Acid Deposition Monitoring Network
in East Asia (EANET)

Report of the Inter-laboratory Comparison Project 2008

11th Inter-laboratory Comparison Project on Wet Deposition

4th Inter-laboratory Comparison Project on Dry Deposition

10th Inter-laboratory Comparison Project on Soil

9th Inter-laboratory Comparison Project on Inland Aquatic Environment

November 2009
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,

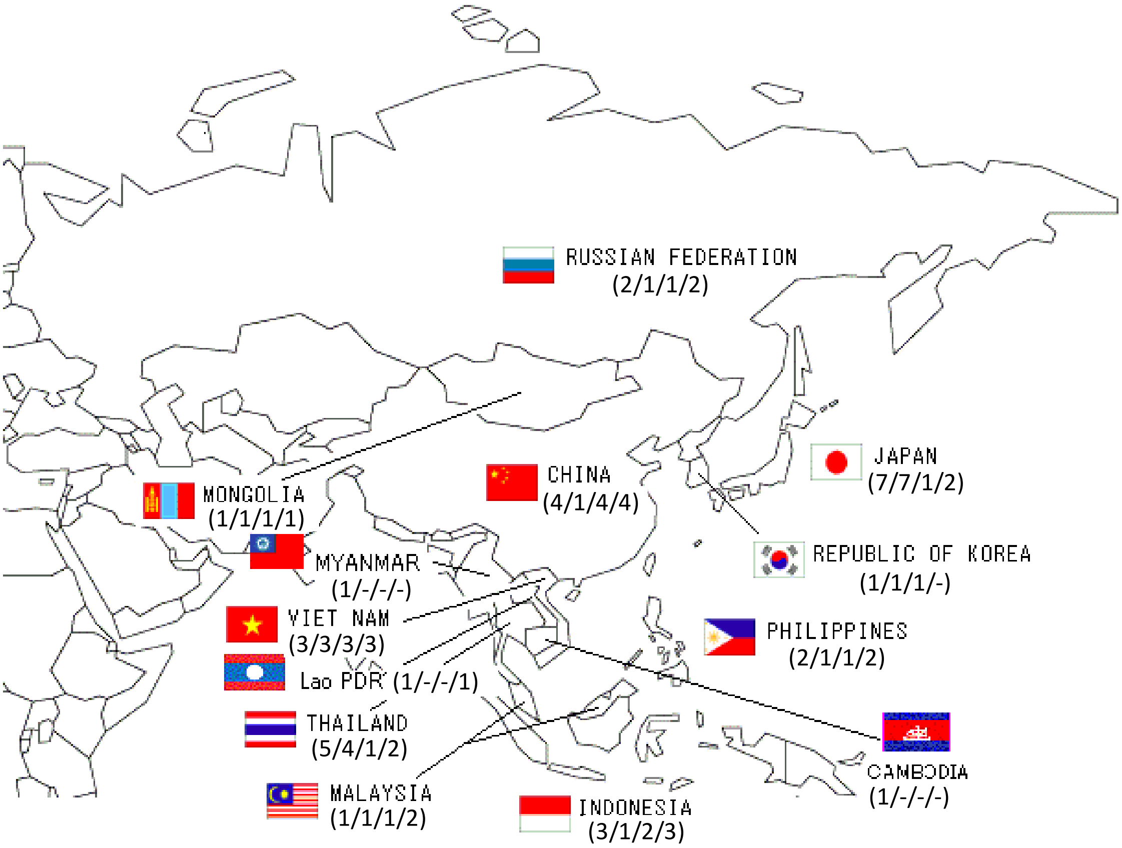
(iii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

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

a. Wet Deposition
b. Dry Deposition
c. Soil
d. Inland aquatic Environment

This report presents the results of the 11th inter-laboratory comparison project on wet deposition, 4th inter-laboratory comparison project on dry deposition, 10th inter-laboratory comparison project on soil, and 9th 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 2008

2. 11th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 11th 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 the 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 15 October 2008. Their analytical results were submitted to the NC by 28 February 2009.

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 the NC. A list of the participating laboratories with the abbreviated name and code are given in Appendix 2.1.

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. 081w (high concentration sample) No. 082w (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. 081w (high concentration)	4.49	3.97	49.5	47.4	75.8	56.8	9.1	25.7	12.6	47.5
No. 082w (low concentration)	5.10	1.18	14.7	16.2	23.4	15.4	3.8	7.6	6.2	14.2

* 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).

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

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).

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

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;

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

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 analytical results from 32 laboratories in the participating countries of EANET. 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 -4.6%(EC) to 2.1%(NH_4^+) for the sample No. 081w, and -2.0%(EC) to 8.8%(Ca^{2+}) for the sample No. 082w.

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

Sample No. 081w

Constituents	Prepared (Vp)	Average (Va)	Va/Vp [%]	S.D.	N	Min.	Max.
pH	4.49	4.54	1.2	0.10	30	4.37	4.84
EC [mS/m]	3.97	3.79	-4.6	0.36	31	2.58	4.87
SO_4^{2-} [µmol/L]	49.5	49.3	-0.4	2.30	30	42.2	54.5
NO_3^- [µmol/L]	47.4	46.4	-2.1	1.88	29	40.4	50.2
Cl^- [µmol/L]	75.8	74.1	-2.2	3.23	29	63.6	82.6
Na^+ [µmol/L]	56.8	56.6	-0.3	2.94	30	49.7	66.7
K^+ [µmol/L]	9.1	9.1	0.1	0.70	30	8.2	11.5
Ca^{2+} [µmol/L]	25.7	26.0	1.2	1.30	28	24.1	29.6
Mg^{2+} [µmol/L]	12.6	12.4	-1.6	0.69	29	10.5	14.0
NH_4^+ [µmol/L]	47.5	48.5	2.1	3.38	30	40.2	55.4

Sample No. 082w

Constituents	Prepared (Vp)	Average (Va)	Va/Vp [%]	S.D.	N	Min.	Max.
pH	5.10	5.14	0.8	0.18	32	4.68	5.68
EC [mS/m]	1.18	1.16	-2.0	0.07	31	0.94	1.31
SO_4^{2-} [µmol/L]	14.7	14.6	-0.5	0.67	29	12.6	15.6
NO_3^- [µmol/L]	16.2	16.1	-0.5	1.16	29	14.0	19.5
Cl^- [µmol/L]	23.4	23.3	-0.6	1.73	30	19.6	28.4
Na^+ [µmol/L]	15.4	16.1	4.4	1.92	30	13.8	22.2
K^+ [µmol/L]	3.8	3.7	-1.5	0.49	30	2.7	4.9
Ca^{2+} [µmol/L]	7.6	8.3	8.8	1.21	29	6.8	11.2
Mg^{2+} [µmol/L]	6.2	6.3	1.9	0.75	30	4.5	8.1
NH_4^+ [µmol/L]	14.2	14.8	4.3	1.35	30	11.9	17.8

Va/Vp : (Va-Vp)/Vp*100

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. 081w (high concentrations) and No. 082w (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. 081w and No. 082w 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)

1) High Concentration Sample No. 081w

The number and percentage of flagged data in the high concentration sample No. 081w are described in Table 2.7. It was founded that 18 analytical data out of 307 exceeded the DQOs within a factor of 2 and was flagged by "E", 3 analytical data out of 307 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" shared about 6.8 percent of all reported data for sample No. 081w.

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. 081w (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	32	27	30	29	28	29	28	27	28	28	286
Data with flag E*	0	3	1	0	2	2	3	2	2	3	18
Data with flag X**	0	2	0	1	0	0	0	0	0	0	3
Flagged data [%]	0.0	15.6	3.2	3.3	6.7	6.5	9.7	6.9	6.7	9.7	6.8

(Total data = 307)

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

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

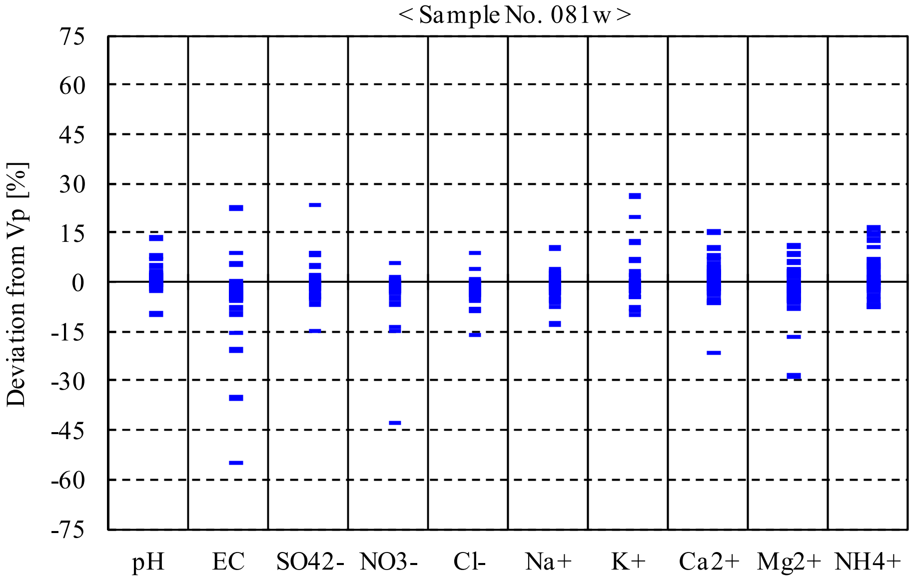


Figure 2.1 Distribution of the data normalized by prepared value in each parameters in the high concentration sample

The parameter which had most flags was EC. 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. 081w

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]	R_1 [%]	R_2 [%]
KH01	4.71	E 3.15	53.7	50.2	75.9	57.6	9.7		13.4	50.1		
CN01	4.38	3.83	49.7	46.1	75.2	55.8	8.8	26.3	13.1	48.7	2.9	5.9
CN02	4.42	3.85	49.7	47.8	75.6	57.3	8.7	25.5	13.0	50.9	2.0	4.5
CN03	4.46	3.84	49.8	46.1	73.6	56.5	8.7	25.3	12.9	48.1	1.1	2.6
CN04	4.46	3.85	50.4	45.9	72.6	57.3	8.3	26.7	14.0	46.9	2.1	2.7
ID01	4.53	4.19	48.7	X 27.1	73.4	56.8	9.0	27.1	12.8	52.6	7.0	-5.4
ID02	4.56	3.74	50.6	41.0	69.3	49.7	9.2	24.3	E 10.5	44.1	-2.8	-1.4
ID03	5.09	X 2.58	42.2	40.4	E 63.6	55.1	E 10.9	E 20.2	12.5	50.7	0.5	4.7
JP01	4.57	3.91	48.7	46.8	71.9	57.5	9.1	E 29.6	13.7	49.4	3.0	-1.1
JP02	4.55	3.88	47.0	45.1	73.0	56.3	8.9	25.8	12.2	47.5	1.1	-1.7
JP03	4.53	3.79	49.7	47.3	75.6	56.1	9.0	26.1	12.1	47.3	-0.9	1.2
JP04	4.54	3.87	51.9	47.5	76.1	55.3	8.7	26.1	12.3	49.2	-1.9	0.5
JP05	4.59	3.80	47.4	46.1	73.1	54.4	9.1	25.2	12.2	48.2	-0.4	-1.7
JP06	4.56	3.80	49.5	47.2	75.5	55.7	9.0	24.2	12.4	45.0	-2.6	-0.4
JP07	4.51	3.81	48.7	47.3	74.8	56.1	9.1	25.3	11.6	46.5	-0.7	1.0
LA01	4.46	E 3.36	48.2	46.1	78.9	58.7	9.7	28.4	12.3	E 55.4	4.0	C 10.6
MY01	4.54	3.78	47.9	46.6	74.3	58.0	8.9	26.5	11.9	45.5	0.3	0.4
MN01	4.57	3.79	46.3	47.6	75.9	56.1	10.2	25.2	11.8	49.8	0.2	-0.5
MM01	4.81	X 1.79										
PH01	4.63	3.78	53.7	46.6	82.6	53.3	9.0	26.5	E 9.0	54.4	-5.7	0.1
PH02	4.84	3.66	49.4	46.7	76.3	62.7	E 11.5	24.9	12.0	50.0	-2.2	-3.6
KR01	4.60	4.32	49.1	44.2	74.2	52.5	8.2	24.8	12.0	44.1	-3.1	-8.8
RU01	4.51	3.94	47.2	46.2	76.0	56.6	8.9	26.5	12.8	46.3	1.1	-0.7
RU02	4.54	3.94	50.2	48.2	71.5	58.3	9.0	27.5	12.3	46.3	0.4	-1.0
TH01	4.57	3.80	49.1	46.6	74.2	58.3	9.4	27.8	13.0	47.1	1.0	0.1
TH02	4.52	3.78	48.9	47.5	75.2	53.8	8.7	24.1	11.9	48.4	-1.7	1.0
TH04	4.05	E 4.87	E 61.1	46.9	69.3	58.8	9.3	26.9	12.3	53.5	I 9.6	C 11.8
TH05	4.48	3.59	47.5	45.9	73.1	55.2	8.4	26.2	12.5	44.1	1.0	4.3
TH06	4.51	3.51	49.2	46.1	72.7	54.8	8.5	25.2	11.7	53.7	1.0	5.4
VN01	4.49	4.07	50.6	47.7	75.6	57.9	8.8	26.4	12.5	50.4	0.6	-0.5
VN02	4.37	3.78	49.7	47.7	E 61.7	E 43.2	E 6.4	24.1	11.7	E 40.2	-1.1	3.7
VN03	4.53	3.60	54.5			E 66.7	8.5			E 61.4		
Vp	4.49	3.97	49.5	47.4	75.8	56.8	9.1	25.7	12.6	47.5	0.0	0.2

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

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

* The abbreviated name and code are given in Appendix 2.1.

I: Poor ion balance (R_1)

C: Poor Conductivity agreement (R_2)

2) Low Concentration Sample No. 082w

For sample No. 082w (low concentrations), the number and percentage of flagged data are described in Table 2.9. It was founded that 33 analytical data out of 306 exceeded the DQOs within a factor of 2 and was flagged by "E", 11 analytical data out of 306 exceeded the DQOs more than a factor of 2 and was flagged by "X". Data flagged by “E” and “X” shared up to 14.3 percent of all reported data for sample No. 082w.
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. 082w (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	32	30	29	27	27	26	23	19	24	25	262
Data with flag E*	0	1	1	2	3	2	7	7	5	5	33
Data with flag X**	0	1	0	1	0	3	1	3	1	1	11
Flagged data [%]	0.0	6.3	3.3	10.0	10.0	16.1	25.8	34.5	20.0	19.4	14.3

(Total data = 306)

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

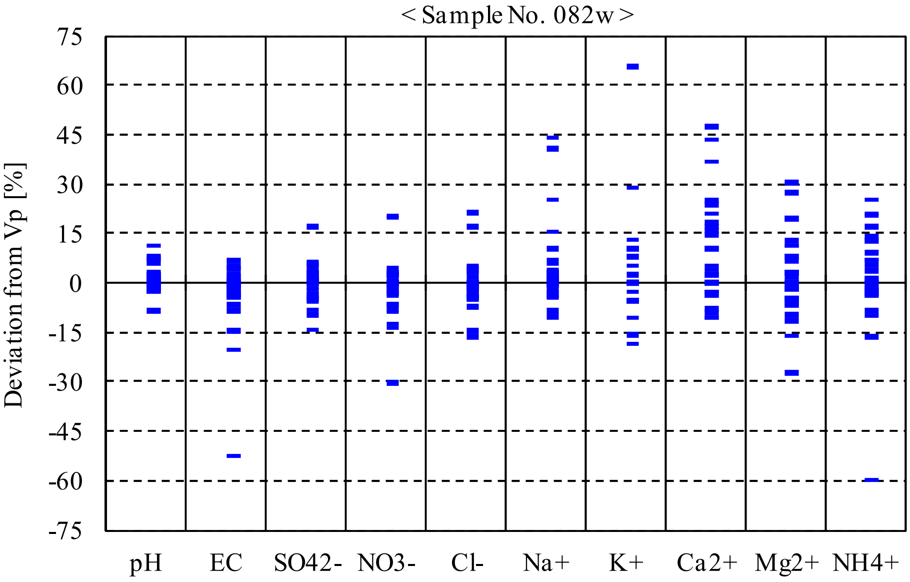


Figure 2.2 Distribution of the data normalized by prepared value for each parameter in the low concentration sample

Cations had a tendency to be flagged in comparison with 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. 082w

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]	R_1 [%]	R_2 [%]
KH01	5.21	1.16	15.1	E 19.5	E 28.4	15.6	4.2		7.0	X 5.7		
CN01	4.97	1.14	15.0	16.6	23.1	15.9	3.8	E 9.0	E 7.4	15.0	5.8	7.1
CN02	4.96	1.18	15.0	16.6	23.8	16.3	4.2	7.8	6.7	15.2	3.6	5.3
CN03	4.99	1.17	14.8	16.7	24.2	15.6	3.8	E 9.2	E 7.4	14.7	4.8	5.3
CN04	5.15	1.18	15.4	16.7	24.6	16.0	3.6	X 10.9	X 8.1	13.7	4.2	1.9
ID01	5.15	1.26	15.2	X 11.3	22.6	15.9	3.6	E 8.8	6.4	E 17.8	7.5	-4.4
ID02	5.19	1.13	15.2	14.8	23.0	15.5	4.1	7.4	E 5.2	12.8	-3.1	-1.5
ID03	5.68	E 0.94	12.6	14.2	20.0	14.8	3.8	6.8	5.8	14.0	0.4	-3.5
JP01	5.27	1.19	14.8	16.2	22.3	17.0	3.6	8.7	E 7.9	E 16.6	5.3	-2.5
JP02	5.09	1.17	14.9	16.1	22.9	15.0	3.6	7.9	6.3	13.8	0.1	0.3
JP03	5.08	1.16	14.8	16.2	23.2	15.3	3.7	7.3	5.9	13.9	-1.0	0.7
JP04	5.09	1.21	15.5	16.1	22.4	14.7	E 3.2	8.0	6.1	16.0	0.5	-0.7
JP05	5.16	1.18	14.7	16.2	23.3	14.1	3.6	7.0	5.9	14.4	-3.1	-2.6
JP06	5.21	1.14	14.9	16.3	22.4	15.6	3.9	7.3	6.4	15.5	0.0	-1.0
JP07	5.08	1.17	14.2	16.0	23.0	15.6	3.8	8.4	6.7	13.8	3.1	0.7
LA01	4.99	1.16	15.6	E 19.4	24.5	X 22.2	4.1	X 10.4	6.6	E 17.2	7.8	9.2
MY01	5.10	1.14	14.0	15.7	22.8	15.6	3.6	7.4	5.5	15.2	1.2	0.5
MN01	5.50	1.01	13.3	15.6	23.4	E 17.8	3.4	E 9.5	6.4	14.0	3.4	0.1
MM01	5.47	X 0.56										
PH01	5.22	1.14	E 17.2	16.9	E 27.4	X 21.7	E 4.9	X 11.2	E 4.5	16.2	1.0	5.1
PH02	5.41	1.13	15.2	16.6	22.5	E 19.3	X 6.3	E 8.9	5.8	13.7	2.2	-2.2
KR01	5.23	1.24	14.2	16.6	22.3	13.8	E 3.1	6.8	5.6	13.9	-4.5	-8.0
RU01	5.04	1.20	14.4	14.0	24.2	15.3	3.6	7.4	6.1	13.0	0.8	-0.6
RU02	5.05	1.19	14.9	14.9	23.2	15.2	3.8	7.4	5.9	13.9	0.4	0.1
TH01	5.14	1.17	14.5	15.8	22.5	15.9	4.2	E 9.4	6.9	14.4	5.0	0.1
TH02	5.15	1.08	13.5	15.1	21.7	14.8	4.0	6.9	5.9	16.0	2.8	1.1
TH04	4.68	1.23	13.9	15.1	E 19.6	16.5	4.2	7.8	6.1	E 17.1	I 16.1	C 13.3
TH05	5.00	1.10	14.0	15.7	22.5	15.0	4.3	8.4	6.9	E 11.9	4.1	5.4
TH06	5.06	1.10	14.8	16.2	21.9	14.0	E 2.8	6.8	5.8	15.5	-1.1	3.2
VN01	5.08	1.23	14.9	15.8	24.2	15.1	E 2.7	E 9.4	6.0	14.6	1.2	-1.0
VN02	4.90	1.31	14.7	15.7	25.7	17.3	E 4.4	7.6	6.3	14.6	4.0	2.2
VN03	5.14	1.03				X 24.1	E 2.7			15.8		
Vp	5.10	1.18	14.7	16.2	23.4	15.4	3.8	7.6	6.2	14.2	0.0	-0.3

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

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

* The abbreviated name and code are given in Appendix 2.1.

I: Poor ion balance (R_1)

C: Poor Conductivity agreement (R_2)

3) 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.

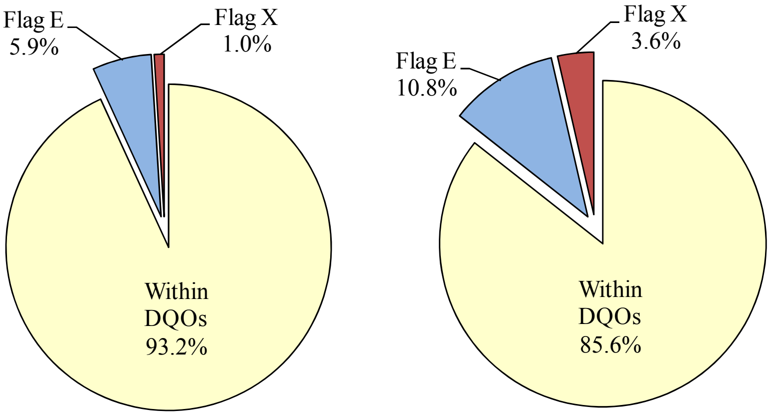


Figure 2.3 Percentage of flagged data for Sample No. 081w and No. 082w (Left: No. 081w, Right: No. 082w)

The percentage of the data within DQOs for the sample No. 081w and 082w were 93.2% and 85.6% respectively. The difference between both samples was 7.6%. In this project, the total number of flagged data was 65 (E: 51, X: 14) among the whole set of 613 data.

4) The number of flagged data of laboratories

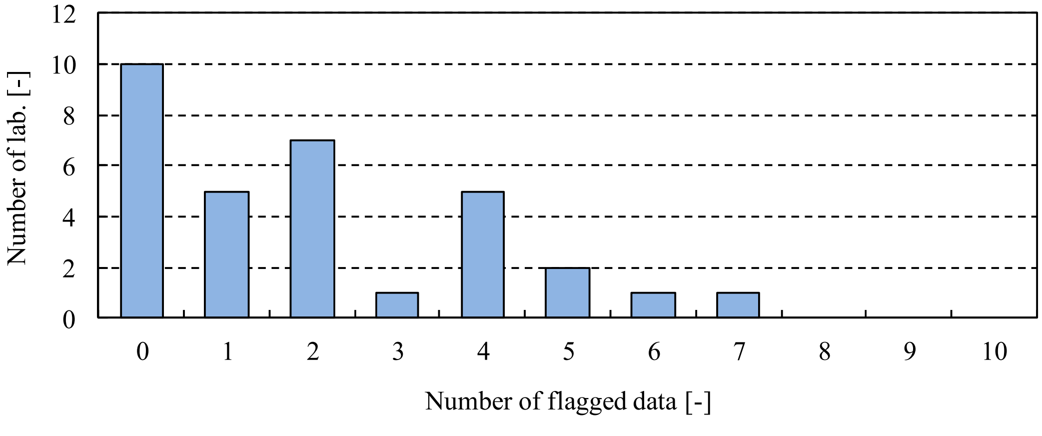


Figure 2.4 The distribution of laboratories with the number of flagged data

The number of flagged data of laboratories are shown in Figure 2.4. The number of laboratories without flagged data was 10, which corresponds to 31.3% 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 and solid lines depict the values dependent on DQOs (15%) and DQOs (30%) respectively.

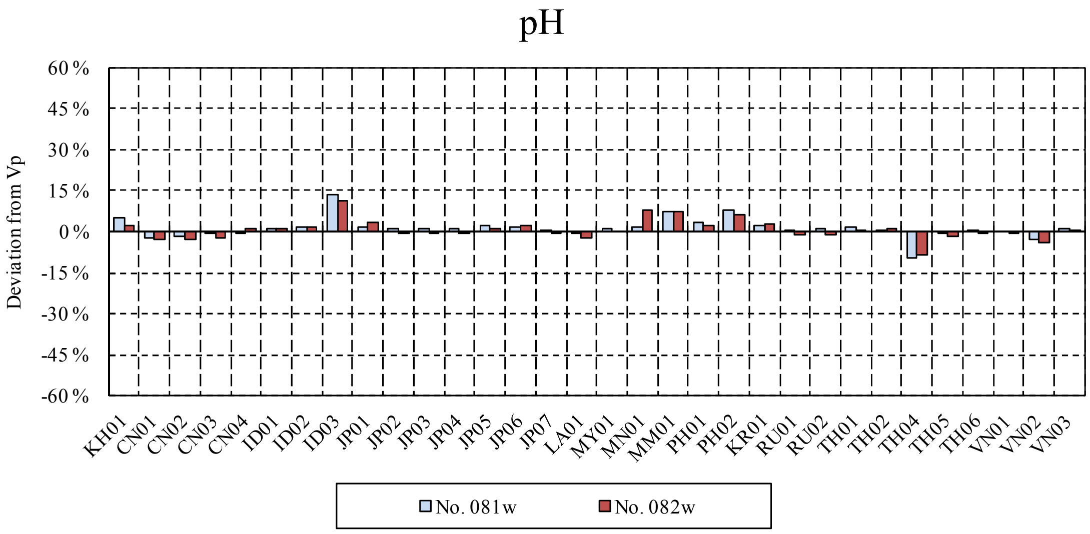
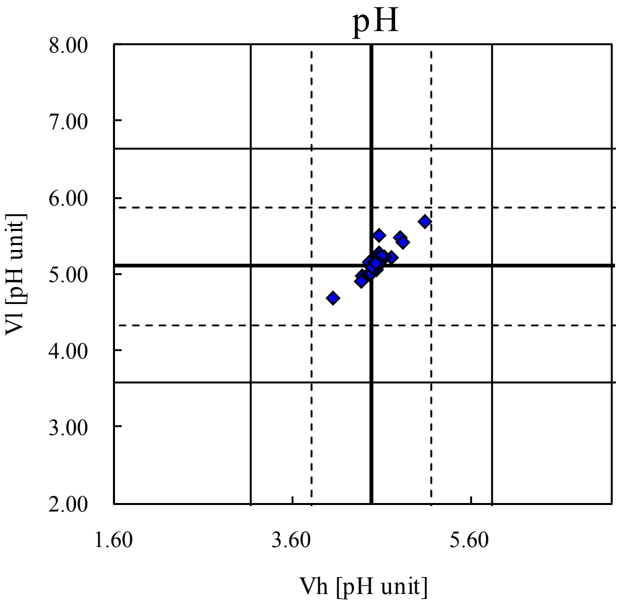


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)



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

Figure 2.6 Scatter diagram for pH

All participating laboratories used pH meter with glass electrode for the measurement of pH. All of obtained data satisfied the DQO of the QA/QC program of EANET.

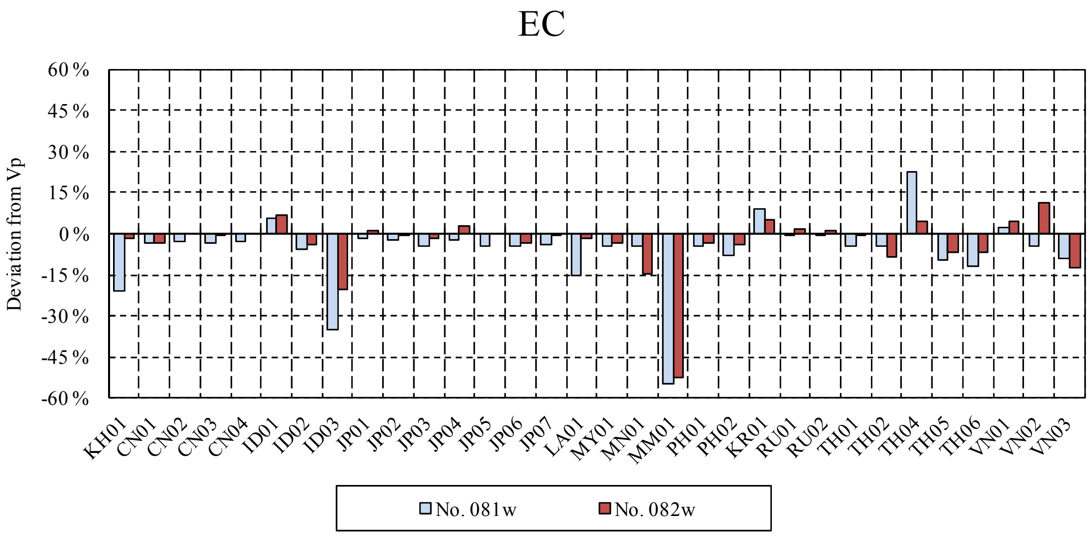
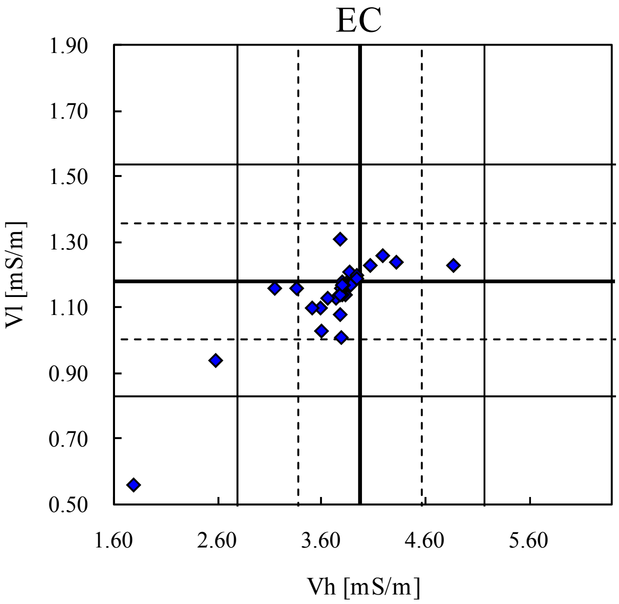


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)



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

Figure 2.8 Scatter diagram for EC

All participating laboratories used conductivity cell for the measurement of EC. The data submitted by KH01, LA01 and TH04 exceeded the DQO in high concentration sample. And the data submitted by ID03 and MM01 exceeded the DQO in both samples.

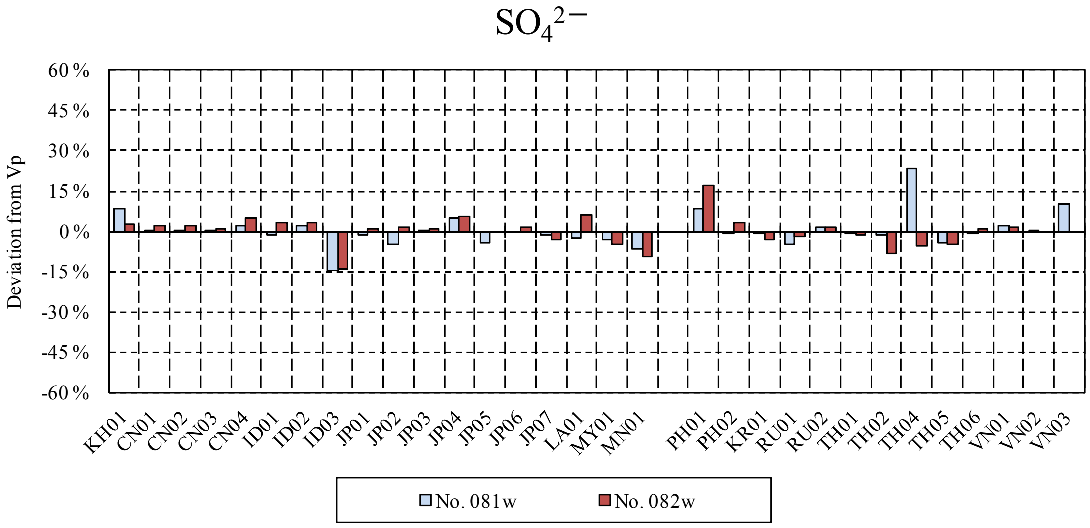
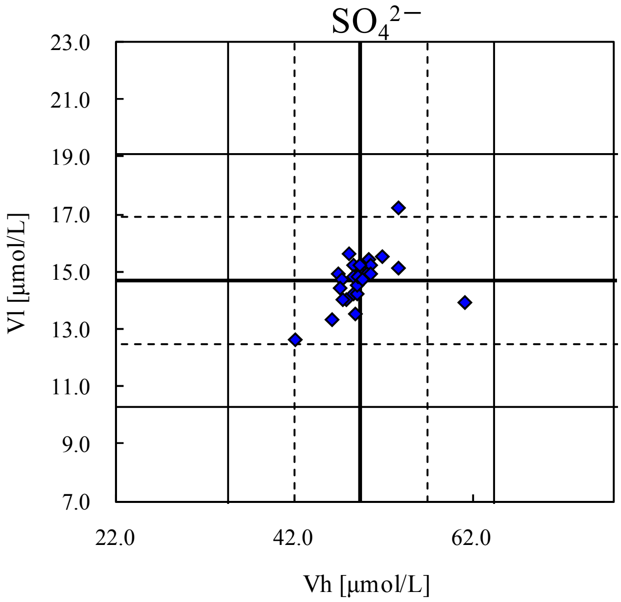


Figure 2.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)



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

Figure 2.10 Scatter diagram for SO_4^{2-}

For the analysis of SO_4^{2-}, 29 laboratories used Ion-chromatography, 2 laboratories (RU02 and VN03) used Spectrophotometry. The data submitted by TH04 in high concentration sample and PH01 in low concentration sample exceeded the DQO and were marked with flag “E”.

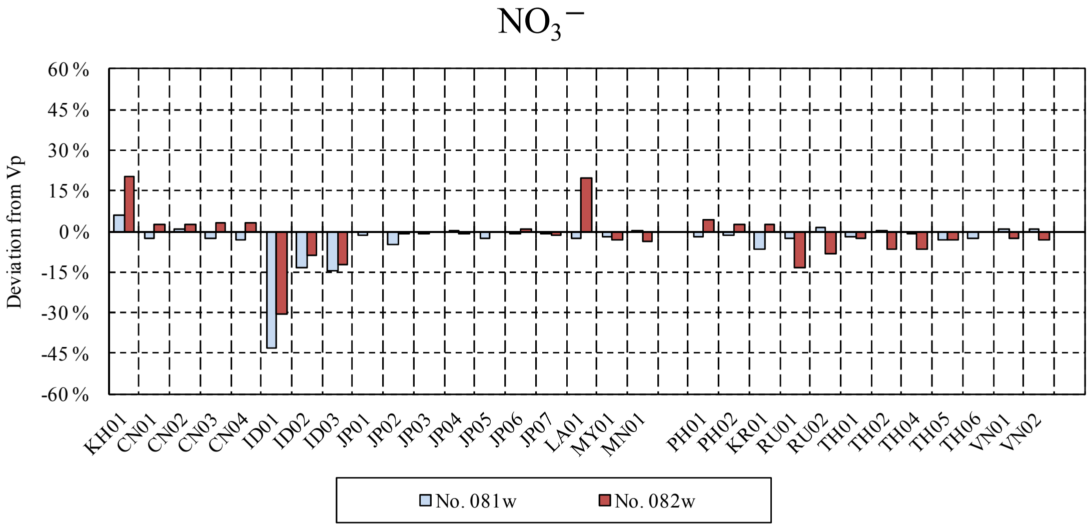
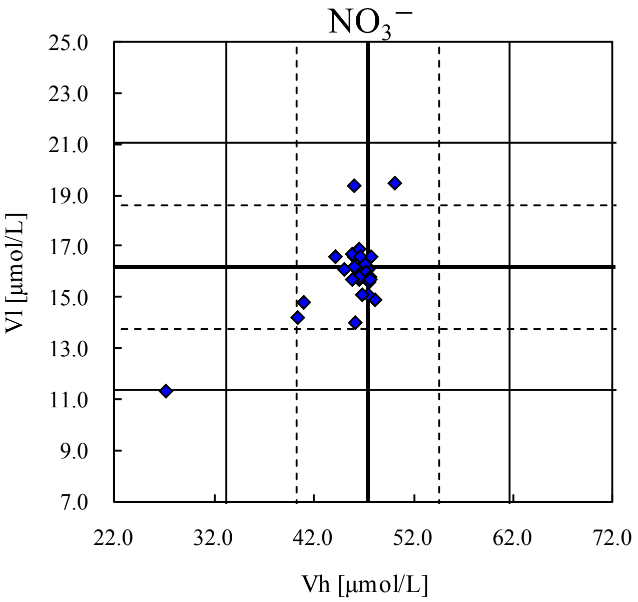


Figure 2.11 Deviation from prepared value for NO_3^- (normalized by prepared value)



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

Figure 2.12 Scatter diagram for NO_3^-

For the analysis of NO_3^-, 29 laboratories used Ion-chromatography, 1 laboratory (RU02) used Spectrophotometry. The data submitted by KH01 and LA01 in low concentration sample exceeded the DQO and was marked with flag “E”. And the data submitted by ID01 in both samples exceeded the DQO more than a factor of 2 and were marked with flag “X”.

