Acid Deposition Monitoring Network
in East Asia (EANET)

Report of the Inter-laboratory Comparison Project 2006

9th Inter-laboratory Comparison Project on Wet Deposition

2nd Inter-laboratory Comparison Project on Dry Deposition

8th Inter-laboratory Comparison Project on Soil

7th Inter-laboratory Comparison Project on Inland Aquatic Environment

November 2007
Network Center for EANET

Contents

1. INTRODUCTION

The inter-laboratory comparison project (round robin analysis survey) was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the Quality Assurance / Quality Control (QA/QC) Program of EANET.

The objectives of the project are, through the evaluation of analytical results, analytical equipment and its operating condition and other practices,

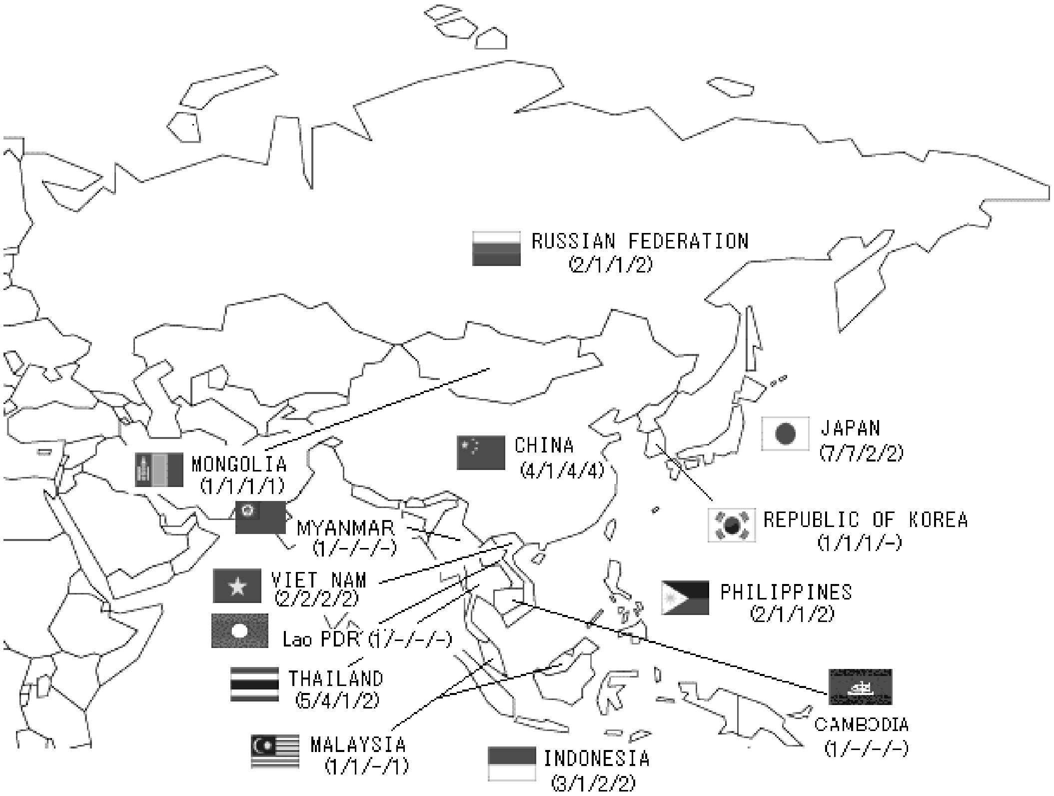
(i) to recognize the analytical precision and accuracy of the measurement in each participating laboratory,
(ii) to give an opportunity to improve the quality of the analysis on wet deposition, dry deposition monitoring (filter pack method), soil monitoring and inland aquatic monitoring of EANET,
(iii)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

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

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

This report presents the results of the 9th inter-laboratory comparison project on wet deposition, 2nd inter-laboratory comparison project on dry deposition, 8th inter-laboratory comparison project on soil, and 7th 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 2006

2. 9th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

2.1 Introduction

In the 9th 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 the results were statistically treated.

The Network Center (NC) shipped the artificial rainwater samples to these laboratories, on 22 November 2006 and all of them submitted their analytical results to NC by 28 February 2007.

2.2 Procedures

2.2.1 Participating Laboratories

A total of 31 laboratories in charge of chemical analysis in the 13 countries of EANET participated in this survey. All the participating laboratories submitted their analytical results to NC. A list of the participating laboratories with the abbreviated name and code are given in APPENDIX 2-1.

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

2.2.2 Description of samples

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

Table 2.1 Description of artificial rainwater samples

Artificial rainwater samples	Amount of each sample	Container	Number of samples	Note
No.061 (high concentration sample) No.062 (low concentration sample)	Approximately 100mL	Poly-propylene bottle 100mL	One bottle each	Known amount of reagents are dissolved in deionized water

The prepared concentrations of ions in the sample No.061 were approximately the same level on slightly lower compared to the high concentration sample of the 2005 project. The concentrations of ions in the sample No.062 were all slightly higher than those in the low concentration sample of the 2005 project. 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.061 (high concentration)	4.72	3.10	45.8	36.3	57.5	44.5	6.9	23.8	11.7	43.9
No.062 (low concentration)	5.15	1.21	16.9	15.0	24.5	20.5	4.9	9.3	3.5	15.1

* For 100 times diluted samples.

2.2.3 Analytical Method and Data Checking Procedures

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

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

Participating laboratories are required to apply the analytical methods and data checking procedures that are specified in the "Technical Manual for Wet Deposition Monitoring in East Asia" and "Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia". Analytical methods specified in the manual are listed in Table 2.3.

Table 2.3 Analytical methods specified in the manual

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

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

Calculation of ion balance (R_1)

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

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

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

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

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

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

(3) Calculation of ion balance (R_1)

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

(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°C.

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

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

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

Table 2.5 Allowable ranges for R_2 in different ranges of EC

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

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

2.3 Results

The NC received the data on analytical results of artificial rainwater samples from 31 laboratories in the participating countries of EANET. Several laboratories measured only pH and EC. The original results from the laboratories are shown in APPENDIX 2-2 and 2-3.

General statistics of obtained data summarized in Table 2.6 were calculated for each constituent of the artificial rainwater samples such as: Average (Va), Minimum (Min.), Maximum (Max.), Standard deviation (S.D.), and Number of data (N). Outlying data, which are apart from the average greater than a factor of 3 of S.D. were not included for this overall project statistics calculation. As shown in Table 2.6, average of submitted data fairly well agreed with the prepared values/concentrations (Vp) except Ca^{2+}. The range of Va/Vp was between –4.5%(EC) to +1.9%(Ca^{2+}) for the sample No.061, and –3.9%(NO_3^-) to 7.9%(Ca^{2+}) for the sample No.062. There were a few laboratories that submitted measured data with considerable differences from prepared concentrations.

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

Constituents	Prepared (Vp)	Average (Va)	Va/Vp (%)	S.D.	N	Min.	Max.
[Sample No.061]							
pH	4.72	4.76	0.9	0.11	30	4.51	5.10
EC(mS/m)	3.10	2.96	-4.5	0.13	30	2.60	3.14
SO_4^{2-}(μmol/L)	45.8	46.0	0.3	1.90	27	41.2	49.9
NO_3^-(μmol/L)	36.3	35.5	-2.3	2.54	27	26.6	39.0
Cl^-(μmol/L)	57.5	57.5	0.0	2.69	27	50.8	64.3
Na^+(μmol/L)	44.5	44.6	0.1	1.97	27	40.2	48.0
K^+(μmol/L)	6.9	6.7	-2.3	0.80	27	5.4	9.8
Ca^{2+}(μmol/L)	23.8	24.2	1.9	1.54	27	21.1	27.4
Mg^{2+}(μmol/L)	11.7	11.6	-1.2	0.58	27	10.5	12.9
NH_4^+(μmol/L)	43.9	44.5	1.3	4.38	28	37.5	56.4
[Sample No.062]							
pH	5.15	5.17	0.4	0.10	30	4.97	5.48
EC(mS/m)	1.21	1.20	-1.1	0.06	30	1.04	1.34
SO_4^{2-}(μmol/L)	16.9	16.9	0.0	1.28	27	13.8	20.3
NO_3^-(μmol/L)	15.0	14.4	-3.9	1.69	28	9.6	17.1
Cl^-(μmol/L)	24.5	24.5	-0.1	2.16	27	18.9	28.9
Na^+(μmol/L)	20.5	20.7	1.1	2.01	28	13.8	24.6
K^+(μmol/L)	4.9	4.8	-1.9	0.54	27	3.5	5.9
Ca^{2+}(μmol/L)	9.3	10.0	7.9	1.31	27	7.7	12.5
Mg^{2+}(μmol/L)	3.5	3.6	2.9	0.41	28	2.9	4.7
NH_4^+(μmol/L)	15.1	15.3	1.6	2.05	28	11.4	20.4

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

Va/Vp (%): {Average(Va) / Prepared (Vp) - 1} X 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 value/concentration and evaluated by the excess of DQOs criteria: the flag "E" was put to the data that exceed DQOs by a factor of 2 (±15% ~ ±30%), and the flag "X" was put to the data that exceed DQOs more than a factor of 2 (<-30% or >30%).

