Acid Deposition Monitoring Network
in East Asia (EANET)

Report of the Inter-laboratory Comparison Project 2007

10th Inter-laboratory Comparison Project on Wet Deposition

3rd Inter-laboratory Comparison Project on Dry Deposition

9th Inter-laboratory Comparison Project on Soil

8th Inter-laboratory Comparison Project on Inland Aquatic Environment

October 2008
Network Center for EANET

Contents

1. INTRODUCTION

The inter-laboratory comparison project (round robin analysis survey) 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 objectives of the project are, through the evaluation of analytical results, analytical equipment and its operating condition and other practices,

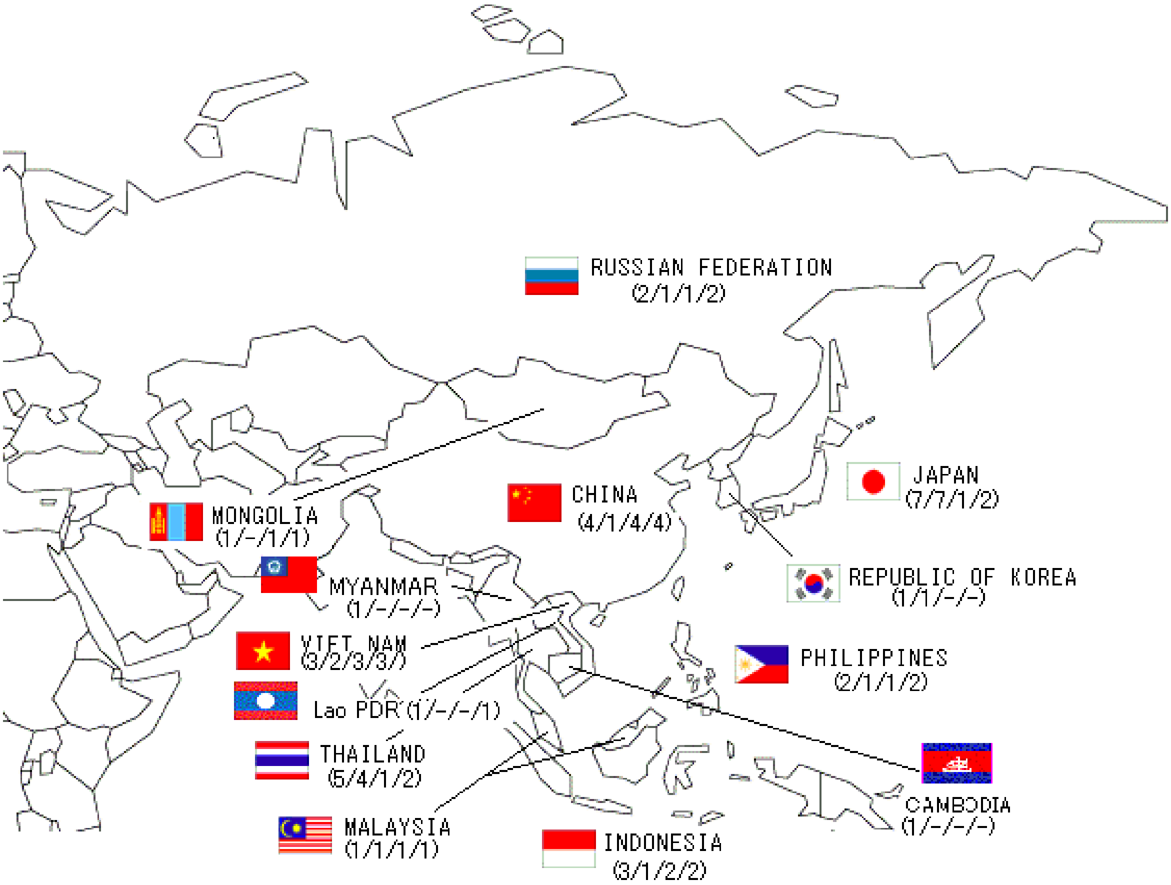
(i) to recognize the analytical precision and accuracy of the measurement in each participating laboratory,
(ii) to give an opportunity to improve the quality of the analysis on wet deposition, dry deposition monitoring (filter pack method), soil monitoring and inland aquatic monitoring of EANET,
(iii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

The inter-laboratory comparison project is implemented by the Network Center of EANET(NC) annually for the following items:

(i) Wet Deposition
(ii) Dry Deposition
(iii) Soil
(iv) Inland Aquatic Environment

This report presents the results of the 10th inter-laboratory comparison project on wet deposition, 3rd inter-laboratory comparison project on dry deposition, 9th inter-laboratory comparison project on soil, and 8th inter-laboratory comparison project on inland aquatic environment.

The number of laboratories from each country that participated in each of the projects are shown in Figure 1.1.



* Figure in parenthesis shows the number of laboratories of each country (Wet/Dry/Soil/Inland aquatic environment)

Figure 1.1 Number of participating laboratories in 2007

2. 10th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 10th Inter-laboratory comparison project on wet deposition, artificial rainwater samples containing known concentrations of major ions were prepared and distributed to the participating countries of EANET by Network Center (NC). The measurement of pH, EC and concentrations of SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ from the participating countries were compared with prepared values and results were statistically treated.

The Network Center (NC) shipped the artificial rainwater samples to laboratories in charge of chemical analysis in EANET on 12 November 2007. Their analytical results were submitted to NC by 29 February 2008.

2.2 Procedures

2.2.1 Participating Laboratories

A total of 32 laboratories in charge of chemical analysis in 13 countries of EANET participated in this survey. All the participating laboratories submitted their analytical results to NC. A list of the participating laboratories with the abbreviated name and code are given in APPENDIX 2-1.

Some laboratories from countries outside the EANET region also participated in the inter-laboratory comparison project. Although the analytical results from these laboratories are presented, they were not evaluated and included in the statistical analysis.

2.2.2 Description of samples

Two kinds of artificial rainwater samples (one with high concentration ions and one with low concentration ions) were distributed to the laboratories. A description of the samples is given in Table 2.1.

Table 2.1 Description of artificial rainwater samples

Artificial rainwater samples	Amount of each sample	Container	Number of samples	Note
No.071w (high concentration sample) No.072w (low concentration sample)	Approximately 100mL	Poly-propylene bottle 100mL	One bottle each	Known amount of reagents are dissolved in de-ionized water

The prepared values/concentrations of analytical parameters in the artificial rainwater samples are described in Table 2.2.

Table 2.2 Prepared values/concentrations of analytical parameters*

	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
No.071w (high concentration)	4.64	3.72	54.9	43.6	69.0	53.4	8.3	28.6	14.0	52.7
No.072w (low concentration)	5.00	1.47	14.0	21.0	38.8	30.8	4.9	6.4	7.0	15.1

* For 100 times diluted samples.

2.2.3 Analytical Method and Data Checking Procedures

Before the measurement, each laboratory should accurately dilute the distributed samples by 100 times following the specified procedure.

All participating laboratories were expected to analyze the diluted samples for the following ten parameters: pH, Electric Conductivity (EC), concentrations of sulfate, nitrate, chloride, sodium ion, potassium ion, calcium ion, magnesium ion and ammonium ion.

Participating laboratories are required to apply the 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 listed in Table 2.3.

Table 2.3 Analytical methods specified in the manual

Parameter	Analytical method
pH	Glass Electrode
EC	Conductivity Cell
SO_4^{2-} NO_3^- Cl^-	Ion Chromatography Spectrophotometry
Na^+ K^+ Ca^{2+} Mg^{2+}	Ion Chromatography Atomic Absorption/Emission Spectrometry
NH_4^+	Ion Chromatography Spectrophotometry (Indophenol Blue)

Checking of analytical results should be performed using the calculation of ion balance (R_1) and total electric conductivity agreement (R_2).

Calculation of ion balance (R_1)

(1)Total anion (**A**) equivalent concentration (μeq /L) is calculated by summing the concentrations of all anions (C: μmol /L).

$$\mathbf{A}\ (\mu eq\ /L) = \sum n\, C_{Ai}\ (\mu mol\ /L) = 2C\ (SO_4^{2-}) + C\ (NO_3^{-}) + C\ (Cl^{-})$$

n, C_{Ai}: electric charge of ion and concentration (μmol /L) of anion “i”.

(2) Total cation (**C**) equivalent concentration (μeq /L) is calculated by summing the concentrations of all cations (C: μmol /L).

$$\mathbf{C}\ (\mu eq\ /L) = \sum n\, C_{Ci}\ (\mu mol\ /L) = 10^{(6\text{-}pH)} + C\ (NH_4^{+}) + C\ (Na^{+}) + C\ (K^{+}) + 2C\ (Ca^{2+}) + 2C\ (Mg^{2+})$$

n, C_{Ci}: electric charge of ion and concentration (μmol /L) of cation “i”.

(3) Calculation of ion balance (R_1)

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

(4) R_1, which is calculated using the above equation, should be compared with standard values in Table 2.4. If R_1 is out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves are recommended.

Table 2.4 Allowable ranges for R_1 in different concentration ranges

C+A (μeq / L)	R_1 (%)
< 50	± 30
50 – 100	± 15
> 100	± 8

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

Comparison between calculated and measured values of electrical conductivity (R_2)

(1) Total electric conductivity (Λ calc) is calculated as follows;

$$\Lambda \text{ calc (mS /m)} = \{349.7 \text{ X } 10^{(6-pH)} + 80.0 \text{ X } 2C(SO_4^{2-}) + 71.5\ C(NO_3^-) \\ +76.3\ C(Cl^-) + 73.5\ C(NH_4^+) + 50.1\ C(Na^+) + 73.5\ C(K^+) \\ + 59.8 \text{ X } 2C(Ca^{2+}) + 53.3 \text{ X } 2C(Mg^{2+})\} / 10000$$

C: Molar concentrations (µmol /L) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25 degrees centigrade.

(2) Ratio (R_2) of calculations (Λ calc) to measurements (Λ meas) in electric conductivity is calculated as follows;

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

(3) R_2, which is calculated using the above equation, is compared with standard values in Table 2.5. If R_2 is out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves are recommended.

Table 2.5 Allowable ranges for R_2 in different ranges of EC

Λ meas (mS/m)	R_2 (%)
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9

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

2.3 Results

The NC received the data on analytical results of artificial rainwater samples from 32 laboratories in the participating countries of EANET. Several laboratories measured only pH and EC. The original results from the laboratories are shown in APPENDIX 2-2 and 2-3.

General statistics of obtained data summarized in Table 2.6 were calculated for each constituent of the artificial rainwater samples such as: Average (Va), 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 overall project statistics calculation. As shown in Table 2.6, average of submitted data fairly well agreed with the prepared values (Vp). The range of Va/Vp was between -4.2%(EC) to 2.9%(NH_4^+) for the sample No.071w, and -3.3%(EC) to 4.3%(NH_4^+) for the sample No.072w. There were a few laboratories that submitted analytical data with considerable differences from prepared concentrations.

Table 2.6 Summary of analytical results of the artificial rainwater samples
(Reported data after removal of outliers)

Sample No.071w

Constituents	Prepared (Vp)	Average (Va)	Va/Vp [%]	S.D.	N	Min.	Max.
pH	4.64	4.67	0.7	0.07	31	4.51	4.88
EC [mS/m]	3.72	3.57	-4.2	0.14	30	3.22	3.80
SO_4^{2-} [μmol/L]	54.9	54.6	-0.6	1.76	29	51.2	58.8
NO_3^- [μmol/L]	43.6	42.9	-1.5	1.48	27	40.6	47.9
Cl^- [μmol/L]	69.0	67.3	-2.5	2.38	26	59.4	70.7
Na^+ [μmol/L]	53.4	53.0	-0.8	1.95	27	47.4	58.2
K^+ [μmol/L]	8.3	8.2	-1.3	1.06	27	4.6	11.1
Ca^+ [μmol/L]	28.6	28.9	1.0	2.33	26	24.5	34.7
Mg^{2+} [μmol/L]	14.0	14.0	-0.2	1.08	27	12.2	17.4
NH_4^+ [μmol/L]	52.7	54.2	2.9	3.33	29	48.1	63.6

Sample No.072w

Constituents	Prepared (Vp)	Average (Va)	Va/Vp [%]	S.D.	N	Min.	Max.
pH	5.00	5.03	0.6	0.12	31	4.70	5.36
EC [mS/m]	1.47	1.42	-3.3	0.09	30	1.24	1.58
SO_4^{2-} [μmol/L]	14.0	13.8	-1.0	0.91	28	11.3	16.5
NO_3^- [μmol/L]	21.0	20.5	-2.1	1.07	27	17.0	23.6
Cl^- [μmol/L]	38.8	37.6	-3.2	2.50	27	30.4	42.6
Na^+ [μmol/L]	30.8	30.9	0.4	1.49	27	26.0	33.6
K^+ [μmol/L]	4.9	5.0	0.6	0.47	26	3.9	6.0
Ca^+ [μmol/L]	6.4	6.5	1.2	0.97	27	4.7	9.6
Mg^{2+} [μmol/L]	7.0	7.3	3.6	0.96	27	6.1	9.5
NH_4^+ [μmol/L]	15.1	15.8	4.3	1.95	29	10.6	19.8

The Data Quality Objectives (DQOs) of EANET was specified by the QA/QC program of the EANET for every constituent to be within ±15% of deviation from prepared value. In this report, analytical data on the artificial rainwater samples were compared with the prepared values and evaluated by the excess over DQOs criteria: the flag "E" was put to the data that exceed DQOs within a factor of 2 (±15% to ±30%), and the flag "X" was put to the data that exceed DQOs more than a factor of 2 (over ±30%).

A set of data for each sample was evaluated by the Data Checking Procedures described in chapter 2.2.3. The flag “I” and the flag “C” were added to the data sets with a poor ion balance and conductivity agreement, respectively.

The results were evaluated by the three aspects:
i) Comparison of concentration dependence on level of their concentration
- sample No.071w (high concentrations) and No.072w (low concentrations),
ii) Comparison of individual parameters,
iii) Comparison of circumstances of analysis in each participating laboratory.

Evaluation of data on both the sample No.071w and No.072w is presented in “2.3.1 Evaluation of laboratories’ performance (by sample)”, evaluation of data for each constituent is presented in “2.3.2 Evaluation of laboratories’ performance (by analytical parameters)”, and evaluation of data by the circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is presented in “2.3.4 Information on Laboratories”.

2.3.1 Evaluation of laboratories’ performance (by sample)

High Concentration Sample No.071w

The number and percentage of flagged data in the high concentration sample No.071w are described in Table 2.7. It was founded that 11 analytical data out of 290 exceeded the DQOs within a factor of 2 and was flagged by "E", 8 analytical data out of 290 exceeded the DQOs more than a factor of 2 and flagged by "X”. Data flagged by "E" and "X" shared about 6.6 percent of all reported data for sample No.071w.

The normalized data by prepared value in each parameter are depicted in Figure 2.1.

Table 2.7 Number of flagged data for the Sample No.071w (High concentrations)

Charactarization of data		pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
Data within DQOs		31	30	29	27	26	27	23	24	26	28	271
Data with flag E*		1	0	0	1	2	1	2	2	1	1	11
Data with flag X**		0	2	0	0	0	0	3	2	1	0	8
Flagged data	[%]	3.1	6.3	0.0	3.6	7.1	3.6	17.9	14.3	7.1	3.4	6.6

(Total data = 290)

*E: Value exceeded the DQOs within a factor of 2

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

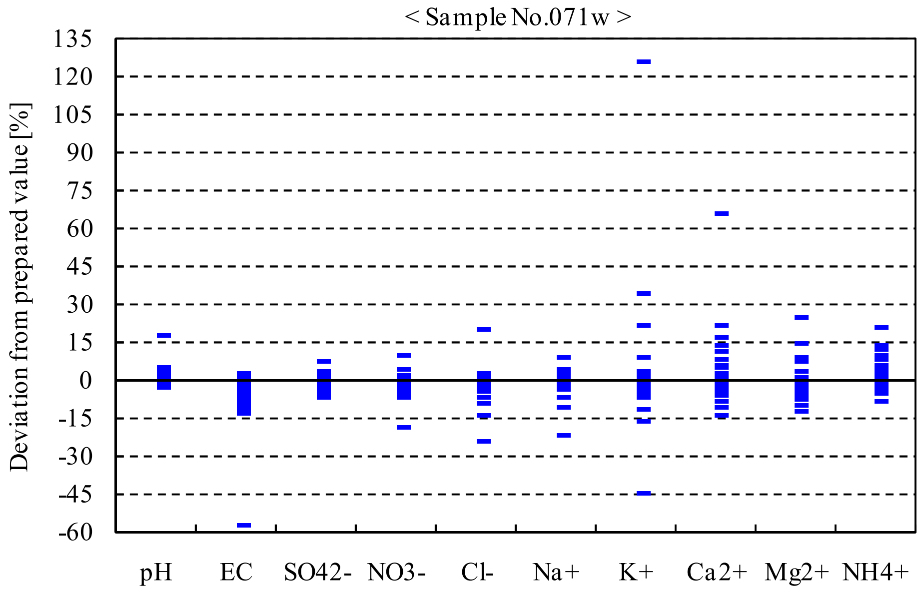


Figure 2.1 Distribution of the data normalized by prepared value in each parameters in the high concentration sample

The parameter which had most flags was K^+. The analytical results of all the laboratories are shown in Table 2.8 with flag E and X marked for values that exceeded DQOs.

Table 2.8 Analytical Results of Sample No.071w

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 [%]
KH01	E 5.44	X 1.34	56.4	43.8	68.4	52.3	8.6	29.3	14.1	59.1	-3.3	C 40.0
CN01	4.60	3.55	54.8	42.5	68.0	54.1	7.9	28.9	13.6	52.6	1.0	3.2
CN02	4.61	3.65	56.5	44.3	68.5	53.0	8.0	30.9	16.0	57.4	2.4	3.2
CN03	4.59	3.59	56.4	43.9	68.3	53.5	8.3	30.2	15.2	56.9	2.2	4.2
CN04	4.59	3.55	55.9	43.1	68.5	53.4	8.3	27.3	14.4	52.4	0.0	3.6
ID01	4.68	3.75	54.5	42.9	E 52.3	49.7	X 18.7	27.0	14.5	55.1	5.4	-2.4
ID02	4.60	3.61	56.8	41.3	62.4	52.0	E 10.1	26.8	13.8	54.4	1.3	2.0
ID03	4.88	3.29	52.4	40.6	59.4	47.4	X 11.1	24.5	12.9	50.6	-1.9	-1.9
JP01	4.69	3.54	53.3	43.4	66.7	53.7	9.0	28.4	13.2	53.4	0.7	0.8
JP02	4.68	3.71	53.1	41.8	67.4	51.4	7.8	29.4	13.9	51.0	0.5	-1.7
JP03	4.64	3.62	54.8	43.0	68.5	53.2	8.4	28.9	13.8	52.3	0.3	1.3
JP04	4.69	3.63	55.3	43.4	68.6	52.0	8.1	29.0	14.0	55.5	-0.1	0.4
JP05	4.73	3.61	53.0	42.5	66.7	51.8	8.3	28.4	13.7	53.1	0.2	-1.4
JP06	4.72	3.67	55.2	43.7	70.3	55.3	8.6	30.0	14.4	52.1	-0.1	-0.5
JP07	4.70	3.62	54.3	43.3	67.1	51.2	8.2	28.3	13.6	50.0	-1.4	-0.9
LA01	4.70	3.34	58.8	47.9	E 82.7	58.2	9.0	X 9.3	X 50.9	E 63.6	4.4	C 10.1
MY01	4.74	3.22	54.8	41.8	69.9	53.2	8.5	27.9	13.4	49.7	-2.1	4.4
MN01	4.58	3.49	54.4	41.4	65.7							
MM01	4.63	X 1.58										
PH01	4.70	3.72	55.4	42.5	68.9	53.8	7.8	31.7	13.3	55.7	1.1	-0.7
PH02	4.81	3.42										
KR01	4.61	3.80	51.4	41.1	66.0	53.5	8.3	X 47.3	E 17.4	57.1	I 13.0	2.3
RU01	4.59	3.69	55.7	41.3	66.6	54.3	7.7	25.4	13.4	55.2	0.3	1.1
RU02	4.66	3.68	53.5	42.5	66.5	54.1	7.3	26.7	13.1	51.9	-0.3	-1.1
TH01	4.68	3.69	55.8	43.6	68.7	53.9	8.4	32.5	15.2	53.6	1.8	0.6
TH02	4.75	3.39	53.7	43.7	69.0	52.8	8.3	28.0	13.3	60.0	0.3	2.5
TH04	4.51	3.77				53.6	8.4	26.1	12.2	51.8		
TH05	4.71	3.38	56.6	45.2	70.7	55.7	7.7	E 33.4	15.0	52.8	0.7	5.0
TH06	4.71	3.49	54.3	41.1	64.3	51.2	E 6.9	27.7	12.6	55.6	0.0	0.4
VN01	4.64	3.61	54.1	43.4	67.6	52.2	7.9	28.9	13.5	52.5	0.3	1.1
VN02	4.66	3.42	51.2	E 35.3	66.0	E 41.6	X 4.6	E 34.7	15.0	48.1	2.8	1.3
VN03	4.78	3.47	51.2							57.6		

E: Value exceeded the DQO(±15) within 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)

Low Concentration Sample No.072w

For sample No.072w (low concentrations), the number and percentage of flagged data are described in Table 2.9. It was founded that 29 analytical data out of 290 exceeded the DQOs within a factor of 2 and was flagged by "E", 12 analytical data out of 290 exceeded the DQOs more than a factor of 2 and was flagged by "X". Data flagged by “E” and “X” shared up to 14.1 percent of all reported data for sample No.072w.

The normalized data by prepared value in each parameter are depicted in Figure 2.2.

Table 2.9 Number of flagged data for the Sample No.072w (low concentrations)

Charactarization of data		pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
Data within DQOs		31	29	26	26	24	26	22	23	20	22	249
Data with flag E*		1	1	3	2	4	2	4	2	5	5	29
Data with flag X**		0	2	0	0	0	0	2	3	3	2	12
Flagged data	[%]	3.1	9.4	10.3	7.1	14.3	7.1	21.4	17.9	28.6	24.1	14.1

(Total data = 290)

*E: Value exceeded the DQOs within a factor of 2
**X: Value exceeded the DQOs more than a factor of 2

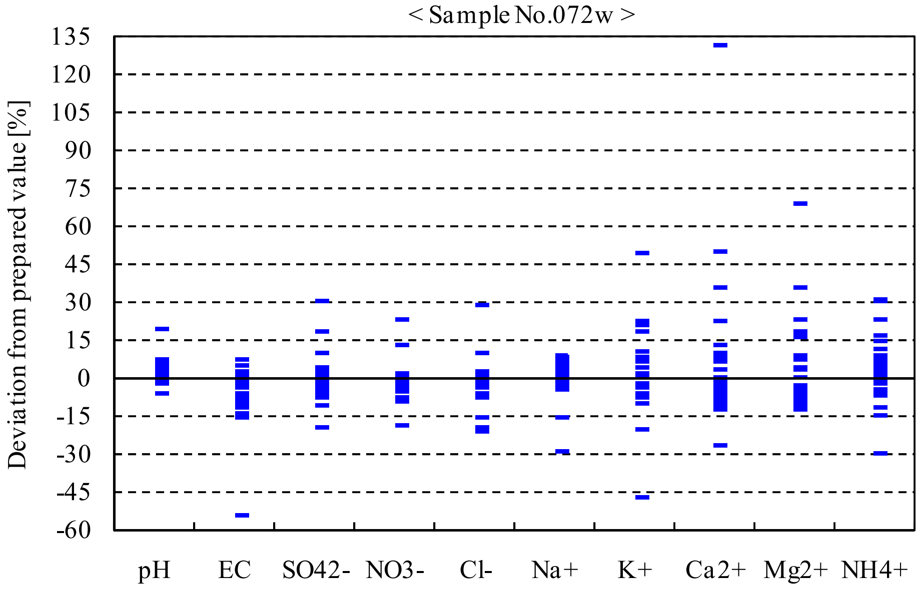


Figure 2.2 Distribution of the data normalized by prepared value for each parameter in the low concentration sample

Cations had a tendency to be flagged more than anions. The analytical results of all the laboratories are shown in Table 2.10 with flag E and X marked for values that exceeded DQOs.

Table 2.10 Analytical Results of Sample No.072w

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 [%]
KH01	E 5.94	X 0.67	E 11.3	21.4	42.6	30.1	5.3	7.0	7.6	13.3	-4.6	C 26.4
CN01	4.94	1.41	13.6	20.1	38.2	31.6	5.0	6.9	6.5	15.9	3.0	3.7
CN02	4.92	1.51	14.6	21.4	38.7	31.6	4.9	5.8	X 9.5	15.9	3.1	2.4
CN03	4.90	1.49	14.4	20.9	38.6	31.8	5.3	6.8	X 9.5	15.6	5.2	3.9
CN04	4.90	1.32	14.5	20.5	38.4	32.4	E 5.8	6.6	E 8.2	15.5	4.3	9.5
ID01	5.08	1.58	13.6	20.9	E 30.4	30.2	X 7.3	7.2	7.5	E 18.6	I 8.9	-6.1
ID02	4.95	1.51	E 16.5	19.9	E 31.1	30.4	4.8	5.9	7.2	E 12.8	0.8	-1.5
ID03	5.36	1.33	13.0	19.0	E 32.8	E 26.0	E 5.9	5.6	6.1	16.4	-1.1	-6.3
JP01	5.07	1.45	13.5	20.9	38.2	31.9	4.8	5.7	6.4	16.2	-0.3	-1.6
JP02	4.99	1.38	13.7	20.5	38.5	30.0	4.9	6.2	7.3	14.9	0.4	3.0
JP03	4.96	1.46	14.1	20.7	38.6	30.5	4.9	6.4	7.0	14.8	0.3	1.4
JP04	5.06	1.49	14.3	20.9	38.1	29.3	4.5	6.3	6.6	17.3	-1.1	-2.2
JP05	5.10	1.45	13.9	20.9	38.7	29.3	4.7	6.1	6.7	15.2	-2.7	-2.4
JP06	5.06	1.50	14.1	21.1	38.9	32.2	5.1	7.0	7.6	E 17.6	2.5	-1.0
JP07	5.03	1.47	13.6	20.9	37.3	29.5	5.2	6.3	6.8	14.4	-0.5	-1.8
LA01	5.17	1.25	15.3	23.6	E 49.9	33.2	5.4	E 4.7	X 11.8	X 19.8	-2.9	11.2
MY01	5.04	E 1.24	13.7	20.0	39.4	30.7	4.8	6.0	6.6	15.7	-0.7	7.1
MN01	4.93	1.32	13.5	E 25.8	38.5							
MM01	4.90	X 0.67										
PH01	5.04	1.50	13.9	20.8	39.0	31.2	4.7	5.9	7.0	14.0	-1.6	-2.5
PH02	5.19	1.41										
KR01	5.05	1.50	12.5	20.1	36.3	31.3	E 6.0	X 9.6	E 8.3	E 10.6	6.4	-2.9
RU01	4.87	1.54	13.2	20.4	35.9	31.3	4.4	5.8	6.6	16.8	4.7	0.5
RU02	5.04	1.47	14.1	19.8	38.3	33.6	4.5	6.1	6.2	15.8	0.8	-1.2
TH01	5.04	1.49	13.8	20.5	38.0	31.5	5.3	E 7.8	E 8.1	15.9	4.2	-0.7
TH02	5.07	1.26	13.0	20.5	38.6	30.7	5.0	6.2	6.7	X 19.7	2.6	6.2
TH04	4.70	1.47				31.2	5.1	6.3	6.3	15.5		
TH05	5.06	1.38	14.6	21.3	39.7	32.8	4.6	X 8.7	E 8.6	14.2	2.5	3.9
TH06	5.09	1.42	13.4	19.4	36.4	29.5	E 3.9	5.6	6.2	17.2	-0.2	-2.5
VN01	5.04	1.46	14.1	21.3	37.4	31.5	4.6	6.1	6.7	15.0	-0.6	-1.1
VN02	5.16	1.36	12.9	E 17.0	37.7	E 21.8	X 2.6	X 14.8	E 8.6	14.8	7.2	0.1
VN03	5.28	1.30	E 18.2							E 18.6		

E: Value exceeded the DQO(±15) within 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)

Comparison of High and Low Concentration Sample

The percentage of flagged data for the high concentration sample and the low concentration sample are shown in Figure 2.3.

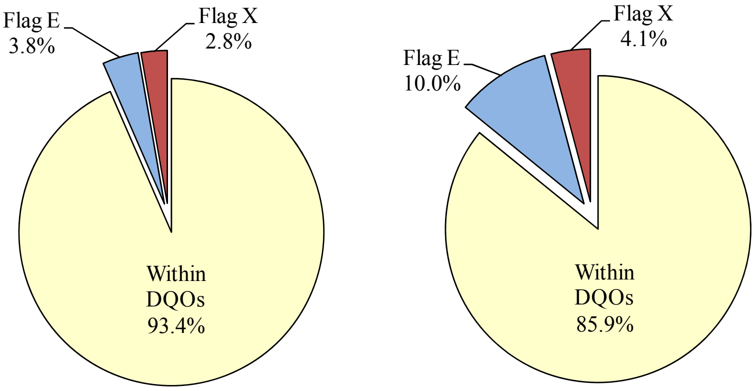


Figure 2.3 Percentage of flagged data for Sample No.071w and No.072w (Left: No.071w, Right: No.072w)

Compared with sample No.072w, prepared values of sample No.071w were 0.9 – 4.5 times higher. The percentage of the data within DQOs for the sample No.071w was 93.4 %, and the percentage of the data within DQOs for the sample No.072w was 85.9 %. The difference between both samples was 7.5%. In this project, the total number of flagged data was 60 (E: 40, X: 20) among the whole set of 580 data.

The number of flagged data of laboratories

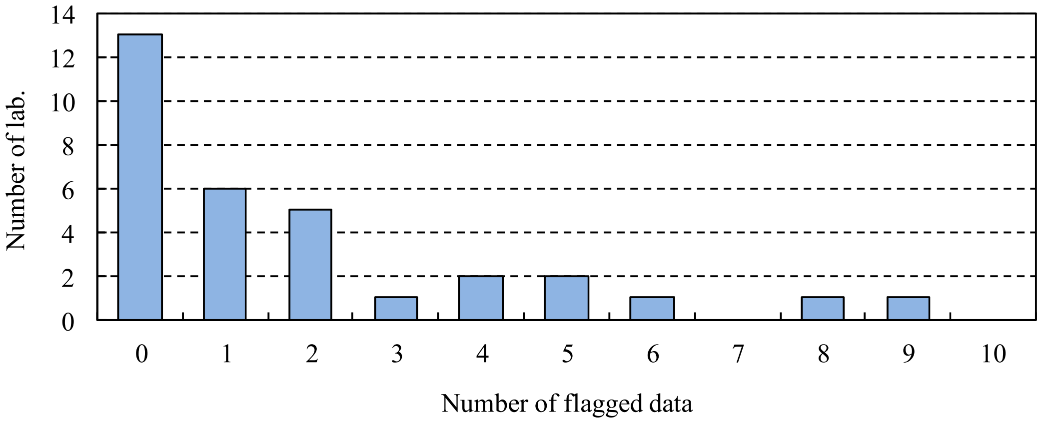


Figure 2.4 The distribution of laboratories with the number of flagged data

The number of flagged data of laboratories are shown in Figure 2.4. The number of laboratories without flagged data was 13, which corresponds to 40.6% of all the participating laboratories.

2.3.2 Evaluation of laboratories' performance with DQOs (by analytical parameters)

The general overviews of data are presented below in Figures 2.5 to 2.24 for each analytical parameter. In scatter diagrams (lower figures), dotted lines depict the values dependent on DQOs (15%) and solid lines depict the values dependent on DQOs (30%).

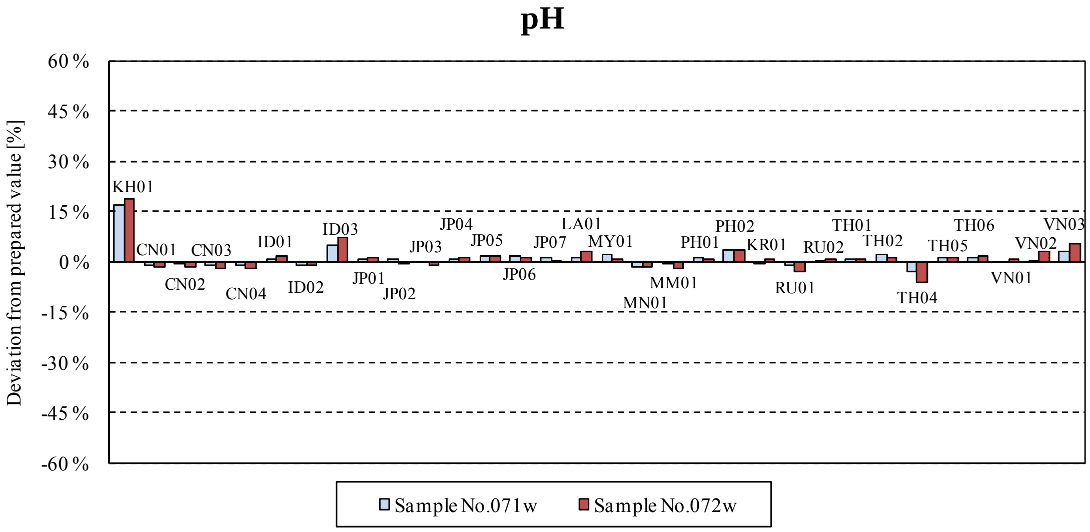


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

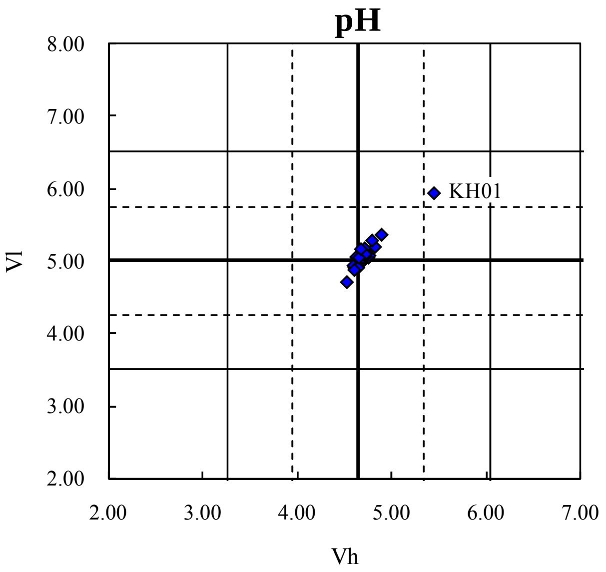


Figure 2.6 Scatter diagram for pH

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

All participating laboratories used pH meter with glass electrode for measurement of pH. All of obtained data satisfied the DQO of the QA/QC program of EANET. Almost of all data submitted by participating laboratories were within ±10% of prepared value.

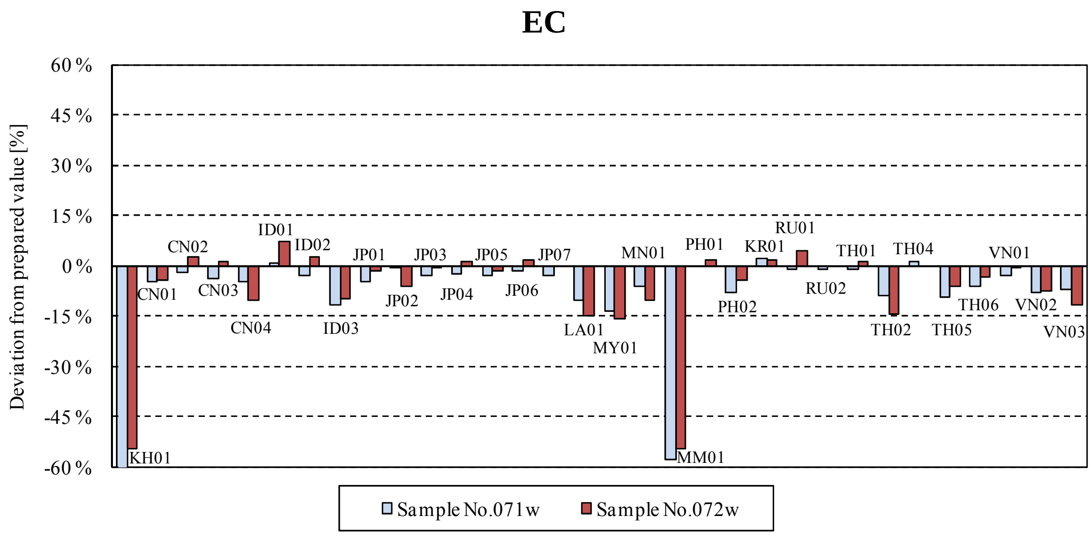


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

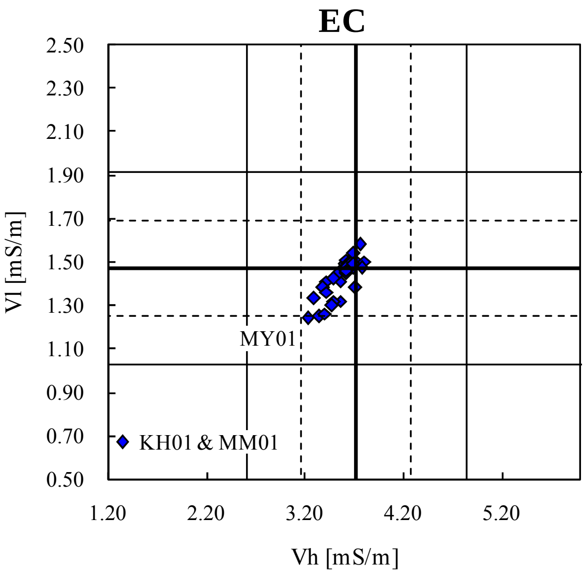


Figure 2.8 Scatter diagram for EC

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

All participating laboratories used conductivity cell for the measurement of EC. Almost of all obtained data that satisfied the DQO of the QA/QC program of the EANET. However, Laboratories KH01 and MM01 reported the data that exceeded the DQO more than a factor of 2 for sample No.071w and 072w.

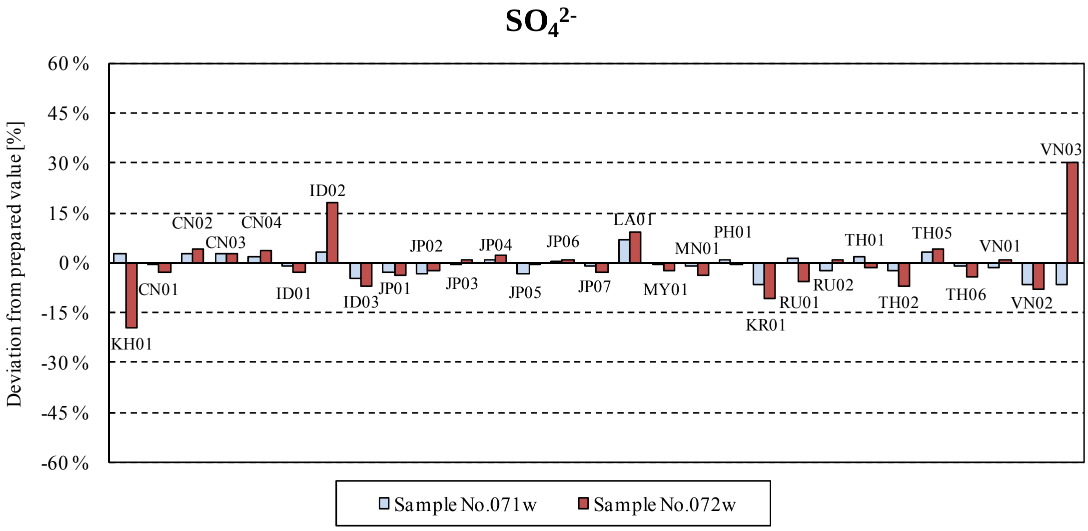


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

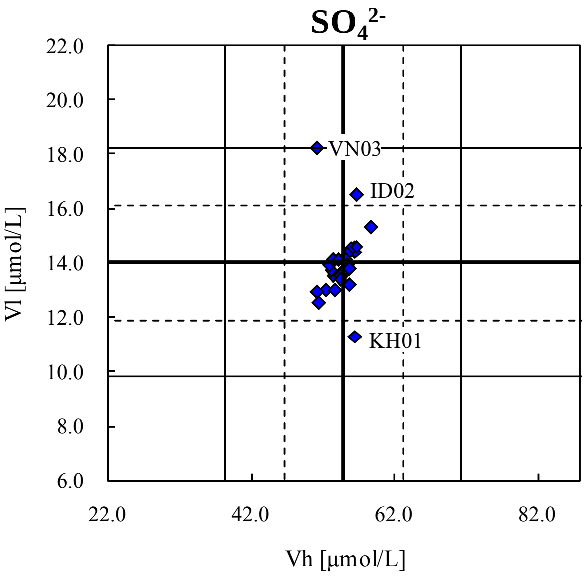


Figure 2.10 Scatter diagram for SO_4^{2-}

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

27 laboratories used ion chromatography for the determination of SO_4^{2-}. Lab.RU02 and Lab.VN03 used spectrophotometry. Data submitted by Laboratories KH01, ID02 and VN03 exceeded the DQO in low concentration sample and were marked with flag “E”.

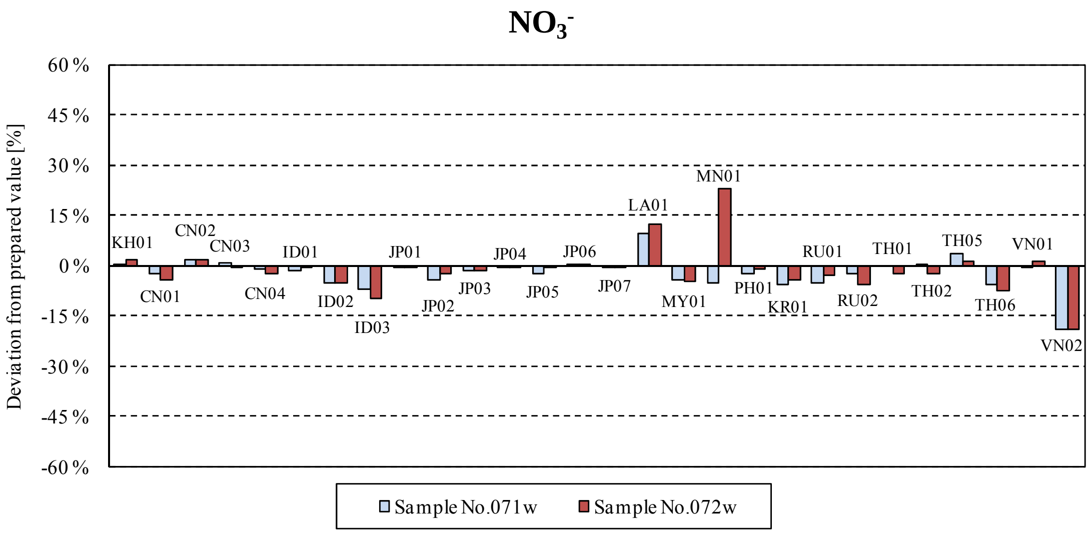


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

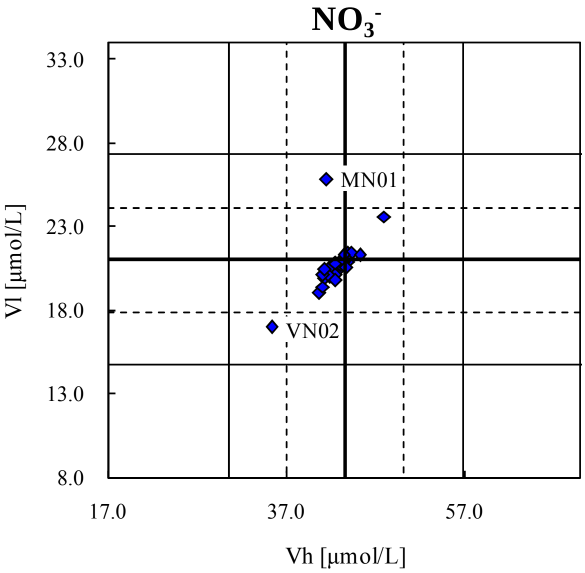


Figure 2.12 Scatter diagram for NO_3^-

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

27 laboratories used ion chromatography for the determination of NO_3^-. One laboratory (RU02) used spectrophotometry. The data submitted by Laboratory MN01 was higher than the prepared value in low concentration sample and was marked with flag “E”. The data of Laboratory VN02 in both samples exceeded the DQO and they were marked with flag “E”.