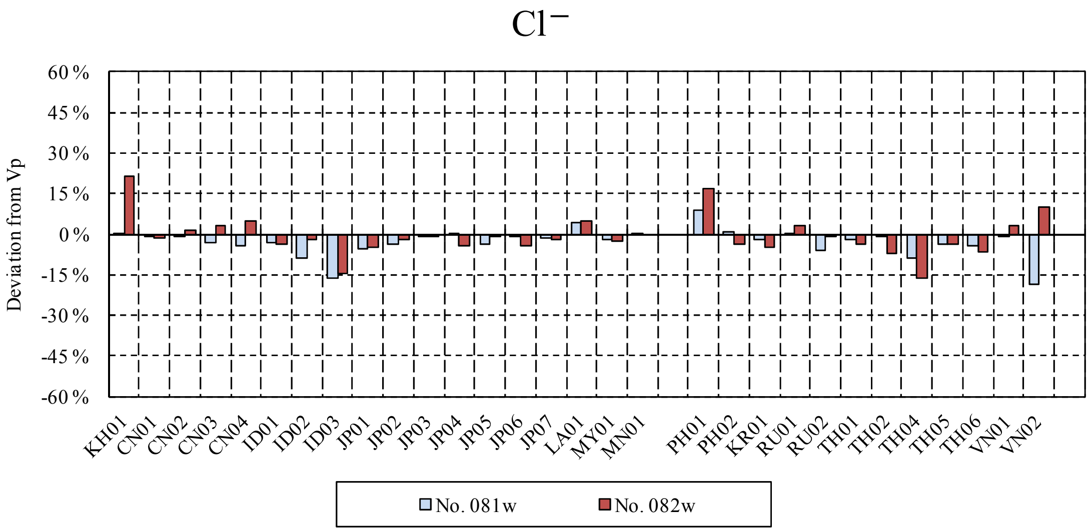
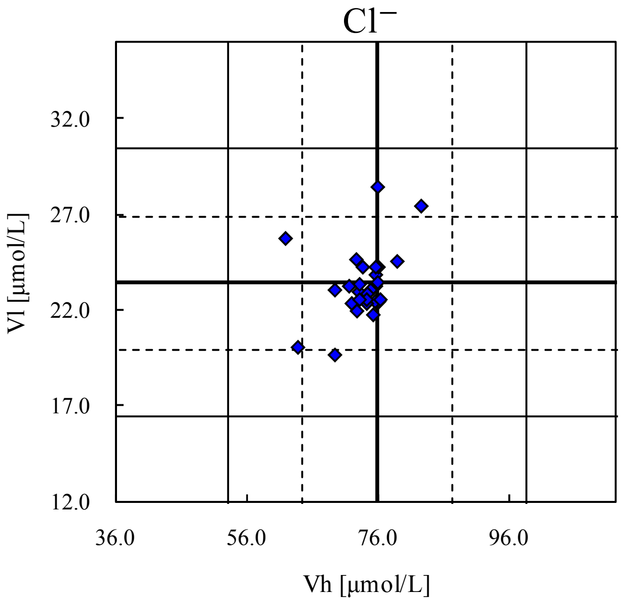


Figure 2.13 Deviation from prepared value for Cl$^-$ (normalized by prepared value)



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

Figure 2.14 Scatter diagram for Cl$^-$

For the analysis of Cl$^-$, 29 laboratories used Ion-chromatography, 1 laboratory (RU02) used titration method. The data submitted by ID03 and VN02 in high concentration sample exceeded the DQO and were marked with flag “E”. The data submitted by KH01, PH01 and TH04 in low concentration sample exceeded the DQO and were marked with flag “E”.

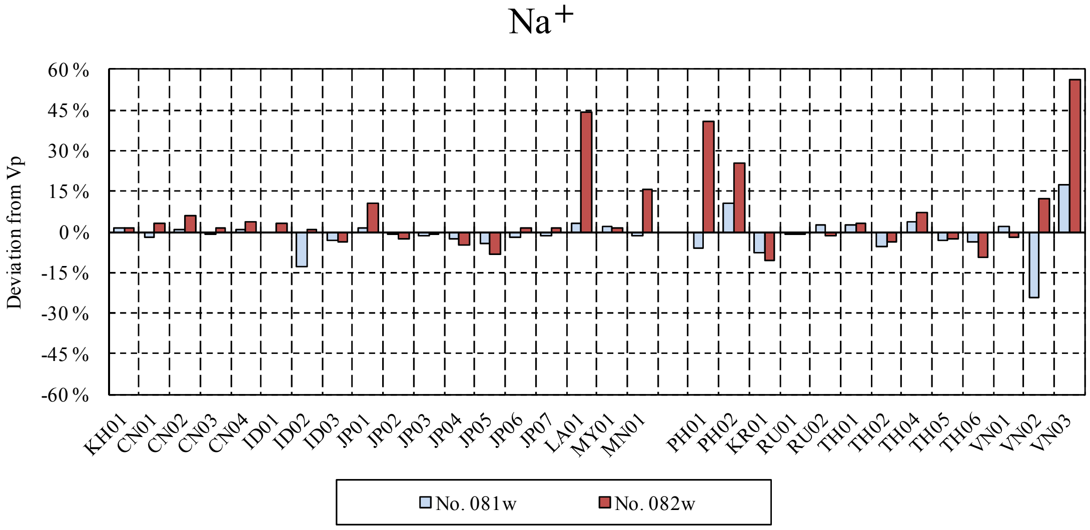
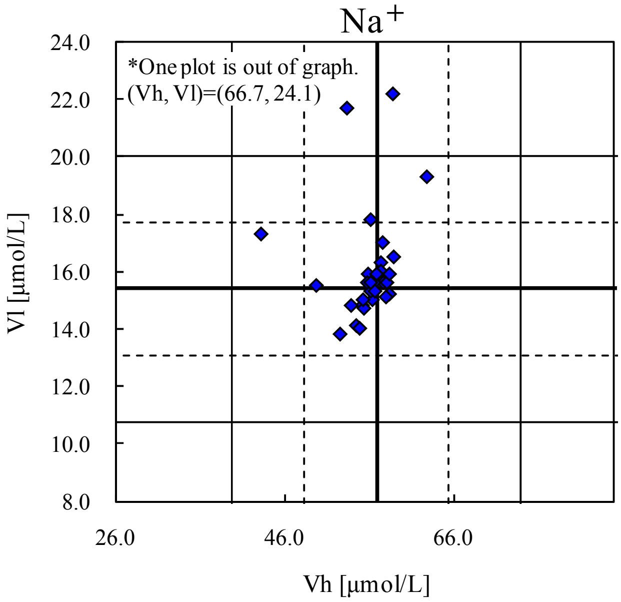


Figure 2.15 Deviation from prepared value for Na$^+$ (normalized by prepared value)



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

Figure 2.16 Scatter diagram for Na$^+$

For the analysis of Na$^+$, 27 laboratories used Ion-chromatography, 3 laboratories (RU01, RU02 and VN03) used Flame (Emission) Photometry, and 1 laboratory (PH02) used Atomic Absorption Spectrometry. The data submitted by VN02 and VN03 in high concentration sample exceeded the DQO and were marked with flag "E". As for low concentration sample, the data of MN01 and PH02 were marked with flag "E" and the data of LA01, PH01 and VN03 were marked with flag "X".

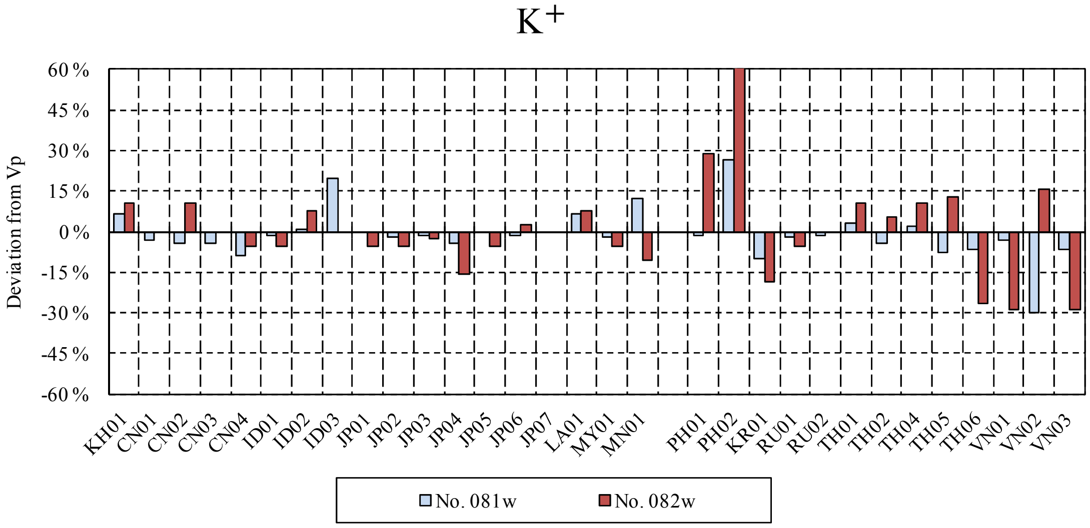
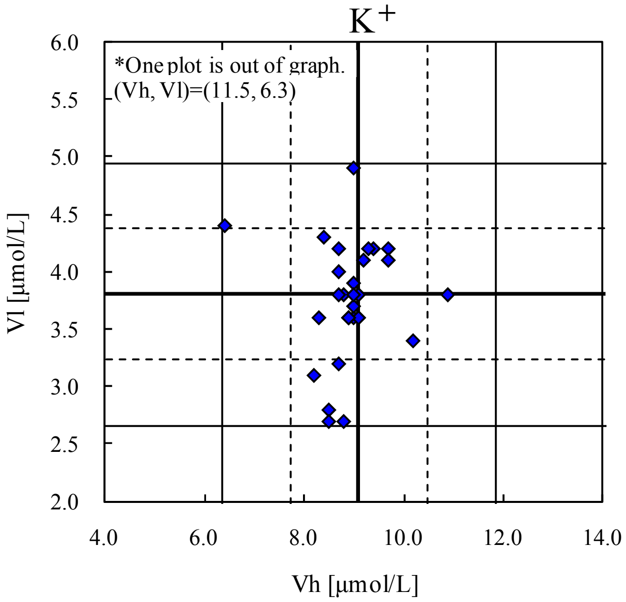


Figure 2.17 Deviation from prepared value for K^+ (normalized by prepared value)



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

Figure 2.18 Scatter diagram for K^+

For the analysis of K^+, 27 laboratories used Ion-chromatography, 3 laboratories (RU01, RU02 and VN03) used Flame (Emission) Photometry, and 1 laboratory (PH02) used Atomic Absorption Spectrometry. The data submitted by ID03, PH02 and VN02 in high concentration sample exceeded the DQO and were marked with flag “E”. As for low concentration sample, 7 data (JP04, PH01, KR01, TH06, VN01, VN02 and VN03) were marked with flag “E” and 1 data (PH02) was marked with flag “X”. Overall, 25.8% of the data for low concentration sample had flags.

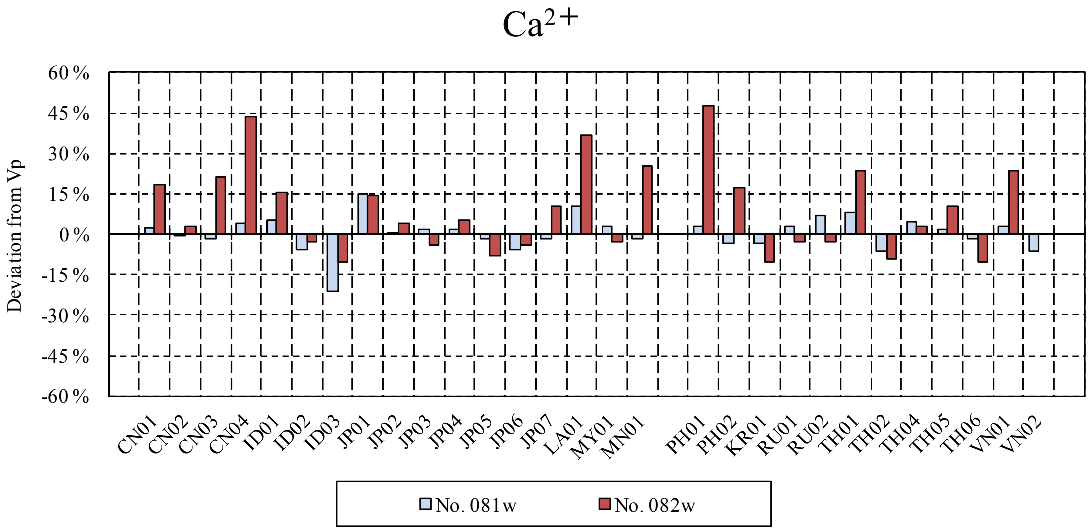
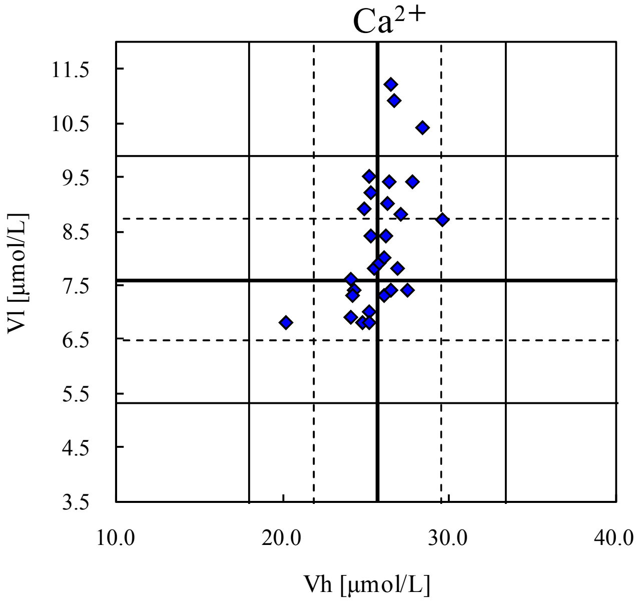


Figure 2.19 Deviation from prepared value for Ca^{2+} (normalized by prepared value)



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

Figure 2.20 Scatter diagram for Ca^{2+}

For the analysis of Ca^{2+}, 26 laboratories used Ion-chromatography, 3 laboratories (PH02, RU01 and RU02) used Atomic Absorption Spectrometry. The data submitted by ID03 and JP01 in high concentration sample exceeded the DQO and marked with flag “E”. As for low concentration sample, 7 data (CN01, CN03, ID01, MN01, PH02, TH01 and VN01) were marked with flag “E” and 3 data (CN04, LA01 and PH01) were marked with flag “X”. Overall, 34.5% of the data for low concentration sample had flags. This was the worst percentage of flagged data in this survey.

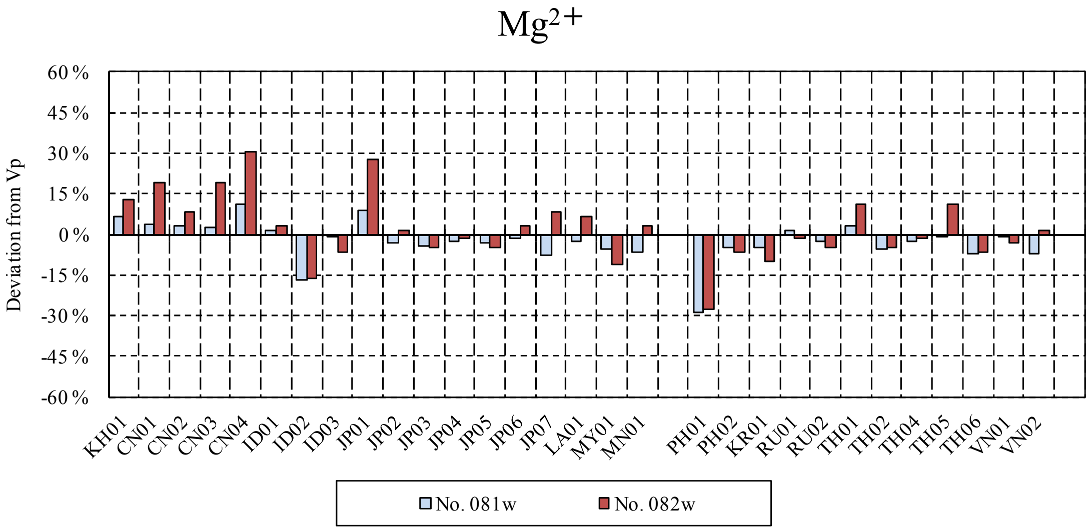
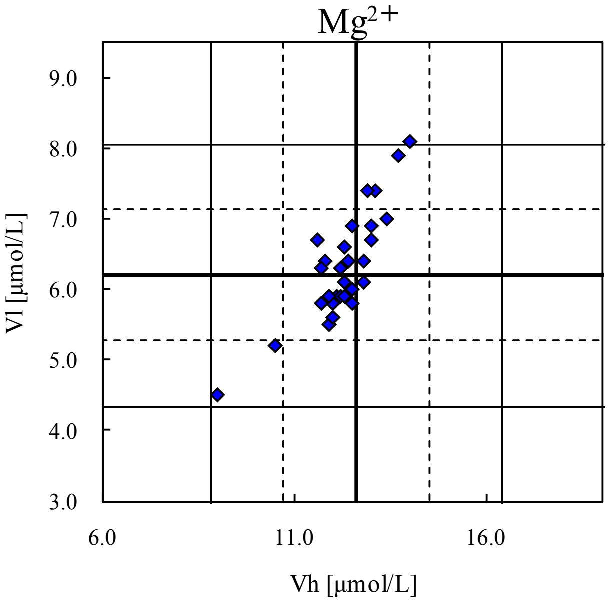


Figure 2.21 Deviation from prepared value for Mg^{2+} (normalized by prepared value)



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

Figure 2.22 Scatter diagram for Mg^{2+}

For the analysis of Mg^{2+}, 27 laboratories used Ion-chromatography, 3 laboratories (PH02, RU01 and RU02) used Atomic Absorption Spectrometry. The data submitted by ID02 and PH01 were marked with flag “E”. As for low concentration sample, 5 data (CN01, CN03, ID02, JP01 and PH01) were marked with flag “E” and 1 data (CN04) was marked with flag “X”. The percentage of flagged data in low concentration sample was 20.0%.

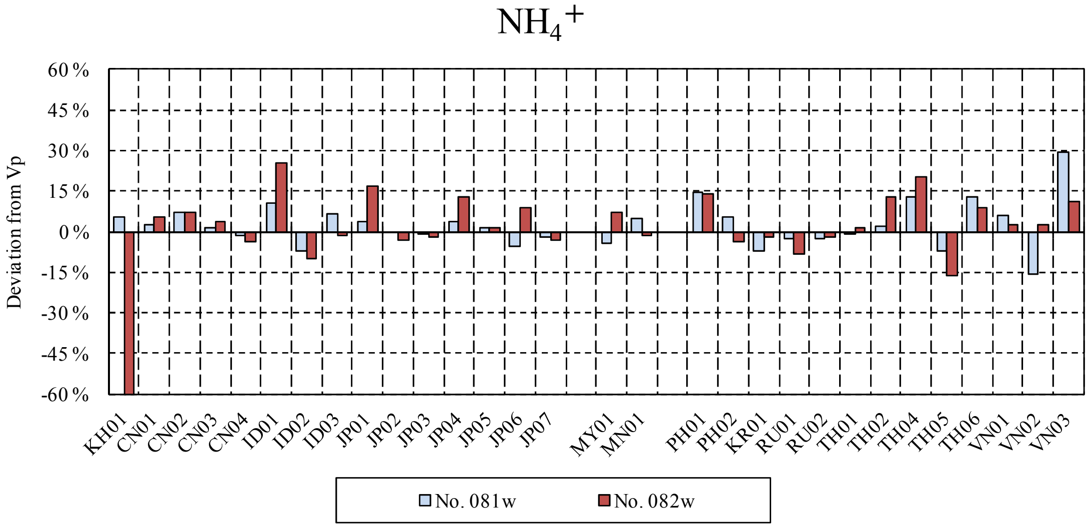
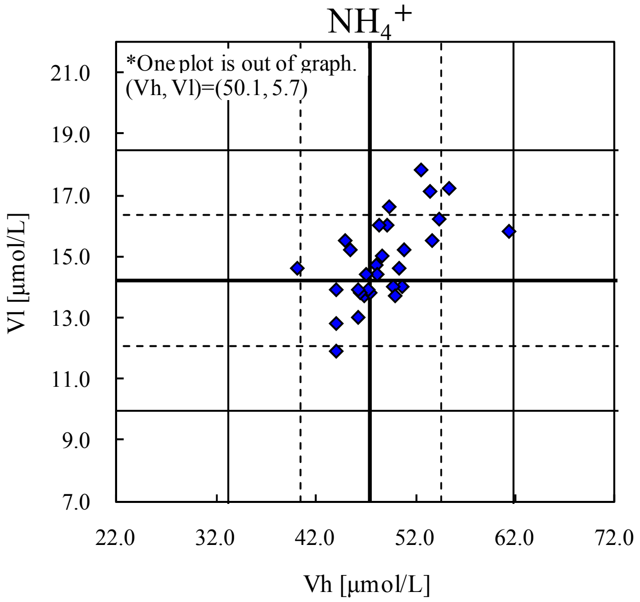


Figure 2.23 Deviation from prepared value for NH_4^+ (normalized by prepared value)



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

Figure 2.24 Scatter diagram for NH_4^+

For the analysis of NH_4^+, 27 laboratories used Ion-chromatography, 3 laboratories (PH02, RU01 and VN03) used Spectrophotometry (Indophenol-blue method), and 1 laboratory (RU02) used Spectrophotometry (Without Indophenol-blue method). The data submitted by LA01, VN02 and VN03 in high concentration sample exceeded the DQO and marked with flag “E”. As for low concentration sample, 5 data (ID01, JP01, LA01, TH04 and TH05) were marked with flag “E” and 1 data (KH01) was marked with flag “X”.

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

The concentrations of the constituents in this survey were settled on the basis of the statistics of monitoring data on wet deposition in EANET. Compared to the samples for 2007's survey, concentrations in sample No. 082w were relatively low.

The relative standard deviations (R.S.D.) of each of the parameters in the sample No. 081w and No. 082w are shown in the Figure 2.25. The highest R.S.D. was for Ca^{2+} in low concentration sample in this survey. The R.S.D. of EC and SO_4^{2-} in the high concentration sample were higher than those of the low concentration sample. As for the other ions, the R.S.D. in the low concentration sample are approximately twice as much as those in the high concentration sample.

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

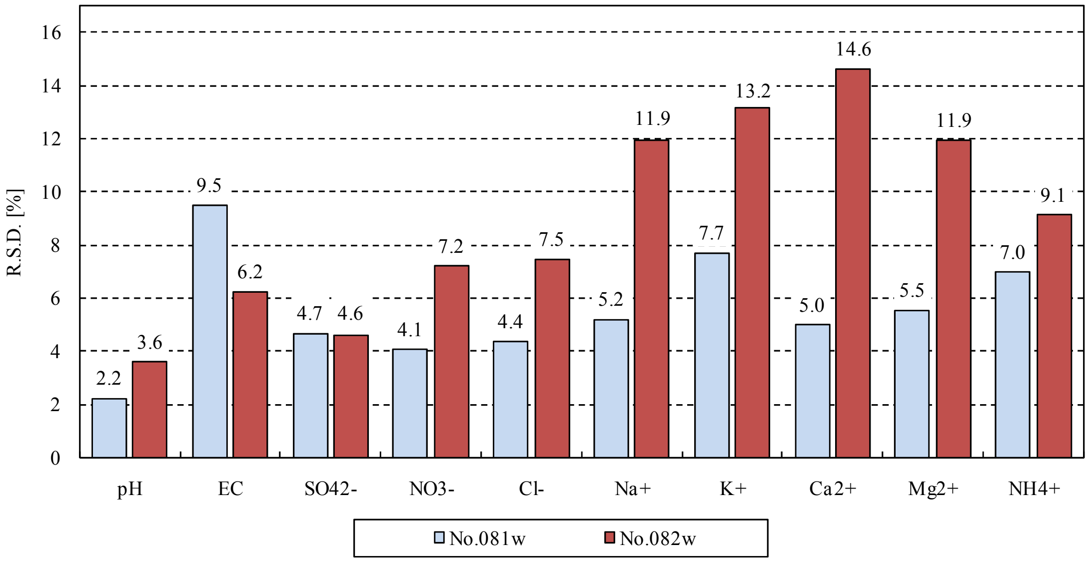


Figure 2.25 Relative standard deviations (R.S.D.) of each constituent

Some laboratories had problems in drawing calibration curves for the analysis of the ions in this project as same as past projects. The person in charge of analysis needs to confirm that the calibration curves are suitable for accurate determination analysis, in accordance with the technical manual. The reliability of the calibration needs to be examined before the analysis of the precipitation samples by using the Standard Reference Materials (SRMs) 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 drawing the calibration curves.

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 chemical analysis of anions, all participating laboratories used the recommended methods (Ion-chromatography or Spectrophotometry) except for 1 laboratory (RU02) in the analysis of Cl^-. RU02 used titration method for the analysis of Cl^- concentration.

As for the chemical analysis of cations, most of the participating laboratories used the recommended methods (Atomic Absorption Spectrometry, Flame (Emission) Spectrometry, Ion-chromatography, or Spectrophotometry with Indophenol-blue). Only RU02 analyzed NH_4^+ by Spectrophotometry without Indophenol-blue.

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

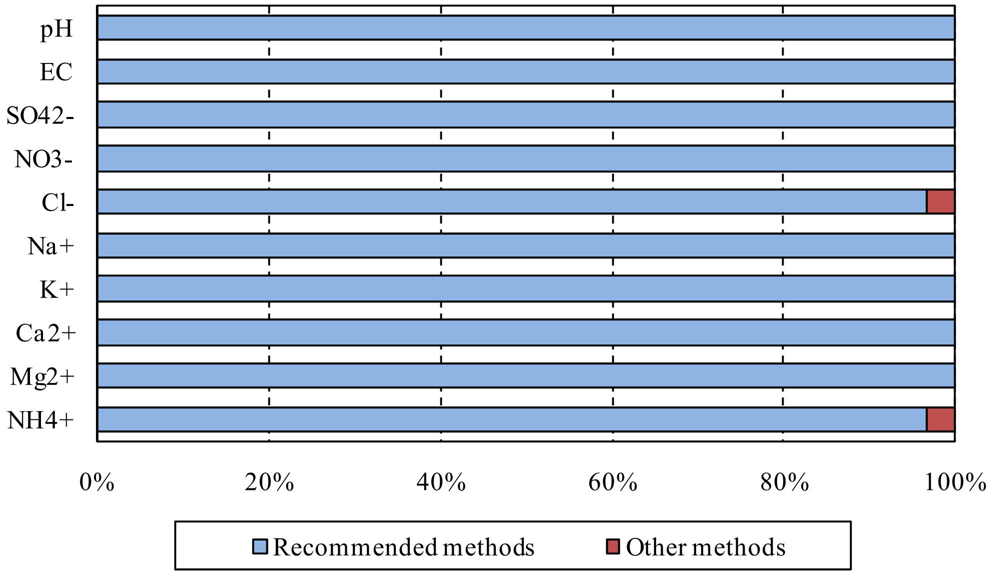


Figure 2.26 Percentage of laboratories that used the recommended methods in the project

Table 2.11 List of analytical methods

Code	Mothod
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. 081w (High concentrations)

Code	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	32									
1		32 (5)								
2					1					
3						1	1 (1)	3	3	
4						3 (1)	3			
5			29 (1)	29 (1)	29 (2)	27 (1)	27 (2)	26 (2)	27 (2)	27 (2)
6										
7			2	1						1
8										3 (1)
9										
10										
11										
Flag E	0	3	1	0	2	2	3	2	2	3
Flag X	0	2	0	1	0	0	0	0	0	0

Sample No. 082w (Low concentrations)

Code	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	32									
1		32 (2)								
2					1					
3						1 (1)	1 (1)	3 (1)	3	
4						3 (1)	3 (1)			
5			29 (1)	29 (3)	29 (3)	27 (3)	27 (6)	26 (9)	27 (6)	27 (6)
6										
7			1	1						1
8										3
9										
10										
11										
Flag E	0	1	1	2	3	2	7	7	5	5
Flag X	0	1	0	1	0	3	1	3	1	1

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

Staff (Number and years of experience)

The number of staffs in charge of measurement is described in Table 2.13. The letters of "A", "B", "C" and "D" represent individuals of staffs in each laboratory who are in charge of measurement. In 17 laboratories, only 1 person carried out the measurements. In the case of laboratories where more than 2 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

Lab. ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	4	A	A	B,C,D	B,C,D	B,C,D	B,C,D	B,C,D		B,C,D	B,C,D
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	3	A	A	B	B	B	C	C	C	C	C
ID02	1	A	A	A	A	A	A	A	A	A	A
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	2	A	A	A	A	B	B	A	A	A	A
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	1	A	A	A	A	A	A	A	A	A	A
MM01	1	A	A								
PH01	3	A	A	B	B	B	C	C	C	C	C
PH02	3	A	A	B	B	B	C	C	C	C	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	B	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	A	A	A
TH05	2	A	A	B	B	B	B	B	B	B	B
TH06	2	A	A	B	B	B	B	B	B	B	B
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	3	A	A	B			C	C			B

Light mesh: Analytical data was marked with flag "E" or "X" in sample No. 081w or No. 082w.

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]

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	6	6	4	4	4	4	4		4	4
CN01	17	17	17	17	17	17	17	17	17	17
CN02	10	10	2	2	2	2	2	2	2	2
CN03	10	10	10	10	10	10	10	10	10	10
CN04	13	13	13	13	13	13	13	13	13	13
ID01	9	9	9	9	9	9	9	9	9	9
ID02	7	7	7	7	7	7	7	7	7	7
ID03	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
JP01	5	5	5	5	5	5	5	5	5	5
JP02	2	2	2	2	2	2	2	2	2	2
JP03	1	1	1	1	1	1	1	1	1	1
JP04	6	6	6	6	6	6	6	6	6	6
JP05	3	3	3	3	3	3	3	3	3	3
JP06	6	6	6	6	6	6	6	6	6	6
JP07	2	2	2	2	2	2	2	2	2	2
LA01	3	3	3	3	3	3	3	3	3	3
MY01	2	2	6	6	6	4	4	4	4	4
MN01	10	10	10	10	10	10	10	10	10	10
MM01	3	3								
PH01	<1	<1	1	1	1	4	4	4	4	4
PH02	1	1	1	1	1	1	1	1	1	1
KR01	10	10	10	10	10	10	10	10	10	10
RU01	5	5	5	5	5	11	11	11	11	5
RU02	5	5	36	36	36	17	17	17	17	5
TH01	11	6	6	6	6	11	11	11	11	11
TH02	1	1	1	1	1	1	1	1	1	1
TH04	7	7	7	7	7	7	7	7	7	7
TH05	5	5	2	2	2	2	2	2	2	2
TH06	7	7	5	5	5	5	5	5	5	5
VN01	24	24	24	24	24	15	15	15	15	15
VN02	2	2	4	4	4	4	4	4	4	4
VN03	2	2	3			5	5			3

Light mesh: Analytical data was marked with flag “E” or “X” in sample No. 081w or No. 082w.

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 11th 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 93.2%. In the case of the low concentration samples, the percentage of data within DQOs in this survey was 85.6%. 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.

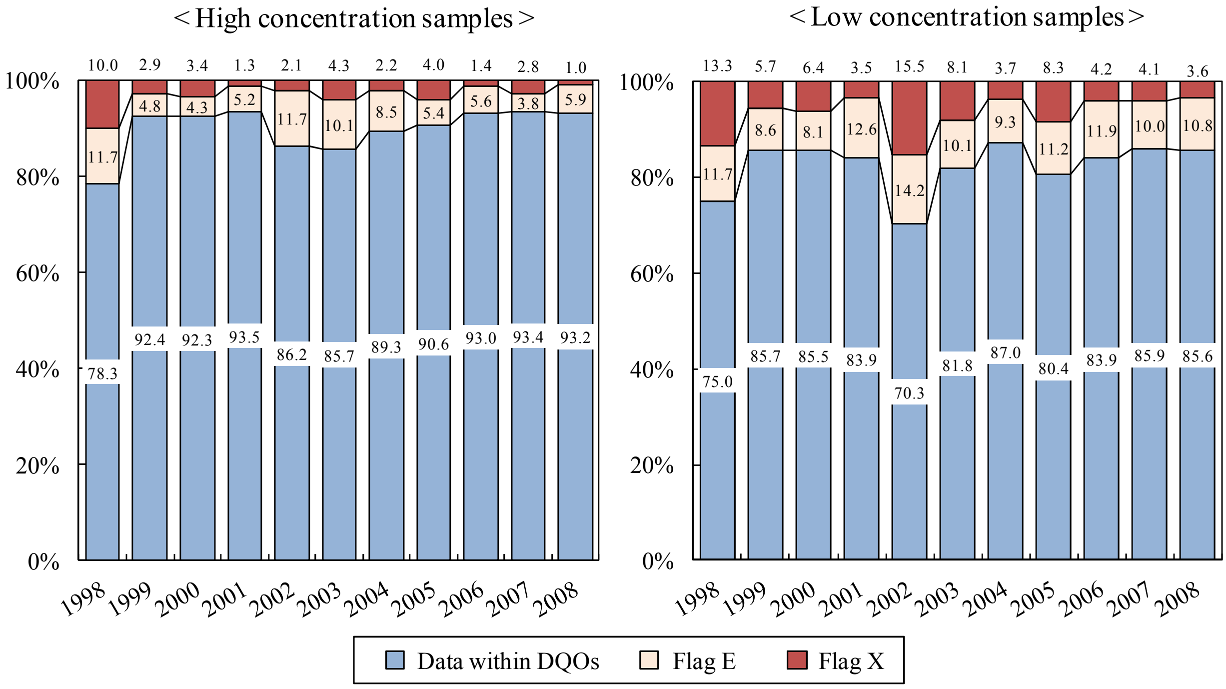


Figure 2.27 Comparison of results from the inter-laboratory comparison projects

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 NO_3^- and Na^+, there was no data marked with flag "X" in previous survey (2007), while some data were marked with flag "X" in this survey. On the other hand, as for the high concentration sample, there was no flag "X", except for NO_3^-.