A set of data for each sample was evaluated by the data checking procedures described in chapter 2.2.3. 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.061 (high concentrations) and No.062 (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.061 and No.062 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 countries’ 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 “2.3.3 Information on Laboratories”.

2.3.1 Evaluation of laboratories' performance (by sample)

High Concentration Sample No.061

The number and percentage of flagged data in the high concentration sample No.061 are described in Table2.7. It was founded that 16 analytical data out of 286 exceeded the DQOs within a factor of 2 and was flagged by "E". 4 analytical data out of 286 exceeded the DQOs more than a factor of 2 and flagged by "X". Data flagged by "E" and "X" shared about 7.0 percent of all reported data for sample No.061.

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.061 (high concentrations)

Characterization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
Data within DQOs	31	29	27	25	27	27	22	26	27	25	266
With flag E*	0	2	1	2	0	1	4	2	1	3	16
With flag X**	0	0	0	1	1	0	2	0	0	0	4
Flagged(%)	0.0	6.5	3.6	10.7	3.6	3.6	21.4	7.1	3.6	10.7	7.0

*E : Value exceeded the DQO within a factor of 2 (Total data=286)

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

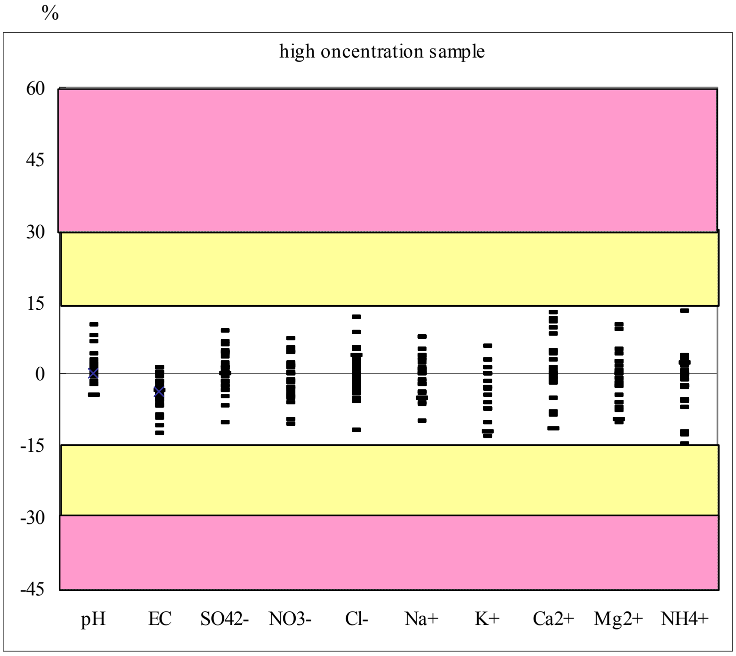


Figure 2.1 Distribution of the data normalized by prepared value in each parameters in the high concentration sample

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

Table 2.8 Analytical Results of Sample No.061

Lab.ID	pH	EC	SO$_4^{2-}$	NO$_3^-$	Cl$^-$	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	NH$_4^+$	R1	R2
	-	(mS/m)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	(μmol/L)	-	-
KH01	5.21	E 2.20	48.0	38.0	59.3	43.6	6.7	23.7	11.6	44.2	-6.0	10.3
CN01	4.70	2.90	46.6	35.3	62.5	41.7	6.4	26.4	11.7	38.3	-2.3	4.1
CN02	4.73	2.97	47.5	38.0	60.8	45.0	6.0	E 30.2	12.2	38.6	-0.2	3.6
CN03	4.74	2.96	47.9	36.5	58.4	44.7	6.6	25.8	11.2	42.9	-1.1	2.7
CN04	4.87	2.82	46.5	36.9	58.7	42.9	7.0	E 27.4	12.0	42.9	-0.9	2.5
ID01	4.65	3.00	44.3	34.2	56.0	48.0	7.1	26.1	12.9	44.9	5.7	3.8
ID02	4.76	2.90	49.9	E 26.6	56.9	45.6	X 9.8	21.8	11.4	45.0	0.2	2.4
ID03	5.04	E 2.60	41.2	32.5	56.5	46.9	6.2	23.8	11.7	E 56.4	5.0	2.7
JP01	4.73	3.00	46.4	36.9	58.8	46.2	7.3	24.1	11.4	45.7	0.1	2.2
JP02	4.73	3.10	45.2	35.0	56.4	43.5	6.9	24.0	11.5	42.7	0.3	-0.9
JP03	4.80	3.02	45.8	35.8	57.2	44.0	6.8	23.6	11.8	44.0	-0.9	-0.6
JP04	4.76	3.01	46.9	37.0	58.2	41.8	6.4	23.5	11.4	42.9	-2.9	0.5
JP05	4.81	2.94	42.8	34.7	50.8	43.6	6.7	23.4	11.7	43.4	2.4	-1.5
JP06	4.78	3.05	45.5	36.8	56.2	45.8	7.1	24.5	11.9	41.5	-0.1	-0.7
JP07	4.83	2.96	48.7	38.1	59.3	46.0	6.9	24.8	11.8	45.4	-2.2	1.6
LA01	5.10	2.72	E 32.5	X 24.9	X 37.2	48.0	E 8.1	26.9	12.8	E 55.1	I 21.9	-5.8
MY01	4.62	2.77	47.7	38.3	60.6	42.8	6.4	23.4	11.0	43.7	-2.3	C 9.0
MN01	4.92	2.94	44.9	34.5	54.6	46.2	X 10.6	26.6	E 13.9	49.7	5.4	0.1
MM01	4.71	2.74										
PH01	4.81	2.99	44.7	35.3	55.2	43.9	E 5.8	25.0	10.8	40.8	-0.6	-1.4
PH02	4.69	2.84										
KR01	4.51	3.00	45.8	E 30.7	59.7	42.3	6.1	21.1	10.6	44.9	1.5	6.8
RU01	4.62	3.11	45.8	36.3	57.5	45.2	7.0	23.4	11.6	42.8	1.0	2.4
RU02	4.74	3.14	46.0	39.0	56.0	48.0	6.9	23.5	11.0	43.8	-0.3	-0.8
TH01	4.77	3.04	46.2	35.7	56.8	45.0	7.0	24.9	12.0	44.7	0.7	0.2
TH02	4.72	3.05	43.6	35.2	55.6	44.9	6.5	23.8	11.5	43.4	1.8	-0.2
TH04	4.75	3.14										
TH05	4.76	2.92	44.5	35.9	57.0	40.2	6.4	23.7	10.5	37.5	-3.4	0.2
TH06	4.75	3.08	44.3	34.6	54.3	42.7	E 5.4	25.0	12.3	E 53.5	4.4	-0.2
VN01	4.70	3.11	49.0	37.2	64.3	44.5	6.7	22.6	10.9	44.8	-4.3	1.8
VN02	4.72	2.99	45.2	32.9	55.1	E 33.9	E 5.8	21.9	11.0	41.6	-3.6	-0.8

E:Value exceeded the DQO(±15) within a factor of 2
I:Poor ion balance (R1)

X:Value exceeded the DQO(±15) more than a factor of 2
C:Poor conductivity agreement (R2)

Low Concentration Sample No.062

For sample No.062 (low concentrations), the number and percentage of flagged data are described in Table2.9. It was founded that 34 analytical data out of 286 exceeded the DQOs within a factor of 2 and was flagged by "E". 12 analytical data out of 286 exceeded the DQOs more than a factor of 2 and was flagged by "X". Data flagged by “E” and “X” shared up to 16.1 percent of all reported data for sample No.062.

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.062 (low concentrations)

Characterization of data	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Total
Data within DQOs	31	30	25	24	24	24	22	17	22	21	240
With flag E*	0	0	3	2	3	3	5	8	5	5	34
With flag X**	0	1	0	2	1	1	1	3	1	2	12
Flagged(%)	0.0	3.2	10.7	14.3	14.3	14.3	21.4	39.3	21.4	25.0	16.1

*E : Value exceeded the DQO within a factor of 2 (Total data=286)

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

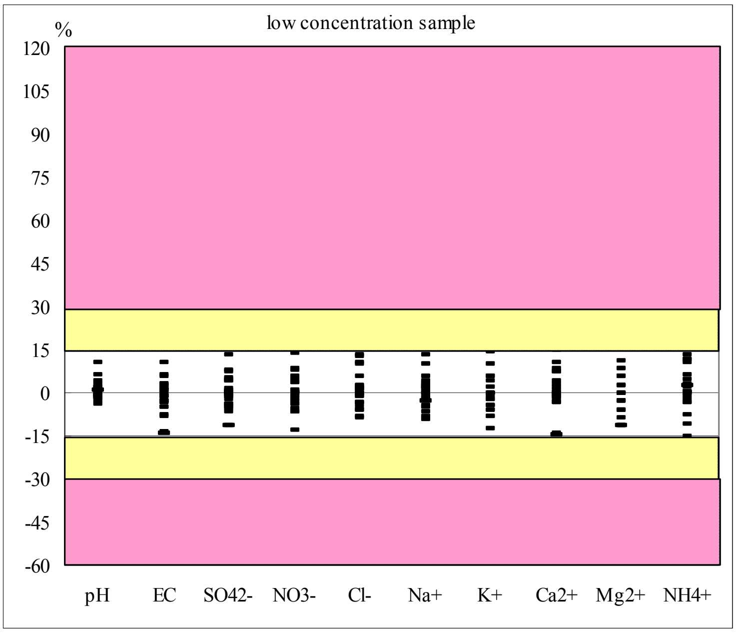


Figure 2.2 Distribution of the data normalized by prepared value for each parameter in the low concentration sample

