

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

Report of the Inter-laboratory Comparison Project 2002 on Wet Deposition

5th Attempt

November 2003

Acid Deposition and Oxidant Research Center

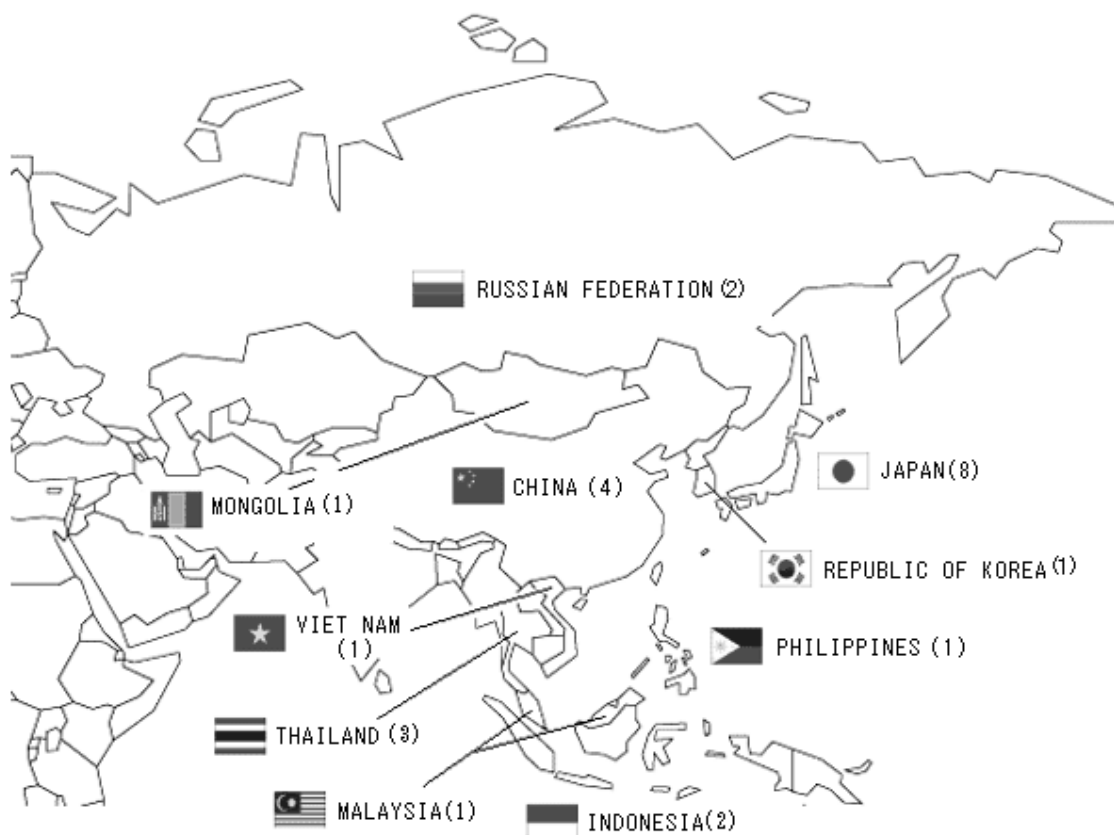
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1. INTRODUCTION

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 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) at the end of 2002. All of the participating laboratories submitted their analytical data to NC. Obtained data for pH, EC and concentrations of SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ were compared with prepared values and statistically treated. List of the participating laboratories, individual analytical data with their laboratory's short name, and various statistical parameters are included in this report.



* Figure in parenthesis shows the number of laboratories of each country (24 laboratories from 10 countries)

Fig.1 Laboratories participated in the Inter-comparison project 2002 of the EANET

2. PROCEDURE

2.1 Participating Laboratories

Twenty-four 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 24 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) 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

Name	Amount of each sample	Container	Number of samples	Note
Artificial rainwater samples No.021 (higher concentration) No.022 (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 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 ₄ ²⁻	micro mole/liter	µmol/L
NO ₃ ⁻	micro mole/liter	µmol/L
Cl ⁻	micro mole/liter	µmol/L
Na ⁺	micro mole/liter	µmol/L
K ⁺	micro mole/liter	µmol/L
Ca ²⁺	micro mole/liter	µmol/L
Mg ²⁺	micro mole/liter	µmol/L
NH ₄ ⁺	micro mole/liter	µmol/L

Table 3 Concentration range of the artificial rainwater samples*

Parameter	Range	Parameter	Range
pH	4.0– 5.5	Na ⁺	1 – 100µmol /L
EC	0.3 – 10.0 mS/m	K ⁺	1 – 50µmol /L
SO ₄ ²⁻	5 – 100µmol/L	Ca ²⁺	1 – 50µmol /L
NO ₃ ⁻	5 – 100µmol/L	Mg ²⁺	1 – 50µmol /L
Cl ⁻	5 – 150µmol /L	NH ₄ ⁺	3 – 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 “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 ₄ ²⁻	Ion Chromatography
NO ₃ ⁻	Spectrophotometry
Cl ⁻	
Na ⁺	Ion Chromatography
K ⁺	Atomic Absorption/Emission Spectrometry
Ca ²⁺	
Mg ²⁺	
NH ₄ ⁺	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 : $\mu\text{mol L}^{-1}$).

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

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

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

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

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

(3) Calculation of ion balance (R_1)

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

(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 (R₂)

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

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

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

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

(3) R₂, which is calculated using the above equation, should be compared with standard values in Table 6. If R₁ is out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves are necessary.

Table 6 Allowable ranges for R₂ in different ranges of EC

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

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

3. RESULTS

The Network Center shipped artificial rainwater samples to 24 laboratories in the participating countries of EANET, and received the data on analytical results from all 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 values/concentrations within a range of $\pm 10\%$. But there are 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	Average	S.D.	N	Min.	Max.
[Sample No.021] pH	4.30	4.32	0.08	24	4.15	4.50
EC(mS/m)	3.75	3.54	0.22	24	2.93	4.03
SO ₄ ²⁻ (μ mol/L)	40.3	40.2	2.57	23	34.4	49.4
NO ₃ ⁻ (μ mol/L)	51.0	51.3	2.91	23	47.8	61.6
Cl ⁻ (μ mol/L)	33.7	32.5	2.82	23	26.0	37.9
Na ⁺ (μ mol/L)	13.7	13.6	1.15	24	11.4	16.5
K ⁺ (μ mol/L)	6.92	7.2	1.12	24	5.3	10.5
Ca ²⁺ (μ mol/L)	19.1	19.2	1.86	24	14.2	23.0
Mg ²⁺ (μ mol/L)	7.02	7.0	0.89	24	5.2	8.9
NH ₄ ⁺ (μ mol/L)	42.4	43.3	3.27	23	38.7	50.8
[Sample No.022] pH	5.15	5.19	0.14	24	4.94	5.61
EC(mS/m)	0.69	0.69	0.04	23	0.59	0.75
SO ₄ ²⁻ (μ mol/L)	8.88	9.0	1.03	23	5.1	10.9
NO ₃ ⁻ (μ mol/L)	8.49	8.5	0.87	23	6.4	11.6
Cl ⁻ (μ mol/L)	9.13	10.0	1.85	23	8.5	15.8
Na ⁺ (μ mol/L)	5.13	4.9	1.05	23	1.8	6.4
K ⁺ (μ mol/L)	1.98	2.0	0.61	23	1.2	3.4
Ca ²⁺ (μ mol/L)	6.61	7.1	1.96	24	2.1	10.0
Mg ²⁺ (μ mol/L)	1.75	1.9	0.52	24	1.1	3.3
NH ₄ ⁺ (μ mol/L)	4.54	4.2	1.04	22	1.3	7.0

(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 in chapter 2.5 .

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.021 (higher concentrations) and No.022 (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.021 and No.022 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.021 (higher concentrations)

Table 8 Numbers of flagged data for the Sample No.021 (higher concentrations)

Flag	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
E	0	3	1	1	3	4	4	2	7	3	28
X	0	0	1	1	1	0	2	0	0	0	5
Data within DQOs	24	21	22	22	20	20	18	22	17	20	206
Flagged(%)	0.0	12.5	8.3	8.3	16.7	16.7	25.0	8.3	29.2	13.0	13.8

Note: ID01 ; no date for the trouble of UV/VIS meter (Total data=239)

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

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

For sample No.021(higher concentrations), 28 analytical data out of 239 exceeded the DQOs by a factor of 2 and flagged by "E". 5 analytical data out of 239 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" were 33 out of 239, shared about 13.8 percents of all reported data for sample No.021 (Fig.2).

Especially measured values of Mg²⁺,K⁺ and Na⁺ have many results with flags. It is necessary to note that concentration of each mentioned constituent was prepared as a half of that in 2001 .