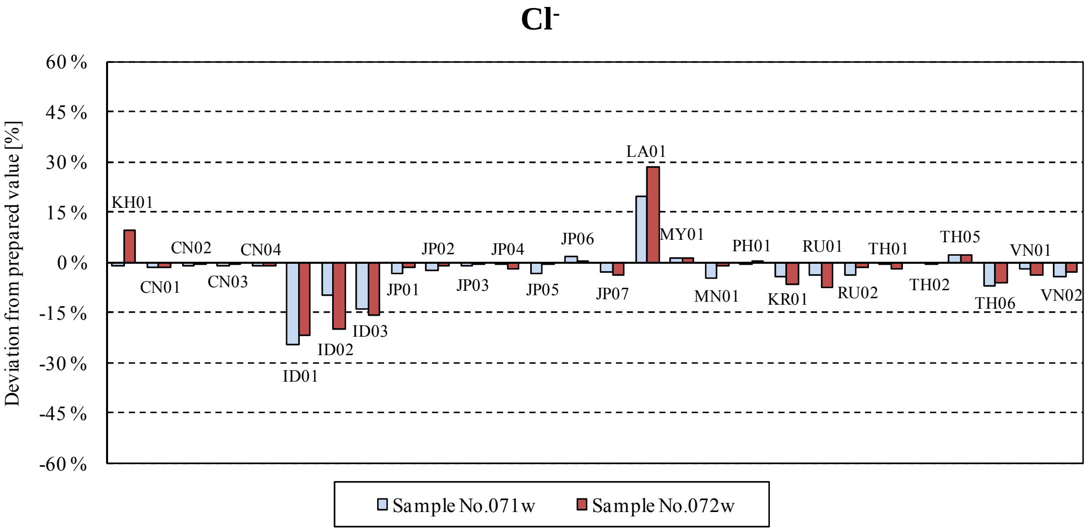


Figure 2.13 Deviation from prepared value for Cl- (normalized by prepared value)

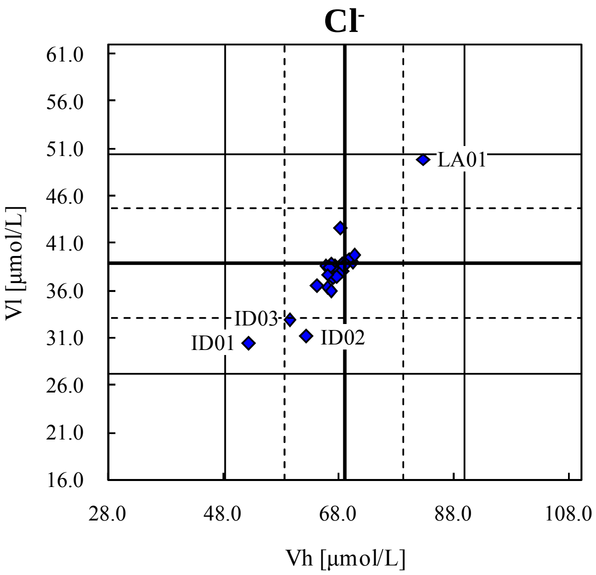


Figure 2.14 Scatter diagram for Cl-

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

27 laboratories used ion chromatography for the determination of Cl-. The Lab.RU02 used titration method. The data of Laboratories LA01 and ID01 in both samples exceeded the DQO and they were marked with flag “E”. The data submitted by Laboratories ID02 and ID03 were lower than the prepared value in low concentration sample and were marked with flag “E”.

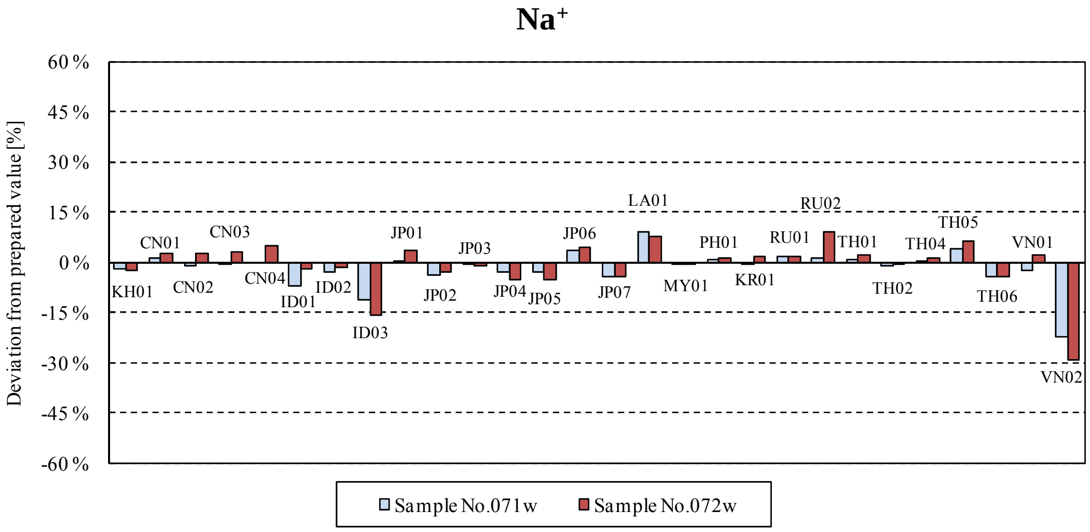


Figure 2.15 Deviation from prepared value for Na^+ (normalized by prepared value)

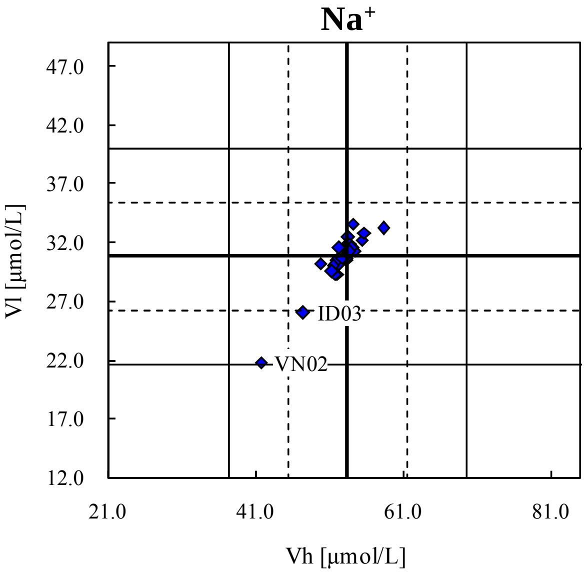


Figure 2.16 Scatter diagram for Na^+

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

26 laboratories used ion chromatography, Lab.RU01 and RU02 used flame (emission) photometry for the determination of Na^+. The data of Laboratory VN02 in both samples exceeded the DQO. The data submitted by ID03 was lower than the prepared value in low concentration sample and were marked with flag “E”.

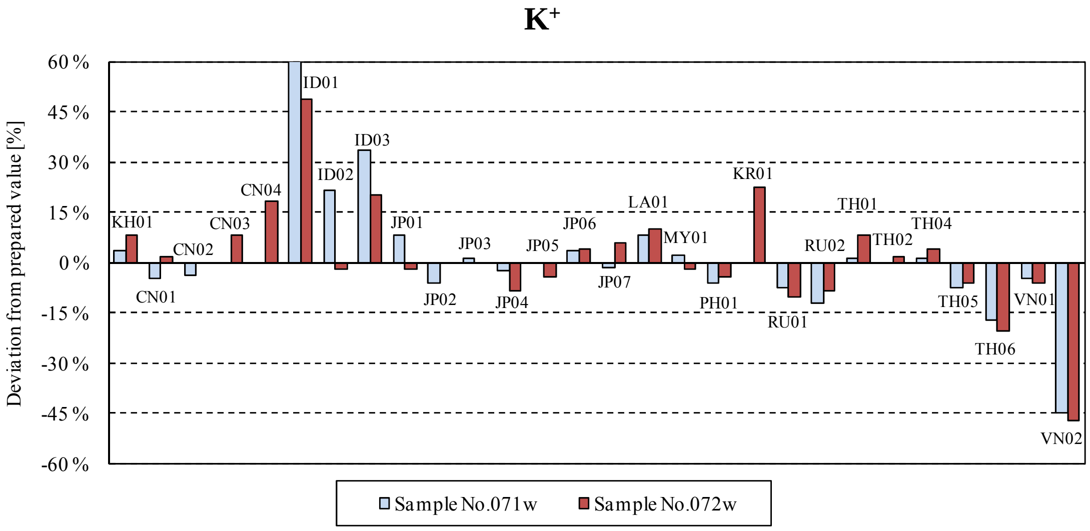


Figure 2.17 Deviation from prepared value for K^+ (normalized by prepared value)

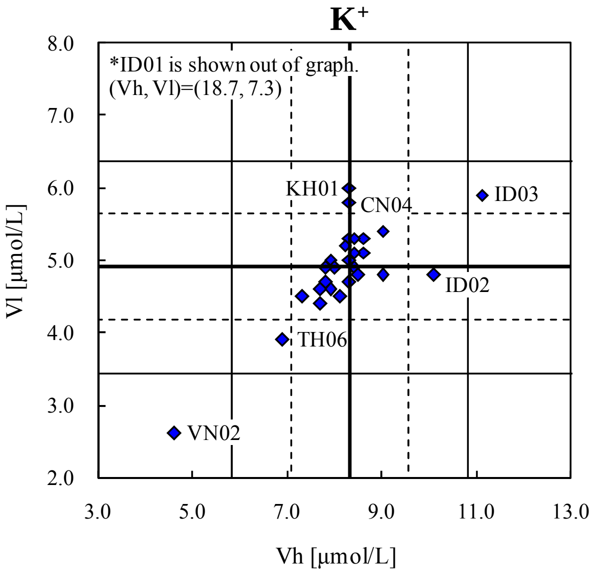


Figure 2.18 Scatter diagram for K^+

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

26 laboratories used ion chromatography, 2 laboratories used flame (emission) photometry, for the determination of K^+ as same as Na^+. Overall, 17.9% of the data for the Sample No.071w had flag. This was the highest percentage in high concentration sample in this survey. The percentage of flagged data in the sample No.072w was 21.4%.

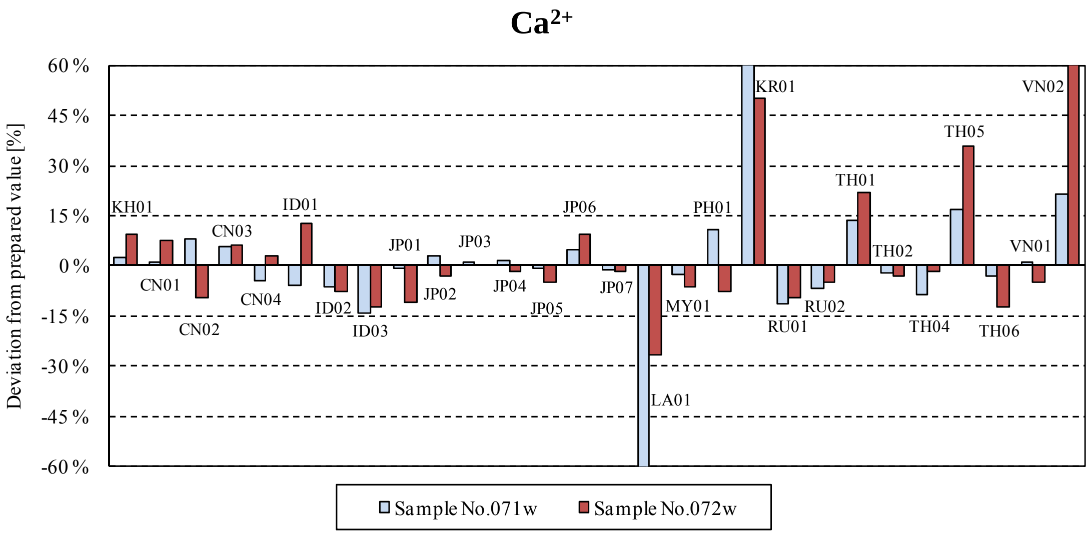


Figure 2.19 Deviation from prepared value for Ca^{2+} (normalized by prepared value)

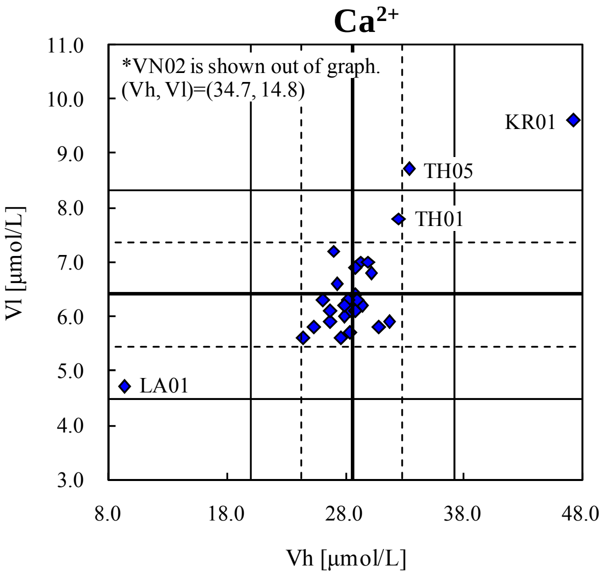


Figure 2.20 Scatter diagram for Ca^{2+}

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

25 laboratories used ion chromatography, 3 laboratories used atomic absorption spectrometry for the determination of Ca^{2+}. The data of Laboratory LA01 in high concentration sample, the data of Laboratories TH05 and VN02 in low concentration sample, and the data of Laboratory KR01 in both samples exceeded the DQO more than a factor of 2 and were marked with flag “X”. The data of Laboratories LA01 and TH01 in low concentration sample and the data of Laboratories TH05 and VN02 in high concentration sample also exceeded the DQO, and they were marked with flag “E”.

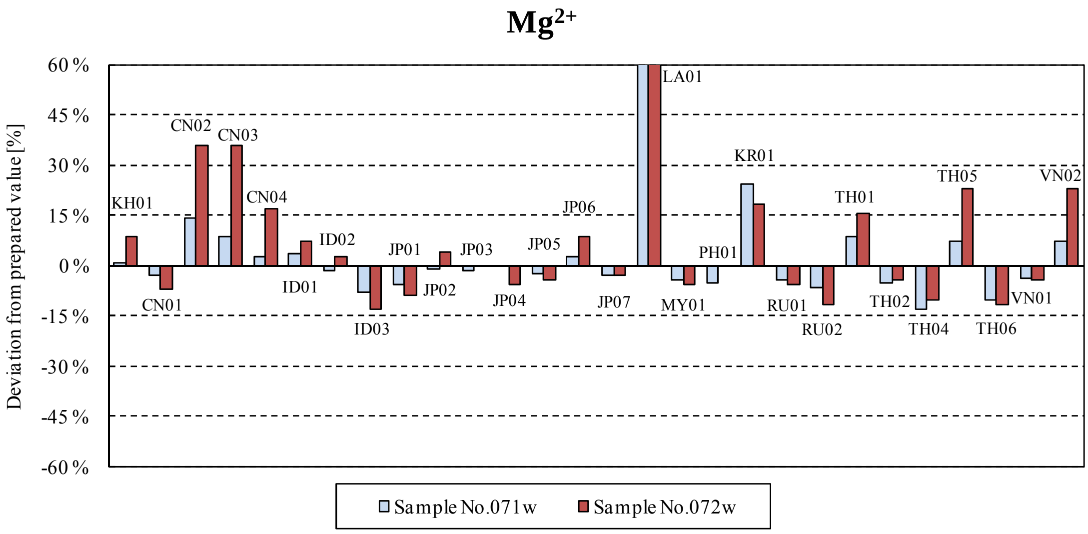


Figure 2.21 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

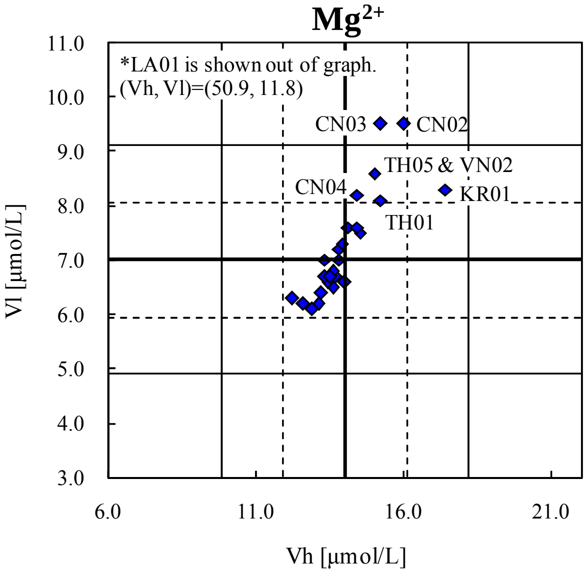


Figure 2.22 Scatter diagram for Mg^{2+}

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

25 laboratories used ion chromatography, 3 laboratories used atomic absorption spectrometry for determination of Mg^{2+}. The percentage of flagged data in low concentration sample was 28.6%. This was the highest percentage in low concentration sample in this survey. On the other hand, the percentage in high concentration sample was 7.1%. There was much difference in the percentage of flagged data between sample No.071w and sample No.072w.

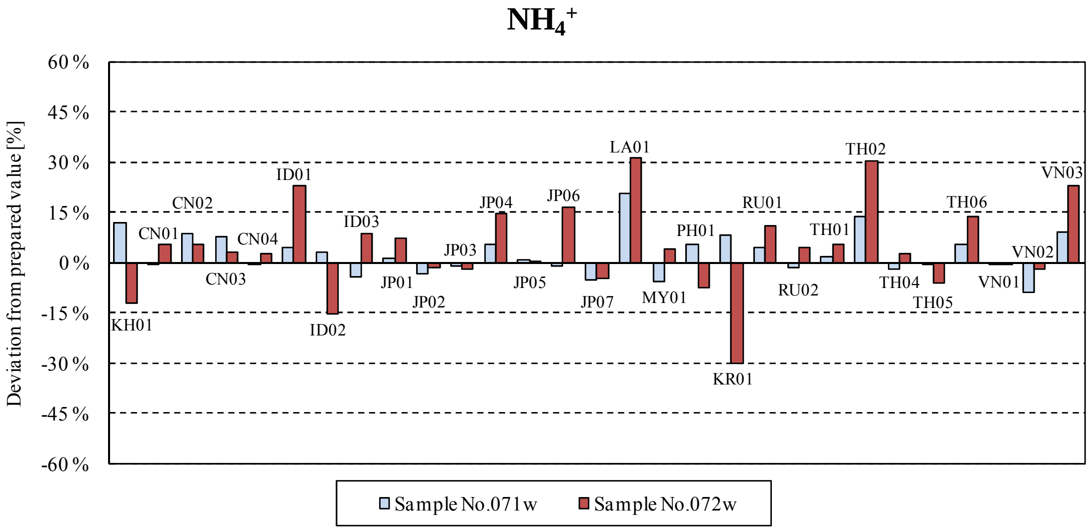


Figure 2.23 Deviation from prepared value for NH_4^+ (normalized by prepared value)

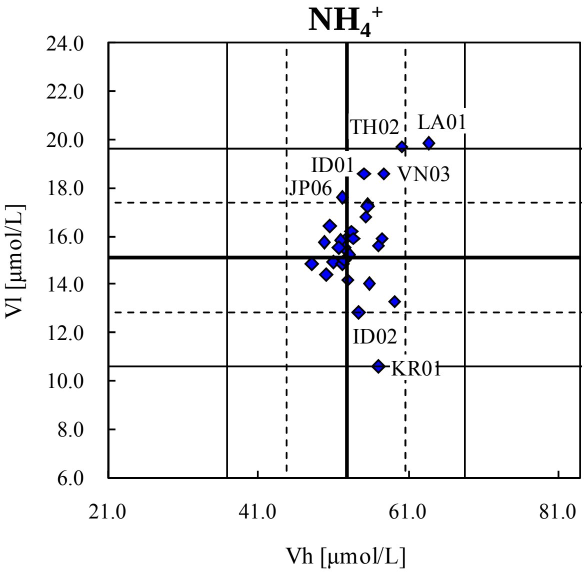


Figure 2.24 Scatter diagram for NH_4^+

(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

26 laboratories used ion chromatography, 2 laboratories used spectrophotometry (indophenol blue), and 1 laboratory used spectrophotometry (others) for the determination of NH_4^+. The data of Laboratories LA01, KR01, and TH02 in low concentration sample exceeded the DQO more than a factor of 2 and they were marked with flag “X”. The data of Laboratories ID01, ID02, JP06, and VN03 in low concentration sample exceeded the DQO and they were marked with flag “E”.

To study the distribution of analytical results, the Z-score method was applied to each parameter. Youden diagrams with Z-score and error evaluations were presented in APPENDIX 2-4.

2.3.3 Overall Evaluation

Some of concentrations of the constituents in this survey were similar to the samples in previous years. Compared to the 2006 survey, concentrations of K^+ and NH_4^+ in low concentration sample were same. The percentage of flagged data for K^+ has decreased from 21.4% in 2006 to 19.2% in 2007, and also the percentage for NH_4^+ has decreased from 10.7% to 3.7%.

The relative standard deviations (R.S.D.) of each of the parameters in the sample No.071w and No.072w are shown in the Figure 2.25. The highest R.S.D. was for Ca^{2+} in low concentration sample in this survey. Only R.S.D. of K^+ in the high concentration sample was higher than that of the low concentration sample. As for the other ions, R.S.D. in the low concentration sample is approximately twice as much as that in the high concentration sample.

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

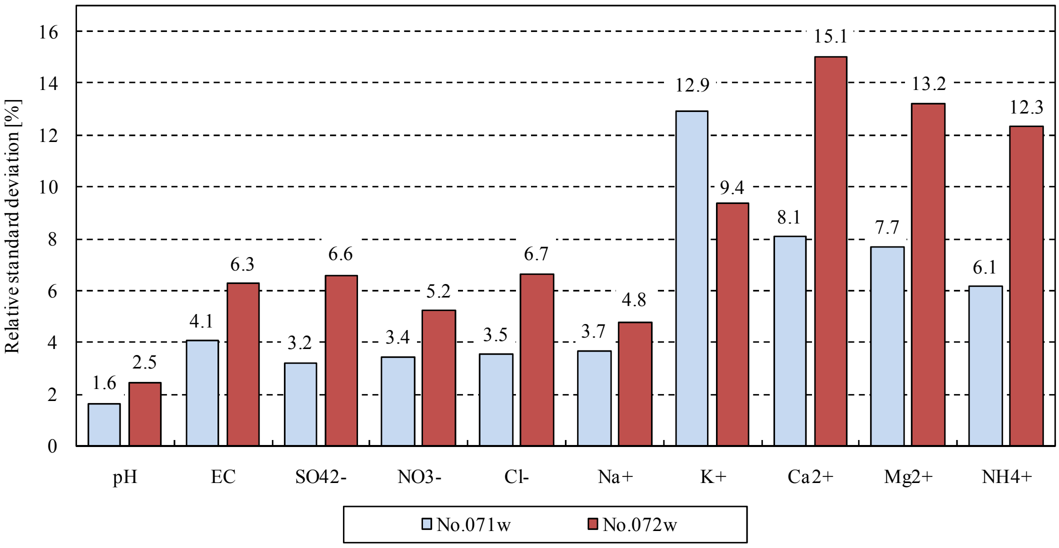


Figure 2.25 Relative standard deviation of each constituent

Some laboratories had problems drawing calibration curves in the determination of the ions in this project as in past projects. The person in charge of analysis needs to confirm the more suitable calibration curve drawn on the chart based on technical manual. The reliability of the calibration needs to be examined before the analysis of the rain samples by using the working standard to avoid the acquisition of low-quality data. In addition, the staff needs to take care to prepare and save a potion of the standard solution for preparing the calibration curve.

2.3.4 Information on laboratories

Methodologies Used

As shown in Figure 2.26, most of the participating laboratories used the recommended methods of EANET. The list of analytical methods is described in the table 2.11.

As for the determination of anions, all participating laboratories used the recommended methods (Ion chromatography or Spectrophotometry) except for one laboratory in the determination of Cl^-. Laboratory RU02 used titration for the determination of Cl^-.

As for the determination of cations, most of the participating laboratories used the recommended methods (Atomic absorption spectrometry, Emission spectrometry, Ion chromatography, or Indophenol spectrophotometry). Laboratory RU02 analyzed NH_4^+ by Spectrophotometry without indophenol.

Table 2.12 presented the number of submitted data and flagged data for each parameter.

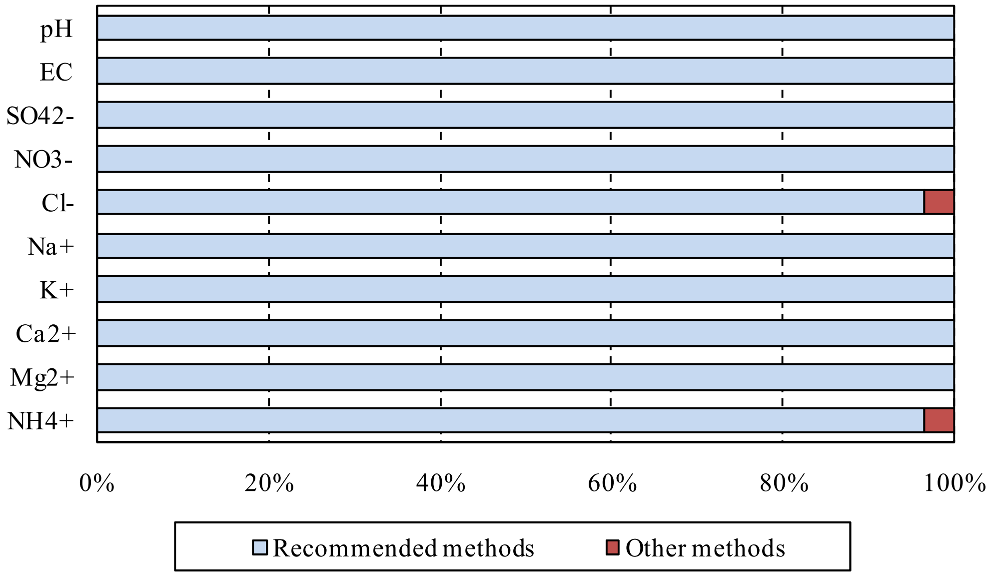


Figure 2.26 Percentage of laboratories that used the recommended methods in the project

Table 2.11 List of analytical 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_4^+)
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
11	Other method

Reverse mesh is the recommended method in EANET

Table 2.12 Number of data measured by each analytical methods

Sample No.071w

Code	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	32 (1)									
1		32 (2)								
2					1					
3								3	3	
4						2	2			
5			27	27 (1)	27 (2)	26 (1)	26 (5)	25 (4)	25 (2)	26 (1)
6										
7			2	1						1
8										2
9										
10										
11										
Flag E	1	0	0	1	2	1	2	2	1	1
Flag X	0	2	0	0	0	0	3	2	1	0

Sample No.072w

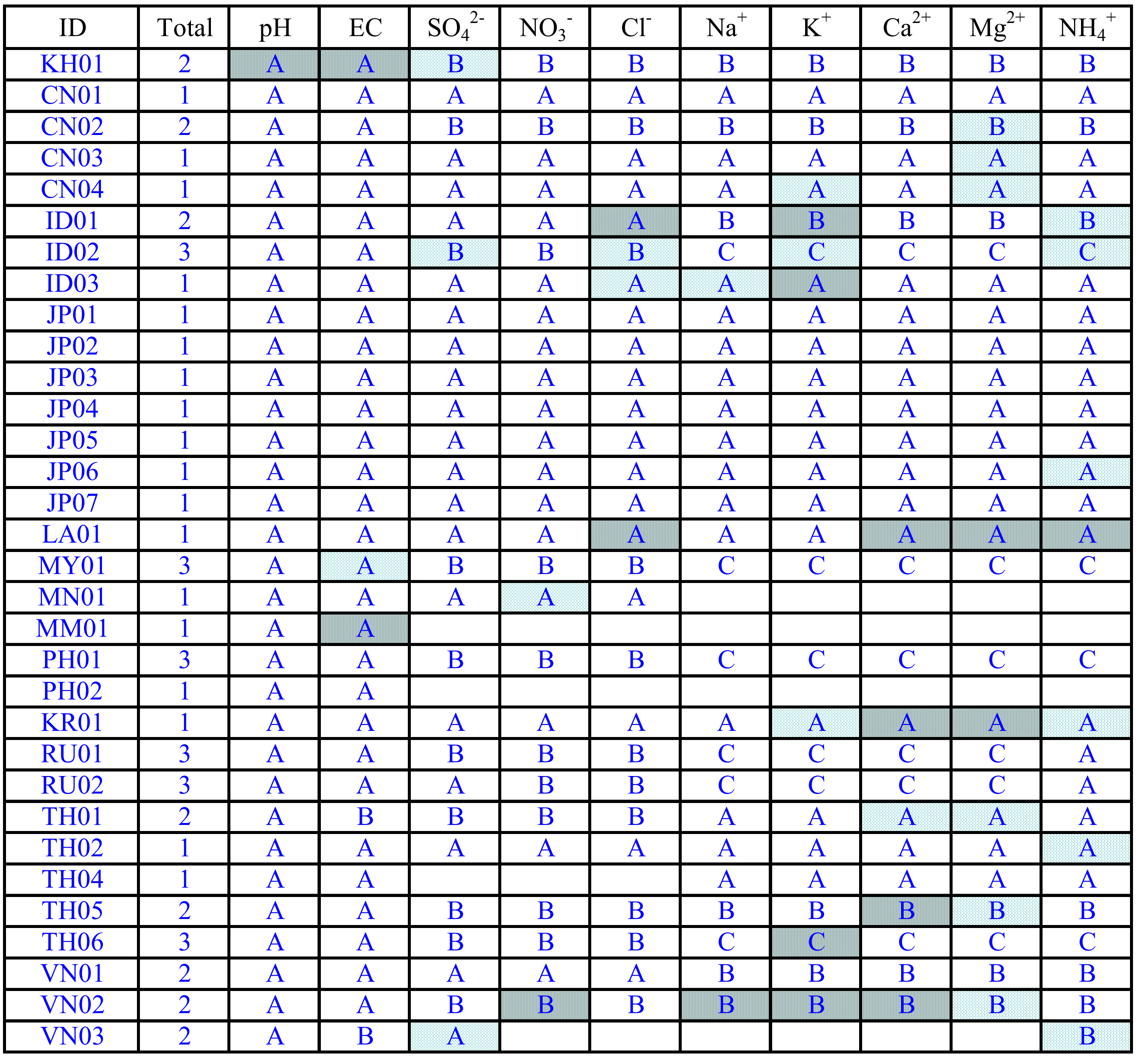
Code	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	32 (1)									
1		32 (3)								
2					1					
3								3	3	
4						2	2			
5			27 (2)	27 (2)	27 (4)	26 (2)	26 (6)	25 (5)	25 (8)	26 (6)
6										
7			2 (1)	1						1
8										2 (1)
9										
10										
11										
Flag E	1	1	3	2	4	2	4	2	5	5
Flag X	0	2	0	0	0	0	2	3	3	2

( ): Number of data flagged by “E” or “X”

Staff (Number and years of experience)

The number of staff in charge of measurement on rainwater samples is described in Table 2.13. “A”, “B”, and “C” represent individuals of staff in each laboratory who are in charge of measurement. In 18 laboratories, only one person carried out measurement of rainwater samples. In 8 laboratories two persons were in charge of the measurements. While in 6 laboratories three persons carried out the measurements. There was no laboratory where more than 4 persons carried out measurements. In the case of laboratories where 3 persons conducted the measurements, their responsibilities were separated according to the methods used for analysis. Relationship between staff number and flagged data could not be identified.

Table 2.13 Staff in charge of measurement



ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	2	A	A	B	B	B	B	B	B	B	B
CN01	1	A	A	A	A	A	A	A	A	A	A
CN02	2	A	A	B	B	B	B	B	B	B	B
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	3	A	A	B	B	B	C	C	C	C	C
ID03	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
LA01	1	A	A	A	A	A	A	A	A	A	A
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	1	A	A	A	A	A					
MM01	1	A	A								
PH01	3	A	A	B	B	B	C	C	C	C	C
PH02	1	A	A								
KR01	1	A	A	A	A	A	A	A	A	A	A
RU01	3	A	A	B	B	B	C	C	C	C	A
RU02	3	A	A	A	B	B	C	C	C	C	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
TH04	1	A	A				A	A	A	A	A
TH05	2	A	A	B	B	B	B	B	B	B	B
TH06	3	A	A	B	B	B	C	C	C	C	C
VN01	2	A	A	A	A	A	B	B	B	B	B
VN02	2	A	A	B	B	B	B	B	B	B	B
VN03	2	A	B	A							B

Light mesh: Analytical data was marked with flag “E” or “X” in sample No.071w or No.072w.

Dark mesh: Analytical data was marked with flag “E” or “X” in both samples.

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" (Table 2.14).

Table 2.14 Years of experience [unit: year]

ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	5	5	3	3	3	3	3	3	3	3
CN01	16	16	16	16	16	16	16	16	16	16
CN02	9	9	1	1	1	1	1	1	1	1
CN03	2	2	2	2	2	2	2	2	2	2
CN04	12	12	12	12	12	12	12	12	12	12
ID01	8	8	8	8	8	8	8	8	8	8
ID02	4	4	2	2	2	6	6	6	6	6
ID03	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
JP01	4	4	4	4	4	4	4	4	4	4
JP02	1	1	1	1	1	1	1	1	1	1
JP03	1	1	1	1	1	1	1	1	1	1
JP04	5	5	5	5	5	5	5	5	5	5
JP05	2	2	2	2	2	2	2	2	2	2
JP06	5	5	5	5	5	5	5	5	5	5
JP07	1	1	1	1	1	1	1	1	1	1
LA01	3	3	3	3	3	3	3	3	3	3
MY01	1	1	5	5	5	7	7	7	7	7
MN01	9	9	9	9	9					
MM01	2	2								
PH01	8	8	7	7	7	11	11	11	11	3
PH02	<1	<1								
KR01	10	10	10	10	10	10	10	10	10	10
RU01	2	2	10	10	10	10	10	10	10	2
RU02	4	4	4	35	35	16	16	16	16	4
TH01	10	5	5	5	5	10	10	10	10	10
TH02	11	11	11	11	11	11	11	11	11	11
TH04	6	6				6	6	6	6	6
TH05	4	4	2	2	2	2	2	2	2	2
TH06	6	6	8	8	8	4	4	4	4	4
VN01	23	23	23	23	23	14	14	14	14	14
VN02	3	3	3	3	3	3	3	3	3	3
VN03	2	2	2							2

Light mesh: Analytical data was marked with flag "E" or "X" in sample No.071w or No.072w.

Dark mesh: Analytical data was marked with flag "E" or "X" in both samples.

2.4 Comparison with past surveys

Since the beginning of EANET, inter-laboratory comparison on wet deposition reached 10th survey. The results showing the percentages of flagged data and percentage of data that satisfied the DQOs are shown in Figure 2.27.

As for the high concentration samples, the percentage of data that satisfied DQOs has increased gradually since 6th survey (2003), and reached to 93.4%. In the case of the low concentration samples, the percentage of data within DQOs in this survey was 85.9%. Although these were not the highest percentages among past 10 surveys, the percentages of data within DQOs are showing a tendency to rise in recent years.

The data quality may have improved due to accumulating effort and experiences in participating laboratories.

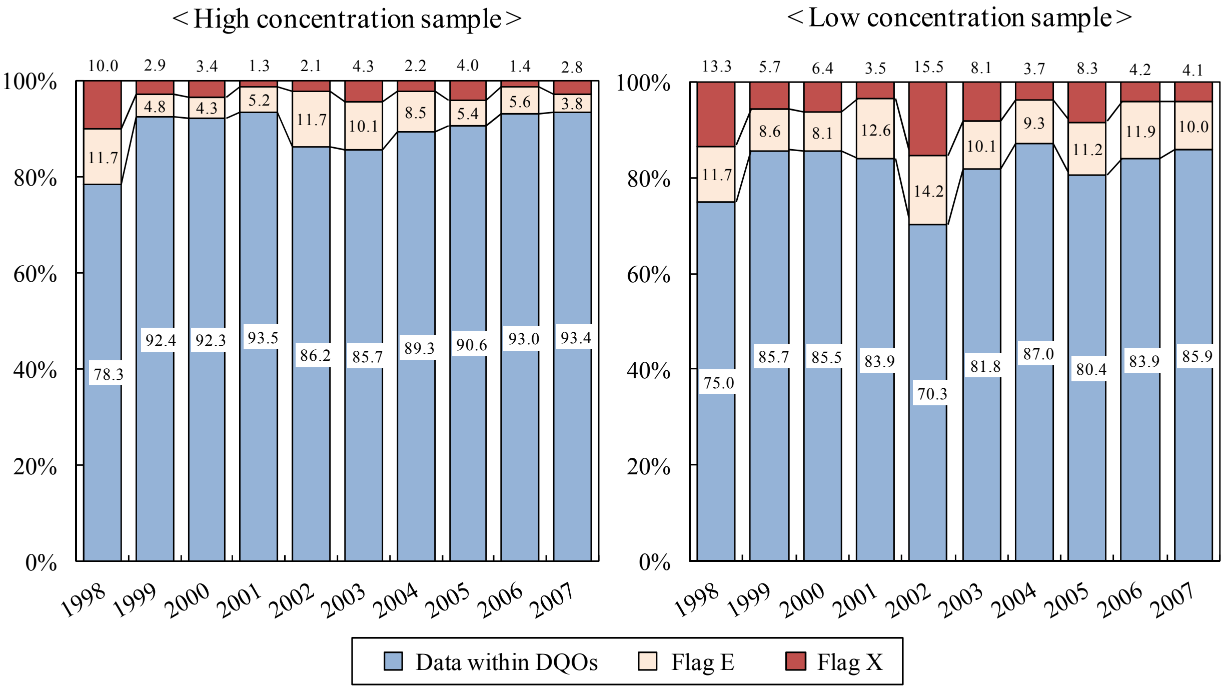


Figure 2.27 Comparison of results from the inter-laboratory comparison projects

The comparison for each parameter in inter-laboratory comparison projects on wet deposition year by year is shown in Figure 2.28. In the results of SO_4^{2-}, there was no flag in high concentration sample for the first time since the beginning of inter-laboratory comparison on wet deposition.

Comparing the percentage of flagged data in low concentration sample from 2001 to 2006 with that of 2007, the result of Ca^{2+} was improved well. On the other hand, as for the results of K^{+} and Mg^{2+} in this survey, the percentage of data flagged “X” increased in both samples.

The concentrations of each parameter in the prepared artificial rainwater of inter-laboratory comparison project of EANET are described in Table 2.15.

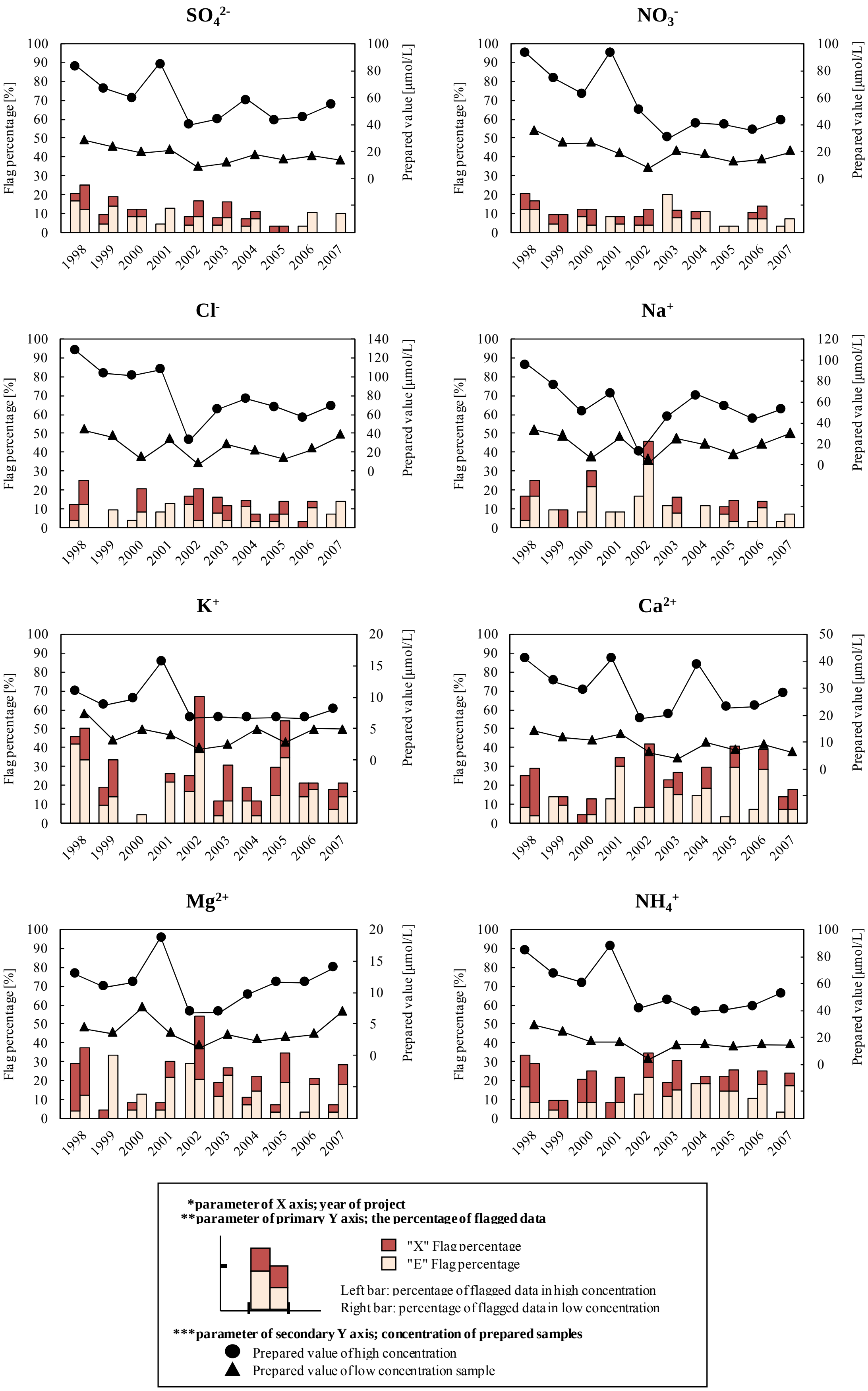


Figure 2.28 Comparison for each parameter in inter-laboratory comparison project

Table 2.15 The prepared values of each parameter in artificial rainwater of inter-laboratory comparison projects in EANET

< High concentration sample >

Year	Sample No.	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.1	4.05	7.94	83.5	93.3	129.0	95.8	11.1	41.1	13.1	84.8
1999	No.1	4.14	6.38	67.0	75.0	104.0	77.0	8.9	33.0	11.0	68.0
2000	No.1	4.10	6.23	59.7	63.3	101.3	51.3	9.9	29.4	11.7	60.5
2001	No.011	4.10	7.45	85.0	93.3	108.4	68.4	15.8	41.1	18.7	87.8
2002	No.021	4.30	3.75	40.3	51.0	33.7	13.7	6.9	19.1	7.0	42.4
2003	No.031	4.52	3.44	44.7	30.9	66.0	46.1	6.9	20.5	7.0	48.3
2004	No.041	4.60	3.94	58.6	41.4	76.7	66.7	6.9	38.9	9.8	39.4
2005	No.051	4.66	3.32	43.7	40.3	68.5	56.5	6.9	23.2	11.7	40.9
2006	No.061	4.72	3.10	45.8	36.3	57.5	44.5	6.9	23.8	11.7	43.9
2007	No.071w	4.64	3.72	54.9	43.6	69.0	53.4	8.3	28.6	14.0	52.7

< Low concentration sample >

Year	Sample No.	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.2	4.51	2.82	29.1	36.1	45.1	33.5	7.4	14.3	4.6	29.5
1999	No.2	4.59	2.30	24.0	27.0	38.0	28.0	3.2	12.0	3.8	25.0
2000	No.2	4.85	1.55	20.1	27.5	15.5	8.7	4.9	11.0	7.8	18.2
2001	No.012	4.82	1.76	21.5	19.4	34.4	27.4	4.0	13.2	3.7	16.7
2002	No.022	5.15	0.69	8.9	8.5	9.1	5.1	2.0	6.6	1.8	4.5
2003	No.032	4.80	1.48	12.0	21.3	29.6	25.6	2.5	4.4	3.4	15.1
2004	No.042	5.00	1.33	17.6	18.4	22.5	20.5	5.0	10.0	2.7	15.1
2005	No.052	5.05	1.05	14.4	13.2	15.3	10.3	3.0	7.6	3.1	13.6
2006	No.062	5.15	1.21	16.9	15.0	24.5	20.5	4.9	9.3	3.5	15.1
2007	No.072w	5.00	1.47	14.0	21.0	38.8	30.8	4.9	6.4	7.0	15.1

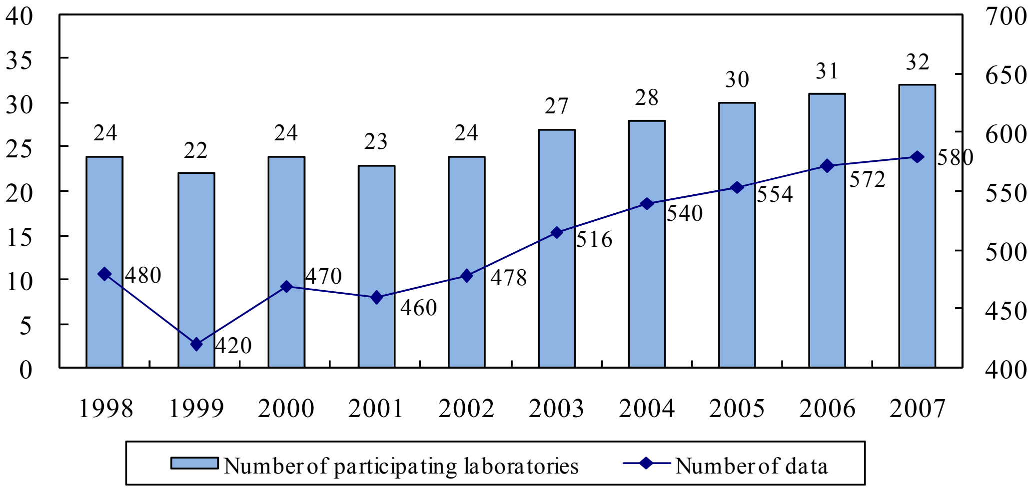


Figure 2.29 The number of participating laboratories and data in the inter-laboratory comparison project on wet deposition

As the figure 2.29 indicates, the number of laboratories participating in the inter-laboratory comparison project on wet deposition has increased since the beginning of the project. In comparison with previous survey, due to the increment of the number of participating laboratory in Viet Nam, the total number of participating laboratories reached 32 in this survey.