Many data on Ca^{2+}, Mg^{2+} and NH_4^+ were marked with flags E or flags X. 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.062

Lab.ID		pH		EC		SO_4^{2-}		NO_3^-		Cl^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		NH_4^+		R1		R2
		-		(mS/m)		(μmol/L)		(μmol/L)		(μmol/L)		(μmol/L)		(μmol/L)		(μmol/L)		(μmol/L)		(μmol/L)		-		-
KH01		5.48	X	1.74		17.6		15.7		25.1		20.4		4.8		9.3		3.5		16.9		-3.4	C	-22.0
CN01		5.20		1.20		17.6		16.2		27.8		21.7		4.3	X	12.5	E	4.1	E	11.5		-1.4		2.0
CN02		5.15		1.20		19.2		17.1		27.1	E	24.3		4.8	X	19.2	X	4.7		13.5	I	8.3		8.4
CN03		5.15		1.28	E	20.3		15.9		27.0		23.2		4.9	X	12.5		3.7		14.0		-1.2		2.1
CN04		5.12		1.20		17.0		15.2		26.0		20.9		4.9	E	11.8		3.6		14.9		2.5		3.0
ID01		5.07		1.34		16.3		14.4		22.4	E	24.6		5.2	E	11.6		3.9		16.7	I	10.7		-1.6
ID02		5.26		1.15		18.3	X	9.6	E	18.9		18.8	E	5.9	E	7.7		3.6	E	11.4		-0.7		-4.6
ID03		5.38		1.05		15.0		13.1		23.3		20.9		4.9		9.1		3.4	X	20.4		6.3		2.0
JP01		5.22		1.20		16.9		15.0		24.9		21.3		4.7		8.0	E	2.9		15.8		-2.8		-1.6
JP02		5.07		1.22		17.2		15.1		24.9		20.2		4.9		10.3		3.7		14.6		1.2		2.3
JP03		5.21		1.21		16.8		14.6		24.4		20.2		4.9		9.4		3.5		15.5		0.0		-1.4
JP04		5.13		1.23		17.1		15.1		24.2		19.5		4.6		9.7		3.3		15.2		-0.5		-0.4
JP05		5.23		1.22		16.7		14.8		24.9		22.6		4.9		9.2		3.4		15.2		0.5		-1.8
JP06		5.20		1.23		16.5		14.8		24.2		21.1		5.0		9.5		3.6		15.2		1.2		-2.0
JP07		5.25		1.18		17.8		15.6		24.9		21.4		5.1		10.0		3.5		15.2		-1.2		0.7
LA01		5.70		1.15	E	12.0	X	10.1	X	16.0	E	23.9	E	5.7	E	11.3	E	4.2	X	20.0	I	24.5		-9.8
MY01		4.97		1.11		17.7		16.3		27.6		19.9		4.7		9.2		3.1		15.4		-2.6		10.7
MN01		5.16		1.21		17.0		14.7		25.0		21.0		5.6	E	11.9	E	4.4	E	17.6		6.4		2.6
MM01		5.11		1.18																				
PH01		5.26		1.17		16.1		14.0		23.7		19.9	E	3.9	E	11.5		3.3	E	12.8		1.3		-1.9
PH02		5.10		1.12																				
KR01		5.21		1.04		15.0	E	12.2	E	19.9		20.0	X	2.6		8.0		3.1		15.5		3.4		0.8
RU01		5.00		1.25		16.7		14.4		25.2		20.6		4.7		9.2		3.2		15.1		1.5		2.2
RU02		5.07		1.25		17.0		15.2		23.0		19.6		4.5		9.6		3.1		16.1		1.3		0.1
TH01		5.18		1.22		15.8		14.0		23.6		21.2		5.2		10.0		3.8		15.6		4.8		-1.5
TH02		5.13		1.17		16.0		14.2		23.7		20.8		4.6		9.0		3.3		16.9		3.1		1.4
TH04		5.12		1.24																				
TH05		5.31		1.18		16.3		15.1		24.6		19.2		4.5	E	10.7		3.6	E	12.1		-2.1		-3.0
TH06		5.10		1.29		16.2		14.0		23.0		18.6	E	3.7		10.1	E	4.1		17.1		4.4		-2.7
VN01		5.13		1.24		18.2		15.6	E	28.9		20.8		5.4	E	10.8		3.8		14.6		-2.2		2.5
VN02		5.16		1.18	E	13.8	E	11.7		22.5	X	13.8	E	3.5		9.0		3.4		14.8		1.6		-5.1

E:Value exceeded the DQO(±15) within a factor of 2 I:Poor ion balance (R1)

X:Value exceeded the DQO(±15) more than a factor of 2 C:Poor conductivity agreement (R2)

Comparison of High and Low Concentration Sample

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

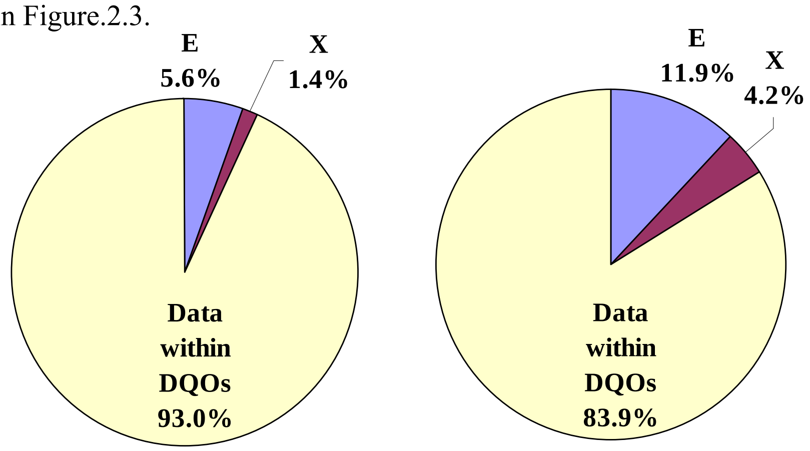


Figure 2.3 Percentage of flagged data for Sample No.061 and No.062

Comparing the prepared value of sample No.061 with that of Sample No.062, values of Sample No.061 were 0.9 - 3.3 times higher than that of sample No.062. The percentage of the data within DQOs for sample No.061 was 93.0 %, and the percentage of the data within DQOs for the sample No.062 was 83.9 %. The difference between both concentration samples was 9.1 %. The number of “E” flagged data in the low concentration sample was 34 and this is 2 times more than that of the high concentration sample. The number of “X” flagged data was 12 and this is 3 times more than that of the high concentration sample. In this project, the total number of flagged data was 66 (E50, X16) among the whole set of 572 data. 5.9% (17 out of 286) data are flagged in both concentration samples.

The number of flagged data of laboratories

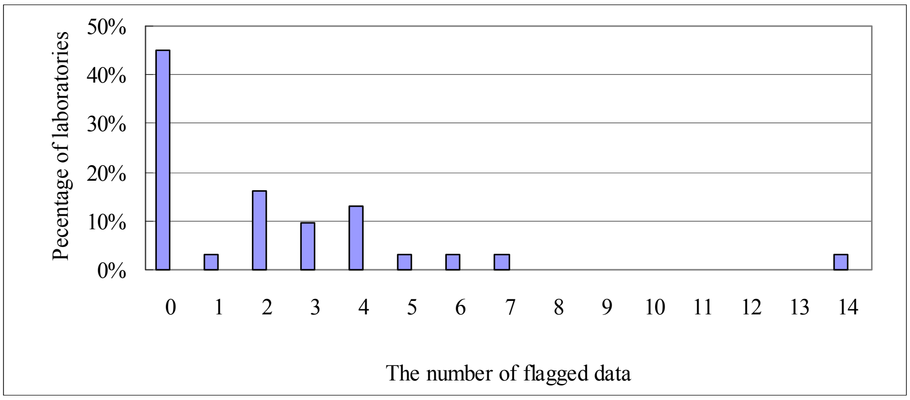


Figure 2.4 The distribution of laboratories with the number of flagged data

The number of flagged data of laboratories are shown in Figure 2.4. The number of laboratories without flagged data was 14, which corresponds to 45% of all the participating laboratories. On the other hand, one laboratory had 14 flagged data.