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

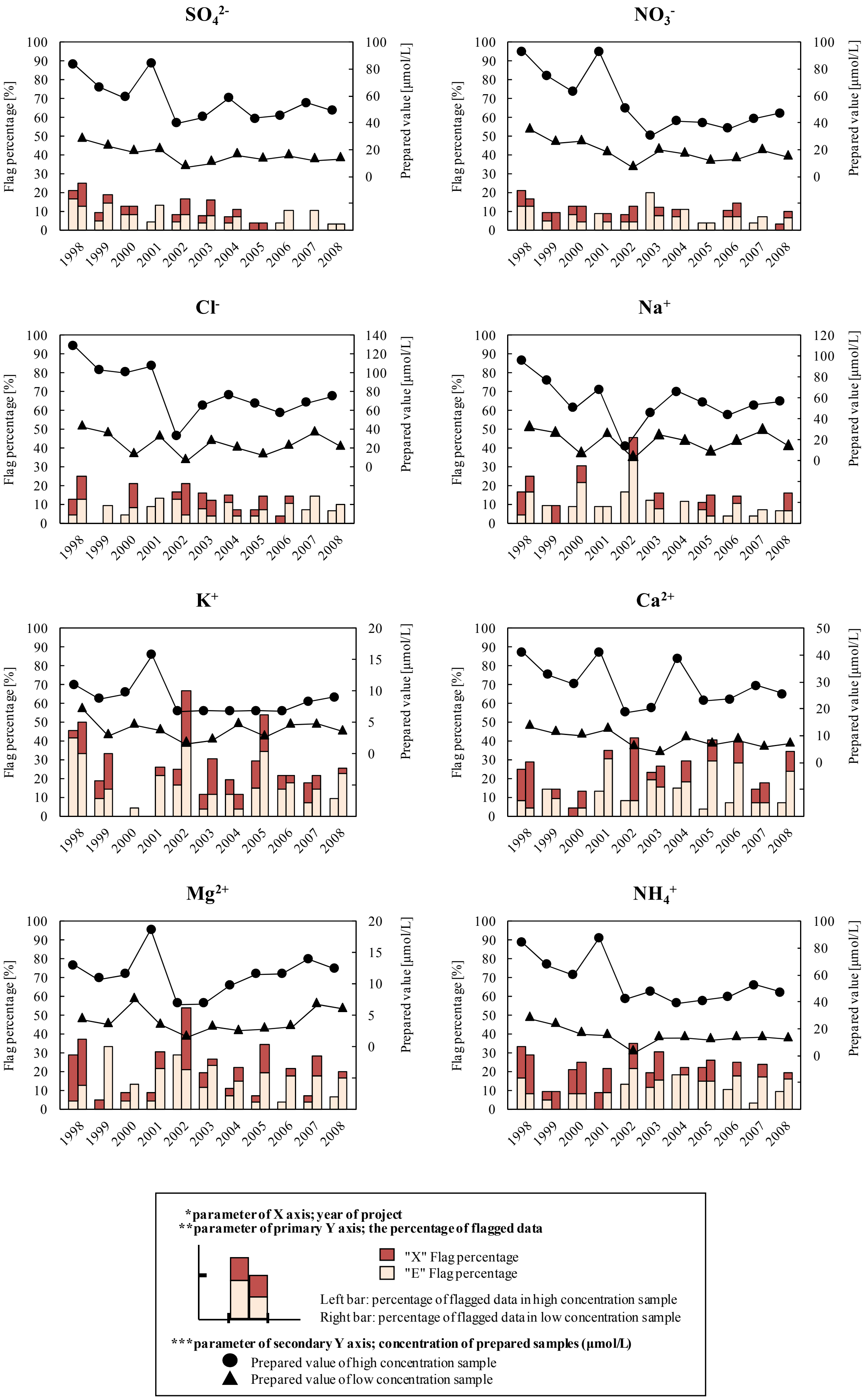


Figure 2.28 Comparison for each parameter in inter-laboratory comparison project

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

< High concentration samples >

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	981	4.05	7.94	83.5	93.3	129.0	95.8	11.1	41.1	13.1	84.8
1999	991	4.14	6.38	67.0	75.0	104.0	77.0	8.9	33.0	11.0	68.0
2000	001	4.10	6.23	59.7	63.3	101.3	51.3	9.9	29.4	11.7	60.5
2001	011	4.10	7.45	85.0	93.3	108.4	68.4	15.8	41.1	18.7	87.8
2002	021	4.30	3.75	40.3	51.0	33.7	13.7	6.9	19.1	7.0	42.4
2003	031	4.52	3.44	44.7	30.9	66.0	46.1	6.9	20.5	7.0	48.3
2004	041	4.60	3.94	58.6	41.4	76.7	66.7	6.9	38.9	9.8	39.4
2005	051	4.66	3.32	43.7	40.3	68.5	56.5	6.9	23.2	11.7	40.9
2006	061	4.72	3.10	45.8	36.3	57.5	44.5	6.9	23.8	11.7	43.9
2007	071w	4.64	3.72	54.9	43.6	69.0	53.4	8.3	28.6	14.0	52.7
2008	081w	4.49	3.97	49.5	47.4	75.8	56.8	9.1	25.7	12.6	47.5

< Low concentration samples >

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	982	4.51	2.82	29.1	36.1	45.1	33.5	7.4	14.3	4.6	29.5
1999	992	4.59	2.30	24.0	27.0	38.0	28.0	3.2	12.0	3.8	25.0
2000	002	4.85	1.55	20.1	27.5	15.5	8.7	4.9	11.0	7.8	18.2
2001	012	4.82	1.76	21.5	19.4	34.4	27.4	4.0	13.2	3.7	16.7
2002	022	5.15	0.69	8.9	8.5	9.1	5.1	2.0	6.6	1.8	4.5
2003	032	4.80	1.48	12.0	21.3	29.6	25.6	2.5	4.4	3.4	15.1
2004	042	5.00	1.33	17.6	18.4	22.5	20.5	5.0	10.0	2.7	15.1
2005	052	5.05	1.05	14.4	13.2	15.3	10.3	3.0	7.6	3.1	13.6
2006	062	5.15	1.21	16.9	15.0	24.5	20.5	4.9	9.3	3.5	15.1
2007	072w	5.00	1.47	14.0	21.0	38.8	30.8	4.9	6.4	7.0	15.1
2008	082w	5.10	1.18	14.7	16.2	23.4	15.4	3.8	7.6	6.2	14.2

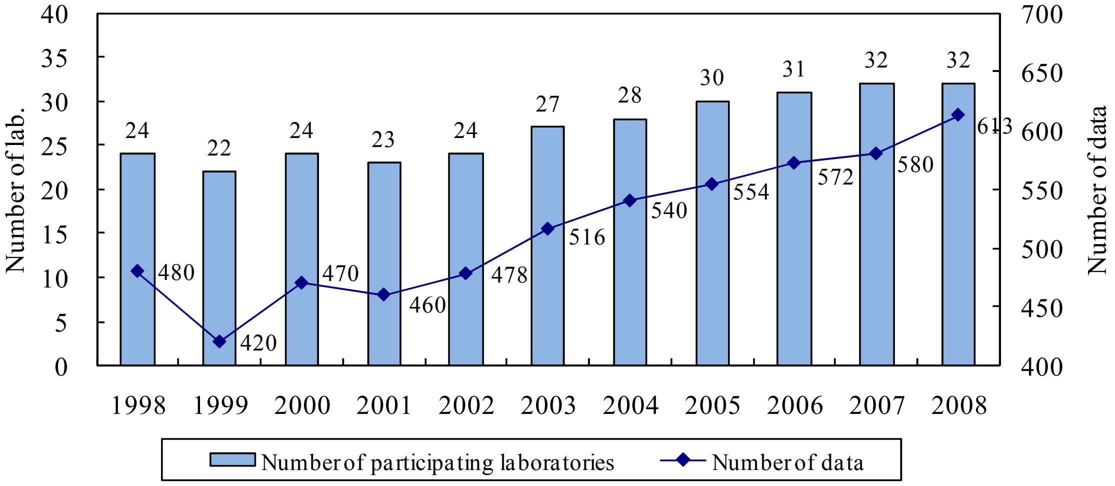


Figure 2.29 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

As the figure 2.29 indicates, the number of data has increased since the beginning of the project. In comparison with previous survey, due to the increment of the number of measurement constituents in PH02, TH04 and VN03, the total number of data reached 613 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.

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11) Network Center for EANET. 2007. Report of the Inter-laboratory Comparison Project 2006

12) Network Center for EANET. 2008. Report of the Inter-laboratory Comparison Project 2007

13) Hilde Th. Uggerud and Anne-Gunn Hjellbrekke. 2008. The twenty-fifth intercomparison of analytical methods within EMEP, Norwegian Institute for Air Research (EMEP/CCC-Report 7/2008).

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) Xiamen Environmental Monitoring Station	**(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, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	**(RU01)**
24) Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	**(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)**

Appendix 2.2 Analytical Results submitted by the laboratories

Appendix Table 2.2.1 Analytical data concerning high conc. sample No. 081w

Sample No. 081w (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	4.71	3.15	53.7	50.2	75.9	57.6	9.7		13.4	50.1
CN01	4.38	3.83	49.7	46.1	75.2	55.8	8.8	26.3	13.1	48.7
CN02	4.42	3.85	49.7	47.8	75.6	57.3	8.7	25.5	13.0	50.9
CN03	4.46	3.84	49.8	46.1	73.6	56.5	8.7	25.3	12.9	48.1
CN04	4.46	3.85	50.4	45.9	72.6	57.3	8.3	26.7	14.0	46.9
ID01	4.53	4.19	48.7	27.1	73.4	56.8	9.0	27.1	12.8	52.6
ID02	4.56	3.74	50.6	41.0	69.3	49.7	9.2	24.3	10.5	44.1
ID03	5.09	2.58	42.2	40.4	63.6	55.1	10.9	20.2	12.5	50.7
JP01	4.57	3.91	48.7	46.8	71.9	57.5	9.1	29.6	13.7	49.4
JP02	4.55	3.88	47.0	45.1	73.0	56.3	8.9	25.8	12.2	47.5
JP03	4.53	3.79	49.7	47.3	75.6	56.1	9.0	26.1	12.1	47.3
JP04	4.54	3.87	51.9	47.5	76.1	55.3	8.7	26.1	12.3	49.2
JP05	4.59	3.80	47.4	46.1	73.1	54.4	9.1	25.2	12.2	48.2
JP06	4.56	3.80	49.5	47.2	75.5	55.7	9.0	24.2	12.4	45.0
JP07	4.51	3.81	48.7	47.3	74.8	56.1	9.1	25.3	11.6	46.5
LA01	4.46	3.36	48.2	46.1	78.9	58.7	9.7	28.4	12.3	55.4
MY01	4.54	3.78	47.9	46.6	74.3	58.0	8.9	26.5	11.9	45.5
MN01	4.57	3.79	46.3	47.6	75.9	56.1	10.2	25.2	11.8	49.8
MM01	4.81	1.79								
PH01	4.63	3.78	53.7	46.6	82.6	53.3	9.0	26.5	9.0	54.4
PH02	4.84	3.66	49.4	46.7	76.3	62.7	11.5	24.9	12.0	50.0
KR01	4.60	4.32	49.1	44.2	74.2	52.5	8.2	24.8	12.0	44.1
RU01	4.51	3.94	47.2	46.2	76.0	56.6	8.9	26.5	12.8	46.3
RU02	4.54	3.94	50.2	48.2	71.5	58.3	9.0	27.5	12.3	46.3
TH01	4.57	3.80	49.1	46.6	74.2	58.3	9.4	27.8	13.0	47.1
TH02	4.52	3.78	48.9	47.5	75.2	53.8	8.7	24.1	11.9	48.4
TH04	4.05	4.87	61.1	46.9	69.3	58.8	9.3	26.9	12.3	53.5
TH05	4.48	3.59	47.5	45.9	73.1	55.2	8.4	26.2	12.5	44.1
TH06	4.51	3.51	49.2	46.1	72.7	54.8	8.5	25.2	11.7	53.7
VN01	4.49	4.07	50.6	47.7	75.6	57.9	8.8	26.4	12.5	50.4
VN02	4.37	3.78	49.7	47.7	61.7	43.2	6.4	24.1	11.7	40.2
VN03	4.53	3.60	54.5			66.7	8.5			61.4
Prepared value	**4.49**	**3.97**	**49.5**	**47.4**	**75.8**	**56.8**	**9.1**	**25.7**	**12.6**	**47.5**
Number of data	30	31	30	29	29	30	30	28	29	30
Average	4.54	3.79	49.3	46.4	74.1	56.6	9.1	26.0	12.4	48.5
Minimum	4.37	2.58	42.2	40.4	63.6	49.7	8.2	24.1	10.5	40.2
Maximum	4.84	4.87	54.5	50.2	82.6	66.7	11.5	29.6	14.0	55.4
Standard deviation	0.10	0.36	2.30	1.88	3.23	2.94	0.70	1.30	0.69	3.38

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

Appendix Table 2.2.2 Analytical data concerning low conc. sample No. 082w

Sample No. 082w (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	5.21	1.16	15.1	19.5	28.4	15.6	4.2		7.0	5.7
CN01	4.97	1.14	15.0	16.6	23.1	15.9	3.8	9.0	7.4	15.0
CN02	4.96	1.18	15.0	16.6	23.8	16.3	4.2	7.8	6.7	15.2
CN03	4.99	1.17	14.8	16.7	24.2	15.6	3.8	9.2	7.4	14.7
CN04	5.15	1.18	15.4	16.7	24.6	16.0	3.6	10.9	8.1	13.7
ID01	5.15	1.26	15.2	11.3	22.6	15.9	3.6	8.8	6.4	17.8
ID02	5.19	1.13	15.2	14.8	23.0	15.5	4.1	7.4	5.2	12.8
ID03	5.68	0.94	12.6	14.2	20.0	14.8	3.8	6.8	5.8	14.0
JP01	5.27	1.19	14.8	16.2	22.3	17.0	3.6	8.7	7.9	16.6
JP02	5.09	1.17	14.9	16.1	22.9	15.0	3.6	7.9	6.3	13.8
JP03	5.08	1.16	14.8	16.2	23.2	15.3	3.7	7.3	5.9	13.9
JP04	5.09	1.21	15.5	16.1	22.4	14.7	3.2	8.0	6.1	16.0
JP05	5.16	1.18	14.7	16.2	23.3	14.1	3.6	7.0	5.9	14.4
JP06	5.21	1.14	14.9	16.3	22.4	15.6	3.9	7.3	6.4	15.5
JP07	5.08	1.17	14.2	16.0	23.0	15.6	3.8	8.4	6.7	13.8
LA01	4.99	1.16	15.6	19.4	24.5	22.2	4.1	10.4	6.6	17.2
MY01	5.10	1.14	14.0	15.7	22.8	15.6	3.6	7.4	5.5	15.2
MN01	5.50	1.01	13.3	15.6	23.4	17.8	3.4	9.5	6.4	14.0
MM01	5.47	0.56								
PH01	5.22	1.14	17.2	16.9	27.4	21.7	4.9	11.2	4.5	16.2
PH02	5.41	1.13	15.2	16.6	22.5	19.3	6.3	8.9	5.8	13.7
KR01	5.23	1.24	14.2	16.6	22.3	13.8	3.1	6.8	5.6	13.9
RU01	5.04	1.20	14.4	14.0	24.2	15.3	3.6	7.4	6.1	13.0
RU02	5.05	1.19	14.9	14.9	23.2	15.2	3.8	7.4	5.9	13.9
TH01	5.14	1.17	14.5	15.8	22.5	15.9	4.2	9.4	6.9	14.4
TH02	5.15	1.08	13.5	15.1	21.7	14.8	4.0	6.9	5.9	16.0
TH04	4.68	1.23	13.9	15.1	19.6	16.5	4.2	7.8	6.1	17.1
TH05	5.00	1.10	14.0	15.7	22.5	15.0	4.3	8.4	6.9	11.9
TH06	5.06	1.10	14.8	16.2	21.9	14.0	2.8	6.8	5.8	15.5
VN01	5.08	1.23	14.9	15.8	24.2	15.1	2.7	9.4	6.0	14.6
VN02	4.90	1.31	14.7	15.7	25.7	17.3	4.4	7.6	6.3	14.6
VN03	5.14	1.03				24.1	2.7			15.8
Prepared value	**5.10**	**1.18**	**14.7**	**16.2**	**23.4**	**15.4**	**3.8**	**7.6**	**6.2**	**14.2**
Number of data	32	31	29	29	30	30	30	29	30	30
Average	5.14	1.16	14.6	16.1	23.3	16.1	3.7	8.3	6.3	14.8
Minimum	4.68	0.94	12.6	14.0	19.6	13.8	2.7	6.8	4.5	11.9
Maximum	5.68	1.31	15.6	19.5	28.4	22.2	4.9	11.2	8.1	17.8
Standard deviation	0.18	0.07	0.67	1.16	1.73	1.92	0.49	1.21	0.75	1.35

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

Appendix 2.3 Normalized Data

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

Appendix Table 2.3.1 Deviation% from prepared values of high conc. sample No. 081w

Sample No. 081w (High concentrations)

Lab. ID	pH [%]	EC [%]	SO_4^{2-} [%]	NO_3^- [%]	Cl^- [%]	Na^+ [%]	K^+ [%]	Ca^{2+} [%]	Mg^{2+} [%]	NH_4^+ [%]
KH01	4.9	-20.7	8.5	5.9	0.1	1.4	6.6		6.3	5.5
CN01	-2.4	-3.5	0.4	-2.7	-0.8	-1.8	-3.3	2.3	4.0	2.5
CN02	-1.6	-3.0	0.4	0.8	-0.3	0.9	-4.4	-0.8	3.2	7.2
CN03	-0.7	-3.3	0.6	-2.7	-2.9	-0.5	-4.4	-1.6	2.4	1.3
CN04	-0.7	-3.0	1.8	-3.2	-4.2	0.9	-8.8	3.9	11.1	-1.3
ID01	0.9	5.5	-1.6	-42.8	-3.2	0.0	-1.1	5.4	1.6	10.7
ID02	1.6	-5.8	2.2	-13.5	-8.6	-12.5	1.1	-5.4	-16.7	-7.2
ID03	13.4	-35.0	-14.7	-14.8	-16.1	-3.0	19.8	-21.4	-0.8	6.7
JP01	1.8	-1.5	-1.6	-1.3	-5.1	1.2	0.0	15.2	8.7	4.0
JP02	1.3	-2.3	-5.1	-4.9	-3.7	-0.9	-2.2	0.4	-3.2	0.0
JP03	0.9	-4.5	0.4	-0.2	-0.3	-1.2	-1.1	1.6	-4.0	-0.4
JP04	1.1	-2.5	4.8	0.2	0.4	-2.6	-4.4	1.6	-2.4	3.6
JP05	2.2	-4.3	-4.2	-2.7	-3.6	-4.2	0.0	-1.9	-3.2	1.5
JP06	1.6	-4.3	0.0	-0.4	-0.4	-1.9	-1.1	-5.8	-1.6	-5.3
JP07	0.4	-4.0	-1.6	-0.2	-1.3	-1.2	0.0	-1.6	-7.9	-2.1
LA01	-0.7	-15.4	-2.6	-2.7	4.1	3.3	6.6	10.5	-2.4	16.6
MY01	1.1	-4.8	-3.2	-1.7	-2.0	2.1	-2.2	3.1	-5.6	-4.2
MN01	1.8	-4.5	-6.5	0.4	0.1	-1.2	12.1	-1.9	-6.3	4.8
MM01	7.1	-54.9								
PH01	3.1	-4.8	8.5	-1.7	9.0	-6.2	-1.1	3.1	-28.6	14.5
PH02	7.8	-7.8	-0.2	-1.5	0.7	10.4	26.4	-3.1	-4.8	5.3
KR01	2.4	8.8	-0.8	-6.8	-2.1	-7.6	-9.9	-3.5	-4.8	-7.2
RU01	0.4	-0.8	-4.6	-2.5	0.3	-0.4	-2.2	3.1	1.6	-2.5
RU02	1.1	-0.8	1.4	1.7	-5.7	2.6	-1.1	7.0	-2.4	-2.5
TH01	1.8	-4.3	-0.8	-1.7	-2.1	2.6	3.3	8.2	3.2	-0.8
TH02	0.7	-4.8	-1.2	0.2	-0.8	-5.3	-4.4	-6.2	-5.6	1.9
TH04	-9.8	22.7	23.4	-1.1	-8.6	3.5	2.2	4.7	-2.4	12.6
TH05	-0.2	-9.6	-4.0	-3.2	-3.6	-2.8	-7.7	1.9	-0.8	-7.2
TH06	0.4	-11.6	-0.6	-2.7	-4.1	-3.5	-6.6	-1.9	-7.1	13.1
VN01	0.0	2.5	2.2	0.6	-0.3	1.9	-3.3	2.7	-0.8	6.1
VN02	-2.7	-4.8	0.4	0.6	-18.6	-23.9	-29.7	-6.2	-7.1	-15.4
VN03	0.9	-9.3	10.1			17.4	-6.6			29.3
Number of data	32	32	31	30	30	31	31	29	30	31
Average	1.3	-6.1	0.4	-3.5	-2.8	-1.0	-0.9	0.5	-2.5	2.9
Minimum	-9.8	-54.9	-14.7	-42.8	-18.6	-23.9	-29.7	-21.4	-28.6	-15.4
Maximum	13.4	22.7	23.4	5.9	9.0	17.4	26.4	15.2	11.1	29.3

Appendix Table 2.3.2 Deviation% from prepared values of low conc. sample No. 082w

Sample No. 082w (Low concentrations)

Lab. ID	pH [%]	EC [%]	SO_4^{2-} [%]	NO_3^- [%]	Cl^- [%]	Na^+ [%]	K^+ [%]	Ca^{2+} [%]	Mg^{2+} [%]	NH_4^+ [%]
KH01	2.2	-1.7	2.7	20.4	21.4	1.3	10.5		12.9	-59.9
CN01	-2.5	-3.4	2.0	2.5	-1.3	3.2	0.0	18.4	19.4	5.6
CN02	-2.7	0.0	2.0	2.5	1.7	5.8	10.5	2.6	8.1	7.0
CN03	-2.2	-0.8	0.7	3.1	3.4	1.3	0.0	21.1	19.4	3.5
CN04	1.0	0.0	4.8	3.1	5.1	3.9	-5.3	43.4	30.6	-3.5
ID01	1.0	6.8	3.4	-30.2	-3.4	3.2	-5.3	15.8	3.2	25.4
ID02	1.8	-4.2	3.4	-8.6	-1.7	0.6	7.9	-2.6	-16.1	-9.9
ID03	11.4	-20.3	-14.3	-12.3	-14.5	-3.9	0.0	-10.5	-6.5	-1.4
JP01	3.3	0.8	0.7	0.0	-4.7	10.4	-5.3	14.5	27.4	16.9
JP02	-0.2	-0.8	1.4	-0.6	-2.1	-2.6	-5.3	3.9	1.6	-2.8
JP03	-0.4	-1.7	0.7	0.0	-0.9	-0.6	-2.6	-3.9	-4.8	-2.1
JP04	-0.2	2.5	5.4	-0.6	-4.3	-4.5	-15.8	5.3	-1.6	12.7
JP05	1.2	0.0	0.0	0.0	-0.4	-8.4	-5.3	-7.9	-4.8	1.4
JP06	2.2	-3.4	1.4	0.6	-4.3	1.3	2.6	-3.9	3.2	9.2
JP07	-0.4	-0.8	-3.4	-1.2	-1.7	1.3	0.0	10.5	8.1	-2.8
LA01	-2.2	-1.7	6.1	19.8	4.7	44.2	7.9	36.8	6.5	21.1
MY01	0.0	-3.4	-4.8	-3.1	-2.6	1.3	-5.3	-2.6	-11.3	7.0
MN01	7.8	-14.4	-9.5	-3.7	0.0	15.6	-10.5	25.0	3.2	-1.4
MM01	7.3	-52.5								
PH01	2.4	-3.4	17.0	4.3	17.1	40.9	28.9	47.4	-27.4	14.1
PH02	6.1	-4.2	3.4	2.5	-3.8	25.3	65.8	17.1	-6.5	-3.5
KR01	2.5	5.1	-3.4	2.5	-4.7	-10.4	-18.4	-10.5	-9.7	-2.1
RU01	-1.2	1.7	-2.0	-13.6	3.4	-0.6	-5.3	-2.6	-1.6	-8.5
RU02	-1.0	0.8	1.4	-8.0	-0.9	-1.3	0.0	-2.6	-4.8	-2.1
TH01	0.8	-0.8	-1.4	-2.5	-3.8	3.2	10.5	23.7	11.3	1.4
TH02	1.0	-8.5	-8.2	-6.8	-7.3	-3.9	5.3	-9.2	-4.8	12.7
TH04	-8.2	4.2	-5.4	-6.8	-16.2	7.1	10.5	2.6	-1.6	20.4
TH05	-2.0	-6.8	-4.8	-3.1	-3.8	-2.6	13.2	10.5	11.3	-16.2
TH06	-0.8	-6.8	0.7	0.0	-6.4	-9.1	-26.3	-10.5	-6.5	9.2
VN01	-0.4	4.2	1.4	-2.5	3.4	-1.9	-28.9	23.7	-3.2	2.8
VN02	-3.9	11.0	0.0	-3.1	9.8	12.3	15.8	0.0	1.6	2.8
VN03	0.8	-12.7				56.5	-28.9			11.3
Number of data	32	32	30	30	30	31	31	29	30	31
Average	0.8	-3.6	0.0	-1.5	-0.6	6.1	0.7	8.8	1.9	2.2
Minimum	-8.2	-52.5	-14.3	-30.2	-16.2	-10.4	-28.9	-10.5	-27.4	-59.9
Maximum	11.4	11.0	17.0	20.4	21.4	56.5	65.8	47.4	30.6	25.4

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:

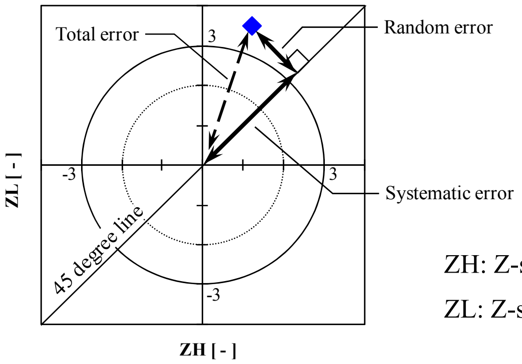
$|Z| \leqq 2$: Satisfactory

$2 < |Z| < 3$: Questionable

$3 \leqq |Z|$: Unsatisfactory

- **Youden diagram**

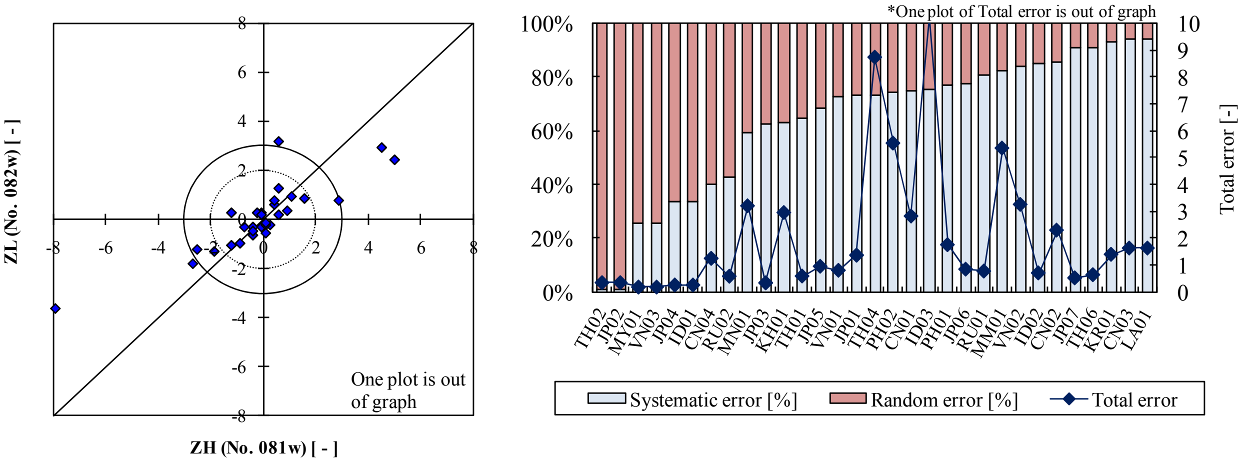
Youden diagram with Z-score provides visual discrimination of outliers from valid results. The outliers are plotted outside the circle whose radius is 3. In addition, all plots on Z-score coordinate can be evaluated by random error and systematic error as shown below:



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

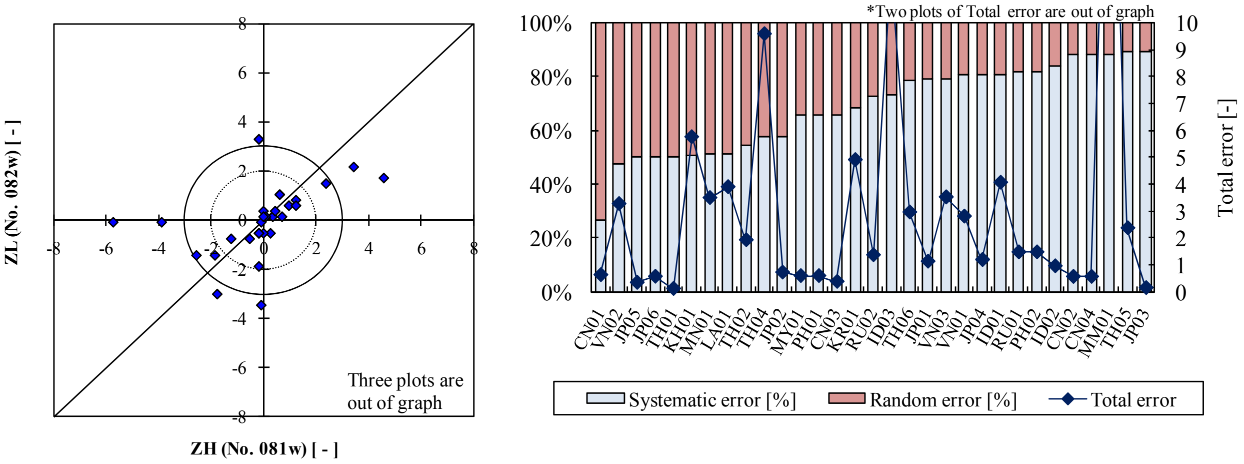
ZL: Z-score for low concentration sample [-]

pH



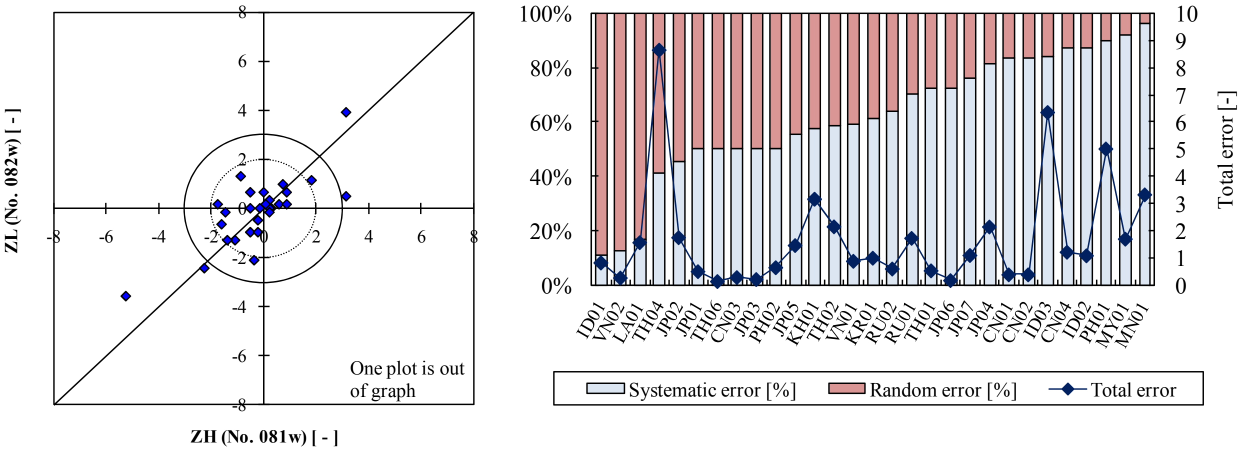
Appendix Figure 2.4.1 Youden diagram with Z-score and Error evaluation for pH

EC



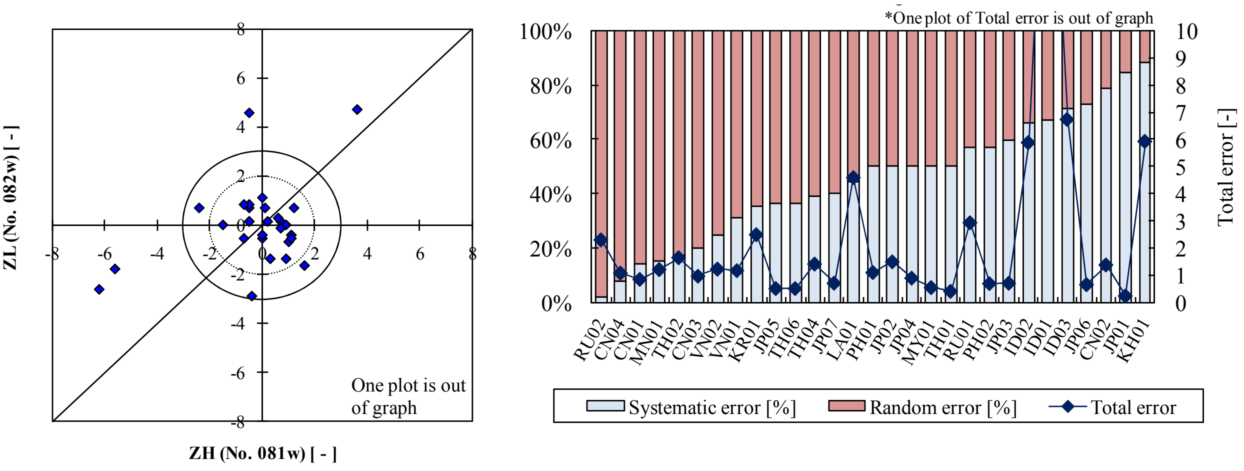
Appendix Figure 2.4.2 Youden diagram with Z-score and Error evaluation for EC

SO_4^{2-}



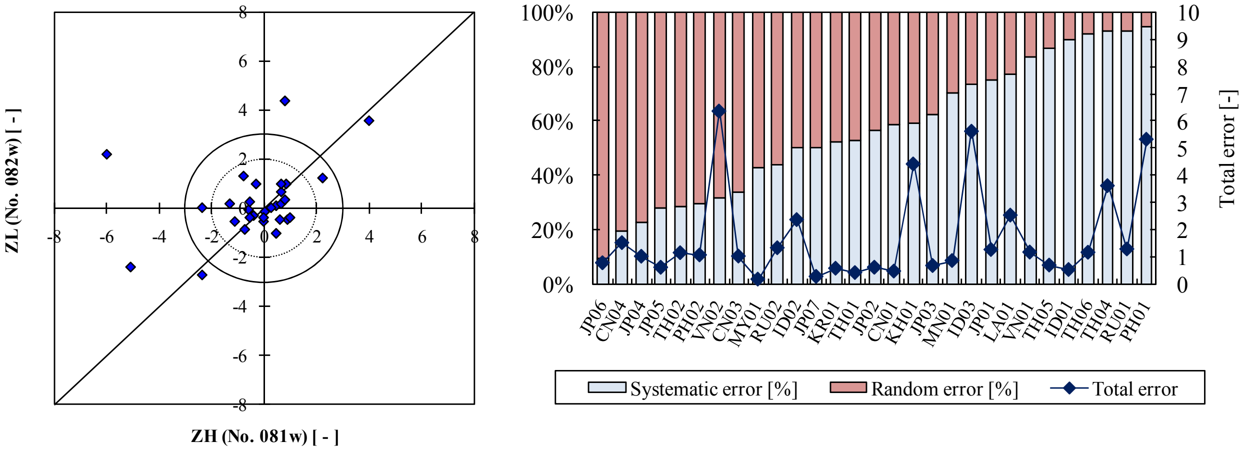
Appendix Figure 2.4.3 Youden diagram with Z-score and Error evaluation for SO_4^{2-}

NO_3^-



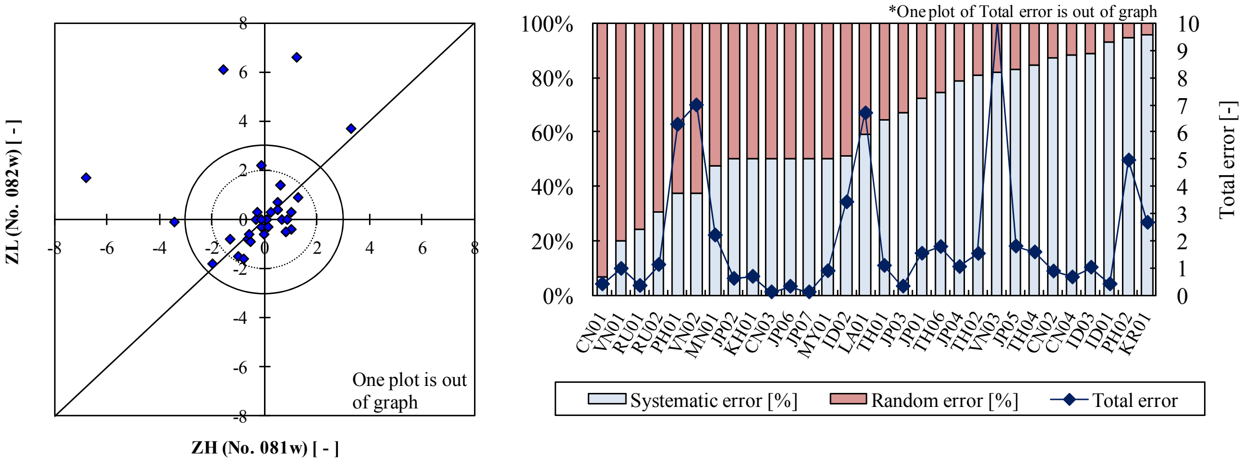
Appendix Figure 2.4.4 Youden diagram with Z-score and Error evaluation for NO_3^-

Cl^-



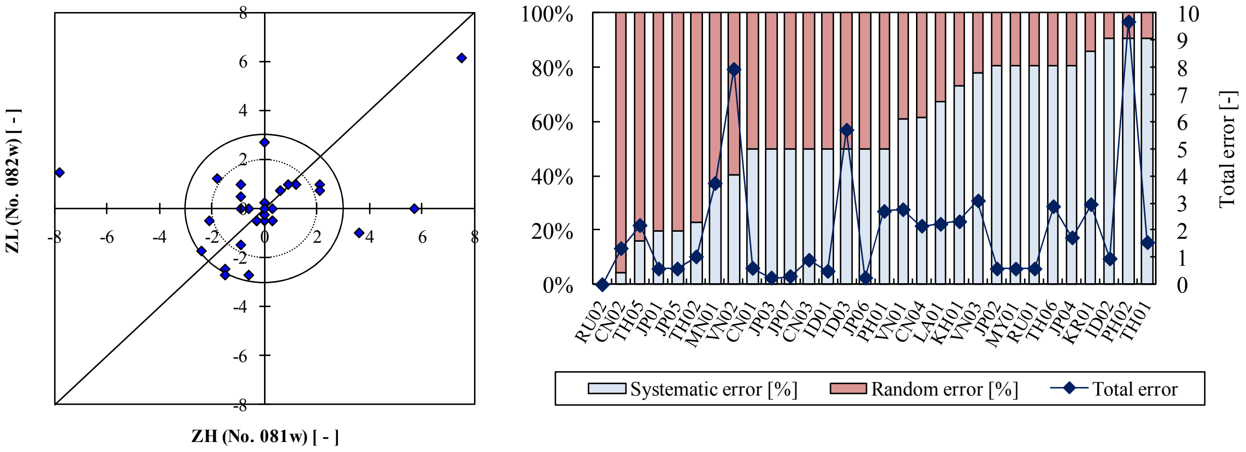
Appendix Figure 2.4.5 Youden diagram with Z-score and Error evaluation for Cl^-