2.5 Recommendations for improvements

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

2.5.1 Measurement and Analysis

1) General

- ►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.

2) Deionized water

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

3) 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 materials should be used as much as possible.

4) 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.

5) Calibration of analytical instruments

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

2.5.2 Evaluation of reliability

1) Sensitivity fluctuation of analytical instruments

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

For example, in 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 should be made, and reference solution should be measured again.
- ►If the retention time changes slowly while the separator column is deteriorating, then adequate actions should 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.

2.5.3 Data control

1) Data checks by the analytical laboratories

- ►When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the percentage 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 questionable quality. When abnormal or unrecorded data is detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

References

1) Guidelines for Acid Deposition Monitoring in East Asia
Adopted at Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.

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 adopted at Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.

3) Report of the Inter-laboratory Comparison Project 1998
(Round robin analysis survey 1st Attempt)
Acid Deposition and Oxidant Research Center, November 1999

4) Report of the Inter-laboratory Comparison Project 1999
(Round robin analysis survey 2nd Attempt)
Acid Deposition and Oxidant Research Center, October 2000

5) Report of the Inter-laboratory Comparison Project 2000 on Wet Deposition (3rd Attempt)
Acid Deposition and Oxidant Research Center, October 2001

6) Report of the Inter-laboratory Comparison Project 2001 on Wet Deposition (4th Attempt)
Acid Deposition and Oxidant Research Center, November 2002

7) Report of the Inter-laboratory Comparison Project 2002 on Wet Deposition (5th Attempt)
Acid Deposition and Oxidant Research Center, November 2003

8) Report of the Inter-laboratory Comparison Project 2003 on Wet Deposition (6th Attempt)
Acid Deposition and Oxidant Research Center, November 2004

9) Report of the Inter-laboratory Comparison Project 2004 on Wet Deposition (7th Attempt)
Acid Deposition and Oxidant Research Center, November 2005

10) Report of the Inter-laboratory Comparison Project 2005 on Wet Deposition (8th Attempt)
Acid Deposition and Oxidant Research Center, November 2006

11) Report of the Inter-laboratory Comparison Project 2006
(9th Inter-laboratory Comparison Project on Wet Deposition)
Network Center for EANET, November 2007

12) ICP-WATERS REPORT, 74/2003 (Intercomparison 0317)
International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes, Norwegian Institute for Water Research, September 2003

Appendix 2-1 List of Participating laboratories

CAMBODIA	**Code**
1) Department of Pollution Control, Ministry of Environment	**(KH01)**
CHINA	
2) Zhuhai Environmental Monitoring Station	**(CN01)**
3) Environmental Monitoring Station of Xiamen	**(CN02)**
4) Xi’an Environmental Monitoring Station	**(CN03)**
5) Chongqing Institute of Environmental Science	**(CN04)**
INDONESIA	
6) Analysis Division, Meteorological and Geophysical Agency (BMG)	**(ID01)**
7) Center for Environmental Impact Control Facilities (PUSARPEDAL) Environmental Impact Management Agency (BAPEDAL)	**(ID02)**
8) Indonesian National Institute of Aeronautic and Space (Lapan)	**(ID03)**
JAPAN	
9) Hokkaido Institute of Environmental Sciences	**(JP01)**
10) Nagano Research Institute for Health and Pollution	**(JP02)**
11) Gifu Prefectural Research Institute of Health and Environmental Science	**(JP03)**
12) Kochi Prefectural Environmental Research Center	**(JP04)**
13) Shimane Prefectural Institute of Public Health and Environmental Science	**(JP05)**
14) Okinawa Research Institute of Health and Environment	**(JP06)**
15) Acid Deposition and Oxidant Research Center (ADORC)	**(JP07)**
LAO PDR	
16) Environment Quality Monitoring Center, Environment Research Institute, Science, Technology and Environment Agency	**(LA01)**
MALAYSIA	
17) Division of Environmental Health, Department of Chemistry	**(MY01)**
MONGOLIA	
18) Central Laboratory of Environmental Monitoring, National Agency for Meteorology, Hydrology and Environmental Monitoring, Ministry of Nature and Environment	**(MN01)**
MYANMAR	
19) Department of Meteorology and Hydrology (DMH)	**(MM01)**

PHILIPPINES	**Code**
20) Research and Development Division, Environmental Management Bureau (EMB-CO), Department of Environment and Natural Resources (DENR)	**(PH01)**
21) Environmental Management Bureau CAR (EMB-CAR),	**(PH02)**

REPUBLIC OF KOREA	
22) Atmospheric Chemistry Division, National Institute of Environment Research (NIER)	**(KR01)**

RUSSIA	
23) Limnological Institute of the Russian Academy of Sciences/Siberian Branch (RAS/SB)	**(RU01)**
24) Primorsky Center for Environmental Monitoring	**(RU02)**

THAILAND	
25) Research and Training Centre (ERTC), Department of Research and Environmental Quality Promotion	**(TH01)**
26) Pollution Control Department (PCD) Ministry of Natural Resources and Environment (MONRE)	**(TH02)**
27) Meteorological Observation Division, Thailand Meteorological Department (TMD)	**(TH04)**
28) Chemistry Department, Science Faculty, Chiangmai University (CMU)	**(TH05)**
29) Khon Kaen University (KKU)	**(TH06)**

VIET NAM	
30) Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE - Vietnam	**(VN01)**
31) Middle of Central Regional Hydro-Meteorological Observatory National Hydro -Meteorological Center (NHMS)	**(VN02)**
32)Sub-Institute of Hydro-Meteorology and Environment of South Vietnam (SIHYMETE)	**(VN03)**

OTHER LABORATORIES

	Code
33) Voeikov Main Geophysical Observatory (MGO)	**(RU03)**
32) Indian Institute of Chemical Technology (IICT)	**(IN01)**
33) National Physical Laboratory (NPL)	**(IN02)**
34) Institute of Minerals and Materials Technology (IMMT)	**(IN03)**
32) Indian Institute of Tropical Meteorology (IITM)	**(IN04)**
34) Stockholm University	**(SE01)**

Appendix 2-2 Analytical Results submitted by the laboratories

Sample No.071w (High concentrations)

< Laboratories in EANET >

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]
KH01	5.44	1.34	56.4	43.8	68.4	52.3	8.6	29.3	14.1	59.1
CN01	4.60	3.55	54.8	42.5	68.0	54.1	7.9	28.9	13.6	52.6
CN02	4.61	3.65	56.5	44.3	68.5	53.0	8.0	30.9	16.0	57.4
CN03	4.59	3.59	56.4	43.9	68.3	53.5	8.3	30.2	15.2	56.9
CN04	4.59	3.55	55.9	43.1	68.5	53.4	8.3	27.3	14.4	52.4
ID01	4.68	3.75	54.5	42.9	52.3	49.7	18.7	27.0	14.5	55.1
ID02	4.60	3.61	56.8	41.3	62.4	52.0	10.1	26.8	13.8	54.4
ID03	4.88	3.29	52.4	40.6	59.4	47.4	11.1	24.5	12.9	50.6
JP01	4.69	3.54	53.3	43.4	66.7	53.7	9.0	28.4	13.2	53.4
JP02	4.68	3.71	53.1	41.8	67.4	51.4	7.8	29.4	13.9	51.0
JP03	4.64	3.62	54.8	43.0	68.5	53.2	8.4	28.9	13.8	52.3
JP04	4.69	3.63	55.3	43.4	68.6	52.0	8.1	29.0	14.0	55.5
JP05	4.73	3.61	53.0	42.5	66.7	51.8	8.3	28.4	13.7	53.1
JP06	4.72	3.67	55.2	43.7	70.3	55.3	8.6	30.0	14.4	52.1
JP07	4.70	3.62	54.3	43.3	67.1	51.2	8.2	28.3	13.6	50.0
LA01	4.70	3.34	58.8	47.9	82.7	58.2	9.0	9.3	50.9	63.6
MY01	4.74	3.22	54.8	41.8	69.9	53.2	8.5	27.9	13.4	49.7
MN01	4.58	3.49	54.4	41.4	65.7					
MM01	4.63	1.58								
PH01	4.70	3.72	55.4	42.5	68.9	53.8	7.8	31.7	13.3	55.7
PH02	4.81	3.42								
KR01	4.61	3.80	51.4	41.1	66.0	53.5	8.3	47.3	17.4	57.1
RU01	4.59	3.69	55.7	41.3	66.6	54.3	7.7	25.4	13.4	55.2
RU02	4.66	3.68	53.5	42.5	66.5	54.1	7.3	26.7	13.1	51.9
TH01	4.68	3.69	55.8	43.6	68.7	53.9	8.4	32.5	15.2	53.6
TH02	4.75	3.39	53.7	43.7	69.0	52.8	8.3	28.0	13.3	60.0
TH04	4.51	3.77				53.6	8.4	26.1	12.2	51.8
TH05	4.71	3.38	56.6	45.2	70.7	55.7	7.7	33.4	15.0	52.8
TH06	4.71	3.49	54.3	41.1	64.3	51.2	6.9	27.7	12.6	55.6
VN01	4.64	3.61	54.1	43.4	67.6	52.2	7.9	28.9	13.5	52.5
VN02	4.66	3.42	51.2	35.3	66.0	41.6	4.6	34.7	15.0	48.1
VN03	4.78	3.47	51.2							57.6
Prepared value	**4.64**	**3.72**	**54.9**	**43.6**	**69.0**	**53.4**	**8.3**	**28.6**	**14.0**	**52.7**
Number of data	31	30	29	27	26	27	27	26	27	29
Average	4.67	3.57	54.6	42.9	67.3	53.0	8.2	28.9	14.0	54.2
Minimum	4.51	3.22	51.2	40.6	59.4	47.4	4.6	24.5	12.2	48.1
Maximum	4.88	3.80	58.8	47.9	70.7	58.2	11.1	34.7	17.4	63.6
Standard deviation	0.07	0.14	1.76	1.48	2.38	1.95	1.06	2.33	1.08	3.33

Note: The outliers judged by 3S.D. method were painted with light mesh and were excluded from statistics.

< Laboratories outside EANET >

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]
RU03	4.65	3.59	18.6	41.7	75.4	50.8	6.3	36.7	14.8	53.0
IN01	4.59	3.46	51.7	41.5	63.0	56.3	6.7	32.1	9.8	48.1
IN02	4.44	4.00	53.1	42.3	67.4	50.6	6.5	29.8	13.3	53.4
IN03	4.42	3.33	55.2	42.5	61.5	72.8	23.2	33.1	17.0	60.5
IN04	4.58	3.48	48.5	40.6	52.6	115.8	9.4	27.3	11.0	91.4
SE01	4.69	3.67	54.1	43.1	68.5	52.6	8.2	28.1	13.1	50.7

Sample No.072w (Low concentrations)

< Laboratories in EANET >

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]
KH01	5.94	0.67	11.3	21.4	42.6	30.1	5.3	7.0	7.6	13.3
CN01	4.94	1.41	13.6	20.1	38.2	31.6	5.0	6.9	6.5	15.9
CN02	4.92	1.51	14.6	21.4	38.7	31.6	4.9	5.8	9.5	15.9
CN03	4.90	1.49	14.4	20.9	38.6	31.8	5.3	6.8	9.5	15.6
CN04	4.90	1.32	14.5	20.5	38.4	32.4	5.8	6.6	8.2	15.5
ID01	5.08	1.58	13.6	20.9	30.4	30.2	7.3	7.2	7.5	18.6
ID02	4.95	1.51	16.5	19.9	31.1	30.4	4.8	5.9	7.2	12.8
ID03	5.36	1.33	13.0	19.0	32.8	26.0	5.9	5.6	6.1	16.4
JP01	5.07	1.45	13.5	20.9	38.2	31.9	4.8	5.7	6.4	16.2
JP02	4.99	1.38	13.7	20.5	38.5	30.0	4.9	6.2	7.3	14.9
JP03	4.96	1.46	14.1	20.7	38.6	30.5	4.9	6.4	7.0	14.8
JP04	5.06	1.49	14.3	20.9	38.1	29.3	4.5	6.3	6.6	17.3
JP05	5.10	1.45	13.9	20.9	38.7	29.3	4.7	6.1	6.7	15.2
JP06	5.06	1.50	14.1	21.1	38.9	32.2	5.1	7.0	7.6	17.6
JP07	5.03	1.47	13.6	20.9	37.3	29.5	5.2	6.3	6.8	14.4
LA01	5.17	1.25	15.3	23.6	49.9	33.2	5.4	4.7	11.8	19.8
MY01	5.04	1.24	13.7	20.0	39.4	30.7	4.8	6.0	6.6	15.7
MN01	4.93	1.32	13.5	25.8	38.5					
MM01	4.90	0.67								
PH01	5.04	1.50	13.9	20.8	39.0	31.2	4.7	5.9	7.0	14.0
PH02	5.19	1.41								
KR01	5.05	1.50	12.5	20.1	36.3	31.3	6.0	9.6	8.3	10.6
RU01	4.87	1.54	13.2	20.4	35.9	31.3	4.4	5.8	6.6	16.8
RU02	5.04	1.47	14.1	19.8	38.3	33.6	4.5	6.1	6.2	15.8
TH01	5.04	1.49	13.8	20.5	38.0	31.5	5.3	7.8	8.1	15.9
TH02	5.07	1.26	13.0	20.5	38.6	30.7	5.0	6.2	6.7	19.7
TH04	4.70	1.47				31.2	5.1	6.3	6.3	15.5
TH05	5.06	1.38	14.6	21.3	39.7	32.8	4.6	8.7	8.6	14.2
TH06	5.09	1.42	13.4	19.4	36.4	29.5	3.9	5.6	6.2	17.2
VN01	5.04	1.46	14.1	21.3	37.4	31.5	4.6	6.1	6.7	15.0
VN02	5.16	1.36	12.9	17.0	37.7	21.8	2.6	14.8	8.6	14.8
VN03	5.28	1.30	18.2							18.6
Prepared value	**5.00**	**1.47**	**14.0**	**21.0**	**38.8**	**30.8**	**4.9**	**6.4**	**7.0**	**15.1**
Number of data	31	30	28	27	27	27	26	27	27	29
Average	5.03	1.42	13.8	20.5	37.6	30.9	5.0	6.5	7.3	15.8
Minimum	4.70	1.24	11.3	17.0	30.4	26.0	3.9	4.7	6.1	10.6
Maximum	5.36	1.58	16.5	23.6	42.6	33.6	6.0	9.6	9.5	19.8
Standard deviation	0.12	0.09	0.91	1.07	2.50	1.49	0.47	0.97	0.96	1.95

Note: The outliers judged by 3S.D. method were painted with light mesh and were excluded from statistics.

< Laboratories outside EANET >

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]
RU03	4.94	1.51	9.1	21.0	42.3	30.1	5.0	1.3	7.4	15.6
IN01	4.96	1.46	13.2	20.3	34.4	36.7	3.8	11.2	4.5	11.1
IN02	4.95	1.34	13.9	22.1	38.7	26.2	3.9	14.1	7.0	12.8
IN03	4.76	1.32	14.3	21.0	37.8	46.3	34.5	16.4	9.4	25.5
IN04	4.89	1.57	11.9	18.5	29.5	72.6	5.0	3.6	4.8	26.5
SE01	5.02	1.50	13.8	20.9	38.6	30.7	4.9	6.4	7.3	15.1

Appendix 2-3 Normalized Data

Deviation from prepared value (Va/Vp): (Average (Va) / Prepared value (Vp) – 1) x 100

Sample No.071w (High concentrations)

< Laboratories in EANET >

Lab. ID	pH [%]	EC [%]	SO_4^{2-} [%]	NO_3^- [%]	Cl^- [%]	Na^+ [%]	K^+ [%]	Ca^{2+} [%]	Mg^{2+} [%]	NH_4^+ [%]
KH01	17.2	-64.0	2.7	0.5	-0.9	-2.1	3.6	2.4	0.7	12.1
CN01	-0.9	-4.6	-0.2	-2.5	-1.4	1.3	-4.8	1.0	-2.9	-0.2
CN02	-0.6	-1.9	2.9	1.6	-0.7	-0.7	-3.6	8.0	14.3	8.9
CN03	-1.1	-3.5	2.7	0.7	-1.0	0.2	0.0	5.6	8.6	8.0
CN04	-1.1	-4.6	1.8	-1.1	-0.7	0.0	0.0	-4.5	2.9	-0.6
ID01	0.9	0.8	-0.7	-1.6	-24.2	-6.9	125.3	-5.6	3.6	4.6
ID02	-0.9	-3.0	3.5	-5.3	-9.6	-2.6	21.7	-6.3	-1.4	3.2
ID03	5.2	-11.6	-4.6	-6.9	-13.9	-11.2	33.7	-14.3	-7.9	-4.0
JP01	1.1	-4.8	-2.9	-0.5	-3.3	0.6	8.4	-0.7	-5.7	1.3
JP02	0.9	-0.3	-3.3	-4.1	-2.3	-3.7	-6.0	2.8	-0.7	-3.2
JP03	0.0	-2.7	-0.2	-1.4	-0.7	-0.4	1.2	1.0	-1.4	-0.8
JP04	1.1	-2.4	0.7	-0.5	-0.6	-2.6	-2.4	1.4	0.0	5.3
JP05	1.9	-3.0	-3.5	-2.5	-3.3	-3.0	0.0	-0.7	-2.1	0.8
JP06	1.7	-1.3	0.5	0.2	1.9	3.6	3.6	4.9	2.9	-1.1
JP07	1.3	-2.7	-1.1	-0.7	-2.8	-4.1	-1.2	-1.0	-2.9	-5.1
LA01	1.3	-10.2	7.1	9.9	19.9	9.0	8.4	-67.5	263.6	20.7
MY01	2.2	-13.4	-0.2	-4.1	1.3	-0.4	2.4	-2.4	-4.3	-5.7
MN01	-1.3	-6.2	-0.9	-5.0	-4.8					
MM01	-0.2	-57.5								
PH01	1.3	0.0	0.9	-2.5	-0.1	0.7	-6.0	10.8	-5.0	5.7
PH02	3.7	-8.1								
KR01	-0.6	2.2	-6.4	-5.7	-4.3	0.2	0.0	65.4	24.3	8.3
RU01	-1.1	-0.8	1.5	-5.3	-3.5	1.7	-7.2	-11.2	-4.3	4.7
RU02	0.4	-1.1	-2.6	-2.5	-3.6	1.3	-12.0	-6.6	-6.4	-1.5
TH01	0.9	-0.8	1.6	0.0	-0.4	0.9	1.2	13.6	8.6	1.7
TH02	2.4	-8.9	-2.2	0.2	0.0	-1.1	0.0	-2.1	-5.0	13.9
TH04	-2.8	1.3				0.4	1.2	-8.7	-12.9	-1.7
TH05	1.5	-9.1	3.1	3.7	2.5	4.3	-7.2	16.8	7.1	0.2
TH06	1.5	-6.2	-1.1	-5.7	-6.8	-4.1	-16.9	-3.1	-10.0	5.5
VN01	0.0	-3.0	-1.5	-0.5	-2.0	-2.2	-4.8	1.0	-3.6	-0.4
VN02	0.4	-8.1	-6.7	-19.0	-4.3	-22.1	-44.6	21.3	7.1	-8.7
VN03	3.0	-6.7	-6.7							9.3
Number of data	32	32	29	28	28	28	28	28	28	29
Average	1.2	-7.7	-0.5	-2.2	-2.5	-1.5	3.4	0.8	9.5	2.8
Minimum	-2.8	-64.0	-6.7	-19.0	-24.2	-22.1	-44.6	-67.5	-12.9	-8.7
Maximum	17.2	2.2	7.1	9.9	19.9	9.0	125.3	65.4	263.6	20.7

< Laboratories outside EANET >

Lab. ID	pH [%]	EC [%]	SO_4^{2-} [%]	NO_3^- [%]	Cl^- [%]	Na^+ [%]	K^+ [%]	Ca^{2+} [%]	Mg^{2+} [%]	NH_4^+ [%]
RU03	0.2	-3.5	-66.1	-4.4	9.3	-4.9	-24.1	28.3	5.7	0.6
IN01	-1.1	-7.0	-5.8	-4.8	-8.7	5.4	-19.3	12.2	-30.0	-8.7
IN02	-4.3	7.5	-3.3	-3.0	-2.3	-5.2	-21.7	4.2	-5.0	1.3
IN03	-4.7	-10.5	0.5	-2.5	-10.9	36.3	179.5	15.7	21.4	14.8
IN04	-1.3	-6.5	-11.7	-6.9	-23.8	116.9	13.3	-4.5	-21.4	73.4
SE01	1.1	-1.3	-1.5	-1.1	-0.7	-1.5	-1.2	-1.7	-6.4	-3.8

Sample No.072w (Low concentrations)

< Laboratories in EANET >

Lab. ID	pH [%]	EC [%]	SO_4^{2-} [%]	NO_3^- [%]	Cl^- [%]	Na^+ [%]	K^+ [%]	Ca^{2+} [%]	Mg^{2+} [%]	NH_4^+ [%]
KH01	18.8	-54.4	-19.3	1.9	9.8	-2.3	8.2	9.4	8.6	-11.9
CN01	-1.2	-4.1	-2.9	-4.3	-1.5	2.6	2.0	7.8	-7.1	5.3
CN02	-1.6	2.7	4.3	1.9	-0.3	2.6	0.0	-9.4	35.7	5.3
CN03	-2.0	1.4	2.9	-0.5	-0.5	3.2	8.2	6.3	35.7	3.3
CN04	-2.0	-10.2	3.6	-2.4	-1.0	5.2	18.4	3.1	17.1	2.6
ID01	1.6	7.5	-2.9	-0.5	-21.6	-1.9	49.0	12.5	7.1	23.2
ID02	-1.0	2.7	17.9	-5.2	-19.8	-1.3	-2.0	-7.8	2.9	-15.2
ID03	7.2	-9.5	-7.1	-9.5	-15.5	-15.6	20.4	-12.5	-12.9	8.6
JP01	1.4	-1.4	-3.6	-0.5	-1.5	3.6	-2.0	-10.9	-8.6	7.3
JP02	-0.2	-6.1	-2.1	-2.4	-0.8	-2.6	0.0	-3.1	4.3	-1.3
JP03	-0.8	-0.7	0.7	-1.4	-0.5	-1.0	0.0	0.0	0.0	-2.0
JP04	1.2	1.4	2.1	-0.5	-1.8	-4.9	-8.2	-1.6	-5.7	14.6
JP05	2.0	-1.4	-0.7	-0.5	-0.3	-4.9	-4.1	-4.7	-4.3	0.7
JP06	1.2	2.0	0.7	0.5	0.3	4.5	4.1	9.4	8.6	16.6
JP07	0.6	0.0	-2.9	-0.5	-3.9	-4.2	6.1	-1.6	-2.9	-4.6
LA01	3.4	-15.0	9.3	12.4	28.6	7.8	10.2	-26.6	68.6	31.1
MY01	0.8	-15.6	-2.1	-4.8	1.5	-0.3	-2.0	-6.3	-5.7	4.0
MN01	-1.4	-10.2	-3.6	22.9	-0.8					
MM01	-2.0	-54.4								
PH01	0.8	2.0	-0.7	-1.0	0.5	1.3	-4.1	-7.8	0.0	-7.3
PH02	3.8	-4.1								
KR01	1.0	2.0	-10.7	-4.3	-6.4	1.6	22.4	50.0	18.6	-29.8
RU01	-2.6	4.8	-5.7	-2.9	-7.5	1.6	-10.2	-9.4	-5.7	11.3
RU02	0.8	0.0	0.7	-5.7	-1.3	9.1	-8.2	-4.7	-11.4	4.6
TH01	0.8	1.4	-1.4	-2.4	-2.1	2.3	8.2	21.9	15.7	5.3
TH02	1.4	-14.3	-7.1	-2.4	-0.5	-0.3	2.0	-3.1	-4.3	30.5
TH04	-6.0	0.0				1.3	4.1	-1.6	-10.0	2.6
TH05	1.2	-6.1	4.3	1.4	2.3	6.5	-6.1	35.9	22.9	-6.0
TH06	1.8	-3.4	-4.3	-7.6	-6.2	-4.2	-20.4	-12.5	-11.4	13.9
VN01	0.8	-0.7	0.7	1.4	-3.6	2.3	-6.1	-4.7	-4.3	-0.7
VN02	3.2	-7.5	-7.9	-19.0	-2.8	-29.2	-46.9	131.3	22.9	-2.0
VN03	5.6	-11.6	30.0							23.2
Number of data	32	32	29	28	28	28	28	28	28	29
Average	1.2	-6.3	-0.3	-1.3	-2.0	-0.6	1.5	5.7	6.2	4.6
Minimum	-6.0	-54.4	-19.3	-19.0	-21.6	-29.2	-46.9	-26.6	-12.9	-29.8
Maximum	18.8	7.5	30.0	22.9	28.6	9.1	49.0	131.3	68.6	31.1

< Laboratories outside EANET >

Lab. ID	pH [%]	EC [%]	SO_4^{2-} [%]	NO_3^- [%]	Cl^- [%]	Na^+ [%]	K^+ [%]	Ca^{2+} [%]	Mg^{2+} [%]	NH_4^+ [%]
RU03	-1.2	2.7	-35.0	0.0	9.0	-2.3	2.0	-79.7	5.7	3.3
IN01	-0.8	-0.7	-5.7	-3.3	-11.3	19.2	-22.4	75.0	-35.7	-26.5
IN02	-1.0	-8.8	-0.7	5.2	-0.3	-14.9	-20.4	120.3	0.0	-15.2
IN03	-4.8	-10.2	2.1	0.0	-2.6	50.3	604.1	156.3	34.3	68.9
IN04	-2.2	6.8	-15.0	-11.9	-24.0	135.7	2.0	-43.8	-31.4	75.5
SE01	0.4	2.0	-1.4	-0.5	-0.5	-0.3	0.0	0.0	4.3	0.0

Appendix 2-4 Youden diagram with Z-score

- **Z-score**

The formula for Z-score calculations is as follows:

$$Z = \frac{X - Q_2}{0.7413 * (Q_3 - Q_1)}$$

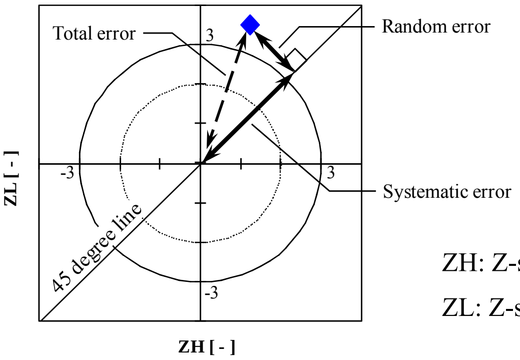
where X: The result obtained by the laboratory
Q_1: The result corresponding to the 1st quartile. (First 25% when ranked in order)
Q_2: The result corresponding to the 2nd quartile. (i.e. Median)
Q_3: The result corresponding to the 3rd quartile. (First 75% when ranked in order)

Z-score given to each laboratory means how close it is to the consensus result. The best Z-score is zero. Generally, the Z-score is evaluated as follows:

$|Z| \leqq 2$: Satisfactory
$2 < |Z| < 3$: Questionable
$3 \leqq |Z|$: Unsatisfactory

- **Youden diagram**

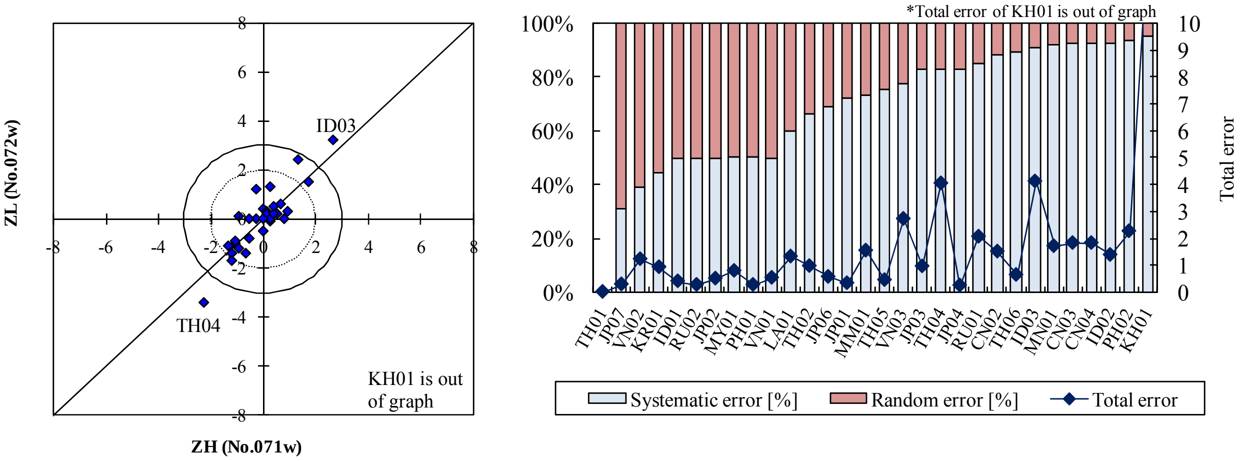
Youden diagram with Z-score provides visual discrimination of outliers from valid results. The outliers are plotted outside the circle whose radius is 3. In addition, all plots on Z-score coordinate can be evaluated by random error and systematic error as shown below:



ZH: Z-score for high concentration sample [-]

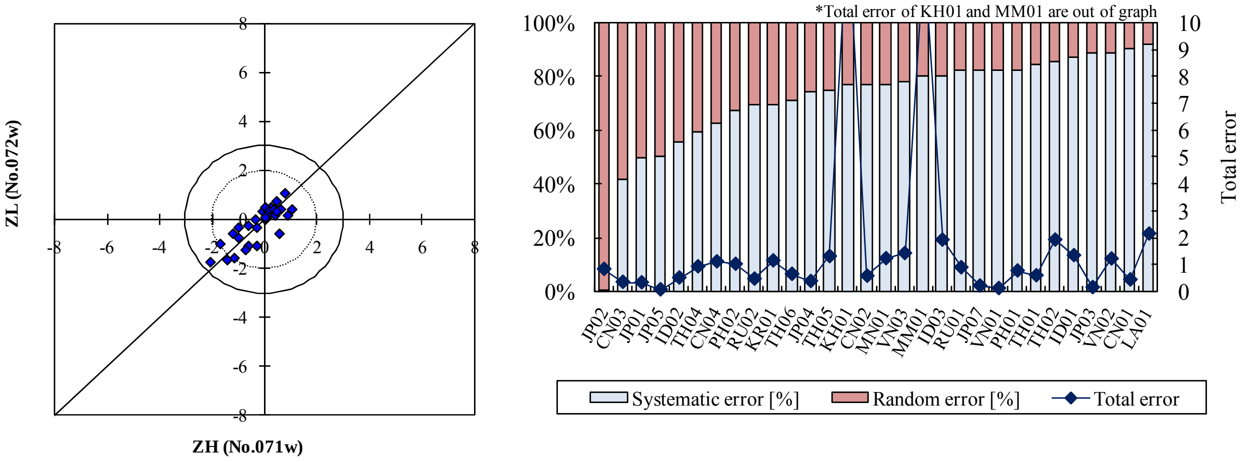
ZL: Z-score for low concentration sample [-]

pH



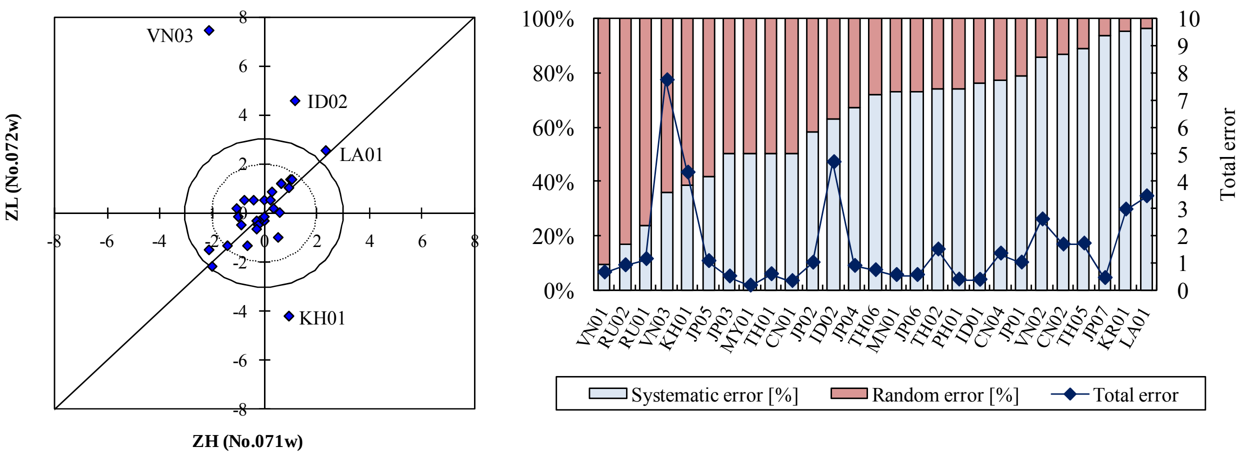
(a) Youden diagram with Z-score and Error evaluation for pH

EC



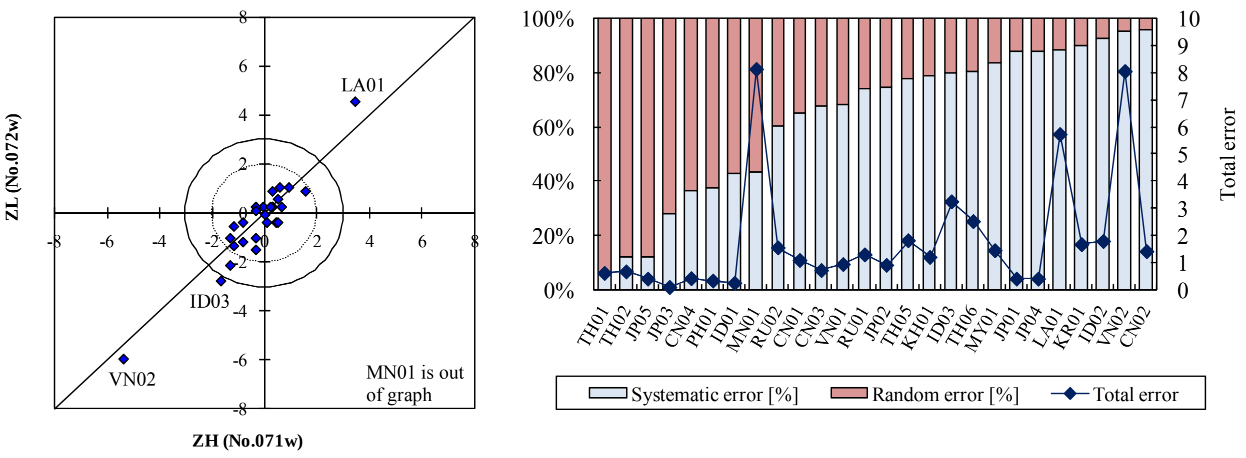
(b) Youden diagram with Z-score and Error evaluation for EC

SO$_4^{2-}$



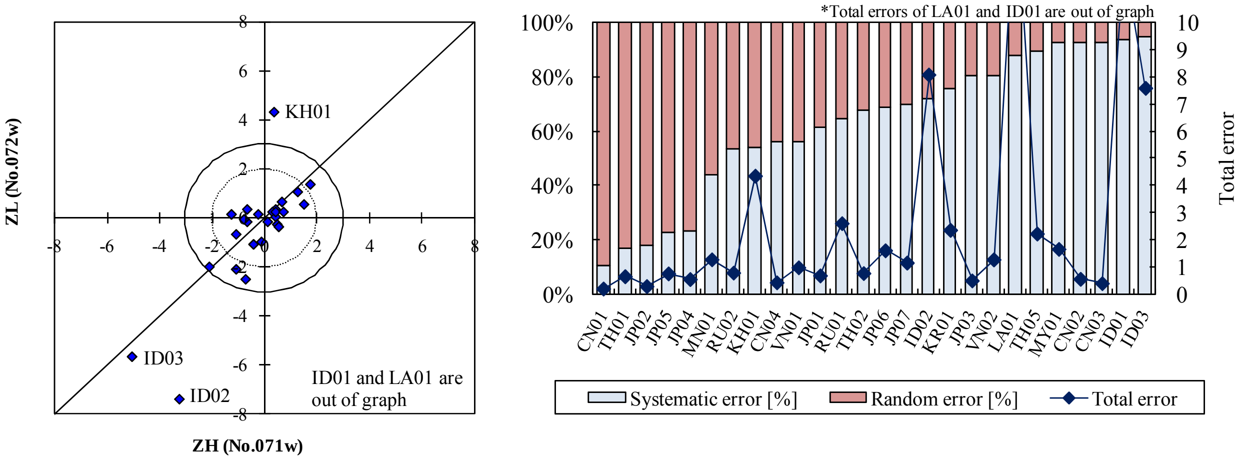
(c) Youden diagram with Z-score and Error evaluation for SO$_4^{2-}$

NO$_3^-$



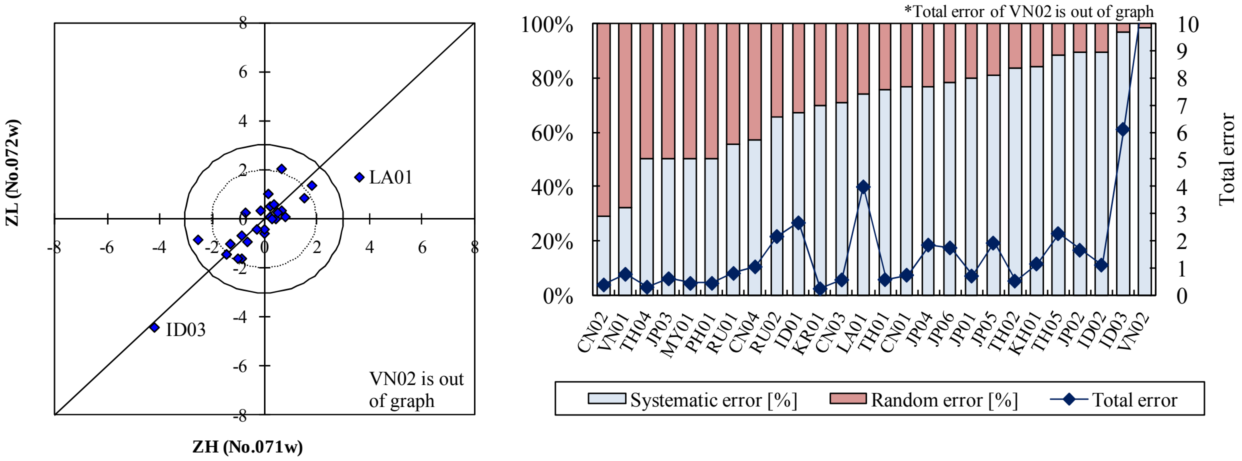
(d) Youden diagram with Z-score and Error evaluation for NO$_3^-$

Cl$^-$



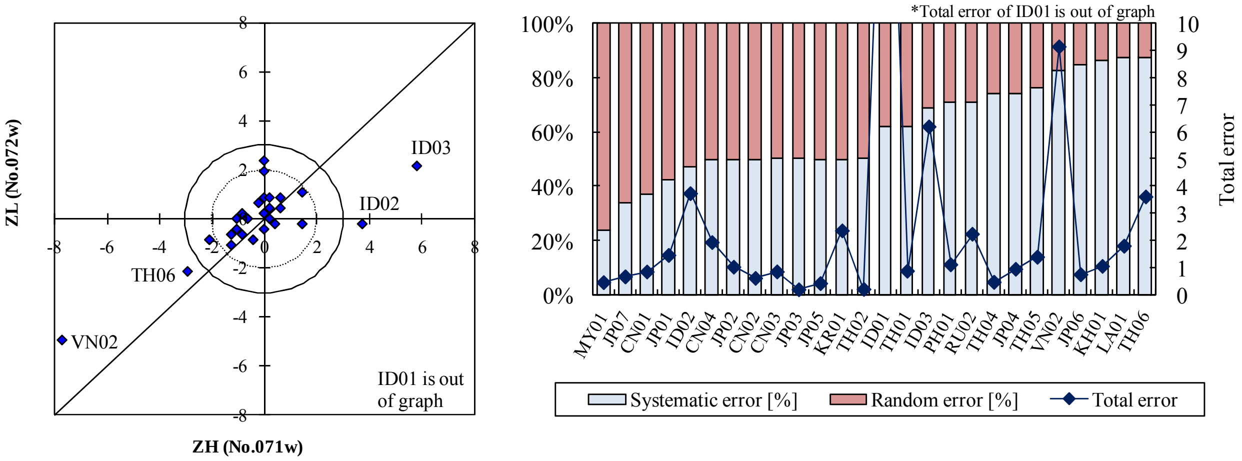
(e) Youden diagram with Z-score and Error evaluation for Cl$^-$