2.3.2 Evaluation of laboratories' performance (by analytical parameters)

The general overviews of data are presented below in Figures 2.5 to 2.14 for each analytical parameter. The results received from each laboratory were normalized by prepared values to evaluate their deviation.

pH

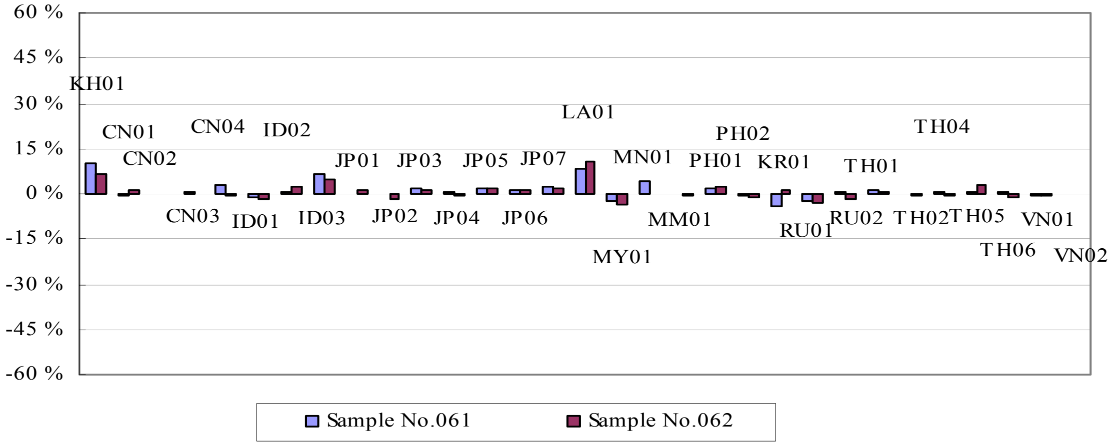


Figure 2.5 Distribution of results for pH (normalized by prepared value)

All participating laboratories used pH meter with glass electrode for measurement of pH. All of obtained data satisfied the DQO of the QA/QC program of EANET. Almost half of participating laboratories submitted slightly higher pH values than the prepared value in both samples.

EC

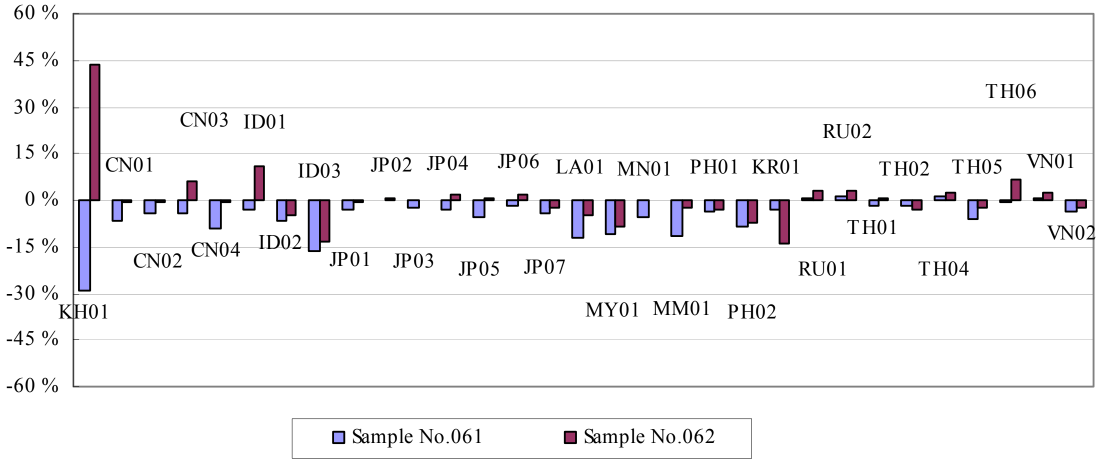


Figure 2.6 Distribution of results for EC (normalized by prepared value)

All participating laboratories used conductivity cell for the measurement of EC. Almost all obtained data that satisfied the DQO of the QA/QC program of the EANET. However, Lab.KH01 reported also for the data that exceeded the DQO for Sample No.061 and Sample No.062.

SO_4^{2-}

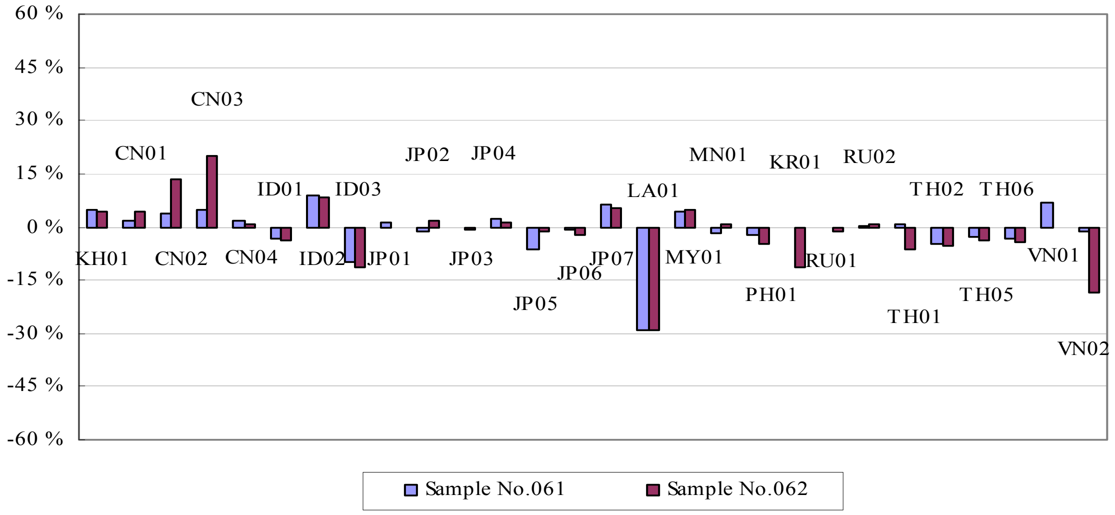


Figure 2.7 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

All of the participating laboratories used ion chromatography for the determination of SO_4^{2-} except for one laboratory (Lab.RU02), which used Spectrophotometry. Data submitted by Lab.LA01 was lower than the prepared value in both samples and marked with flag “E”.

NO_3^-

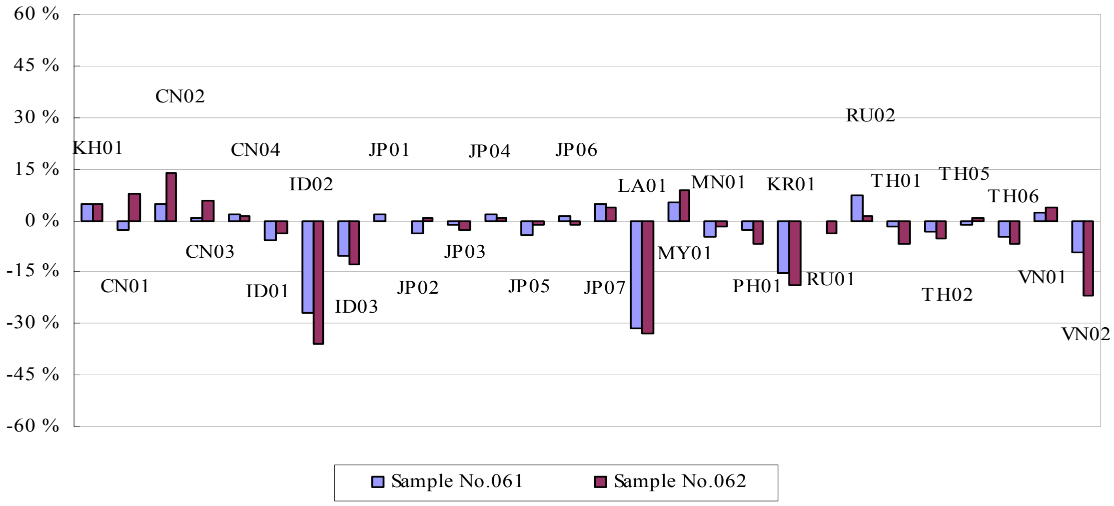


Figure 2.8 Distribution of results for NO_3^- (normalized by prepared concentration)

All of the participating laboratories used ion chromatography for the determination of NO_3^- except for one laboratory (Lab.RU02), which used Spectrophotometry. Data of Lab.ID03 and LA01 were flagged in both samples. All flagged data were lower than the prepared value.