Na^+



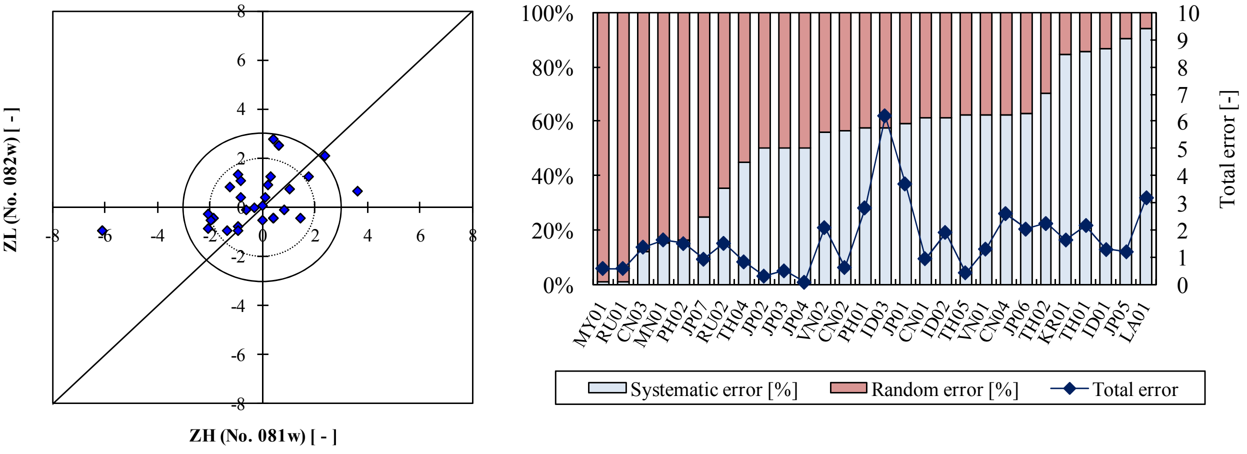
Appendix Figure 2.4.6 Youden diagram with Z-score and Error evaluation for Na^+

K^+



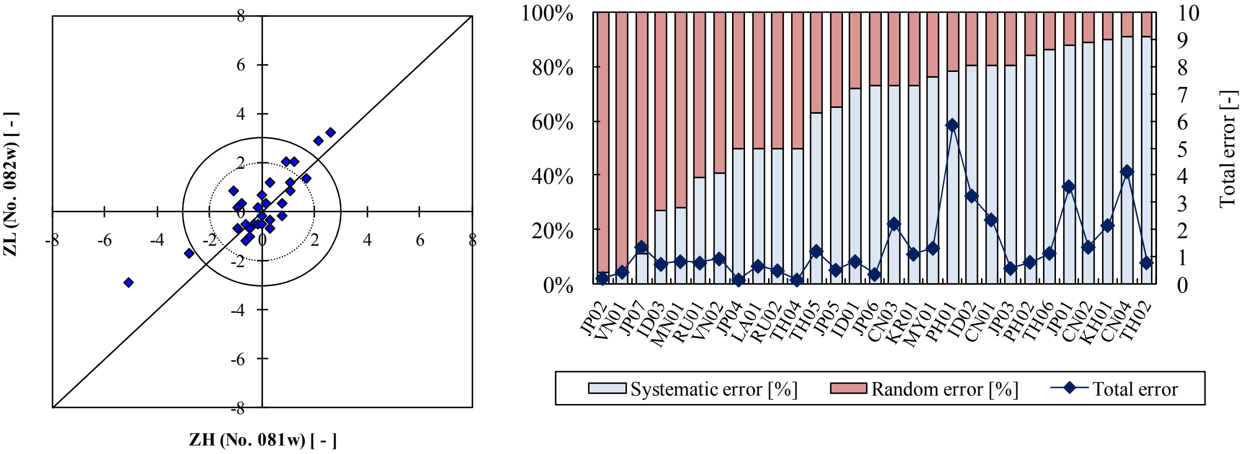
Appendix Figure 2.4.7 Youden diagram with Z-score and Error evaluation for K^+

Ca^{2+}



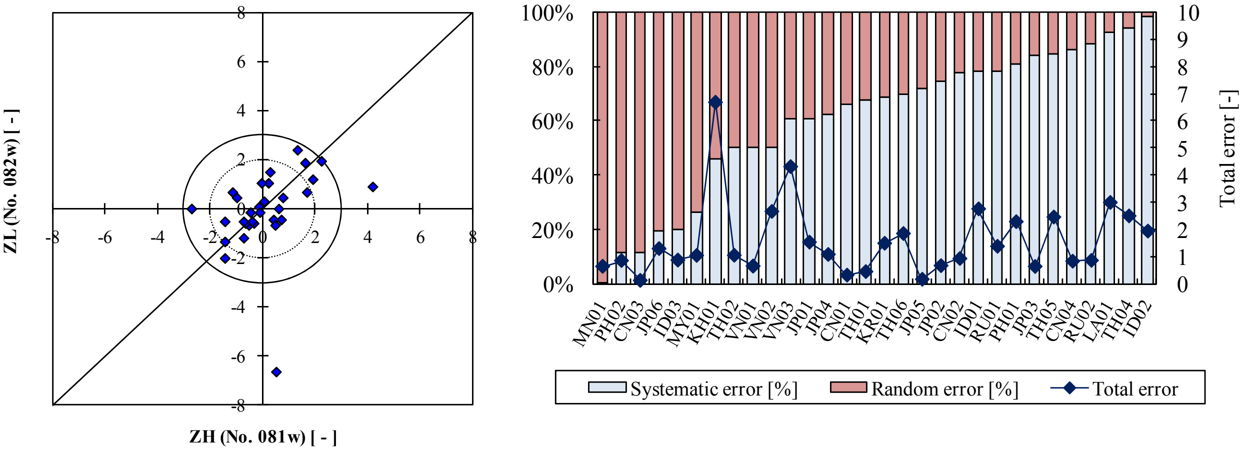
Appendix Figure 2.4.8 Youden diagram with Z-score and Error evaluation for Ca^{2+}

Mg^{2+}



Appendix Figure 2.4.9 Youden diagram with Z-score and Error evaluation for Mg^{2+}

NH_4^+



Appendix Figure 2.4.10 Youden diagram with Z-score and Error evaluation for NH_4^+

Appendix Table 2.4.1 Judgment of outliers with Youden diagram method for high conc. sample No. 081w

Sample No. 081w (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	4.71	3.15	53.7	50.2	75.9	57.6	9.7		13.4	50.1
CN01	4.38	3.83	49.7	46.1	75.2	55.8	8.8	26.3	13.1	48.7
CN02	4.42	3.85	49.7	47.8	75.6	57.3	8.7	25.5	13.0	50.9
CN03	4.46	3.84	49.8	46.1	73.6	56.5	8.7	25.3	12.9	48.1
CN04	4.46	3.85	50.4	45.9	72.6	57.3	8.3	26.7	14.0	46.9
ID01	4.53	4.19	48.7	27.1	73.4	56.8	9.0	27.1	12.8	52.6
ID02	4.56	3.74	50.6	41.0	69.3	49.7	9.2	24.3	10.5	44.1
ID03	5.09	2.58	42.2	40.4	63.6	55.1	10.9	20.2	12.5	50.7
JP01	4.57	3.91	48.7	46.8	71.9	57.5	9.1	29.6	13.7	49.4
JP02	4.55	3.88	47.0	45.1	73.0	56.3	8.9	25.8	12.2	47.5
JP03	4.53	3.79	49.7	47.3	75.6	56.1	9.0	26.1	12.1	47.3
JP04	4.54	3.87	51.9	47.5	76.1	55.3	8.7	26.1	12.3	49.2
JP05	4.59	3.80	47.4	46.1	73.1	54.4	9.1	25.2	12.2	48.2
JP06	4.56	3.80	49.5	47.2	75.5	55.7	9.0	24.2	12.4	45.0
JP07	4.51	3.81	48.7	47.3	74.8	56.1	9.1	25.3	11.6	46.5
LA01	4.46	3.36	48.2	46.1	78.9	58.7	9.7	28.4	12.3	55.4
MY01	4.54	3.78	47.9	46.6	74.3	58.0	8.9	26.5	11.9	45.5
MN01	4.57	3.79	46.3	47.6	75.9	56.1	10.2	25.2	11.8	49.8
MM01	4.81	1.79								
PH01	4.63	3.78	53.7	46.6	82.6	53.3	9.0	26.5	9.0	54.4
PH02	4.84	3.66	49.4	46.7	76.3	62.7	11.5	24.9	12.0	50.0
KR01	4.60	4.32	49.1	44.2	74.2	52.5	8.2	24.8	12.0	44.1
RU01	4.51	3.94	47.2	46.2	76.0	56.6	8.9	26.5	12.8	46.3
RU02	4.54	3.94	50.2	48.2	71.5	58.3	9.0	27.5	12.3	46.3
TH01	4.57	3.80	49.1	46.6	74.2	58.3	9.4	27.8	13.0	47.1
TH02	4.52	3.78	48.9	47.5	75.2	53.8	8.7	24.1	11.9	48.4
TH04	4.05	4.87	61.1	46.9	69.3	58.8	9.3	26.9	12.3	53.5
TH05	4.48	3.59	47.5	45.9	73.1	55.2	8.4	26.2	12.5	44.1
TH06	4.51	3.51	49.2	46.1	72.7	54.8	8.5	25.2	11.7	53.7
VN01	4.49	4.07	50.6	47.7	75.6	57.9	8.8	26.4	12.5	50.4
VN02	4.37	3.78	49.7	47.7	61.7	43.2	6.4	24.1	11.7	40.2
VN03	4.53	3.60	(54.5)			66.7	8.5			61.4
Prepared value	**4.49**	**3.97**	**49.5**	**47.4**	**75.8**	**56.8**	**9.1**	**25.7**	**12.6**	**47.5**
Number of data	26	22	25	25	25	25	26	26	26	29
Average	4.53	3.81	49.2	46.7	74.3	56.3	8.9	25.8	12.4	48.4
Minimum	4.38	3.51	47.0	44.2	69.3	52.5	8.2	24.1	11.6	40.2
Maximum	4.71	4.07	51.9	48.2	78.9	58.8	9.7	27.8	13.4	55.4
Standard deviation	0.07	0.12	1.16	0.90	1.92	1.50	0.36	1.02	0.47	3.42

Note: The outliers judged by Youden diagram method were painted with light mesh and were excluded from statistics.
The data in parentheses were not evaluated by Youden diagram method because of the lack of necessary parameters, and were excluded from statistics.

Appendix Table 2.4.2 Judgment of outliers with Youden diagram method for low conc. sample No. 082w

Sample No. 082w (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	5.21	1.16	15.1	19.5	28.4	15.6	4.2		7.0	5.7
CN01	4.97	1.14	15.0	16.6	23.1	15.9	3.8	9.0	7.4	15.0
CN02	4.96	1.18	15.0	16.6	23.8	16.3	4.2	7.8	6.7	15.2
CN03	4.99	1.17	14.8	16.7	24.2	15.6	3.8	9.2	7.4	14.7
CN04	5.15	1.18	15.4	16.7	24.6	16.0	3.6	10.9	8.1	13.7
ID01	5.15	1.26	15.2	11.3	22.6	15.9	3.6	8.8	6.4	17.8
ID02	5.19	1.13	15.2	14.8	23.0	15.5	4.1	7.4	5.2	12.8
ID03	5.68	0.94	12.6	14.2	20.0	14.8	3.8	6.8	5.8	14.0
JP01	5.27	1.19	14.8	16.2	22.3	17.0	3.6	8.7	7.9	16.6
JP02	5.09	1.17	14.9	16.1	22.9	15.0	3.6	7.9	6.3	13.8
JP03	5.08	1.16	14.8	16.2	23.2	15.3	3.7	7.3	5.9	13.9
JP04	5.09	1.21	15.5	16.1	22.4	14.7	3.2	8.0	6.1	16.0
JP05	5.16	1.18	14.7	16.2	23.3	14.1	3.6	7.0	5.9	14.4
JP06	5.21	1.14	14.9	16.3	22.4	15.6	3.9	7.3	6.4	15.5
JP07	5.08	1.17	14.2	16.0	23.0	15.6	3.8	8.4	6.7	13.8
LA01	4.99	1.16	15.6	19.4	24.5	22.2	4.1	10.4	6.6	17.2
MY01	5.10	1.14	14.0	15.7	22.8	15.6	3.6	7.4	5.5	15.2
MN01	5.50	1.01	13.3	15.6	23.4	17.8	3.4	9.5	6.4	14.0
MM01	5.47	0.56								
PH01	5.22	1.14	17.2	16.9	27.4	21.7	4.9	11.2	4.5	16.2
PH02	5.41	1.13	15.2	16.6	22.5	19.3	6.3	8.9	5.8	13.7
KR01	5.23	1.24	14.2	16.6	22.3	13.8	3.1	6.8	5.6	13.9
RU01	5.04	1.20	14.4	14.0	24.2	15.3	3.6	7.4	6.1	13.0
RU02	5.05	1.19	14.9	14.9	23.2	15.2	3.8	7.4	5.9	13.9
TH01	5.14	1.17	14.5	15.8	22.5	15.9	4.2	9.4	6.9	14.4
TH02	5.15	1.08	13.5	15.1	21.7	14.8	4.0	6.9	5.9	16.0
TH04	4.68	1.23	13.9	15.1	19.6	16.5	4.2	7.8	6.1	17.1
TH05	5.00	1.10	14.0	15.7	22.5	15.0	4.3	8.4	6.9	11.9
TH06	5.06	1.10	14.8	16.2	21.9	14.0	2.8	6.8	5.8	15.5
VN01	5.08	1.23	14.9	15.8	24.2	15.1	2.7	9.4	6.0	14.6
VN02	4.90	1.31	14.7	15.7	25.7	17.3	4.4	7.6	6.3	14.6
VN03	5.14	1.03				24.1	2.7			15.8
Prepared value	**5.10**	**1.18**	**14.7**	**16.2**	**23.4**	**15.4**	**3.8**	**7.6**	**6.2**	**14.2**
Number of data	26	22	25	25	25	25	26	26	26	29
Average	5.11	1.16	14.8	16.0	23.1	15.5	3.8	8.2	6.3	14.8
Minimum	4.96	1.08	13.5	14.0	21.7	13.8	2.7	6.8	5.5	11.9
Maximum	5.27	1.23	15.6	16.9	24.6	17.8	4.9	11.2	7.4	17.8
Standard deviation	0.08	0.04	0.49	0.66	0.79	0.88	0.47	1.17	0.51	1.36

Note: The outliers judged by Youden diagram method were painted with light mesh and were excluded from statistics.
The data in parentheses were not evaluated by Youden diagram method because of the lack of necessary parameters, and were excluded from statistics.

3. 4th 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 October 2008. 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

21 laboratories in charge of chemical analysis in 10 countries of EANET participated in the fourth attempt. NC shipped the sample filters to all of these laboratories in 10 countries. 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.081d-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.081d-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.082d-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.082d-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.083d-1	Alkali-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by K_2CO_3
No.083d-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.081d-1, No.082d-1, No.083d-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.081d-2, No.082d-2, No.083d-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 <u>**the net amount**</u> 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.081d-1,No.081d-2,No.082d-1 and No.082d-2;
$M_{sol,\ Blank}$: the averaged net amount (μg) in the extracting solutions from the blank filters, No.083d-1 and No.083d-2.

3.3 Results

NC distributed the sample filters to 21 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 -1.8% (SO_4^{2-}) to 3.3% (NH_4^+) for Sample No.081d (low amount), and from -1.0% (Cl^-, NH_4^+) to 0% (SO_4^{2-}) for Sample No.082d (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 by 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.081d (low amount) and No.082d (high amount); ii) Individual parameters; iii) Circumstances of analysis in each participating laboratory. The evaluation of results on both of Sample No.081d and No.082d is presented in “3.3.1 Evaluation of Laboratories’ Performance (by sample)”. The evaluation of results for each constituent is presented in “3.3.2 Evaluation of Laboratories’ Performance (by analytical parameters)”. Then the evaluation of results on both two samples and each constituent is presented in “3.3.3 Overall Evaluation”. 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 “3.3.4 Information on Laboratories”.

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

Constituents	Prepared * (Vp)	Average (Va)	$\Delta V/Vp$ * (%)	S.D.	Number (N)	Min.	Max.
Sample No.081d (Low)							
SO_4^{2-} (µg)	30.0	28.2	-1.8	2.69	18	21.4	30.7
Cl^-(µg)	2.50	2.37	-1.3	0.33	19	1.85	3.33
NH_4^+(µg)	5.60	5.93	3.3	0.94	20	4.35	8.99
Sample No.082d (High)							
SO_4^{2-}(µg)	110	110	0	10.6	20	89.7	138
Cl^-(µg)	32.0	31.0	-1.0	2.64	19	25.7	34.9
NH_4^+(µg)	35.0	34.0	-1.0	3.23	20	26.5	38.1

* 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.081d (low amount), 11 analytical data in 59 submitted results exceeded the DQOs (±15%) by a factor of 2 (±30%) and were flagged by "E". Also 4 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". A number of flagged data was 15 and the ratio of the flagged data was about 25.4 percents in total for Sample No.081d (Figure 3.2, Table 3.4 and 3.5)

Table 3.4 Number of flagged data for Sample No.081d(low amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	3	3	5	11
Flag X *	1	1	2	4
Data within DQOs	15	15	14	44
Ratio of Flagged (%)	21.1	21.1	33.3	25.4

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

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

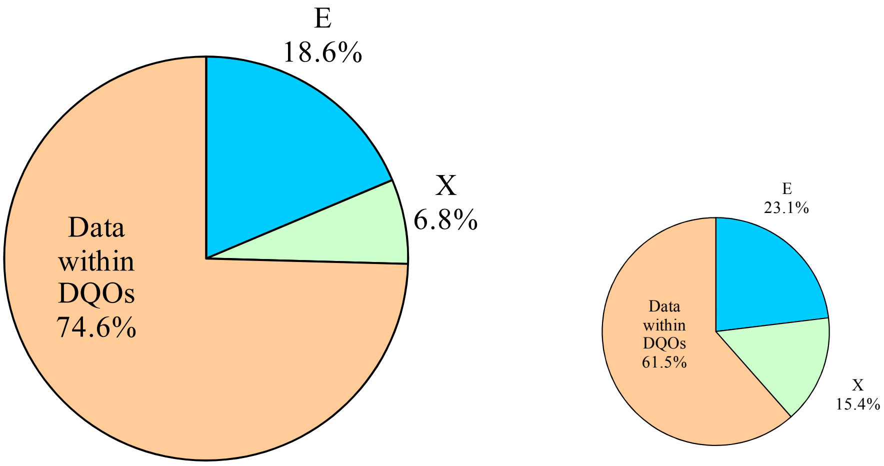


Figure 3.2 Percentage of flagged data for Sample No.081d (low amount)

Table 3.5 Averaged analytical results of Sample No.081d (low amount)

Lab. Code	SO_4^{2-} (µg)		Cl^- (µg)		NH_4^+ (µg)	
CN01	E	21.4		2.35	X	1.08
ID01		27.0	X	3.33		5.76
JP01		29.6		2.15		5.49
JP02		28.6	E	3.02		6.03
JP03		30.2		2.31		5.35
JP04		30.3		2.55		5.71
JP06		30.1		2.25		5.61
JP07		29.9		2.31		6.08
JP08		30.7		2.33		5.58
KR01		28.6		2.43		5.98
MY01		27.3		2.33		5.74
MN01		29.5		2.60		5.13
PH01	X	10.7		2.20	X	8.99
RU01					E	6.66
TH01	E	24.6	E	2.09	E	6.63
TH02		30.2		2.20	E	6.87
TH03		27.8		2.25		5.44
TH04		28.7		2.26		5.97
VN01	E	22.7	E	1.85		5.26
VN02		29.6		2.21	E	4.35
VN03					E	4.34

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

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

Sample with high amount of Ions

For Sample No.082d (high amount), 9 analytical data in 60 submitted results exceeded the DQOs (±15%) by a factor of 2 (±30%) and were flagged by "E". Also 1 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 16.7 percents in total for Sample No.082d (Fig.3.3). Results of SO_4^{2-} and Cl^- have no flags of "X". (Table 3.6 and 3.7)

Table 3.6 Number of flagged data for Sample No.082d (high amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E*	4	3	2	9
Flag X*	0	0	1	1
Data within DQOs	16	16	18	50
Ratio of Flagged (%)	20.0	15.8	14.3	16.7

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

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

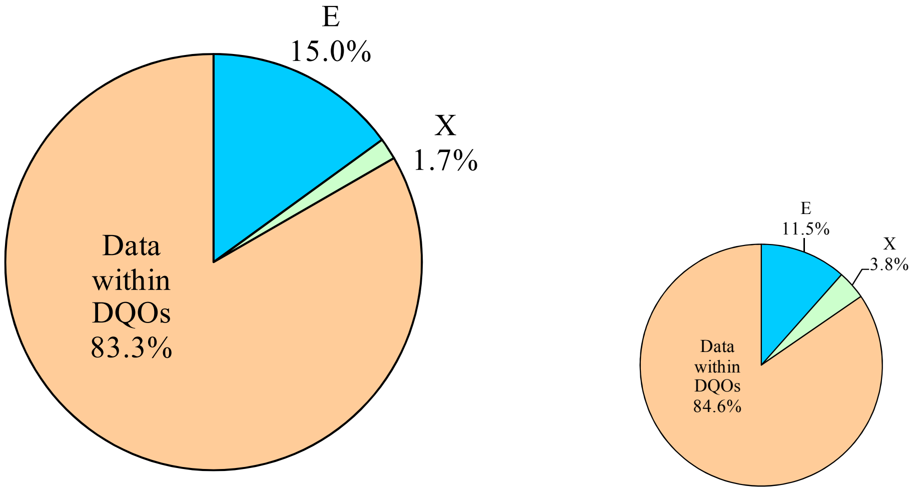


Figure 3.3 Percentage of flagged data for Sample No.082d (high amount)

Table 3.7 Averaged analytical results of Sample No.082d (high amount)

Lab. Code	SO_4^{2-} (μg)		Cl^- (μg)		NH_4^+ (μg)	
CN01	E	92.6		32.6	E	27.7
ID01		106	E	26.2		32.1
JP01		118		33.5		34.2
JP02		109		31.7		34.2
JP03		114		33.1		34.5
JP04		113		32.8		35.9
JP06		114		33.0		36.7
JP07		115		31.5		30.7
JP08		114		31.4		35.9
KR01		113		33.0		35.8
MY01		106		30.9		31.6
MN01		111		30.1		38.1
PH01	E	138	E	26.2		32.1
RU01	E	90.5				37.2
TH01		105		29.4		37.8
TH02		114		34.9		31.7
TH03		108		30.5		36.5
TH04		113		33.0		36.5
VN01	E	89.7	E	25.7		33.2
VN02		112		29.3	E	26.5
VN03					X	19.8

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

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

Blank Sample Analysis

Sample No.083d (No.083d-1 and No.083d-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 0.18μg, 0.70μg, and 0.24μg, respectively. Blank values were detected in wide range including 0μg. Table 3.9 shows the ratio of blank value to analytical result. Reverse mesh indicates that there was a flag for Sample No.081d or 082d. Although the blank values were relatively higher, flags were not appeared at some laboratories. 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.083d (blank)

Lab. Code	SO_4^{2-} (µg)	Cl^- (µg)	NH_4^+ (µg)
CN01	0.00	0.98	0.00
ID01	0.00	0.00	0.00
JP01	0.18	0.41	0.37
JP02	0.00	0.91	0.97
JP03	0.21	0.65	0.24
JP04	0.36	0.65	0.16
JP05	0.29	1.09	0.17
JP06	0.00	0.72	0.20
JP07	0.00	0.47	0.49
KR01	0.15	0.70	0.20
MY01	0.14	0.62	0.18
MN01	1.80	0.60	1.13
PH01	0.00	0.00	0.00
RU01	-	-	0.16
TH01	0.17	0.81	0.60
TH02	0.60	1.67	0.00
TH03	0.00	0.96	0.00
TH04	0.41	0.54	0.24
VN01	4.01	1.09	0.48
VN02	3.52	0.66	0.93
VN03	-	-	5.25
Average	0.71	0.78	0.62
Median	0.18	0.70	0.24
Minimum	0.00	0.00	0.00
Maximum	4.01	1.67	5.25
Standard deviation	1.20	0.35	1.13

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	0.03	🟨 0.00	🟨 0.00	0.42	🟧 0.00
ID01	0.00	0.00	0.00	0.00	🟨 0.00	0.00
JP01	0.00	0.01	0.01	0.01	0.19	0.07
JP02	0.00	0.03	0.03	0.00	🟨 0.30	0.16
JP03	0.00	0.02	0.01	0.01	0.28	0.04
JP04	0.00	0.02	0.00	0.01	0.25	0.03
JP05	0.00	0.03	0.00	0.01	0.48	0.03
JP06	0.00	0.02	0.01	0.00	0.31	0.03
JP07	0.00	0.01	0.01	0.00	0.20	0.09
KR01	0.00	0.02	0.01	0.01	0.29	0.03
MY01	0.00	0.02	0.01	0.01	0.27	0.03
MN01	0.02	0.02	0.03	0.06	0.23	0.22
PH01	🟨 0.01	🟨 0.05	0.04	🟧 0.16	0.55	🟧 0.14
RU01	🟨 -	-	0.00	-	-	🟨 0.02
TH01	0.00	0.03	0.02	🟨 0.01	🟨 0.39	🟨 0.09
TH02	0.01	0.05	0.00	0.02	0.76	🟨 0.00
TH03	0.00	0.03	0.00	0.00	0.43	0.00
TH04	0.00	0.02	0.01	0.01	0.24	0.04
VN01	🟨 0.04	🟨 0.04	0.02	🟨 0.18	🟨 0.59	0.09
VN02	0.03	0.02	🟧 0.04	0.12	0.30	🟧 0.21
VN03	-	-	🟧 0.27	-	-	🟧 1.21

🟧 : Flagged data of "E" for Sample No.081d or No.082d

🟨 : Flagged data of "X" for Sample No.081d or No.082d

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)

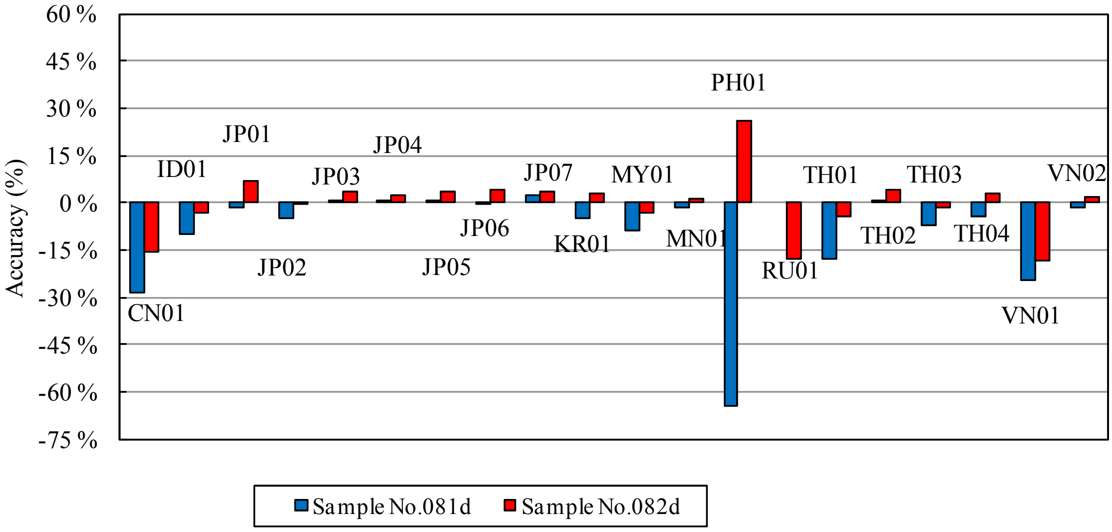


Figure 3.4 Distribution of results for SO_4^{2-} (normalized by prepared value)

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

Analytical Method			
Ion Chromatography	20/20		

Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.081d	3	1	21.1
Sample No.082d	4	0	20.0

All of the participating laboratories used Ion Chromatography for the determination of SO_4^{2-}. “E” flags appeared at 3 laboratories for Sample No.081d and “X” flags appeared 1 laboratory. 4 of the data for Sample No.082d marked “E” flags. “X” flag did not appear for No.082d. Particularly the data of PH01 exceeded “prepared value” more than 60%.

Cl^- (Chloride)

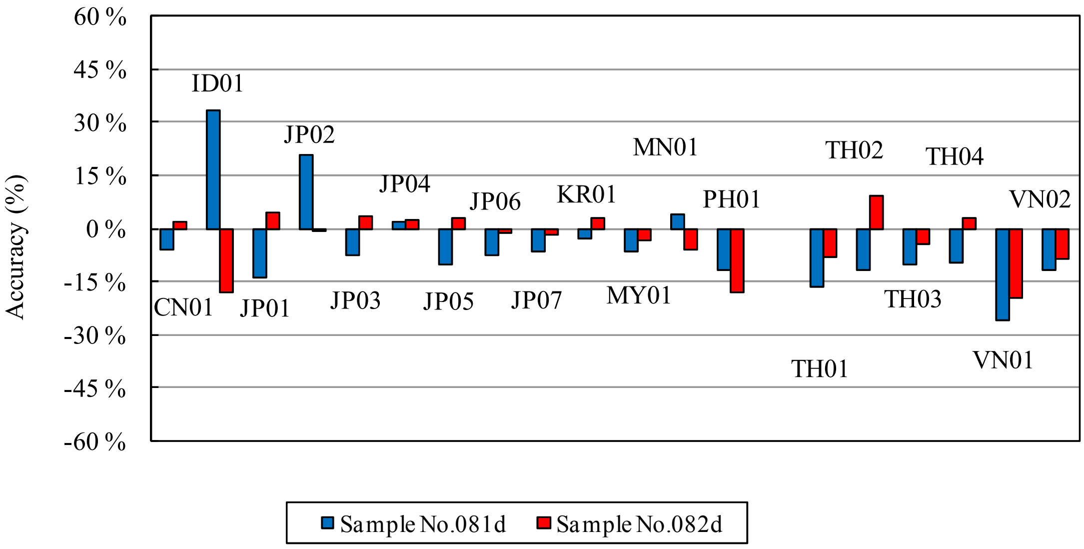


Figure 3.5 Distribution of results for Cl^- (normalized by prepared value)

Table 3.11 Analytical method and flagged data of Cl^-

Analytical Method			
Ion Chromatography	19/19		

Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.081d	3	1	21.1
Sample No.082d	3	0	15.8

As same with the analysis of SO_4^{2-}, all laboratories used Ion Chromatography for the determination of Cl^-. "E" flags appeared at 3 laboratories for Sample No.081d and "X" flags appeared 1 laboratory. 3 of the data for Sample No.082d marked "E" flags. "X" flag did not appear for No.082d.

NH_4^+ (Ammonium)

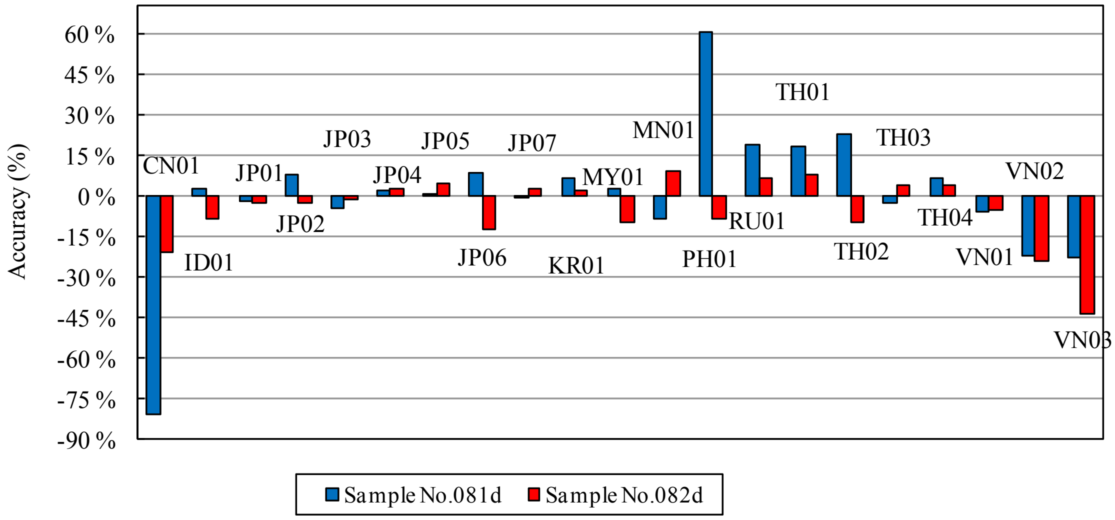


Figure 3.6 **Distribution of results for NH_4^+ (normalized by prepared value)**

Table 3.12 **Analytical method and flagged data of NH_4^+**

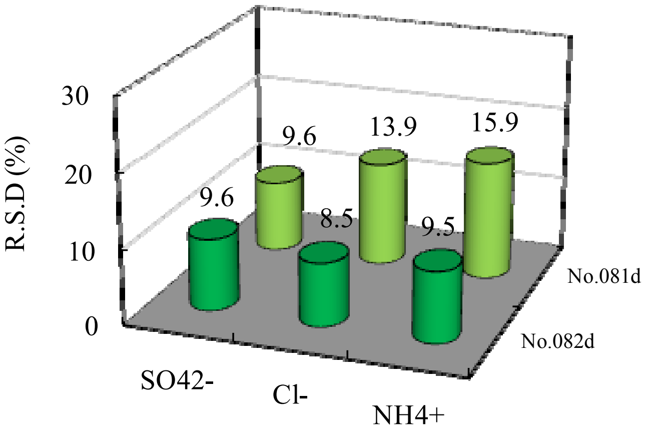
Analytical Method			
Ion Chromatography	20/21		
Spectrometry (Nessler)	1/21		
Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.081d	5	2	33.3
Sample No.082d	2	1	14.3

20 laboratories used Ion Chromatography and 1 laboratory used Nessler Spectrophotometry. The ratio of the flagged data for Sample No.081d, which had low amount, was higher than that for Sample No.082d which had high amount. There were 5 “E” flags and 2 “X” flags for Sample No.081d, and 2 “E” flags and 1 “X” flag for Sample No.082d,.

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.081d and No.082d are shown in Figure 3.7. The values of R.S.D for Sample No.081d were higher than those for Sample No.082d. Especially, R.S.D. of Cl^- and NH_4^+ for Sample No.081d showed relatively higher value compared with the others, which were almost the same as the first to third attempt, 2005-2007. The use of inappropriate range for the calibration standard solution can be pointed out as one of the reasons for unsatisfied 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^+, 20 of 21 laboratories used Ion Chromatography and 1 laboratory used Spectrophotometry. However, spectrophotometry other than Indophenol blue method was used.

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	
JP05	Ion Chromatography	
JP06	Ion Chromatography	
JP07	Ion Chromatography	
KR01	Ion Chromatography	
MY01	Ion Chromatography	
MN01	Ion Chromatography	
PH01	Ion Chromatography	
RU01	Ion Chromatography	Spectrophotometry(Nessler)
TH01	Ion Chromatography	
TH02	Ion Chromatography	
TH03	Ion Chromatography	
TH04	Ion Chromatography	
VN01	Ion Chromatography	
VN02	Ion Chromatography	
VN03	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 7.6 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.081d and/or 082d. Reverse mesh with dark color indicate flagged data in both of Sample No.081d and No.082d.

Table 3.14 Years of experience (unit: year)

Lab. Code	SO_4^{2-}	Cl^-	NH_4^+
CN01	-	-	-
ID01	7	7	7
JP01	24	24	24
JP02	25	25	25
JP03	2	2	2
JP04	1	1	1
JP06	1	1	1
JP07	6	6	6
JP08	4	4	4
KR01	10	10	10
MY01	6	6	6
MN01	10	10	1o
PH01	1	1	1
RU01	17	-	17
TH01	1	1	1
TH02	5	5	5
TH03	2	2	2
TH04	6	6	11
VN01	15	15	15
VN02	4	4	4
VN03			3

(Note) Reverse mesh: Flagged data in Sample No.081d and/or No.082d (Dark color: Flagged data in both of Sample No.081d and No.082d)

Flagged Data

In the results of Sample No.081d and 082d, the total number of flagged data was 25 (E: 20, X: 5) among the whole of 119 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 9 (43%). The number of laboratories that submitted data with less than 2 flagged values were 12 (57%) in this attempt. There were four 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.

