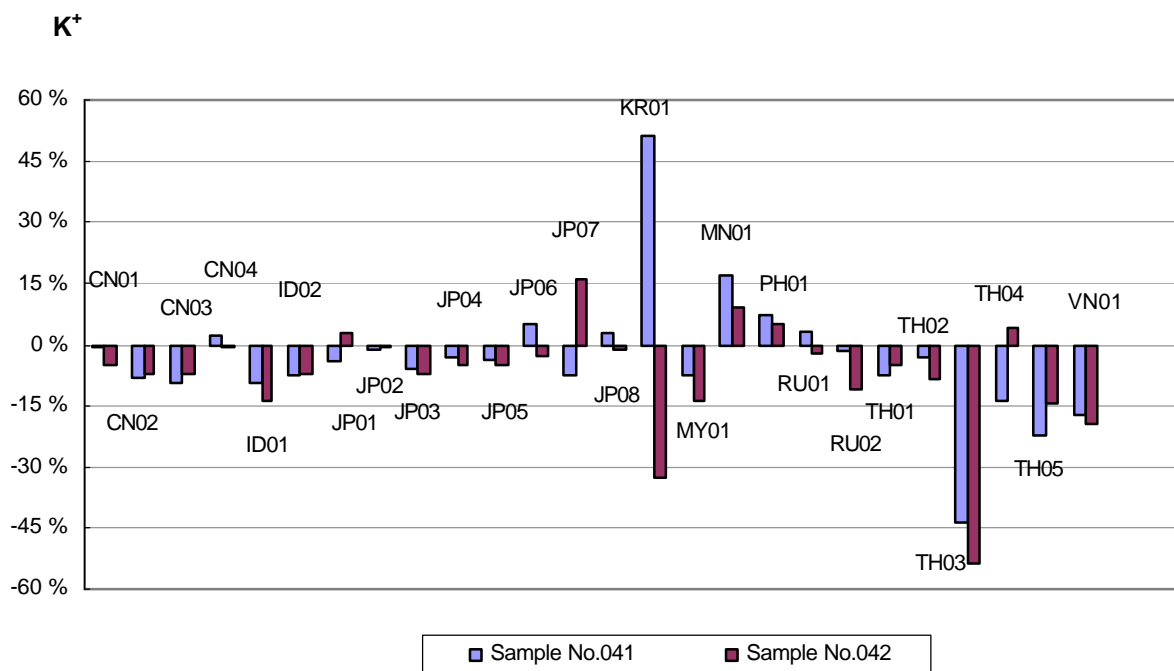
Ion chromatography	22/26
Atomic absorption spectrometry	3/26
Flame (emission) spectrometry	1/26

**Flagged data**

	E	X	Flagged (%)
Sample No.041	0	0	0.0
Sample No.042	3	0	11.5

22 laboratories used ion chromatography, 3 laboratories used atomic absorption spectrometry (Lab. KR01 PH01, RU01), and 1 Laboratory used flame (emission) photometry (Lab.RU02) for the determination of Na<sup>+</sup>.

The concentrations of the sample No.041 and No.042 were 1.5 times higher than that of the sample No.031 and No.032 respectively. There was no flag in the sample No.041. And for the sample No.042 the ratio of flagged data decreased a little.



**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	22/26
Atomic absorption spectrometry	3/26
Flame (emission) spectrometry	1/26

**Flagged data**

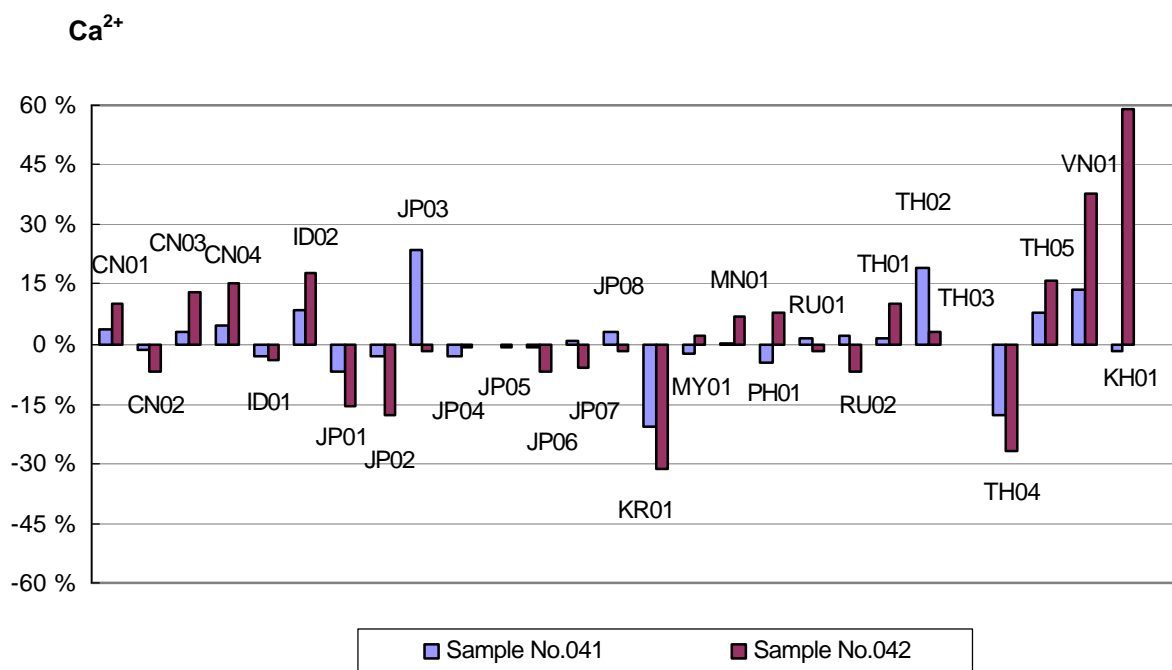
	E	X	Flagged (%)
Sample No.041	3	2	19.2
Sample No.042	1	2	11.5