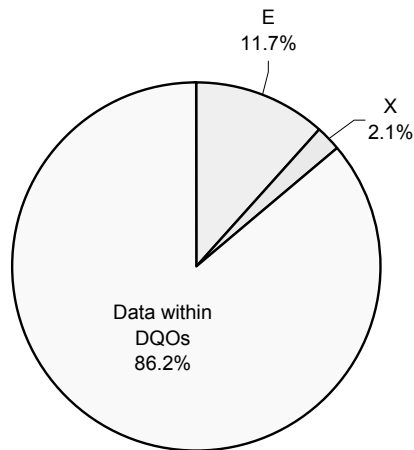


Fig.2 Percentage of flagged data for Sample No.021

Table9 Analytical Results of Sample No.021 (Higher concentrations)

Lab. ID	pH	EC (mS/m)	SO ₄ ²⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)	Cl ⁻ (μmol/L)	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	NH ₄ ⁺ (μmol/L)	R1	R2
	-										-	-
CN01	4.24	3.64	40.1	50.8	33.5	12.8	7.0	20.5	7.1	42.8	3.2	5.0
CN02	4.22	3.63	40.3	51.0	34.0	14.1	6.9	20.4	6.8	43.5	3.9	6.5
CN03	4.24	3.66	39.4	50.8	32.7	12.9	7.1	20.4	7.3	43.0	4.0	4.6
CN04	4.23	3.59	39.6	50.7	32.7	13.2	7.1	20.1	7.1	42.9	4.1	6.1
ID01	4.16	3.57	X 57.9	E 61.6	X 51.3	12.9	6.0	E 14.2	E 8.9	-	-	-
ID02	4.40	3.56	43.0	48.1	37.9	14.6	X 10.5	18.5	7.1	E 50.3	-1.7	-0.4
JP01	4.34	3.69	38.0	49.7	29.7	13.4	6.3	17.8	6.8	41.4	0.2	-2.8
JP02	4.35	3.54	40.3	51.0	33.1	E 16.2	7.0	19.9	7.9	38.8	-0.7	0.3
JP03	4.34	3.50	40.5	50.8	33.0	12.1	5.9	17.7	6.5	41.4	-3.5	0.7
JP04	4.38	3.47	40.4	51.1	32.6	14.4	E 8.1	20.5	6.9	43.0	-0.8	0.2
JP05	4.33	3.70	40.1	50.7	31.5	13.3	6.4	18.2	E 5.4	39.8	-2.8	-1.9
JP06	4.36	3.66	34.4	47.8	E 26.0	E 11.6	6.9	19.0	6.6	45.1	5.3	-4.3
JP07	4.32	3.54	39.8	49.2	31.1	13.3	6.1	16.5	E 5.7	40.5	-2.5	0.4
JP08	4.37	3.46	39.9	50.4	33.0	13.7	7.4	19.1	7.3	41.8	-1.5	0.3
KR01	3.07	E 3.07	39.6	54.4	37.8	E 16.5	X 9.3	21.5	8.0	E 50.8	-1.2	3.4
MY01	4.26	3.51	39.2	50.7	34.3	12.8	E 5.3	16.4	E 5.2	40.6	-2.1	4.3
MN01	4.36	3.57	38.9	49.9	E 26.7	13.5	7.6	17.7	7.4	41.1	0.5	-2.1
PH01	4.36	3.44	40.2	51.3	32.6	E 11.4	E 8.5	21.0	E 5.5	43.7	-1.3	1.4
RU01	4.28	3.68	38.1	52.3	34.2	14.1	7.5	18.1	7.1	42.8	1.4	1.8
RU02	4.30	4.03	43.3	57.5	34.6	14.0	E 8.0	E 23.0	E 8.2	46.6	0.7	-0.9
TH01	4.35	3.62	41.1	51.1	32.7	14.3	6.2	19.6	7.1	44.0	-1.0	-0.5
TH02	4.15	3.70	40.6	49.2	31.4	13.2	6.7	19.6	7.0	43.9	7.4	C 9.4
TH03	4.42	E 3.13	39.1	50.6	33.8	13.9	7.8	19.3	6.7	38.7	-3.9	2.5
VN01	4.45	E 2.93	E 49.4	X 28.3	E 27.9	13.3	6.9	21.0	E 8.1	E 49.7	2.7	5.4

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

I:Poor ion balance (R1)

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

C:Poor Conductivity agreement (R2)

Sample No.022 (lower concentrations)

Table 10 Number of flagged data for the Sample No.022 (lower concentrations)

Flag	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total
E	0	1	2	1	1	8	9	2	5	5	34
X	0	0	2	2	4	3	7	8	8	3	37
Data within DQOs	24	23	20	21	19	13	8	14	11	16	169
Flagged(%)	0.0	4.2	16.7	12.5	20.8	45.8	66.7	41.7	54.2	33.3	29.6

Note: no NH₄⁻ data for ID01 due to the trouble of UV/VIS meter (Total data=239)

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

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

For sample No.022 (lower concentrations), 34 analytical data out of 239 exceeded the DQOs by a factor of 2 and flagged by "E". 37 analytical data out of 239 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" were 71 analytical data out of 239, shared up to 29.6 percents of all reported data for sample No.022 (Fig.3).

Many data on K⁺ and Na⁺ are marked with flags E. Many data on Ca²⁺, Mg²⁺, K⁺ are marked with flags X.(Table 11)

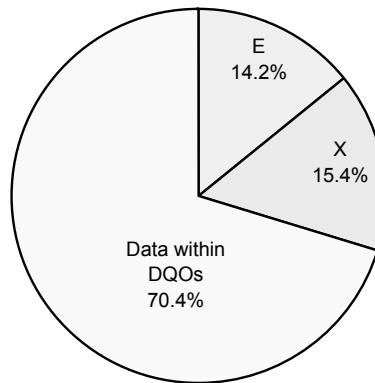


Fig.3 Percentage of flagged data for Sample No.022

Evaluation

The number of flagged data for Sample No.022 was more about 2.5 times in the rate of flagged data as compared with Sample No.021. It indicates the difficulty of the analysis of lower concentration sample, particularly for K⁺, Mg²⁺, Na⁺, Ca²⁺. The reason why quantity of flagged data was increased is clarified in chapter 5.

Table11 Analytical Results of Sample No.022 (Lower concentrations)

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	R1	R2
	-	(mS/m)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	-	-
CN01	5.09	0.70	E 10.3	9.1	9.8	5.3	E 2.5	X 9.8	E 2.2	E 3.2	4.4	6.5
CN02	5.12	0.71	E 10.9	9.2	10.3	5.8	E 1.6	7.6	1.7	4.2	-4.5	3.7
CN03	5.10	0.71	10.0	9.0	9.6	4.9	E 2.3	X 10.0	E 2.1	E 3.3	5.0	4.9
CN04	5.08	0.69	10.0	8.9	9.7	5.1	X 2.9	X 10.0	X 2.5	E 3.5	7.4	8.0
ID01	5.11	0.74	X 16.0	X 11.6	X 20.5	X 1.8	E 1.4	X 3.6	1.8		I -49.3	6.8
ID02	5.28	0.67	9.0	7.8	X 15.8	X 9.1	E 1.4	X 2.1	1.8	X 18.2	0.2	4.8
JP01	5.23	0.70	8.7	8.2	8.5	5.3	1.7	5.8	1.7	4.6	-2.4	-5.3
JP02	5.21	0.70	8.9	8.1	9.1	E 6.1	2.1	X 9.0	E 2.1	4.2	7.6	-0.6
JP03	5.14	0.65	9.0	8.7	9.1	E 3.8	X 1.3	6.3	1.6	4.5	-4.6	2.5
JP04	5.33	0.66	8.8	8.3	8.8	5.2	2.2	6.2	E 1.3	E 5.5	-3.2	-4.6
JP05	5.22	0.71	8.6	8.2	8.8	4.9	1.9	6.9	1.6	4.6	0.3	-4.7
JP06	5.21	0.74	8.8	8.4	8.8	E 3.7	E 1.6	E 5.4	X 1.1	5.1	-8.1	-8.2
JP07	5.15	0.66	8.9	8.3	E 10.6	E 5.9	1.9	5.8	1.5	3.9	-4.7	2.1
JP08	5.28	0.63	9.0	8.6	9.0	5.1	2.0	7.0	1.8	4.3	-1.9	0.2
KR01	5.46	0.59	8.8	8.8	11.9	4.6	3.4	7.2	1.7	4.1	-6.9	0.7
MY01	5.13	0.72	8.7	8.4	9.5	4.5	X 1.2	6.0	X 1.1	4.0	-6.2	-3.2
MN01	5.18	0.71	8.9	8.5	9.6	E 4.1	X 2.8	6.6	X 3.3	3.9	1.8	-1.3
PH01	5.23	0.75	8.7	8.3	8.8	X 3.2	X 3.4	7.5	X 1.1	E 3.2	-2.4	-8.1
RU01	5.05	0.75	9.7	8.1	9.8	4.5	E 1.7	5.8	1.6	4.4	-4.2	0.2
RU02	5.00	E 0.85	9.7	9.3	9.2	5.2	1.9	7.2	E 2.1	4.3	2.7	-1.7
TH01	5.19	0.69	8.9	8.5	9.4	E 6.0	E 1.4	X 9.4	X 2.3	X 1.3	4.0	-0.2
TH02	4.94	0.70	9.2	E 6.4	9.0	5.1	E 2.3	7.1	1.7	X 7.0	12.4	10.2
TH03	5.23	0.64	8.3	8.0	9.1	E 6.1	X 4.6	E 8.6	X 2.5	5.0	13.1	4.3
VN01	5.61	0.69	X 5.1	X 22.2	X 15.2	E 6.4	E 1.8	X 10.0	X 2.6	4.9	-7.7	-1.4

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 their deviation. The numbers of flagged data were indicated in table for each analytical parameter.

PH

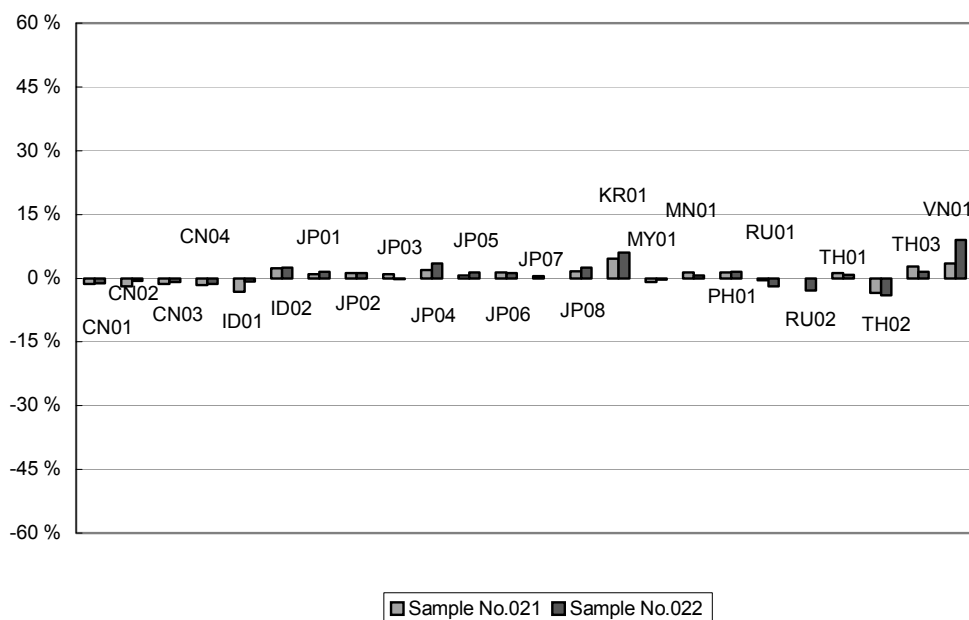


Fig.4 Distribution of pH data normalized by prepared value

Table 12 Analytical method and flagged data of pH

Analytical Method

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

Flagged data

	E	X	Flagged (%)
Sample No.021	0	0	0
Sample No.022	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.021 and No.022 were good to be 1.9% and 2.7% correspondently.