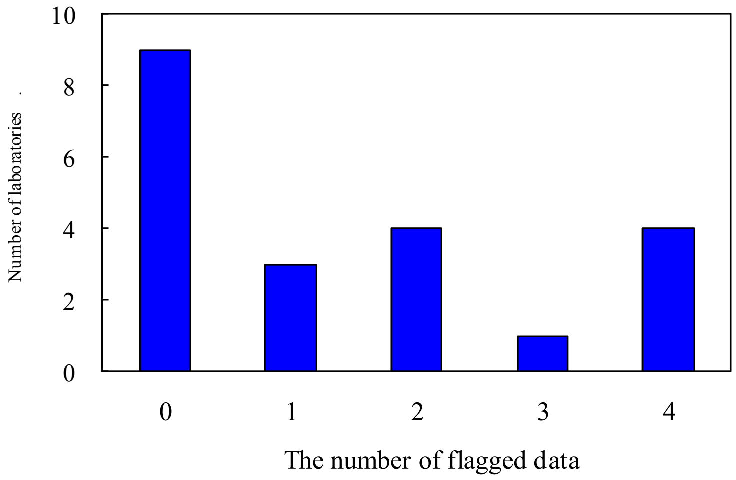


Figure 3.8 Distribution of laboratories with the number of flagged data

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	**20.8**	208	**22.5**	225	**35.7**	357
ID01	5.21	**52.1**	**14.1**	141	11.1	111
JP01	10.4	209	**28.3**	566	**22.3**	557
JP02	0.52	104	1.41	70.5	2.78	139
JP03	5.21	156	2.82	84.6	5.54	111
JP04	1.04	104	2.82	141	2.77	277
JP05	1.04	521	1.41	705	2.77	1390
JP06	1.67	83.4	**4.54**	227	4.43	221
JP07	0.31	62.4	0.85	169	1.66	166
KR01	20.8	146	2.82	56.4	5.55	111
MY01	1.04	62.5	1.41	113	2.77	166
MN01	4.37	125	**5.64**	169	11.1	111
PH01	2.08	208	**5.64**	564	2.77	111
RU01	6.24	**20.8**	-	-	5.56	222
TH01	1.04	62.5	2.82	169	0.55	166
TH02	2.08	62.4	**5.64**	169	4.43	111
TH03	1.04	104	2.82	282	5.54	443
TH04	0.10	83.3	0.28	226	1.11	139
VN01	2.08	104	2.82	141	5.54	277
VN02	2.08	**52.0**	2.82	70.5	4.43	111
VN03	-	-	-	-	2.50	40.0
Sample No.081d	15.6		3.52		15.5	
Sample No.082d		57.3		45.1		97.0

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

Reverse mesh: Flagged data in Sample No.081d and/or No.082d (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 reached 4th survey. 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 amount samples, the percentage of data that satisfied DQOs are almost over 80%. In the case of the low amount samples, the percentage of data in this survey was 74.6%. These are the highest percentages among past 4 surveys.

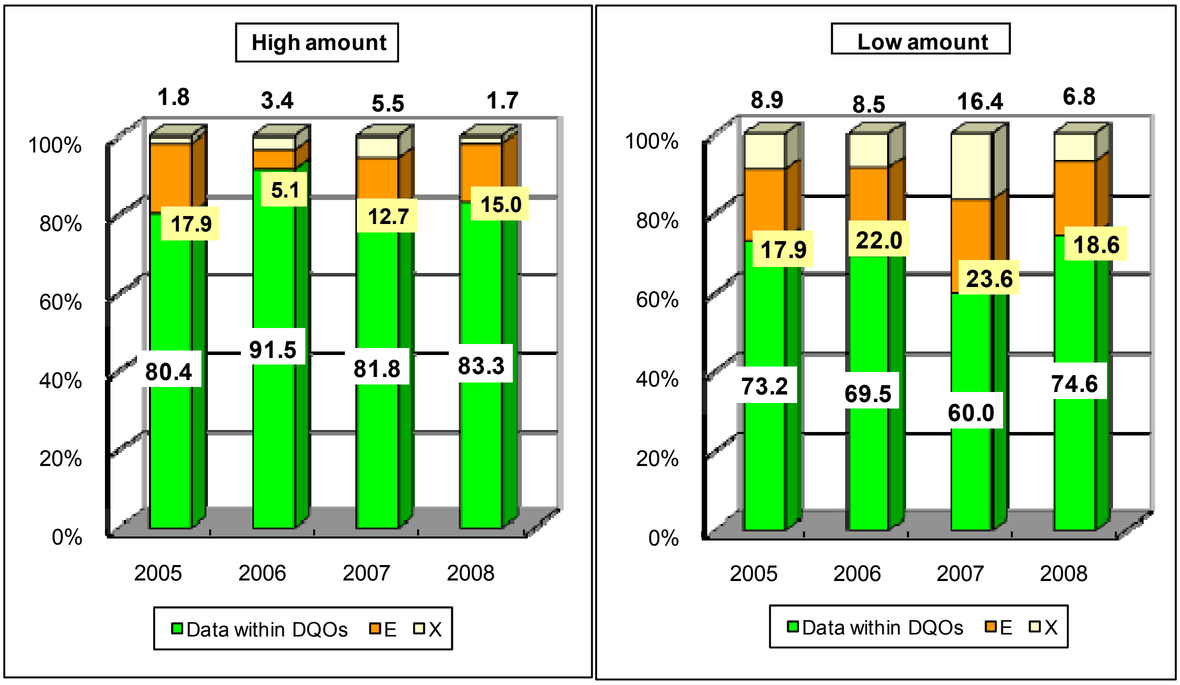


Figure 3.9 Comparison of results from the inter-laboratory comparison projects

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 high amount samples of each year. Comparing the percentage of flagged data in Cl^- and NH_4^+ from 1st to 4th comparison, the percentage of flagged data in 2008 was dencreased in Cl^- low amount sample though prepared value didn't change so much.

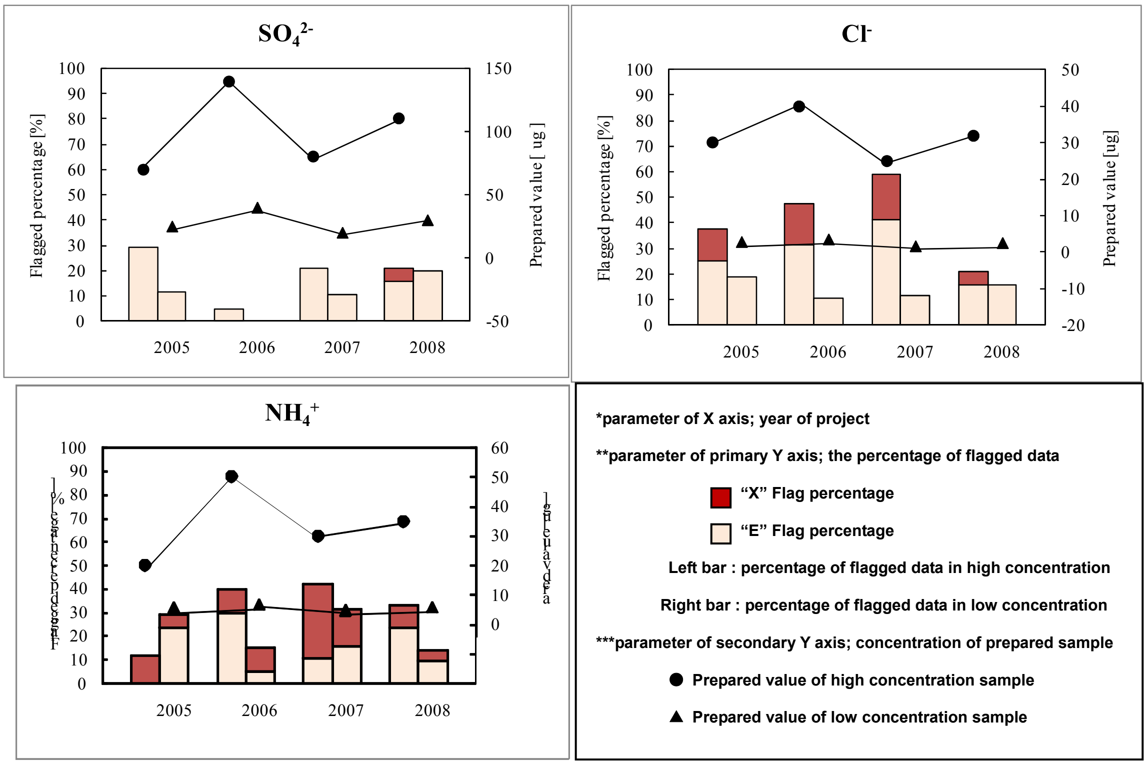


Figure 3.10 Comparison for each parameter in inter-laboratory comparison project

References

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

2) EANET, March 2000. Technical Documents for Wet Deposition Monitoring in East Asia adopted at : The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.

3) EANET, November 2003. Technical Documents for Filter Pack Method in East Asia 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)**
2. INDONESIA	
2) Environmental Management Center (PUSARPEDAL)	**(ID01)**
3. 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)**
4.RRPUBLIC OF KOREA	
10) National Institute of Environmental Research	**(KR01)**
5. MALAYSIA	
11) Department of Chemistry	**(MY01)**
6. MONGOLIA	
12) Central Laboratory of Environment and Metrology	**(MN01)**
7. PHILIPPINES	
13) Environmental Management Bureau (EMB)	**(PH01)**
8. RUSSIA	
14) Limnological Institute, Russian Academy of Sciences/Siberian Branch	**(RU01)**
9. THAILAND	
15) Pollution Control Department (PCD)	**(TH01)**
16) Khon Kaen University (KKU)	**(TH02)**
17) Chiang Mai University (CMU)	**(TH03)**
18) Environmental Research and Training Center (ERTC)	**(TH04)**
10.VIET NAM	
19) Center for Environmental Research, Institute of Meteorology and Hydrology	**(VN01)**
20) Mid-central Regional Hydro Meteorological Center	**(VN02)**
21) Sub-institute of Hydrometeorology and Environment of South Vietnam	**(VN03)**

Appendix 3-2 Summary of data

Appendix Table 3.2(1) Analytical results of Sample No.081d (low amount)

Lab. ID	SO_4^{2-} (µg)	Cl^- (µg)	NH_4^+ (µg)
CN01	21.4	2.35	1.08
ID01	27.0	3.33	5.76
JP01	29.6	2.15	5.49
JP02	28.6	3.02	6.03
JP03	30.2	2.31	5.35
JP04	30.3	2.55	5.71
JP05	30.1	2.25	5.61
JP06	29.9	2.31	6.08
JP07	30.7	2.33	5.58
KR01	28.6	2.43	5.98
MY01	27.3	2.33	5.74
MN01	29.5	2.60	5.13
PH01	10.7	2.20	8.99
RU01			6.66
TH01	24.6	2.09	6.63
TH02	30.2	2.20	6.87
TH03	27.8	2.25	5.44
TH04	28.7	2.26	5.97
VN01	22.7	1.85	5.26
VN02	29.6	2.21	4.35
VN03			4.34
Prepared value	30.0	2.50	5.60
Number of data	19	19	21
Average	27.2	2.37	5.62
Minimum	10.7	1.85	1.08
Maximum	30.7	3.33	8.99
Standard deviation	4.78	0.33	1.42

Appendix Table 3.2(2) Analytical results of Sample No.082d (high amount)

Lab. ID	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	92.6	32.6	27.7
ID01	106	26.2	32.1
JP01	118	33.5	34.2
JP02	109	31.7	34.2
JP03	114	33.1	34.5
JP04	113	32.8	35.9
JP05	114	33.0	36.7
JP06	115	31.5	30.7
JP07	114	31.4	35.9
KR01	113	33.0	35.8
MY01	106	30.9	31.6
MN01	111	30.1	38.1
PH01	138	26.2	32.1
RU01	90.5		37.2
TH01	105	29.4	37.8
TH02	114	34.9	31.7
TH03	108	30.5	36.5
TH04	113	33.0	36.5
VN01	89.7	25.7	33.2
VN02	112	29.3	26.5
VN03			19.8
Prepared value	110	32.0	35.0
Number of data	20	19	21
Average	110	31.0	33.3
Minimum	89.7	25.7	19.8
Maximum	138	34.9	38.1
Standard deviation	10.6	2.64	4.41

4. 10th 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 10th project, NC provided two soil samples (No.081 and 082) 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

Sixteen laboratories of 10 countries participated in the 10th 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. 081: Brown forest soil (Cambisols)
Sample No. 082: Red soil (Acrisols)

Soils for Sample No. 081 and 082 were collected in a forest of Japanese cypress (*Chamaecyparis obtusa*) and a secondary forest of *Castanopsis* sp. and *Quercus* sp. in Fukuoka 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. 081 and 082
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) **<u>Repeat the procedure 1) - 7) twice.</u>**

(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. The outline of the results are discussed here mainly for the verified data, although the statistics were calculated for both entire (non-verified) data and verified data. 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 verified data, the variations (CVs) of pH(H_2O) and pH(KCl) were very small, 2.1 – 3.5%. CVs for other parameters except Ex-Ca of No. 081 and Ex-K of No. 082 were improved after removing outliers, when compared with the entire data. CVs of Ex-acidity and Al were 17 – 30%. CVs of Ex-H were still relatively large, probably because the values calculated based on Ex-acidity and Ex-Al including 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" and "vn02", 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. 081								
Number of Laboratories	16	16	14	14	14	14	16	16	16
Total average	5.3	4.2	1.04	0.49	0.15	0.14	2.20	1.97	0.59
Median	5.4	4.2	1.13	0.49	0.16	0.07	1.41	1.06	0.33
Maximum	5.7	4.6	1.80	0.81	0.23	1.02	13.84	15.28	3.95
Minimum	4.1	3.7	0.00	0.00	0.00	0.00	0.89	0.63	0.04
Standard deviation	0.4	0.2	0.61	0.18	0.05	0.26	3.12	3.57	0.93
CV (%)*1	7.9	4.4	58.1	36.3	35	185	141.9	181.2	157
	No. 082								
Number of Laboratories	16	16	14	14	14	14	16	16	16
Total average	4.2	3.7	0.20	0.30	0.24	0.15	9.70	8.40	1.38
Median	4.2	3.6	0.13	0.29	0.26	0.07	9.63	8.23	1.23
Maximum	5.3	4.8	0.67	0.50	0.43	1.13	14.13	11.70	2.88
Minimum	3.6	3.4	0.01	0.00	0.00	0.00	5.18	6.23	0.00
Standard deviation	0.4	0.3	0.19	0.12	0.10	0.29	2.05	1.39	0.74
CV (%)*1	8.8	8.9	96.7	41.0	43	187	21.1	16.6	54

(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. 081								
Number of Laboratories	14	14	13	12	11	12	13	13	15
Total average	5.4	4.2	1.04	0.50	0.16	0.07	1.37	1.03	0.37
Median	5.5	4.2	1.16	0.49	0.16	0.06	1.39	1.01	0.31
Maximum	5.7	4.3	1.80	0.62	0.23	0.15	2.04	1.62	0.83
Minimum	5.0	4.0	0.00	0.37	0.12	0.00	0.89	0.63	0.04
Standard deviation	0.2	0.1	0.63	0.07	0.03	0.04	0.30	0.30	0.26
CV (%)*1	3.5	2.1	60.7	14.9	19.8	61.4	21.8	29.3	71.2
	No. 082								
Number of Laboratories	11	13	13	13	14	12	16	16	15
Total average	4.2	3.6	0.16	0.32	0.24	0.07	9.70	8.40	1.47
Median	4.2	3.6	0.09	0.29	0.26	0.06	9.63	8.23	1.23
Maximum	4.4	3.7	0.39	0.50	0.43	0.11	14.13	11.70	2.88
Minimum	4.0	3.4	0.01	0.16	0.00	0.00	5.18	6.23	0.70
Standard deviation	0.1	0.1	0.14	0.09	0.10	0.03	2.05	1.39	0.66
CV (%)*1	3.0	2.2	86.8	28.2	43.4	49.7	21.1	16.6	45.2

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

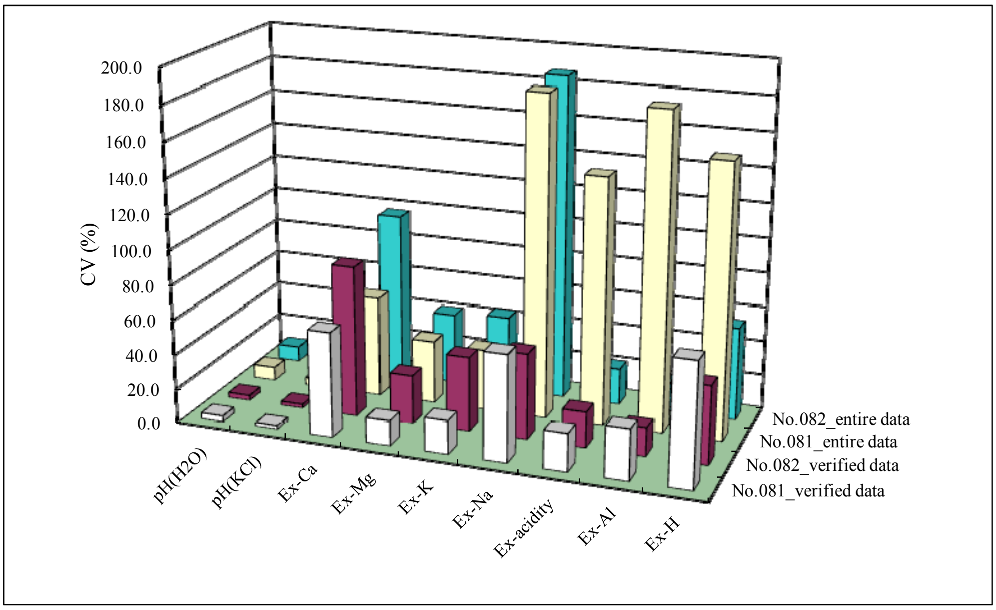


Figure 4.1 CV among laboratories

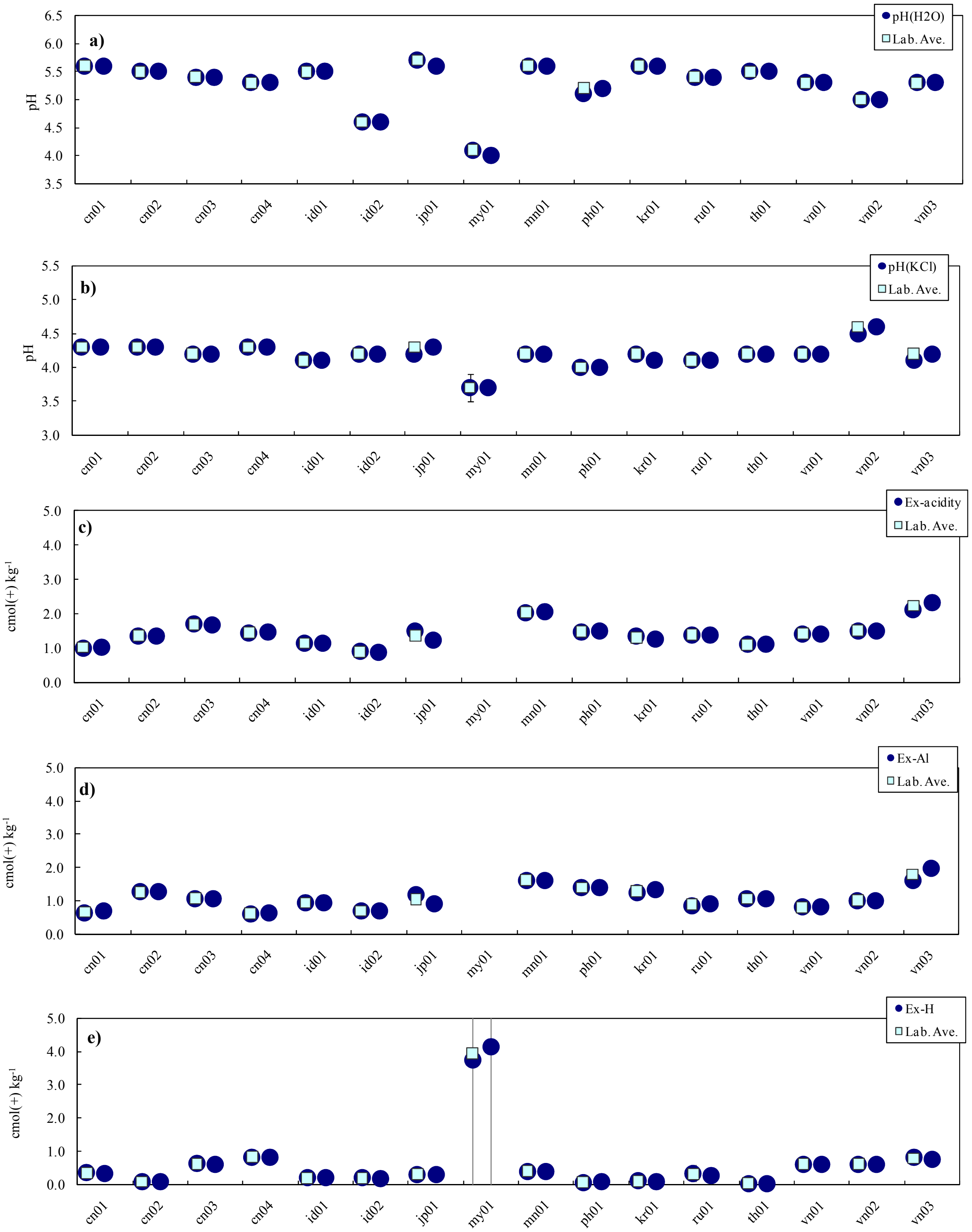


Figure 4.2-1 Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 081. Error bar shows standard deviation of triplicate analysis.

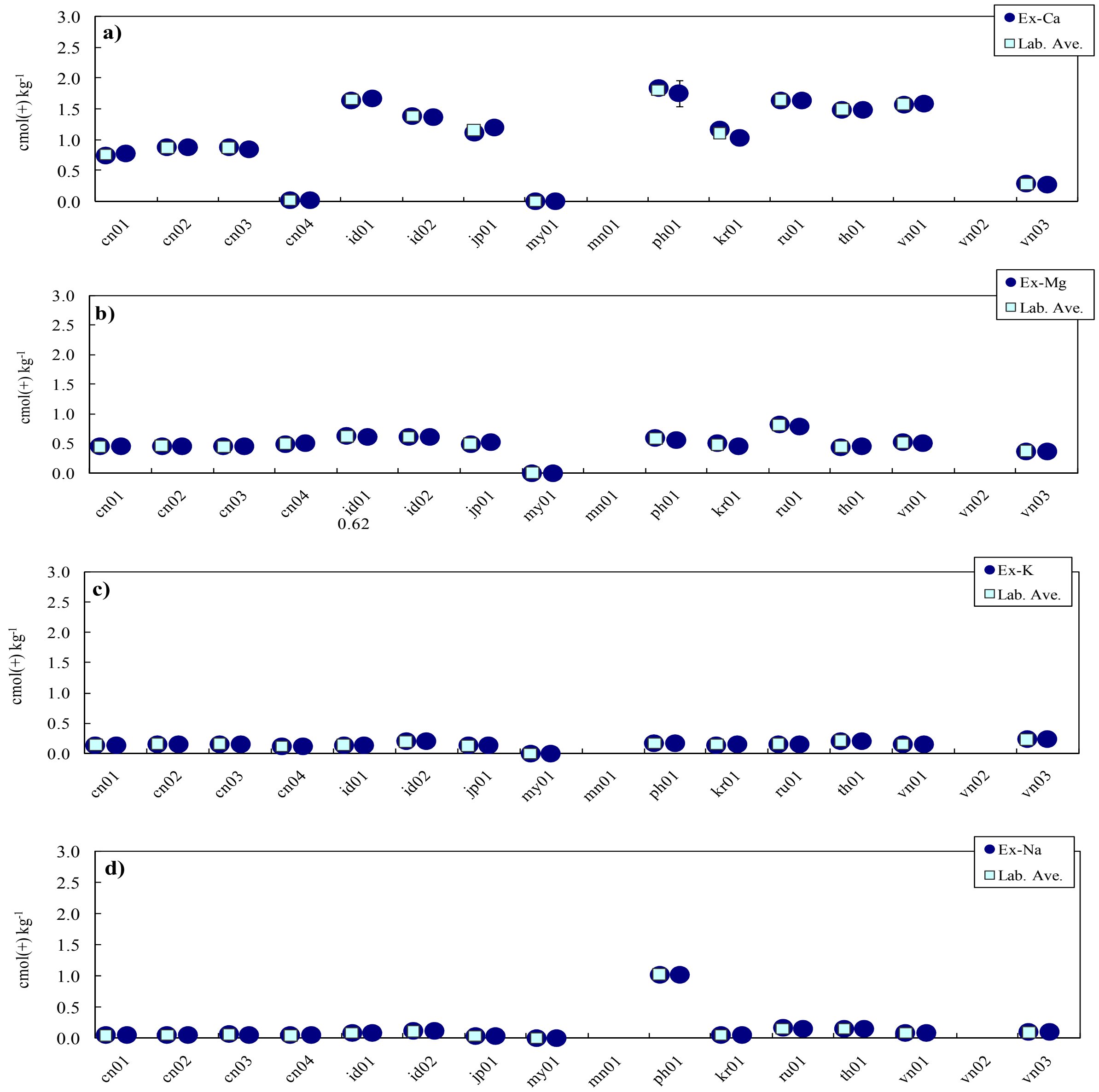


Figure 4.2-2 Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 081. Error bar shows standard deviation of triplicate analysis.

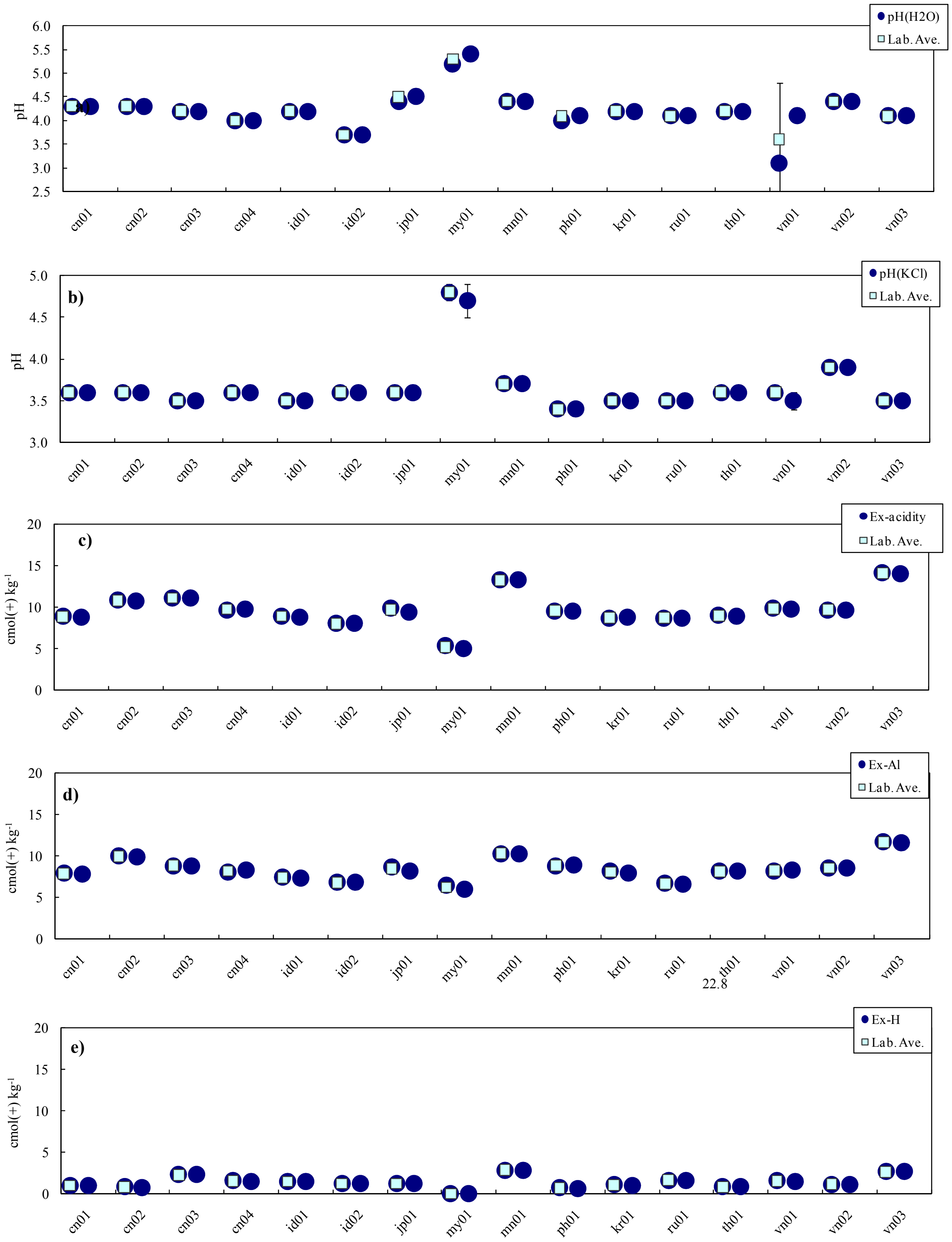


Figure 4.2-3 Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 082. Error bar shows standard deviation of triplicate analysis.

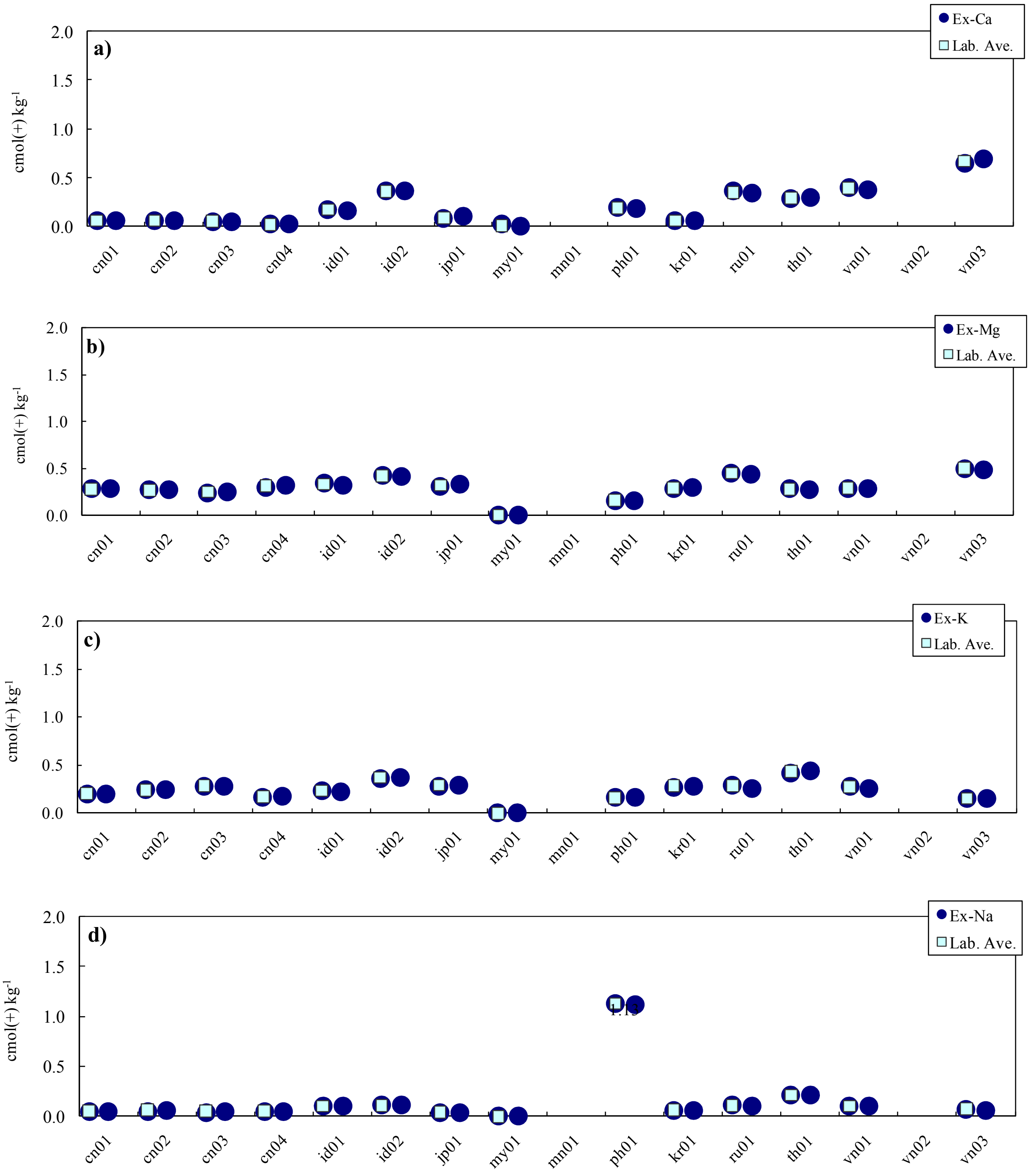


Figure 4.2-4 Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 082. Error bar shows standard deviation of triplicate analysis.

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.

The 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. “jp01” in Ex-acidity and -Al of No. 081, “my01” in Ex-Al and -H of No. 081, etc. As for the Cochran method, very small difference of the repeat analyses was detected in some laboratories since the repeatability of other laboratories were extremely high. Then, the rest of data were tested by Grubbs method (examination of the average value of each laboratory), and the laboratories, which have remarkably large or small average, were judged as outliers: e.g. “id02” in pH (H_2O) of No. 081, “my01” in pH (H_2O), pH (KCl), Ex-Mg, Ex-K, and Ex-acidity of No. 081, etc.

In a laboratory, more than three outliers were detected. It was suggested that some systematic errors in the analytical procedures might occur in such a laboratory.

Table 4.3-1. Data verified by Cochran-Grubbs methods: No. 081

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	5.6	4.3	0.75	0.45	0.14	0.04	1.00	0.64	0.36
	2nd	5.6	4.3	0.77	0.45	0.14	0.04	1.03	0.70	0.34
cn02	1st	5.5	4.3	0.87	0.46	0.16	0.05	1.36	1.27	0.09
	2nd	5.5	4.3	0.87	0.46	0.16	0.05	1.36	1.27	0.09
cn03	1st	5.4	4.2	0.88	0.45	0.16	0.06	1.71	1.06	0.65
	2nd	5.4	4.2	0.85	0.45	0.16	0.05	1.67	1.07	0.61
cn04	1st	5.3	4.3	0.02	0.49	0.12	0.04	1.43	0.61	0.82
	2nd	5.3	4.3	0.02	0.51	0.12	0.04	1.47	0.64	0.83
id01	1st	5.5	4.1	1.64	0.62	0.14	0.08	1.15	0.95	0.20
	2nd	5.5	4.1	1.66	0.61	0.14	0.08	1.13	0.93	0.20
id02	1st	4.6*g	4.2	1.39	0.61	0.20	0.11	0.90	0.70	0.20
	2nd	4.6*g	4.2	1.37	0.61	0.20	0.11	0.88	0.70	0.19
jp01	1st	5.7	4.2	1.12	0.48	0.13	0.03	1.5*c	1.19*c	0.31
	2nd	5.6	4.3	1.20	0.52	0.13	0.03	1.22*c	0.91*c	0.31
my01	1st	4.1*g	3.7*g	0.00	0.00*g	0.00*g	0.00	13.83*g	14.99*c	3.76*c
	2nd	4.0*g	3.7*g	0.00	0.00*g	0.00*g	0.00	13.84*g	15.56*c	4.14*c
mn01	1st	5.6	4.2					2.02	1.62	0.40
	2nd	5.6	4.2					2.05	1.62	0.40
ph01	1st	5.1	4.0	1.84	0.60	0.17	1.01*g	1.46	1.40	0.07
	2nd	5.2	4.0	1.76	0.56	0.17	1.02*g	1.49	1.40	0.08
kr01	1st	5.6	4.2	1.17*c	0.50	0.14*c	0.05	1.34	1.24	0.12
	2nd	5.6	4.1	1.02*c	0.46	0.16*c	0.05	1.27	1.34	0.10
ru01	1st	5.4	4.1	1.64	0.82*g	0.16	0.16*c	1.39	0.85	0.34
	2nd	5.4	4.1	1.63	0.79*g	0.16	0.14*c	1.39	0.92	0.27
th01	1st	5.5	4.2	1.48	0.43	0.20*c	0.15	1.10	1.06	0.04
	2nd	5.5	4.2	1.49	0.45	0.21*c	0.14	1.10	1.06	0.04
vn01	1st	5.3	4.2	1.57	0.52	0.15	0.08	1.41	0.81	0.61
	2nd	5.3	4.2	1.58	0.51	0.15	0.08	1.42	0.81	0.61
vn02	1st	5.0	4.5*g					1.50	1.01	0.61
	2nd	5.0	4.6*g					1.50	1.01	0.61
vn03	1st	5.3	4.1	0.28	0.37	0.23	0.09	2.13*c	1.60*c	0.83
	2nd	5.3	4.2	0.27	0.37	0.23	0.09	2.32*c	1.98*c	0.75

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. 082

Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
cn01	1st	4.3	3.6	0.06	0.28	0.20	0.05	8.90	7.93	0.97
	2nd	4.3	3.6	0.06	0.28	0.20	0.05	8.82	7.83	0.99
cn02	1st	4.3	3.6	0.06	0.27	0.24	0.05	10.82	9.98	0.85
	2nd	4.3	3.6	0.06	0.27	0.24	0.06	10.74	9.95	0.80
cn03	1st	4.2	3.5	0.05	0.24	0.28	0.04	11.13	8.82	2.32
	2nd	4.2	3.5	0.05	0.25	0.28	0.05	11.13	8.86	2.28
cn04	1st	4.0	3.6	0.02	0.30	0.16	0.05	9.70	8.10	1.61
	2nd	4.0	3.6	0.02	0.32	0.18	0.05	9.81	8.32	1.49
id01	1st	4.2	3.5	0.17	0.34	0.23	0.10	8.98	7.50	1.48
	2nd	4.2	3.5	0.16	0.32	0.22	0.10	8.85	7.36	1.49
id02	1st	3.7*g	3.6	0.36	0.42	0.36	0.11	8.02	6.80	1.22
	2nd	3.7*g	3.6	0.36	0.41	0.37	0.11	8.03	6.79	1.24
jp01	1st	4.4*c	3.6	0.08	0.31	0.28	0.03	9.90	8.71	1.19
	2nd	4.5*c	3.6	0.10	0.33	0.29	0.04	9.47	8.23	1.25
my01	1st	5.2*c	4.8*c	0.02	0.00*g	0.00	0.00	5.36	6.50	-0.28*c
	2nd	5.4*c	4.7*c	0.00	0.00*g	0.00	0.00	5.00	5.96	0.00*c
mn01	1st	4.4	3.7					13.29	10.30	2.88
	2nd	4.4	3.7					13.29	10.30	2.88
ph01	1st	4.0*c	3.4	0.19	0.15	0.16	1.13*g	9.57	8.83	0.75
	2nd	4.1*c	3.4	0.18	0.16	0.16	1.12*g	9.59	8.93	0.65
kr01	1st	4.2	3.5	0.06	0.28	0.27	0.06	8.63	8.14	1.13
	2nd	4.2	3.5	0.06	0.30	0.28	0.06	8.78	7.97	0.97
ru01	1st	4.1	3.5	0.36	0.45	0.29	0.11	8.71	6.73	1.59
	2nd	4.1	3.5	0.34	0.44	0.26	0.10	8.68	6.59	1.66
th01	1st	4.2	3.6	0.28	0.28	0.42	0.21*g	8.99	8.16	0.83
	2nd	4.2	3.6	0.30	0.27	0.44	0.21*g	8.98	8.16	0.82
vn01	1st	3.1*c	3.6*c	0.40	0.29	0.28	0.10	9.88	8.24	1.57
	2nd	4.1*c	3.5*c	0.38	0.29	0.26	0.10	9.72	8.26	1.46
vn02	1st	4.4	3.9*g					9.68	8.54	1.17
	2nd	4.4	3.9*g					9.67	8.53	1.17
vn03	1st	4.1	3.5	0.65*g	0.50	0.15	0.07	14.17	11.77	2.66
	2nd	4.1	3.5	0.69*g	0.49	0.15	0.06	14.09	11.63	2.67

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) were smaller than 1.0%, and those of Ex-acidity and Al were smaller than 4%.