22 laboratories used ion chromatography for the determination of K<sup>+</sup>, 3 laboratories used atomic absorption spectrometry and one laboratory used flame (emission) photometry.

The ratio of flagged data in the sample of higher concentration is higher than the one of lower concentration. Comparing the ratio of flagged data with 2003 project, it was decreased significantly for the sample No.042. Otherwise the number of flagged data in the sample No.041 was increased.

The concentration K<sup>+</sup> of deionized water in Lab. MN01 was higher and this seemed to affect on analytical data.

Lab.TH03 reported the values approximately of a half of the prepared value for the sample No.042.



**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	22/27
Atomic absorption photometry	5/27

**Flagged data**

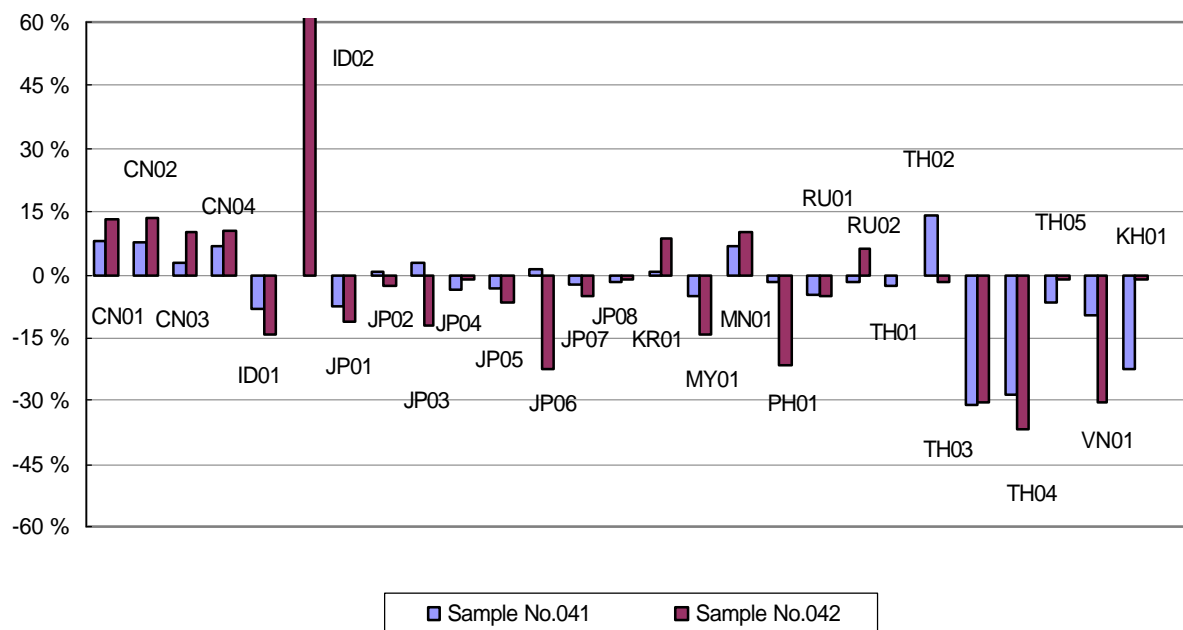
	E	X	Flagged (%)
Sample No.041	4	0	14.8
Sample No.042	5	3	29.6

22 laboratories used ion chromatography, and 5 laboratories used atomic absorption spectrometry for the determination of Ca<sup>2+</sup>.