Na$^+$



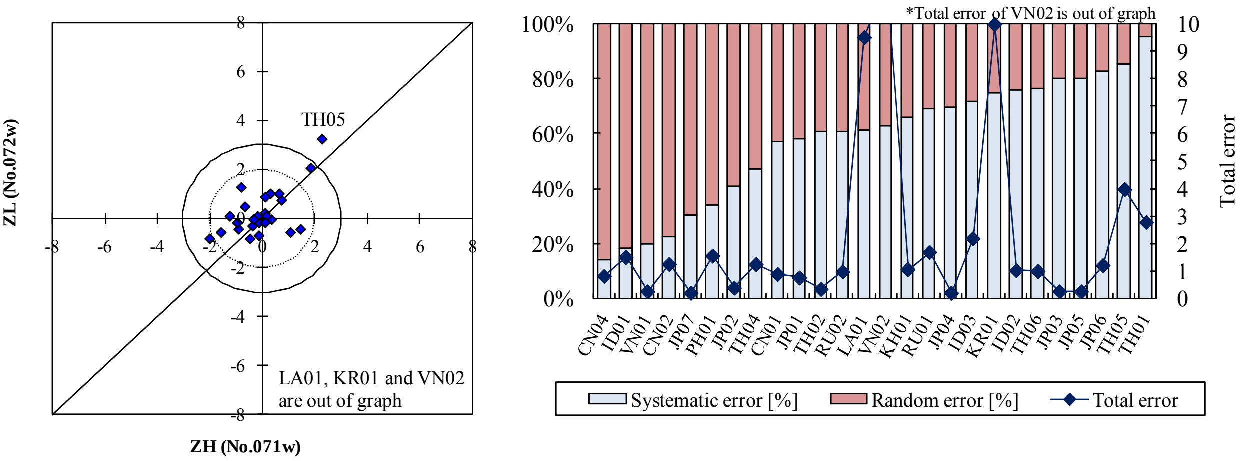
(f) Youden diagram with Z-score and Error evaluation for Na$^+$

K$^+$



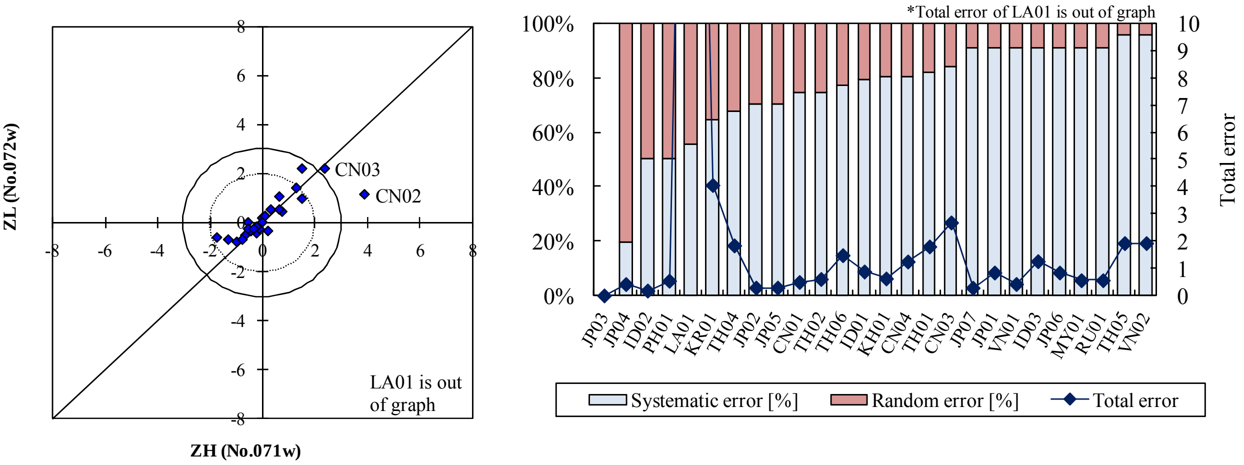
(g) Youden diagram with Z-score and Error evaluation for K$^+$

Ca^{2+}



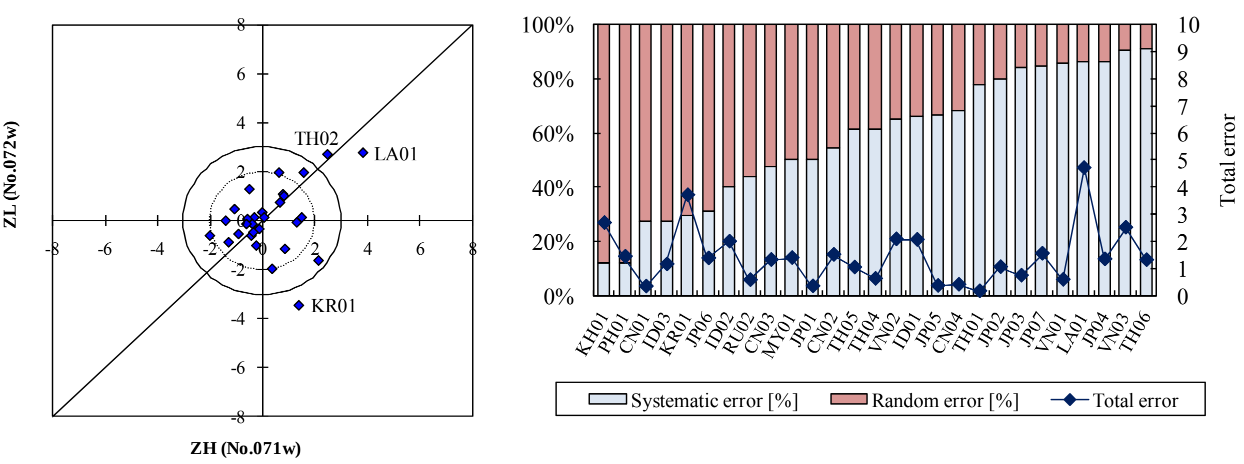
(h) Youden diagram with Z-score and Error evaluation for Ca^{2+}

Mg^{2+}



(i) Youden diagram with Z-score and Error evaluation for Mg^{2+}

NH_4^+



(j) Youden diagram with Z-score and Error evaluation for NH_4^+

(k) Judgment of outliers with Youden diagram method for sample No.071w

Sample No.071w (High 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]
KH01	5.44	1.34	56.4	43.8	68.4	52.3	8.6	29.3	14.1	59.1
CN01	4.60	3.55	54.8	42.5	68.0	54.1	7.9	28.9	13.6	52.6
CN02	4.61	3.65	56.5	44.3	68.5	53.0	8.0	30.9	16.0	57.4
CN03	4.59	3.59	56.4	43.9	68.3	53.5	8.3	30.2	15.2	56.9
CN04	4.59	3.55	55.9	43.1	68.5	53.4	8.3	27.3	14.4	52.4
ID01	4.68	3.75	54.5	42.9	52.3	49.7	18.7	27.0	14.5	55.1
ID02	4.60	3.61	56.8	41.3	62.4	52.0	10.1	26.8	13.8	54.4
ID03	4.88	3.29	52.4	40.6	59.4	47.4	11.1	24.5	12.9	50.6
JP01	4.69	3.54	53.3	43.4	66.7	53.7	9.0	28.4	13.2	53.4
JP02	4.68	3.71	53.1	41.8	67.4	51.4	7.8	29.4	13.9	51.0
JP03	4.64	3.62	54.8	43.0	68.5	53.2	8.4	28.9	13.8	52.3
JP04	4.69	3.63	55.3	43.4	68.6	52.0	8.1	29.0	14.0	55.5
JP05	4.73	3.61	53.0	42.5	66.7	51.8	8.3	28.4	13.7	53.1
JP06	4.72	3.67	55.2	43.7	70.3	55.3	8.6	30.0	14.4	52.1
JP07	4.70	3.62	54.3	43.3	67.1	51.2	8.2	28.3	13.6	50.0
LA01	4.70	3.34	58.8	47.9	82.7	58.2	9.0	9.3	50.9	63.6
MY01	4.74	3.22	54.8	41.8	69.9	53.2	8.5	27.9	13.4	49.7
MN01	4.58	3.49	54.4	41.4	65.7					
MM01	4.63	1.58								
PH01	4.70	3.72	55.4	42.5	68.9	53.8	7.8	31.7	13.3	55.7
PH02	4.81	3.42								
KR01	4.61	3.80	51.4	41.1	66.0	53.5	8.3	47.3	17.4	57.1
RU01	4.59	3.69	55.7	41.3	66.6	54.3	7.7	25.4	13.4	55.2
RU02	4.66	3.68	53.5	42.5	66.5	54.1	7.3	26.7	13.1	51.9
TH01	4.68	3.69	55.8	43.6	68.7	53.9	8.4	32.5	15.2	53.6
TH02	4.75	3.39	53.7	43.7	69.0	52.8	8.3	28.0	13.3	60.0
TH04	4.51	3.77				53.6	8.4	26.1	12.2	51.8
TH05	4.71	3.38	56.6	45.2	70.7	55.7	7.7	33.4	15.0	52.8
TH06	4.71	3.49	54.3	41.1	64.3	51.2	6.9	27.7	12.6	55.6
VN01	4.64	3.61	54.1	43.4	67.6	52.2	7.9	28.9	13.5	52.5
VN02	4.66	3.42	51.2	35.3	66.0	41.6	4.6	34.7	15.0	48.1
VN03	4.78	3.47	51.2							57.6
Prepared value	**4.64**	**3.72**	**54.9**	**43.6**	**69.0**	**53.4**	**8.3**	**28.6**	**14.0**	**52.7**
Number of data	29	30	25	24	23	25	23	24	25	26
Average	4.67	3.57	54.4	42.9	67.8	53.0	8.2	28.4	13.8	53.5

Note: The outliers judged by Youden diagram method were painted with light mesh and were excluded from statistics.

(l) Judgment of outliers with Youden diagram method for sample No.072w

Sample No.072w (Low 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]
KH01	5.94	0.67	11.3	21.4	42.6	30.1	5.3	7.0	7.6	13.3
CN01	4.94	1.41	13.6	20.1	38.2	31.6	5.0	6.9	6.5	15.9
CN02	4.92	1.51	14.6	21.4	38.7	31.6	4.9	5.8	9.5	15.9
CN03	4.90	1.49	14.4	20.9	38.6	31.8	5.3	6.8	9.5	15.6
CN04	4.90	1.32	14.5	20.5	38.4	32.4	5.8	6.6	8.2	15.5
ID01	5.08	1.58	13.6	20.9	30.4	30.2	7.3	7.2	7.5	18.6
ID02	4.95	1.51	16.5	19.9	31.1	30.4	4.8	5.9	7.2	12.8
ID03	5.36	1.33	13.0	19.0	32.8	26.0	5.9	5.6	6.1	16.4
JP01	5.07	1.45	13.5	20.9	38.2	31.9	4.8	5.7	6.4	16.2
JP02	4.99	1.38	13.7	20.5	38.5	30.0	4.9	6.2	7.3	14.9
JP03	4.96	1.46	14.1	20.7	38.6	30.5	4.9	6.4	7.0	14.8
JP04	5.06	1.49	14.3	20.9	38.1	29.3	4.5	6.3	6.6	17.3
JP05	5.10	1.45	13.9	20.9	38.7	29.3	4.7	6.1	6.7	15.2
JP06	5.06	1.50	14.1	21.1	38.9	32.2	5.1	7.0	7.6	17.6
JP07	5.03	1.47	13.6	20.9	37.3	29.5	5.2	6.3	6.8	14.4
LA01	5.17	1.25	15.3	23.6	49.9	33.2	5.4	4.7	11.8	19.8
MY01	5.04	1.24	13.7	20.0	39.4	30.7	4.8	6.0	6.6	15.7
MN01	4.93	1.32	13.5	25.8	38.5					
MM01	4.90	0.67								
PH01	5.04	1.50	13.9	20.8	39.0	31.2	4.7	5.9	7.0	14.0
PH02	5.19	1.41								
KR01	5.05	1.50	12.5	20.1	36.3	31.3	6.0	9.6	8.3	10.6
RU01	4.87	1.54	13.2	20.4	35.9	31.3	4.4	5.8	6.6	16.8
RU02	5.04	1.47	14.1	19.8	38.3	33.6	4.5	6.1	6.2	15.8
TH01	5.04	1.49	13.8	20.5	38.0	31.5	5.3	7.8	8.1	15.9
TH02	5.07	1.26	13.0	20.5	38.6	30.7	5.0	6.2	6.7	19.7
TH04	4.70	1.47				31.2	5.1	6.3	6.3	15.5
TH05	5.06	1.38	14.6	21.3	39.7	32.8	4.6	8.7	8.6	14.2
TH06	5.09	1.42	13.4	19.4	36.4	29.5	3.9	5.6	6.2	17.2
VN01	5.04	1.46	14.1	21.3	37.4	31.5	4.6	6.1	6.7	15.0
VN02	5.16	1.36	12.9	17.0	37.7	21.8	2.6	14.8	8.6	14.8
VN03	5.28	1.30	18.2							18.6
Prepared value	**5.00**	**1.47**	**14.0**	**21.0**	**38.8**	**30.8**	**4.9**	**6.4**	**7.0**	**15.1**
Number of data	29	30	25	24	23	25	23	24	25	26
Average	5.03	1.42	13.7	20.6	38.1	31.0	5.0	6.3	7.1	15.7

Note: The outliers judged by Youden diagram method were painted with light mesh and were excluded from statistics.

3. 3rd INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

3.1 Introduction

In the inter-laboratory comparison for dry deposition, impregnated filters which contain three ions, SO_4^{2-}, Cl^-, and NH_4^+, were prepared and distributed to the participating laboratories by the Network Center (NC) in November 2007. Most of the laboratories participating in EANET activities joined this activity and submitted their analytical results to NC. Obtained results for the amount of SO_4^{2-}, Cl^-, and NH_4^+ on the distributed filters were compared with the prepared values and statistically treated.

3.2 Procedures

3.2.1 Participating Laboratories

Nineteen laboratories in charge of chemical analysis in 8 countries of EANET participated in the third attempt. NC shipped the sample filters to all of these laboratories. The names of the participating laboratories are presented in *Appendix 3-1*.

3.2.2 Description of Samples

Sample filters, on which low and high amount of salts (ions) were impregnated, were prepared and distributed to the laboratories as well as blank filters. The details of the sample filters are described in Table 3.1. The information on the analytical precision and accuracy on the individual parameters were summarized through the statistical treatment of the submitted analytical results from each participating laboratory.

Table 3.1 Outline of distributed filter samples

Name	Details	Container	Number of filters	Note
No.071d-1	Alkali-Impregnated filter (low amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by K_2CO_3
No.071d-2	Acid-Impregnated filter (low amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by H_3PO_4

No.072d-1	Alkali-Impregnated filter (high amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by K_2CO_3
No.072d-2	Acid-Impregnated filter (high amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by H_3PO_4
No.073d-1	Alkali-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by K_2CO_3
No.073d-2	Acid-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by H_3PO_4

3.2.3 Parameters analyzed

All participating laboratories were expected to analyze the sample filters and submit the results as the net amount of three kinds of contained salts, Sulfate, Chloride and Ammonium, in the units of microgram (μg).

3.2.4 Analytical Methodologies

The recommended procedures for sampling and analysis on filter pack method are described in EANET Document, “Technical Document for Filter Pack Method in EAST Asia” (NC, 2003). Each sample filter was put in a centrifuging tube and distributed to the participating laboratories. Thus, extracting solvent could be poured directly into the centrifuging tube and then the extract operation could be carried out.

Extraction procedure was carried out according to the following procedures;

(1) In the case of Sample No.071d-1, No.072d-1, No.073d-1, pour exactly 20 mL H_2O_2 solution (0.05%-v/v) into the centrifuging tube, then shake or vibrate the tubes during 20 minutes for extractions using shaker or ultrasonic bath.
(2) In the case of Sample No.071d-2, No.072d-2, No.073d-2, pour exactly 20 mL deionized water into the centrifuging tube, then shake or vibrate the tubes during 20 minutes for the extractions using shaker or ultrasonic bath.
(3) Filter the insoluble matters out of the extracted solutions using a membrane filter (pore size 0.45μm) previously well washed by pure water (more than 100mL).

Note 1) Put a name on each sample tube and keep them in the refrigerator.
Note 2) Carry out the analysis as soon as possible after the extraction process.

Participating laboratories were expected to use the same analytical methods. Analytical methods specified in the Technical Document are described in Table 3.2.

Table 3.2 Analytical methods specified in the Technical Document

Parameter	Analytical method
SO_4^{2-}	Ion Chromatography
Cl^-	Spectrophotometry
NH_4^+	Ion Chromatography Spectrophotometry (Indophenol Blue)

3.2.5 Data Checking Procedures

It was requested that the results were reported as **the net amount** of each salt contained in sample filters. The net amount can be determined by:

$$M_{sol} = C_{sol} \times V_{sol} \qquad (1)$$

where M_{sol} : the net amount of each component in the extracting solution (µg);
C_{sol} : concentration of each component in the extracting solution (mg/L);
V_{sol} : volume of the extracting solution (mL).

The net values of absolute amount should be calculated by:

$$\text{net } M_{sol} = M_{sol,\ Sample} - M_{sol,\ Blank} \qquad (2)$$

where $M_{sol,\ Sample}$: the net amount (µg) of each component in the extracting solution from the sample filters, No.071d-1,No.071d-2,No.072d-1 and No.072d-2;
$M_{sol,\ Blank}$: the averaged net amount (µg) in the extracting solutions from the blank filters, No.073d-1 and No.073d-2.

3.3 Results

NC distributed the sample filters to 19 laboratories in the participating countries of EANET, and received the data on analytical results. Outline of the submitted results are summarized in Table 3.3. Statistics such as Average, Minimum (Min.), Maximum (Max.), Standard deviation (S.D.) and Number of data (N) were calculated for each analyzed ion. Outlying result which was apart from the average greater than a factor of 3 of S.D. was not included for this statistical calculation. Statistics summary of every result is described in *Appendix 3.2*. As shown in Table 3.3, averages of submitted results were fairly well agreed with the prepared values within a range from -16.5% (Cl^-) to 2.8% (NH_4^+) for Sample No.071d (low amount), and from -4.9% (Cl^-) to -1.5% (NH_4^+) for Sample No.072d (high amount). But there were laboratories of which submitted results were considerably different from prepared values.

The Data Quality Objectives (DQOs) of EANET was specified as ±15% for every constituent by the QA/QC program in EANET. In this report, detected values of three filters (a, b, c) were averaged for every Sample No. and the averaged values were compared with the prepared values taking the DQOs into account. The flag "E" was put to the result of which accuracy exceeded DQOs within a factor of 2 (±15% ~ ±30%), and the flag "X" was put to the data of which accuracy exceeded DQOs more than a factor of 2 (<-30% or >30%).

$$\text{Accuracy (\%)} = (\text{Obtained result} - \text{Prepared value}) / \text{Prepared value} * 100 \qquad (3)$$

Flag E: $-30\% \leq \text{Accuracy} < -15\%$ or $15\% < \text{Accuracy} \leq 30\%$
Flag X: $\text{Accuracy} < -30\%$ or $30\% < \text{Accuracy}$

The results were evaluated by the comparison analyses of i) Concentration dependence between Sample No.071d (low amount) and No.072d (high amount); ii) Individual parameters; iii) Circumstances of analysis in each participating laboratory. The evaluation of results on both of Sample No.071d and No.072d is presented in “3.3.1 Comparison by Sample”. The evaluation of results for each constituent is presented in “3.3.2 Analytical Parameters”. And the evaluation of results by the circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is presented in “3.3.3 Circumstances of Sample Analysis”.

Table 3.3 Summary of analytical results of the sample filters (Reported data after removing outliers)

Constituents	Prepared * (Vp)	Average (Va)	ΔV/Vp * (%)	S.D.	Number (N)	Min.	Max.
Sample No.071d (Low)							
SO_4^{2-} (μg)	20.0	18.5	-7.5	1.96	19	14.4	20.9
Cl^-(μg)	1.60	1.34	-16.5	0.37	17	0.56	2.14
NH_4^+(μg)	4.60	4.73	2.8	1.37	19	2.07	7.6
Sample No.072d (High)							
SO_4^{2-}(μg)	80.0	77.2	-3.5	6.20	19	65.1	90.5
Cl^-(μg)	25.0	23.8	-4.9	1.76	17	20.7	28.2
NH_4^+(μg)	30.0	29.5	-1.5	6.54	19	19.7	47.6

* Prepared: Prepared values which were expected to be extracted from each filter

* ΔV: Average (Va) - Prepared (Vp)

3.3.1 Evaluation of Laboratories' Performance (by sample)

Sample with low amount of Ions

For Sample No.071d (low amount), 13 analytical data in 55 submitted results exceeded the DQOs (±15%) within a factor of 2 (±30%) and were flagged by "E". Also 9 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". A number of flagged data was 22 and the ratio of the flagged data was about 40 percent in total for Sample No.071d (Figure 3.2). Result of SO_4^{2-} had no flags of "X". (Table 3.4 and 3.5)

Table 3.4 Number of flagged data for Sample No.071d (low amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	4	7	2	13
Flag X *	0	3	6	9
Data within DQOs	15	7	11	33
Ratio of Flagged (%)	21.1	58.8	42.1	40.0

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

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

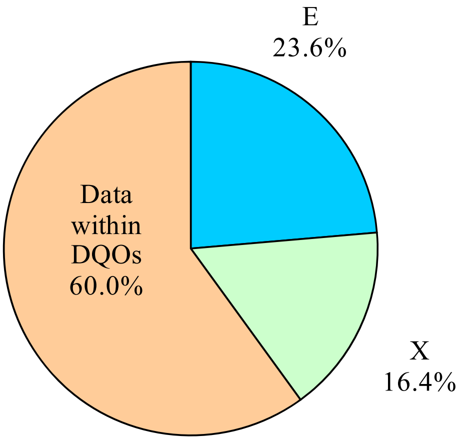


Figure 3.2 **Percentage of flagged data for Sample No.071d (low amount)**

Table 5 **Averaged analytical results of Sample No.071d (low amount)**

Lab. Code		SO_4^{2-} (μg)		Cl^- (μg)		NH_4^+ (μg)
CN01	E	15.9	X	1.0	X	6.7
ID01		20.2	X	0.6	E	3.8
JP01		18.5	E	1.2	X	2.8
JP02		20.2	E	2.0	E	3.8
JP03		19.1		1.4		4.2
JP04		18.8		1.4		4.6
JP06		19.4	E	1.4		4.7
JP07		19.7	E	1.3		5.1
JP08		18.8	X	2.1		4.0
KR01	E	14.4		1.48	X	7.6
MY01		19.8		1.6		4.9
PH01	E	14.9	X	1.1		5.1
RU01		20.2		-	X	6.1
TH01		18.9	X	1.05		5.2
TH02		18.5	E	1.33	X	6.4
TH03		20.9	E	1.28		4.6
TH04	E	16.5		1.36	X	3.1
VN01		20.6	E	1.1		5.2
VN02	E	16.3		-	X	2.1

(Note) E: Value exceeded the DQO (±15%) within a factor of 2

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

<u>Sample with high amount of Ions</u>

For Sample No.072d (high amount), 7 analytical data in 55 submitted results exceeded the DQOs (±15%) within a factor of 2 (±30%) and were flagged by "E". Also 3 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". A number of flagged data was 10 and the ratio of the flagged data was about 18.2 percent in total for Sample No.072d (Fig.3). Result of SO_4^{2-} had no flags of "X". (Table 3.6 and 3.7)

Table 3.6 Number of flagged data for Sample No.072d (high amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	2	2	3	7
Flag X *	0	0	3	3
Data within DQOs	17	15	13	45
Ratio of Flagged Data (%)	10.5	11.8	31.6	18.2

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

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

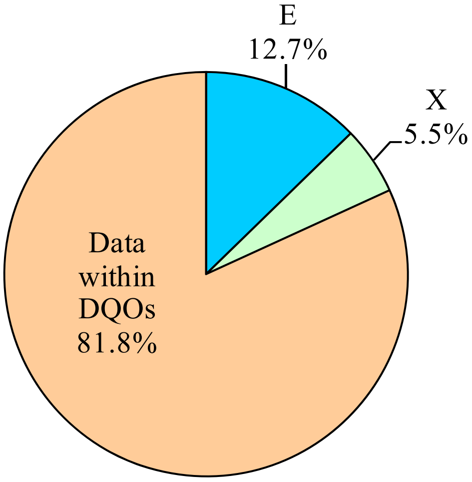


Figure 3.3 Percentage of flagged data for Sample No.072d (high amount)

Table 3.7 Averaged analytical results of Sample No.072d (high amount)

Lab. Code	SO_4^{2-} (μg)		Cl^- (μg)		NH_4^+ (μg)	
CN01		68.3		24.8	X	47.6
ID01		90.5		23.0		26.0
JP01		80.4		24.1	X	19.7
JP02		77.5		23.5		26.1
JP03		75.6		23.2		28.1
JP04		79.5		24.9		29.4
JP06		76.2		24.0		28.2
JP07		77.9		23.3		26.5
JP08		76.2		23.2		28.5
KR01	E	66.1		23.1	X	40.6
MY01		86.8		28.2		32.1
PH01	E	65.1	E	20.7		30.7
RU01		79.0		-		30.2
TH01		79.9		25.2		27.1
TH02		78.1		22.3		33.3
TH03		79.5		25.4	E	35.3
TH04		73.5		24.5	E	21.1
VN01		81.4	E	20.8		28.5
VN02		74.7		-	E	22.4

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

Blank Sample Analysis

Sample No.073d (No.073d-1 and No.073d-2) was supplied for the implementation of blank analysis. Obtained results are summarized in Table 3.8. Medians of SO_4^{2-}, Cl^- and NH_4^+ were 0.44μg, 0.89μg, and 0.40μg, respectively. Blank values were detected in wide range including 0μg. Table 9 shows the ratio of blank value to analytical result. Reverse mesh indicates that there was a flag for Sample No.071d or 072d. Although the blank values were relatively high in some laboratories, these laboratories did not have flags for their analytical results. As a result, a clear relationship between the blank values and the flagged data was not found.

Table 3.8 Analytical results of Sample No.073d (blank)

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	0.00	1.21	0.00
ID01	0.00	0.00	0.00
JP01	0.13	0.65	0.13
JP02	0.27	1.15	0.88
JP03	0.00	0.89	0.33
JP04	0.45	0.72	0.23
JP06	0.51	1.21	0.21
JP07	0.19	0.48	0.48
JP08	0.88	1.08	0.69
KR01	2.41	0.74	0.00
MY01	0.19	0.66	0.31
PH01	1.39	1.20	0.69
RU01	6.29	-	2.78
TH01	0.15	1.22	0.47
TH02	2.40	2.40	0.00
TH03	0.59	1.11	0.49
TH04	0.44	0.83	0.61
VN01	0.20	0.64	0.40
VN02	3.29	-	2.16
Average	1.04	0.95	0.43
Median	0.44	0.89	0.40
Minimum	0.00	0.00	0.00
Maximum	6.29	2.40	2.78
Standard deviation	1.59	0.50	1.03

Table 3.9 The ratio of blank to analytical results (V_{blank} /V_{result})

Lab. Code	High amount SO_4^{2-}	High amount Cl^-	High amount NH_4^+	Low amount SO_4^{2-}	Low amount Cl^-	Low amount NH_4^+
CN01	0.00	0.05	0.00	0.00	1.20	0.00
ID01	0.00	0.00	0.00	0.00	0.00	0.00
JP01	0.00	0.03	0.01	0.01	0.57	0.05
JP02	0.00	0.05	0.03	0.01	0.57	0.23
JP03	0.00	0.04	0.01	0.00	0.64	0.08
JP04	0.01	0.03	0.01	0.02	0.50	0.05
JP06	0.01	0.05	0.01	0.03	0.90	0.05
JP07	0.00	0.02	0.02	0.01	0.37	0.09
JP08	0.01	0.05	0.02	0.05	0.50	0.17
KR01	0.04	0.03	0.00	0.17	0.50	0.00
MY01	0.00	0.02	0.01	0.01	0.40	0.06
PH01	0.02	0.06	0.02	0.09	1.13	0.14
RU01	0.08	-	0.09	0.31	-	0.46
TH01	0.00	0.05	0.02	0.01	1.16	0.09
TH02	0.03	0.11	0.00	0.13	1.80	0.00
TH03	0.01	0.04	0.01	0.03	0.87	0.10
TH04	0.01	0.04	0.02	0.03	0.61	0.20
VN01	0.00	0.03	0.01	0.01	0.57	0.08
VN02	0.04	-	0.10	0.20	-	1.05

🟧 : Flagged data of "E" for Sample No.071d or No.072d

🟨 : Flagged data of "X" for Sample No.071d or No.072d

3.3.2 Evaluation of Laboratories' Performance (by analytical parameters)

The general overviews of the results were presented below in Figures and Tables for each analytical parameter (SO_4^{2-}, Cl^- and NH_4^+). The results received from each laboratory were normalized by prepared values to evaluate their deviation. The numbers of flagged data were also shown in tables for each analytical parameter.

SO_4^{2-} (Sulfate)

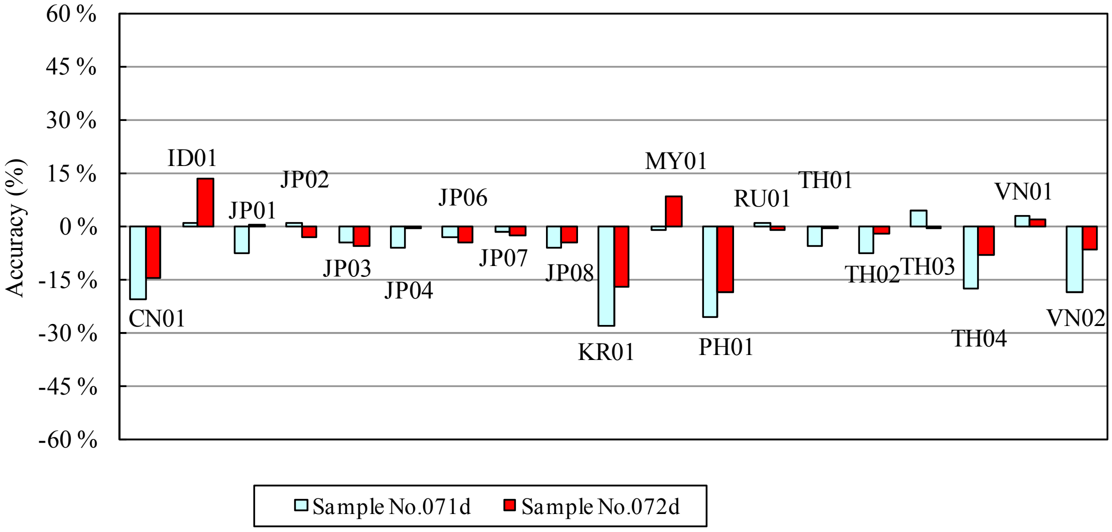


Figure 3.4 Distribution of results for SO_4^{2-} (normalized by prepared value)

Table 3.10 Analytical method and flagged data of SO_4^{2-}

Analytical Method			
Ion Chromatography	19/19		
Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.071d	4	0	21.1
Sample No.072d	2	0	10.5

All of the participating laboratories used Ion Chromatography for the determination of SO_4^{2-}. "E" flags appeared at 4 laboratories for Sample No.071d, and 2 laboratories for Sample No.072d. On the other hand, "X" flag did not appear for both samples.

Cl$^-$ (Chloride)

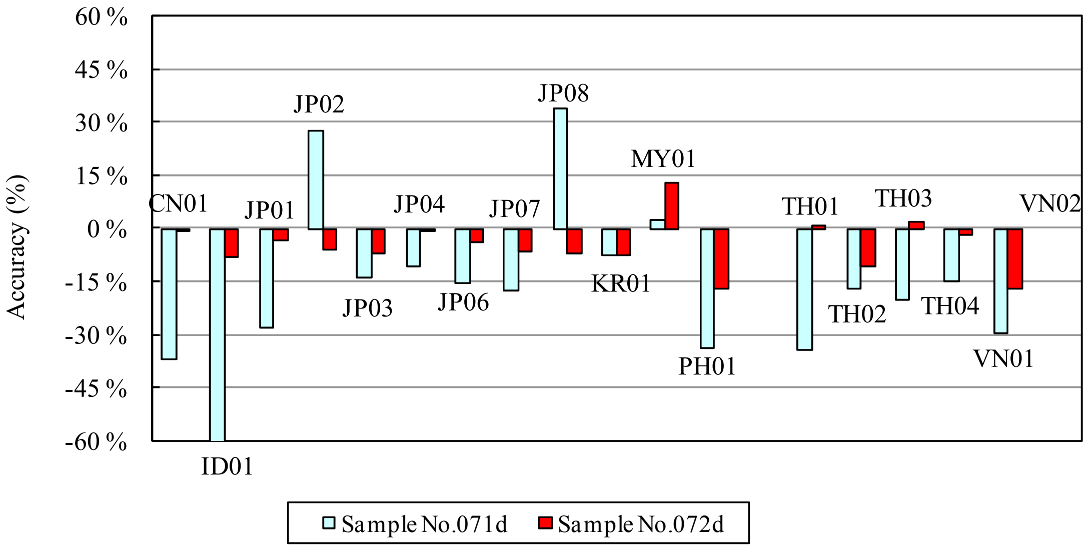


Figure 3.5 Distribution of results for Cl$^-$ (normalized by prepared value)

Table 3.11 Analytical method and flagged data of Cl$^-$

Analytical Method			
Ion Chromatography	17/17		

Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.071d	7	3	58.8
Sample No.072d	2	0	11.8

As same with the analysis of SO_4^{2-}, all laboratories used Ion Chromatography for the determination of Cl$^-$. “E” flags appeared at 7 laboratories for Sample No.071d and “X” flags appeared 3 laboratories. 2 of the data for Sample No.072d marked “E” flags. “X” flag did not appear for No.072d. Particularly the data of ID01 exceeded “prepared value” more than 60%. The ratio of the flagged data for Sample No.071d, which had low amount, was higher than that for Sample No.072d which had high amount.

NH_4^+ (Ammonium)

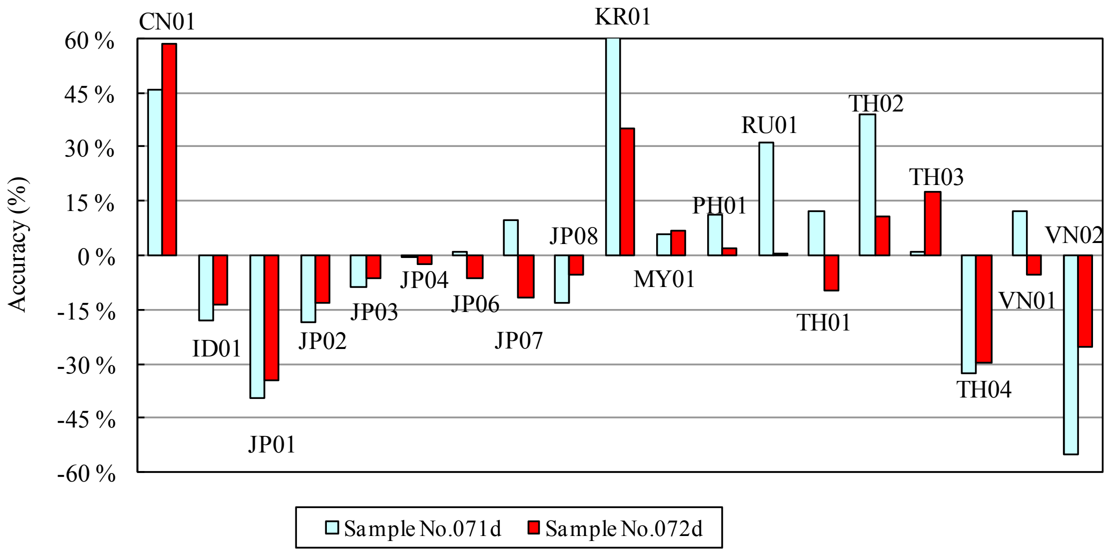


Figure 3.6 Distribution of results for NH_4^+ (normalized by prepared value)

Table 3.12 Analytical method and flagged data of NH_4^+

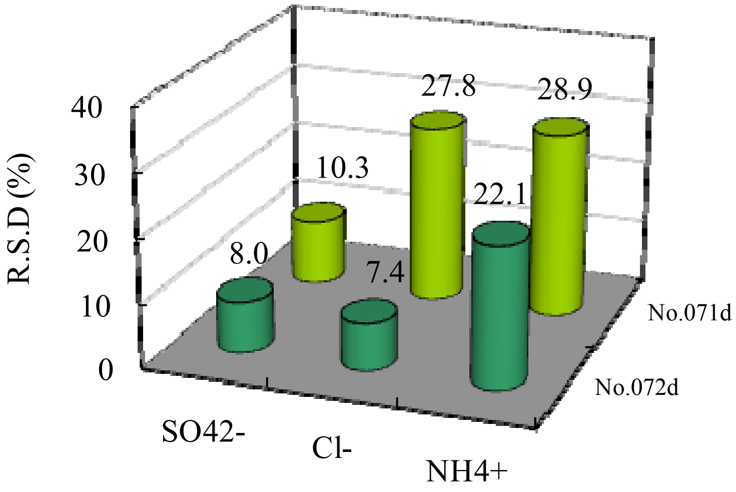
Analytical Method			
Ion Chromatography	17/19		
Spectrometry (Indophenol blue)	1/19		
Spectrometry (Nessler)	1/19		
Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.071d	2	6	42.1
Sample No.072d	3	3	31.6

19 laboratories used recommended analytical method of EANET for the determination of NH_4^+; 17 laboratories used Ion Chromatography and 1 laboratory used Indophenol Spectrophotometry. 1 laboratory used Spectrophotometry other than Indophenol blue method. The ratio of the flagged data for Sample No.071d, which had low amount, was higher than that for Sample No.072d which had high amount. There were 2 “E” flags and 6 “X” flags for Sample No.071d.

3.3.3 Overall Evaluation

Relative Standard Deviation (R.S.D)

The values of the relative standard deviation (R.S.D) for the results of Sample No.071d and No.072d are shown in Figure 3.7. The values of R.S.D for Sample No.071d were higher than those for Sample No.072d. Especially, R.S.D. of Cl^- and NH_4^+ for Sample No.071d showed relatively higher value compared with the others, which were the same as the first and second attempt, 2005-2006. The use of inappropriate range for the calibration standard solution can be pointed out as one of the reasons for unsatisfactory result. The calibration standard solution used in each laboratory is summarized in Table 3.15.



R.S.D (%) = (Standard deviation / Average) x 100(Reported data after removing the outliers)

Figure 3.7 Relative standard deviation of each analyzed constituent

3.3.4 Information on Laboratories

Methodologies Used

As shown in Table 3.13, most of participating laboratories used recommended methods of EANET. All laboratories used Ion Chromatography for the determination of anions. As for determination of NH_4^+, 17 of 19 laboratories used Ion Chromatography and 1 laboratory used Indophenol Spectrophotometry. However, 1 laboratory used the Spectrophotometry other than Indophenol blue method.

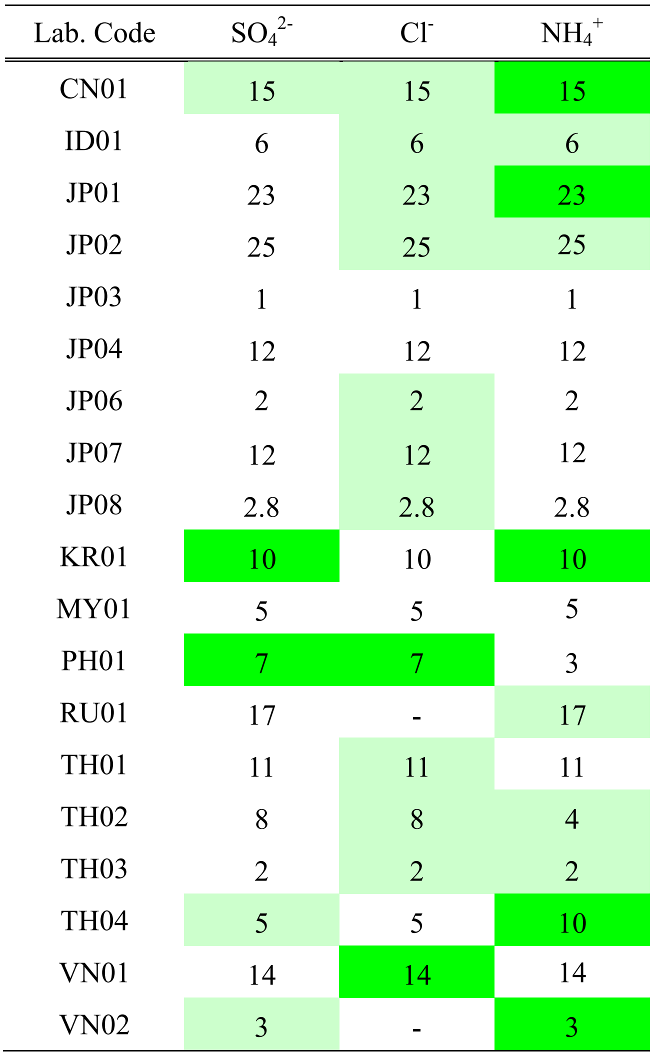
Table 3.13 Analytical methods used for sample analysis

Lab. Code	SO_4^{2-},Cl^-	NH_4^+
CN01	Ion Chromatography	
ID01	Ion Chromatography	
JP01	Ion Chromatography	
JP02	Ion Chromatography	
JP03	Ion Chromatography	
JP04	Ion Chromatography	
JP06	Ion Chromatography	
JP07	Ion Chromatography	
JP08	Ion Chromatography	
KR01	Ion Chromatography	
MY01	Ion Chromatography	
PH01	Ion Chromatography	Indophenol Spectrophotometry
RU01	Ion Chromatography	Spectrophotometry(Nessler)
TH01	Ion Chromatography	
TH02	Ion Chromatography	
TH03	Ion Chromatography	
TH04	Ion Chromatography	
VN01	Ion Chromatography	
VN02	Ion Chromatography	

Staff (number and years of experience)

According to the information about "years of experience for staff in charge" obtained through this project, clear evidence for the relationship with data quality was not found. The average of the years of experience was 9.5 years. Years of experience for staff in charge are summarized in Table 3.14. Reverse mesh in Table 3.14 indicates that there was a flag for Sample No.071d and/or 072d. Reverse mesh with dark color indicate flagged data in both of Sample No.071d and No.072d.

Table 3.14 Years of experience (unit: year)



Lab. Code	SO$_4^{2-}$	Cl$^-$	NH$_4^+$
CN01	15	15	15
ID01	6	6	6
JP01	23	23	23
JP02	25	25	25
JP03	1	1	1
JP04	12	12	12
JP06	2	2	2
JP07	12	12	12
JP08	2.8	2.8	2.8
KR01	10	10	10
MY01	5	5	5
PH01	7	7	3
RU01	17	-	17
TH01	11	11	11
TH02	8	8	4
TH03	2	2	2
TH04	5	5	10
VN01	14	14	14
VN02	3	-	3

(Note) Reverse mesh: Flagged data in Sample No.071d and/or No.072d (Dark color: Flagged data in both of Sample No.071d and No.072d)

Flagged Data

In the results of Sample No.071d and 072d, the total number of flagged data was 32 (E: 20, X: 12) among the whole of 110 values. The attribution of flagged data in each laboratory was presented in Figure 3.8. The number of laboratories with good results without flagged data was 3 (17%). The number of laboratories that submitted data with less than 2 flagged values were 8 (45%) in this attempt. There were three laboratories which had more than 4 flagged data. The analytical procedures in this laboratory should be reconsidered as well as quality of standard solutions, and so on.