Cl^-

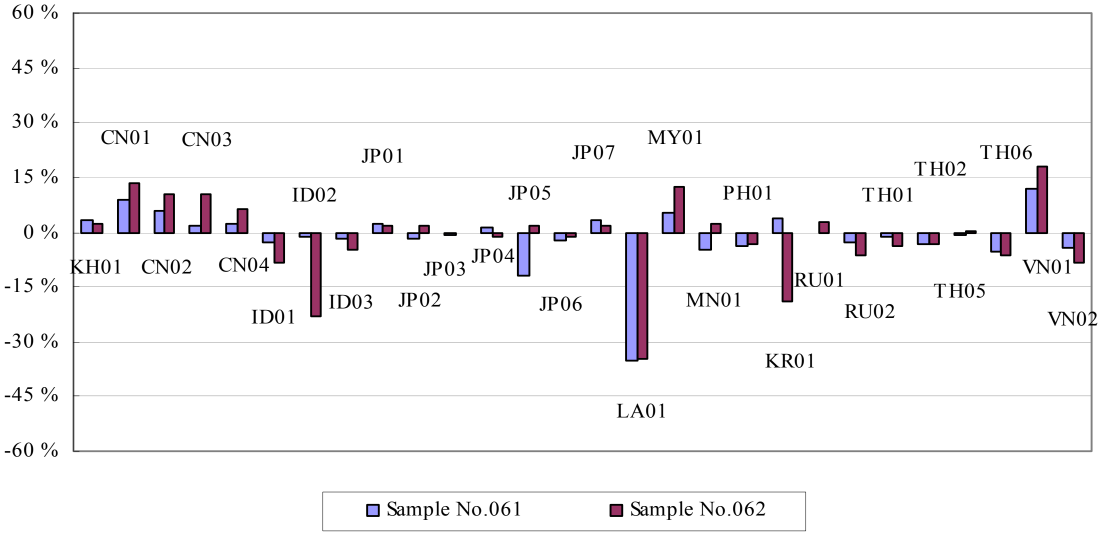


Figure 2.9 **Distribution of results for Cl^- (normalized by prepared concentration)**

27 laboratories used ion chromatography for the determination of Cl^-. The Lab.RU02 used titration method. The data of Lab.LA01 in both samples exceeded the DQOs and more than a factor of 2 they marked with flag “X”.

Na^+

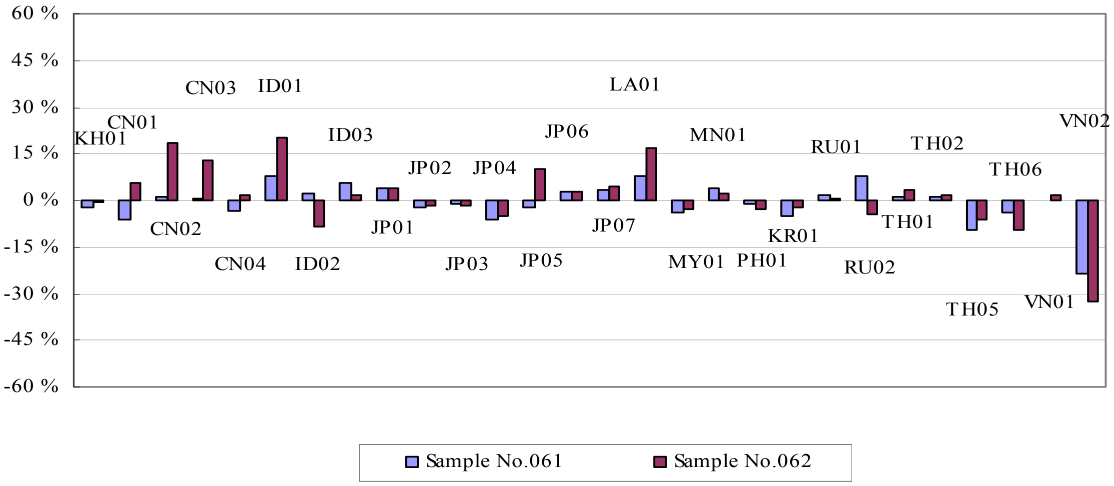


Figure 2.10 **Distribution of results for Na^+ (normalized by prepared concentration)**

25 laboratories used ion chromatography, 1 laboratories used atomic absorption spectrometry (Lab.ID02), and 2 laboratories used flame (emission) photometry (Lab.RU01, RU02) for the determination of Na^+. The normalized percentage of data from 75% (21 / 28) laboratories tended to be in same direction.

K^+

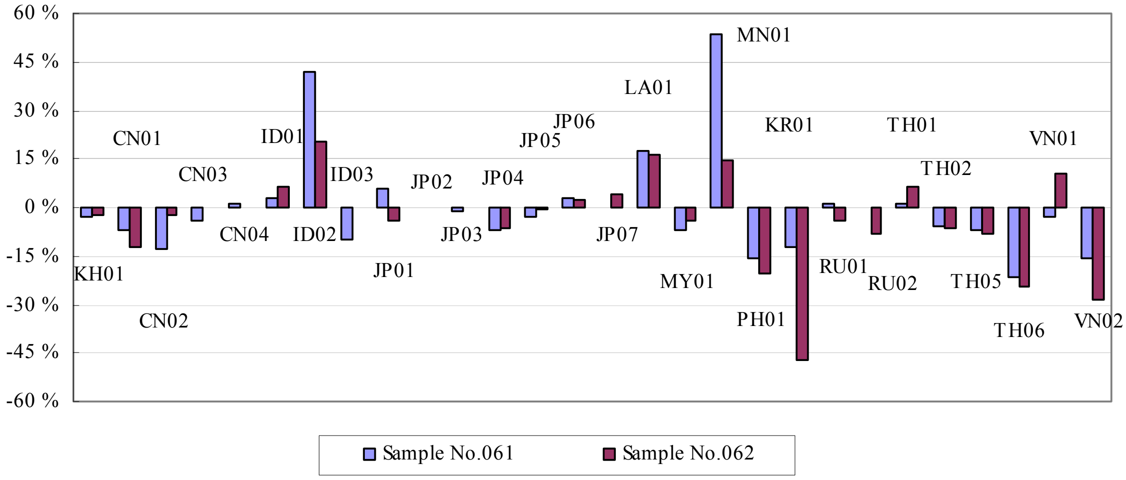


Figure 2.11 Distribution of results for K^+ (normalized by prepared concentration)

25 laboratories used ion chromatography, 1 laboratories used atomic absorption spectrometry and 2 laboratories used flame (emission) photometry, for the determination of K^+ as same as Na^+. 21.4% of the data for the Sample No.061 had the flag and this was the highest percentage in the Sample No.061 in this survey. The percentage of flagged data in the sample No.062 was also 21.4%.

Ca^{2+}

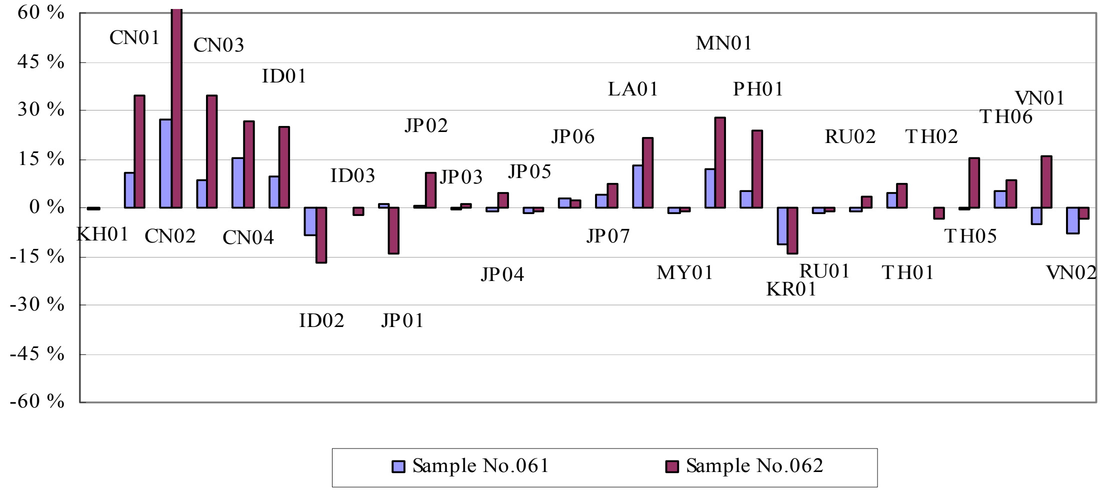


Figure 2.12 Distribution of results for Ca^{2+} (normalized by prepared concentration)

25 laboratories used ion chromatography, 3 laboratories used atomic absorption spectrometry for the determination of Ca^{2+}. The percentage of flagged data in low concentration sample was 39.3%. This was the highest percentage in this survey. On the other hand, the percentage in high concentration sample was 7.1%. There were much difference with the flagged percentage in both samples.

Mg^{2+}

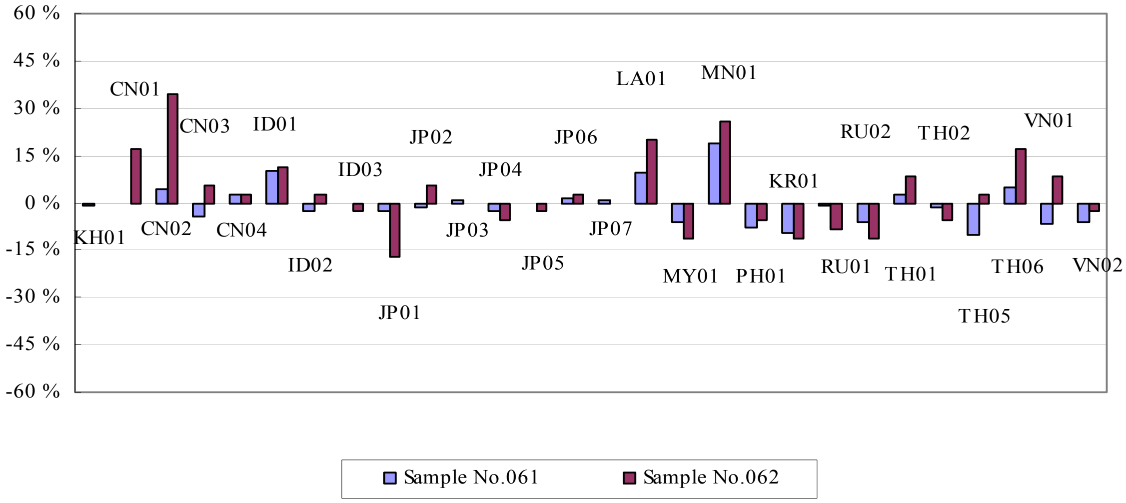


Figure 2.13 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Ion chromatography and atomic absorption spectrometry were used in the analysis of Mg^{2+} same as for Ca^{2+} except Lab.KR01. The Lab.KR01 used the atomic absorption spectrometry. The all flagged data were measured by ion chromatography. The data in Lab.MN01 marked with “E” flag. Both data were higher than the levels of DQOs.