The ratio of flagged data in the sample No.041 decreased a little. 8 laboratories had flagged data of the lower concentration sample in this year.

There were many flagged data in the samples No.041. The concentration of Ca<sup>2+</sup> (10.0 μmol/L) in the sample No.042 was 2 times higher than that of the project 2003. However the ratio of flagged data increased. This indicates the analysis of Ca<sup>2+</sup> is difficult and should be carried out with particular attention to analytical condition of the equipments, preparation of standard solution and so on.

**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	22/27
Atomic absorption spectrometry	5/27

**Flagged data**

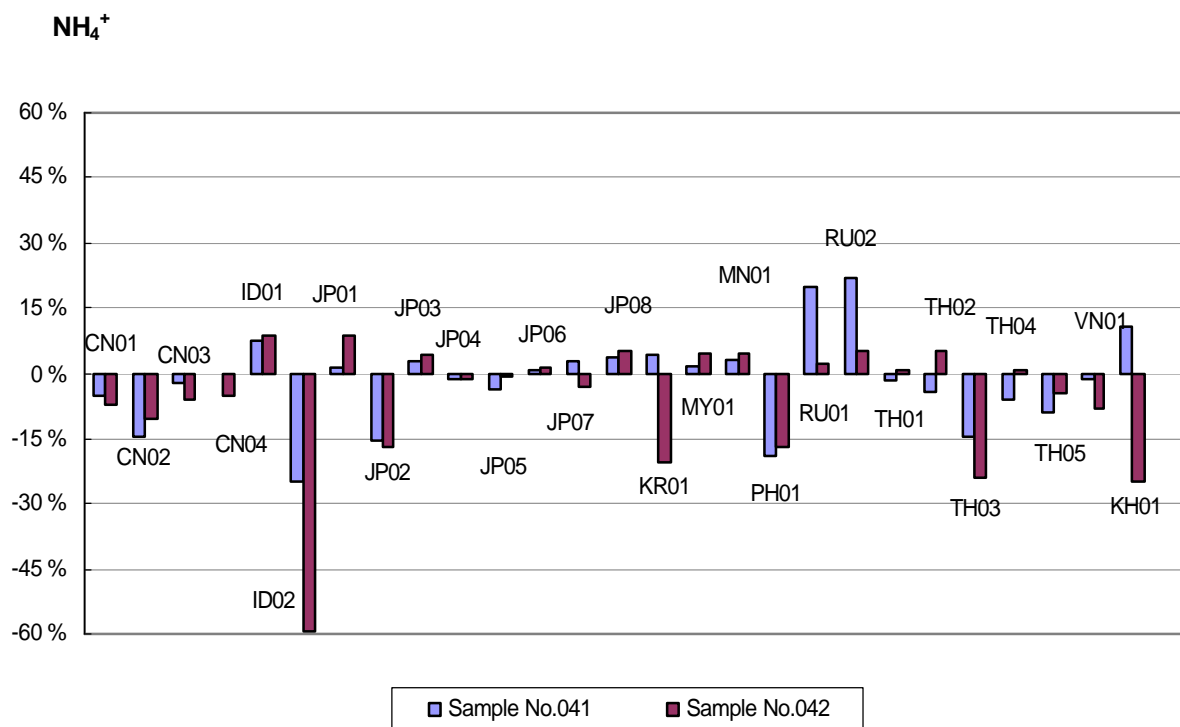
	E	X	Flagged (%)
Sample No.041	2	1	11.1
Sample No.042	4	2	22.2

Ion chromatography and atomic absorption spectrometry were used in the analysis of Mg<sup>2+</sup>.

The flagged ratio for the higher concentration sample decreased almost twice and for the lower concentration sample less than in last project.

The data of Lab.TH05 exceeded 30% for both sample No.041 and No.042.

Lab.ID02 reported the values approximately twice higher than the prepared concentration of the sample No.042. The flagged data for ID02 would be caused by the preparation of standard solution.



**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	22/27
Spectrometry (Indophenol blue)	2/27
Other method (Spectrometry)	1/27
Other method (Colorimetry)	2/27

**Flagged data**

	E	X	Flagged (%)
Sample No.041	5	0	18.5
Sample No.042	5	1	22.2

24 laboratories used recommended analytical method of EANET for the determination of NH<sub>4</sub><sup>+</sup>: 22 laboratories used ion chromatography; two laboratories used spectrometry (Indophenol blue). One laboratory used spectrometry without using indophenol blue method; Two laboratories used Colorimetry.

Although the concentration of sample No.042 (15.1mol/ L) was same as the sample No.032 (project 2003), the ratio of flagged data in sample No.042 were lower than that in the project 2003.