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 smaller than 3%.

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 4% in pH(H_2O) and pH(KCl). CVs of exchangeable base cations were relatively large. In particular, CVs of exchangeable Ca and Na were larger than 50%. Those of Ex-acidity and Al were smaller than 30%.

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. 081								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	16	16	14	14	14	14	16	16	16
Total sum of square	256846	160961	7642	1654	162	136	44605	35611	3241
ST/lmd	2675	1677	91	20	2	2	465	371	34
Number of Data	96	96	84	84	84	84	96	96	96
Total sum	506.8	401.2	87.42	40.67	12.74	11.66	211.20	188.71	56.93
Total average	5.3	4.2	1.04	0.48	0.15	0.14	2.20	1.97	0.59
Sum of square inter-laboratories (S_R)	16.2	2.5	28.58	2.41	0.22	5.07	877.18	1143.19	78.04
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.06	0.01	0.00	0.00	0.19	0.86	0.23
Sum of square repeatablility (S_r)	0.1	0.1	0.16	0.02	0.00	0.00	0.40	0.47	188.11
Total sum of square (S_T)	16.3	2.6	28.79	2.43	0.23	5.07	877.77	1144.51	266.38
Inter-laboratories degree of freedom (ϕ_R)	15	15	13	13	13	13	15	15	15
Within-laboratory degree of freedom (ϕ_{RW})	16	16	14	14	14	14	16	16	16
Repeatability degree of freedom (ϕ_r)	64	64	56	56	56	56	64	64	64
Total degree of freedom (ϕ_T)	95	95	83	83	83	83	95	95	95
Inter-laboratories variance ($V_R = S_R/\phi_R$)	1.08	0.17	2.198	0.185	0.017	0.390	58.479	76.213	5.202
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.004	0.001	0.000	0.000	0.012	0.054	0.015
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.006	0.007	2.939
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.18	0.03	0.366	0.031	0.003	0.065	9.744	12.693	0.865
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	0.002	0.015	-0.975
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.006	0.007	2.939
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.4	0.2	0.61	0.18	0.05	0.25	3.12	3.56	0.93
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.04	0.01	0.00	0.00	0.06	0.13	0.07
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.05	0.02	0.01	0.01	0.08	0.09	1.71
Inter-laboratories precision CV (%)	8.0	4.0	58.16	36.27	35.21	183.61	141.91	181.31	157.02
Within-laboratory precision CV (%)	0.4	0.7	3.64	3.04	2.94	3.21	2.86	6.81	11.76
Repeatability precision CV (%)	0.6	0.8	5.10	3.72	3.87	6.53	3.58	4.34	289.10
Reproducibility limit ($R = D(2, 0.95)*s_R$)	1.19	0.47	1.695	0.492	0.150	0.714	8.741	9.979	2.607
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.05	0.08	0.106	0.041	0.012	0.012	0.176	0.375	0.195
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.12	0.175	0.059	0.019	0.030	0.260	0.281	5.658
Statistics	No. 082								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	16	16	14	14	14	14	16	16	16
Total sum of square	164268	122990	273	615	397	161	867115	649829	17237
ST/lmd	1711	1281	3	7	5	2	9032	6769	180
Number of Data	96	96	84	84	84	84	96	96	96
Total sum	405.3	350.7	16.51	24.80	19.93	12.69	931.19	806.12	131.29
Total average	4.2	3.7	0.20	0.30	0.24	0.15	9.70	8.40	1.37
Sum of square inter-laboratories (S_R)	12.0	9.3	2.88	1.15	0.82	6.32	376.67	174.78	51.70
Sum of square within-laboratory (S_{RW})	1.6	0.0	0.00	0.00	0.00	0.00	0.61	1.03	0.24
Sum of square repeatablility (S_r)	6.1	0.1	0.01	0.01	0.00	0.02	0.57	0.80	1.08
Total sum of square (S_T)	19.7	9.4	2.89	1.16	0.82	6.34	377.84	176.62	53.02
Inter-laboratories degree of freedom (ϕ_R)	15	15	13	13	13	13	15	15	15
Within-laboratory degree of freedom (ϕ_{RW})	16	16	14	14	14	14	16	16	16
Repeatability degree of freedom (ϕ_r)	64	64	56	56	56	56	64	64	64
Total degree of freedom (ϕ_T)	95	95	83	83	83	83	95	95	95
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.80	0.62	0.221	0.088	0.063	0.486	25.111	11.652	3.447
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.10	0.00	0.000	0.000	0.000	0.000	0.038	0.065	0.015
Repeatability variance ($V_r = S_r/\phi_r$)	0.09	0.00	0.000	0.000	0.000	0.000	0.009	0.013	0.017
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.12	0.10	0.037	0.015	0.010	0.081	4.179	1.931	0.572
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	0.010	0.017	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.09	0.00	0.000	0.000	0.000	0.000	0.009	0.013	0.017
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.4	0.3	0.19	0.12	0.10	0.28	2.05	1.39	0.76
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.2	0.0	0.01	0.01	0.01	0.00	0.11	0.15	0.07
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.3	0.0	0.01	0.01	0.01	0.02	0.09	0.11	0.13
Inter-laboratories precision CV (%)	8.7	8.8	97.70	41.10	43.11	188.39	21.09	16.60	55.42
Within-laboratory precision CV (%)	4.3	0.6	5.50	2.83	3.49	3.26	1.16	1.75	5.12
Repeatability precision CV (%)	7.3	1.1	6.93	3.80	3.93	13.14	0.97	1.34	9.51
Reproducibility limit ($R = D(2, 0.95)*s_R$)	1.02	0.90	0.538	0.340	0.286	0.797	5.728	3.902	2.122
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.51	0.06	0.030	0.023	0.023	0.014	0.315	0.411	0.196
Repeatability limit ($r = D(3, 0.95)*s_r$)	1.02	0.13	0.045	0.037	0.031	0.066	0.311	0.370	0.429

Table 4.4-2 Analysis of variance for the verified data

Statistics	No. 081								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	14	13	12	11	12	13	13	15
Total sum of square	206934	123623	6537	1283	113	22	11378	6410	1104
ST/lmd	2464	1472	84	18	2	0	146	82	12
Number of Data	84	84	78	72	66	72	78	78	90
Total sum	454.9	351.6	80.85	35.82	10.61	4.68	106.67	80.06	33.22
Total average	5.4	4.2	1.04	0.50	0.16	0.07	1.37	1.03	0.37
Sum of square inter-laboratories (S_R)	2.8	0.6	28.56	0.36	0.06	0.10	6.41	6.56	5.84
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.02	0.01	0.00	0.00	0.02	0.03	0.02
Sum of square repeatablility (S_r)	0.0	0.0	0.15	0.01	0.00	0.00	0.08	0.08	0.29
Total sum of square (S_T)	2.8	0.6	28.73	0.38	0.07	0.10	6.50	6.66	6.16
Inter-laboratories degree of freedom (ϕ_R)	13	13	12	11	10	11	12	12	14
Within-laboratory degree of freedom (ϕ_{RW})	14	14	13	12	11	12	13	13	15
Repeatability degree of freedom (ϕ_r)	56	56	52	48	44	48	52	52	60
Total degree of freedom (ϕ_T)	83	83	77	71	65	71	77	77	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.21	0.04	2.380	0.032	0.006	0.009	0.534	0.546	0.417
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.002	0.001	0.000	0.000	0.001	0.002	0.001
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.003	0.000	0.000	0.000	0.001	0.001	0.005
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.04	0.01	0.396	0.005	0.001	0.002	0.089	0.091	0.069
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	0.000	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	0.001	0.001	0.005
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.2	0.1	0.63	0.07	0.03	0.04	0.30	0.30	0.26
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.02	0.01	0.00	0.00	0.02	0.03	0.02
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.05	0.02	0.01	0.01	0.04	0.04	0.07
Inter-laboratories precision CV (%)	3.5	2.0	60.76	14.76	20.30	60.52	21.81	29.40	71.45
Within-laboratory precision CV (%)	0.3	0.6	2.37	2.95	0.99	4.19	1.51	2.66	5.82
Repeatability precision CV (%)	0.5	0.5	5.20	3.39	3.83	10.88	2.79	3.76	18.95
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.53	0.24	1.763	0.206	0.091	0.110	0.835	0.845	0.738
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.05	0.07	0.069	0.041	0.004	0.008	0.058	0.076	0.060
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.06	0.178	0.056	0.020	0.023	0.126	0.127	0.231

Statistics	No. 082								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	11	13	13	13	14	12	16	16	15
Total sum of square	77785	76840	156	615	397	22	867115	649829	17237
ST/lmd	1179	985	2	8	5	0	9032	6769	192
Number of Data	66	78	78	78	84	72	96	96	96
Total sum	278.9	277.2	12.48	24.80	19.93	4.69	931.19	806.12	131.29
Total average	4.2	3.6	0.16	0.32	0.24	0.07	9.70	8.40	1.37
Sum of square inter-laboratories (S_R)	1.0	0.4	1.42	0.59	0.82	0.08	376.67	174.78	39.61
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.61	1.03	0.12
Sum of square repeatablility (S_r)	0.0	0.0	0.01	0.01	0.00	0.00	0.57	0.80	0.60
Total sum of square (S_T)	1.1	0.4	1.43	0.60	0.82	0.08	377.84	176.62	40.33
Inter-laboratories degree of freedom (ϕ_R)	10	12	12	12	13	11	15	15	14
Within-laboratory degree of freedom (ϕ_{RW})	11	13	13	13	14	12	16	16	15
Repeatability degree of freedom (ϕ_r)	44	52	52	52	56	48	64	64	60
Total degree of freedom (ϕ_T)	65	77	77	77	83	71	95	95	89
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.10	0.04	0.118	0.049	0.063	0.007	25.111	11.652	2.829
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.000	0.000	0.000	0.038	0.065	0.008
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.009	0.013	0.010
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.02	0.01	0.020	0.008	0.010	0.001	4.179	1.931	0.470
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	0.010	0.017	-0.001
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.009	0.013	0.010
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.14	0.09	0.10	0.03	2.05	1.39	0.69
Within-laboratory standard deviation ($s_{RW} = SQRT(s_r^2/3 + s_c^2)$)	0.0	0.0	0.01	0.01	0.01	0.00	0.11	0.15	0.05
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.01	0.01	0.01	0.01	0.09	0.11	0.10
Inter-laboratories precision CV (%)	3.1	2.2	87.70	28.35	43.11	51.80	21.09	16.60	50.21
Within-laboratory precision CV (%)	0.3	0.0	5.39	2.73	3.49	7.46	1.16	1.75	3.70
Repeatability precision CV (%)	0.7	0.0	7.91	3.67	3.93	8.86	0.97	1.34	7.32
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.37	0.22	0.393	0.252	0.286	0.094	5.728	3.902	1.923
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.03	0.00	0.024	0.024	0.023	0.014	0.315	0.411	0.142
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.09	0.00	0.042	0.038	0.031	0.019	0.311	0.370	0.331

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 used AAS for measurement of Ex-Ca and Mg, and 6 laboratories used FEP for Ex-K and Na. Years in use of instruments were varied from 1 to 21 for AAS and from 3 to 20 for FEP. All the laboratories except “vn01” and “vn03” applied Sr or La for measurement of Ex-Ca and Mg by AAS.

As for procedures for extraction of Ex-base cations, 8 laboratories used percolation tube procedures, 3 laboratories used Buchner funnel procedures, 2 laboratory used centrifuge procedures, and 1 laboratory used automatic extractor procedures. 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 64 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, although a few laboratories might conduct the instrumental analysis of both samples in a same day.

Table 4.5. Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience Chemical	Soil	Number of analyst	Years of experience Chemical	Soil	
cn01	1	23	5	1	23	5	s
cn02	1	13	10	1	n	n	d
cn03	1	11	11	1	18	18	d
cn04	3	14	4	2	14	4	s
id01	1	6	3	1	6	3	s
id02	2	n	n	1	11	9	d
jp01	1	6	4	1	6	4	s
my01	2	4	4	1	4	4	s
mn01	-	-	-	1	15	15	-
ph01	1	20	1	1	32	32	d
kr01	1	10	10	1	10	10	s
ru01	1	13	13	1	13	13	s
th01	2	4/4	2/0	2	4/4	2/0	s
vn01	1	16	11	1	16	11	s
vn02	-	-	-	1	6	2	-
vn03	1	5	5	1	3	3	-

Note: -, Not measured; n, no information; 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.081	AAS	3	AAS	3	Sr	FEP	3	FEP	3	Sr
	No.082	AAS	3	AAS	3	Sr	FEP	3	FEP	3	Sr
cn02	No.081	AAS	18	AAS	18	Sr	AAS	18	AAS	18	Sr
	No.082	AAS	18	AAS	18	Sr	AAS	18	AAS	18	Sr
cn03	No.081	AAS	11	AAS	11	Sr	AAS	11	AAS	11	Sr
	No.082	AAS	11	AAS	11	Sr	AAS	11	AAS	11	Sr
cn04	No.081	AAS	10	AAS	10	Sr	FEP	10	FEP	10	Cs
	No.082	AAS	10	AAS	10	Sr	FEP	10	FEP	10	Cs
id01	No.081	AAS	3	AAS	3	La	AAS	3	AAS	3	La
	No.082	AAS	3	AAS	3	La	AAS	3	AAS	3	La
id02	No.081	AAS	21	AAS	21	(Sr)	AAS	21	AAS	21	+
	No.082	AAS	21	AAS	21	(Sr)	AAS	21	AAS	21	+
jp01	No.081	AAS	5	AAS	5	Sr	FEP	5	FEP	5	na
	No.082	AAS	5	AAS	5	Sr	FEP	5	FEP	5	na
my01	No.081	AAS	5	AAS	5	Sr	FEP	5	FEP	5	La
	No.082	AAS	5	AAS	5	Sr	FEP	5	FEP	5	La
mn01	No.081	-	-	-	-	-	-	-	-	-	-
	No.082	-	-	-	-	-	-	-	-	-	-
ph01	No.081	AAS	11	AAS	11	Sr	AAS	11	AAS	11	na
	No.082	AAS	11	AAS	11	Sr	AAS	11	AAS	11	na
kr01	No.081	AAS	2	AAS	2	Sr	FEP	2	FEP	2	na
	No.082	AAS	2	AAS	2	Sr	FEP	2	FEP	2	na
ru01	No.081	AAS	20	AAS	20	(Sr)	FEP	20	FEP	20	+
	No.082	AAS	20	AAS	20	(Sr)	FEP	20	FEP	20	+
th01	No.081	AAS	1	AAS	1	Sr	AAS	1	AAS	1	Sr
	No.082	AAS	1	AAS	1	Sr	AAS	1	AAS	1	Sr
vn01	No.081	AAS	2	AAS	2	na	AAS	2	AAS	2	na
	No.082	AAS	2	AAS	2	na	AAS	2	AAS	2	na
vn02	No.081	-	-	-	-	-	-	-	-	-	-
	No.082	-	-	-	-	-	-	-	-	-	-
vn03	No.081	AAS	3	AAS	3	na	AAS	3	AAS	3	na
	No.082	AAS	3	AAS	3	na	AAS	3	AAS	3	na

Lab.	Sample	Procedures for extraction of Ex-base cations	Ex-Acidity, Al and H		
			method	Size of burette (ml)	
				Capacity	Minimum graduate
cn01	No.081 No.082	Percolation tube	Titration	25	0.1
cn02	No.081 No.082	Automatic extractor	Titration	5	0.00125
cn03	No.081 No.082	Percolation tube	Titration	50	0.1
cn04	No.081 No.082	Centrifuge	Titration	25	0.1
id01	No.081 No.082	Percolation tube	Titration	25	0.05
id02	No.081 No.082	Percolation tube	Titration	50	0.02
jp01	No.081 No.082	Percolation tube	Titration	25	0.1
my01	No.081 No.082	Buchner funnel	Titration	25	0.05
mn01	No.081 No.082	-	Titration	25	0.1
ph01	No.081 No.082	Buchner funnel	Titration	50	0.01
kr01	No.081 No.082	Percolation tube	Titration	10	0.02
ru01	No.081 No.082	Percolation tube	Titration	50	0.1
th01	No.081 No.082	Percolation tube	Titration	25	0.05
vn01	No.081 No.082	Buchner funnel	Titration	10	0.02
vn02	No.081 No.082	-	Titration	10	0.05
vn03	No.081 No.082	Centrifuge	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	9-Jan	2	2	15-Jan	5	0	15-Jan	5	0	6-Feb	2	2
	2nd	11-Jan	2		15-Jan	3		15-Jan	3		8-Feb	2	
cn02	1st	8-Jan	2	15	10-Jan	3	14	10-Jan	3	14	7-Jan	2	15
	2nd	23-Jan	2		24-Jan	3		24-Jan	3		22-Jan	2	
cn03	1st	23-Feb	1	1	12-Feb	2	7	12-Feb	2	7	19-Jan	5	38
	2nd	24-Feb	1		19-Feb	2		19-Feb	2		26-Feb	7	
cn04	1st	12-Jan	1	23	23-Jan	2	25	23-Jan	2	25	13-Jan	2	24
	2nd	4-Feb	1		17-Feb	2		17-Feb	2		6-Feb	2	
id01	1st	6-Jan	1	13	22-Jan	15	0	16-Jan	9	6	8-Jan	1	12
	2nd	19-Jan	1		22-Jan	3		22-Jan	3		20-Jan	1	
id02	1st	1-Feb	16	0	1-Feb	16	0	1-Feb	16	0	1-Feb	16	0
	2nd	1-Feb	16		1-Feb	16		1-Feb	16		1-Feb	16	
jp01	1st	1-Dec	1	59	17-Dec	9	64	17-Dec	9	64	28-Jan	9	21
	2nd	29-Jan	1		19-Feb	2		19-Feb	4		18-Feb	3	
my01	1st	4-Feb	1	1	3-Mar	2	2	3-Mar	2	2	9-Feb	1	1
	2nd	5-Feb	1		5-Mar	2		5-Mar	2		10-Feb	1	
mn01	1st	19-Feb	1	0		-	-		-	-	18-Feb	1	1
	2nd	19-Feb	1			-			-		19-Feb	1	
ph01	1st	7-Apr	1	7	23-Apr	1	7	23-Apr	1	7	9-Apr	1	7
	2nd	14-Apr	1		30-Apr	1		30-Apr	1		16-Apr	1	
kr01	1st	27-May	1	7	27-May	8	9	26-May	7	15	22-May	3	28
	2nd	3-Jun	2		5-Jun	3		10-Jun	8		19-Jun	2	
ru01	1st	25-Feb	1	1	17-Feb	2	3	17-Feb	2	3	21-Feb	1	1
	2nd	26-Feb	1		20-Feb	2		20-Feb	2		22-Feb	1	
th01	1st	26-May	1	1	1-Jun	5	6	1-Jun	5	6	27-May	1	3
	2nd	27-May	1		7-Jun	3		7-Jun	3		30-May	1	
vn01	1st	8-Jan	3	14	8-Jan	3	14	8-Jan	3	14	8-Jan	3	14
	2nd	22-Jan	3		22-Jan	3		22-Jan	3		22-Jan	3	
vn02	1st	7-Jan	1	1		-	-		-	-	7-Jan	1	1
	2nd	8-Jan	1			-			-		8-Jan	1	
vn03	1st	9-Jan	1	0	9-Feb	1	0	9-Feb	1	0	17-Feb	1	0
	2nd	9-Jan	1		9-Feb	1		9-Feb	1		17-Feb	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.

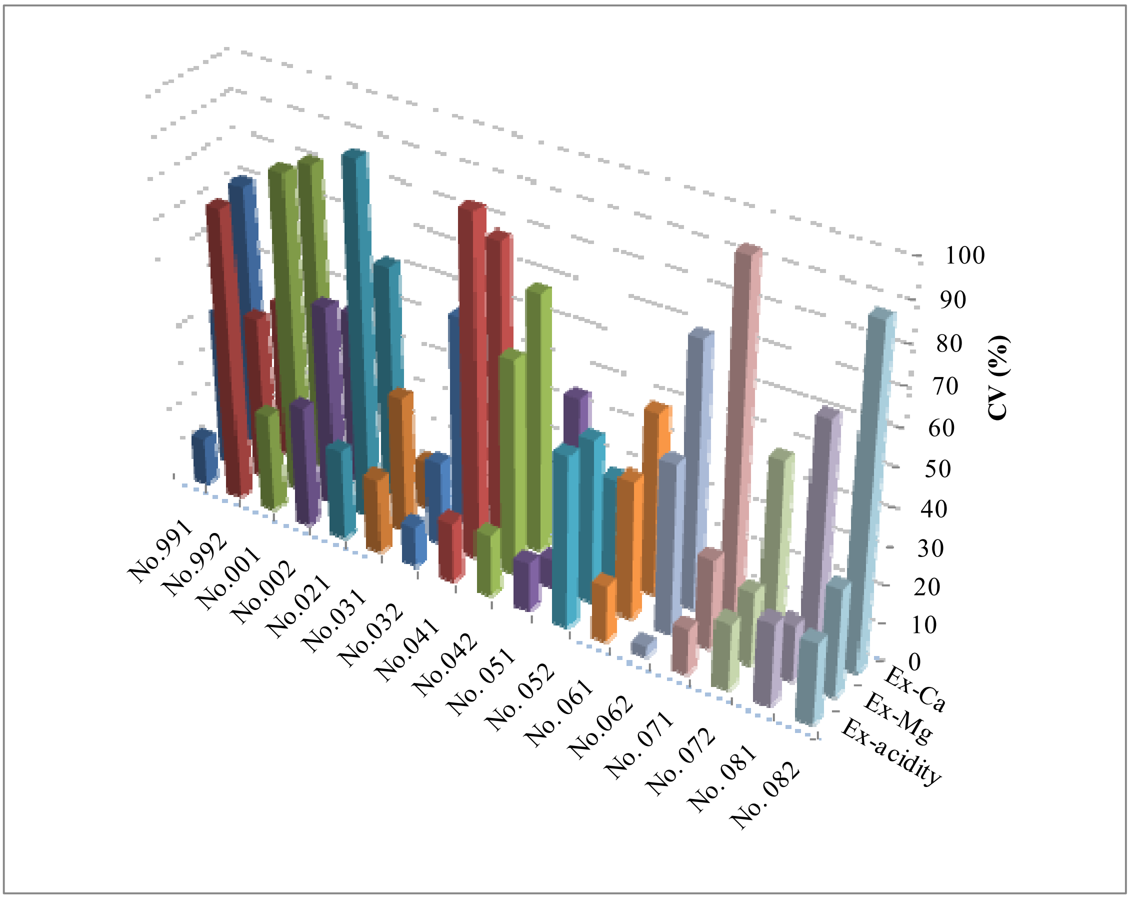


Figure 4.3 Comparison with inter-laboratories standard deviations (CV%) of the past surveys for Ex-Ca, Mg, and acidity

4.5 Recommendations for Improvement

A few laboratories showed significantly different values in pH (H_2O) and pH (KCl). Since measurement of pH required only balance, deionized water/1M KCl, and the pH meter, the main cause may be identified easily. The deionized water or pH electrode used for analysis should firstly be checked. Moreover, some reported values of exchangeable base cations could be identified as outliers within the laboratory, since they were minus or zero. Not only analytical procedures but also reporting procedures should be checked carefully in the respective laboratories.

References

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

2) EANET, 2000. 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	
11) Soil and Groundwater Research Team, NIER	
8. RUSSIA	
12) Limnological Institute Russian Academy of Science/Siberian Branch	**ru01**
9. THAILAND	
13) King Mongkut's University of Technology Thonburi	**th01**
10. VIET NAM	
14) Center for Environmental Research, Institute of Meteorology and Hydrology, MoNRE	**vn01**
15) Environment Analysis Laboratory II area, Middle of Central regional Hydro-Meteorological Observatory, National Hydro-Meteorological Center, MoNRE	**vn02**
16) Environmental Research Division, National Hydro-Meteorological Center, MoNRE	**Vn03**

Appendix Table 4.2-1 Entire data of pH in Sample No.081

Lab.	pH(H_2O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	5.6	5.6 (0.0)	5.6	4.3	4.3 (0.0)	4.3
			5.6			4.3
			5.6			4.3
		5.6 (0.1)	5.5		4.3 (0.0)	4.3
			5.6			4.3
			5.6			4.3
cn02	5.5	5.5 (0.0)	5.5	4.3	4.3 (0.0)	4.3
			5.5			4.3
			5.5			4.3
		5.5 (0.0)	5.5		4.3 (0.1)	4.3
			5.5			4.3
			5.5			4.2
cn03	5.4	5.4 (0.0)	5.4	4.2	4.2 (0.0)	4.2
			5.4			4.2
			5.4			4.2
		5.4 (0.1)	5.4		4.2 (0.0)	4.2
			5.5			4.2
			5.4			4.2
cn04	5.3	5.3 (0.1)	5.4	4.3	4.3 (0.0)	4.3
			5.3			4.3
			5.3			4.3
		5.3 (0.0)	5.3		4.3 (0.0)	4.3
			5.3			4.3
			5.3			4.3
id01	5.5	5.5 (0.0)	5.5	4.1	4.1 (0.0)	4.1
			5.5			4.1
			5.5			4.1
		5.5 (0.0)	5.5		4.1 (0.0)	4.1
			5.5			4.1
			5.5			4.1
id02	4.6	4.6 (0.0)	4.6	4.2	4.2 (0.0)	4.2
			4.6			4.2
			4.6			4.2
		4.6 (0.0)	4.6		4.2 (0.0)	4.2
			4.6			4.2
			4.6			4.2
jp01	5.7	5.7 (0.0)	5.7	4.3	4.2 (0.0)	4.2
			5.7			4.2
			5.7			4.2
		5.6 (0.1)	5.6		4.3 (0.0)	4.3
			5.7			4.3
			5.6			4.3
my01	4.1	4.1 (0.1)	4.0	3.7	3.7 (0.2)	3.6
			4.1			3.9
			4.1			3.7
		4.0 (0.1)	4.1		3.7 (0.1)	3.8
			4.0			3.7
			4.0			3.7
mn01	5.6	5.6 (0.0)	5.6	4.2	4.2 (0.0)	4.2
			5.6			4.2
			5.6			4.2
		5.6 (0.0)	5.6		4.2 (0.0)	4.2
			5.6			4.2
			5.6			4.2
ph01	5.2	5.1 (0.1)	5.1	4.0	4.0 (0.0)	4.0
			5.1			4.0
			5.2			4.0
		5.2 (0.1)	5.2		4.0 (0.0)	4.0
			5.1			4.0
			5.2			4.0
kr01	5.6	5.6 (0.0)	5.6	4.2	4.2 (0.1)	4.2
			5.6			4.2
			5.6			4.1
		5.6 (0.0)	5.6		4.1 (0.0)	4.1
			5.6			4.1
			5.6			4.1
ru01	5.4	5.4 (0.0)	5.4	4.1	4.1 (0.0)	4.1
			5.4			4.1
			5.4			4.1
		5.4 (0.0)	5.4		4.1 (0.0)	4.1
			5.4			4.1
			5.4			4.1
th01	5.5	5.5 (0.0)	5.5	4.2	4.2 (0.0)	4.2
			5.5			4.2
			5.5			4.2
		5.5 (0.0)	5.5		4.2 (0.0)	4.2
			5.5			4.2
			5.5			4.2
vn01	5.3	5.3 (0.0)	5.3	4.2	4.2 (0.0)	4.2
			5.3			4.2
			5.3			4.2
		5.3 (0.0)	5.3		4.2 (0.0)	4.2
			5.3			4.2
			5.3			4.2
vn02	5.0	5.0 (0.0)	5.0	4.6	4.5 (0.0)	4.5
			5.0			4.5
			5.0			4.5
		5.0 (0.0)	5.0		4.6 (0.1)	4.5
			5.0			4.6
			5.0			4.6
vn03	5.3	5.3 (0.0)	5.3	4.2	4.1 (0.0)	4.1
			5.3			4.1
			5.3			4.1
		5.3 (0.1)	5.2		4.2 (0.1)	4.2
			5.3			4.1
			5.3			4.2

Note: Value in parenthesis showed standard deviation of triplicate analyses

Appendix Table 4.2-2 Entire data of exchangeable base cations in Sample No.081

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	0.76	0.75 (0.01)	0.74	0.45	0.45 (0.01)	0.46	0.14	0.14 (0.00)	0.14	0.04	0.04 (0.00)	0.04
			0.74			0.44			0.14			0.04
			0.76			0.44			0.14			0.04
		0.77 (0.04)	0.75		0.45 (0.02)	0.44		0.14 (0.01)	0.14		0.04 (0.00)	0.04
			0.82			0.47			0.15			0.04
			0.74			0.45			0.14			0.04
cn02	0.87	0.87 (0.00)	0.87	0.46	0.46 (0.00)	0.46	0.16	0.16 (0.00)	0.16	0.05	0.05 (0.00)	0.05
			0.87			0.46			0.16			0.05
			0.87			0.46			0.16			0.05
		0.87 (0.01)	0.88		0.46 (0.01)	0.47		0.16 (0.00)	0.16		0.05 (0.01)	0.06
			0.87			0.46			0.16			0.05
			0.87			0.46			0.16			0.05
cn03	0.87	0.88 (0.06)	0.92	0.45	0.45 (0.01)	0.44	0.16	0.16 (0.01)	0.17	0.06	0.06 (0.02)	0.07
			0.91			0.46			0.16			0.04
			0.82			0.45			0.15			0.06
		0.85 (0.02)	0.85		0.45 (0.01)	0.44		0.16 (0.01)	0.16		0.05 (0.00)	0.05
			0.87			0.45			0.17			0.05
			0.84			0.45			0.16			0.05
cn04	0.02	0.02 (0.00)	0.02	0.50	0.49 (0.01)	0.49	0.12	0.12 (0.00)	0.12	0.04	0.04 (0.00)	0.04
			0.02			0.50			0.12			0.04
			0.02			0.49			0.12			0.04
		0.02 (0.00)	0.02		0.51 (0.01)	0.50		0.12 (0.00)	0.12		0.04 (0.00)	0.04
			0.02			0.51			0.12			0.04
			0.02			0.51			0.12			0.04
id01	1.65	1.64 (0.03)	1.67	0.62	0.62 (0.02)	0.63	0.14	0.14 (0.01)	0.14	0.08	0.08 (0.01)	0.09
			1.62			0.60			0.14			0.08
			1.64			0.62			0.15			0.08
		1.66 (0.02)	1.67		0.61 (0.01)	0.60		0.14 (0.00)	0.14		0.08 (0.00)	0.08
			1.67			0.61			0.14			0.08
			1.63			0.62			0.14			0.08
id02	1.38	1.39 (0.01)	1.38	0.61	0.61 (0.01)	0.62	0.20	0.20 (0.01)	0.20	0.11	0.11 (0.01)	0.11
			1.39			0.60			0.21			0.11
			1.40			0.60			0.20			0.12
		1.37 (0.01)	1.36		0.61 (0.01)	0.60		0.20 (0.01)	0.20		0.11 (0.01)	0.11
			1.36			0.62			0.21			0.12
			1.38			0.62			0.20			0.11
jp01	1.16	1.12 (0.08)	1.16	0.50	0.48 (0.04)	0.50	0.13	0.13 (0.01)	0.14	0.03	0.03 (0.01)	0.03
			1.17			0.51			0.14			0.03
			1.02			0.44			0.12			0.04
		1.20 (0.09)	1.20		0.52 (0.01)	0.51		0.13 (0.00)	0.13		0.03 (0.01)	0.03
			1.29			0.53			0.13			0.03
			1.12			0.51			0.13			0.04
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 Table 4.2-2 (continued)

mn01												
ph01	1.80	1.84 (0.10)	1.86	0.58	0.60 (0.02)	0.62	0.17	0.17 (0.01)	0.18	1.02	1.01 (0.03)	1.03
			1.73			0.61			0.18			1.02
			1.92			0.58			0.16			0.97
		1.76 (0.21)	1.99		0.56 (0.05)	0.51		0.17 (0.01)	0.17		1.02 (0.01)	1.02
			1.59			0.58			0.16			1.02
			1.71			0.60			0.18			1.01
kr01	1.10	1.17 (0.05)	1.23	0.48	0.50 (0.01)	0.50	0.15	0.14 (0.01)	0.15	0.05	0.05 (0.01)	0.06
			1.15			0.49			0.14			0.05
			1.14			0.50			0.14			0.05
		1.02 (0.03)	1.03		0.46 (0.02)	0.46		0.16 (0.01)	0.16		0.05 (0.00)	0.05
			0.98			0.44			0.16			0.05
			1.04			0.47			0.17			0.05
ru01	1.64	1.64 (0.01)	1.65	0.81	0.82 (0.04)	0.86	0.16	0.16 (0.01)	0.16	0.15	0.16 (0.00)	0.16
			1.63			0.83			0.16			0.16
			1.65			0.78			0.15			0.16
		1.63 (0.03)	1.66		0.79 (0.03)	0.82		0.16 (0.01)	0.16		0.14 (0.01)	0.14
			1.61			0.79			0.16			0.14
			1.62			0.77			0.15			0.15
th01	1.49	1.48 (0.03)	1.49	0.44	0.43 (0.02)	0.41	0.21	0.20 (0.01)	0.20	0.15	0.15 (0.02)	0.17
			1.44			0.43			0.19			0.13
			1.50			0.45			0.20			0.15
		1.49 (0.02)	1.47		0.45 (0.01)	0.46		0.21 (0.01)	0.21		0.14 (0.01)	0.15
			1.51			0.44			0.20			0.14
			1.50			0.45			0.21			0.14
vn01	1.58	1.57 (0.02)	1.57	0.52	0.52 (0.02)	0.53	0.15	0.15 (0.01)	0.15	0.08	0.08 (0.01)	0.09
			1.58			0.53			0.15			0.09
			1.55			0.50			0.14			0.07
		1.58 (0.02)	1.56		0.51 (0.01)	0.50		0.15 (0.01)	0.14		0.08 (0.01)	0.07
			1.59			0.51			0.15			0.08
			1.58			0.52			0.15			0.08
vn02												
vn03	0.28	0.28 (0.01)	0.27	0.37	0.37 (0.00)	0.37	0.23	0.23 (0.01)	0.23	0.09	0.09 (0.00)	0.09
			0.28			0.37			0.24			0.09
			0.28			0.37			0.23			0.09
		0.27 (0.01)	0.28		0.37 (0.02)	0.37		0.23 (0.01)	0.23		0.09 (0.01)	0.08
			0.28			0.36			0.23			0.08
			0.26			0.39			0.24			0.10

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

Appendix Table 4.2-3. Entire data of exchangeable acidity and acid cations in Sample No. 081