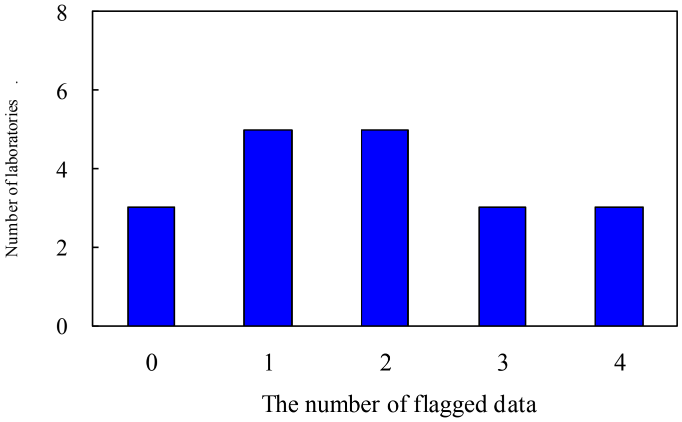


Figure 3.8 Distribution of laboratories with the number of flagged data

Calibration standard solution

Table 3.15 shows the lowest (except to zero) and highest concentrations of the calibration standard solution for the analytical methods used in each laboratory, and also shows the prepared values in the unit of µmol/L. The concentrations of the standard solution in some laboratories were not in the appropriate range for the sample analysis. Flagged data mainly appeared for the laboratories of which the standard solution was not in the appropriate range. A boldfaced number in Table 3.15 indicates that the value of standard solution was less than the prepared value of the low amount sample or more than the prepared value of the high amount sample.

Prepared value should be put between lowest and highest standard solution. However some laboratories used inappropriate solution, especially the flagged data usually appeared for Cl^- in such a case that the lowest standard solution was not less than the prepared value. Thus, it is suggested that if the obtained results is not in the range of the calibration standard, the chemical analysis should be done again by using appropriate range of standard solution.

Table 3.15 Ranges of the calibration standard solution in each laboratory

	SO_4^{2-} (μmol/L)		Cl^- (μmol/L)		NH_4^+ (μmol/L)	
Lab. Code	Lowest	Highest	Lowest	Highest	Lowest	Highest
CN01	8.24	83.1	**22.3**	225.3	18.6	178.8
ID01	5.21	41.67	**14.08**	112.68	11.11	88.89
JP01	5.21	104.17	**14.13**	282.65	11.17	279.17
JP02	0.52	52.08	1.41	141.04	2.78	277.78
JP03	5.21	156	**2.82**	84.6	5.54	111
JP04	1.04	104.1	**2.82**	141.04	2.77	277.16
JP06	1.04	520.51	1.41	705.22	2.77	1385.81
JP07	1.67	83.36	**4.54**	226.80	4.43	221.48
JP08	0.21	62.45	0.56	169.25	1.11	110.86
KR01	5.02	58.46	**12.75**	53.64	**27.72**	221.75
MY01	1.04	83.28	1.41	141.04	2.77	166.30
PH01	1.04	208.20	**2.82**	282.09	2.77	110.86
RU01	6.24	**20.81**	-	-	5.56	222.22
TH01	0.10	104.10	0.28	282.09	0.55	554.32
TH02	2.08	62.42	**5.64**	169.25	4.43	110.86
TH03	2.08	62.46	**2.82**	56.42	5.54	110.86
TH04	0.10	83.28	0.28	225.67	1.11	138.58
VN01	2.08	104.10	**2.82**	141.04	5.54	277.16
VN02	2.08	52.05	-	-	4.43	110.86
Sample No.071d	10.4		2.26		12.8	
Sample No.072d		41.6		35.3		83.1

(Note) Boldfaced number: Standard solution was less/more than the prepared value of low/high amount, respectively.

Reverse mesh: Flagged data in Sample No.071d and/or No.072d (Dark color: Flagged data "X")

Lowest and Highest: lowest/highest concentrations of the calibration standard solution for the analytical methods

3.3.5. Comparison with past surveys

Since 2005, inter-laboratory comparison on dry deposition have been carried out 3 times. The results showing the percentages of flagged data and percentage of data that satisfied the DQOs are shown in Figure 3.9.

As for the high concentration samples, the percentage of data that satisfied DQOs are above 80%. In the case of the low concentration samples, the percentage of data in this survey was 60.0%. This is the lowest percentage among past 3 surveys.

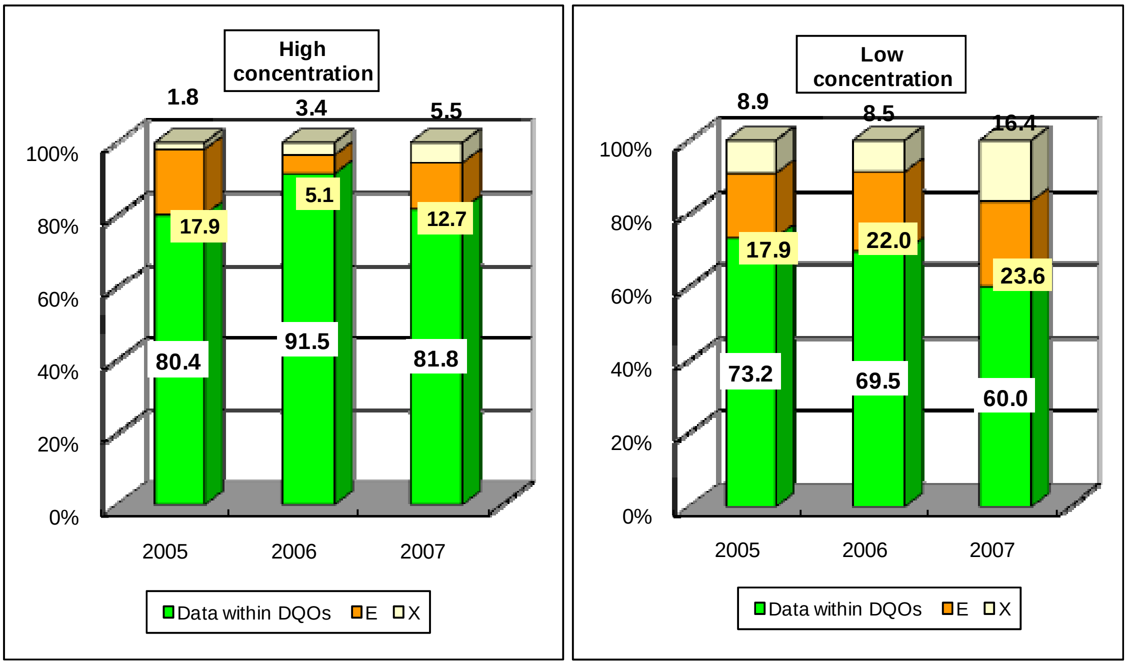


Figure 3.9 Comparison of results from the inter-laboratory comparison projects

The comparison for each parameter in inter-laboratory comparison projects on dry deposition year by year is shown in Figure 3.10. In the results of SO_4^{2-}, there was no flag “X” in each concentration or each year. Comparing the percentage of flagged data in Cl^- and NH_4^+ from project with the previous 2 projects, the percentage of flagged data had increased in both samples, especially that in Cl- low concentration samples were remarkably increased.

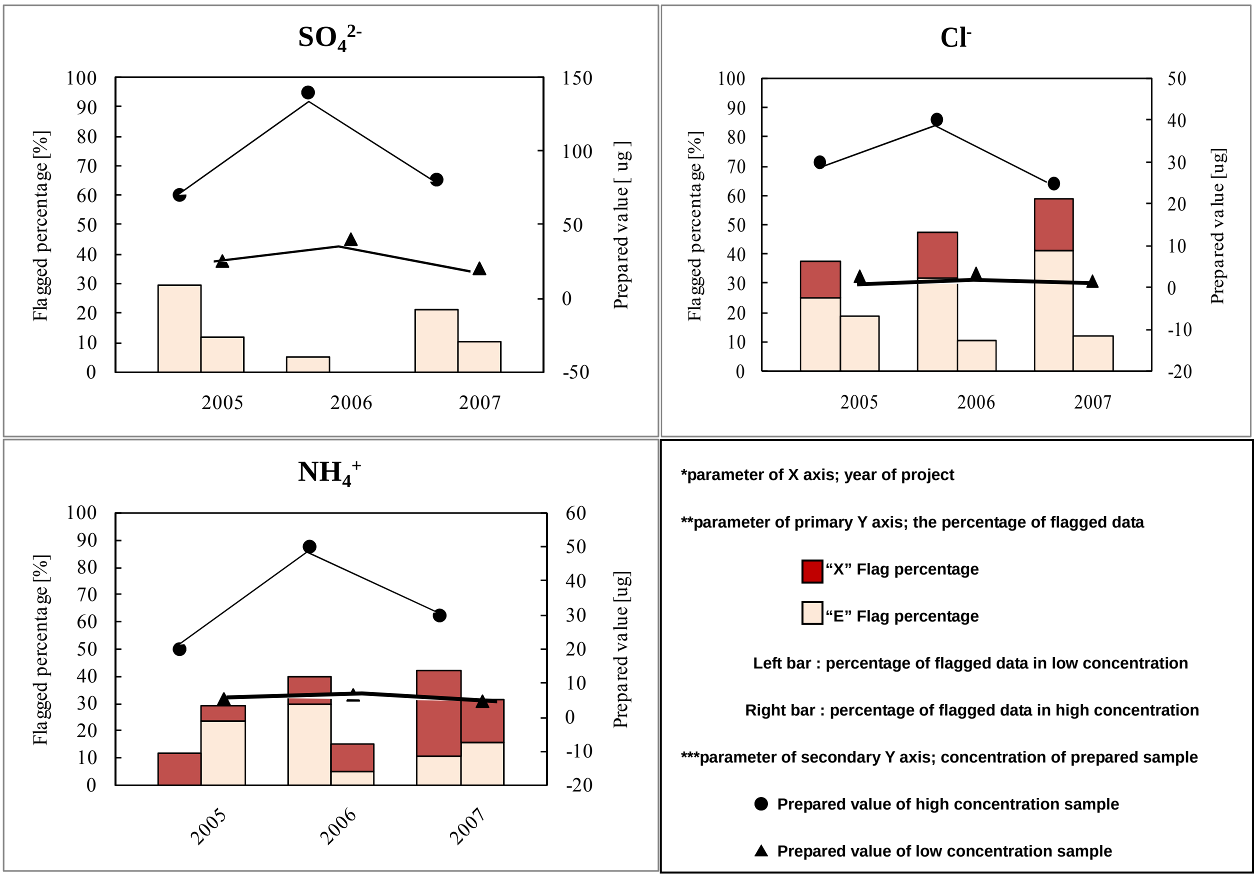


Figure 3.10 Comparison for each parameter in inter-laboratory comparison project

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
March 2000 adopted at:
The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.

3) Technical Documents for Filter Pack Method in East Asia
November 2003 adopted at:
The Third Session of the Scientific Advisory Committee (SAC3)

Appendix 3-1 Participating laboratories

Countries / Laboratories	**Code**
1. China	
1) Xiamen Environmental Monitoring Central Station	**(CN01)**
1. INDONESIA	
2) Environmental Management Center (PUSARPEDAL)	**(ID01)**
2. JAPAN	
3) Hokkaido Institute of Environmental Sciences	**(JP01)**
4) Niigata Prefectural Institute of Public Health and Environmental Sciences	**(JP02)**
5) Nagano Environmental Conservation Research Institute	**(JP03)**
6) Gifu Prefectural Institute of Health and Environmental Science	**(JP04)**
7) Shimane Prefectural Institute of Public Health and Environmental Science	**(JP06)**
8) Okinawa Prefectural Institute of Health and Environment	**(JP07)**
9) Acid Deposition and Oxidant Research Center (ADORC)	**(JP08)**
3. MALAYSIA	
10) Department of Chemistry	**(MY01)**
4. PHILIPPINES	
11) Environmental Management Bureau (EMB)	**(PH01)**
5. REPUBLIC OF KOREA	
12) National Institute of Environmental Research (NIER)	**(KR01)**
6. RUSSIA	
13) Limnological Institute, Russian Academy of Sciences/Siberian Branch	**(RU01)**
7. THAILAND	
14) Pollution Control Department (PCD)	**(TH01)**
15) Khon Kaen University (KKU)	**(TH02)**
16) Chiang Mai University (CMU)	**(TH03)**
17) Environmental Research and Training Center (ERTC)	**(TH04)**
8.VIET NAM	
18) Center for Environmental Research, Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)	**(VN01)**
19) Mid-central Regional Hydro Meteorological Center	**(VN02)**

Appendix 3-2 Summary of data

Analytical results of Sample No.071d (low amount)

Lab. ID	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	15.9	2.21	6.71
ID01	20.2	0.56	3.79
JP01	18.5	1.15	2.79
JP02	20.2	2.04	3.76
JP03	19.1	1.38	4.20
JP04	18.8	1.43	4.62
JP06	19.4	1.35	4.66
JP07	19.7	1.32	5.06
JP08	18.8	2.14	4.01
KR01	14.4	1.48	7.63
MY01	19.8	1.64	4.89
PH01	14.9	1.06	5.12
RU01	20.2	-	6.05
TH01	18.9	1.05	5.18
TH02	18.5	1.33	6.40
TH03	20.9	1.28	4.65
TH04	16.5	1.28	3.10
VN01	20.6	1.13	5.18
VN02	16.3	-	2.07
Prepared value	20.0	1.60	4.60
Number of data	19	17	19
Average	18.5	1.34	4.73
Minimum	14.4	0.56	2.07
Maximum	20.9	2.14	7.63
Standard deviation	1.96	0.37	1.37

Analytical results of Sample No.072d (high amount)

Lab. ID	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	68.3	26.0	47.6
ID01	90.5	23.0	26.0
JP01	80.4	24.1	19.7
JP02	77.5	23.5	26.1
JP03	75.6	23.2	28.1
JP04	79.5	24.9	29.4
JP06	76.2	24.0	28.2
JP07	77.9	23.3	26.5
JP08	76.2	23.2	28.5
KR01	66.1	23.1	40.6
MY01	86.8	28.2	32.1
PH01	65.1	20.7	30.7
RU01	79.0	-	30.2
TH01	79.9	25.2	27.1
TH02	78.1	22.3	33.3
TH03	79.5	25.4	35.3
TH04	73.5	24.5	21.1
VN01	81.4	20.8	28.5
VN02	74.7	-	22.4
Prepared value	80.0	25.0	30.0
Number of data	19	17	19
Average	77.2	23.8	29.5
Minimum	65.1	20.7	19.7
Maximum	90.5	28.2	47.6
Standard deviation	6.04	1.71	6.36

4. 9th INTER-LABORATORY COMPARISON PROJECT ON SOIL

4.1 Introduction

The Inter-laboratory comparison project on soil sample analysis started in 1999 as one of the activities within the QA/QC program on Soil and Vegetation Monitoring. The inter-laboratories precision should be clarified as well as the within-laboratory and repeatability precisions in the project to improve the analytical quality of the EANET laboratories. Factors related to the precisions have been discussed through the previous projects.

Soil analysis has relatively complicated procedures and many steps compared with analysis of water samples. Steps in the procedures of soil analysis may be related to the variation among laboratories; e.g. extraction, instrumental analysis and/or titration. Results of the first three projects from 1999 to 2001 suggested that instrumental analysis have relatively large effect on the total precision of soil analysis, and the following analytical conditions could affect results:

- Addition of La or Sr solution for AAS analysis of Ex-Ca
- Preparation method of standard solution
- Instrument for Ex-K and Na analysis

The participating laboratories shared the information on these possible factors to improve the precisions.

Moreover, other possible factors, such as level of the concentrations, were suggested in the previous projects. Further investigation should be considered taking concentrations of the samples into account.

In the 9th project, NC provided two soil samples (No.071 and 072) to laboratories to improve the inter-laboratories precision further more by standardization of the methods. In this report, the data from participating laboratories were evaluated statistically according to the QA/QC program for soil monitoring, and the results may be utilized for estimation of inter-laboratory variability in soil monitoring, and provide useful information to improve precision of soil analysis on EANET.

4.2 Procedures

4.2.1 Participating Laboratories

Fifteen laboratories of 9 countries participated in the 9th project. Names of the participating laboratories are listed in Appendix 4-1.

4.2.2 Description of Samples

The characteristics of the soil samples were as follows:

Sample No. 071: Red soil (Acrisols)
Sample No. 072: Brown forest soil (Cambisols)

Soils for Sample No. 071 and 072 were collected in Hiba (*Thujopsis dolabrata*) and Japanese cedar (*Cryptomeria japonica*) forests respectively in Ishikawa Prefecture.

Soil was collected from B-horizon in the forest floor. The soils was air-dried, sieved to separate the fine earth fraction (< 2 mm), and mixed well by the following procedures: the bulk sample was divided into two parts, each part was mixed well, the parts were joined and mixed well, and then the sample was divided again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of ca. 500 g were weighed out, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (20kGy) for distributing (exporting) to the participating countries.

4.2.3 Parameters Analyzed

All the participating laboratories were expected to measure all the parameters (Table 4.1).

Table 4.1. Parameters to be measured

Parameters	Unit	No. 061 and 062
a) Moisture Content	wt %	M
b) pH (H_2O)		M
c) pH (KCl)		M
d) Exchangeable Ca	cmol(+) kg^{-1}	M
e) Exchangeable Mg	cmol(+) kg^{-1}	M
f) Exchangeable K	cmol(+) kg^{-1}	M
g) Exchangeable Na	cmol(+) kg^{-1}	M
h) Exchangeable Acidity	cmol(+) kg^{-1}	M
i) Exchangeable Al	cmol(+) kg^{-1}	M
j) Exchangeable H	cmol(+) kg^{-1}	M

M: Mandatory items

“Exchangeable” were abbreviated to “Ex-“ in this report; e.g. Ex-Ca, Ex-Mg, etc.

4.2.4 Analytical Methodologies

All the procedures for chemical analysis were carried out basically according to the “Technical Manual for Soil and Vegetation Monitoring in East Asia” (2nd ISAG, 2000).

In the respective laboratories, all the parameters except moisture content were analyzed three times under the same conditions (repeatability condition: analyst, time, and instrument are the same; three replicates). Then, under within-laboratory-reproducibility condition (part or all of analyst, time, and instrument are different), all the analytical procedures should be repeated twice.

Moisture content was analyzed with three replicates, and the average is used for calculation of all the parameters.

4.2.4.1 Standardization of methods

All the procedures for chemical analysis should be carried out basically according to the “Technical Documents for Soil and Vegetation Monitoring in East Asia (March 2000, Adopted at: The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia)”.

In the 8th project,

(1) **Atomic absorption spectrometry (AAS)** method should be used basically for analysis of Ex-Ca, Mg, K and Na. (If it is impossible to use AAS, Flame (emission) photometry method is allowable for Ex-K and Na).
(2) **Titration method** should be used for analysis of EX-acidity, Al and H.
(3) **Calibration curve method** should be used for determination of Ex-Ca, Mg, K and Na.
(4) The Samples should be extracted and diluted with **1M CH_3COONH_4 (pH 7.0)** for analysis of Ex-Ca, Mg, K and Na. Then, 1M CH_3COONH_4 (pH 7.0) solution should be used to prepare each standard solution as the solvent.
(5) **Sr** should be added to the samples and each standard solution to eliminate the interference of the sample for analysis of Ex-Ca and Mg. These are to be the same concentration Sr. (If Sr can not be obtained, La is allowable.)

4.2.4.2 Procedures for Ex-base cations

(1) Extract from air-dry sample with 1M CH_3COONH_4 (pH 7.0) solution. (According to the “Technical Documents for Soil and Vegetation Monitoring in East Asia”)

(2) Pipette an appropriate aliquot of the soil extract into volumetric flask and add 100g-Sr/L solution to be 1000mg-Sr/L as final concentration Sr. ($SrCl_2$ solution eliminates the interference of the sample.) And then make to volume with 1M CH_3COONH_4 (pH 7.0). This solution is named " Prepared sample".

(3) Prepare three "prepared samples".

(4) Prepare each standard solution with diluting 1M CH_3COONH_4 (pH 7.0) solution.

(5) Add 100g-Sr/L solution to each standard solution to be the same concentration $SrCl_2$ as the sample.

(6) Analyze the standard solution and the prepared samples by AAS.

(7) Store the calibration curves certainly and report them together with reporting formats.

(8) **Repeat the procedure 1) - 7) twice.**

(9) Calculation of content in the soil

Content in the soil could be calculated by the following formulas:

Ex-Ca (cmol(+)/kg soil) = [A * B * V * mcf]/[10 * 20.04 * S]

Ex-Mg (cmol(+)/kg soil) = [A * B * V * mcf]/[10 * 12.15 * S]

Ex-K (cmol(+)/kg soil) = [A * B * V* mcf]/[10 * 39.10 * S]

Ex-Na (cmol(+)/kg soil) = [A * B * V* mcf]/[10 * 23.00 * S]

Where

A = Measurement values of prepared (diluted) samples (mg/L)

B = Dilution ratio (B = 2, if 25mL sample was diluted to 50 mL for making prepared sample.)

mcf = Moisture correction factor (Measured value)

S = Weight of air-dry sample (g)

V = Volume of extract (mL)

4.2.4.3 Procedures for Ex-acidity

(1) Extraction and titration would be carried out according to the "Technical Documents for Soil and Vegetation Monitoring in East Asia" basically.

(2) Prepare three samples. Analyze each sample and at least one blank.

(3) Repeat the procedure twice

(4) Calculation of content in the soil

Content in the soil could be calculated by the following formulas:

Ex-Acidity (cmol (+)/kg) = $[(A_{NaOH} - bl_{NaOH}) * M_{NaOH} * c * 100 * mcf] / S$

Ex-Al (cmol (+)/kg) = $[(A_{HCl} - bl_{HCl}) * M_{HCl} * c * 100 * mcf] / S$

Ex-H (cmol (+)/kg) = $[(A_{NaOH} - bl_{NaOH}) * M_{NaOH} - (A_{HCl} - bl_{HCl}) * M_{HCl}] * c * 100 * mcf] / S$

Where

A_{NaOH} = Titration volume of 0.025 M NaOH solution needed for percolate (mL)

A_{HCl} = Titration volume of 0.02 M HCl solution needed for percolate (mL)

bl_{NaOH} = Titration volume of 0.025M NaOH solution needed for blank (mL)

bl_{HCl} = Titration volume of 0.02M HCl solution needed for blank (mL)
M_{NaOH} = Molarity of NaOH solution (mol/L)
M_{HCl} = Molarity of HCl solution (mol/L)
S = Weight of air-dry sample (g)
c = Aliquot factor (c = 2, if 50mL percolate of 100mL is used.)

4.2.4.4 Reporting

(1) Preparation of the report

Digital formats (Microsoft Excel) for reporting were provided to the participating laboratories, and the laboratories were requested to fill in the formats. Contents in the soil sample would be calculated automatically by the formula above if the formats were filled in.

(2) Submission of the report

Data reporting formats together with all of the copy of calibration curve were submitted by using digital devices.

4.2.5 Data Checking Procedures

Data were statistically evaluated according to the following procedures described in the "Technical Manual for Soil and Vegetation Monitoring in East Asia" (2nd ISAG, 2000). Data of the soil content with one decimal place for pH and two decimal places for Ex-cations and acidity were used for the analysis.

1) Verification of data

Evenness of within-laboratory precision was verified by Cochran methods, then the laboratory averages was verified by Grubbs methods.

2) Analysis of variance and estimation of precision

Total variation among laboratories includes within-laboratory and inter-laboratories variation. As described in the following equation, Total sum of square (S_T) is consisted of Sum of square inter-laboratories (S_R), Sum of square within-laboratory (S_{RW}) and Sum of square repeatability (S_r).

$$S_T = S_R + S_{RW} + S_r$$

Based on the above equation, Inter-laboratories variance, Within-laboratory-reproducibility variance, and Repeatability variance were calculated, and then the precisions were estimated.

3) Calculation of permissible tolerance

Permissible tolerances were calculated based on the above precisions.

4.3 Results

4.3.1 Outline of Laboratories' Performance

Basic statistics calculated from the laboratory averages are presented in Table 4.2 for the respective parameters, and especially coefficients of variation (CVs) among laboratories were shown in Figure 4.1. For both entire (non-verified) data and verified data, the statistics were calculated. Outliers detected by Cochran-Grubbs methods were removed for the verified data. Detailed data on the Cochran-Grubbs methods were shown in the next section.

As for the entire data, the variations (CVs) among the participating laboratories were different in parameter. CVs were relatively small, 3.0 – 9.4%, in pH(H_2O) and pH(KCl) probably due to their simple analytical procedures and logarithmic values as discussed in the previous reports (ADORC, 2001a; 2000b). However, these values were higher than those of the previous projects; e.g. 2.0 - 3.7% in the 8th project. CVs in exchangeable cations were relatively large, and remarkably large CVs (larger than 100%) were observed especially in Ex-Ca of No. 072 and Ex-Na of both samples. On the other hand, variations in Ex-acidity and Al were relatively small, 27 – 31%, also probably due to their relatively simple titration procedures. However, these values were also higher than those of the previous projects; e.g. 15 - 21% in the 8th project.

As for the verified data, the variations (CVs) of pH(H_2O) and pH(KCl) were very small, 2.3 – 3.1%. CVs for other parameters except Ex-Ca of No. 071 were improved after removing outliers. CVs of Ex-acidity and Al were 12 – 18%. CVs of Ex-H were still relatively large, probably because the values calculated based on Ex-acidity and Ex-Al included errors of these parameters.

The averages of triplicate analyses (three-time analysis in repeatability condition) and the average of repeat analyses (in within-laboratory-reproducibility condition) in each laboratory were shown in Figure 4.2-1, 4.2-2, 4.2-3 and 4.2-4. Error bar shows standard deviation of triplicate analyses but it cannot be found in most figures due to its small length. This indicates that triplicate analyses were carried out with high precision under the repeatability condition. Averages of triplicate samples for the respective laboratories were of similar values, and the repeat analyses might also be carried out with high precision under the within-laboratory-reproducibility condition.

Three laboratories, “mn01”, “vn02”, and “vn03”, did not analyze Ex-base cations.

Table 4.2. Basic statistics of the entire data and the verified data

(Entire data)

Statistics	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol(+) kg^{-1}						
	No. 071								
Number of Laboratories	15	15	12	12	12	12	15	15	15
Total average	4.6	3.7	0.19	1.00	0.41	0.30	16.13	14.98	2.11
Median	4.6	3.7	0.17	0.86	0.36	0.13	16.78	16.43	1.67
Maximum	4.9	3.9	0.45	3.28	1.44	1.73	20.36	20.31	11.94
Minimum	3.6	3.5	0.00	0.00	0.00	0.00	3.39	2.87	0.00
Standard deviation	0.3	0.1	0.16	0.78	0.38	0.49	4.49	4.12	2.85
CV (%)[*1]	6.6	3.0	82.1	78.2	94	162	27.8	27.5	135
	No. 072								
Number of Laboratories	15	15	12	12	12	12	15	15	15
Total average	5.1	4.2	2.82	0.67	0.21	0.30	3.32	2.96	0.59
Median	5.1	4.1	2.20	0.56	0.16	0.13	3.54	3.02	0.53
Maximum	5.4	5.6	11.57	2.05	0.66	1.89	4.77	4.49	1.51
Minimum	4.4	4.0	0.01	0.00	0.00	0.00	0.82	0.53	0.05
Standard deviation	0.2	0.4	3.01	0.49	0.20	0.52	0.91	0.92	0.38
CV (%)[*1]	4.4	9.4	106.7	73.7	92	172	27.4	31.1	64

(Verified data)[*2]

Statistics	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol(+) kg^{-1}						
	No. 071								
Number of Laboratories	13	15	10	10	10	9	12	12	14
Total average	4.6	3.7	0.18	0.87	0.26	0.11	17.79	15.89	1.41
Median	4.6	3.7	0.13	0.86	0.30	0.12	18.49	16.65	1.40
Maximum	4.9	3.9	0.45	1.29	0.39	0.22	20.36	20.31	2.71
Minimum	4.4	3.5	0.00	0.58	0.00	0.00	14.73	9.89	0.00
Standard deviation	0.1	0.1	0.17	0.21	0.13	0.06	2.14	2.67	0.89
CV (%)[*1]	3.1	3.0	92.7	23.6	51.2	52.8	12.0	16.8	63.2
	No. 072								
Number of Laboratories	14	14	10	8	12	8	14	9	13
Total average	5.1	4.1	1.72	0.56	0.21	0.09	3.49	2.94	0.47
Median	5.1	4.1	1.98	0.56	0.16	0.10	3.57	3.13	0.51
Maximum	5.4	4.3	2.67	0.70	0.66	0.14	4.77	3.35	0.77
Minimum	5.0	4.0	0.01	0.35	0.00	0.00	2.49	2.13	0.05
Standard deviation	0.1	0.1	0.80	0.11	0.20	0.05	0.61	0.43	0.20
CV (%)[*1]	2.4	2.3	46.8	19.3	92.0	55.0	17.5	14.5	43.2

Note: *1. CV, Coefficient of variance (%) = (standard deviation/average)*100 *2.Outliers judged by Cochran-Grubbs methods and calculation mistakes were removed.

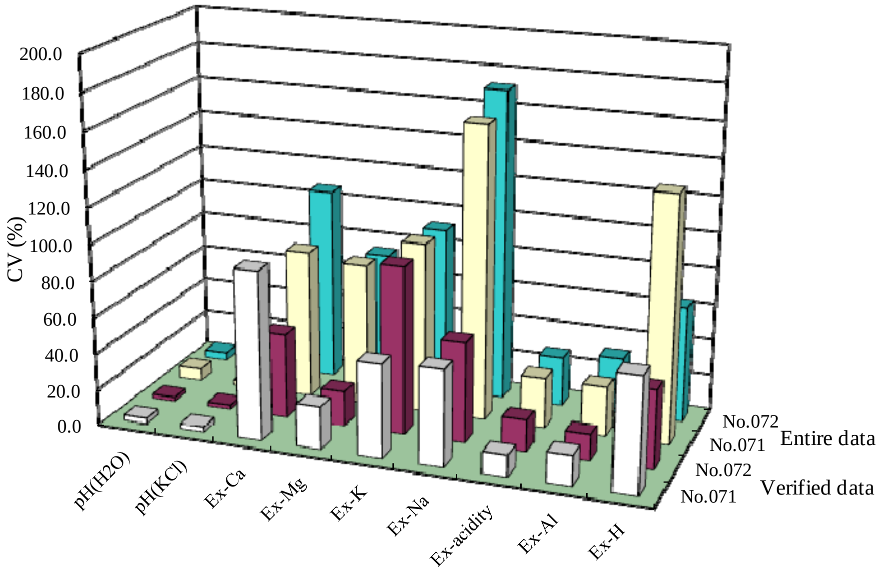


Figure 4.1. CV among laboratories

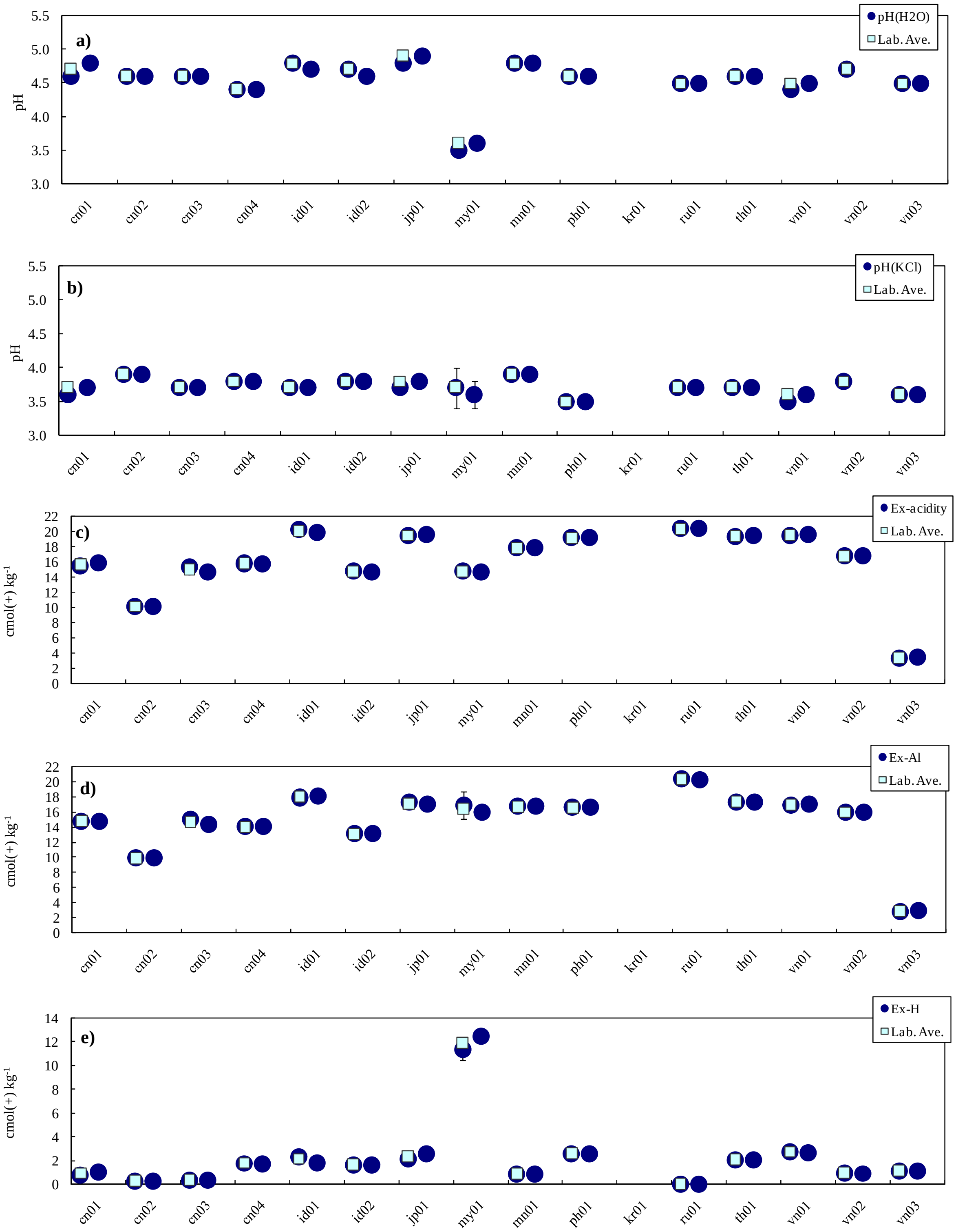


Figure 4.2-1 Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 071. Error bar shows standard deviation of triplicate analysis.

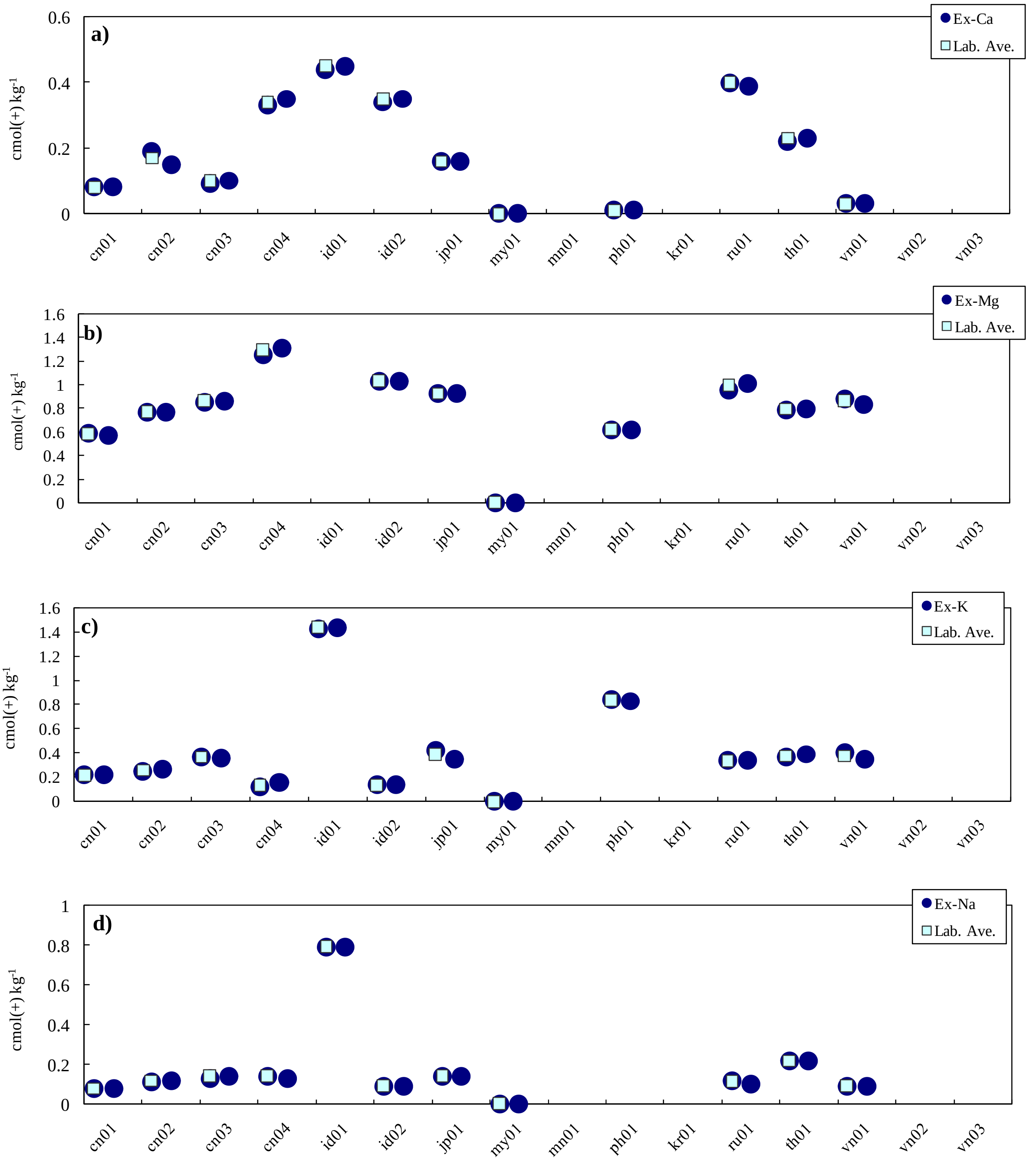


Figure 4.2-2 Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 071. Error bar shows standard deviation of triplicate analysis.

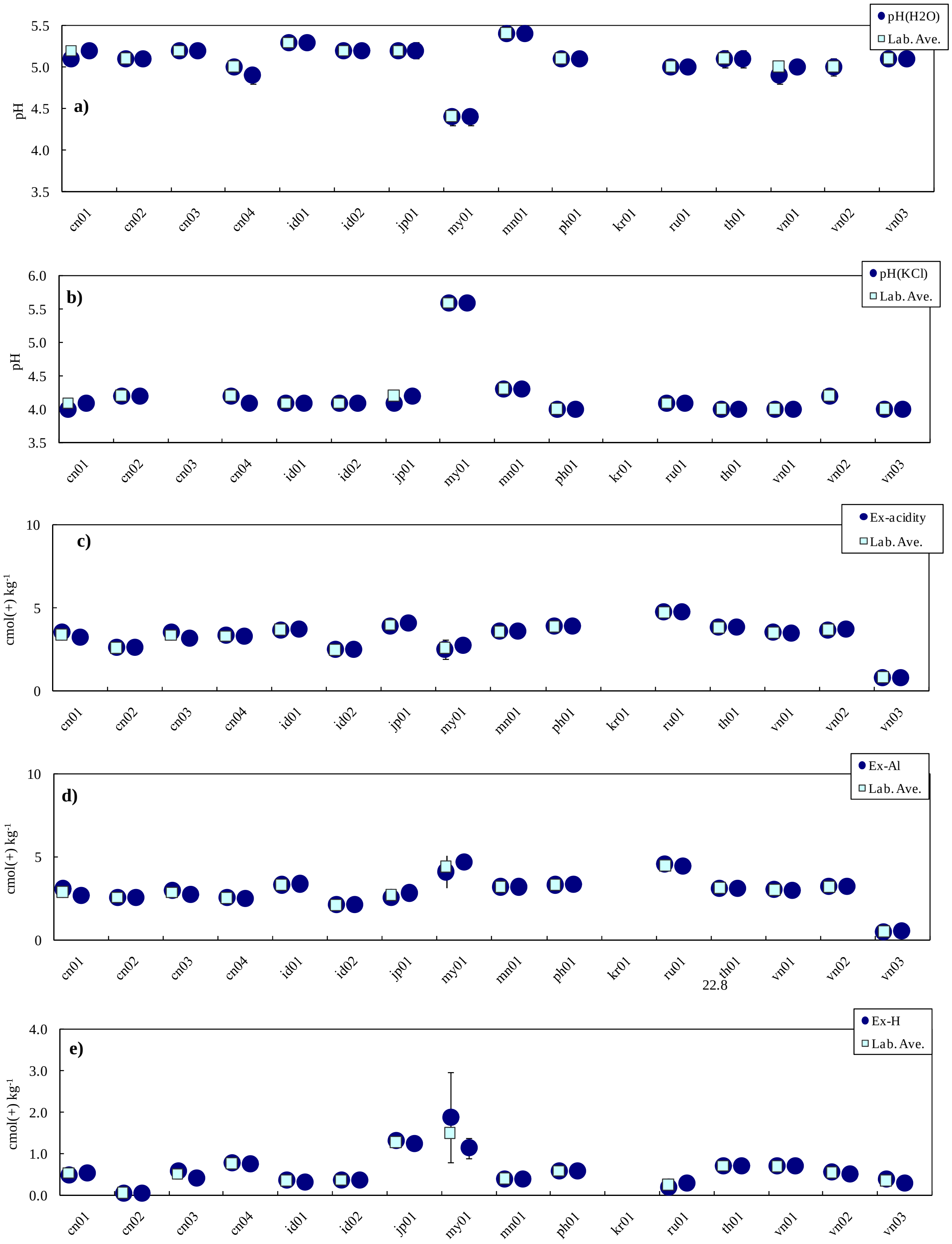


Figure 4.2-3 Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 072. Error bar shows standard deviation of triplicate analysis.

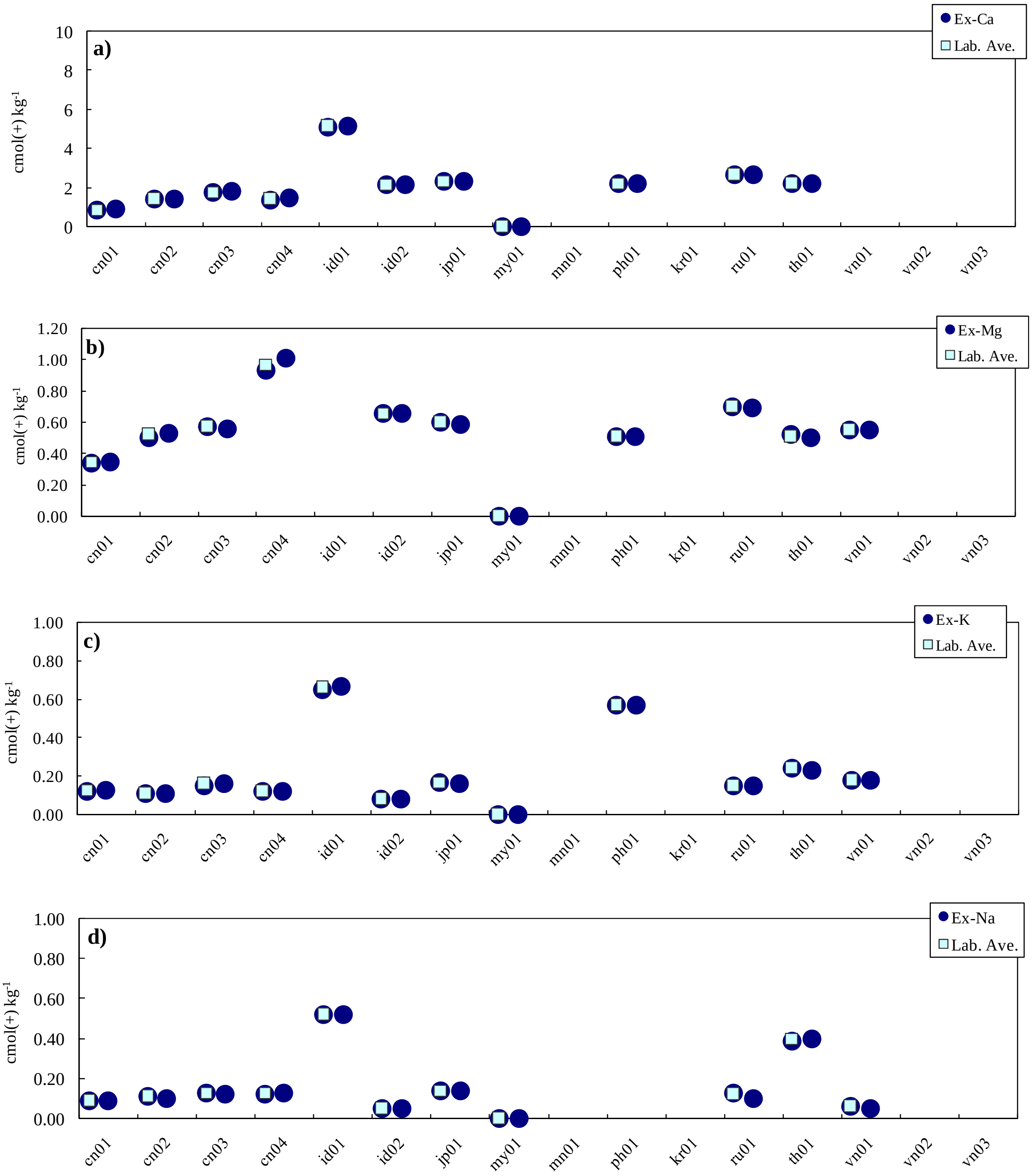


Figure 4.2-4 Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 072. Error bar shows standard deviation of triplicate analysis.