## Overall Evaluation

The concentrations of anions in the samples No.041 were approximately the same as of project 2003 sample except  $\text{Ca}^{2+}$ . The concentration of ions in the sample No.042 with low concentration was the same as the project 2003 <sup>+</sup> in the range of ratio 0.76 to 1.45 times except  $\text{K}^+$  and  $\text{Ca}^{2+}$ .

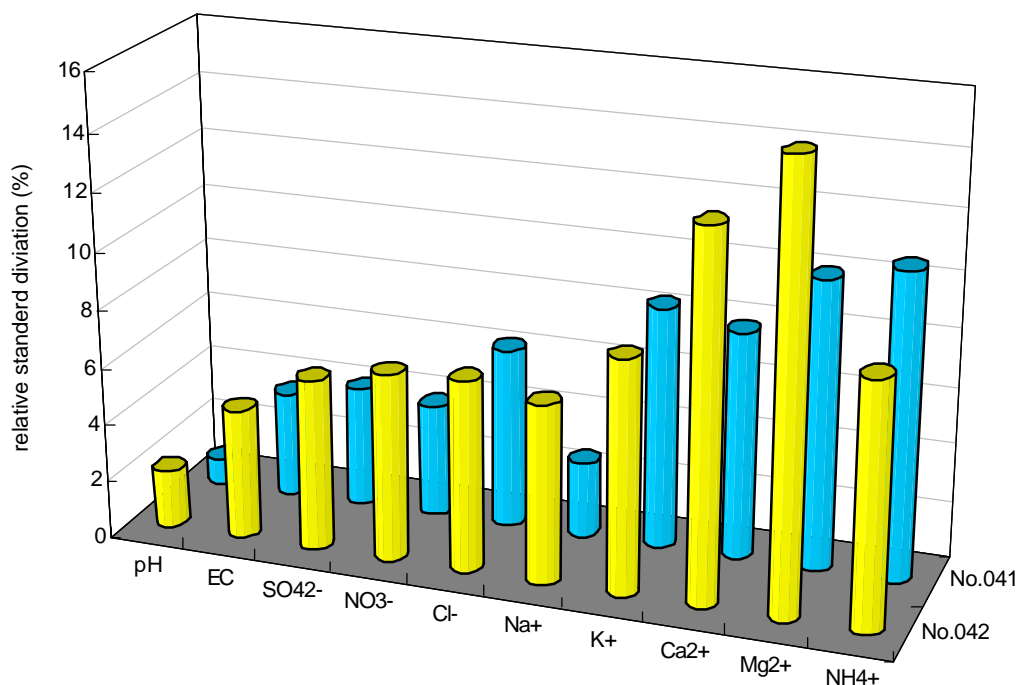
The relative standard deviation (R.S.D) of the sample No.041 and No.042 are shown in the figure 14. The R.S.D of each parameter was same or less comparing to the project 2003 except  $\text{Mg}^{2+}$  of the sample No.42.

Comparing the ratio of the flagged data, the ratios of the sample No.031 (2003) and the sample No.041 (with higher concentration) were 14.3% and 10.7% respectively. The ratio of the sample No.032 (2003) and No.042 (with lower concentration) were 18.2% and 13.0% respectively.

As reported in the “Report of the Inter-laboratory Comparison Project 2003 on Wet Deposition” the ratio of flagged data was affected by the concentration of the ions.

In this project, as same as project 2003, there are some laboratories having problems in the determination of the ions and the measurement of pH and EC.

Main reasons of the flagged data were an incorrect deriving of the calibration curve. The person in charge of analysis should confirm the calibration curve drawn on the chart. And before the analysis of the rain samples, the reliability of the calibration should be examined by using the working standard. This practice would avoid the acquisition of low-trust data.



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

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

### 3.3 Circumstance of Sample Analysis

#### Methods Used

As shown in Fig.15, the most of participating laboratories used recommended methods of EANET.

There are 25/27 laboratories used ion chromatography for the determination of anions. One laboratory used Spectrophotometry in the determination of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . and another laboratory used Nephelometry(\*), or Colorimetry(\*). And two laboratories used Titration in the determination of  $\text{Cl}^-$ .

As for determination of the cations, 22 of 26 laboratories used ion chromatography. 3 ( $\text{Na}^+$ ,  $\text{K}^+$ ) and 4 ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) laboratories used Atomic Absorption Spectrometry. One laboratory used Emission Spectrometry ( $\text{Na}^+$ ,  $\text{K}^+$ ). Regarding the  $\text{NH}_4^+$ , two laboratories used Indophenol Spectrophotometry, one laboratory used Spectrophotometry, and two laboratories used the Colorimetry.