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+) kg^{-1}								
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	1.02	1.00 (0.04)	1.00	0.67	0.64 (0.02)	0.64	0.35	0.36 (0.02)	0.36
			0.97			0.63			0.34
			1.04			0.66			0.38
		1.03 (0.02)	1.02		0.70 (0.04)	0.66		0.34 (0.02)	0.36
			1.03			0.70			0.33
			1.05			0.73			0.32
cn02	1.36	1.36 (0.00)	1.36	1.27	1.27 (0.01)	1.26	0.09	0.09 (0.01)	0.10
			1.36			1.26			0.10
			1.36			1.28			0.08
		1.36 (0.00)	1.36		1.27 (0.01)	1.26		0.09 (0.01)	0.10
			1.36			1.26			0.10
			1.36			1.28			0.08
cn03	1.69	1.71 (0.07)	1.72	1.07	1.06 (0.04)	1.07	0.63	0.65 (0.10)	0.65
			1.77			1.02			0.75
			1.64			1.09			0.55
		1.67 (0.04)	1.64		1.07 (0.07)	0.99		0.61 (0.05)	0.65
			1.72			1.09			0.62
			1.66			1.12			0.55
cn04	1.45	1.43 (0.02)	1.44	0.63	0.61 (0.01)	0.61	0.83	0.82 (0.01)	0.83
			1.44			0.61			0.83
			1.41			0.60			0.81
		1.47 (0.01)	1.46		0.64 (0.01)	0.65		0.83 (0.02)	0.81
			1.48			0.63			0.85
			1.47			0.65			0.82
id01	1.14	1.15 (0.00)	1.15	0.94	0.95 (0.02)	0.92	0.20	0.20 (0.02)	0.23
			1.15			0.96			0.19
			1.15			0.96			0.19
		1.13 (0.03)	1.15		0.93 (0.02)	0.92		0.20 (0.05)	0.23
			1.15			0.92			0.23
			1.10			0.96			0.14
id02	0.89	0.90 (0.01)	0.89	0.70	0.70 (0.01)	0.71	0.20	0.20 (0.02)	0.18
			0.89			0.69			0.20
			0.91			0.71			0.21
		0.88 (0.01)	0.89		0.70 (0.02)	0.71		0.19 (0.01)	0.18
			0.87			0.67			0.20
			0.89			0.71			0.18
jp01	1.36	1.50 (0.16)	1.38	1.05	1.19 (0.03)	1.19	0.31	0.31 (0.17)	0.19
			1.68			1.16			0.51
			1.44			1.21			0.23
		1.22 (0.12)	1.35		0.91 (0.03)	0.91		0.31 (0.12)	0.44
			1.15			0.93			0.22
			1.15			0.88			0.27
my01	13.84	13.83 (0.31)	14.17	15.28	14.99 (0.31)	14.92	3.95	3.76 (6.52)	11.29
			13.56			14.72			0.00
			13.76			15.32			0.00
		13.84 (0.15)	13.81		15.56 (0.31)	15.83		4.14 (7.17)	12.42
			14.01			15.63			0.00
			13.71			15.22			0.00

Appendix Table 4.2-3 (continued)

mn01	2.04	2.02 (0.00)	2.02	1.62	1.62 (0.00)	1.62	0.40	0.40 (0.00)	0.40
			2.02			1.62			0.40
			2.02			1.62			0.40
		2.05 (0.06)	2.02		1.62 (0.00)	1.62		0.40 (0.00)	0.40
			2.02			1.62			0.40
			2.12			1.62			0.40
ph01	1.48	1.46 (0.03)	1.50	1.40	1.40 (0.01)	1.41	0.08	0.07 (0.03)	0.10
			1.44			1.39			0.05
			1.44			1.39			0.05
		1.49 (0.04)	1.53		1.40 (0.09)	1.49		0.08 (0.05)	0.04
			1.45			1.32			0.13
			1.48			1.40			0.08
kr01	1.31	1.34 (0.07)	1.30	1.29	1.24 (0.06)	1.31	0.11	0.12 (0.06)	0.19
			1.30			1.21			0.09
			1.42			1.21			0.09
		1.27 (0.03)	1.25		1.34 (0.05)	1.29		0.10 (0.05)	0.15
			1.26			1.37			0.07
			1.30			1.37			0.07
ru01	1.39	1.39 (0.09)	1.34	0.89	0.85 (0.12)	0.92	0.31	0.34 (0.24)	0.20
			1.50			0.92			0.20
			1.34			0.71			0.61
		1.39 (0.05)	1.42		0.92 (0.00)	0.92		0.27 (0.12)	0.41
			1.34			0.92			0.20
			1.42			0.92			0.20
th01	1.10	1.10 (0.05)	1.15	1.06	1.06 (0.04)	1.10	0.04	0.04 (0.01)	0.05
			1.06			1.02			0.04
			1.10			1.06			0.04
		1.10 (0.00)	1.10		1.06 (0.00)	1.06		0.04 (0.00)	0.04
			1.10			1.06			0.04
			1.10			1.06			0.04
vn01	1.42	1.41 (0.03)	1.43	0.81	0.81 (0.00)	0.81	0.61	0.61 (0.04)	0.63
			1.43			0.81			0.63
			1.37			0.81			0.56
		1.42 (0.04)	1.37		0.81 (0.00)	0.81		0.61 (0.04)	0.56
			1.44			0.81			0.63
			1.44			0.81			0.63
vn02	1.50	1.50 (0.03)	1.52	1.01	1.01 (0.00)	1.01	0.61	0.61 (0.00)	0.61
			1.47			1.01			0.61
			1.52			1.01			0.61
		1.50 (0.03)	1.52		1.01 (0.00)	1.01		0.61 (0.00)	0.61
			1.52			1.01			0.61
			1.47			1.01			0.61
vn03	2.23	2.13 (0.02)	2.12	1.79	1.60 (0.04)	1.62	0.79	0.83 (0.03)	0.81
			2.12			1.62			0.81
			2.16			1.55			0.87
		2.32 (0.03)	2.28		1.98 (0.03)	2		0.75 (0.04)	0.73
			2.34			1.94			0.8
			2.34			2			0.73

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

Appendix Table 4.3-1 Entire data of pH in Sample No. 082

Lab.	pH(H_2O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	4.3	4.3 (0.0)	4.3	3.6	3.6 (0.0)	3.6
			4.3			3.6
			4.3			3.6
		4.3 (0.0)	4.3		3.6 (0.0)	3.6
			4.3			3.6
			4.3			3.6
cn02	4.3	4.3 (0.0)	4.3	3.6	3.6 (0.0)	3.6
			4.3			3.6
			4.3			3.6
		4.3 (0.0)	4.3		3.6 (0.0)	3.6
			4.3			3.6
			4.3			3.6
cn03	4.2	4.2 (0.0)	4.2	3.5	3.5 (0.0)	3.5
			4.2			3.5
			4.2			3.5
		4.2 (0.0)	4.2		3.5 (0.0)	3.5
			4.2			3.5
			4.2			3.5
cn04	4.0	4.0 (0.0)	4.0	3.6	3.6 (0.0)	3.6
			4.0			3.6
			4.0			3.6
		4.0 (0.0)	4.0		3.6 (0.0)	3.6
			4.0			3.6
			4.0			3.6
id01	4.2	4.2 (0.0)	4.2	3.5	3.5 (0.0)	3.5
			4.2			3.5
			4.2			3.5
		4.2 (0.0)	4.2		3.5 (0.0)	3.5
			4.2			3.5
			4.2			3.5
id02	3.7	3.7 (0.0)	3.7	3.6	3.6 (0.0)	3.6
			3.7			3.6
			3.7			3.6
		3.7 (0.0)	3.7		3.6 (0.0)	3.6
			3.7			3.6
			3.7			3.6
jp01	4.5	4.4 (0.0)	4.4	3.6	3.6 (0.0)	3.6
			4.4			3.6
			4.4			3.6
		4.5 (0.0)	4.5		3.6 (0.0)	3.6
			4.5			3.6
			4.5			3.6
my01	5.3	5.2 (0.1)	5.2	4.8	4.8 (0.1)	4.9
			5.1			4.8
			5.2			4.8
		5.4 (0.1)	5.4		4.7 (0.2)	4.8
			5.3			4.5
			5.4			4.9
mn01	4.4	4.4 (0.1)	4.4	3.7	3.7 (0.0)	3.7
			4.4			3.7
			4.5			3.7
		4.4 (0.1)	4.5		3.7 (0.0)	3.7
			4.4			3.7
			4.4			3.7
ph01	4.1	4.0 (0.1)	4.1	3.4	3.4 (0.0)	3.4
			3.9			3.4
			4.0			3.4
		4.1 (0.0)	4.1		3.4 (0.0)	3.4
			4.1			3.4
			4.1			3.4
kr01	4.2	4.2 (0.0)	4.2	3.5	3.5 (0.0)	3.5
			4.2			3.5
			4.2			3.5
		4.2 (0.1)	4.3		3.5 (0.0)	3.5
			4.2			3.5
			4.2			3.5
ru01	4.1	4.1 (0.1)	4.1	3.5	3.5 (0.0)	3.5
			4.1			3.5
			4.2			3.5
		4.1 (0.0)	4.1		3.5 (0.0)	3.5
			4.1			3.5
			4.1			3.5
th01	4.2	4.2 (0.0)	4.2	3.6	3.6 (0.0)	3.6
			4.2			3.6
			4.2			3.6
		4.2 (0.0)	4.2		3.6 (0.0)	3.6
			4.2			3.6
			4.2			3.6
vn01	4.1	4.1 (0.0)	4.1	3.6	3.6 (0.0)	3.6
			4.1			3.6
			*1.1			3.6
		4.1 (0.0)	4.1		3.5 (0.1)	3.5
			4.1			3.5
			4.1			3.6
vn02	4.4	4.4 (0.1)	4.4	3.9	3.9 (0.0)	3.9
			4.5			3.9
			4.4			3.9
		4.4 (0.0)	4.4		3.9 (0.0)	3.9
			4.4			3.9
			4.4			3.9
vn03	4.1	4.1 (0.0)	4.1	3.5	3.5 (0.0)	3.5
			4.1			3.5
			4.1			3.5
		4.1 (0.0)	4.1		3.5 (0.0)	3.5
			4.1			3.5
			4.1			3.5

Note: Value in parenthesis showed standard deviation of triplicate analyses; An obvious typing mistake at vn01 was ommited for the average.

Appendix Table 4.3-2 Entire data of exchangeable base cations in Sample No. 082

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	0.06	0.06 (0.00)	0.06	0.28	0.28 (0.00)	0.28	0.20	0.20 (0.01)	0.21	0.05	0.05 (0.00)	0.05
			0.06			0.28			0.21			0.05
			0.06			0.28			0.19			0.05
		0.06 (0.01)	0.06		0.28 (0.01)	0.29		0.20 (0.01)	0.20		0.05 (0.01)	0.04
			0.05			0.27			0.19			0.05
			0.06			0.29			0.21			0.05
cn02	0.06	0.06 (0.00)	0.06	0.27	0.27 (0.00)	0.27	0.24	0.24 (0.01)	0.24	0.06	0.05 (0.00)	0.05
			0.06			0.27			0.24			0.05
			0.06			0.27			0.23			0.05
		0.06 (0.00)	0.06		0.27 (0.00)	0.27		0.24 (0.00)	0.24		0.06 (0.00)	0.06
			0.06			0.27			0.24			0.06
			0.06			0.27			0.24			0.06
cn03	0.05	0.05 (0.00)	0.05	0.25	0.24 (0.01)	0.24	0.28	0.28 (0.01)	0.29	0.05	0.04 (0.00)	0.04
			0.05			0.24			0.29			0.04
			0.05			0.23			0.27			0.04
		0.05 (0.01)	0.04		0.25 (0.01)	0.24		0.28 (0.01)	0.27		0.05 (0.00)	0.05
			0.05			0.26			0.29			0.05
			0.05			0.25			0.29			0.05
cn04	0.02	0.02 (0.00)	0.02	0.31	0.30 (0.00)	0.30	0.17	0.16 (0.00)	0.16	0.05	0.05 (0.00)	0.05
			0.02			0.30			0.16			0.05
			0.02			0.30			0.16			0.05
		0.02 (0.00)	0.02		0.32 (0.00)	0.32		0.18 (0.01)	0.17		0.05 (0.00)	0.05
			0.02			0.32			0.18			0.05
			0.02			0.32			0.18			0.05
id01	0.17	0.17 (0.01)	0.18	0.33	0.34 (0.01)	0.33	0.23	0.23 (0.00)	0.23	0.10	0.10 (0.01)	0.11
			0.16			0.34			0.23			0.10
			0.16			0.34			0.23			0.10
		0.16 (0.00)	0.16		0.32 (0.01)	0.32		0.22 (0.00)	0.22		0.10 (0.00)	0.10
			0.16			0.32			0.22			0.10
			0.16			0.31			0.22			0.10
id02	0.36	0.36 (0.01)	0.35	0.42	0.42 (0.02)	0.44	0.37	0.36 (0.01)	0.36	0.11	0.11 (0.01)	0.12
			0.37			0.40			0.36			0.11
			0.36			0.42			0.35			0.11
		0.36 (0.01)	0.35		0.41 (0.01)	0.42		0.37 (0.01)	0.36		0.11 (0.01)	0.11
			0.35			0.40			0.37			0.10
			0.37			0.42			0.37			0.12
jp01	0.09	0.08 (0.02)	0.06	0.32	0.31 (0.01)	0.31	0.29	0.28 (0.01)	0.29	0.04	0.03 (0.01)	0.03
			0.08			0.32			0.28			0.03
			0.09			0.31			0.28			0.04
		0.10 (0.01)	0.10		0.33 (0.01)	0.32		0.29 (0.01)	0.28		0.04 (0.01)	0.04
			0.10			0.33			0.29			0.05
			0.09			0.33			0.29			0.03
my01	0.01	0.02 (0.00)	0.02	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00	0.00	0.00 (0.00)	0.00
			0.02			0.00			0.00			0.00
			0.02			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 Table 4.3-2 (continued)

mn01												
ph01	0.19	0.19 (0.01)	0.18	0.16	0.15 (0.01)	0.14	0.16	0.16 (0.00)	0.16	1.13	1.13 (0.08)	1.06
			0.19			0.15			0.16			1.21
			0.19			0.16			0.16			1.12
		0.18 (0.02)	0.16		0.16 (0.01)	0.16		0.16 (0.00)	0.16		1.12 (0.07)	1.05
			0.20			0.17			0.16			1.13
			0.19			0.15			0.16			1.18
kr01	0.06	0.06 (0.01)	0.06	0.29	0.28 (0.01)	0.28	0.28	0.27 (0.01)	0.26	0.06	0.06 (0.01)	0.06
			0.07			0.29			0.28			0.07
			0.06			0.28			0.27			0.06
		0.06 (0.01)	0.06		0.30 (0.01)	0.30		0.28 (0.01)	0.29		0.06 (0.00)	0.06
			0.06			0.30			0.27			0.06
			0.05			0.31			0.29			0.06
ru01	0.35	0.36 (0.00)	0.36	0.45	0.45 (0.03)	0.45	0.28	0.29 (0.01)	0.29	0.11	0.11 (0.01)	0.12
			0.36			0.48			0.28			0.11
			0.36			0.42			0.29			0.11
		0.34 (0.05)	0.36		0.44 (0.03)	0.46		0.26 (0.03)	0.28		0.10 (0.02)	0.11
			0.37			0.46			0.28			0.11
			0.28			0.41			0.23			0.08
th01	0.29	0.28 (0.01)	0.29	0.28	0.28 (0.01)	0.28	0.43	0.42 (0.02)	0.43	0.21	0.21 (0.01)	0.22
			0.28			0.28			0.43			0.20
			0.28			0.29			0.40			0.20
		0.30 (0.02)	0.28		0.27 (0.01)	0.27		0.44 (0.02)	0.42		0.21 (0.01)	0.21
			0.29			0.27			0.44			0.22
			0.32			0.28			0.45			0.20
vn01	0.39	0.40 (0.00)	0.40	0.29	0.29 (0.01)	0.29	0.27	0.28 (0.01)	0.28	0.10	0.10 (0.00)	0.10
			0.40			0.30			0.27			0.10
			0.40			0.29			0.28			0.10
		0.38 (0.01)	0.38		0.29 (0.01)	0.29		0.26 (0.01)	0.26		0.10 (0.00)	0.10
			0.39			0.29			0.25			0.10
			0.38			0.30			0.26			0.10
vn02												
vn03	0.67	0.65 (0.03)	0.66	0.50	0.50 (0.01)	0.51	0.15	0.15 (0.00)	0.15	0.07	0.07 (0.01)	0.07
			0.62			0.50			0.15			0.06
			0.68			0.50			0.15			0.08
		0.69 (0.01)	0.69		0.49 (0.02)	0.50		0.15 (0.01)	0.16		0.06 (0.00)	0.06
			0.68			0.51			0.15			0.06
			0.70			0.47			0.15			0.06

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

Appendix Table 4.3-3 Entire data of exchangeable acidity and acid cations in Sample No. 082

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+) kg^{-1}								
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	8.86	8.90 (0.06)	8.88	7.88	7.93 (0.03)	7.95	0.98	0.97 (0.05)	0.92
			8.85			7.89			0.97
			8.97			7.95			1.02
		8.82 (0.07)	8.76		7.83 (0.08)	7.75		0.99 (0.02)	1.01
			8.81			7.82			0.98
			8.89			7.91			0.98
cn02	10.78	10.82 (0.13)	10.90	9.97	9.98 (0.12)	10.10	0.83	0.85 (0.08)	0.80
			10.90			9.96			0.94
			10.67			9.87			0.80
		10.74 (0.19)	10.85		9.95 (0.17)	10.05		0.80 (0.00)	0.80
			10.52			9.75			0.80
			10.85			10.05			0.80
cn03	11.13	11.13 (0.06)	11.07	8.84	8.82 (0.15)	8.86	2.30	2.32 (0.18)	2.21
			11.15			8.94			2.22
			11.18			8.65			2.53
		11.13 (0.04)	11.10		8.86 (0.07)	8.78		2.28 (0.04)	2.32
			11.12			8.88			2.24
			11.18			8.91			2.27
cn04	9.76	9.70 (0.01)	9.70	8.21	8.10 (0.01)	8.09	1.55	1.61 (0.01)	1.62
			9.70			8.10			1.61
			9.71			8.10			1.61
		9.81 (0.01)	9.80		8.32 (0.01)	8.32		1.49 (0.01)	1.48
			9.80			8.32			1.48
			9.82			8.33			1.50
id01	8.92	8.98 (0.00)	8.98	7.43	7.50 (0.00)	7.50	1.49	1.48 (0.00)	1.48
			8.98			7.50			1.48
			8.98			7.50			1.48
		8.85 (0.06)	8.88		7.36 (0.05)	7.33		1.49 (0.11)	1.55
			8.88			7.33			1.55
			8.78			7.42			1.36
id02	8.03	8.02 (0.01)	8.03	6.80	6.80 (0.02)	6.83	1.23	1.22 (0.02)	1.20
			8.01			6.79			1.22
			8.03			6.79			1.24
		8.03 (0.03)	8.06		6.79 (0.00)	6.79		1.24 (0.02)	1.26
			8.01			6.79			1.22
			8.03			6.79			1.24
jp01	9.69	9.90 (0.10)	9.99	8.47	8.71 (0.31)	8.97	1.22	1.19 (0.31)	1.02
			9.79			8.79			1.00
			9.91			8.37			1.54
		9.47 (0.24)	9.51		8.23 (0.11)	8.11		1.25 (0.31)	1.40
			9.69			8.24			1.45
			9.22			8.33			0.89
my01	5.18	5.36 (0.22)	5.43	6.23	6.50 (0.33)	6.86	0.00	0.00 (0.00)	0.00
			5.11			6.22			0.00
			5.54			6.43			0.00
		5.00 (0.18)	5.11		5.96 (0.22)	5.75		0.00 (0.00)	0.00
			4.79			6.18			0.00
			5.11			5.96			0.00

Appendix Table 4.3-3 (continued)

mn01	13.29	13.29 (0.00)	13.29	10.30	10.30 (0.00)	10.30	2.88	2.88 (0.00)	2.88
			13.29			10.30			2.88
			13.29			10.30			2.88
		13.29 (0.00)	13.29		10.30 (0.00)	10.30		2.88 (0.00)	2.88
			13.29			10.30			2.88
			13.29			10.30			2.88
ph01	9.58	9.57 (0.08)	9.65	8.88	8.83 (0.06)	8.89	0.70	0.75 (0.04)	0.75
			9.50			8.79			0.71
			9.57			8.80			0.78
		9.59 (0.08)	9.60		8.93 (0.08)	8.91		0.65 (0.03)	0.69
			9.50			8.87			0.63
			9.66			9.02			0.64
kr01	8.71	8.63 (0.11)	8.75	8.06	8.14 (0.11)	8.24	1.05	1.13 (0.11)	1.13
			8.59			8.03			1.03
			8.55			8.14			1.24
		8.78 (0.04)	8.74		7.97 (0.13)	7.83		0.97 (0.05)	0.92
			8.81			7.99			1.00
			8.79			8.08			1.00
ru01	8.70	8.71 (0.05)	8.74	6.66	6.73 (0.00)	6.73	1.63	1.59 (0.12)	1.66
			8.65			6.73			1.45
			8.74			6.73			1.66
		8.68 (0.05)	8.65		6.59 (0.12)	6.52		1.66 (0.00)	1.66
			8.65			6.52			1.66
			8.74			6.73			1.66
th01	8.99	8.99 (0.06)	8.95	8.16	8.16 (0.03)	8.14	0.83	0.83 (0.03)	0.81
			9.06			8.19			0.87
			8.97			8.16			0.82
		8.98 (0.06)	8.93		8.16 (0.05)	8.16		0.82 (0.05)	0.77
			8.98			8.12			0.86
			9.04			8.21			0.83
vn01	9.80	9.88 (0.08)	9.93	8.25	8.24 (0.01)	8.23	1.52	1.57 (0.03)	1.59
			9.93			8.23			1.59
			9.79			8.25			1.54
		9.72 (0.06)	9.79		8.26 (0.01)	8.25		1.46 (0.07)	1.54
			9.69			8.26			1.42
			9.69			8.26			1.42
vn02	9.68	9.68 (0.03)	9.71	8.54	8.54 (0.06)	8.57	1.17	1.17 (0.06)	1.14
			9.66			8.47			1.24
			9.66			8.57			1.14
		9.67 (0.03)	9.65		8.53 (0.06)	8.57		1.17 (0.06)	1.14
			9.7			8.57			1.14
			9.65			8.46			1.24
vn03	14.13	14.17 (0.12)	14.1	11.70	11.77 (0.00)	11.77	2.67	2.66 (0.09)	2.77
			14.3			11.77			2.61
			14.1			11.77			2.61
		14.09 (0.02)	14.1		11.63 (0.00)	11.63		2.67 (0.00)	2.67
			14.06			11.63			2.67
			14.1			11.63			2.67

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

5. 9th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

In the 9th 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 October 2008. All the participating laboratories submitted their analytical data to NC. The measurement 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 22 laboratories on October 15 in 2008, and all laboratories submitted their analytical data to NC by February 28 in 2009. 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 Indonesia (Lab.ID id03), Malaysia (Lab. ID my02) and Lao PDR(Lab. ID la01) participated for the first time in this inter-laboratory comparison project on inland aquatic environment. The laboratory id03 and la01 submitted all the parameters and the laboratory my02 submitted the data of 3 parameters, pH, EC and Alkalinity. And the laboratory vn03 submitted the all data except NO_3^-.

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 are required to apply the analytical methods and data checking procedures that are 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) $= 10^{(6-pH)} + C(NH_4^+) + C(Na^+) + C(K^+)$
$+ C(Ca^{2+}) + C(Mg^{2+})$

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

(3) Calculation of ion balance (R_1)

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

(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;

$$\Lambda\text{calc (mS/m)} = \{349.7 \times 10^{(3\text{-pH})} + 80.0 \times C (SO_4^{2-}) + 71.5 \times C (NO_3^-) + 76.3 \times C (Cl^-) + 73.5 \times C (NH_4^+) + 50.1 \times C (Na^+) + 73.5 \times C (K^+) + 59.8 \times C (Ca^{2+}) + 53.3 \times C (Mg^{2+}) + 44.5 \times (ALK)\}/10000$$

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;

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

(3) R_2, which is calculated using the above equation, is compared with standard values in Table 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 APPENDIX5-2 and APPENDIX5-3. 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. is not included for the calculation in Table 5.7. 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

(Reported data after outliers were removed)

Constituents		Prepared	Average	S.D.	N	Min.	Max.
pH		7.41	7.29	0.14	21	7.01	7.62
EC	(mS/m)	6.57	6.27	0.16	18	5.95	6.68
Alkalinity	(meq/L)	0.238	0.245	0.027	20	0.216	0.319
SO_4^{2-}	(mg/L)	6.72	6.45	0.60	21	5.15	7.75
NO_3^-	(mg/L)	0.82	0.80	0.08	19	0.68	0.99
Cl^-	(mg/L)	5.80	5.59	0.57	20	4.53	6.77
Na^+	(mg/L)	5.78	5.63	0.45	18	4.41	6.67
K^+	(mg/L)	1.21	1.18	0.18	17	0.76	1.45
Ca^{2+}	(mg/L)	2.48	2.56	0.46	21	1.33	3.36
Mg^{2+}	(mg/L)	1.59	1.53	0.20	21	1.05	1.98
NH_4^+	(mg/L)	0.29	0.29	0.07	21	0.17	0.46

(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	3	2	4	2	4	3	2	2	3	4	29	12.4%
X	0	0	3	0	1	1	2	4	4	1	6	22	9.4%
Data within DQOs	22	19	17	17	17	16	16	15	15	17	11	182	78.1%
Flagged(%)	0.0	13.6	22.7	19.0	15.0	23.8	23.8	28.6	28.6	19.0	47.6	21.9	

*E : Value exceeded the DQO by 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%)

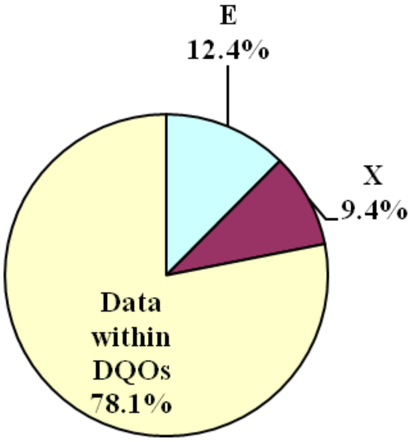


Figure 5.1 Percentage of flagged data

The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 12.4% of all reported data of samples. And the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 9.4% of all reported data of samples. And the percentage of flagged cations was larger than that of anions. Especially the percentage of flagged K^+, Ca^{2+} and NH_4^+ exceeded more than 25%.

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	Share
0	5	23%
1	8	36%
2	1	5%
3	2	9%
4	2	9%
5	1	5%
6	1	5%
7	1	5%
8	0	0%
9	1	5%
Total	22	100%

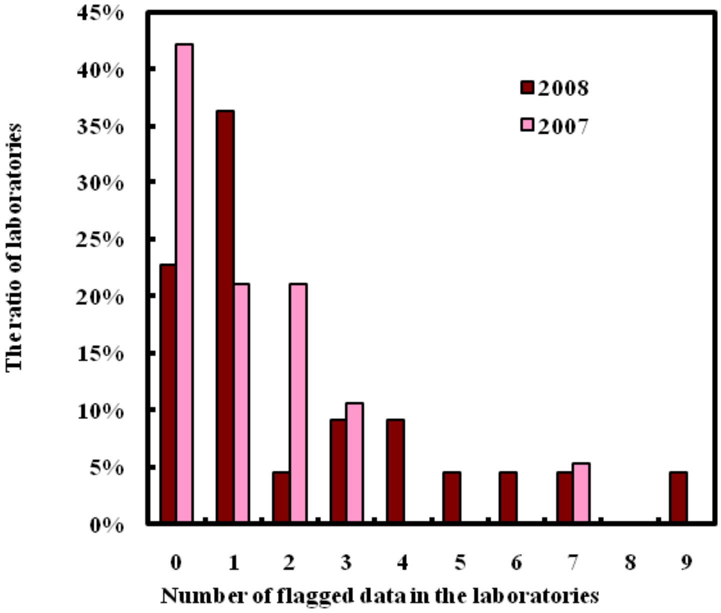


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 42% in last attempt (2007), but that of this year was 23%. There was a laboratory that has nine flagged data in this attempt.

Table 5.10 Analytical Results of Sample No.081 (artificial inland aquatic environment sample : EANET in 2008)

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)	R1 -	R2 -
cn01	7.27	6.20	0.22	6.93	0.82	5.83	5.66	1.20	2.65	1.64	E 0.34	1.62	3.16
cn02	7.27	6.18	0.22	6.47	0.88	5.71	5.74	1.22	E 3.03	1.47	0.32	3.52	2.96
cn03	7.27	6.16	0.23	6.67	0.89	5.71	5.65	1.17	2.75	1.63	0.29	1.79	3.20
cn04	7.27	6.51	0.24	6.70	0.82	5.74	5.65	1.16	2.75	1.69	0.28	1.39	0.89
id01	7.30	6.28	0.27	6.08	E 0.68	5.01	5.23	1.10	2.30	1.39	0.26	-4.65	-1.32
id02	7.10	6.40	X 0.32	E 5.70	0.78	5.05	X 9.30	E 1.45	2.50	X 1.05	0.26	5.89	5.59
id03	7.80	6.68	E 0.28	E 5.15	X 0.30	E 6.77	E 6.76	X 0.34	X 1.69	E 1.14	E 0.23	I -8.27	-3.54
jp01	7.30	6.30	0.24	6.66	0.79	5.71	5.74	1.19	2.49	1.57	0.31	-0.25	1.84
jp02	7.47	6.10	0.25	6.64	0.71	5.44	5.83	1.18	X 1.33	E 1.98	X 0.19	-2.39	1.53
la01	7.62	E 5.39	X 2.59	E 5.35	0.72	E 4.53	X 23.42	1.24	2.73	1.67	E 0.34	I -35.80	C 58.36
mn01	7.28	6.19	0.23	6.38	0.76	6.15	5.83	1.20	2.54	1.60	X 0.39	1.41	3.31
my01	7.36	6.35	0.25	6.53	0.78	5.58	5.73	1.18	2.45	1.66	0.29	0.30	1.30
my02	7.36	E 8.34	0.25										
ph01	7.25	6.29	0.23	E 7.75	0.84	E 6.77	6.00	E 1.40	E 2.97	1.57	0.31	-0.50	6.36
ph02	7.34	6.33	X 0.41	6.25	E 0.99	5.43	E 6.67	X 3.20	X 3.36	E 1.32	X 0.42	-2.73	C 11.39
ru01	7.08	6.31	0.22	6.84	0.94	6.01	5.53	1.22	2.31	1.61	X 0.46	-0.38	1.86
ru02	7.10	6.35	0.22	6.45	0.85	5.72	5.50	1.20	2.30	1.55	0.32	-0.22	-0.25
th01	7.34	6.21	0.22	6.62	0.77	5.64	5.76	1.25	2.62	1.61	E 0.22	3.06	1.82
th02	7.34	6.12	0.27	6.30	0.75	4.95	5.73	1.19	2.81	1.42	X 0.19	-0.06	2.18
vn01	7.38	6.24	0.24	6.80	0.80	E 4.89	E 4.41	X 0.76	2.59	1.50	0.30	-5.10	-1.94
vn02	7.37	5.95	0.22	5.83	0.70	5.23	5.05	X 0.76	2.35	1.54	X 0.17	-0.86	-0.90
vn03	7.01	E 8.36	E 0.28	7.32		X 3.40	5.66	1.33	X 3.23	1.45	0.29		
Expected value	7.41	6.57	0.24	6.72	0.82	5.80	5.78	1.21	2.48	1.59	0.29	-	-

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

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

I:Poor ion balance (R1)

C:Rich Conductivity agreement (R2)

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.

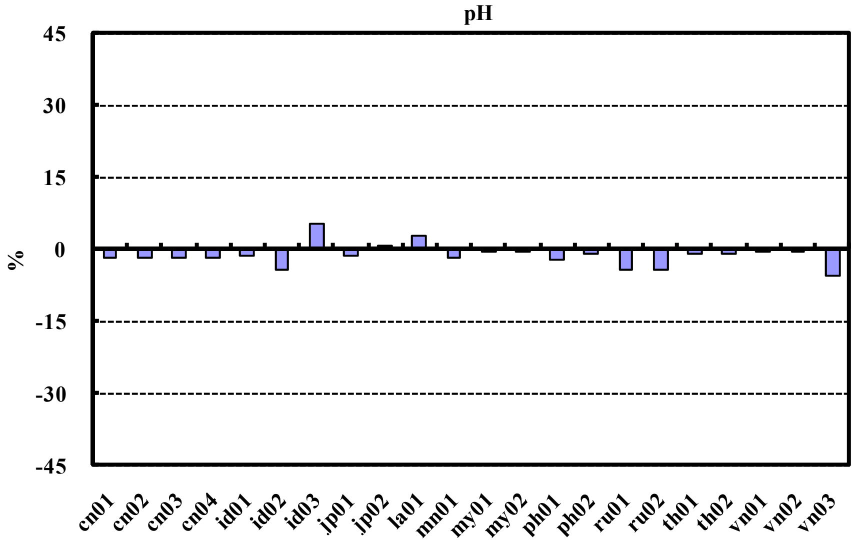


Figure 5.3 Distribution of results for pH (normalized by prepared value)

All obtained data of pH were within DQOs.

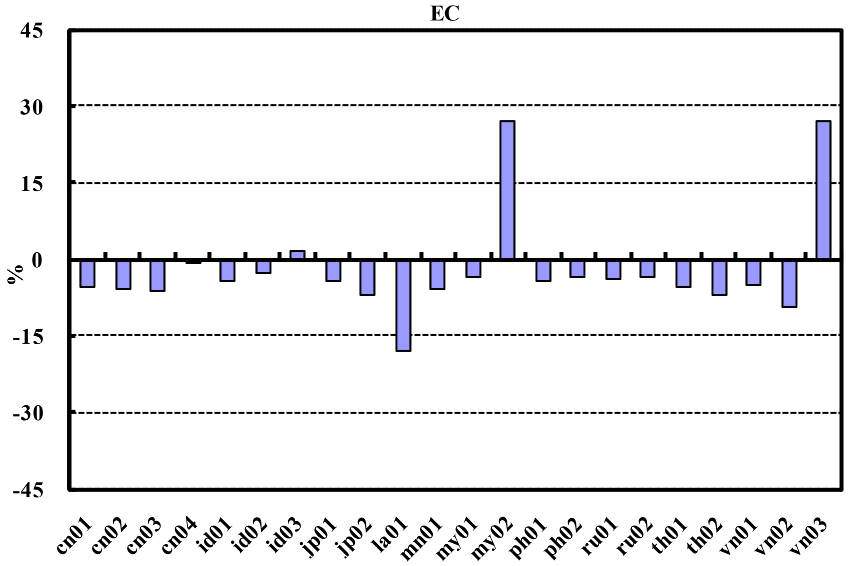


Figure 5.4 Distribution of results for EC (normalized by prepared value)

Three data were flagged. All the rest data of EC were within DQOs.

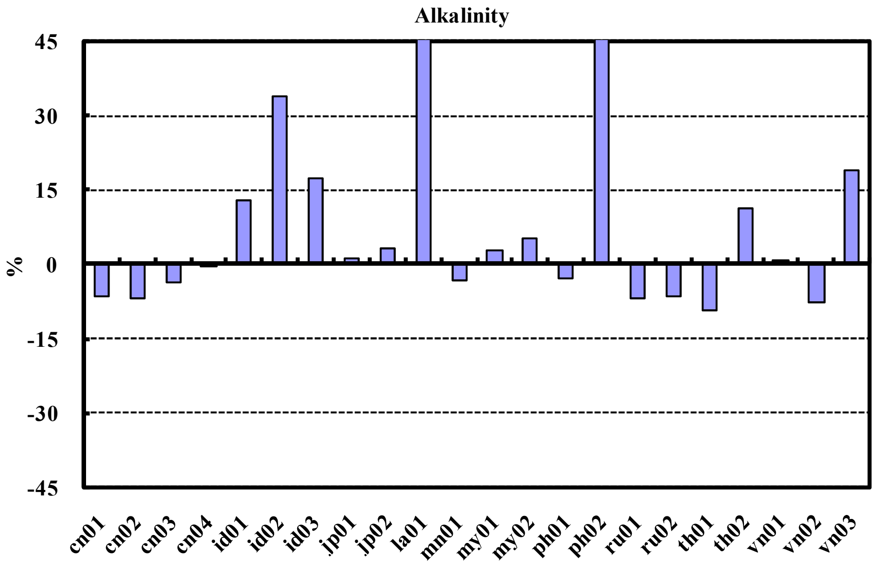


Figure 5.5 Distribution of results for Alkalinity (normalized by prepared concentration)

Five data were flagged. And there were some data near the flag.