EC

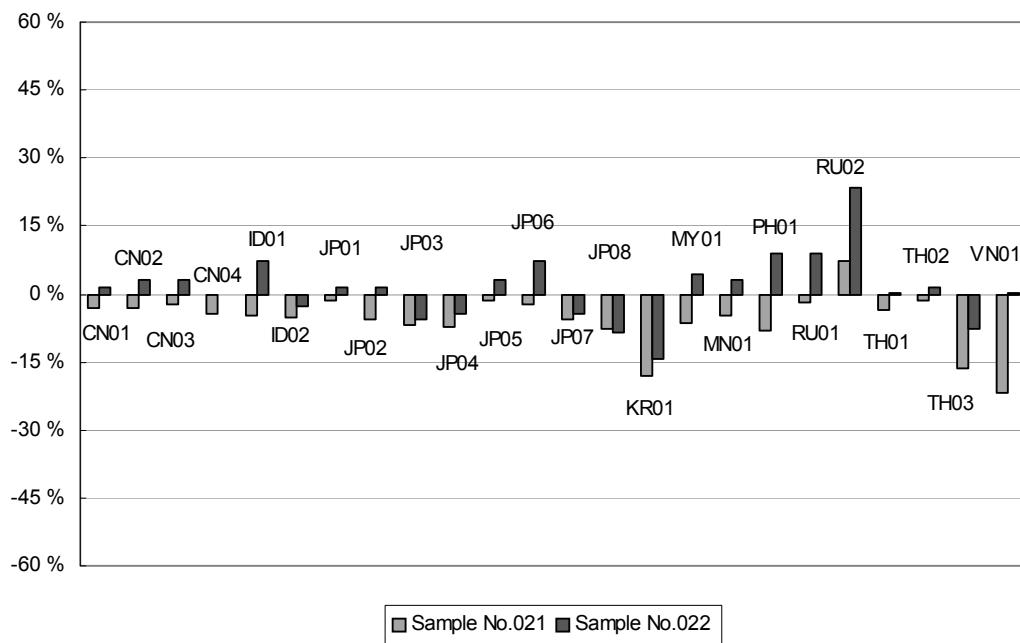


Fig.5 Distribution of EC data normalized by prepared value

Table 13 Analytical method and flagged data of EC

Analytical Method

Conductivity meter and cell	24/24
-----------------------------	-------

Flagged data

	E	X	Flagged (%)
Sample No.021	3	0	12.5
Sample No.022	1	0	4.2

All participating laboratories used conductivity cell for the measurement of EC. Obtained data were almost agreed with the prepared values. However, Lab.RU02,KR01,TH03 and VN01 submitted results flagged by “E”. 70% of the Laboratories reported lower data than prepared value for Sample No.021. On the other hand many laboratories reported higher data than prepared value for No.022.

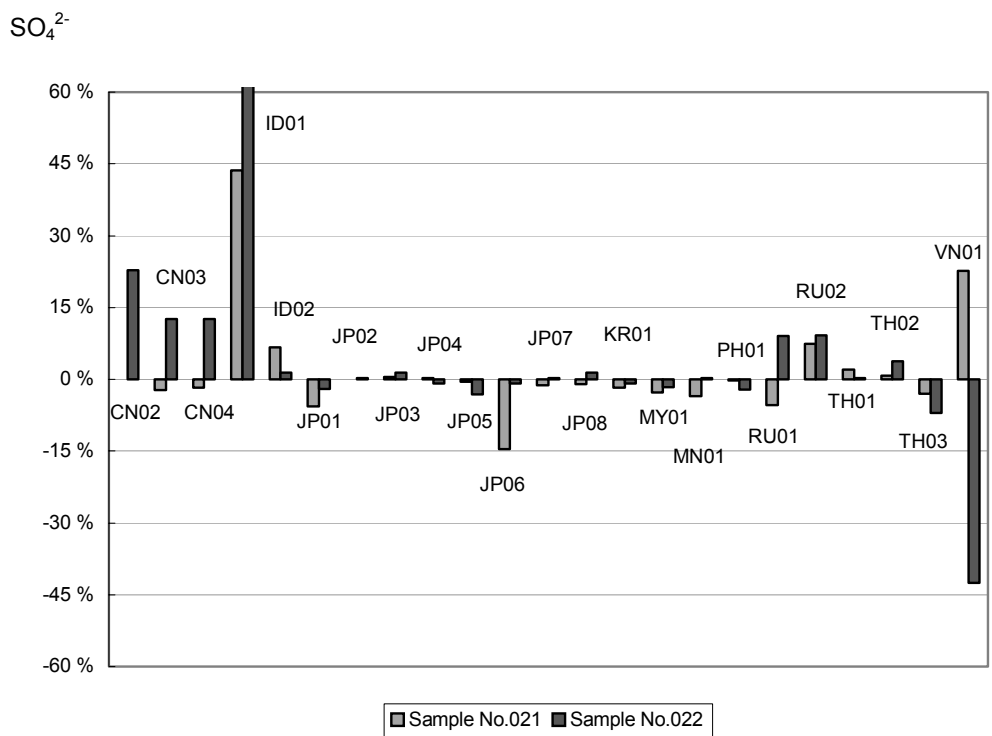


Fig.6 Distribution of SO₄²⁻ data normalized by prepared concentration

Table 14 Analytical method and flagged data of SO₄²⁻

Analytical Method

Ion chromatography	22/24
Spectrophotometry	2/24

Flagged data

	E	X	Flagged (%)
Sample No.021	1	1	8.3
Sample No.022	2	2	16.7

All of the participating laboratories used ion chromatography for the determination of SO₄²⁻ except for two laboratories (Lab.RU02,VN01), which used spectrophotometry. Lab.ID01 reported outlier over 30% than prepared value for both samples. It seemed to be the calibration error in the analysis by using ion chromatograph. Lab.VN01 reported below -30% than prepared value for sample No.022. It seemed to be a problem in the analytical procedure with spectrophotometry. The data which exceeds 3 times of standard deviation from average value were rejected in statistics.

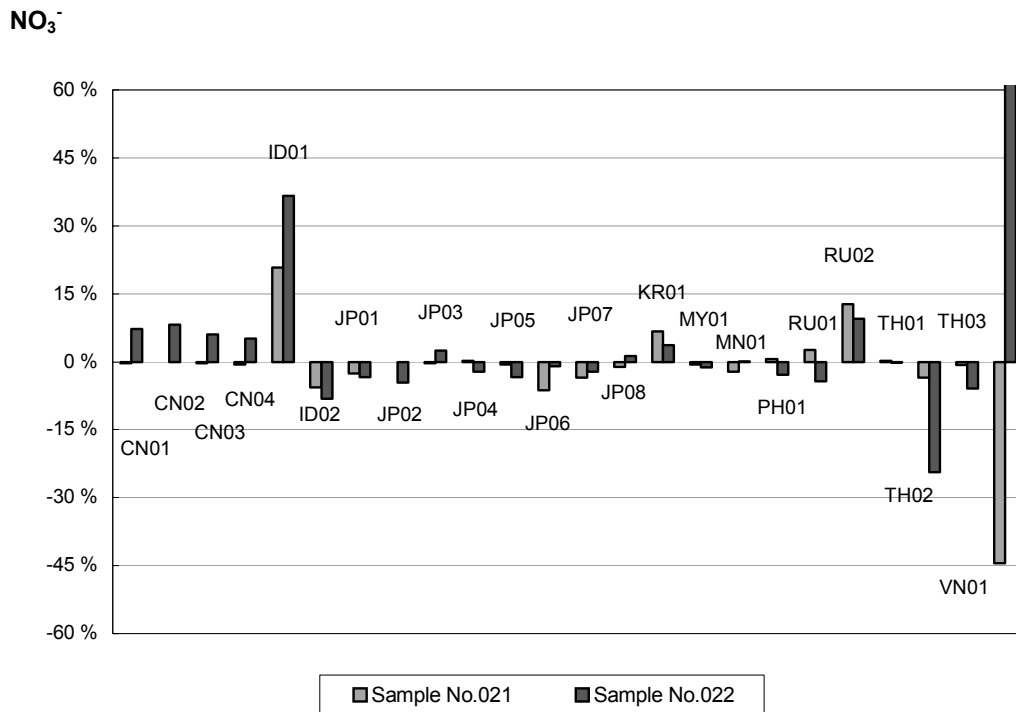


Fig.7 Distribution of NO₃⁻ data normalized by prepared concentration

Table 15 Analytical method and flagged data of NO₃⁻

Analytical Method

Ion chromatography	22/24
Spectrophotometry	1/24
Other method (Colorimetry)	1/24

Flagged data

	E	X	Flagged (%)
Sample No.021	1	1	8.3
Sample No.022	1	2	12.5

The data of both Lab.ID01 (obtained by ion chromatography) and Lab.VN01 (obtained by spectrophotometry) were flagged. The results of Lab.ID01 were 15% higher than the prepared value. It seemed to be the calibration error in the analysis same as SO₄²⁻. The results of Lab.VN01 exceed ±30% than the prepared value for the both samples No.021 and No.022. It seemed to be a problem in the analytical procedure with spectrophotometry method as same as SO₄²⁻.