\*:Nephelometry and Colorimetry are included in Spectrophotometry

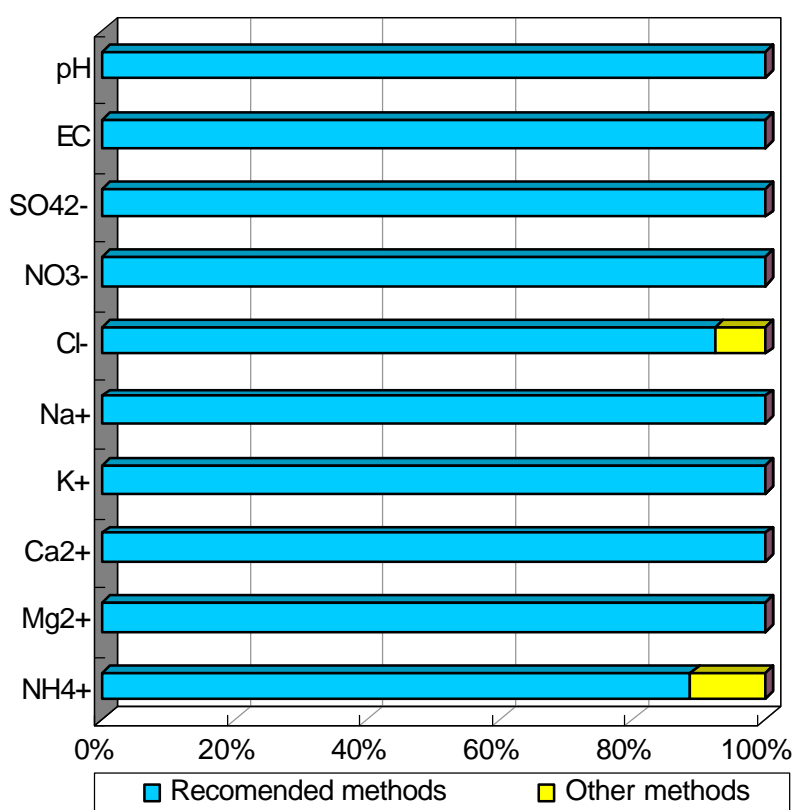


Fig.15 Ratio of recommended method used in the project

**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 (NH <sub>4</sub> <sup>+</sup> )
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
11	Other method

**SampleNo.041**

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	28(1)									
1		28(2)								
2					2(1)					
3						3	3(1)	5(1)	5(1)	
4						1	1			
5			25(1)	25(2)	25(3)	22	22(4)	22(3)	22(2)	22(2)
6										
7			2(1)	2(1)						3(2)
8										2(1)
9										
10										
11										
Flagged E	1	2	1	2	3	0	3	4	2	5
Flagged X	0	0	1	1	1	0	2	0	1	0

**Sample No.042**

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	28									
1		28(1)								
2					2					
3						3(2)	3(1)	5(2)	4(1)	
4						1(1)	1			
5			25(2)	25(2)	25(2)	22	22(2)	22(6)	22(5)	22(3)
6										
7			2(1)	2(1)						3(1)
8										2(2)
9										
10										
11										
Flagged E	0	1	2	3	1	3	1	5	4	5
Flagged X	0	0	1	0	1	0	2	3	2	1

**Table 23 Number of laboratories used different analytical method**

Reverse mesh is recommended method of EANET

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

## Number of staff in charge of measurement

The number of staff in charge of measurement on rainwater samples is described in Table 24. In 18 laboratories only one person carried out measurement of rainwater samples. In 5 laboratories two persons carried it. Three persons carried it in 4 laboratories. And four persons made measurements in one.

In the laboratories where 3 persons carried out measurement, their responsibilities were separated according to the methods used for analysis such as pH-EC, anions and cations (CN02, MY01, TH05), pH-EC-NH<sub>4</sub><sup>+</sup>, anions and cations (RU01). In PH01, 4 persons carried out measurement and their responsibilities were separated pH-EC, anions, cations and NH<sub>4</sub><sup>+</sup>.

**Table 24 Staff in charge of measurement**

Lab.ID	Total	pH	EC	SO <sub>4</sub> 2-	NO <sub>3</sub> -	Cl-	Na+	K+	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	3	A	A	B	B	B	C	C	C	C	C
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	2	A	A	A	A	A	B	B	B	B	B
ID02	1	A	A	A	A	A	A	A	A	A	A
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	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	B	B	B	B	A	A	A	A	A
PH01	4	A	A	B	B	B	C	C	C	C	D
RU01	3	A	A	B	B	B	C	C	C	C	A
RU02	1	A	A	A	A	A	A	A	A	A	A
TH01	2	A	B	B	B	B	A	A	A	A	A
TH02	1	A	A	A	A	A	A	A	A	A	A
TH03	1	A	A	A	A	A	A	A	A	A	A
TH04	1	A	A	A	A	A	A	A	A	A	A
TH05	3	A	A	B	B	B	C	C	C	C	C
VN01	2	A	A	B	B	B	A	A	A	A	A
KH01	2	A	A	A	B	A					B
LA01	1	A	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.041 and/or sample No.042.