NH_4^+

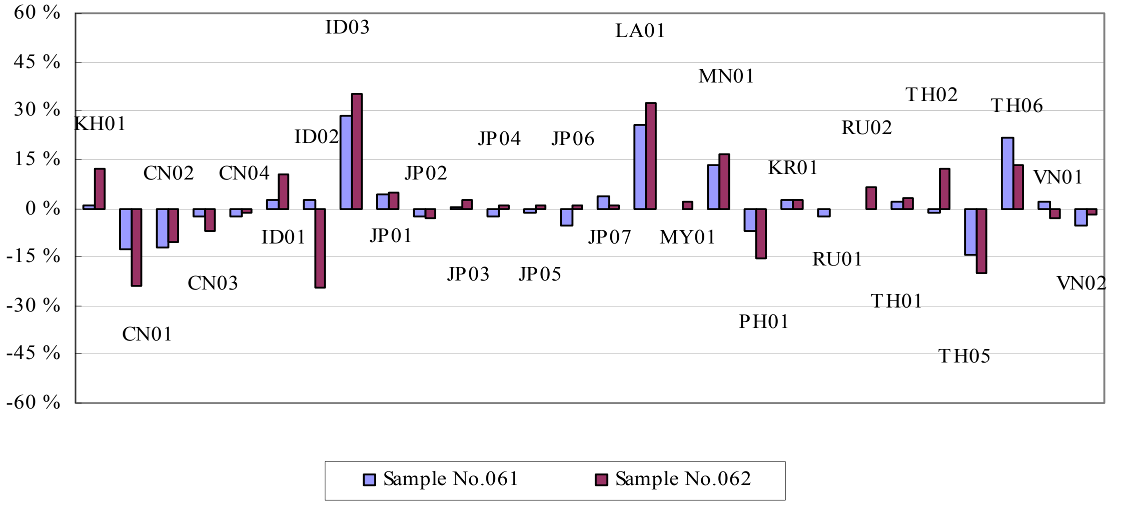


Figure 2.14 Distribution of results for NH_4^+ (normalized by prepared concentration)

25 laboratories used recommended analytical method of EANET for the determination of NH_4^+: 24 laboratories used ion chromatography; 2 laboratories (Lab.PH01, RU01) used spectrophotometry (Indophenol blue); 1 laboratories used spectrophotometry (others). (Lab. RU02) Lab. ID03 and LA01 submitted the data flagged in both samples. These data were higher than each prepared value.

For future elaboration, distribution of each parameter is presented using a scatter diagram as shown in the APPENDIX 2-4. The code names of the laboratories that exceeded the DQOs are shown.

To study the deviation from the actual values, the Z-score (by robust way) method was applied to each parameter. Z-score bar charts and Youden diagrams were presented in APPENDIX 2-5.

2.3.3 Overall Evaluation

Some of concentrations of the constituents in this survey were similar to the samples in previous years. Compared to the 2005 survey, concentrations of K^+ and Ca^{2+} in high concentration sample were same. The percentage of flagged data for K^+ has decreased from 29.6% in 2005 to 21.4% in 2006 but the percentage for Ca^{2+} has increased from 3.7% to 7.1%. As for low concentration sample, the concentrations for K^+ and NH_4^+ were same to those in 2004. Comparing percentage of flagged data in 2006 with that in 2004, the percentage of flagged data for both K^+ and NH_4^+ had increased from 11.5% to 21.4% and from 22.2% to 25.0%, respectively in 2006.

The relative standard deviations (R.S.D.) of each of the parameters in the sample No.061 and No.062 are shown in the Figure 2.15. The highest R.S.D. in both samples was for NH_4^+ in the low concentration sample in this survey. Only R.S.D. of K^+ in the high concentration sample was higher than that of the low concentration sample. R.S.D. of NH_4^+ is almost same level in both concentration samples. As for the other ions, R.S.D. in the low concentration sample is approximately twice higher than that in the high concentration sample.

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

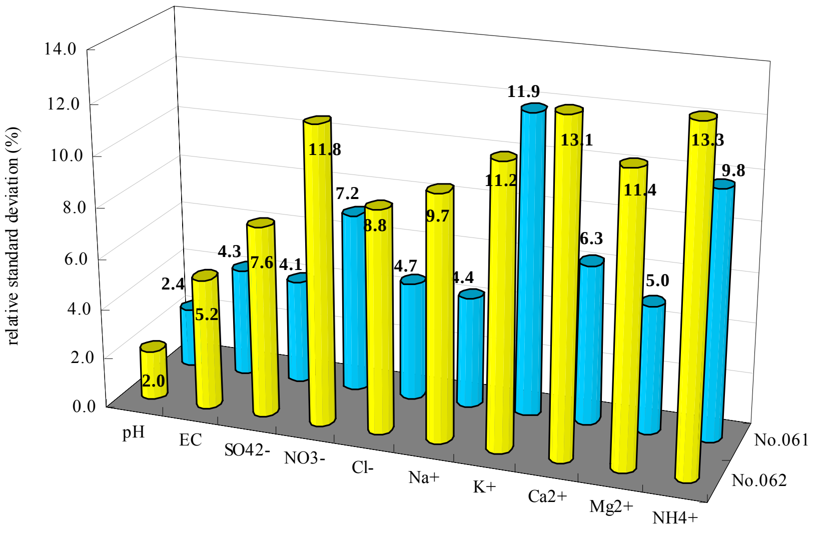


Figure 2.15 Relative standard deviation of each constituent data

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

2.3.4 Information on laboratories

<u>Methodologies Used</u>

As shown in Figure 2.16, most of the participating laboratories used the recommended methods of EANET. Regarding the determination of anions, 27 laboratories used ion chromatography. One laboratory used Spectrophotometry, and Titration in the determination of SO_4^{2-}, NO_3^- and Cl^-, respectively.

As for determination of the all cations, 24 out of 28 laboratories used ion chromatography. One laboratory analyzed Mg^{2+} by Atomic Absorption Spectrometry and analyzed other cations by ion chromatography. Two laboratories used Emission Spectrometry for measurement of Na^+ and K^+, and used Atomic Absorption Spectrometry for measurement of Ca^{2+} and Mg^{2+}. One laboratory used Atomic Absorption Spectrometry for measurement of Na^+, K^+, Ca^{2+} and Mg^{2+}. Regarding NH_4^+, two laboratories used Indophenol Spectrophotometry and one laboratory used the other Spectrophotometry, There relationship between recommended analytical methods and flagged data was not clear.

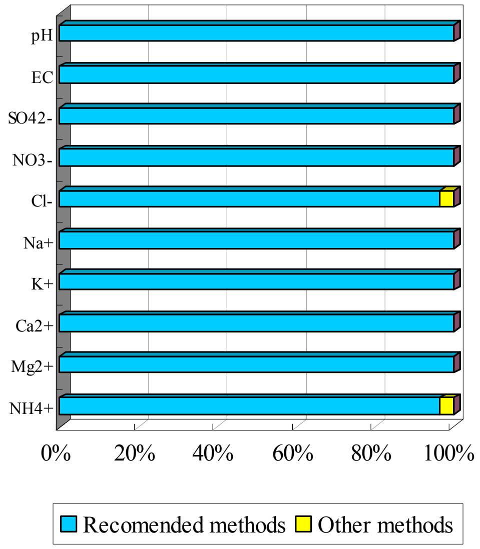


Figure 2.16 Percentage of laboratories with the recommended methods used in the project

The list of analytical methods was described in the table 2.11. Reverse mesh is recommended method of EANET. Table 2.12 presented the number of submitted data and flagged data for each parameter.