Cl⁻

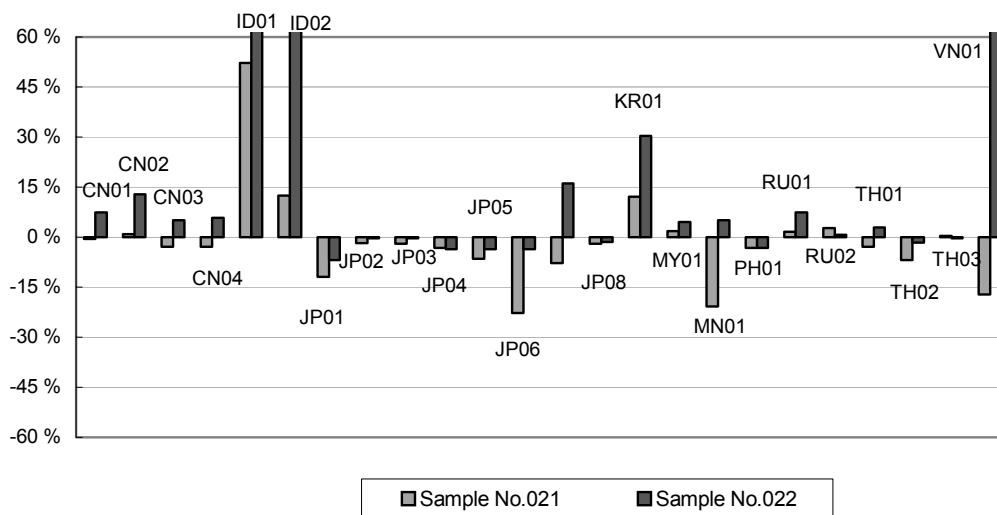


Fig.8 Distribution of Cl⁻ data normalized by prepared concentration

Table 16 Analytical method and flagged data of Cl⁻

Analytical Method

Ion chromatography	22/24
Titration	2/24

Flagged data

	E	X	Flagged (%)
Sample No.021	3	1	16.7
Sample No.022	1	4	20.8

Same as SO₄²⁻ and NO₃⁻, most of laboratories used ion chromatography for the determination of Cl⁻. Two laboratories (Lab.RU02 and VN01) used titration method for the determination of Cl⁻. As for the sample No.022, the data of four Lab. (ID01, ID02, KR01, VN01) exceeded 30%. It seemed to be a calibration error for ID01, ID02, while a problem was occurred in the analytical procedure for VN01.

Na⁺

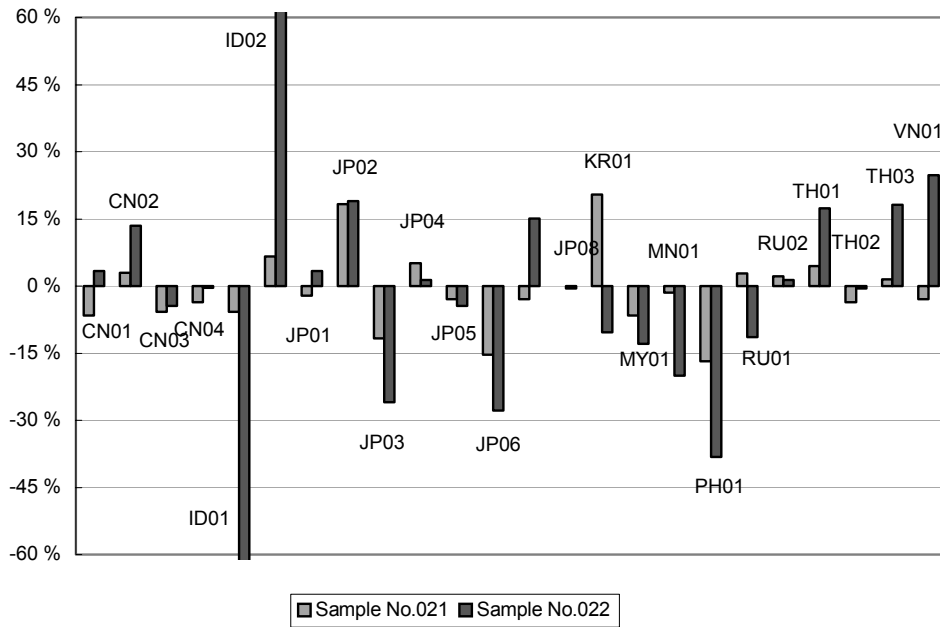


Fig.9 Distribution of Na⁺ data normalized by prepared concentration

Table 17 Analytical method and flagged data of Na⁺

Analytical Method

Ion chromatography	18/24
Atomic absorption spectrometry	4/24
Flame (emission) spectrometry	2/24

Flagged data

	E	X	Flagged (%)
Sample No.021	4	0	16.7
Sample No.022	8	3	45.8

18 laboratories used ion chromatography, 4 laboratories used atomic absorption photometry (Lab.ID01,ID02,KR01,PH01), and 2 Laboratories used flame (emission) photometry (Lab.RU01,RU02) for the determination of Na⁺.

As for the lower concentration sample No.022, half of the data have flags. And flag X is marked on the data that obtained by the Atomic absorption spectrometry.

It is clear that determination might be difficult because of low concentration of Na⁺.

On the other hand, there were only 4 flagged data for the sample with higher concentration.

And there was no clear difference among data obtained by these three analytical methods for the sample No.021.

K⁺

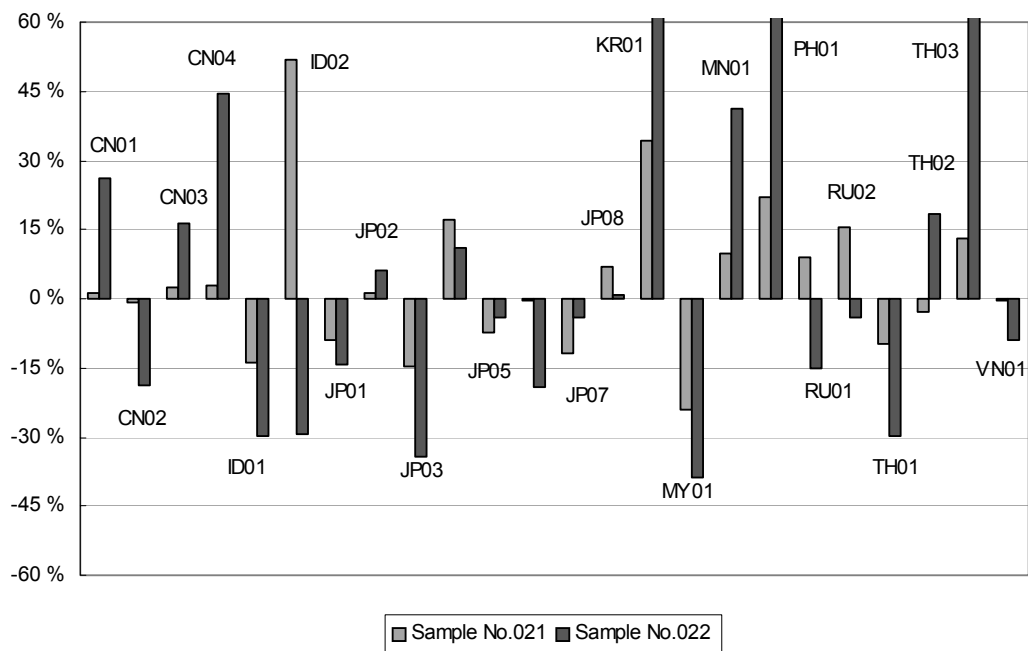


Fig.10 Distribution of K⁺ data normalized by prepared concentration

Table 18 Analytical method and flagged data of K⁺

Analytical Method

Ion chromatography	18/24
Atomic absorption spectrometry	4/24
Flame (emission) spectrometry	2/24

Flagged data

	E	X	Flagged (%)
Sample No.021	4	2	25.0
Sample No.022	9	7	66.7

Same as for Na⁺, 18 laboratories used ion chromatography, 4 laboratories used atomic absorption and 2 laboratories used flame (emission) photometry, for the determination of K⁺.

There was difference in data obtained by different analytical methods for Sample No.021. Most of the values measured by ion chromatography were satisfied with the DQOs. But four sixths of the data by atomic absorption/flame (emission) spectrometry was flagged as out of the DQOs.

There were 16 flagged data for the sample No.022 with the concentration to be close to the minimum determination limit for K⁺ by both ion chromatography and atomic absorption photometry,.

It seemed that the results were affected by the difficulty of making the calibration curve and/or blank value of the water used for the dilution.

Ca²⁺

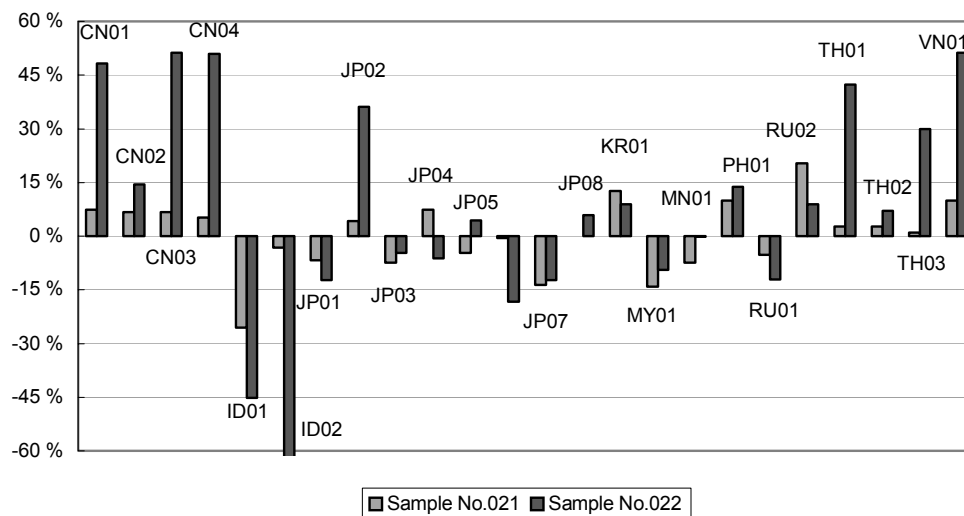


Fig.11 Distribution of Ca²⁺ data normalized by prepared concentration

Table 19 Analytical method and flagged data of Ca²⁺

Analytical Method

Ion chromatography	18/24
Atomic absorption photometry	4/24
Flame (emission) photometry	2/24

Flagged data

	E	X	Flagged (%)
Sample No.021	2	0	8.3
Sample No.022	2	8	41.7

Same as for Na⁺ and K⁺, ion chromatography and atomic absorption /flame (emission) photometry, were used for the analysis of Ca²⁺.