Reverse mesh with dark are flagged data of both sample No.041 and No.042

## Years of experience (Acid rain)

According to 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. In the Lab. JP02, JP06 and MY01 this year project was the first experience for the staff.

The average of the years of the experience in each analysis was in the range from 5.98 (EC) to 6.98 (anions). The average in 2003 project was the range from 5.11 to 6.18. The reason why the average in this year was about one year higher than that in last year was that there were the cases that same person analyzed in almost the laboratories.

**Table 25 Years of experience**

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	13	13	13	13	13	13	13	13	13	13
CN02	6	6	13	13	13	3	3	3	3	3
CN03	6	6	6	6	6	6	6	6	6	6
CN04	9	9	9	9	9	9	9	9	9	9
ID01	5	5	5	5	5	5	5	5	5	5
ID02	7	7	7	7	7	7	7	7	7	7
JP01	20	20	20	20	20	20	20	20	20	20
JP02	1	1	1	1	1	1	1	1	1	1
JP03	7	7	7	7	7	7	7	7	7	7
JP04	2	2	2	2	2	2	2	2	2	2
JP05	2	2	2	2	2	2	2	2	2	2
JP06	1	1	1	1	1	1	1	1	1	1
JP07	2	2	2	2	2	2	2	2	2	2
JP08	2	2	2	2	2	2	2	2	2	2
KR01	5	5	5	5	5	5	5	5	5	5
MY01	0.5	0.5	1	1	1	3	3	3	3	3
MN01	7	7	7	7	7	7	7	7	7	7
PH01	4	4	3.5	3.5	3.5	8	8	8	8	2.5
RU01	7	7	14	14	14	7	7	7	7	7
RU02	32	32	32	32	32	32	32	32	32	32
TH01	7	2	2	2	2	7	7	7	7	7
TH02	8	8	8	8	8	8	8	8	8	8
TH03	2	2	2	2	2	2	2	2	2	2
TH04	2	2	2	2	2	2	2	2	2	2
TH05	3	3	3	3	3	3	3	3	3	3
VN01	10	10	19	19	19	10	10	10	10	10
KH01	2	2	2	2	2					2
LA01	2	2								

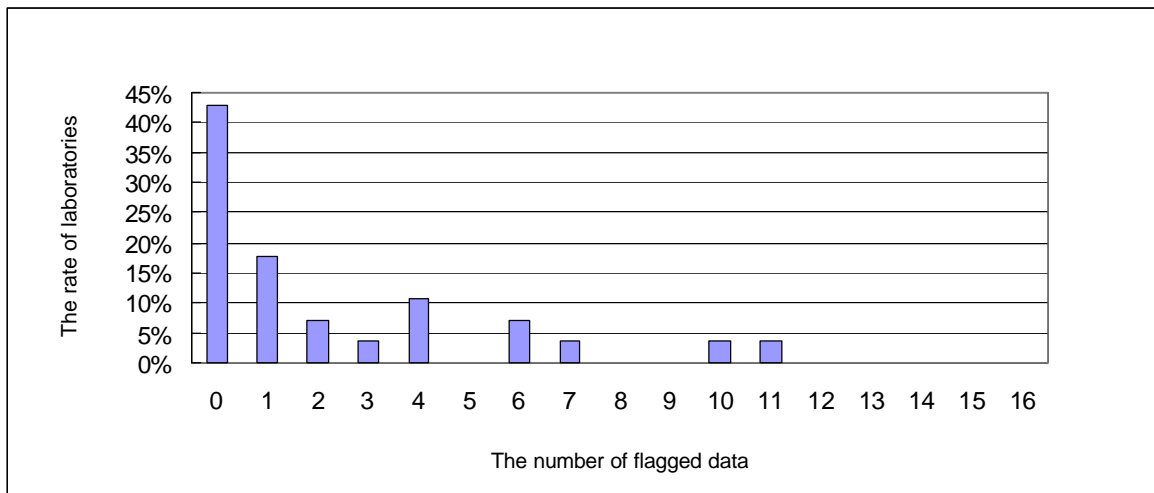
Unit: year

Reverse mesh: Flagged data of “E” or “X” in sample No.041 and/or sample No.042

Reverse mesh with dark are flagged date of both sample No.041 and No.042

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	12	43%
1	5	18%
2	2	7%
3	1	4%
4	3	11%
5	0	0%
6	2	7%
7	1	4%
8	0	0%
9	0	0%
10	1	4%
11	1	4%
12	0	0%
13	0	0%
14	0	0%
15	0	0%
16	0	0%

In this project, the total number of flagged data was 64 (E48, X16) among the whole set of 540 data. The attribution of flagged data in each laboratory was presented in Table 26.