4.3.2 Detection of outliers

The results of verification by Cochran-Grubbs methods were presented in Table 4.3-1 and 4.3-2.

Laboratories, which have large difference in repeat analyses, were judged as outliers by Cochran method (examination of the evenness of within-laboratory precision): e.g. “cn01” in Ex-Al of No. 072, “cn03” in Ex-acidity of No. 071, “my01” in Ex-Al of No. 071, “jp01” in Ex-Al of No. 072, etc. Then, the rest of data were tested, and laboratories, which have remarkably large or small average, were judged as outliers by Grubbs method (examination of the average value of each laboratory): e.g. “id01” in Ex-Mg, K and Na of No. 071, “ph01” in Ex-Na and Ex-K of No. 071, “th01” in Ex-Na of No. 072, “vn03” in Ex-acidity and Al of No. 071, etc.

In a few laboratories, more than three outliers were detected. It was suggested that some systematic errors in the analytical procedures might occur in such laboratories. No outlier was detected in pH (KCl) of No. 071, and Ex-K of No. 072. One to three outliers were detected in most parameters.

Table 4.3-1. Data verified by Cochran-Grubbs methods: No. 071

Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
				cmol(+) kg^{-1}						
cn01	1st	4.6*c	3.6	0.08	0.59	0.22	0.08	15.51	14.74	0.77
	2nd	4.8*c	3.7	0.08	0.57	0.22	0.08	15.84	14.78	1.06
cn02	1st	4.7	3.9	0.19*c	0.77	0.25	0.11	10.15*g	9.90	0.26
	2nd	4.7	3.9	0.15*c	0.77	0.27	0.12	10.13*g	9.88	0.25
cn03	1st	4.6	3.7	0.09	0.85	0.37	0.13	15.31*c	14.94*c	0.37
	2nd	4.6	3.7	0.09	0.86	0.36	0.13	14.7*c	14.36*c	0.34
cn04	1st	4.4	3.8	0.33*c	1.26	0.12	0.13	15.80	14.04	1.76
	2nd	4.4	3.8	0.35*c	1.32	0.16	0.13	15.76	14.01	1.74
id01	1st	4.7	3.7	0.44	3.26*g	1.43*g	0.79*g	20.22	17.88	2.34
	2nd	4.7	3.7	0.45	3.29*g	1.43*g	0.80*g	19.90	18.06	1.84
id02	1st	4.7	3.8	0.35	1.03	0.14	0.09	14.73	13.06	1.67
	2nd	4.6	3.8	0.35	1.03	0.14	0.09	14.72	13.06	1.66
jp01	1st	4.8	3.7	0.16	0.93	0.42	0.14	19.40	17.27	2.14
	2nd	4.9	3.8	0.16	0.93	0.35	0.14	19.53	16.97	2.56
my01	1st	3.6*g	3.7	0.00	0.00*g	0.00	0.00	14.76	16.87*c	11.36*c
	2nd	3.6*g	3.6	0.00	0.00*g	0.00	0.00	14.69	15.98*c	12.51*c
mn01	1st	4.8	3.9					17.82	16.72	0.88
	2nd	4.8	3.9					17.82	16.72	0.88
ph01	1st	4.6	3.5	0.01	0.62	0.84*g	1.73*g	19.16	16.58	2.58
	2nd	4.6	3.5	0.01	0.62	0.83*g	1.73*g	19.15	16.55	2.60
kr01	1st									
	2nd									
ru01	1st	4.5	3.7	0.40	0.96	0.34	0.13*c	20.38	20.36	0.00
	2nd	4.5	3.7	0.39	1.00	0.34	0.10*c	20.33	20.25	0.00
th01	1st	4.6	3.7	0.22	0.79	0.37	0.22	19.38	17.31	2.07
	2nd	4.6	3.7	0.23	0.80	0.39	0.22	19.40	17.33	2.08
vn01	1st	4.4	3.5	0.03	0.88	0.40	0.10	19.43	16.89	2.72
	2nd	4.5	3.6	0.03	0.83	0.35	0.09	19.58	17.06	2.69
vn02	1st	4.7	3.8					16.73	15.99	0.97
	2nd							16.82	15.92	0.90
vn03	1st	4.5	3.6					3.35*g	2.80*g	1.14
	2nd	4.5	3.6					3.43*g	2.92*g	1.11

Note: The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g, respectively.

Table 4.3-2. Data verified by Cochran-Grubbs methods: No. 072

Lab.	Repeat analysis	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
				cmol(+) kg^{-1}						
cn01	1st	5.1	4.0	0.87	0.34	0.13	0.09	3.58	3.08*c	0.50
	2nd	5.2	4.1	0.89	0.34	0.13	0.09	3.24	2.69*c	0.55
cn02	1st	5.1	4.2	1.41	0.50*c	0.11	0.11	2.61	2.56	0.05
	2nd	5.1	4.2	1.45	0.53*c	0.11	0.10	2.63	2.58	0.05
cn03	1st	5.2	4.1	1.77	0.57	0.15	0.13	3.56	2.97*c	0.59
	2nd	5.2	4.1	1.79	0.56	0.16	0.12	3.19	2.77*c	0.42
cn04	1st	5.0	4.2	1.36	0.93*c	0.12	0.12	3.34	2.55	0.79
	2nd	4.9	4.1	1.49	1.01*c	0.12	0.13	3.29	2.53	0.75
id01	1st	5.3	4.1	5.09*g	2.04*g	0.65	0.53*g	3.68	3.32	0.36
	2nd	5.3	4.1	5.17*g	2.05*g	0.67	0.52*g	3.71	3.38	0.34
id02	1st	5.2	4.1	2.18	0.65	0.07	0.04	2.49	2.13	0.36
	2nd	5.2	4.1	2.18	0.65	0.08	0.04	2.49	2.13	0.36
jp01	1st	5.2	4.1	2.34	0.60	0.17	0.13	3.90	2.59*c	1.31*g
	2nd	5.2	4.2	2.34	0.59	0.16	0.14	4.09	2.85*c	1.24*g
my01	1st	4.4*g	5.6*g	0.01	0.00*g	0.00	0.00	2.50	4.11*c	1.88*c
	2nd	4.4*g	5.6*g	0.00	0.00*g	0.00	0.00	2.73	4.68*c	1.13*c
mn01	1st	5.4	4.3					3.60	3.20	0.40
	2nd	5.4	4.3					3.60	3.20	0.40
ph01	1st	5.1	4.0	2.24	0.51	0.57	1.89*g	3.90	3.32	0.58
	2nd	5.1	4.0	2.24	0.51	0.57	1.89*g	3.91	3.33	0.58
kr01	1st									
	2nd									
ru01	1st	5.0	4.1	2.68	0.70	0.15	0.13*c	4.77	4.54*c	0.20
	2nd	5.0	4.1	2.65	0.69	0.15	0.10*c	4.77	4.44*c	0.30
th01	1st	5.1	4.0	2.22	0.52	0.24	0.39*g	3.84	3.12	0.71
	2nd	5.1	4.0	2.21	0.51	0.23	0.40*g	3.83	3.12	0.71
vn01	1st	4.9	4.0	11.65*g	0.55	0.18	0.06	3.55	3.02	0.70
	2nd	5.0	4.0	11.49*g	0.55	0.18	0.05	3.52	3.00	0.70
vn02	1st	5.0	4.2					3.68	3.21	0.56
	2nd							3.74	3.21	0.53
vn03	1st	5.1	4.0					0.83*g	0.51g	0.40
	2nd	5.1	4.0					0.81*g	0.55*g	0.30

Note: The outliers judged by Cochran and Grubbs methods were marked with asterisk c and g, respectively.

4.3.3 Overall analysis

Analysis of variance (ANOVA) for the entire data and verified data were shown in Table 4.4-1 and 4.4-2, respectively. “Repeatability-precision”, “within-laboratory-precision” and “inter-laboratories-precision” were estimated. In the following section, the results of verified data were mainly discussed (see Table 4.4-2).

1) Repeatability-precision

Repeatability standard deviations were relatively small for most of the parameters in the verified data, and CVs of most parameters were smaller than 10%. Especially CVs of pH(H_2O) and pH(KCl) in No.072 were smaller than 1.0%, and those of Ex-acidity and Al were mostly smaller 1.0% except for Ex-acidity of No. 072.

It seems that triplicate analyses were carried out under the same condition. Process on extraction, dilution of the sample, and stability of the instruments might affect the results. The small CVs suggested that the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

2) Within-laboratory precision

Within-laboratory standard deviations were also relatively small for most of the parameters in the verified data, and CVs of most parameters were smaller than 10%. Especially CVs of Ex-acidity and Al were mostly smaller 1.0% except for Ex-acidity of No. 072.

For most parameters, the CVs were smaller than those of repeatability precision. It was suggested that the average of triplicate analyses under the repeatability condition could be representative value for the analysis in a laboratory. It was also suggested that the participating laboratories could analyze the parameters with their own standard procedures.

3) Inter-laboratories precision

CVs of the inter-laboratories precision were smaller than 5% in pH(H_2O) and pH(KCl) of No. 071. CVs of exchangeable base cations were mostly larger than 40%, while those of Ex-acidity and Al were mostly smaller than 20%.

4) Calculation of permissible tolerance

As for the repeatability limit and within-laboratory reproducibility limit, values might be enough small, and it could be used as a reference value for the repeat analysis on the instrumental analysis in the respective laboratories. As for the reproducibility limit, inter-laboratories precision should be improved for Ex-base cations, and then the discussion should be carried out.

Table 4.4-1 Analysis of variance for the entire data

Statistics	No. 071								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	14	12	12	12	12	15	15	15
Total sum of square	141903	96970	190	5165	856	478	2107607	1816241	36001
ST/lmd	1689	1154	3	72	12	7	23418	20180	400
Number of Data	83	84	72	72	72	72	90	90	90
Total sum	376.7	311.4	13.79	71.87	29.25	21.87	1451.76	1347.68	189.74
Total average	4.5	3.7	0.19	1.00	0.41	0.30	16.13	14.97	2.11
Sum of square inter-laboratories (S_R)	8.4	1.0	1.64	40.34	9.66	16.00	1695.16	1424.91	682.43
Sum of square within-laboratory (S_{RW})	3.9	0.1	0.00	0.01	0.01	0.00	0.97	1.98	2.78
Sum of square repeatablility (S_r)	15.4	0.3	0.00	0.02	0.00	0.02	0.84	7.39	2.43
Total sum of square (S_T)	27.8	1.4	1.65	40.37	9.68	16.02	1696.97	1434.28	687.64
Inter-laboratories degree of freedom (ϕ_R)	13	13	11	11	11	11	14	14	14
Within-laboratory degree of freedom (ϕ_{RW})	14	14	12	12	12	12	15	15	15
Repeatability degree of freedom (ϕ_r)	56	56	48	48	48	48	60	60	60
Total degree of freedom (ϕ_T)	83	83	71	71	71	71	89	89	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.65	0.08	0.149	3.667	0.879	1.455	121.083	101.779	48.745
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.28	0.00	0.000	0.001	0.001	0.000	0.065	0.132	0.185
Repeatability variance ($V_r = S_r/\phi_r$)	0.28	0.01	0.000	0.000	0.000	0.000	0.014	0.123	0.041
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.06	0.01	0.025	0.611	0.146	0.242	20.170	16.941	8.093
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	0.017	0.003	0.048
Repeatability component of variance ($s_r^2 = V_r$)	0.28	0.01	0.000	0.000	0.000	0.000	0.014	0.123	0.041
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.3	0.1	0.16	0.78	0.38	0.49	4.49	4.12	2.85
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.3	0.0	0.01	0.02	0.02	0.01	0.15	0.21	0.25
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.5	0.1	0.01	0.02	0.01	0.02	0.12	0.35	0.20
Inter-laboratories precision CV (%)	7.2	3.1	82.38	78.32	94.19	162.10	27.85	27.50	135.20
Within-laboratory precision CV (%)	6.7	1.0	5.06	1.86	4.60	1.69	0.91	1.40	11.78
Repeatability precision CV (%)	11.6	2.1	5.00	1.83	2.46	6.16	0.73	2.34	9.55
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.92	0.32	0.442	2.189	1.071	1.379	12.578	11.532	7.981
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.86	0.10	0.027	0.052	0.052	0.014	0.412	0.588	0.695
Repeatability limit ($r = D(3, 0.95)*s_r$)	1.73	0.25	0.032	0.060	0.033	0.062	0.390	1.158	0.665

Statistics	No. 072								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	15	15	12	12	12	12	15	15	15
Total sum of square	195895	133810	41270	2281	234	470	88881	70815	2832
ST/lmd	2177	1487	573	32	3	7	988	787	31
Number of Data	87	87	72	72	72	72	90	90	90
Total sum	442.6	365.8	203.15	47.76	15.31	21.69	298.13	266.11	53.22
Total average	5.1	4.2	2.82	0.66	0.21	0.30	3.31	2.96	0.59
Sum of square inter-laboratories (S_R)	41.5	37.3	599.71	15.88	2.59	18.02	69.07	71.03	12.04
Sum of square within-laboratory (S_{RW})	37.5	26.5	0.08	0.01	0.00	0.00	0.53	0.89	0.93
Sum of square repeatablility (S_r)	0.1	0.0	0.13	0.01	0.01	0.01	0.99	2.41	2.72
Total sum of square (S_T)	79.1	63.9	599.92	15.90	2.59	18.03	70.60	74.34	15.68
Inter-laboratories degree of freedom (ϕ_R)	14	14	11	11	11	11	14	14	14
Within-laboratory degree of freedom (ϕ_{RW})	15	15	12	12	12	12	15	15	15
Repeatability degree of freedom (ϕ_r)	60	60	48	48	48	48	60	60	60
Total degree of freedom (ϕ_T)	89	89	71	71	71	71	89	89	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	2.97	2.67	54.519	1.444	0.235	1.638	4.934	5.074	0.860
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	2.50	1.77	0.007	0.001	0.000	0.000	0.036	0.059	0.062
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.017	0.040	0.045
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.08	0.15	9.085	0.240	0.039	0.273	0.816	0.836	0.133
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.83	0.59	0.001	0.000	0.000	0.000	0.006	0.006	0.006
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.017	0.040	0.045
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.7	0.7	3.01	0.49	0.20	0.52	0.91	0.92	0.38
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.9	0.8	0.05	0.02	0.01	0.01	0.11	0.14	0.14
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.05	0.01	0.01	0.01	0.13	0.20	0.21
Inter-laboratories precision CV (%)	13.8	15.9	106.83	73.94	93.09	173.45	27.38	31.10	64.02
Within-laboratory precision CV (%)	18.0	18.3	1.67	2.90	2.50	2.81	3.29	4.76	24.28
Repeatability precision CV (%)	0.7	0.6	1.88	2.06	4.86	4.01	3.88	6.78	35.98
Reproducibility limit ($R = D(2, 0.95)*s_R$)	1.97	1.87	8.440	1.373	0.554	1.463	2.539	2.575	1.060
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	2.56	2.15	0.132	0.054	0.015	0.024	0.305	0.394	0.402
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.11	0.08	0.175	0.045	0.034	0.040	0.424	0.662	0.702

Note: The data of "vn02" was not applied for the analysis of pH(H_2O) and pH(KCl) since the repeat analysis was not submitted for these parameters.

Table 4.4-2 Analysis of variance for the verified data

Statistics	No. 071								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	12	14	10	10	10	9	12	12	14
Total sum of square	107060	96970	115	2727	245	37	1639783	1308805	13957
ST/lmd	1487	1154	2	45	4	1	22775	18178	166
Number of Data	71	84	60	60	60	54	72	72	84
Total sum	327.2	311.4	10.73	52.22	15.64	6.06	1280.54	1144.03	118.14
Total average	4.6	3.7	0.18	0.87	0.26	0.11	17.79	15.89	1.41
Sum of square inter-laboratories (S_R)	2.9	1.0	1.49	2.28	0.96	0.17	301.61	471.02	61.86
Sum of square within-laboratory (S_{RW})	3.9	0.1	0.00	0.01	0.01	0.00	0.41	0.26	0.80
Sum of square repeatablility (S_r)	15.4	0.3	0.00	0.01	0.00	0.00	0.69	0.52	0.60
Total sum of square (S_T)	22.2	1.4	1.50	2.30	0.98	0.17	302.71	471.80	63.27
Inter-laboratories degree of freedom (ϕ_R)	11	13	9	9	9	8	11	11	13
Within-laboratory degree of freedom (ϕ_{RW})	12	14	10	10	10	9	12	12	14
Repeatability degree of freedom (ϕ_r)	48	56	40	40	40	36	48	48	56
Total degree of freedom (ϕ_T)	71	83	59	59	59	53	71	71	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.26	0.08	0.166	0.253	0.107	0.021	27.419	42.820	4.759
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.32	0.00	0.000	0.001	0.001	0.000	0.034	0.022	0.057
Repeatability variance ($V_r = S_r/\phi_r$)	0.32	0.01	0.000	0.000	0.000	0.000	0.014	0.011	0.011
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	-0.01	0.01	0.028	0.042	0.018	0.004	4.564	7.133	0.784
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.000	0.000	0.000	0.006	0.004	0.016
Repeatability component of variance ($s_r^2 = V_r$)	0.32	0.01	0.000	0.000	0.000	0.000	0.014	0.011	0.011
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.2	0.1	0.17	0.21	0.13	0.06	2.14	2.67	0.89
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.3	0.0	0.00	0.02	0.02	0.00	0.11	0.08	0.14
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.6	0.1	0.01	0.02	0.01	0.01	0.12	0.10	0.10
Inter-laboratories precision CV (%)	4.5	3.1	92.93	23.58	51.14	52.91	12.02	16.81	63.32
Within-laboratory precision CV (%)	7.1	1.0	2.00	2.26	7.79	3.13	0.60	0.53	9.83
Repeatability precision CV (%)	12.3	2.1	5.26	2.20	3.61	6.97	0.67	0.65	7.36
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.58	0.32	0.465	0.575	0.373	0.166	5.986	7.480	2.494
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.92	0.10	0.010	0.055	0.057	0.010	0.297	0.238	0.387
Repeatability limit ($r = D(3, 0.95)*s_r$)	1.87	0.25	0.031	0.063	0.031	0.026	0.396	0.342	0.342

Statistics	No. 072								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	14	10	8	12	8	14	9	13
Total sum of square	173056	110490	10597	705	234	17	85972	25205	1332
ST/lmd	2060	1315	177	15	3	0	1023	467	17
Number of Data	81	81	60	48	72	48	84	54	78
Total sum	416.0	332.4	102.94	26.56	15.31	4.13	293.21	158.76	36.49
Total average	5.1	4.1	1.72	0.55	0.21	0.09	3.49	2.94	0.47
Sum of square inter-laboratories (S_R)	40.0	22.8	34.97	0.47	2.59	0.10	29.13	8.67	2.95
Sum of square within-laboratory (S_{RW})	37.5	26.5	0.03	0.00	0.00	0.00	0.53	0.01	0.08
Sum of square repeatablility (S_r)	0.1	0.0	0.11	0.01	0.01	0.00	0.97	0.03	0.19
Total sum of square (S_T)	77.6	49.3	35.10	0.48	2.59	0.10	30.64	8.71	3.22
Inter-laboratories degree of freedom (ϕ_R)	13	13	9	7	11	7	13	8	12
Within-laboratory degree of freedom (ϕ_{RW})	14	14	10	8	12	8	14	9	13
Repeatability degree of freedom (ϕ_r)	56	56	40	32	48	32	56	36	52
Total degree of freedom (ϕ_T)	83	83	59	47	71	47	83	53	77
Inter-laboratories variance ($V_R = S_R/\phi_R$)	3.08	1.76	3.885	0.068	0.235	0.014	2.241	1.084	0.246
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	2.68	1.89	0.003	0.000	0.000	0.000	0.038	0.001	0.006
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.017	0.001	0.004
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.07	-0.02	0.647	0.011	0.039	0.002	0.367	0.180	0.040
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.89	0.63	0.000	0.000	0.000	0.000	0.007	0.000	0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.017	0.001	0.004
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.7	0.5	0.80	0.11	0.20	0.05	0.61	0.42	0.20
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.9	0.8	0.03	0.01	0.01	0.01	0.11	0.02	0.05
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.05	0.01	0.01	0.01	0.13	0.03	0.06
Inter-laboratories precision CV (%)	13.9	13.2	46.90	19.20	93.09	55.55	17.51	14.45	43.28
Within-laboratory precision CV (%)	18.4	19.4	1.86	1.09	2.50	6.05	3.23	0.55	9.92
Repeatability precision CV (%)	0.6	0.5	3.04	2.38	4.86	7.50	3.77	1.00	12.85
Reproducibility limit ($R = D(2, 0.95)*s_R$)	2.01	1.51	2.253	0.297	0.554	0.134	1.711	1.190	0.567
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	2.65	2.22	0.089	0.017	0.015	0.015	0.316	0.045	0.130
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.06	0.172	0.043	0.034	0.021	0.434	0.097	0.198

Note: The data of "vn02" was not applied for the analysis of pH(H_2O) and pH(KCl) since the repeat analysis was not submitted for these parameters.

4.3.4 Information on Laboratories

1) Number of analysts and their experience

Number of analysts and years of their experience were shown in Table 4.5. As for the number of analysts, it seemed that the same analyst carried out the repeat analyses in most laboratories for all parameters. No relationship between the number of analyst and the outliers was suggested. As for years of experience on soil analysis, clear relationship between the experience and the outliers was not suggested.

2) Analytical instruments and condition of instruments

Analytical instruments used for the measurement, procedures for extraction of Ex-base cations, and size of burette used for the titration method in Ex-acidity were shown in Table 4.6. All the laboratories except "th01" used AAS for measurement of Ex-Ca and Mg, and 5 laboratories used FEP for Ex-K and Na. Years in use of instruments were varied from 1 to 21 for AAS and from 4 to 9 for FEP. All the laboratories except "vn01" applied Sr or La for measurement of Ex-Ca and Mg by AAS.

As for procedures for extraction of Ex-base cations, 9 laboratories used percolation tube procedures, 2 laboratories used Buchner funnel procedures, and one laboratory used centrifuge procedures and automatic extractor procedures, respectively. No clear difference was observed among data by different procedures. As for size of burette for titration of Ex-acidity, capacities were varied from 5 to 50 ml, and minimum graduates were 0.02, 0.05 or 0.1 ml in most laboratories.

3) Date of analysis

Date of analysis in the respective laboratories and days used for the analysis were shown in Table 4.7. Most laboratories carried out the analysis by February. There were no significant implication between date of analysis and the data. Days used for the analysis were only one or two days in most laboratories. Interval between the first and second analyses of the repeat analyses was varied from 0 (in a same day) to 47 days. It was suggested that repeat analyses would be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at SAC3. Mostly half of the laboratories followed the recommendation.

Table 4.5. Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of	Years of experience		
		Chemical	Soil		Chemical	Soil	
cn01	1	22	4	1	22	4	s
cn02	1	12	9	1	2	2	d
cn03	1	10	10	1	16	16	d
cn04	2	6/13	3/3	1	13	3	s
id01	1	5	2	1	5	2	s
id02	1	26	26	1	11	9	d
jp01	1	5	3	1	5	3	s
my01	2	3	3	1	3	3	s
mn01	-	-	-	1	14	14	-
ph01	1	16	16	1	31	31	d
kr01							
ru01	1	11	11	1	11	11	s
th01	2	3/3	1/0	2	3/3	1/0	s
vn01	1	15	10	1	15	10	s
vn02	-	-	-	1	5	3	-
vn03	-	-	-	1	4	2	-

Note: -, Not measured; s, Same analysts; d, Different analysts

Table 4.6 Analytical instruments and their conditions for exchangeable cations

Lab.	Sample	Ex-Ca		Ex-Mg			Ex-K		Ex-Na		
		Instrument	Years[*1]	Instrument	Years		Instrument	Years	Instrument	Years	
cn01	No.071	AAS	2	AAS	2	Sr	FEP	2	FEP	2	Sr
	No.072	AAS	2	AAS	2	Sr	FEP	2	FEP	2	Sr
cn02	No.071	AAS	18	AAS	18	(Sr)	AAS	18	AAS	18	+
	No.072	AAS	18	AAS	18	(Sr)	AAS	18	AAS	18	+
cn03	No.071	AAS	10	AAS	10	Sr	AAS	10	AAS	10	Sr
	No.072	AAS	10	AAS	10	Sr	AAS	10	AAS	10	Sr
cn04	No.071	AAS	9	AAS	9	Sr	FEP	9	FEP	9	Cs
	No.072	AAS	9	AAS	9	Sr	FEP	9	FEP	9	Cs
id01	No.071	AAS	2	AAS	2	La	AAS	2	AAS	2	La
	No.072	AAS	2	AAS	2	La	AAS	2	AAS	2	La
id02	No.071	AAS	21	AAS	21	(Sr)	AAS	21	AAS	21	+
	No.072	AAS	21	AAS	21	(Sr)	AAS	21	AAS	21	+
jp01	No.071	AAS	4	AAS	4	Sr	FEP	4	FEP	4	na
	No.072	AAS	4	AAS	4	Sr	FEP	4	FEP	4	na
my01	No.071	AAS	5	AAS	5	Sr	FEP	5	FEP	5	La
	No.072	AAS	5	AAS	5	Sr	FEP	5	FEP	5	La
mn01	No.071	-	-	-	-	-	-	-	-	-	-
	No.072	-	-	-	-	-	-	-	-	-	-
ph01	No.071	AAS	17	AAS	17	Sr	AAS	17	AAS	17	na
	No.072	AAS	17	AAS	17	Sr	AAS	17	AAS	17	na
kr01											
ru01	No.071	AAS	+	AAS	+	+	FEP	+	FEP	+	+
	No.072	AAS	+	AAS	+	+	FEP	+	FEP	+	+
th01	No.071	ICP	13	ICP	13	Sr	ICP	13	ICP	13	Sr
	No.072	ICP	13	ICP	13	Sr	ICP	13	ICP	13	Sr
vn01	No.071	AAS	1	AAS	1	na	AAS	1	AAS	1	na
	No.072	AAS	1	AAS	1	na	AAS	1	AAS	1	na
vn02	No.071	-	-	-	-	-	-	-	-	-	-
	No.072	-	-	-	-	-	-	-	-	-	-
vn03	No.071	-	-	-	-	-	-	-	-	-	-
	No.072	-	-	-	-	-	-	-	-	-	-

Lab.	Sample	Procedures for extraction of Ex-base cations	Ex-Acidity, Al and H		
			method	Size of burette (ml)	
				Capacity	Minimum graduate
cn01	No.071 No.072	Percolation tube	Titration	50	0.1
cn02	No.071 No.072	Automatic	Titration	5	0.00125
cn03	No.071 No.072	Percolation tube	Titration	50	0.1
cn04	No.071 No.072	Centrifuge	Titration	25	0.1
id01	No.071 No.072	Percolation tube	Titration	25	0.05
id02	No.071 No.072	Percolation tube	Titration	50	0.02
jp01	No.071 No.072	Percolation tube	Titration	25/10 (NaOH/HCl)	0.1/0.05 (NaOH/HCl)
my01	No.071 No.072	Percolation tube	Titration	25	0.05
mn01	No.071 No.072	-	Titration	25	0.1
ph01	No.071 No.072	Buchner funnel	Titration	50	0.01
kr01					
ru01	No.071 No.072	Percolation tube	Titration	50	0.1
th01	No.071 No.072	Percolation tube	Titration	50	0.1
vn01	No.071 No.072	Buchner funnel	Titration	10	0.02
vn02	No.071 No.072	-	Titration	10	0.05
vn03	No.071 No.072	-	Titration	10	0.02

Note: AAS, Atomic absorption spectrometry; FEP, Flame (emission) photometry; na, Not added; -, Not measured; +, No information. *1. Years in use of instrument.

Table 4.7 Date of analysis

Lab.	Repeat	pH			Ex-Ca and Mg			Ex-K and Na			Ex-acidity, Al and H		
		Date[*1]	Analysis[*2]	Interval[*3]	Date[*1]	Analysis[*2]	Interval[*3]	Date[*1]	Analysis[*2]	Interval[*3]	Date[*1]	Analysis[*2]	Interval[*3]
			Days			Days			Days			Days	
cn01	1st	8-Jan	1	13	16-Jan	2	2	16-Jan	2	2	14-Jan	2	5
	2nd	21-Jan	1		18-Jan	2		18-Jan	2		19-Jan	2	
cn02	1st	22-Jan	1	2	26-Jan	5	14	26-Jan	5	14	23-Jan	2	2
	2nd	24-Jan	1		9-Feb	5		9-Feb	5		25-Jan	2	
cn03	1st	20-Feb	1	4	14-Feb	2	4	14-Feb	2	4	7-Jan	5	47
	2nd	24-Feb	1		18-Feb	1		18-Feb	1		23-Feb	4	
cn04	1st	12-Jan	1	23	23-Jan	2	23	23-Jan	2	23	13-Jan	3	23
	2nd	4-Feb	1		15-Feb	2		15-Feb	2		5-Feb	3	
id01	1st	7-Jan	1	10	29-Jan	13	0	29-Jan	13	0	9-Jan	1	13
	2nd	17-Jan	1		29-Jan	6		29-Jan	6		22-Jan	1	
id02	1st	1-Mar	76	0	1-Mar	76	0	1-Mar	76	0	1-Mar	76	0
	2nd	1-Mar	76		1-Mar	76		1-Mar	76		1-Mar	76	
jp01	1st	4-Dec	1	35	10-Jan	3	29	17-Dec	14	24	22-Jan	6	17
	2nd	8-Jan	1		8-Feb	2		10-Jan	3		8-Feb	2	
my01	1st	22-Apr	2	0	25-Apr	2	18	25-Apr	2	0	6-May	1	1
	2nd	22-Apr	2		13-May	2		25-Apr	2		7-May	1	
mn01	1st		1	0		-	-		-	-	21-Feb	1	1
	2nd		1			-			-		22-Feb	1	
kr01	1st												
	2nd												
ru01	1st	21-Feb	6	2	26-Feb	3	2	26-Feb	3	2	25-Feb	2	2
	2nd	23-Feb	6		28-Feb	3		28-Feb	3		27-Feb	2	
th01	1st	20-Mar	1	15	22-Mar	2	14	22-Mar	2	14	23-Mar	1	16
	2nd	4-Apr	1		5-Apr	2		5-Apr	2		8-Apr	1	
vn01	1st	8-Jan	1	3	8-Jan	1	3	8-Jan	1	3	8-Jan	1	3
	2nd	11-Jan	1		11-Jan	1		11-Jan	1		11-Jan	1	
vn02	1st	15-Jan	1	0		-	-		-	-	18-Jan	2	0
	2nd	15-Jan	1			-			-		18-Jan	2	
vn03	1st	9-Jan	1	1		-	-		-	-	25-Jan	1	0
	2nd	10-Jan	1			-			-		25-Jan	1	

Note: *1. Finish date of 1st and 2nd analyses. *2. Days used for analysis. *3. Interval between the repeat analyses. +, not reported.

4.4 Comparison with Past Surveys

By using digital formats, no obvious calculation mistake was found in the data. Moreover, most laboratories followed the standard procedures for the analysis. It seemed that the inter-laboratories standard deviations (CV%) of the recent projects were slightly improved compared with those of the past surveys, although sometimes the CV of Ex-Ca was still relatively large, as shown in Figure 4.3.

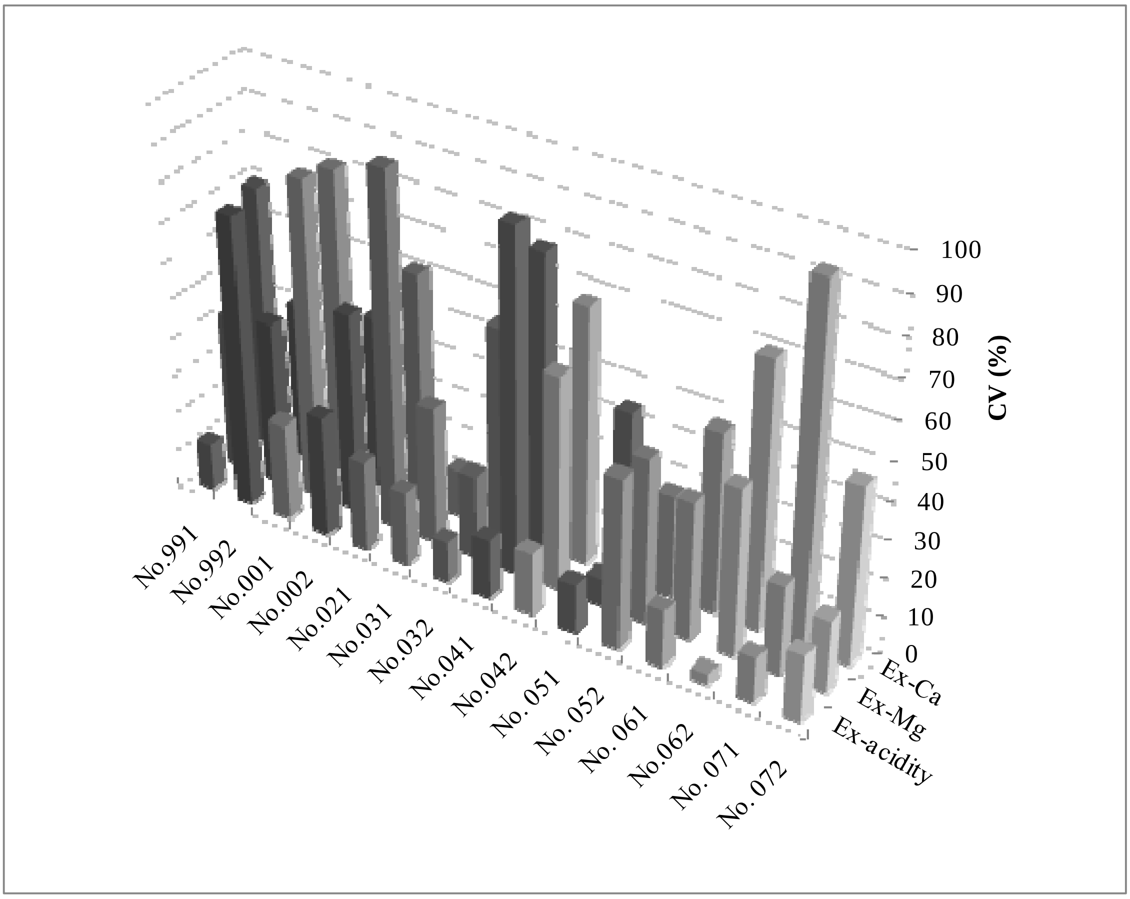


Figure 4.3 Comparison with inter-laboratories standard deviations (CV%) of the past surveys for Ex-Ca, Mg, and acidity

4.5 Recommendations for Improvement

Repeatability precisions and within-laboratory-reproducibility precisions were worse in pH (H_2O) and pH (KCl) than those of the last projects. Efforts should be made to improve the precision. Especially for Ex-base cations, analytical procedures should be checked carefully in the respective laboratories.

It was noted that a few laboratories made systematic mistakes on the analysis showing three or four outliers. The laboratories are encouraged to clarify causes of such systematic mistakes. NC will support this trial.

References

1) Environment Agency, Government of Japan (1997): Monitoring Guidelines and Technical Manuals for Soil and Vegetation Monitoring.

2) The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia (2000): Technical Manuals for Soil and Vegetation Monitoring in East Asia.

3) Japanese Standard Association (1991): General rules for permissible tolerance of chemical analyses and physical tests (JIS Z-8402-$_{1991}$), Japanese Industrial Standard.

4) Acid Deposition and Oxidant Research Center (2001a): Report of the inter-laboratory comparison project 1999 on soil.

5) Acid Deposition and Oxidant Research Center (2001b): Report of the inter-laboratory comparison project 2000 on soil.

6) Acid Deposition and Oxidant Research Center (2002): Report of the inter-laboratory comparison project 2001 on soil.

Appendix 4.1 Participating laboratories

1. CHINA	
1) Chongqing Institute of Environmental Science	**cn01**
2) Xi'an Environmental Monitoring Station	**cn02**
3) Xiamen Environmental Monitoring Central Station	**cn03**
4) Zhuhai Environmental Protected Monitoring Station	**cn04**
2. INDONESIA	
5) Air Quality Laboratory, Environmental Management Center	**id01**
6) Soil Research Institute	**id02**
3. JAPAN	
7) Shimane Agricultural Technology Center	**jp01**
4. Malaysia	
8) Universiti Putra Malaysia	**my01**
5. MONGOLIA	
9) Central Laboratory of Environmental Monitoring	**mn01**
6. PHILIPPINES	
10) University of the Philippines, Los Baños	**ph01**
7. Republic of KOREA	
(not participated this year)	
8. RUSSIA	
11) Limnological Institute Russian Academy of Science/Siberian Branch	**ru01**
9. THAILAND	
12) King Mongkut’s University of Technology Thonburi	**th01**
10. VIET NAM	
13) Center for Environmental Research, Institute of Meteorology and Hydrology, MoNRE	**vn01**
14) Environment Analysis Laboratory II area, Middle of Central regional Hydro-Meteorological Observatory, National Hydro-Meteorological Center, MoNRE	**vn02**
15) Environmental Research Division, National Hydro-Meteorological Center, MoNRE	**Vn03**

Appendix 4.2-1 Entire data of pH in Sample No.071

Lab.	pH(H_2O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	4.7	4.6 (0.0)	4.6	3.7	3.6 (0.0)	3.6
			4.6			3.6
			4.6			3.6
		4.8 (0.1)	4.8		3.7 (0.0)	3.7
			4.8			3.7
			4.7			3.7
cn02	4.6	4.6 (0.1)	4.6	3.9	3.9 (0.1)	3.9
			4.6			3.8
			4.7			3.9
		4.6 (0.1)	4.6		3.9 (0.0)	3.9
			4.6			3.9
			4.7			3.9
cn03	4.6	4.6 (0.0)	4.6	3.7	3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
		4.6 (0.0)	4.6		3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
cn04	4.4	4.4 (0.0)	4.4	3.8	3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8
		4.4 (0.1)	4.5		3.8 (0.1)	3.9
			4.4			3.8
			4.4			3.8
id01	4.8	4.8 (0.1)	4.8	3.7	3.7 (0.0)	3.7
			4.7			3.7
			4.8			3.7
		4.7 (0.0)	4.7		3.7 (0.0)	3.7
			4.7			3.7
			4.7			3.7
id02	4.7	4.7 (0.1)	4.7	3.8	3.8 (0.0)	3.8
			4.7			3.8
			4.6			3.8
		4.6 (0.0)	4.6		3.8 (0.1)	3.8
			4.6			3.7
			4.6			3.8
jp01	4.9	4.8 (0.0)	4.8	3.8	3.7 (0.0)	3.7
			4.8			3.7
			4.8			3.7
		4.9 (0.0)	4.9		3.8 (0.0)	3.8
			4.9			3.8
			4.9			3.8
my01	3.6	3.5 (0.1)	3.5	3.7	3.7 (0.3)	3.5
			3.6			3.5
			3.5			4.1
		3.6 (0.0)	3.6		3.6 (0.2)	3.5
			3.6			3.5
			3.6			3.8
mn01	4.8	4.8 (0.0)	4.8	3.9	3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
		4.8 (0.0)	4.8		3.9 (0.0)	3.9
			4.8			3.9
			-			3.9
ph01	4.6	4.6 (0.0)	4.6	3.5	3.5 (0.0)	3.5
			4.6			3.5
			4.6			3.5
		4.6 (0.0)	4.6		3.5 (0.0)	3.5
			4.6			3.5
			4.6			3.5
kr01						0.0
						0.0
						0.0
						0.0
						0.0
						0.0
ru01	4.5	4.5 (0.1)	4.5	3.7	3.7 (0.0)	3.7
			4.5			3.7
			4.6			3.7
		4.5 (0.0)	4.5		3.7 (0.0)	3.7
			4.5			3.7
			4.5			3.7
th01	4.6	4.6 (0.0)	4.6	3.7	3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
		4.6 (0.0)	4.6		3.7 (0.0)	3.7
			4.6			3.7
			4.6			3.7
vn01	4.5	4.4 (0.0)	4.4	3.6	3.5 (0.1)	3.5
			4.4			3.6
			4.4			3.5
		4.5 (0.0)	4.5		3.6 (0.0)	3.6
			4.5			3.6
			4.5			3.6
vn02	4.7	4.7 (0.0)	4.7	3.8	3.8 (0.0)	3.8
			4.7			3.8
			4.7			3.8
vn03	4.5	4.5 (0.0)	4.5	3.6	3.6 (0.0)	3.6
			4.5			3.6
			4.5			3.6
		4.5 (0.0)	4.5		3.6 (0.0)	3.6
			4.5			3.6
			4.5			3.6

Note: Value in parenthesis showed standard deviation of triplicate analyses.