There was no clear difference in data obtained by these analytical methods. The flagged data in sample No.022 were noticeable same as K⁺ because of the lower concentration.

Mg²⁺

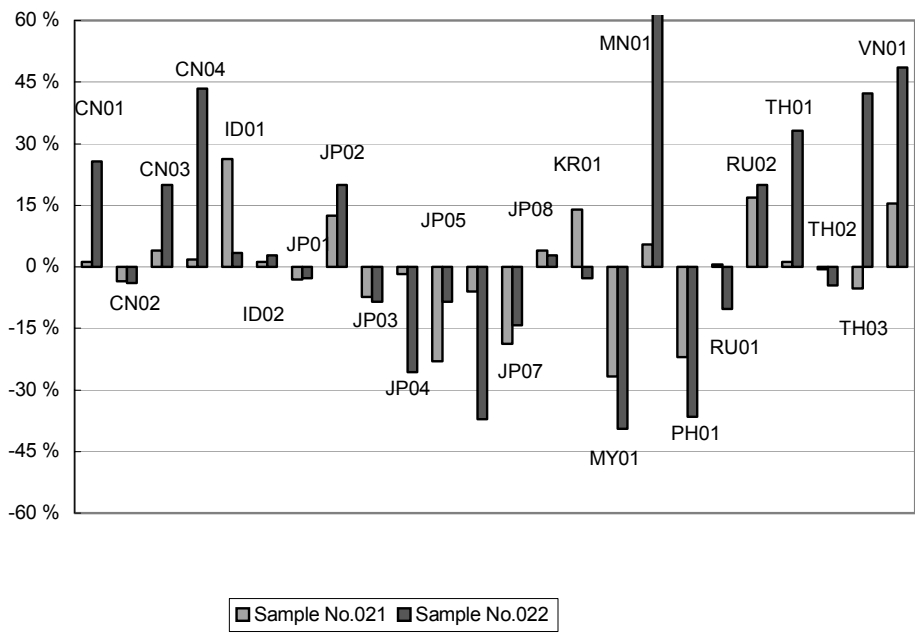


Fig.12 Distribution of Mg²⁺ data normalized by prepared concentration

Table 20 Analytical method and flagged data of Mg²⁺

Analytical Method

Ion chromatography	18/24
Atomic absorption spectrometry	4/24
Flame (emission) spectrometry	2/24

Flagged data

	E	X	Flagged (%)
Sample No.021	7	0	29.2
Sample No.022	5	8	54.2

Ion chromatography, atomic absorption /flame (emission) photometry were used in the analysis of Mg²⁺ same as for Na⁺, K⁺ and Ca²⁺.

18 laboratories used ion chromatography, 6 laboratories used atomic absorption/flame (emission) photometry as analytical instruments for the determination of Mg²⁺.

Flags were put on for more than half of the data in sample No.022. But there was no clear difference of data obtained by these analytical methods.

The number of flagged data on Mg²⁺ were as same as for K⁺.

NH₄⁺

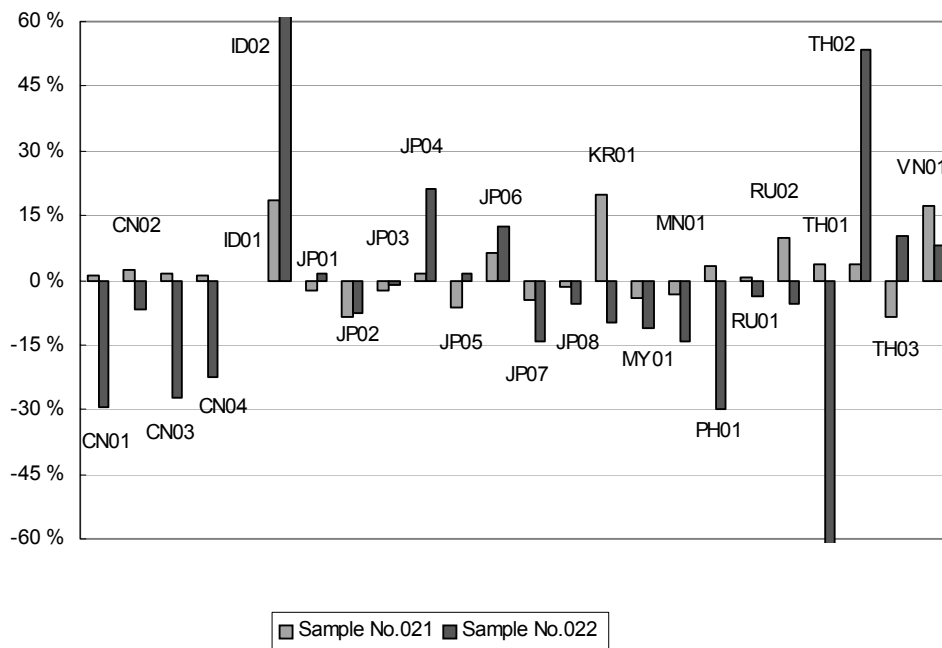


Fig.13 Distribution of NH₄⁺ data normalized by prepared concentration

Table 21 Analytical method and flagged data of NH₄⁺

Analytical Method

Ion chromatography	17/23
Spectrometry (Indophenol blue)	6(3)/23

Note: no data from ID01, due to trouble of UV/VIS meter

Flagged data

	E	X	Flagged (%)
Sample No.021	3	0	13.0
Sample No.022	5	3	33.3

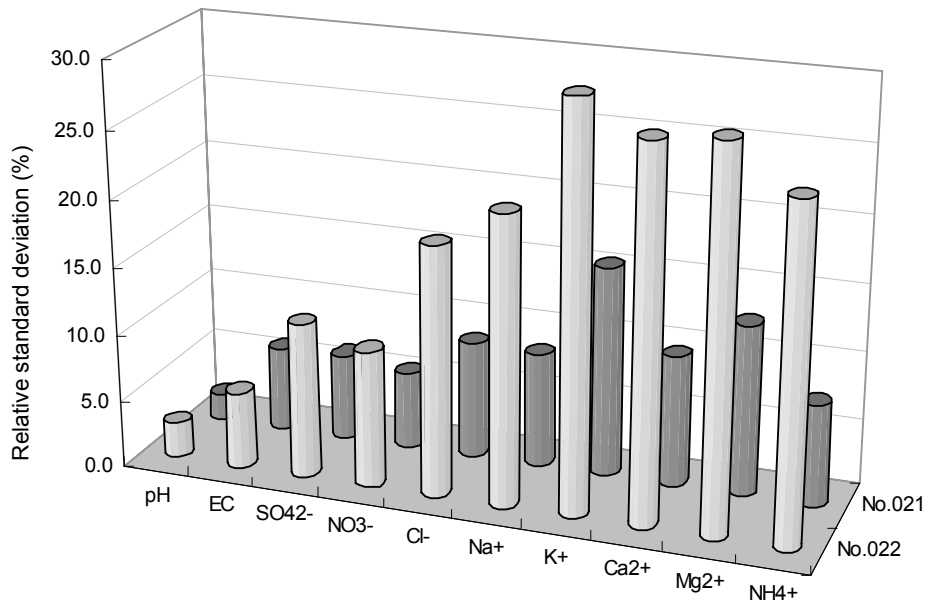
19 laboratories used recommended analytical method of EANET for the determination of NH₄⁺: 17 laboratories used ion chromatography; 3 laboratories used spectrometry (Indophenol blue). 3 laboratories used spectrometry without using indophenol blue method.

Three laboratories (Lab.ID02, TH01, TH02) submitted significantly different data of the sample No.022 comparing with prepared value. Lab.ID02 used spectrometry (indophenol blue), and both Lab.TH01 and TH02 used ion chromatography .

Overall Evaluation

All data on pH were satisfied the required DQOs values for wet deposition monitoring in EANET. The concentrations of anions and cations in samples of 2002 project were approximately as a half of ones of previous years both in high and low concentration samples. Especially concentration of all cations was below $10 \mu\text{mol/L}$ and was close to the minimum determination limits level. As a result, data on cations in sample No.022 were varied within 21~30% range as R.S.D. (Fig.14).

The analysis of ion concentrations are expected to be carried out carefully according to SOPs prepared for all operation steps which could affect the accuracy of measurements.



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

Fig.14 Relative standard deviation of each constituent data

3.3 Circumstance of Sample Analysis

Methods Used

As shown in Fig.15, most of participating laboratories made use of recommended methods of EANET. As for the number of laboratories that used ion chromatography, more than 18 laboratories used it at this time although 15 laboratories used it at last time. The codes for the various analytical methods used in this project are indicated in Table 22. Not recommended methods of EANET were used in some laboratories for chloride-ion.