The number of excellent laboratories without flagged data was 12, which was equivalent to about 43% of the all-participating laboratories. The number of laboratories that submitted less than 2 flagged data were 17(60%)during the comparison test carried out in 2003, but there were 17 (63%) laboratories this time.

There was one laboratory that produced more than 10 flagged data. One laboratory should make more efforts for preparing standard solutions and also for the operation of the equipment.

## Water temperature at measurement (pH and EC)

As described in Table 27, most of the participating laboratories measured pH and EC at temperature around 25°C as recommended condition by EANET. Unfortunately, even though measure temperature was around 25°C, one laboratory had the flagged data in pH measurement and two laboratories had the flagged data in EC measurement.

**Table 27 Water temperature at measurement (pH and EC)**

lab.ID	pH		EC	
	No.041	No.042	No.041	No.042
CN01	25	25	25	25
CN02	14	14	14	14
CN03	25.0	25.0	25.0	25.0
CN04	23.6	24.2	24.2	24.3
ID01	25	25	25	25
ID02	25.0	25.0	25.0	25.0
JP01	24.7-24.8	24.3-25.3	24.4-24.8	24.4-24.8
JP02	25.0	25.0	25.0	25.0
JP03	24.7	24.7	24.5	24.5
JP04	24.9	24.9	24.9	24.9
JP05	24.9	24.9	24.7	24.5
JP06	25.0	25.0	25.0	25.0
JP07	24.6-25.0	24.6-25.0	24.6-25.0	24.6-25.0
JP08	25.0	25.0	25.0	25.0
KR01	25.0	25.0	25.0	25.0
MY01	25	25	25	25
MN01	25	25	25	25
PH01	25	25	25	25
RU01	25	25	25	25
RU02	25	25	25	25
TH01	25	25	25	25
TH02	25	25	25	25
TH03	25	25	25	25
TH04	25	25	25	25
TH05	25	25	25	25
VN01	25	25	25	25
KH01	25	25	25	25
LA01	25.2	25.2	25.2	25.2

Unit: degrees centigrade

Reverse mesh with light are flagged data of "E"

Reverse mesh with dark are flagged date of "X"

#### 4. COMPARISON OF 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup> AND 7<sup>th</sup> SURVEY

The inter-laboratory comparison surveys were carried out 7 times, so far their results with the ratios of flagged data are shown in Fig. 17. The rate of data that satisfied the required data quality objectives (DQOs) increased from 75-78% to 84-93% until the 4<sup>th</sup> (2001) survey. The data quality seemed to be improved by accumulating experiences. But on the 5<sup>th</sup> project (2002), both DQOs on the higher concentration sample and the lower concentration sample decreased because the ion concentrations were a half of their content in the samples of previous projects (Table 28).

In both the higher concentration sample (correspond to the sample NO.041 on 7<sup>th</sup> project) and the lower concentration sample (correspond to the sample NO.042 on 7<sup>th</sup> project), the number of data within DQOs increased in 7<sup>th</sup> project. Especially for the sample No.42, the number of data within DQOs was the best among all surveys. It seems that the quality of the ion analysis was improved in many laboratories.