Table 2.11 List of methods

Code	Method
0	pH meter with electrode
1	Conductivity cell
2	Titration
3	Atomic Absorption Spectrometry
4	Emission Spectrometry
5	Ion chromatography
6	Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES)
7	Spectrophotometry
8	Indophenol Spectrophotometry (NH_4^+)
9	Inductively Coupled Plasma - Mass Spectrometry (ICP - MS)
10	Graphite Furnace Atomic Absorption spectrometry (GFAA)
11	Other method

Table 2.12 Number of laboratories that used different analytical method

SampleNo.061

Method	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	31									
1		31(2)								
2					1					
3						1	1(1)	3	4	
4						2	2			
5			27(1)	27(3)	27(1)	25(1)	25(5)	25(2)	24(1)	25(3)
6										
7			1	1						1
8										2
9										
10										
11										
Flag E	0	2	1	2	0	1	4	2	1	3
Flag X	0	0	0	1	1	0	2	0	0	0

Sample No.062

Method	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	31									
1		31(1)								
2					1					
3						1	1(1)	3(1)	4	
4						2	2			
5			27(3)	27(4)	27(4)	25(4)	25(5)	25(10)	24(6)	25(6)
6										
7			1	1						1
8										2(1)
9										
10										
11										
Flag E	0	0	3	2	3	3	5	8	5	5
Flag X	0	1	0	2	1	1	1	3	1	2

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

Code number of method is shown in Table 2.11

Staff (Number and years of experience)

The number of staff in charge of measurement on rainwater samples is described in Table 2.13. “A”, “B”, and “C” represent individuals of staff in each laboratory who are in charge of measurement. In 16 laboratories, only one person carried out measurement of rainwater samples. In 8 laboratories two persons carried it. In 6 laboratories three persons carried it. There was no laboratory where more than 4 people carried out measurements. In the laboratories that 3 persons conducted the measurements, their responsibilities were basically separated according to the methods used for analysis such as pH-EC, anions and cations (KH01, MY01, RU01, TH01). In PH01 staff in charge of measurement for NH_4^+ was “A”. In RU02, staff in charge of measurement for SO_4^{2-} was “A”. Relationship between staff number and flagged data could not be identified.

Table 2.13 Staff in charge of measurement

Lab.ID	Total	pH	EC	$SO4^{2-}$	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	3	A	A	B	B	B	C	C	C	C	C
CN01	1	A	A	A	A	A	A	A	A	A	A
CN02	2	A	A	B	B	B	B	B	B	B	B
CN03	1	A	A	A	A	A	A	A	A	A	A
CN04	1	A	A	A	A	A	A	A	A	A	A
ID01	2	A	A	A	A	A	B	B	B	B	B
ID02	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	*										
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	B	B	B	B	A	A	A	A	A
MM01	2	A	B								
PH01	3	A	A	B	B	B	C	C	C	C	A
PH02	1	A	A								
KR01	1	A	A	A	A	A	A	A	A	A	A
RU01	3	A	A	B	B	B	C	C	C	C	C
RU02	3	A	A	A	B	B	C	C	C	C	A
TH01	2	A	B	B	B	B	A	A	A	A	A
TH02	1	A	A	A	A	A	A	A	A	A	A
TH04	1	A	A								
TH05	2	A	A	B	B	B	B	B	B	B	B
TH06	3	A	A	B	B	B	C	C	C	C	C
VN01	2	A	A	A	A	A	B	B	B	B	B
VN02	2	A	A	B	B	B	B	B	B	B	B

Reverse mesh: Flagged data of “E” or “X” in sample No.061 and/or sample No.062.

Reverse mesh with dark are flagged data of both sample No.061 and No.062

* 2 staffs’ name was reported in LA01 data.

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

Lab.ID	Total	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	3	5	5	1	1	1	1	1	1	1	1
CN01	1	15	15	15	15	15	15	15	15	15	15
CN02	2	8	8	14	14	14	14	14	14	14	14
CN03	1	8	8	8	8	8	8	8	8	8	8
CN04	1	11	11	11	11	11	11	11	11	11	11
ID01	2	7	7	7	7	7	7	7	7	7	7
ID02	1	3	3	3	3	3	3	3	3	3	3
ID03	1	1	1	1	1	1	1	1	1	1	1
JP01	1	22	22	22	22	22	22	22	22	22	22
JP02	1	2	2	2	2	2	2	2	2	2	2
JP03	1	4	4	4	4	4	4	4	4	4	4
JP04	1	4	4	4	4	4	4	4	4	4	4
JP05	1	3	3	3	3	3	3	3	3	3	3
JP06	1	2	2	2	2	2	2	2	2	2	2
JP07	1	2	2	2	2	2	2	2	2	2	2
LA01	*	2	2	2	2	2	2	2	2	2	2
MY01	3	2	2	4	4	4	2	2	2	2	2
MN01	2	8	8	8	8	8	8	8	8	8	8
MM01	2	0.5	0.5								
PH01	3	7	7	5.5	5.5	5.5	10	10	10	10	2
PH02	1	0	0								
KR01	1	7	7	7	7	7	7	7	7	7	7
RU01	3	9	9	16	16	16	9	9	9	9	9
RU02	3	3	3	3	34	34	15	15	15	15	3
TH01	2	9	4	4	4	4	9	9	9	9	9
TH02	1	10	10	10	10	10	10	10	10	10	10
TH04	1	5	5								
TH05	2	4	4	2	2	2	2	2	2	2	2
TH06	3	5	5	7	7	7	3	3	3	3	3
VN01	2	22	22	22	22	22	13	13	13	13	13
VN02	2	2	2	2	2	2	2	2	2	2	2

Unit: year

Reverse mesh: Flagged data of “E” or “X” in sample No.061 and/or sample No.062

Reverse mesh with dark are flagged date of both sample No.061 and No.062

2.4 Comparison with past surveys

Since the beginning of EANET inter-laboratory comparison surveys have been carried out 9 times, so far and the results showing the percentages of flagged data and percentage of data that satisfied the DQOs are shown in Figure 2.17. The percentage of data that satisfied the required the DQOs increased until the 4th (2001) survey for both types of samples. The data quality may have improved due to laboratories by accumulating experiences. But on the 5th project (2002), the percentages within the DQOs in the high concentration sample and the low concentration sample decreased because the ion concentrations were set lower than that of previous years. The percentage of value that satisfied the DQOs increased again from the 6th survey (2003) to the 8th survey (2005) for the high concentration sample.

Overall, it can be conducted that for the high concentration sample, the number of data within the DQOs has increased from the first survey (1998) to the 9th survey (2006). In the case of the low concentration sample, the performance of the laboratories in the 5th to 9th survey (2002-2006) fluctuated but compared to last year has shown improvement.

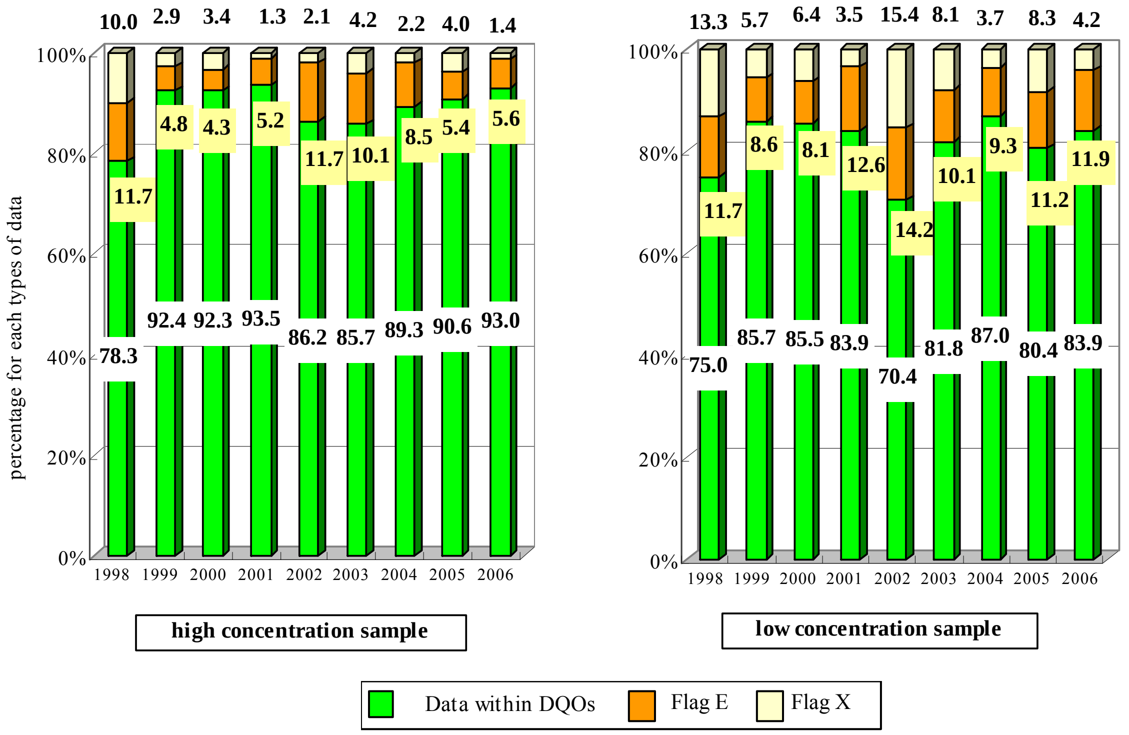


Figure 2.17 Comparison of results from the inter-laboratory comparison projects

The comparison for each parameter in inter-laboratory comparison projects on wet deposition year by year is shown in Figure 2.18. Percentage of flagged data in SO_4^{2-} has decreased. Comparing the percentage of flagged data from 2003 to 2006 with those from 1998 to 2002, percentage of data flagged “X” in result of NO_3^- and Na^+, percentages of flagged data are less than 20% between 2003 and 2006 in both concentration samples.