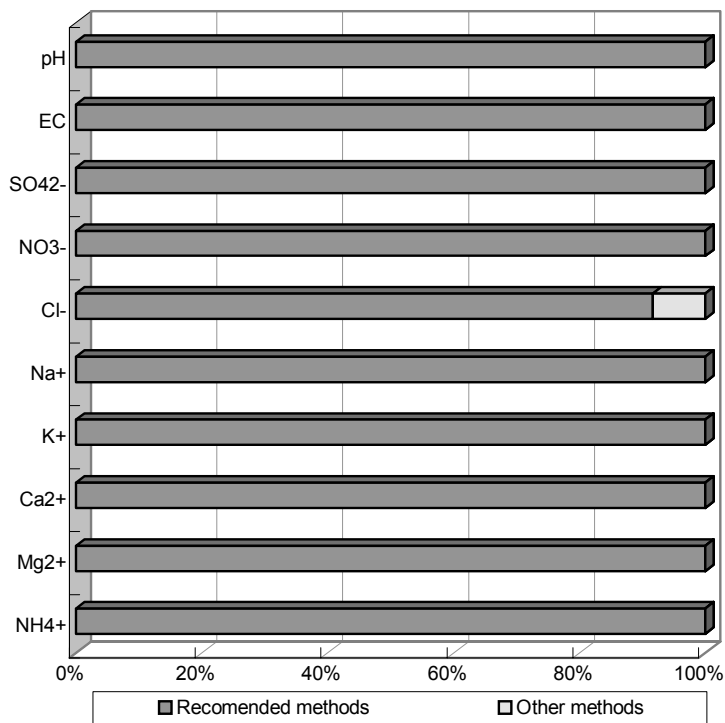


Fig.15 Ratio of recommended method used in the project

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 Number of laboratories used different analytical method

SampleNo.021

Method	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
0	24									
1		24(3)								
2					2(1)					
3						4(2)	4(3)	6(2)	6(3)	
4						2	2(1)			
5			22 (1)	22(1)	22(2)	18(2)	18(2)	18	18(4)	17(1)
6										
7			2(1)	2(1)						3
8										3(2)
9										
10										
X										
Flagged E	0	3	1	1	3	4	4	2	7	3
Flagged X	0	0	1	1	1	0	2	0	0	0

Sample No.022

Method	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
0	24									
1		24(1)								
2					2(1)					
3						4(3)	4(4)	6(2)	6(2)	
4						2	2(1)			
5			22(1)	22(2)	22(4)	18(8)	18(11)	18(8)	18(11)	17(6)
6										
7			2(1)	2(1)						3
8										3(2)
9										
10										
X										
Flagged E	0	1	2	1	1	8	9	2	5	5
Flagged X	0	0	2	2	4	3	7	8	8	3

Reverse mesh is recommended method of EANET

(): Number of data 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. Only one person carried out measurement of rainwater samples in fourteen laboratories. In other laboratories, from 2 to 4 persons carried out measurement, and usually their responsibilities were separated according to the methods used for analysis such as anions and cations. In most laboratories there are several staffs allotted to carry out the analysis of the round robin samples. Anions and cations were analyzed separately by different persons in 8 participating laboratories.

Table 24 Staff in charge of measurement

Lab.ID	Total	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
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	C	C	C	B	B	A	B	A
ID02	3	A	A	A	A	A	B	B	B	B	C
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	2	A	A	B	B	B	A	A	A	A	A
MN01	2	A	B	A	A	B	B	B	B	B	B
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	A	A	A	B	B	B	B	B
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	A	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.021 and/or sample No.022.

Reverse mesh with dark are flagged data of both sample No.021 and No.022

Years of experience

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.

Table 25 Years of experience

Unit: year

Lab.ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
CN01	11	11	11	11	11	11	11	11	11	11
CN02	15	15	11	11	11	2	2	2	2	2
CN03	3	3	3	3	3	3	3	3	3	3
CN04	7	7	7	7	7	7	7	7	7	7
ID01	3	3	13	13	13	3	3	3	3	3
ID02	5	5	5	5	5	3	3	3	3	1
JP01	18	18	18	18	18	18	18	18	18	18
JP02	1	1	1	1	1	1	1	1	1	1
JP03	5	5	5	5	5	5	5	5	5	5
JP04	14	14	14	14	14	14	14	14	14	14
JP05	6	6	6	6	6	6	6	6	6	6
JP06	2	2	2	2	2	2	2	2	2	2
JP07	4	4	4	4	4	4	4	4	4	4
JP08	2	2	2	2	2	2	2	2	2	2
KR01	3	3	3	3	3	3	3	3	3	3
MY01	5	5	5	5	5	5	5	5	5	5
MN01	5	7	5	5	7	7	7	7	7	7
PH01	3	3	1.5	1.5	1.5	6	6	6	6	0.3
RU01	5	5	5	5	5	3	3	3	3	5
RU02	1	1	1	1	1	1	1	1	1	1
TH01	1	4	1	1	1	4	4	4	4	4
TH02	8	8	2	2	2	2	2	2	2	2
TH03	1	1	1	1	1	1	1	1	1	1
VN01	16	16	7	7	7	16	16	16	16	16

Reverse mesh: Flagged data of “E” or “X” in sample No.021 and/or sample No.022

Reverse mesh with dark are flagged date of both sample No.021 and No.022

1 year means experience with one year or less

The number of flagged data in laboratories.

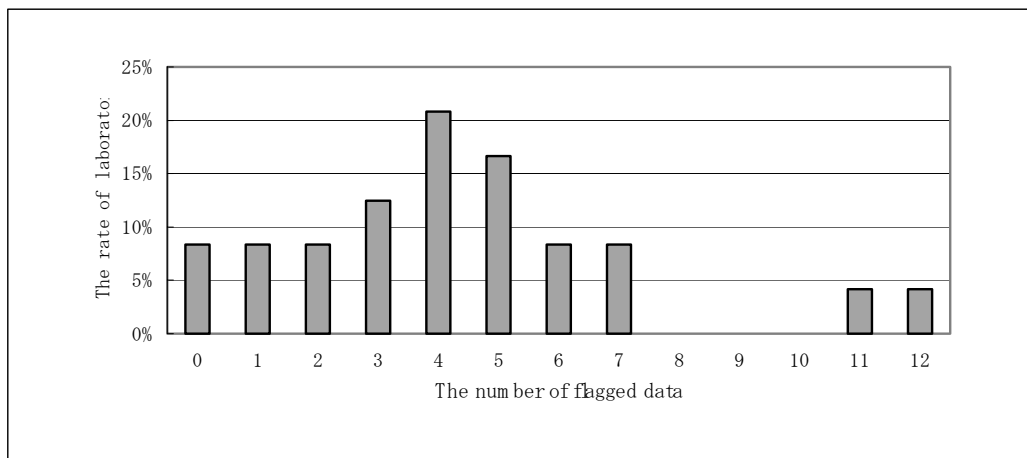


Fig.16 The distribution of laboratories with the number of flagged data

Table 26 Number of flagged data in each laboratory.

Number of flagged data	Number of laboratories	Share
0	2	8%
1	2	8%
2	2	8%
3	3	13%
4	5	21%
5	4	17%
6	2	8%
7	2	8%
8	0	0%
9	0	0%
10	0	0%
11	1	4%
12	1	4%

In this project, the total number of flagged data was 101(E59, X42) among the whole set of 478 data. The attribution of flagged data in each laboratory was presented in Table 26.

Number of excellent laboratories without flagged data was 2, which was equivalent to about 8% of the all-participating laboratories. The number of laboratories that submitted less than 2 flagged data were 16 (70%) during the comparison test carried out in 2001, but there were only 6 (24%) laboratories this time. Laboratories which provided from 3 to 5 marked values are accounted as 50%(12 Lab.) of the all-participating laboratories. There were two laboratories that produced more than 11 flagged data. These laboratories should make more efforts for preparing standard solutions and also in 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. There were two laboratories that water temperature was less than 20 °C. However, these laboratories reported adequate data.

Table 27 Water temperature at measurement (pH and EC)

Unit: degrees centigrade

Lab.ID	PH No.021	pH No.022	EC No.021	EC No.022
CN01	25	25	25	25
CN02	25	25	25	25
CN03	11	11	11	11
CN04	18.5	18.7	18.5	18.7
ID01	25	25	25	25
ID02	25	25	25	25
JP01	24.9~25.7	25.0~26.1	22.3~23.0	24.9~25.7
JP02	25.1	25.1	25	25.1
JP03	24.8	24.8	24.8	24.8
JP04	25.1	24.9	25.2	25.2
JP05	22.5	22.5	22.5	22.5
JP06	25	25	25	25
JP07	24.8~25.0	24.8~25.0	24.9~25.0	24.9~25.0
JP08	25	25	25	25
KR01	25	25	E 25	25
MY01	24.6	26.5	26.5	25.5
MN01	25	25	25	25
PH01	25	25	25	25
RU01	25	25	25	25
RU02	20	20	20	E 20
TH01	25.1	25.1	25.1	25.1
TH02	25	25	25	25
TH03	25	25	E 25	25
VN01	25	25	E 25	25

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

4. COMPARISON OF 1st, 2nd, 3rd, 4th AND 5th SURVEY

The inter-comparison surveys were carried out 5 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 2nd (1999), 3rd (2000), and 4th (2001) survey, the rates of DQOs were increased up to 84-93%. The data quality seemed to be improved by accumulating experiences. But in the 5th (2002) project, unfortunately, number of flagged data is doubled in comparison with the 4th for both samples. In this survey we distributed two samples which ion concentration was a half of their content in samples of previous projects. The concentration of ions in the sample No.022 were within the range found in precipitation. In trace analysis, contamination from used instrument, measurement apparatus and water for dilution might be considered. In order to obtain the data of satisfied quality, items mentioned should be taken into account faithfully.