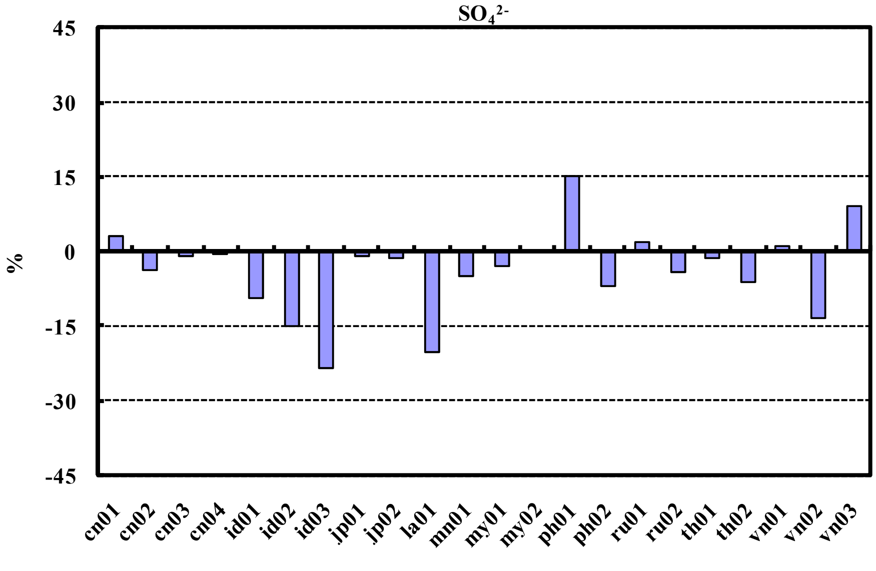


Figure 5.6 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

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

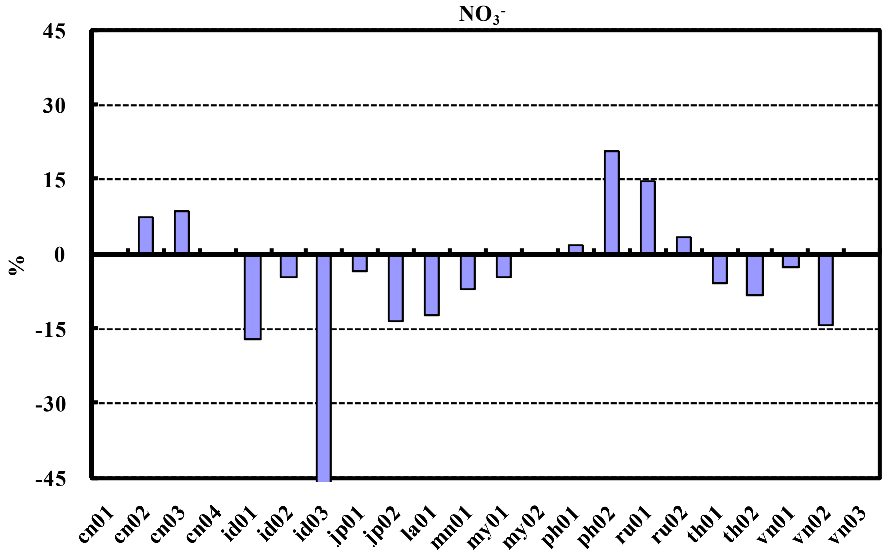


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

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

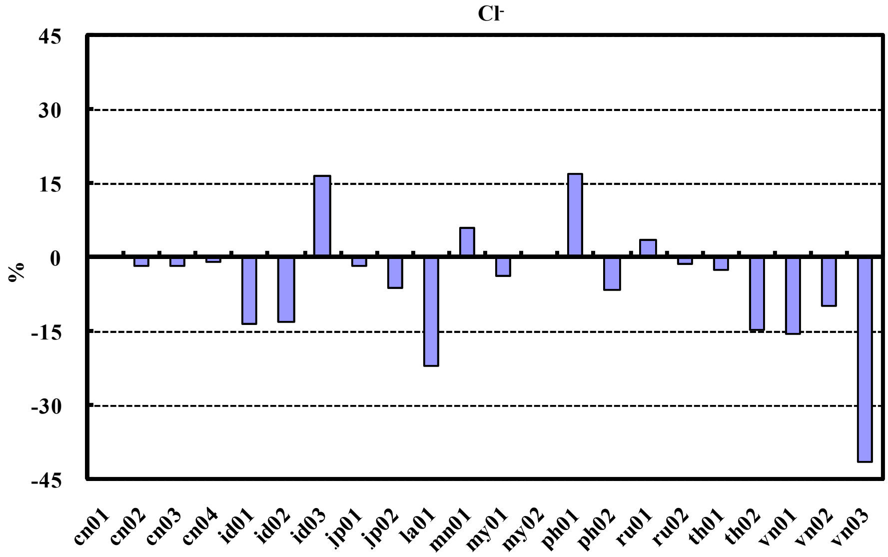


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

Most of participating laboratories used ion chromatography for the determination of Cl^- and four laboratories used titration method. Data from five laboratories were flagged. Three of the samples which had flagged data were analyzed by ion chromatography method, and the other two were analyzed by titration method.

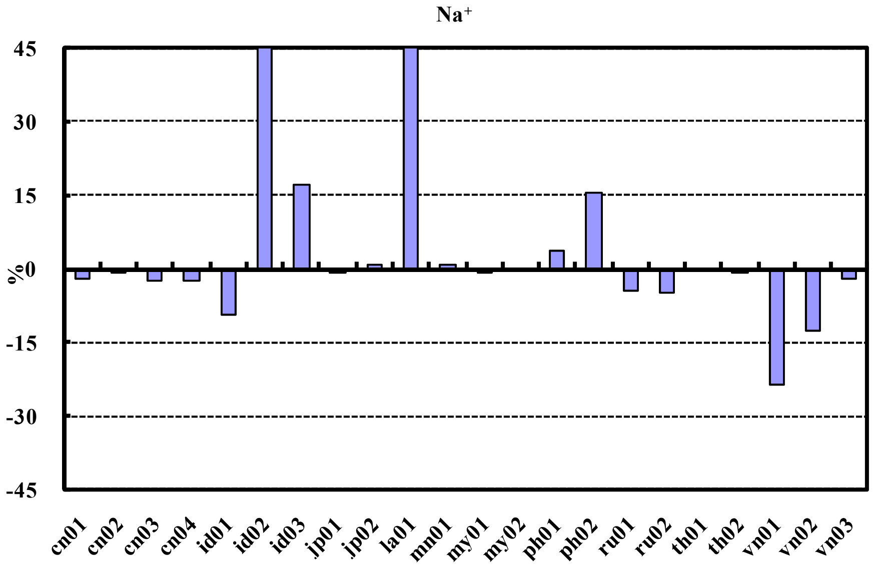


Figure 5.9 Distribution of results for Na^+ (normalized by prepared concentration)

Most of participating laboratories used ion chromatography, while six laboratories used atomic absorption/flame (emission) photometry for the determination of Na^+. Data from five 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 three data were obtained from the use of atomic absorption/flame (emission) photometry method.

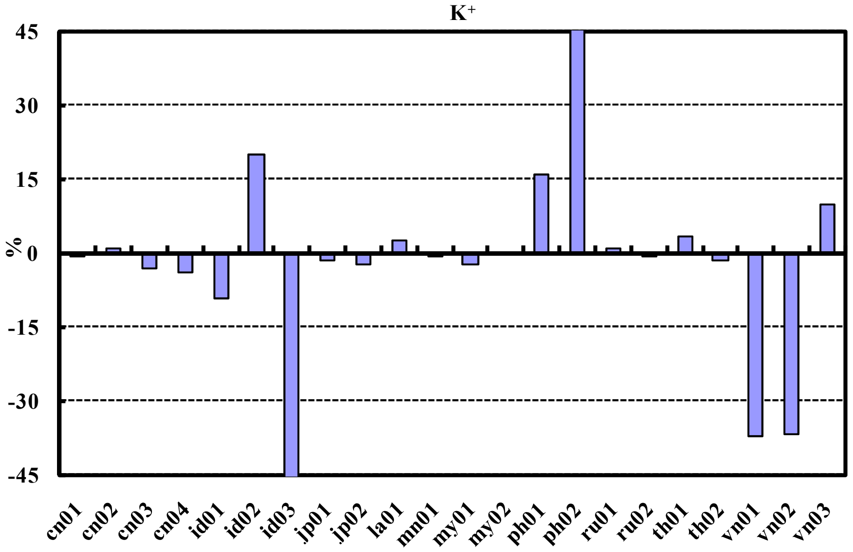


Figure 5.10 Distribution of results for K^+ (normalized by prepared concentration)

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

Data from six laboratories were flagged. Especially four data were significantly deviated from prepared value. Three flagged data were obtained from the use of ion chromatography method, and three data were obtained from the use of atomic absorption/flame (emission) photometry method.

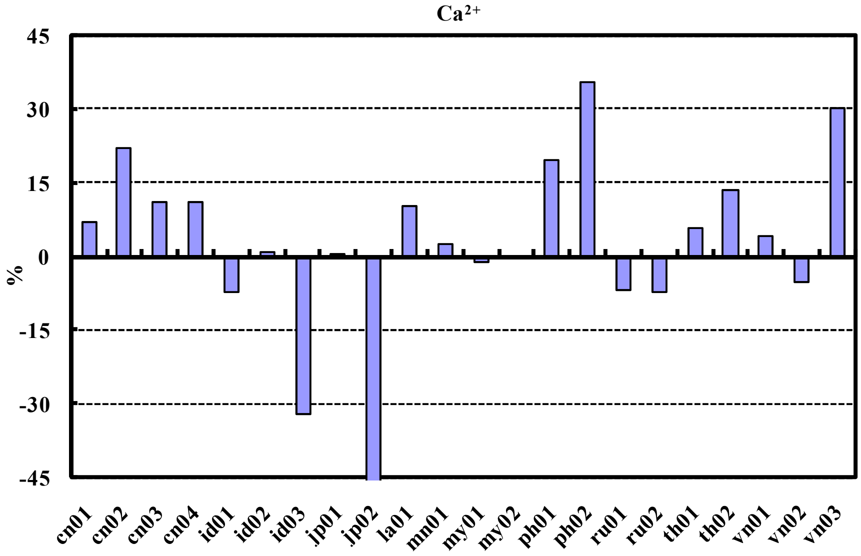


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Most of participating laboratories used ion chromatography, 5 laboratories used atomic absorption/flame (emission) photometry and 1 laboratory used titration (other method) for the determination of Ca^{2+}. Data from six laboratories were flagged. Three flagged data were obtained from the use of ion chromatography method, and three data were obtained from the use of atomic absorption/flame (emission) photometry method

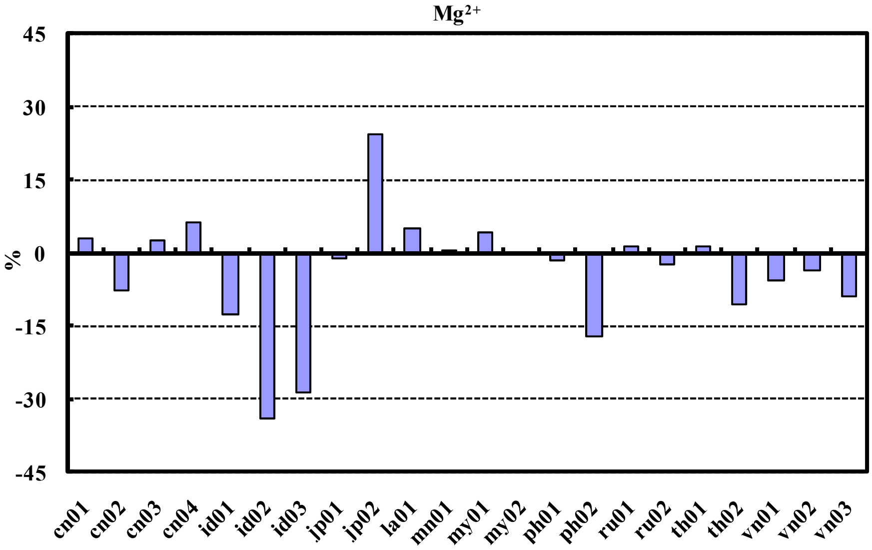


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Most of participating laboratories used ion chromatography, 5 laboratories used atomic absorption/flame (emission) photometry and 1 laboratory used titration (other method) for the determination of Mg^{2+}. Data from 4 laboratories were flagged. One flagged data were obtained from the use of ion chromatography method, two data were obtained from the use of atomic absorption/flame (emission) photometry and one data was obtained from the use of titration.

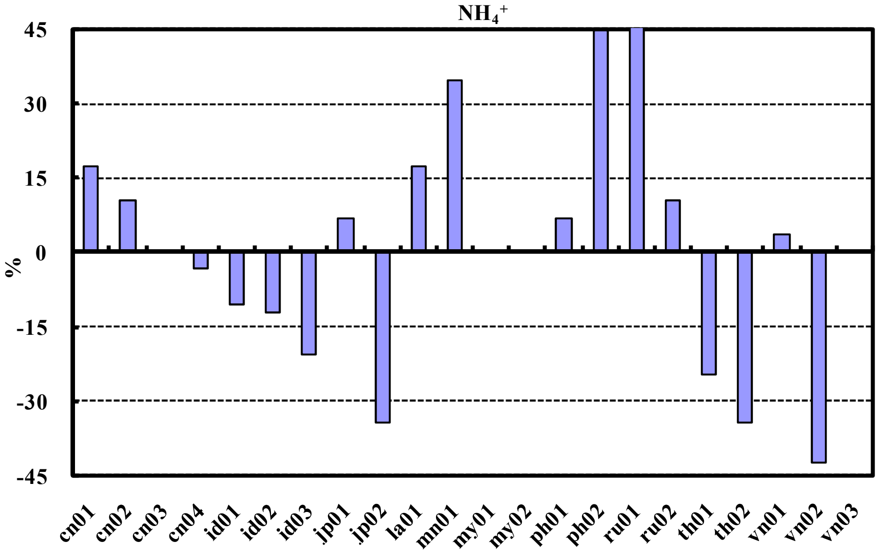


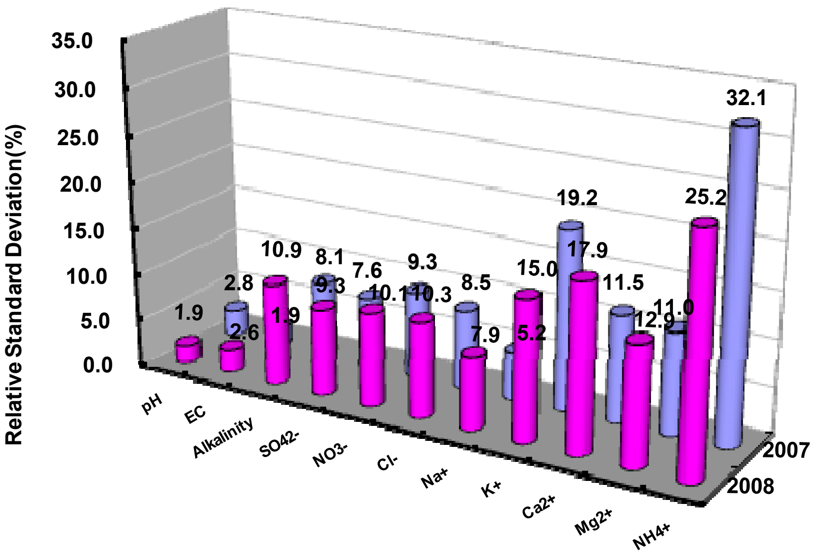
Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Among 20 participating laboratories, 13 laboratories used ion chromatography, 5 laboratories used spectrophotometer (Indophenol) and 2 laboratories used spectrophotometer (other method) for the determination of NH_4^+. Data from 10 laboratories were flagged. Especially six data were significantly deviated from prepared value. Six flagged data were obtained by ion chromatography method, three data were obtained by indophenol method, and 1 data was obtained by spectrophotometry except indophenol method.

NH_4^+ was the parameter that has the highest flagged percentage in this attempt. It had also the highest flagged percentage in the attempt in 2003-2009. It may be necessary to pay more attention to the accuracy of NH_4^+ analyze in the inland water sample in each laboratories.

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 (2007).



(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 deviations of most cations results from laboratories were larger than other parameters. Those of last attempt were also larger than other parameters. It may be necessary to pay more attention to the variation among the laboratories of cations analyze in the inland water than other analytical parameters.

5.3.4 Information on laboratories

Methodologies used

The percentages 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.

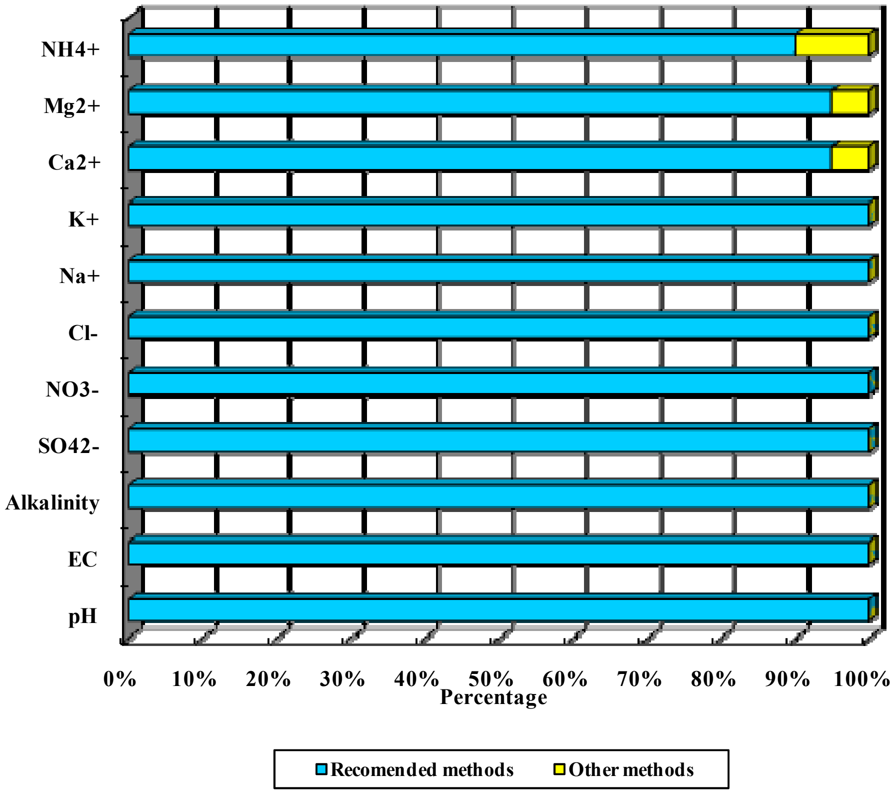


Figure 5.15 Percentage of laboratories using the recommended methods

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	22										
1		22(3)									
2			22(5)			4(2)			1	1(1)	
3							6(3)	6(3)	5(3)	5(2)	
4				17(2)	16(2)	17(3)	15(2)	15(3)	15(3)	15(1)	14(6)
5											
6											
7				4(2)	4(1)						2(1)
8											5(3)
9											
10											
11											
Flagged E	0	3	2	4	2	4	3	2	2	3	4
Flagged X	0	0	3	0	1	1	2	4	4	1	6

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 Ca^{2+}, Mg^{2+} and NH_4^+. Two laboratories used spectrophotometer instead of indophenol blue for NH_4^+ analysis, and one of them was flagged. One laboratory used titration method for Ca^{2+}, Mg^{2+} and its Mg^{2+} data was flagged.

The percentages of flagged cations were larger than those of anions. For the determination of cations, most of participating laboratories used ion chromatography, and some of them used atomic absorption/flame (emission) photometry. There is a tendency the laboratories without ion chromatography have many flagged data more than laboratories with IC.

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	2	A	A	B	A	A	A	A	A	A	A	A
id02	6	A	A	A	B	C	A	D	E	B	B	F
id03	5	A	A	A	B	C	D	E	E	E	E	D
jp01	1	A	A	A	A	A	A	A	A	A	A	A
jp02	3	A	A	B	B	C	B	B	B	B	B	C
la01	1	A	A	A	A	A	A	A	A	A	A	A
mn01	2	A	A	B	A	A	A	A	A	A	A	A
my01	3	A	A	A	B	B	B	C	C	C	C	C
my02	1	A	A	A								
ph01	3	A	A	A	B	B	B	C	C	C	C	C
ph02	3	A	A	B	C	C	C	B	B	B	B	A
ru01	5	A	B	A	C	C	C	D	D	D	D	E
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	2	A	A	A	B	B	B	B	B	B	B	B
vn01	2	A	A	A	B	B	B	B	B	B	B	B
vn02	2	A	A	A	B	B	B	B	B	B	B	B
vn03	3	A	B	B	B		B	A	A	C	C	B

"-" : No information, "A", "B", "C", "D" ,"E" and "F" 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 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	17	17	17	17	17	17	17	17	17	17	17
cn02	18	18	3	2	2	2	2	2	2	2	2
cn03	13	13	13	13	13	13	13	13	13	13	13
cn04	23	23	23	23	23	23	23	23	23	23	23
id01	11	11	11	6	11	11	11	11	11	11	11
id02	27	27	27	32	32	27	5	26	32	32	5
id03	12	12	12	4	19	26	9	9	9	9	26
jp01	1	1	1	1	1	1	1	1	1	1	1
jp02	24	24	12	12	3	12	12	12	12	12	3
la01	3	3	3	3	3	3	3	3	3	3	3
mn01	14	14	10	14	14	14	14	14	14	14	14
my01	2	2	2	6	6	6	5	5	5	5	5
my02	2	2	2								
ph01	1	1	1	1	1	1	20	20	20	20	20
ph02	17	17	4	17	17	17	4	4	4	4	17
ru01	6	15	6	13	13	13	23	23	23	23	15
ru02	48	48	48	14	14	48	17	17	17	17	14
th01	11	6	11	6	6	6	11	11	11	11	11
th02	4	4	4	11	11	11	11	11	11	11	11
vn01	6	6	6	16	16	16	16	16	16	16	16
vn02	4	4	4	11	11	11	11	11	11	11	11
vn03	5	3	3	3		3	5	5	2	2	3

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 9 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.

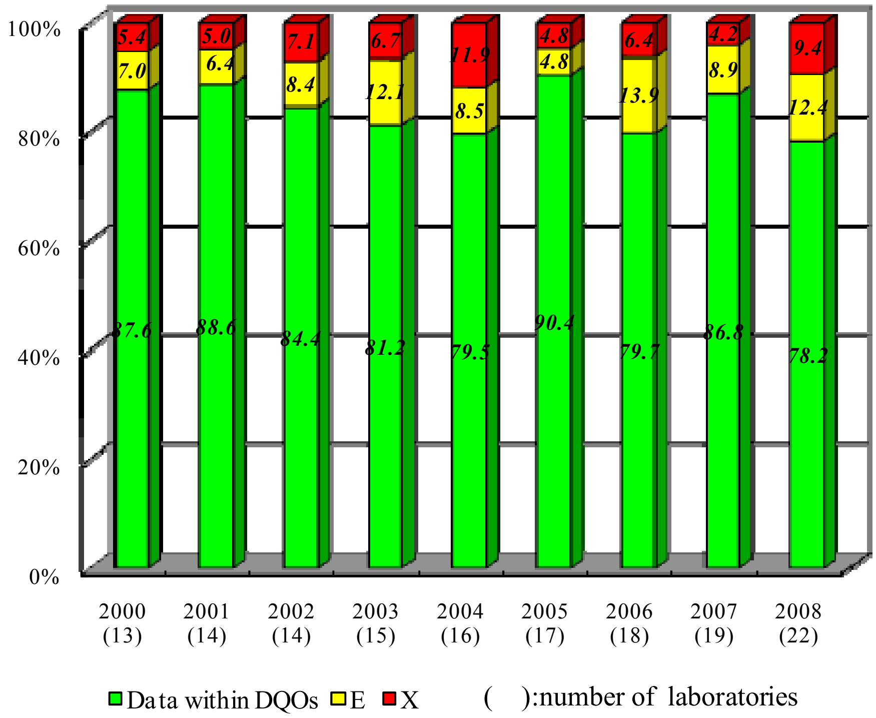


Figure 5. 16 Comparison of the results from the inter-laboratory comparison projects

The graph shows the number of laboratories increase and data within DQOs decrease.

The comparison for each parameter from 1st to 9th project with the percentage of flagged data is shown in Figure 5.17.

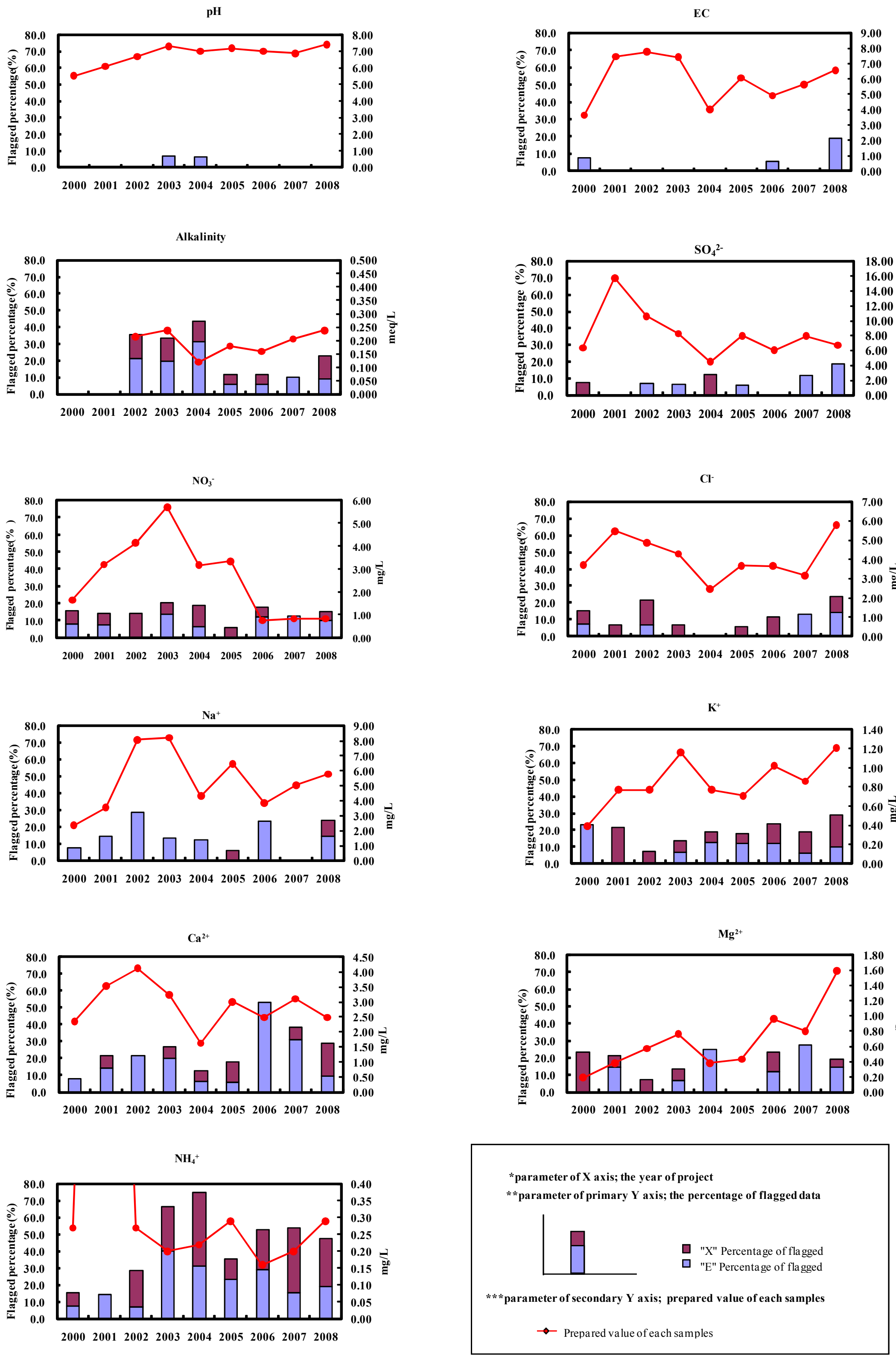


Figure 5.17 Comparison of the percentage of flagged data for each parameter in inter-laboratory comparison projects

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

The percentages of flagged cations were larger than those of anions in this project. Especially the percentages of flagged K^+, Ca^{2+} and NH_4^+ were more than 25%. 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 - 9th project was relatively high. It was not clear why the number of flagged data for Ca^{2+} increased. In this project the percentage flagged K^+ was also relatively high with of unknown origin. But it seems that there is necessity to pay attention to the analysis of K^+, Ca^{2+} and NH_4^+ in inland aquatic 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 aquatic 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.

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9) Network Center for EANET. Report of the Inter-laboratory Comparison Project 2006

10) Network Center for EANET. Report of the Inter-laboratory Comparison Project 2007

Appendix 5.1 Participating laboratories

CHINA	
1) Zhuhai Environmental Monitoring Station	(cn01)
2) Xiamen Environmental Monitoring Central Station	(cn02)
3) Xi'an Environmental Monitoring Station	(cn03)
4) Chongqing Institute of Environmental Science	(cn04)
INDONESIA	
5) Environmental Management Center (EMC)	(id01)
6)Research Center for Water Resources(RCWR), Agency for Research and Development, Ministry of Public Works	(id02)
7)Research Center for Limnology (RCL) Indonesian Institute of Sciences(LIPI) Cibinong Sciences Center	(id03)
JAPAN	
8) Gifu Prefectural Institute of Health and Environmental Science	(jp01)
9) Shimane Prefectural Institute of Public Health and Environmental Science	(jp02)
Lao PDR	
10)Environment Quality Monitoring Centre, Environment Research Institute, Water Resources and Environment Administration	(la01)
MALAYSIA	
11)Division of Environmental Health, Department of Chemistry(DOC)	(my01)
12)Faculty of Applied Science University Technology Mara (UiTM)	(my02)
MONGOLIA	
13)Central Laboratory of Environmental Monitoring(CLEM)	(mn01)
PHILIPPINES	
14)Environmental Management Bureau (EMB),	(ph01)
15)Environmental Management Bureau Cordillera Administrative Region (EMB-CAR),	(ph02)
RUSSIA	
16)Limnologcal Institute of Russian Academy of Science/Siberian Branch (RAS/SB)	(ru01)
17)Primorskii Environmental Monitoring Center of Roshydromet (Laboratory for Monitoring of inland water Pollution)	(ru02)
THAILAND	
18)Environmental Research and Training Center (ERTC)	(th01)
19)Air Quality and Noise Management Division, Pollution Control Department(PCD) Ministry of Science Technology and Environment(MSTE)	(th02)
VIET NAM	
20) Middle of Central regional Hydro-Meteorological Observatory National Hydro -Meteorological Center (NHMS)	(vn01)
21) Environmental Laboratory - Center for Environmental Research - Vietnam	(vn02)

Institute of Meteorology, Hydrology and Environment (IMHEN)

22)Environmental research Division, Sub-Institute of HydroMeteorology and Environment of South Vietnam (SIHYMETE) (vn03)

Appendix Table 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	7.27	6.20	0.223	6.93	0.82	5.83	5.66	1.20	2.65	1.64	0.34
cn02	7.27	6.18	0.222	6.47	0.88	5.71	5.74	1.22	3.03	1.47	0.32
cn03	7.27	6.16	0.229	6.67	0.89	5.71	5.65	1.17	2.75	1.63	0.29
cn04	7.27	6.51	0.237	6.70	0.82	5.74	5.65	1.16	2.75	1.69	0.28
id01	7.30	6.28	0.269	6.08	0.68	5.01	5.23	1.10	2.30	1.39	0.26
id02	7.10	6.40	0.319	5.70	0.78	5.05	9.30	1.45	2.50	1.05	0.26
id03	7.80	6.68	0.279	5.15	0.30	6.77	6.76	0.34	1.69	1.14	0.23
jp01	7.30	6.30	0.241	6.66	0.79	5.71	5.74	1.19	2.49	1.57	0.31
jp02	7.47	6.10	0.246	6.64	0.71	5.44	5.83	1.18	1.33	1.98	0.19
la01	7.62	5.39	2.590	5.35	0.72	4.53	23.42	1.24	2.73	1.67	0.34
mn01	7.28	6.19	0.230	6.38	0.76	6.15	5.83	1.20	2.54	1.60	0.39
my01	7.36	6.35	0.245	6.53	0.78	5.58	5.73	1.18	2.45	1.66	0.29
my02	7.36	8.34	0.250								
ph01	7.25	6.29	0.231	7.75	0.84	6.77	6.00	1.40	2.97	1.57	0.31
ph02	7.34	6.33	0.410	6.25	0.99	5.43	6.67	3.20	3.36	1.32	0.42
ru01	7.08	6.31	0.222	6.84	0.94	6.01	5.53	1.22	2.31	1.61	0.46
ru02	7.10	6.35	0.223	6.45	0.85	5.72	5.50	1.20	2.30	1.55	0.32
th01	7.34	6.21	0.216	6.62	0.77	5.64	5.76	1.25	2.62	1.61	0.22
th02	7.34	6.12	0.265	6.30	0.75	4.95	5.73	1.19	2.81	1.42	0.19
vn01	7.38	6.24	0.240	6.80	0.80	4.89	4.41	0.76	2.59	1.50	0.30
vn02	7.37	5.95	0.220	5.83	0.70	5.23	5.05	0.76	2.35	1.54	0.17
vn03	7.01	8.36	0.283	7.32		3.40	5.66	1.33	3.23	1.45	0.29
Expected value	7.41	6.57	0.238	6.72	0.82	5.80	5.78	1.21	2.48	1.59	0.29
Number of data	22	22	22	21	20	21	21	21	21	21	21
Average	7.31	6.42	0.359	6.45	0.78	5.49	6.71	1.24	2.56	1.53	0.29
Minimum	7.01	5.39	0.216	5.15	0.30	3.40	4.41	0.34	1.33	1.05	0.17
Maximum	7.80	8.36	2.590	7.75	0.99	6.77	23.42	3.20	3.36	1.98	0.46

blank : not analyzed

Appendix Table 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	-1.9	-5.6	-6.3	3.1	0.0	0.5	-2.1	-0.8	6.9	3.1	17.2
cn02	-1.9	-5.9	-6.7	-3.7	7.3	-1.6	-0.7	0.8	22.2	-7.5	10.3
cn03	-1.9	-6.2	-3.8	-0.7	8.5	-1.6	-2.2	-3.3	10.9	2.5	0.0
cn04	-1.9	-0.9	-0.4	-0.3	0.0	-1.0	-2.2	-4.1	10.9	6.3	-3.4
id01	-1.5	-4.4	13.0	-9.5	-17.1	-13.6	-9.5	-9.1	-7.3	-12.6	-10.3
id02	-4.2	-2.6	34.0	-15.2	-4.9	-12.9	60.9	19.8	0.8	-34.0	-12.1
id03	5.3	1.7	17.4	-23.4	-63.4	16.7	17.0	-71.7	-31.9	-28.5	-20.6
jp01	-1.5	-4.1	1.3	-0.9	-3.7	-1.6	-0.7	-1.7	0.4	-1.3	6.9
jp02	0.8	-7.2	3.4	-1.2	-13.4	-6.2	0.9	-2.5	-46.4	24.5	-34.5
la01	2.8	-18.0	988.2	-20.4	-12.2	-21.9	305.2	2.5	10.1	5.0	17.2
mn01	-1.8	-5.8	-3.4	-5.1	-7.3	6.0	0.9	-0.8	2.4	0.6	34.5
my01	-0.7	-3.3	2.9	-2.8	-4.9	-3.8	-0.9	-2.5	-1.2	4.4	0.0
my02	-0.7	26.9	5.0								
ph01	-2.2	-4.3	-2.9	15.3	1.9	16.8	3.8	15.7	19.6	-1.5	6.9
ph02	-0.9	-3.7	72.3	-7.0	20.7	-6.4	15.4	164.5	35.5	-17.0	44.8
ru01	-4.5	-4.0	-6.7	1.8	14.6	3.6	-4.3	0.8	-6.9	1.3	58.6
ru02	-4.2	-3.3	-6.3	-4.0	3.3	-1.4	-4.8	-0.8	-7.3	-2.5	10.3
th01	-1.0	-5.5	-9.3	-1.4	-6.0	-2.7	-0.3	3.4	5.8	1.4	-24.7
th02	-1.0	-6.8	11.3	-6.3	-8.5	-14.7	-0.9	-1.7	13.3	-10.7	-34.5
vn01	-0.4	-5.0	0.8	1.1	-2.6	-15.7	-23.6	-37.4	4.2	-5.5	3.4
vn02	-0.6	-9.4	-7.6	-13.2	-14.4	-9.8	-12.7	-36.9	-5.4	-3.4	-42.4
vn03	-5.4	27.2	18.9	8.9		-41.4	-2.1	9.9	30.2	-8.8	0.0
Minimum	-5.4	-18.0	-9.3	-23.4	-63.4	-41.4	-23.6	-71.7	-46.4	-34.0	-42.4
Maximum	5.3	27.2	988.2	15.3	20.7	16.8	305.2	164.5	35.5	24.5	58.6
Average	-1.3	-2.3	50.7	-4.0	-5.1	-5.4	16.0	2.1	3.2	-4.0	1.3

blank : not analyzed

6. ACKKNOWLEDGEMENT

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7. CONTACT INFORMATION

Please address all inquiries, comments and suggestions to:

Acid Deposition and Oxidant Research Center (ADORC)
1182, Sowa, Nishi-ku, Niigata-shi, 950-2144, Japan
Tel: +81 25-263-0550
Fax: +81 25-263-0567
E-mail: eanetdata@adorc.gr.jp
URL: http://www.eanet.cc

Contact person:

Name	Department & E-mail address
Mr. Shinji NAKAYAMA (EANET QA/QC Manager)	Dept. Head, Data Management Department E-mail: nakayama@adorc.gr.jp