Appendix 4.2-2 Entire data of exchangeable base cations in Sample No.071

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	cmol(+) kg^{-1}											
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	0.08	0.08 (0.01)	0.08	0.58	0.59 (0.02)	0.61	0.22	0.22 (0.00)	0.22	0.08	0.08 (0.00)	0.08
			0.08			0.57			0.22			0.08
			0.07			0.59			0.22			0.08
		0.08 (0.01)	0.08		0.57 (0.04)	0.61		0.22 (0.01)	0.23		0.08 (0.00)	0.08
			0.07			0.55			0.21			0.08
			0.08			0.54			0.22			0.08
cn02	0.17	0.19 (0.01)	0.20	0.77	0.77 (0.01)	0.76	0.26	0.25 (0.02)	0.26	0.12	0.11 (0.01)	0.10
			0.18			0.78			0.22			0.10
			0.18			0.76			0.26			0.12
		0.15 (0.02)	0.16		0.77 (0.01)	0.77		0.27 (0.02)	0.27		0.12 (0.00)	0.12
			0.13			0.76			0.25			0.12
			0.15			0.78			0.28			0.12
cn03	0.10	0.09 (0.01)	0.09	0.86	0.85 (0.04)	0.86	0.37	0.37 (0.01)	0.37	0.14	0.13 (0.01)	0.13
			0.08			0.81			0.36			0.13
			0.10			0.88			0.37			0.14
		0.10 (0.01)	0.10		0.86 (0.02)	0.87		0.36 (0.01)	0.36		0.14 (0.01)	0.13
			0.10			0.87			0.37			0.14
			0.09			0.84			0.36			0.14
cn04	0.34	0.33 (0.01)	0.34	1.29	1.26 (0.03)	1.23	0.14	0.12 (0.02)	0.14	0.14	0.14 (0.02)	0.12
			0.33			1.27			0.12			0.14
			0.33			1.29			0.11			0.15
		0.35 (0.01)	0.35		1.31 (0.04)	1.31		0.16 (0.01)	0.15		0.13 (0.01)	0.13
			0.36			1.35			0.17			0.14
			0.35			1.28			0.15			0.13
id01	0.45	0.44 (0.01)	0.44	3.28	3.26 (0.02)	3.28	1.44	1.43 (0.01)	1.42	0.79	0.79 (0.00)	0.79
			0.45			3.24			1.43			0.79
			0.44			3.27			1.44			0.79
		0.45 (0.02)	0.43		3.29 (0.02)	3.27		1.44 (0.02)	1.44		0.79 (0.01)	0.80
			0.45			3.30			1.42			0.79
			0.46			3.29			1.45			0.79
id02	0.35	0.34 (0.01)	0.34	1.03	1.03 (0.01)	1.04	0.14	0.14 (0.00)	0.14	0.09	0.09 (0.01)	0.10
			0.35			1.02			0.14			0.09
			0.34			1.04			0.14			0.08
		0.35 (0.01)	0.35		1.03 (0.01)	1.02		0.14 (0.00)	0.14		0.09 (0.01)	0.08
			0.35			1.04			0.14			0.10
			0.34			1.02			0.14			0.10
jp01	0.16	0.16 (0.01)	0.16	0.93	0.93 (0.01)	0.92	0.39	0.42 (0.02)	0.43	0.14	0.14 (0.00)	0.14
			0.16			0.92			0.43			0.14
			0.17			0.94			0.40			0.14
		0.16 (0.01)	0.15		0.93 (0.01)	0.94		0.35 (0.01)	0.35		0.14 (0.00)	0.14
			0.17			0.92			0.35			0.14
			0.15			0.92			0.36			0.14
my01	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00
			0.00			0.00			0.00			0.00
			0.00			0.00			0.00			0.00
		0.00 (0.00)	0.00		0.00 (0.00)	0.00		0.00 (0.00)	0.00		0.00 (0.00)	0.00
			0.00			0.00			0.00			0.00
			0.00			0.00			0.00			0.00

Appendix 4.2-2 (continued)

mn01												
ph01	0.01	0.01 (0.01)	0.02	0.62	0.62 (0.01)	0.62	0.84	0.84 (0.00)	0.84	1.73	1.73 (0.06)	1.79
			0.01			0.62			0.84			1.73
			0.01			0.63			0.84			1.67
		0.01 (0.01)	0.02		0.62 (0.01)	0.62		0.83 (0.02)	0.84		1.73 (0.06)	1.73
			0.01			0.63			0.84			1.67
			0.01			0.62			0.81			1.79
kr01												
ru01	0.40	0.40 (0.02)	0.42	0.99	0.96 (0.02)	0.97	0.34	0.34 (0.00)	0.34	0.11	0.12 (0.01)	0.13
			0.39			0.94			0.34			0.12
			0.40			0.97			0.34			0.12
		0.39 (0.01)	0.40		1.01 (0.01)	1.01		0.34 (0.00)	0.34		0.10 (0.01)	0.11
			0.39			1.01			0.34			0.10
			0.39			1.00			0.34			0.10
th01	0.23	0.22 (0.02)	0.24	0.80	0.79 (0.01)	0.79	0.38	0.37 (0.01)	0.37	0.22	0.22 (0.02)	0.22
			0.23			0.79			0.37			0.24
			0.20			0.78			0.38			0.21
		0.23 (0.02)	0.21		0.80 (0.02)	0.78		0.39 (0.01)	0.39		0.22 (0.01)	0.23
			0.24			0.80			0.40			0.21
			0.24			0.82			0.39			0.22
vn01	0.03	0.03 (0.00)	0.03	0.86	0.88 (0.00)	0.88	0.38	0.40 (0.01)	0.40	0.09	0.09 (0.01)	0.10
			0.03			0.88			0.39			0.09
			0.03			0.88			0.40			0.09
		0.03 (0.00)	0.03		0.83 (0.01)	0.84		0.35 (0.01)	0.36		0.09 (0.01)	0.10
			0.03			0.84			0.35			0.09
			0.03			0.82			0.35			0.09
vn02												
vn03												

Note: Value in parenthesis showed standard deviation of triplicate analyses.

Appendix 4.2-3. Entire data of exchangeable acidity and acid cations in Sample No. 071

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+) kg^{-1}								
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	15.68	15.51 (0.05)	15.45	14.76	14.74 (0.12)	14.74	0.92	0.77 (0.12)	0.71
			15.54			14.62			0.91
			15.54			14.85			0.69
		15.84 (0.20)	16.07		14.78 (0.06)	14.85		1.06 (0.14)	1.22
			15.72			14.74			0.98
			15.72			14.74			0.98
cn02	10.14	10.15 (0.01)	10.15	9.89	9.90 (0.01)	9.89	0.26	0.26 (0.01)	0.26
			10.15			9.90			0.25
			10.16			9.90			0.26
		10.13 (0.01)	10.14		9.88 (0.01)	9.88		0.25 (0.01)	0.26
			10.14			9.89			0.25
			10.12			9.88			0.25
cn03	15.01	15.31 (0.20)	15.21	14.65	14.94 (0.14)	14.93	0.36	0.37 (0.09)	0.28
			15.17			14.81			0.36
			15.54			15.09			0.46
		14.70 (0.16)	14.77		14.36 (0.12)	14.45		0.34 (0.07)	0.32
			14.51			14.23			0.28
			14.81			14.40			0.41
cn04	15.78	15.79 (0.02)	15.79	14.03	14.04 (0.02)	14.05	1.76	1.76 (0.03)	1.74
			15.81			14.02			1.79
			15.78			14.04			1.75
		15.76 (0.02)	15.76		14.01 (0.01)	14.02		1.75 (0.02)	1.74
			15.74			14.01			1.73
			15.77			14.01			1.77
id01	20.06	20.22 (0.23)	20.29	17.97	17.88 (0.00)	17.88	2.10	2.35 (0.23)	2.42
			20.41			17.88			2.53
			19.97			17.88			2.09
		19.90 (0.06)	19.86		18.06 (0.16)	17.97		1.84 (0.09)	1.89
			19.97			18.24			1.73
			19.86			17.97			1.89
id02	14.73	14.73 (0.02)	14.75	13.06	13.06 (0.02)	13.04	1.67	1.67 (0.03)	1.71
			14.71			13.06			1.65
			14.73			13.08			1.65
		14.72 (0.03)	14.75		13.06 (0.02)	13.04		1.66 (0.06)	1.71
			14.73			13.06			1.67
			14.69			13.08			1.60
jp01	19.47	19.40 (0.02)	19.42	17.12	17.27 (0.26)	17.57	2.35	2.13 (0.25)	1.85
			19.40			17.10			2.30
			19.39			17.14			2.25
		19.53 (0.23)	19.27		16.97 (0.18)	16.88		2.56 (0.21)	2.39
			19.66			16.85			2.80
			19.67			17.18			2.49
my01	14.73	14.76 (0.11)	14.76	16.43	16.87 (1.82)	18.87	11.94	11.36 (0.89)	10.55
			14.65			15.32			12.32
			14.87			16.43			11.21
		14.69 (0.23)	14.43		15.98 (0.23)	15.76		12.51 (0.34)	12.21
			14.87			15.98			12.88
			14.76			16.21			12.43

Appendix 4.2-3 (continued)

mn01	17.82	17.82 (0.00)	17.82	16.72	16.72 (0.00)	16.72	0.88	0.88 (0.00)	0.88
			17.82			16.72			0.88
			17.82			16.72			0.88
		17.82 (0.00)	17.82		16.72 (0.00)	16.72		0.88 (0.00)	0.88
			17.82			16.72			0.88
			17.82			16.72			0.88
ph01	19.16	19.16 (0.02)	19.18	16.57	16.58 (0.04)	16.61	2.60	2.59 (0.01)	2.58
			19.16			16.59			2.58
			19.14			16.54			2.60
		19.15 (0.03)	19.18		16.55 (0.04)	16.59		2.60 (0.01)	2.60
			19.12			16.52			2.60
			19.14			16.55			2.59
kr01									
ru01	20.36	20.38 (0.18)	20.59	20.31	20.36 (0.00)	20.36	0.00	0.00 (0.00)	0.00
			20.28			20.36			0.00
			20.28			20.36			0.00
		20.33 (0.09)	20.28		20.26 (0.18)	20.36		0.00 (0.00)	0.00
			20.44			20.36			0.00
			20.28			20.05			0.00
th01	19.39	19.38 (0.04)	19.36	17.32	17.31 (0.03)	17.29	2.07	2.07 (0.01)	2.06
			19.42			17.34			2.08
			19.35			17.29			2.06
		19.40 (0.04)	19.43		17.33 (0.03)	17.35		2.07 (0.01)	2.08
			19.36			17.29			2.06
			19.42			17.34			2.08
vn01	19.50	19.43 (0.13)	19.28	16.98	16.89 (0.26)	16.59	2.71	2.72 (0.13)	2.87
			19.50			17.04			2.65
			19.50			17.04			2.65
		19.57 (0.25)	19.28		17.07 (0.05)	17.04		2.69 (0.24)	2.42
			19.72			17.12			2.78
			19.72			17.04			2.87
vn02	16.78	16.73 (0.03)	16.75	15.96	16.00 (0.06)	15.96	0.94	0.97 (0.06)	1.01
			16.69			16.07			0.9
			16.75			15.96			1.01
		16.82 (0.03)	16.86		15.92 (0.06)	15.85		0.90 (0.00)	0.9
			16.8			15.96			0.9
			16.8			15.96			0.9
vn03	3.39	3.35 (0.05)	3.38	2.87	2.80 (0.22)	3.05	1.13	1.14 (0.02)	1.15
			3.38			2.71			1.16
			3.29			2.63			1.12
		3.43 (0.05)	3.46		2.93 (0.06)	2.94		1.11 (0.06)	1.1
			3.38			2.86			1.17
			3.46			2.98			1.06

Note: Value in parenthesis showed standard deviation of triplicate analyses.

Appendix 4.3-1 Entire data of pH in Sample No. 072

Lab.	pH(H_2O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	5.2	5.1 (0.0)	5.1	4.1	4.0 (0.1)	4.1
			5.1			4.0
			5.1			4.0
		5.2 (0.0)	5.2		4.1 (0.0)	4.1
			5.2			4.1
			5.2			4.1
cn02	5.1	5.1 (0.0)	5.1	4.2	4.2 (0.0)	4.2
			5.1			4.2
			5.1			4.2
		5.1 (0.0)	5.1		4.2 (0.0)	4.2
			5.1			4.2
			5.1			4.2
cn03	5.2	5.2 (0.0)	5.2	4.1	4.1 (0.0)	4.1
			5.2			4.1
			5.2			4.1
		5.2 (0.0)	5.2		4.1 (0.0)	4.1
			5.2			4.1
			5.2			4.1
cn04	5.0	5.0 (0.0)	5.0	4.2	4.2 (0.0)	4.2
			5.0			4.2
			5.0			4.2
		4.9 (0.1)	5.0		4.1 (0.0)	4.1
			4.9			4.1
			4.9			4.1
id01	5.3	5.3 (0.0)	5.3	4.1	4.1 (0.0)	4.1
			5.3			4.1
			5.3			4.1
		5.3 (0.0)	5.3		4.1 (0.0)	4.1
			5.3			4.1
			5.3			4.1
id02	5.2	5.2 (0.0)	5.2	4.1	4.1 (0.0)	4.1
			5.2			4.1
			5.2			4.1
		5.2 (0.0)	5.2		4.1 (0.0)	4.1
			5.2			4.1
			5.2			4.1
jp01	5.2	5.2 (0.0)	5.2	4.2	4.1 (0.0)	4.1
			5.2			4.1
			5.2			4.1
		5.2 (0.1)	5.3		4.2 (0.0)	4.2
			5.2			4.2
			5.2			4.2
my01	4.4	4.4 (0.1)	4.5	5.6	5.6 (0.1)	5.6
			4.4			5.5
			4.4			5.6
		4.4 (0.1)	4.5		5.6 (0.1)	5.6
			4.4			5.5
			4.4			5.6
mn01	5.4	5.4 (0.0)	5.4	4.3	4.3 (0.0)	4.3
			5.4			4.3
			5.4			4.3
		5.4 (0.0)	5.4		4.3 (0.0)	4.3
			5.4			4.3
			5.4			4.3
ph01	5.1	5.1 (0.0)	5.1	4.0	4.0 (0.0)	4.0
			5.1			4.0
			5.1			4.0
		5.1 (0.0)	5.1		4.0 (0.0)	4.0
			5.1			4.0
			5.1			4.0
kr01						
ru01	5.0	5.0 (0.0)	5.0	4.1	4.1 (0.0)	4.1
			5.0			4.1
			5.0			4.1
		5.0 (0.0)	5.0		4.1 (0.0)	4.1
			5.0			4.1
			5.0			4.1
th01	5.1	5.1 (0.1)	5.1	4.0	4.0 (0.1)	4.0
			5.2			4.1
			5.1			4.0
		5.1 (0.1)	5.2		4.0 (0.1)	4.1
			5.1			4.0
			5.1			4.0
vn01	5.0	4.9 (0.1)	4.9	4.0	4.0 (0.0)	4.0
			4.9			4.0
			5.0			4.0
		5.0 (0.0)	5.0		4.0 (0.0)	4.0
			5.0			4.0
			5.0			4.0
vn02	5.0	5.0 (0.1)	5.1	4.2	4.2 (0.0)	4.2
			4.9			4.2
			5			4.2
vn03	5.1	5.1 (0.0)	5.1	4.0	4.0 (0.0)	4
			5.1			4
			5.1			4
		5.1 (0.0)	5.1		4.0 (0.0)	4
			5.1			4
			5.1			4

Note: Value in parenthesis showed standard deviation of triplicate analyses.

Appendix 4.3-2 Entire data of exchangeable base cations in Sample No. 072

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	cmol(+) kg^{-1}											
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	0.88	0.87 (0.10)	0.98	0.35	0.34 (0.02)	0.36	0.13	0.12 (0.01)	0.13	0.09	0.09 (0.01)	0.10
			0.82			0.33			0.12			0.09
			0.81			0.33			0.12			0.09
		0.89 (0.07)	0.96		0.35 (0.03)	0.38		0.13 (0.01)	0.13		0.09 (0.01)	0.09
			0.89			0.33			0.12			0.09
			0.83			0.33			0.13			0.10
cn02	1.43	1.41 (0.07)	1.43	0.52	0.50 (0.02)	0.52	0.11	0.11 (0.00)	0.11	0.11	0.11 (0.00)	0.11
			1.46			0.49			0.11			0.11
			1.33			0.48			0.11			0.11
		1.45 (0.03)	1.48		0.53 (0.02)	0.51		0.11 (0.00)	0.11		0.10 (0.01)	0.11
			1.42			0.54			0.11			0.10
			1.44			0.55			0.11			0.10
cn03	1.78	1.77 (0.05)	1.77	0.57	0.57 (0.02)	0.58	0.16	0.15 (0.01)	0.15	0.13	0.13 (0.01)	0.13
			1.73			0.55			0.15			0.12
			1.82			0.57			0.16			0.13
		1.79 (0.03)	1.77		0.56 (0.01)	0.56		0.16 (0.01)	0.16		0.12 (0.01)	0.13
			1.79			0.56			0.16			0.12
			1.82			0.57			0.15			0.12
cn04	1.43	1.36 (0.04)	1.35	0.97	0.93 (0.02)	0.93	0.12	0.12 (0.02)	0.12	0.13	0.12 (0.01)	0.13
			1.32			0.91			0.10			0.11
			1.40			0.95			0.14			0.11
		1.49 (0.02)	1.50		1.01 (0.02)	1.03		0.12 (0.01)	0.13		0.13 (0.01)	0.14
			1.47			1.00			0.12			0.12
			1.49			1.01			0.12			0.14
id01	5.13	5.09 (0.10)	5.14	2.05	2.04 (0.01)	2.03	0.66	0.65 (0.00)	0.65	0.52	0.52 (0.01)	0.53
			4.98			2.05			0.65			0.52
			5.15			2.05			0.65			0.52
		5.17 (0.01)	5.18		2.05 (0.01)	2.06		0.67 (0.03)	0.70		0.52 (0.01)	0.52
			5.16			2.04			0.66			0.52
			5.17			2.05			0.65			0.53
id02	2.18	2.18 (0.01)	2.18	0.66	0.66 (0.01)	0.65	0.08	0.08 (0.01)	0.08	0.05	0.05 (0.01)	0.05
			2.18			0.67			0.07			0.05
			2.17			0.65			0.08			0.04
		2.18 (0.01)	2.19		0.66 (0.01)	0.67		0.08 (0.00)	0.08		0.05 (0.01)	0.04
			2.18			0.65			0.08			0.05
			2.18			0.65			0.08			0.05
jp01	2.35	2.34 (0.02)	2.32	0.60	0.60 (0.01)	0.60	0.17	0.17 (0.00)	0.17	0.14	0.14 (0.01)	0.14
			2.34			0.59			0.17			0.13
			2.35			0.60			0.17			0.14
		2.35 (0.05)	2.33		0.59 (0.02)	0.61		0.16 (0.01)	0.16		0.14 (0.01)	0.15
			2.31			0.58			0.16			0.13
			2.40			0.59			0.15			0.13
my01	0.01	0.01 (0.00)	0.01	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00
			0.01			0.00			0.00			0.00
			0.01			0.00			0.00			0.00
		0.00 (0.00)	0.00		0.00 (0.00)	0.00		0.00 (0.00)	0.00		0.00 (0.00)	0.00
			0.00			0.00			0.00			0.00
			0.00			0.00			0.00			0.00

Appendix 4.3-2 (continued)

mn01												
ph01	2.24	2.24 (0.03)	2.20	0.51	0.51 (0.01)	0.51	0.57	0.57 (0.02)	0.56	1.89	1.89 (0.03)	1.91
			2.26			0.52			0.60			1.85
			2.26			0.51			0.56			1.91
		2.24 (0.03)	2.26		0.51 (0.01)	0.52		0.57 (0.02)	0.60		1.89 (0.03)	1.85
			2.26			0.51			0.56			1.91
			2.20			0.51			0.56			1.91
kr01												
ru01	2.67	2.68 (0.11)	2.59	0.70	0.70 (0.02)	0.68	0.15	0.15 (0.00)	0.15	0.12	0.13 (0.01)	0.12
			2.80			0.71			0.15			0.14
			2.64			0.70			0.15			0.14
		2.66 (0.12)	2.61		0.69 (0.02)	0.67		0.15 (0.01)	0.16		0.10 (0.00)	0.10
			2.79			0.71			0.15			0.10
			2.57			0.68			0.14			0.10
th01	2.21	2.22 (0.01)	2.21	0.51	0.52 (0.01)	0.53	0.24	0.24 (0.01)	0.23	0.40	0.39 (0.01)	0.39
			2.23			0.52			0.24			0.38
			2.21			0.52			0.24			0.40
		2.20 (0.01)	2.20		0.50 (0.01)	0.50		0.23 (0.00)	0.23		0.40 (0.01)	0.41
			2.21			0.51			0.23			0.41
			2.20			0.50			0.23			0.39
vn01	11.57	11.65 (0.03)	11.65	0.55	0.55 (0.00)	0.55	0.18	0.18 (0.00)	0.18	0.06	0.06 (0.00)	0.06
			11.68			0.55			0.18			0.06
			11.63			0.55			0.18			0.06
		11.49 (0.06)	11.54		0.55 (0.01)	0.55		0.18 (0.01)	0.18		0.05 (0.00)	0.05
			11.43			0.54			0.19			0.05
			11.50			0.55			0.18			0.05
vn02												
vn03												

Note: Value in parenthesis showed standard deviation of triplicate analyses.

Appendix 4.3-3 Entire data of exchangeable acidity and acid cations in Sample No. 072

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+) kg^{-1}								
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	3.41	3.58 (0.01)	3.59	2.89	3.08 (0.02)	3.06	0.53	0.50 (0.03)	0.52
			3.59			3.08			0.50
			3.57			3.10			0.47
		3.24 (0.01)	3.24		2.69 (0.04)	2.70		0.55 (0.03)	0.54
			3.24			2.72			0.52
			3.23			2.65			0.58
cn02	2.62	2.61 (0.07)	2.61	2.57	2.56 (0.07)	2.55	0.05	0.05 (0.00)	0.05
			2.68			2.63			0.05
			2.55			2.50			0.05
		2.63 (0.04)	2.68		2.58 (0.05)	2.63		0.05 (0.00)	0.05
			2.61			2.55			0.05
			2.61			2.55			0.05
cn03	3.38	3.56 (0.17)	3.73	2.88	2.98 (0.33)	3.22	0.51	0.59 (0.18)	0.52
			3.56			3.11			0.45
			3.39			2.60			0.79
		3.19 (0.04)	3.16		2.77 (0.04)	2.74		0.42 (0.05)	0.42
			3.23			2.77			0.46
			3.18			2.81			0.37
cn04	3.32	3.34 (0.01)	3.35	2.54	2.55 (0.01)	2.55	0.77	0.79 (0.01)	0.80
			3.34			2.56			0.78
			3.33			2.55			0.78
		3.29 (0.01)	3.29		2.53 (0.01)	2.53		0.75 (0.01)	0.76
			3.30			2.53			0.76
			3.28			2.54			0.74
id01	3.70	3.68 (0.06)	3.71	3.35	3.32 (0.03)	3.35	0.35	0.36 (0.05)	0.36
			3.71			3.30			0.41
			3.61			3.31			0.31
		3.71 (0.00)	3.71		3.38 (0.05)	3.43		0.33 (0.05)	0.28
			3.71			3.35			0.36
			3.71			3.35			0.36
id02	2.49	2.49 (0.02)	2.50	2.13	2.13 (0.02)	2.15	0.36	0.36 (0.04)	0.35
			2.50			2.11			0.40
			2.46			2.13			0.33
		2.49 (0.02)	2.50		2.13 (0.02)	2.11		0.36 (0.05)	0.40
			2.46			2.15			0.31
			2.50			2.13			0.37
jp01	4.00	3.90 (0.14)	3.87	2.72	2.59 (0.09)	2.63	1.28	1.31 (0.08)	1.25
			4.05			2.65			1.40
			3.77			2.49			1.29
		4.09 (0.06)	4.16		2.84 (0.02)	2.87		1.24 (0.04)	1.29
			4.06			2.83			1.23
			4.04			2.83			1.21
my01	2.62	2.50 (0.57)	2.93	4.40	4.11 (0.98)	4.68	1.51	1.88 (1.09)	0.96
			2.71			4.68			1.60
			1.86			2.98			3.09
		2.73 (0.27)	2.98		4.68 (0.21)	4.68		1.14 (0.25)	1.28
			2.77			4.89			0.85
			2.45			4.47			1.28

Appendix 4.3-3 (continued)

mn01	3.60	3.60 (0.00)	3.60	3.20	3.20 (0.00)	3.20	0.40	0.40 (0.00)	0.40
			3.60			3.20			0.40
			3.60			3.20			0.40
		3.60 (0.00)	3.60		3.20 (0.00)	3.20		0.40 (0.00)	0.40
			3.60			3.20			0.40
			3.60			3.20			0.40
ph01	3.91	3.90 (0.01)	3.91	3.33	3.32 (0.00)	3.32	0.58	0.58 (0.01)	0.59
			3.89			3.32			0.57
			3.91			3.32			0.59
		3.91 (0.02)	3.91		3.33 (0.03)	3.30		0.58 (0.02)	0.61
			3.89			3.32			0.57
			3.93			3.36			0.57
kr01									
ru01	4.77	4.77 (0.09)	4.87	4.49	4.54 (0.17)	4.64	0.25	0.20 (0.17)	0.30
			4.72			4.34			0.30
			4.72			4.64			0.00
		4.77 (0.09)	4.72		4.44 (0.17)	4.34		0.30 (0.00)	0.30
			4.72			4.64			0.30
			4.87			4.34			0.30
th01	3.84	3.84 (0.06)	3.87	3.13	3.13 (0.05)	3.18	0.71	0.71 (0.05)	0.69
			3.87			3.10			0.77
			3.77			3.10			0.67
		3.83 (0.05)	3.86		3.12 (0.04)	3.17		0.71 (0.05)	0.69
			3.77			3.10			0.67
			3.86			3.09			0.77
vn01	3.54	3.55 (0.08)	3.64	3.02	3.03 (0.02)	3.04	0.70	0.70 (0.07)	0.77
			3.51			3.04			0.64
			3.51			3.00			0.68
		3.52 (0.02)	3.51		3.00 (0.00)	3.00		0.70 (0.03)	0.68
			3.51			3.00			0.68
			3.55			3.00			0.73
vn02	3.71	3.68 (0.03)	3.72	3.21	3.21 (0.00)	3.21	0.54	0.56 (0.00)	0.56
			3.66			3.21			0.56
			3.66			3.21			0.56
		3.74 (0.03)	3.72		3.21 (0.00)	3.21		0.52 (0.06)	0.56
			3.77			3.21			0.45
			3.72			3.21			0.56
vn03	0.82	0.83 (0.09)	0.92	0.53	0.51 (0.06)	0.52	0.35	0.40 (0.06)	0.39
			0.83			0.56			0.35
			0.75			0.45			0.47
		0.81 (0.06)	0.75		0.55 (0.02)	0.56		0.30 (0.02)	0.31
			0.87			0.56			0.31
			0.8			0.52			0.27

Note: Value in parenthesis showed standard deviation of triplicate analyses.

5. 8th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

In the 8th inter-laboratory comparison of inland aquatic environment, artificial inland aquatic environment samples containing known concentrations of major ions, were prepared and sent to the participating countries of EANET by the Network Center (NC) in November 2007. All the participating laboratories submitted their analytical data to NC. The measurements of pH, EC, alkalinity and concentrations of SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ from the participating countries were compared with prepared values and the results were statistically treated.

5.2 Procedure

5.2.1 Participating Laboratories

The Network Center (NC) shipped artificial inland aquatic environment samples to all 19 laboratories on November 22 in 2007, and all laboratories submitted their analytical data to NC by February 29 in 2008. A list of the participating laboratories with their abbreviated name, and the code are given in Appendix 5-1. For this attempt, the laboratory of Viet Num (Lab.ID vn.03) participated for the first time in this inter-laboratory comparison project on inland aquatic environment. This laboratory submitted the data of six parameters, pH, EC, Alkalinity and concentrations of SO_4^{2-}, Cl^-, and NH_4.$^+$

5.2.2 Description Samples

A description of the samples is given in Table 5.1.

Table 5.1 Description of the artificial inland aquatic environment sample

Name	Amount of the sample	Container	Number of samples	Note
Artificial inland aquatic environment sample	Approximately 1L	Poly-propylene bottle 1L	One bottle	To analyze directly

The analytical parameters are shown in Table 5.2.

Table 5.2 Analytical parameters

Analytical Parameter	Reporting Units	
pH	pH units	-
EC	milli siemens/meter	mS/m
Alkalinity	milli equivalent/liter	meq/L
SO_4^{2-}	milli gram/liter	mg/L
NO_3^-	milli gram/liter	mg/L
Cl^-	milli gram/liter	mg/L
Na^+	milli gram/liter	mg/L
K^+	milli gram/liter	mg/L
Ca^{2+}	milli gram/liter	mg/L
Mg^{2+}	milli gram/liter	mg/L
NH_4^+	milli gram/liter	mg/L

The participating laboratories were informed that concentration of each parameter was prepared within the range described in Table 5.3.

Table 5.3 Concentration range of artificial inland aquatic environment sample

Parameter	Range	Parameter	Range
pH	5.0 – 8.0	Na^+	2 – 20 mg/L
EC	1.5 – 15 mS/m	K^+	0.2 – 2.0 mg/L
Alkalinity	0.05 – 0.5 meq/L	Ca^{2+}	1 – 10 mg/L
SO_4^{2-}	2 – 20 mg/L	Mg^{2+}	0.2 – 2.0 mg/L
NO_3^-	0.5 – 5 mg/L	NH_4^+	0.05 – 0.5 mg/L
Cl^-	1 – 10 mg/L		

5.2.3 Parameters analyzed

Participating laboratories were required to apply the analytical methods and data checking procedures specified in the “Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)” and the “QA/QC Program for Monitoring on Inland Aquatic Environment in East Asia (2000)”. Analytical methods specified in the manual are described in Table 5.4.

Table 5.4 Analytical methods specified in the manual

Parameter	Analytical method
pH	Glass electrode
EC	Conductivity cell
Alkalinity	Titration by Burette or Digital Burette with pH Meter (end-point pH4.8)
SO_4^{2-} NO_3^-	Ion Chromatography or Spectrophotometry
Cl^-	Ion Chromatography or Titration
Na^+ K^+ Ca^{2+} Mg^{2+}	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH_4^+	Ion Chromatography or Spectrophotometry (Indophenol blue)

5.2.4 Data Checking Procedures

a) Calculation of ion balance (R_1)

(1) Total anion (A) equivalent concentration (μeq/L) is calculated by sum up the concentration of anions (C: μmol/L) and Alkalinity (ALK: μeq/L). Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

$\boldsymbol{A}$ (μeq/L) $=\Sigma n\, C_{Ai}$ (μmol/L) $= C(SO_4^{2-}) + C(NO_3^-) + C(Cl^-) + (ALK)$

C_{Ai}: electric charge of ion and concentration (μmol/L) of anion “i”.

(2) Total cation (C) equivalent concentration (μeq/L) is calculated by sum up the concentration of all cations (C: μmol/L).

$\boldsymbol{C}$ (μeq/L) $= \Sigma n\, C_{Ci}$ (μmol/L) $= 10^{(6\text{-pH})} + C(NH_4^+) + C(Na^+) + C(K^+)$

$+ C(Ca^{2+}) + C(Mg^{2+})$

C_{Ci}: electric charge of ion and concentration (μmol/L) of cation “i”.

(3) Calculation of ion balance (R_1)

$R_1 = 100 \times (\boldsymbol{C}\text{-}\boldsymbol{A}) / (\boldsymbol{C}+\boldsymbol{A})$ [%]

(4) R_1, which is calculated using the above equation, should be compared with standard values in Table 5.5. Re-measurement, check with standard solutions, and/or inspection of calibration curves should be undertaken, when R_1 is not within the range.

Table 5.5 Allowable ranges for R_1 in different concentration ranges

(C+A) [μeq/L]	R_1 [%]
< 50	+30 ~ -30
50 ~ 100	+15 ~ -15
>100	+8 ~ - 8

Reference: “Technical Manual for Monitoring on Inland Aquatic Environment in East Asia (2000)”

b) Comparison between calculated and measured electrical conductivity (R_2)

(1) Total electric conductivity (Λcalc) is calculated as follows;

$$\Lambda calc\ (mS/m) = \{349.7 \times 10^{(6-pH)} + 80.0 \times C(SO_4^{2-}) + 71.5 \times C(NO_3^-) + 76.3 \times C(Cl^-) + 73.5 \times C(NH_4^+) + 50.1 \times C(Na^+) + 73.5 \times C(K^+) + 59.8 \times C(Ca^{2+}) + 53.3 \times C(Mg^{2+}) + 44.5 \times (ALK)\}/10000$$

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_3^-).

(2) Ratio (R_2) of calculations (Λcalc) to measurements (Λcalc) in electric conductivity is calculated as follows;

$$R_2 = 100 \times (\Lambda calc - \Lambda meas)/(\Lambda calc + \Lambda meas)\ [\%]$$

(3) R_2, which is calculated using the above equation, is compared with standard values in Table 5.6. Re-measurement, check with standard solutions, and/or inspection of calibration curves are necessary, when R_2 is not within the range.

Table 5.6 Allowable ranges for R_2 in different concentration ranges

Λmeas[mS/m]	R_2 [%]
< 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)"

5.3 Results

5.3.1 Outline of Results

Original data from the laboratories are shown in Appendix 5-2 and Appendix 5-3. Table 5.7 shows the summary of analytical result. Statistics calculated for each constituent of the artificial inland aquatic environment samples were: Average, Standard deviation (S.D.), Number of data (N), Minimum (Min.) and Maximum (Max.). Outlying data that apart from the average greater than a factor of 3 of S.D. were not included in the calculation. As shown in Table 5.7, average of submitted data agreed fairly well with the prepared value/concentration within a range of ±10%.

Table 5.7 Summary of analytical results of the artificial inland aquatic environment sample

Constituents		Prepared	Average	S.D	N	Min.	Max.
pH		6.88	7.12	0.20	19	6.6	7.39
EC	(mS/m)	5.64	5.36	0.10	19	5.15	5.56
Alkalinity	(meq/L)	0.206	0.206	0.017	18	0.178	0.246
SO_4^{2-}	(mg/L)	7.96	7.75	0.59	18	6.2	9.17
NO_3^-	(mg/L)	0.82	0.77	0.07	17	0.59	0.91
Cl^-	(mg/L)	3.16	3.00	0.25	18	2.23	3.3
Na^+	(mg/L)	5.05	4.87	0.25	16	4.44	5.34
K^+	(mg/L)	0.86	0.84	0.16	16	0.36	1.15
Ca^{2+}	(mg/L)	3.1	3.40	0.39	16	2.65	4.12
Mg^{2+}	(mg/L)	0.8	0.81	0.09	16	0.63	0.96
NH_4^+	(mg/L)	0.2	0.17	0.06	17	0.08	0.311

(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 EANET is specified for every constituent as ± 15% by the QA/QC program of the EANET. In this report, analytical data on artificial inland aquatic environmental samples is compared with the prepared value/concentration and evaluated by the DQO criteria: the flag "E" is put to the data that exceed DQO within a factor of 2 (±15% - ±30%) and the flag "X" is put to the data that exceed DQO more than a factor of 2 (<-30% or >30%). Data set for each sample was evaluated by the data checking procedures described in chapter 5.2.4 of this report. The results were evaluated following the two aspects: i) comparison of individual parameters, and ii) comparison of circumstance of analysis in each participating laboratory. Evaluation of data for each constituent is presented in “5.3.2 Evaluation of laboratories’ performance (by analytical parameters)”, and evaluation of data by circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is described in “5.3.4 Information on laboratories”.

Table 5.8 shows the number of flagged data for each parameters and Figure 5.1 shows the percentage of flagged data.

Table 5.8 Number of flagged data

Flag*	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total	Ratio
E	0	0	1	2	2	2	0	1	4	3	2	17	8.9%
X	0	0	0	0	0	0	0	2	1	0	5	8	4.2%
Data within DQOs	19	19	17	16	15	16	16	13	11	13	10	165	86.8%
Flagged(%)	0.0	0.0	5.6	11.1	11.8	11.1	0.0	18.8	31.3	18.8	41.2	13.2	

*E : Value exceeded the DQO within a factor of 2 of the DQO (±15% - ±30%)

*X : Value exceeded the DQO more than a factor of 2 of the DQO (<-30% or >30%)

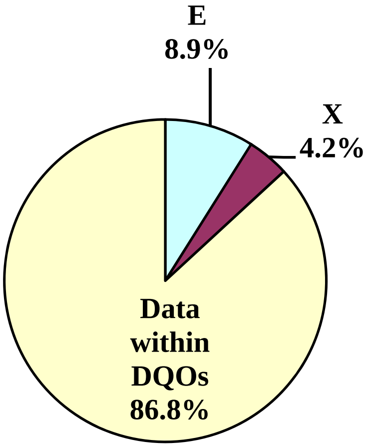


Figure 5.1 Percentage of flagged data

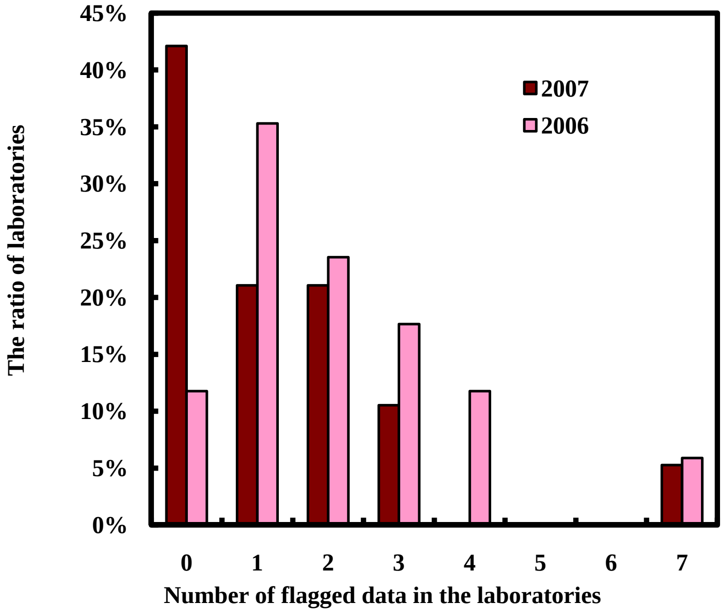
The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 8.9% of all reported data of samples. And the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 4.2% of all reported data of samples. And the percentage of flagged cations was larger than that of anions. Especially the percentage of flagged Ca^{2+} and NH_4^+ exceeded more than 30%.

The distribution of flagged data in each laboratory is shown in Table 5.9 and Figure 5.2.

Table 5.9 Number of flagged data in each laboratory

Number of flagged data	Number of laboratories	Percentage
0	8	42%
1	4	21%
2	4	21%
3	2	11%
4	0	0%
5	0	0%
6	0	0%
7	1	5%
Total	19	100%

Figure 5.2 Distribution of laboratories with the number of flagged data



The percentage of the laboratories without flagged data was 12% in last attempt (2006), but that of this year was 42%. There was a laboratory that has seven flagged data in this attempt.

Table 5.10 Analytical Results of Sample No.071 (artificial inland aquatic environment sample : EANET in 2007)

Lab. ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	-	(mS/m)	(meq/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	-	-
cn01	7.11	5.34	0.21	7.91	0.76	3.08	4.98	0.82	3.21	0.80	0.22	0.53	2.64
cn02	7.11	5.37	0.20	8.17	0.81	3.15	5.34	0.86	E 3.79	E 0.93	X 0.09	5.73	4.77
cn03	7.10	5.32	0.21	7.61	0.82	2.98	5.12	0.82	E 3.76	0.92	X 0.08	4.68	4.04
cn04	7.11	5.31	0.21	7.61	0.79	2.93	5.10	0.80	3.48	0.84	0.18	2.83	3.42
id01	7.03	5.47	0.21	E 9.17	0.91	3.01	5.07	0.89	3.13	0.91	0.22	-0.91	3.70
id02	6.60	5.47	E 0.25	E 6.20	E 0.59	3.28	4.62	X 1.15	E 3.61	E 0.96	X 0.31	3.03	2.57
jp01	6.99	5.37	0.20	7.91	0.77	3.06	4.94	0.85	3.00	0.76	0.22	-0.57	1.43
jp02	7.26	5.37	0.21	8.00	0.80	3.29	5.10	0.85	2.65	E 0.63	E 0.14	-5.10	0.87
mn01	7.23	5.33	0.19	7.91	0.75	2.98							
my01	6.76	5.22	0.22	8.39	0.83	3.30	5.05	E 0.72	3.56	0.77	0.20	-1.29	6.24
ph01	7.39	5.38	0.18	8.22	0.81	3.19	4.92	0.86	3.47	0.81	0.18	3.27	2.48
ph02	7.38	5.20											
ru01	7.25	5.53	0.20	7.65	0.75	2.90	4.44	0.97	3.13	0.72	0.19	-1.25	-1.54
ru02	7.26	5.56	0.20	7.50	0.82	3.08	4.65	0.89	3.06	0.76	E 0.14	-0.36	-1.83
th01	6.95	5.15	0.18	7.94	0.78	3.11	4.98	0.85	3.14	0.81	0.19	3.13	3.22
th02	7.11	5.33	0.22	7.25	0.75	E 2.61	4.99	0.83	E 3.95	0.90	0.18	6.76	3.48
vn01	7.11	5.36	0.21	7.79	E 0.64	2.99	4.44	X 0.36	X 4.12	0.80	0.18	2.32	2.35
vn02	7.15	5.44	0.21	7.61	0.81	3.02	4.98	0.98	3.20	0.76	X 0.13	0.15	1.20
vn03	7.38	5.37	0.23	7.45		E 2.23					X 0.12		
Expected value	6.88	5.64	0.21	7.96	0.82	3.16	5.05	0.86	3.10	0.80	0.20	-	-

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

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

5.3.2 Evaluation of laboratories' performance (by analytical parameters)

The general overviews of data are presented below in Figures 5.3 to 5.13. for each analytical parameter. The results received from each laboratory are normalized by prepared values to evaluate deviation from prepared values.

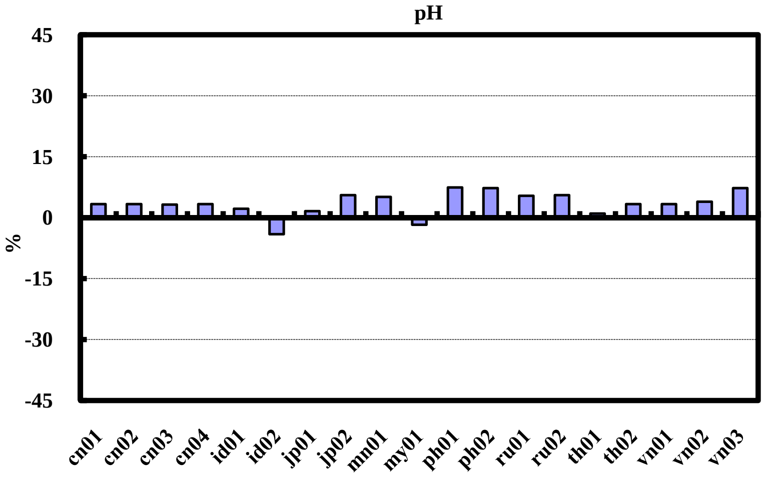


Figure 5.3 Distribution of results for pH (normalized by prepared value)

All obtained data of pH were within DQOs.

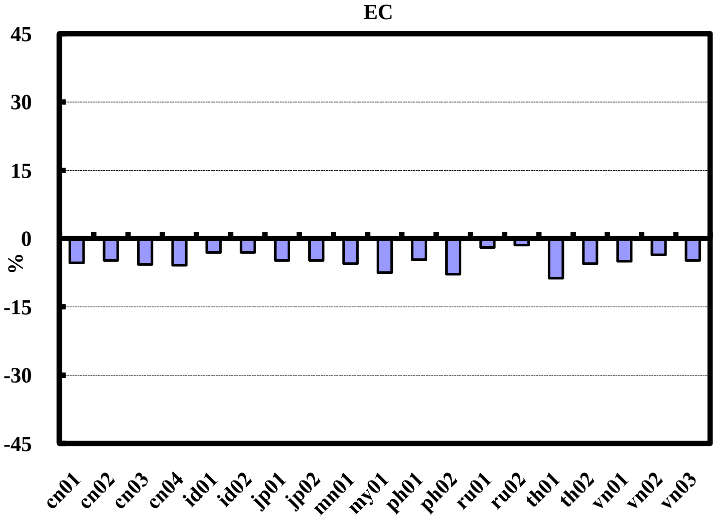


Figure 5.4 Distribution of results for EC (normalized by prepared value)

All obtained data of EC were within DQOs.

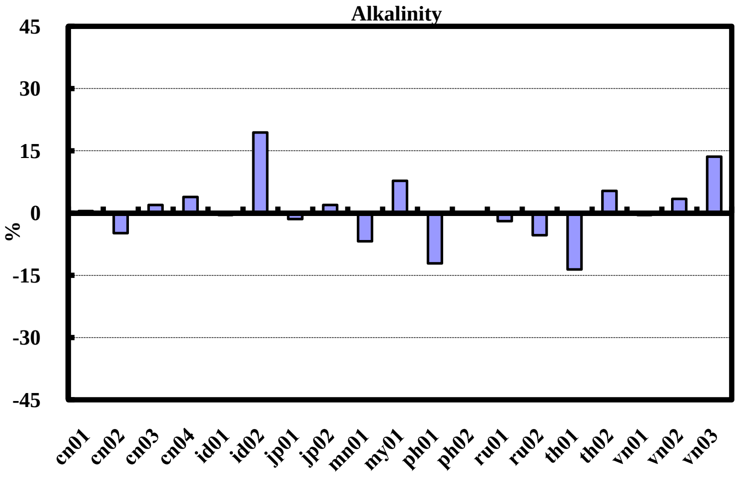


Figure 5.5 Distribution of results for Alkalinity (normalized by prepared concentration)

One data was flagged. And there were some data near the flag.