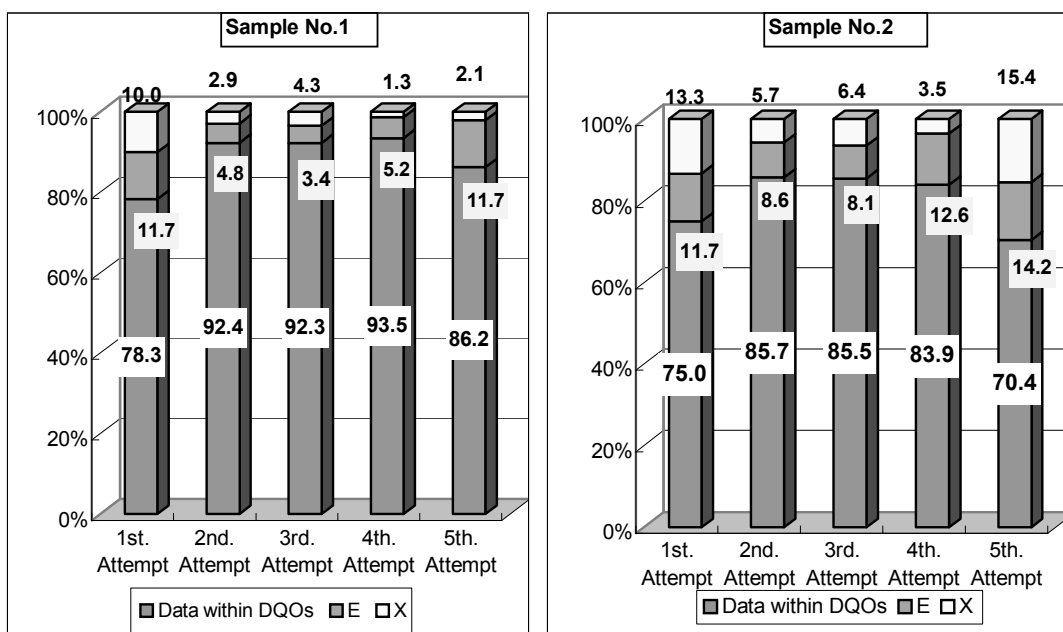


Fig. 17 Comparison of 1st, 2nd, 3rd, 4th and 5th inter-laboratory comparison project

5. THE RELATIONSHIP BETWEEN CONCENTRATION OF THE IONS AND THE NUMBER OF FLAGGED DATA

In this project 2002 a lot of flagged data were found in the results especially in cations.

The prepared values in two samples with high concentration and low concentration were about half of those prepared values for project 2001.

The relationship between total flag number and concentration of ions are shown in Fig. 18 for SO_4^{2-} , Na^+ and Mg^{2+} to clarify the tendency of dependence of flagged number on the concentration using the previous project data listed in Table 28. The highlighted values in Fig. 18 show this project's ion concentrations.

The plots of $29.1 \mu\text{mol/L}$, $83.5 \mu\text{mol/L}$ in SO_4^{2-} , $33.5 \mu\text{mol/L}$ in Na^+ , and $13.1 \mu\text{mol/L}$ in Mg^{2+} have a lot of flagged data respectively compare with other plots. It might have been reported without well evaluation because those data were obtained on the first project started in 1998.

It is found that the numbers of flagged data have tendencies to increase when the concentrations of ions are decreased for SO_4^{2-} , Na^+ and Mg^{2+} . This result means that measurements become more difficult when the concentration decreases. So it is required that analysis has to be carried out very carefully in the trace analysis.

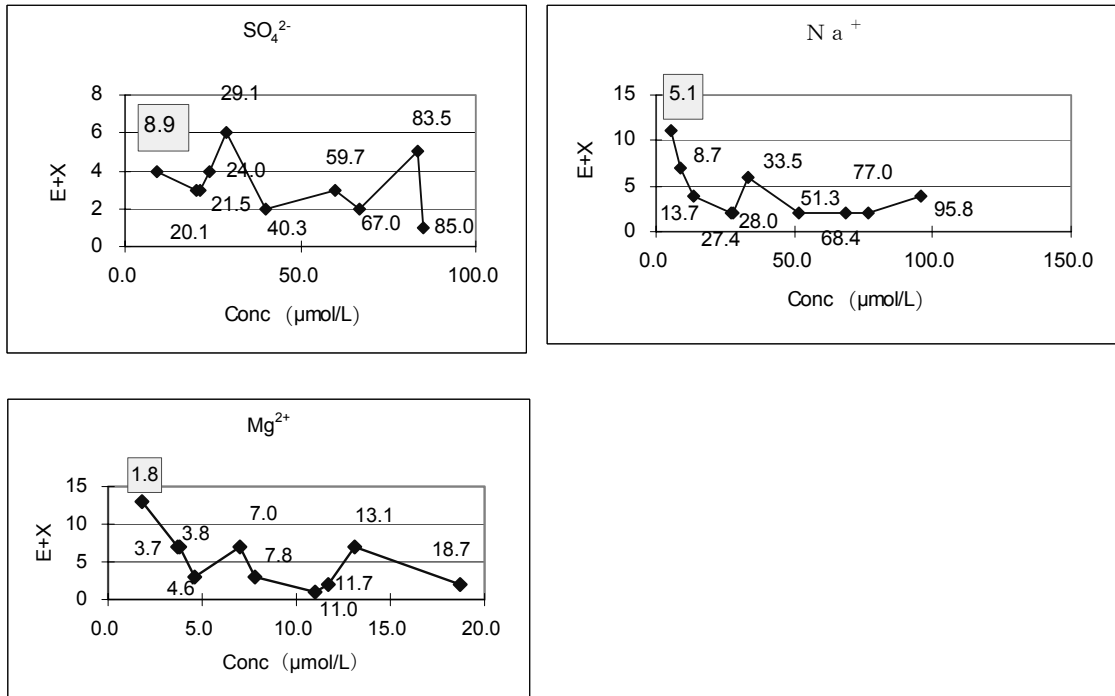


Fig. 18 Concentration of the ions and the number of flagged data

Table 28 The prepared values of each parameter in artificial rainwater of inter-laboratory comparison projects of EANET

		pH (-)	EC (mS/m)	SO ₄ ²⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)	Cl ⁻ (μmol/L)	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	NH ₄ ⁺ (μmol/L)
1998	No.981	4.05	7.94	83.5	93.3	129	95.8	11.1	41.1	13.1	84.8
	No.982	4.51	2.82	29.1	36.1	45.1	33.5	7.42	14.3	4.6	29.5
1999	No.991	4.14	6.38	67	75.0	104	77.0	8.9	33.0	11.0	68.0
	No.992	4.59	2.30	24.0	27.0	38.0	28.0	3.2	12.0	3.8	25.0
2000	No.001	4.10	6.23	59.7	63.3	101.3	51.3	9.9	29.4	11.7	60.5
	No.002	4.85	1.55	20.1	27.5	15.5	8.7	4.9	11.0	7.8	18.2
2001	No.011	4.10	7.45	85.0	93.3	108.4	68.4	15.8	41.1	18.7	87.8
	No.012	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	69	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

6. FOR IMPROVEMENT OF MEASUREMENT PRECISIONS

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

6.1 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, 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) 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.

6.2 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.

6.3 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.

7. REFERENCES

- 1) Guidelines for Acid Deposition Monitoring in East Asia
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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 1st. Attempt) November 1999.
- 4) Report of the Inter-laboratory Comparison Project 1999
(Round robin analysis survey 2nd. Attempt) October 2000
- 5) Report of the Inter-laboratory Comparison Project 2000
(Round robin analysis survey 3rd. Attempt) October 2001
- 6) Report of the Inter-laboratory Comparison Project 2001
(Round robin analysis survey 4th. Attempt) November 2002

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APPENDIX 2 Original data

Sample No.021 (higher concentrations)

	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
	-	mS/m	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
CN01	4.24	3.64	40.1	50.8	33.5	12.8	7.0	20.5	7.1	42.8
CN02	4.22	3.63	40.3	51.0	34.0	14.1	6.9	20.4	6.8	43.5
CN03	4.24	3.66	39.4	50.8	32.7	12.9	7.1	20.4	7.3	43.0
CN04	4.23	3.59	39.6	50.7	32.7	13.2	7.1	20.1	7.1	42.9
ID01	4.16	3.57	57.9	61.6	51.3	12.9	6.0	14.2	8.9	
ID02	4.40	3.56	43.0	48.1	37.9	14.6	10.5	18.5	7.1	50.3
JP01	4.34	3.69	38.0	49.7	29.7	13.4	6.3	17.8	6.8	41.4
JP02	4.35	3.54	40.3	51.0	33.1	16.2	7.0	19.9	7.9	38.8
JP03	4.34	3.50	40.5	50.8	33.0	12.1	5.9	17.7	6.5	41.4
JP04	4.38	3.47	40.4	51.1	32.6	14.4	8.1	20.5	6.9	43.0
JP05	4.33	3.70	40.1	50.7	31.5	13.3	6.4	18.2	5.4	39.8
JP06	4.36	3.66	34.4	47.8	26.0	11.6	6.9	19.0	6.6	45.1
JP07	4.32	3.54	39.8	49.2	31.1	13.3	6.1	16.5	5.7	40.5
JP08	4.37	3.46	39.9	50.4	33.0	13.7	7.4	19.1	7.3	41.8
KR01	4.50	3.07	39.6	54.4	37.8	16.5	9.3	21.5	8.0	50.8
MY01	4.26	3.51	39.2	50.7	34.3	12.8	5.3	16.4	5.2	40.6
MN01	4.36	3.57	38.9	49.9	26.7	13.5	7.6	17.7	7.4	41.1
PH01	4.36	3.44	40.2	51.3	32.6	11.4	8.5	21.0	5.5	43.7
RU01	4.28	3.68	38.1	52.3	34.2	14.1	7.5	18.1	7.1	42.8
RU02	4.30	4.03	43.3	57.5	34.6	14.0	8.0	23.0	8.2	46.6
TH01	4.35	3.62	41.1	51.1	32.7	14.3	6.2	19.6	7.1	44.0
TH02	4.15	3.70	40.6	49.2	31.4	13.2	6.7	19.6	7.0	43.9
TH03	4.42	3.13	39.1	50.6	33.8	13.9	7.8	19.3	6.7	38.7
VN01	4.45	2.93	49.4	28.3	27.9	13.3	6.9	21.0	8.1	49.7
Prepared value	4.30	3.75	40.3	51.0	33.7	13.7	6.9	19.1	7.0	42.4
Data count	24	24	24	24	24	24	24	24	24	23
Average	4.32	3.54	41.0	50.4	33.3	13.6	7.2	19.2	7.0	43.3
Minimum	4.15	2.93	34.4	28.3	26.0	11.4	5.3	14.2	5.2	38.7
Maximum	4.50	4.03	57.9	61.6	51.3	16.5	10.5	23.0	8.9	50.8
Standard deviation	0.08	0.22	4.33	5.41	4.67	1.15	1.12	1.86	0.89	3.27