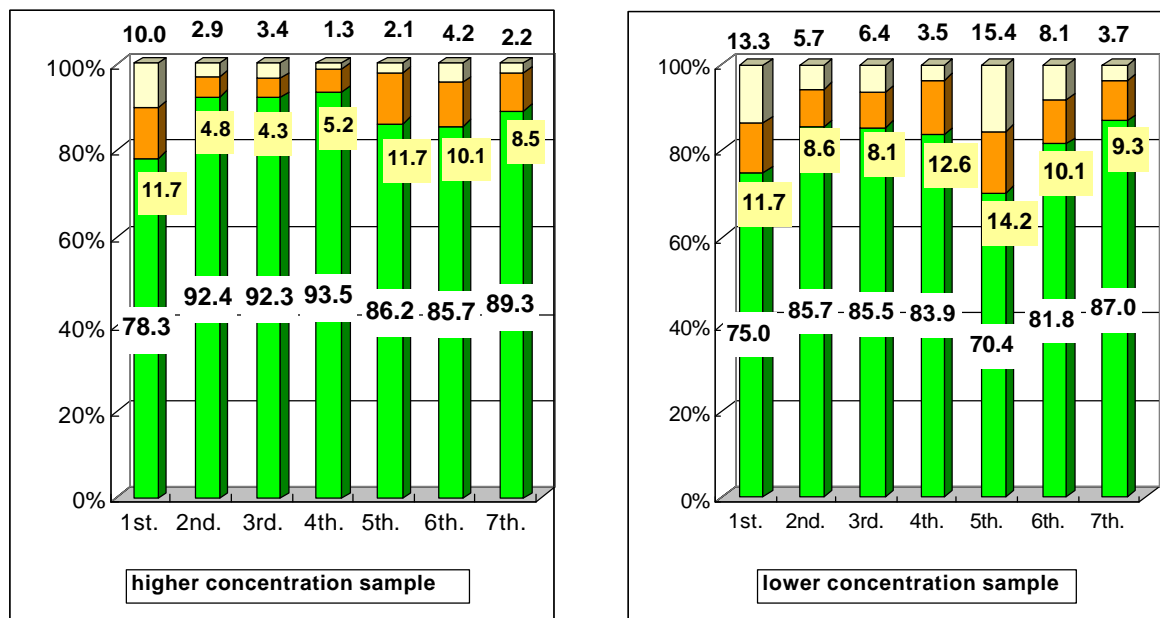


Fig. 17 Comparison of 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> inter-laboratory comparison project



**Table 28 The prepared values of each parameter of artificial rainwater of inter  
–laboratory comparison projects of EANET**

		pH (-)	EC (mS/m)	SO <sub>4</sub> <sup>2-</sup> (μmol/L)	NO <sub>3</sub> <sup>-</sup> (μmol/L)	Cl <sup>-</sup> (μmol/L)	Na <sup>+</sup> (μmol/L)	K <sup>+</sup> (μmol/L)	Ca <sup>2+</sup> (μmol/L)	Mg <sup>2+</sup> (μmol/L)	NH <sub>4</sub> <sup>+</sup> (μmol/L)
1998	No.1	4.05	7.94	83.5	93.3	129.0	95.8	11.1	41.1	13.1	84.8
	No.2	4.51	2.82	29.1	36.1	45.1	33.5	7.4	14.3	4.6	29.5
1999	No.1	4.14	6.38	67.0	75.0	104.0	77.0	8.9	33.0	11.0	68.0
	No.2	4.59	2.30	24.0	27.0	38.0	28.0	3.2	12.0	3.8	25.0
2000	No.1	4.10	6.23	59.7	63.3	101.3	51.3	9.9	29.4	11.7	60.5
	No.2	4.85	1.55	20.1	27.5	15.5	8.7	4.9	11.0	7.8	18.2
2001	No.11	4.10	7.45	85.0	93.3	108.4	68.4	15.8	41.1	18.7	87.8
	No.12	4.82	1.76	21.5	19.4	34.4	27.4	4.0	13.2	3.7	16.7
2002	No.021	4.30	3.75	40.3	51.0	33.7	13.7	6.9	19.1	7.0	42.4
	No.022	5.15	0.69	8.9	8.5	9.1	5.1	2.0	6.6	1.8	4.5
2003	No.031	4.52	3.44	44.7	30.9	66.0	46.1	6.9	20.5	7.0	48.3
	No.032	4.80	1.48	12.0	21.3	29.6	25.6	2.5	4.4	3.4	15.1
<b>2004</b>	<b>No.041</b>	<b>4.60</b>	<b>3.94</b>	<b>58.6</b>	<b>41.4</b>	<b>76.7</b>	<b>66.7</b>	<b>6.9</b>	<b>38.9</b>	<b>9.8</b>	<b>39.4</b>
	<b>No.042</b>	<b>5.00</b>	<b>1.33</b>	<b>17.6</b>	<b>18.4</b>	<b>22.5</b>	<b>20.5</b>	<b>5.0</b>	<b>10.0</b>	<b>2.7</b>	<b>15.1</b>

## 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 (Standard operating procedures)** must be prepared for the management of apparatus, reagents, and procedure of operation.
- 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) Reference Materials

- In order to assure the reliability and traceability of measurements, the reference materials 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 analytical results of reference materials 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 materials 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, or when R1 and/or R2 (See page 5, 6) is out of allowable range, 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
- 6) Report of the Inter-laboratory Comparison Project 2001  
(Round robin analysis survey 4<sup>th</sup> Attempt) November 2002
- 7) Report of the Inter-laboratory Comparison Project 2002  
(Round robin analysis survey 5<sup>th</sup>. Attempt) November 2003
- 8) Report of the Inter-laboratory Comparison Project 2003  
(Round robin analysis survey 6<sup>th</sup> Attempt) November 2004

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