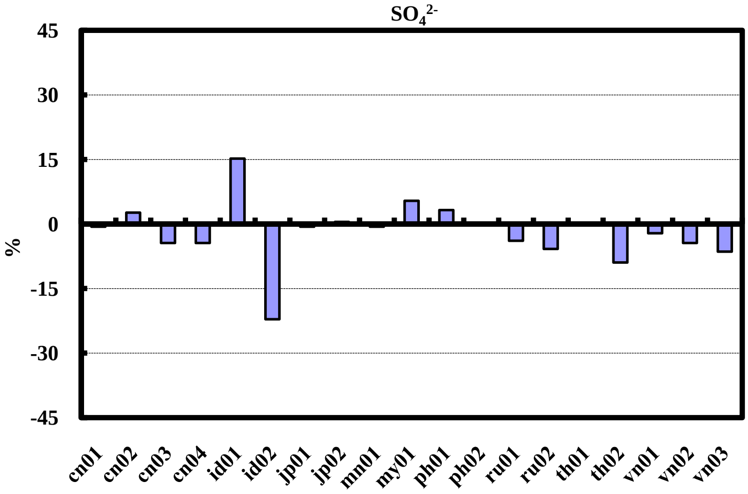


Figure 5.6 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

Data from two laboratories were flagged. Most of participating laboratories used ion chromatography for the determination of SO_4^{2-} and there was a flagged data analyzed with it. While three laboratories used spectrophotometry and there was a flagged data analyzed with it, too.

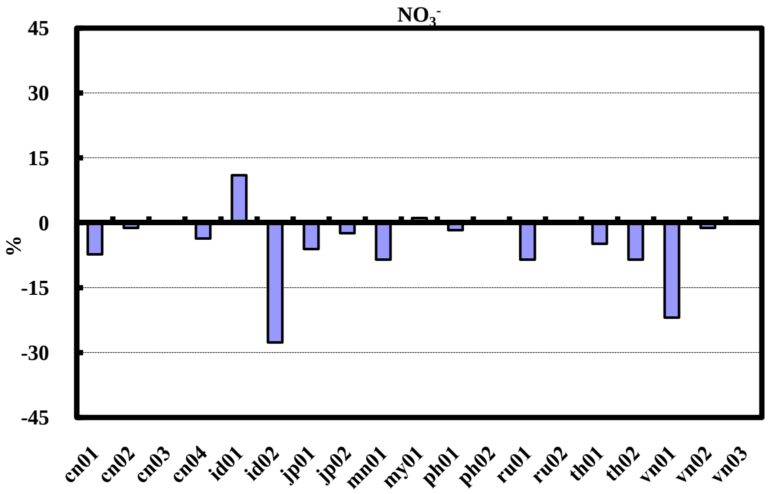


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

Most of the participating laboratories used ion chromatography for the determination of NO_3^-, while three laboratories used spectrophotometry. Data from two laboratories were flagged. One of the samples which had flagged data were analyzed with ion chromatography method and other one was analyzed with spectrophotometry .

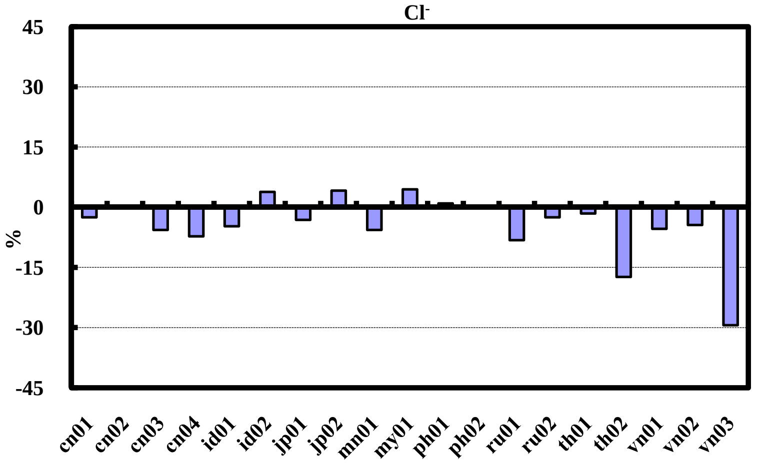


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

Most of participating laboratories used ion chromatography for the determination of Cl^- and three laboratories used titration method. One of the samples which had flagged data was analyzed by ion chromatography method, and the other one was analyzed by titration method.

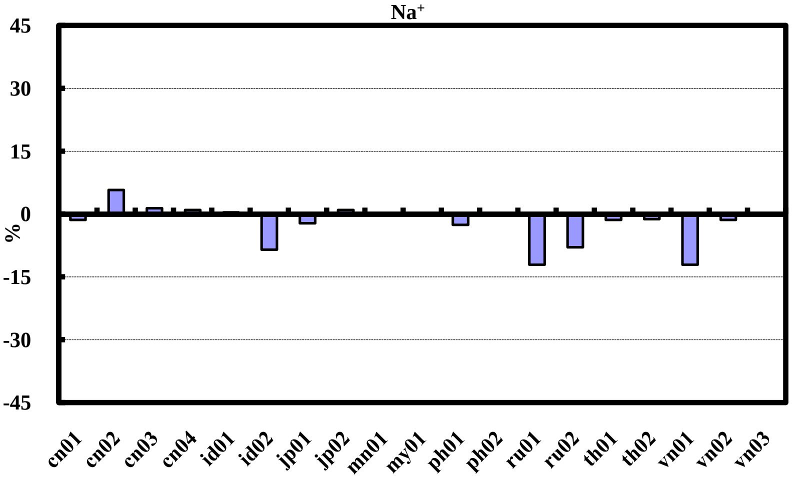


Figure 5.9 Distribution of results for Na^+ (normalized by prepared concentration)

All obtained data of EC were within DQOs.

Most of participating laboratories used ion chromatography, while 3 laboratories used atomic absorption/flame (emission) photometry for the determination of Na^+.

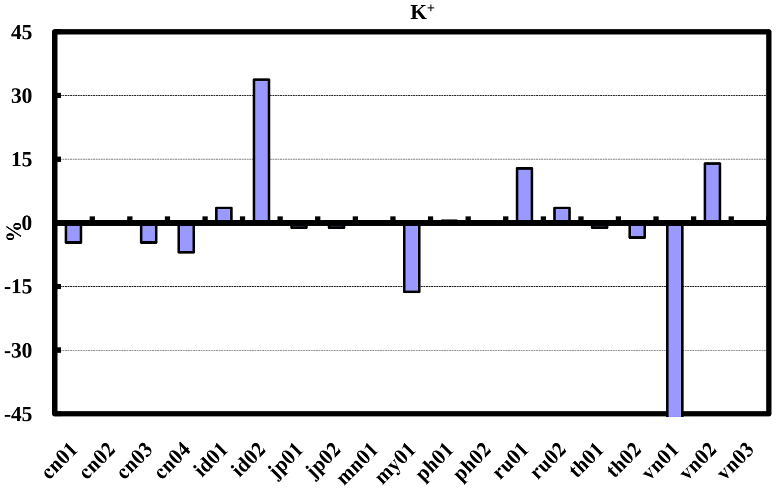


Figure 5.10 Distribution of results for K^+ (normalized by prepared concentration)

Most of participating laboratories used ion chromatography, and 3 laboratories used atomic absorption/flame (emission) photometry for the determination of K^+.

Data from 3 laboratories were flagged. Especially two data were significantly deviated from prepared value. Two flagged data were obtained from the use of ion chromatography method, and one data was obtained from the use of atomic absorption/flame (emission) photometry method.

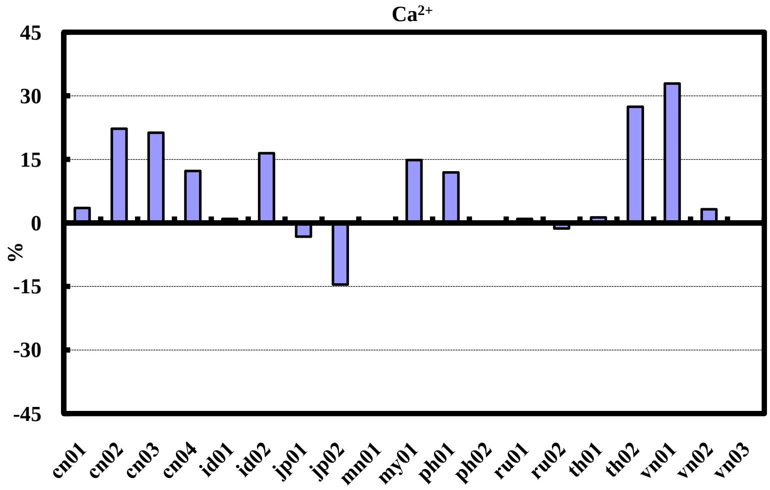


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Ca^{2+} was one of the parameters that have the highest flagged percentage in this attempt. Most of participating laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Ca^{2+}. Data from 5 laboratories were flagged. 4 flagged data were obtained from the use of ion chromatography method, and one data was obtained from the use of atomic absorption/flame (emission)photometry method

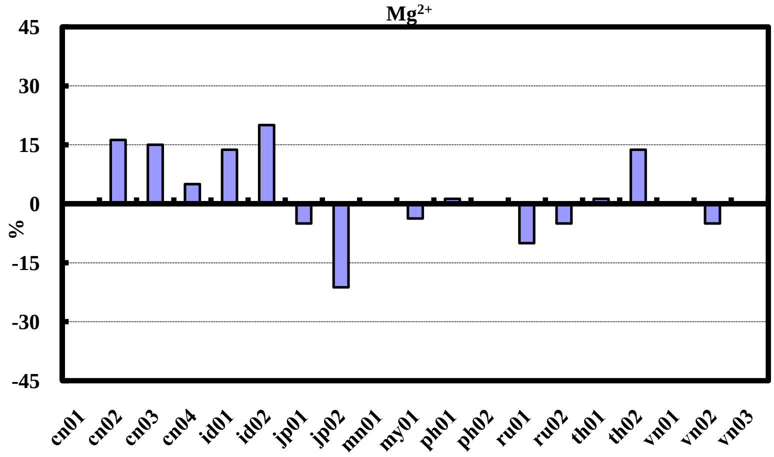


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Most of participating laboratories used ion chromatography, 3 laboratories used atomic absorption/flame (emission) photometry and 1 laboratory used titration (other method) for the determination of Mg^{2+}. Data from 3 laboratories were flagged. Two flagged data were obtained from the use of ion chromatography method, and one data was obtained from the use of titration.

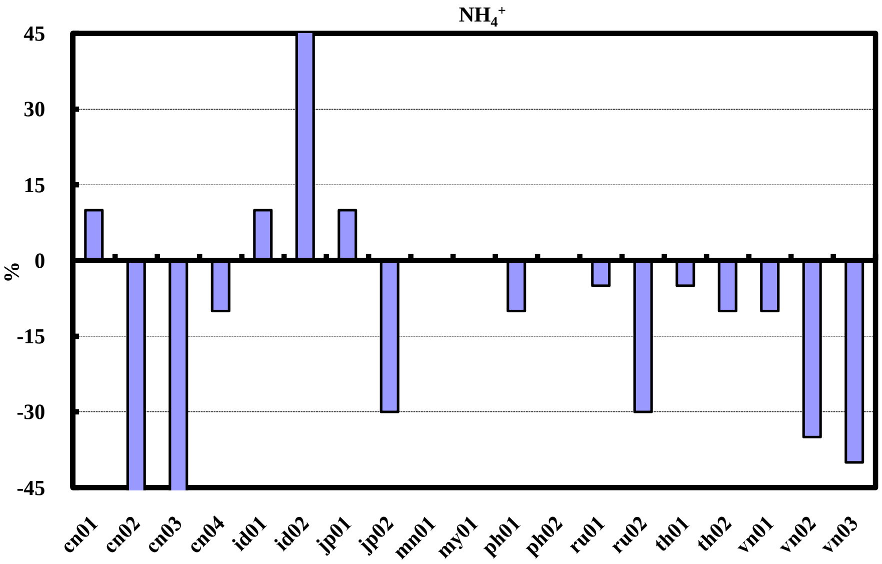


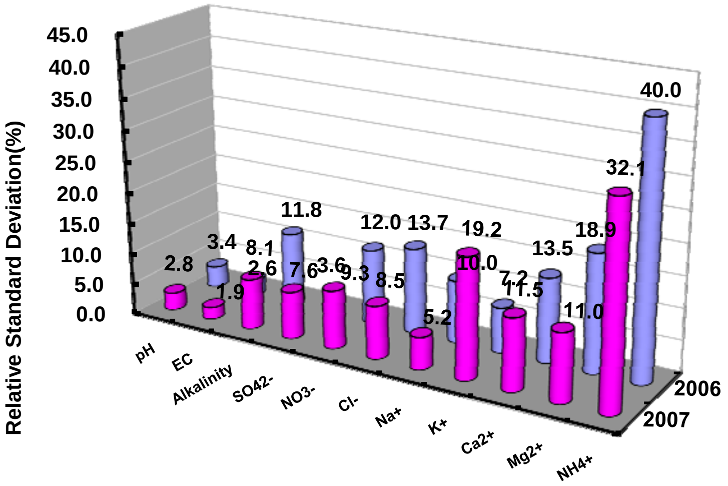
Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Among 17 participating laboratories, 12 laboratories used ion chromatography, 3 laboratories used spectrophotometry (Indophenol) and 2 laboratories used spectrophotometry (other method) for the determination of NH_4^+. Data from 7 laboratories were flagged. Especially 5 data were significantly deviated from prepared value. 3 flagged data were obtained by ion chromatography method, 3 data were obtained by indophenol method, and 1 data was obtained by spectrophotometry except indophenol method.

NH_4^+ was one of the parameters that have the highest flagged percentage in this attempt. It had also the highest flagged percentage in the attempt in 2003-2007. It may be necessary to pay more attention to the analysis of NH_4^+ in the inland water sample in each laboratory to achieve better accuracies.

5.3.3 Overall Evaluation

Calculated relative standard deviation of the whole sets of analytical data is presented in Figure 5.14 with comparison to last attempt (2006).



(Relative standard deviation (%) = Standard deviation / Average x 100, Reported data after outliers were removed)

Figure 5.14 Relative standard deviation of each constituent

The relative standard deviation of NH_4^+ results from laboratories was larger than other ions. That of last attempt was also larger than other ions. It may be necessary to pay more attention to the variation among the laboratories of NH_4^+ analyze in the inland water than another analytical parameters.

5.3.4 Information on laboratories

Methodologies used

The percentage of laboratories using the recommended methods are shown in Fig. 5.15, and the codes used for the various analytical methods are shown in Table 5.11 and 5.12.

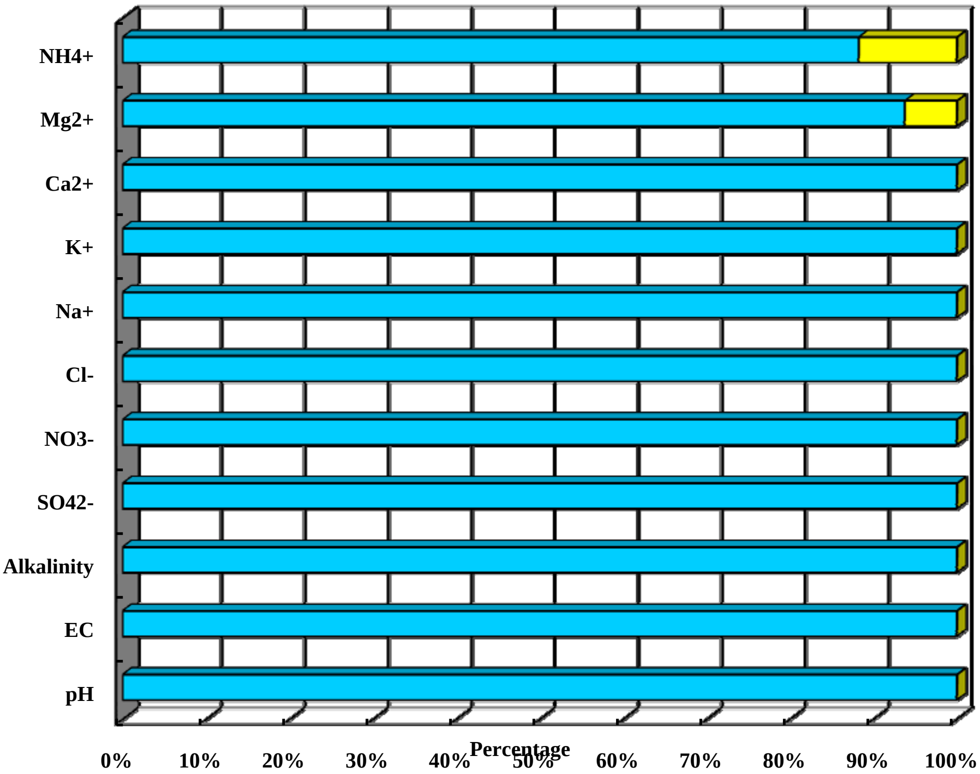


Figure 5.15 Percentage of laboratories using the recommended methods

Table 5.11 List of methods

Code	Method
0	pH meter with electrode
1	Conductivity cell
2	Titration
3	Atomic absorption / Flame (emission) photometry
4	Ion chromatography
5	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
6	Calculation
7	Spectrophotometry
8	Spectrophotometry (Indophenol blue)
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
11	Other method

Table 5.12 Analytical methods

Code	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	19										
1		19									
2			18(1)			3(1)				1(1)	
3							3	3(1)	4(1)	3	
4				15(1)	14(1)	15(1)	13	13(2)	12(4)	12(2)	12(3)
5											
6											
7				3(1)	3(1)						2(1)
8											3(3)
9											
10											
11											
Flagged E	0	0	1	2	2	2	0	1	4	3	2
Flagged X	0	0	0	0	0	0	0	2	1	0	5

Reverse mesh is a recommended method of EANET

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

The participating laboratories used recommended methods of EANET except measurement of Mg^{2+} and NH_4^+. Two laboratories used spectrophotometry instead of indophenol blue for NH_4^+ analysis, and one of them was flagged. One laboratory used titration method for Mg^{2+}, and its data was flagged.

The percentage of flagged cations was larger than that of anions. For the determination of cations, most of participating laboratories used ion chromatography, and some of them used atomic absorption/flame (emission) photometry. But no clear relationship between analytical methods and flagged data was observed.

Staff (numbers and years of experience)

Number of staff in charge of measurement in each laboratory is shown in Table 5.13.

Table 5.13 Staff in charge of measurement

Lab.ID	Total	pH	EC	Alkalinity	SO$_4^{2-}$	NO3$^-$	Cl$^-$	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	NH4$^+$
cn01	1	A	A	A	A	A	A	A	A	A	A	A
cn02	3	A	A	B	C	C	C	C	C	C	C	C
cn03	1	A	A	A	A	A	A	A	A	A	A	A
cn04	1	A	A	A	A	A	A	A	A	A	A	A
id01	3	A	A	A	B	B	B	C	C	C	C	C
id02	5	A	A	B	A	B	C	D	E	E	C	B
jp01	1	A	A	A	A	A	A	A	A	A	A	A
jp02	2	A	A	B	B	A	B	B	B	B	B	A
mn01	2	A	A	B	B	B						
my01	4	A	A	B	C	C	C	D	D	D	D	D
ph01	3	A	A	A	B	B	B	C	C	C	C	C
ph02	1	A	A									
ru01	4	A	A	B	C	C	C	D	D	D	D	A
ru02	3	A	A	A	B	B	A	C	C	C	C	B
th01	2	A	B	A	B	B	B	A	A	A	A	A
th02	1	A	A	A	A	A	A	A	A	A	A	A
vn01	2	A	A	A	B	B	B	B	B	B	B	B
vn02	2	A	A	B	A	A	A	B	B	B	B	B
vn03	2	A	B	B	A		B					A

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

Reverse mesh : "E" or "X" in sample flagged Data.

There were no clear relationship between data quality and the number of staff in charge of measurement.

Years of experience of staff in each laboratory are shown in Table 5.14.

Table 5.14 Years of experience

Unit : year

Lab.ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
cn01	16	16	16	16	16	16	16	16	16	16	16
cn02	17	17	1.5	2	2	2	2	2	2	2	2
cn03	2	2	2	2	2	2	2	2	2	2	2
cn04	22	22	22	22	22	22	22	22	22	22	22
id01	5	5	5	5	5	5	10	10	10	10	10
id02	26	26	4	26	4	31	25	17	17	31	4
jp01	2	2	2	2	2	2	2	2	2	2	2
jp02	3	3	12	12	3	12	12	12	12	12	3
mn01	13	13	9	13	13	13					
my01	1	1	3	5	5	5	7	7	7	7	7
ph01	8	8	8	7	7	7	11	11	11	11	11
ph02	16	16									
ru01	14	14	5	12	12	12	22	22	22	22	14
ru02	47	47	47	13	13	47	16	16	16	16	13
th01	10	5	10	5	5	5	10	10	10	10	10
th02	4	4	4	4	4	4	4	4	4	4	4
vn01	5	5	5	15	15	15	15	15	15	15	15
vn02	25	25	15	25	25	25	15	15	15	15	15
vn03	4	2	2	4		2					4

Reverse mesh:Data were Flagged by “E” or “X” in sample

1 year means experienced with one year or less.

There were no clear relationship between data quality and years of experience.

5.4. Comparison with past surveys

The inter-laboratory comparison projects of EANET have been carried out 8 times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure.5.16.

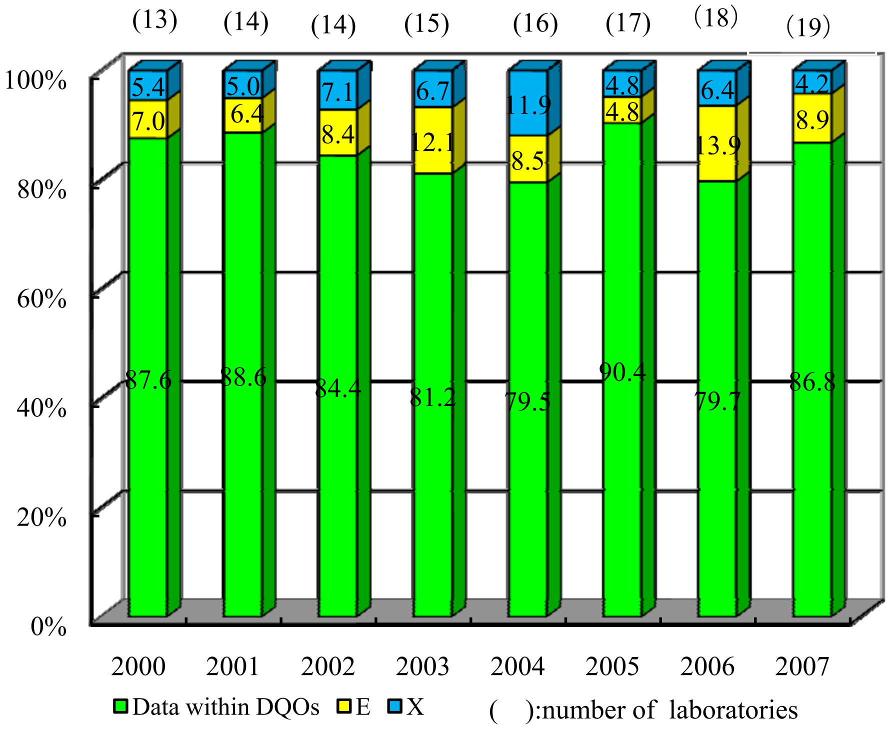
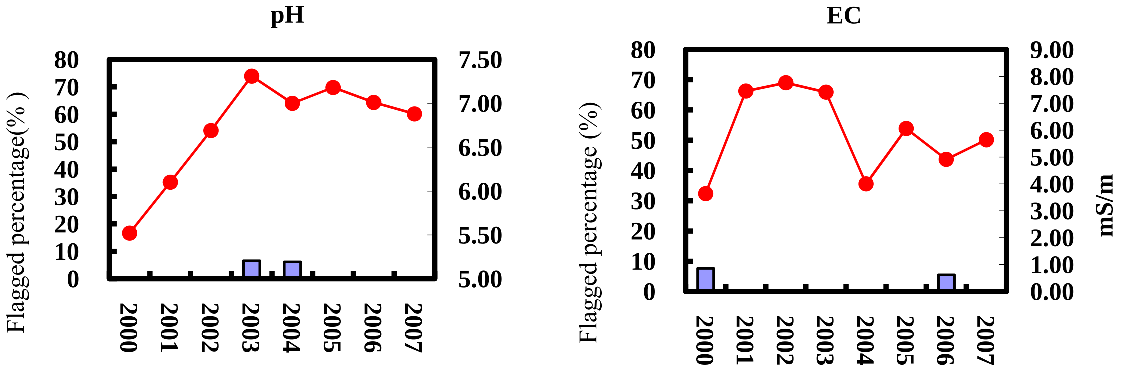
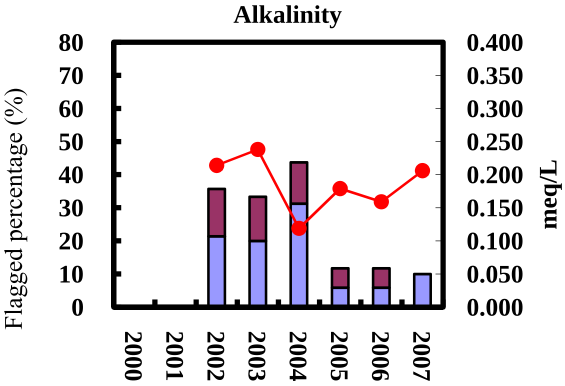


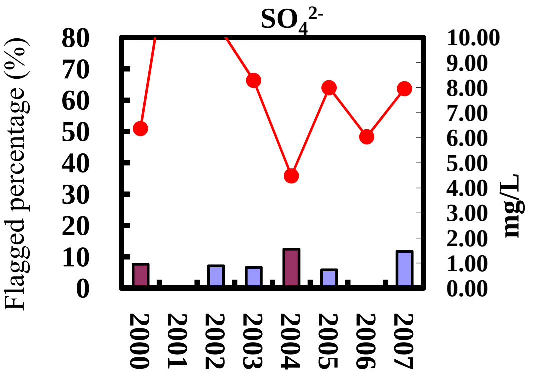
Figure 5. 16 Comparison of the results from the inter-laboratory comparison projects

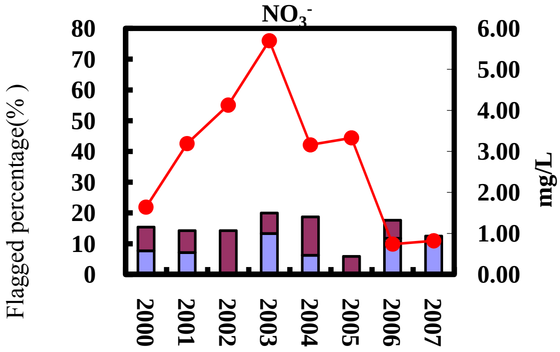
The graph shows the number of laboratories had increased and the percentage of data within DQOs had increased compared to 2006, but is still lower than the value achieved in 2005.

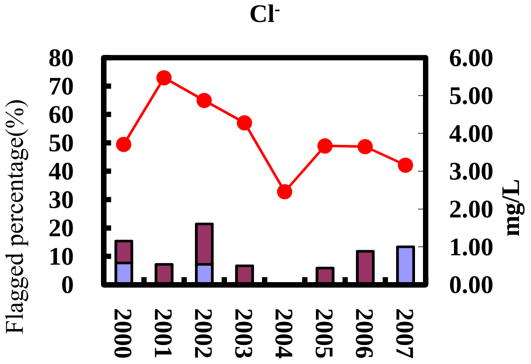
The comparison for each parameter from 1st to 8th project with the percentage of flagged data is shown in Figure 5.17.

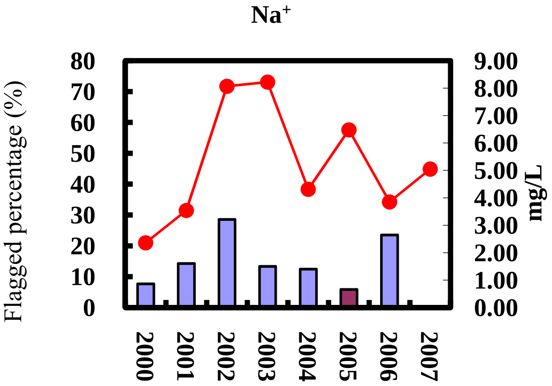


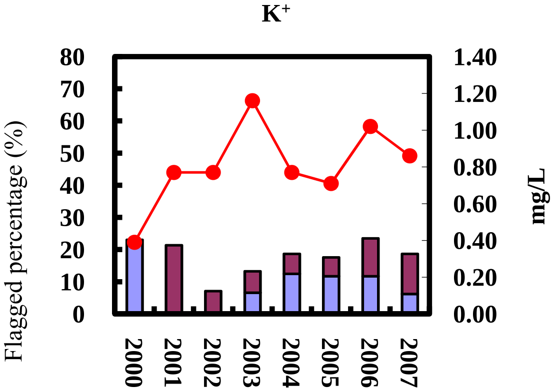

Alkalinity
Flagged percentage (%)
80
70
60
50
40
30
20
10
0
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
meq/L
2000
2001
2002
2003
2004
2005
2006
2007

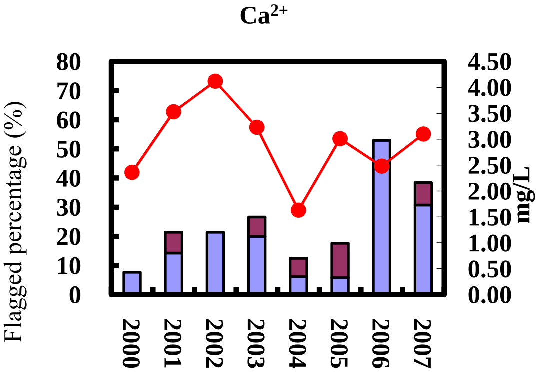

SO_4^{2-}
Flagged percentage (%)
80
70
60
50
40
30
20
10
0
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007

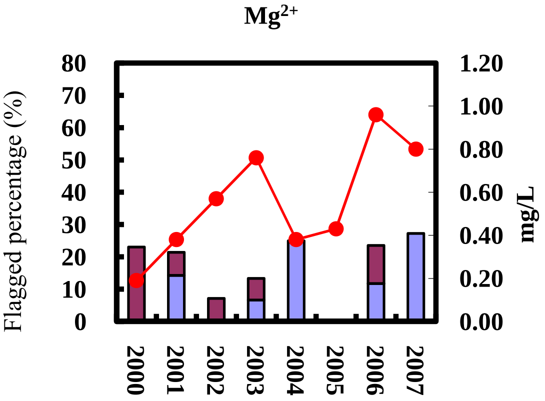

NO_3^-
Flagged percentage(%)
80
70
60
50
40
30
20
10
0
6.00
5.00
4.00
3.00
2.00
1.00
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007


Cl^-
Flagged percentage(%)
80
70
60
50
40
30
20
10
0
6.00
5.00
4.00
3.00
2.00
1.00
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007


Na^+
Flagged percentage (%)
80
70
60
50
40
30
20
10
0
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007


K^+
Flagged percentage (%)
80
70
60
50
40
30
20
10
0
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007


Ca^{2+}
Flagged percentage (%)
80
70
60
50
40
30
20
10
0
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007


Mg^{2+}
Flagged percentage (%)
80
70
60
50
40
30
20
10
0
1.20
1.00
0.80
0.60
0.40
0.20
0.00
mg/L
2000
2001
2002
2003
2004
2005
2006
2007

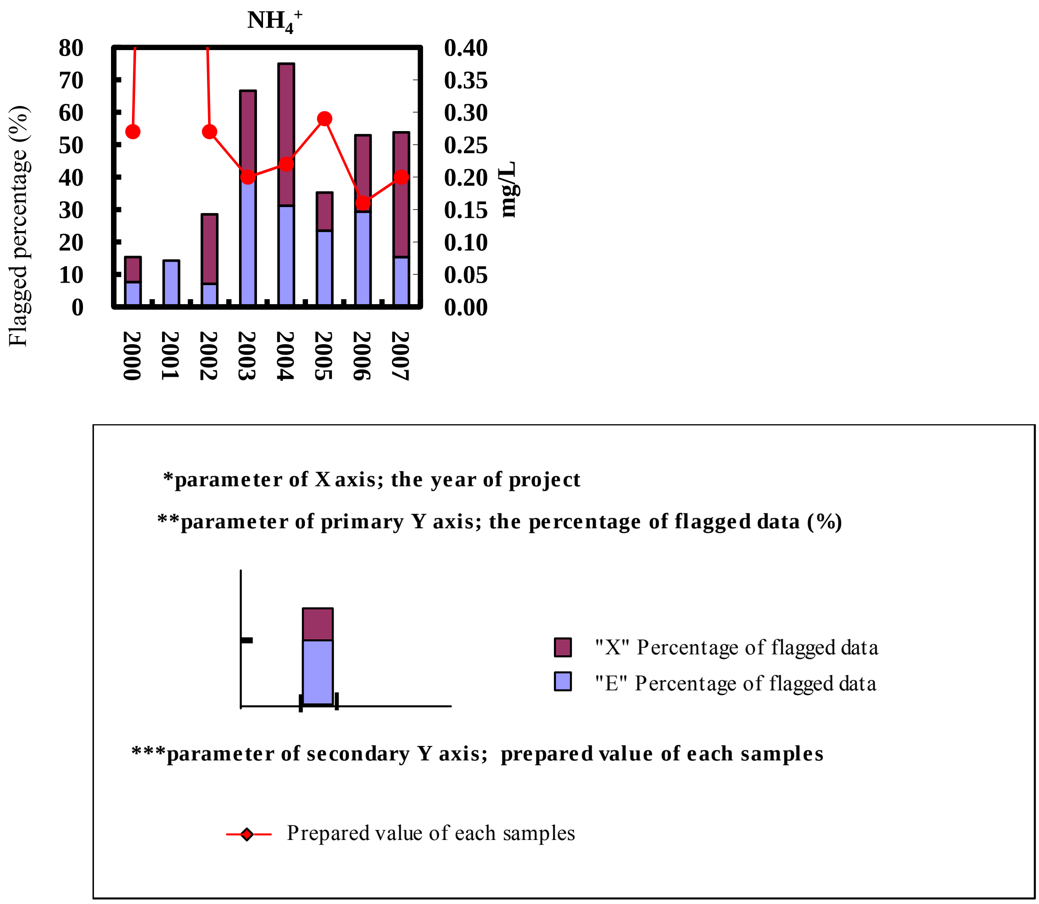


Figure 5.17 Comparison of the percentage of flagged data for each parameter in inter-laboratory comparison projects

The percentage of flagged data of NH_4^+ increased when the prepared concentration of NH_4^+ was low. And the percentage of flagged data of alkalinity decreased. Concerning other parameters, there were no clear relationship between the concentration and the percentage of flagged data.

The percentage of flagged cations was larger than that of anions in this project. Especially the percentage of flagged Ca^{2+} and NH_4^+ exceeded more than 30%. The percentage of flagged NH_4^+ was larger than other parameters in every survey except 1st- 3rd project. The percentage of flagged Ca^{2+} of 7th and 8th project were relatively high.. It was not clear why the number of flagged data for Ca^{2+} increased. But it seems that there is necessity to pay attention to the analysis of Ca^{2+} and NH_4^+ in inland water.

5.5. Recommendations for improvement

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

The analytical method for analyzing an inland-water sample is almost the same as that for analyzing wet deposition samples. Therefore the recommendations for improvements listed below are similar.

5.5.1 Measurement and Analysis

1) General

- ►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.

2) Deionized water

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

3) 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 materials should be used as much as possible.

4) 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.

5) Calibration of analytical instruments

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

5.5.2 Evaluation of reliability

1) Sensitivity fluctuation of analytical instruments

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

For example, in Ion chromatography

► A new calibration should be performed before the measurements are reached to over 30 samples.

► 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 should be made, and reference solution should be measured again.

► If the retention time changes slowly while the separator column is deteriorating, then adequate actions should 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.

5.5.3 Data control

1) Data checks by the analytical laboratories

► When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the percentage 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 questionable quality. When abnormal or unrecorded data is detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

References

1) Technical Manual for Monitoring on Inland Aquatic Environment in East Asia: Adopted at The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia

2) Quality Assurance / Quality Control (QA/QC) Program for Monitoring on Inland Aquatic Environment in East Asia: Adopted at The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia

3) Report on the Inter-laboratory Comparison Project 2000 on Inland Aquatic Environment, 1St attempt, November 2001, 2nd attempt, November 2002, 3rd attempt, November 2003, 4th attempt, November 2004, and 5th attempt, November 2004 , 6th attempt, November 2005 and 7th attempt, October 2006.

Appendix 5.1 Participating laboratories

CHINA

1) Zhuhai Environmental Monitoring Station	(cn01)
2) Environmental Monitoring Station of Xiamen	(cn02)
3) Xi’an Environmental Monitoring Station	(cn03)
4) Chongqing Institute of Environmental Science	(cn04)

INDONESIA

5) Environmental Management Center (EMC) Serpong Indonesia	(id01)
6) Research Institute for Water Resources(RIWR), Agency for Research and Development, Ministry of Settlement and Regional Infrastructures	(id02)

JAPAN

7) Gifu Prefectural Institute of Health and Environmental Science	(jp01)
8) Shimane Prefectural Institute of Public Health and Environmental Science	(jp02)

MALAYSIA

9) Division of Environmental Health, Department of Chemistry	(my01)

MONGOLIA

10) Central Laboratory of Environmental Monitoring,	(mn01)

PHILIPPINES

11) Environmental Management Bureau (EMB),	(ph01)
12) Environmental Management Bureau Cordillera Administrative Region Baguio City (EMB-CAR),	(ph02)

RUSSIA

13) Limnologcal Institute of Russian Academy of Science/Siberian Branch(RAS/SB)	(ru01)
14) Primorskii Environmental Monitoring Center of Roshydromet (Laboratory for Monitoring of Atomosphere and Soil Pollution)	(ru02)

THAILAND

15) Environmental Research and Training Center (ERTC)	(th01)
16) Air Quality and Noise Management Division, Pollution Control Department(PCD) Ministry of Science Technology and Environment(MSTE)	(th02)

VIET NAM

17) Institute of Meteorology and Hydrology (IMH) Hydrometeorological Service of Viet Nam (HMS)	(vn01)
18) Middle of Central regional Hydro-Meteorological Observatory National Hydro -Meteorological Center (NHMS)	(vn 02)
19) Environmental research Division, Sub-Institute of HydroMeteorology and Environment of South Vietnam (SIHYMETE)	(vn 03)

Appendix 5.2

Results submitted by the laboratories

Lab. ID	pH -	EC (mS/m)	Alkalinity (meq/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)
cn01	7.11	5.34	0.207	7.91	0.76	3.08	4.98	0.82	3.21	0.80	0.22
cn02	7.11	5.37	0.196	8.17	0.81	3.15	5.34	0.86	3.79	0.93	0.09
cn03	7.10	5.32	0.210	7.61	0.82	2.98	5.12	0.82	3.76	0.92	0.08
cn04	7.11	5.31	0.214	7.61	0.79	2.93	5.10	0.80	3.48	0.84	0.18
id01	7.03	5.47	0.205	9.17	0.91	3.01	5.07	0.89	3.13	0.91	0.22
id02	6.60	5.47	0.246	6.20	0.59	3.28	4.62	1.15	3.61	0.96	0.31
jp01	6.99	5.37	0.203	7.91	0.77	3.06	4.94	0.85	3.00	0.76	0.22
jp02	7.26	5.37	0.210	8.00	0.80	3.29	5.10	0.85	2.65	0.63	0.14
mn01	7.23	5.33	0.192	7.91	0.75	2.98					
my01	6.76	5.22	0.222	8.39	0.83	3.30	5.05	0.72	3.56	0.77	0.20
ph01	7.39	5.38	0.181	8.22	0.81	3.19	4.92	0.86	3.47	0.81	0.18
ph02	7.38	5.20									
ru01	7.25	5.53	0.202	7.65	0.75	2.90	4.44	0.97	3.13	0.72	0.19
ru02	7.26	5.56	0.195	7.50	0.82	3.08	4.65	0.89	3.06	0.76	0.14
th01	6.95	5.15	0.178	7.94	0.78	3.11	4.98	0.85	3.14	0.81	0.19
th02	7.11	5.33	0.217	7.25	0.75	2.61	4.99	0.83	3.95	0.91	0.18
vn01	7.11	5.36	0.205	7.79	0.64	2.99	4.44	0.36	4.12	0.80	0.18
vn02	7.15	5.44	0.213	7.61	0.81	3.02	4.98	0.98	3.20	0.76	0.13
vn03	7.38	5.37	0.234	7.45		2.23					0.12
Expected	6.88	5.64	0.206	7.96	0.82	3.16	5.05	0.86	3.10	0.80	0.20
Number of	19	19	18	18	17	18	16	16	16	16	17
Average	7.12	5.36	0.206	7.75	0.77	3.00	4.87	0.84	3.40	0.81	0.17
Minimum	6.60	5.15	0.178	6.20	0.59	2.23	4.44	0.36	2.65	0.63	0.08
Maximum	7.39	5.56	0.246	9.17	0.91	3.30	5.34	1.15	4.12	0.96	0.31

blank : not analyzed

Appendix 5.3

Data normalized by prepared value

(Original data / Expected Value - 1) * 100

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO_4^{2-} (%)	NO_3^- (%)	Cl^- (%)	Na^+ (%)	K^+ (%)	Ca^{2+} (%)	Mg^{2+} (%)	NH_4^+ (%)
cn01	3.3	-5.3	0.5	-0.6	-7.3	-2.5	-1.4	-4.7	3.5	0.0	10.0
cn02	3.3	-4.8	-4.9	2.6	-1.2	-0.3	5.7	0.0	22.3	16.3	-55.0
cn03	3.2	-5.7	1.9	-4.4	0.0	-5.7	1.4	-4.7	21.3	15.0	-60.0
cn04	3.3	-5.9	3.9	-4.4	-3.7	-7.3	1.0	-7.0	12.3	5.0	-10.0
id01	2.2	-3.0	-0.5	15.2	11.0	-4.7	0.4	3.5	1.0	13.8	10.0
id02	-4.1	-3.0	19.4	-22.1	-27.7	3.8	-8.5	33.7	16.5	20.0	55.5
jp01	1.6	-4.8	-1.5	-0.6	-6.1	-3.2	-2.2	-1.2	-3.2	-5.0	10.0
jp02	5.5	-4.8	1.9	0.5	-2.4	4.1	1.0	-1.2	-14.5	-21.3	-30.0
mn01	5.1	-5.5	-6.8	-0.6	-8.5	-5.7					
my01	-1.7	-7.4	7.8	5.4	1.1	4.4	0.0	-16.3	14.8	-3.8	0.0
ph01	7.4	-4.6	-12.1	3.3	-1.7	0.9	-2.6	0.5	11.9	1.3	-10.0
ph02	7.3	-7.8									
ru01	5.4	-2.0	-1.9	-3.9	-8.5	-8.2	-12.1	12.8	1.0	-10.0	-5.0
ru02	5.5	-1.4	-5.3	-5.8	0.0	-2.5	-7.9	3.5	-1.3	-5.0	-30.0
th01	1.0	-8.7	-13.6	-0.3	-4.9	-1.6	-1.4	-1.2	1.3	1.3	-5.0
th02	3.3	-5.5	5.3	-8.9	-8.5	-17.4	-1.2	-3.5	27.4	13.8	-10.0
vn01	3.3	-5.0	-0.5	-2.1	-22.0	-5.4	-12.1	-58.1	32.9	0.0	-10.0
vn02	3.9	-3.5	3.4	-4.4	-1.2	-4.4	-1.4	14.0	3.2	-5.0	-35.0
vn03	7.3	-4.8	13.6	-6.4		-29.4					-40.0
Minimum	-4.1	-8.7	-13.6	-22.1	-27.7	-29.4	-12.1	-58.1	-14.5	-21.3	-60.0
Maximum	7.4	-1.4	19.4	15.2	11.0	4.4	5.7	33.7	32.9	20.0	55.5

blank : not analyzed

6. ACKKNOWLEDGEMENT

ADORC wishes to thank Toyama Prefecture for their cooperation in the collection of soil samples used for the soil inter-laboratory comparison project.

7. CONTACT INFORMATION

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