Sample No.022 (lower concentrations)

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
	-	mS/m	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
CN01	5.09	0.70	10.3	9.1	9.8	5.3	2.5	9.8	2.2	3.2
CN02	5.12	0.71	10.9	9.2	10.3	5.8	1.6	7.6	1.7	4.2
CN03	5.10	0.71	10.0	9.0	9.6	4.9	2.3	10.0	2.1	3.3
CN04	5.08	0.69	10.0	8.9	9.7	5.1	2.9	10.0	2.5	3.5
ID01	5.11	0.74	16.0	11.6	20.5	1.8	1.4	3.6	1.8	-
ID02	5.28	0.67	9.0	7.8	15.8	9.1	1.4	2.1	1.8	18.2
JP01	5.23	0.70	8.7	8.2	8.5	5.3	1.7	5.8	1.7	4.6
JP02	5.21	0.70	8.9	8.1	9.1	6.1	2.1	9.0	2.1	4.2
JP03	5.14	0.65	9.0	8.7	9.1	3.8	1.3	6.3	1.6	4.5
JP04	5.33	0.66	8.8	8.3	8.8	5.2	2.2	6.2	1.3	5.5
JP05	5.22	0.71	8.6	8.2	8.8	4.9	1.9	6.9	1.6	4.6
JP06	5.21	0.74	8.8	8.4	8.8	3.7	1.6	5.4	1.1	5.1
JP07	5.15	0.66	8.9	8.3	10.6	5.9	1.9	5.8	1.5	3.9
JP08	5.28	0.63	9.0	8.6	9.0	5.1	2.0	7.0	1.8	4.3
KR01	5.46	0.59	8.8	8.8	11.9	4.6	3.4	7.2	1.7	4.1
MY01	5.13	0.72	8.7	8.4	9.5	4.5	1.2	6.0	1.1	4.0
MN01	5.18	0.71	8.9	8.5	9.6	4.1	2.8	6.6	3.3	3.9
PH01	5.23	0.75	9.7	8.3	8.8	3.2	3.4	7.5	1.1	3.2
RU01	5.05	0.75	8.7	8.1	9.8	4.5	1.7	5.8	1.6	4.4
RU02	5.00	0.85	9.7	9.3	9.2	5.2	1.9	7.2	2.1	4.3
TH01	5.19	0.69	8.9	8.5	9.4	6.0	1.4	9.4	2.3	1.3
TH02	4.94	0.70	9.2	6.4	9.0	5.1	2.3	7.1	1.7	7.0
TH03	5.23	0.64	8.3	8.0	9.1	6.1	4.6	8.6	2.5	5.0
VN01	5.61	0.69	5.1	22.2	15.2	6.4	1.8	10.0	2.6	4.9
Prepared value	5.15	0.69	8.9	8.5	9.1	5.1	2.0	6.6	1.8	4.5
Data count	24	24	24	24	24	24	24	24	24	23
Average	5.19	0.70	9.3	9.1	10.4	5.1	2.1	7.1	1.9	4.8
Minimum	4.94	0.59	5.1	6.4	8.5	1.8	1.2	2.1	1.1	1.3
Maximum	5.61	0.85	16.0	22.2	20.5	9.1	4.6	10.0	3.3	18.2
Standard deviation	0.14	0.05	1.73	2.86	2.78	1.32	0.78	1.96	0.52	3.03

APPENDIX 3 Normalized values by prepared value

Normalized by prepared value Sample No.021

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
CN01	98.6	97.1	99.5	99.6	99.4	93.4	101.2	107.3	101.1	100.9
CN02	98.1	96.8	100.0	100.0	100.9	102.9	99.3	106.8	96.4	102.6
CN03	98.6	97.6	97.8	99.6	97.0	94.2	102.6	106.8	104.0	101.4
CN04	98.4	95.7	98.3	99.4	97.0	96.4	102.9	105.2	101.7	101.2
ID01	96.7	95.2	143.7	120.8	152.2	94.2	86.0	74.5	126.2	
ID02	102.3	94.9	106.7	94.3	112.5	106.6	151.7	96.9	101.1	118.6
JP01	100.9	98.4	94.3	97.5	88.1	97.8	91.0	93.2	96.9	97.6
JP02	101.2	94.4	100.0	100.0	98.2	118.2	101.2	104.2	112.5	91.5
JP03	100.9	93.3	100.5	99.6	97.9	88.3	85.3	92.7	92.6	97.6
JP04	101.9	92.5	100.2	100.2	96.7	105.1	117.1	107.3	98.3	101.4
JP05	100.7	98.7	99.5	99.4	93.5	97.1	92.5	95.3	76.9	93.9
JP06	101.4	97.6	85.4	93.7	77.2	84.7	99.7	99.5	94.0	106.4
JP07	100.5	94.4	98.8	96.5	92.3	97.1	88.2	86.4	81.2	95.5
JP08	101.6	92.3	99.0	98.8	97.9	100.0	106.9	100.0	104.0	98.6
KR01	104.7	81.9	98.3	106.7	112.2	120.4	134.4	112.6	114.0	119.8
MY01	99.1	93.6	97.3	99.4	101.8	93.4	76.0	85.9	73.4	95.8
MN01	101.4	95.2	96.5	97.8	79.2	98.5	109.8	92.7	105.4	96.9
PH01	101.4	91.7	99.8	100.6	96.7	83.2	122.1	109.9	78.1	103.1
RU01	99.5	98.1	94.5	102.5	101.6	102.8	109.0	94.7	100.6	100.9
RU02	100.0	107.5	107.4	112.7	102.7	102.2	115.6	120.4	116.8	109.9
TH01	101.2	96.5	102.0	100.2	97.0	104.4	90.0	102.6	101.1	103.8
TH02	96.5	98.7	100.7	96.5	93.2	96.4	97.3	102.6	99.4	103.5
TH03	102.8	83.5	97.0	99.2	100.3	101.5	113.0	101.0	94.7	91.3
VN01	103.5	78.1	122.6	55.5	82.8	97.1	99.7	109.9	115.4	117.2
Minimum	96.5	78.1	85.4	55.5	77.2	83.2	76.0	74.5	73.4	91.3
Maximum	103.5	107.5	143.7	120.8	152.2	118.2	151.7	120.4	126.2	119.8
Average	100.3	94.9	101.8	98.4	98.1	98.1	102.5	99.8	98.8	102.2

Normalized by prepared value Sample No.022

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
CN01	98.8	101.6	116.0	107.2	107.3	103.3	126.3	148.3	125.7	70.5
CN02	99.4	103.0	122.7	108.1	112.8	113.5	81.3	114.4	96.0	93.2
CN03	99.0	103.0	112.6	106.0	105.1	95.5	116.2	151.3	120.0	72.7
CN04	98.6	99.7	112.6	105.1	105.7	99.6	144.4	151.0	143.4	77.3
ID01	99.2	107.4	180.2	136.6	224.5	34.7	70.2	54.8	103.4	
ID02	102.5	97.2	101.4	91.9	173.1	177.4	70.7	31.8	102.9	400.9
JP01	101.6	101.6	98.0	96.6	93.1	103.3	85.9	87.7	97.1	101.3
JP02	101.2	101.6	100.2	95.4	99.7	118.9	106.1	136.2	120.0	92.5
JP03	99.8	94.3	101.4	102.5	99.7	74.1	65.7	95.3	91.4	99.1
JP04	103.5	95.8	99.1	97.8	96.4	101.4	111.1	93.8	74.3	121.1
JP05	101.4	103.0	96.8	96.6	96.4	95.5	96.0	104.4	91.4	101.3
JP06	101.2	107.4	99.1	98.9	96.4	72.1	80.8	81.7	62.9	112.3
JP07	100.0	95.8	100.2	97.8	116.1	115.0	96.0	87.7	85.7	85.9
JP08	102.5	91.4	101.4	101.3	98.6	99.4	101.0	105.9	102.9	94.7
KR01	106.0	85.6	99.1	103.7	130.3	89.7	171.7	108.9	97.1	90.3
MY01	99.6	104.5	98.3	98.7	104.5	87.1	61.1	90.6	60.6	88.8
MN01	100.6	103.0	100.2	100.1	105.1	79.9	141.4	99.8	188.6	85.9
PH01	101.6	108.9	97.9	97.2	96.7	61.8	169.2	113.8	63.4	70.0
RJ01	98.1	108.9	109.0	95.6	107.4	88.5	84.8	87.9	89.7	96.3
RJ02	97.1	123.4	109.2	109.5	100.8	101.4	96.0	108.9	120.0	94.7
TH01	100.8	100.1	100.2	99.8	103.0	117.3	70.2	142.4	133.1	27.8
TH02	95.9	101.6	103.7	75.6	98.4	99.4	118.2	107.1	95.4	153.5
TH03	101.6	92.5	93.0	94.1	99.6	118.1	232.3	130.0	142.3	110.4
VN01	108.9	100.1	57.4	261.5	166.5	124.8	90.9	151.3	148.6	107.9
Minimum	95.9	91.4	57.4	75.6	93.1	34.7	61.1	31.8	60.6	27.8
Maximum	108.9	123.4	180.2	261.5	224.5	177.4	232.3	151.3	188.6	400.9
Average	100.56	102.00	104.8	107.6	113.3	99.2	105.0	107.6	106.9	106.5