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

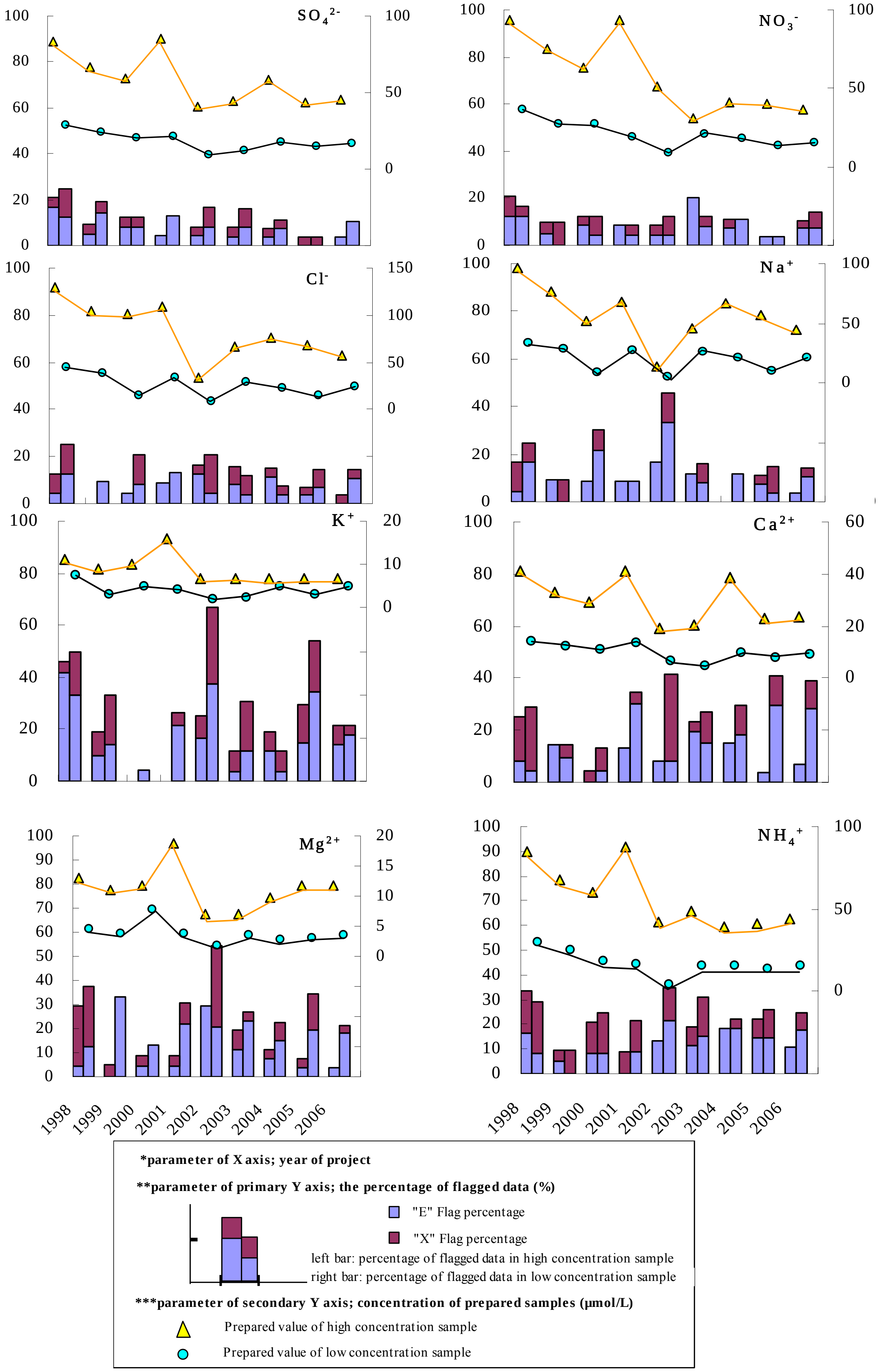


Figure 2.18 Comparison for each parameter in inter-laboratory comparison project

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

Attempt			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)
1	1998	No.1	4.05	7.94	83.5	93.3	129	95.8	11.1	41.1	13.1	84.8
		No.2	4.51	2.82	29.1	36.1	45.1	33.5	7.42	14.3	4.6	29.5
2	1999	No.1	4.14	6.38	67	75.0	104	77.0	8.9	33.0	11.0	68.0
		No.2	4.59	2.30	24.0	27.0	38.0	28.0	3.2	12.0	3.8	25.0
3	2000	No.1	4.10	6.23	59.7	63.3	101.3	51.3	9.9	29.4	11.7	60.5
		No.2	4.85	1.55	20.1	27.5	15.5	8.7	4.9	11.0	7.8	18.2
4	2001	No.11	4.10	7.45	85.0	93.3	108.4	68.4	15.8	41.1	18.7	87.8
		No.12	4.82	1.76	21.5	19.4	34.4	27.4	4.00	13.2	3.7	16.7
5	2002	No.021	4.30	3.75	40.3	51.0	33.7	13.7	6.92	19.1	7.02	42.4
		No.022	5.15	0.69	8.88	8.49	9.13	5.13	1.98	6.6	1.75	4.54
6	2003	No.031	4.52	3.44	44.7	30.9	66.0	46.1	6.9	20.5	7.0	48.3
		No.032	4.80	1.48	12.0	21.3	29.6	25.6	2.5	4.4	3.4	15.1
7	2004	No.041	4.60	3.94	58.6	41.4	76.7	66.7	6.9	38.9	9.8	39.4
		No.042	5.00	1.33	17.6	18.4	22.5	20.5	5.0	10.0	2.7	15.1
8	2005	No.051	4.66	3.32	43.7	40.3	68.5	56.5	6.9	23.2	11.7	40.9
		No.052	5.05	1.05	14.4	13.2	15.3	10.3	3.0	7.6	3.1	13.6
9	**2006**	**No.061**	**4.72**	**3.1**	**45.8**	**36.3**	**57.5**	**44.5**	**6.9**	**23.8**	**11.7**	**43.9**
		No.062	**5.15**	**1.21**	**16.9**	**15.0**	**24.5**	**20.5**	**5.0**	**9.3**	**3.5**	**15.1**

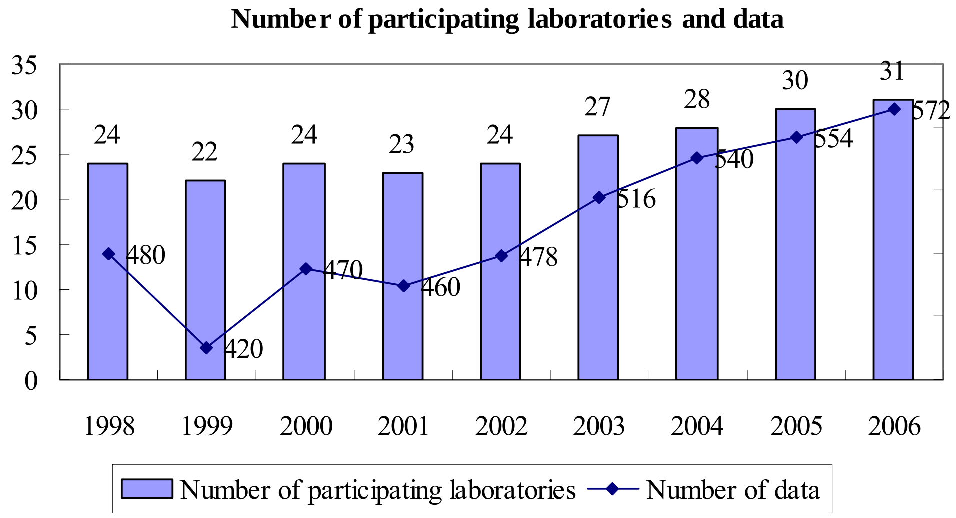


Figure. 2.19 The number of participating laboratories and data in the Inter-laboratory comparison project on wet deposition

The number of laboratories participating in the inter-laboratory comparison project on wet deposition has increased since the start of this activity (Figure 2.19). In the first survey started in 1998 only 24 laboratories from 10 countries participated in the inter-laboratory comparison project. Some countries increase the number of participating laboratories. Cambodia and Lao PDR have participated since the 6th Inter-laboratory comparison project on wet deposition in 2003 and Myanmar have participated in this survey from 2005.

2.5 Recommendations for improvements

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

2.5.1 Measurement and Analysis

1) General

- ►Clearance from contamination of the apparatus, materials and reagents used for measurement and analysis must be confirmed beforehand.
- ►Blank values of target substances should be as low as possible.
- ►Measurement and analysis should be conducted by persons who are well trained.
- ►To maintain high analytical quality, **SOPs** must be prepared for the management of apparatus, reagents, and procedure of operation.

2) Deionized water

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

3) Certified materials and certified samples

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

4) Pretreatment of samples at analytical laboratory

- ►Conductivity and pH should be measured as soon as possible after sample receiving, and checking agreement of samples and sample list.
- ►Effort should be made to start analysis of the other parameters within a week of sample arrival in the laboratory and to complete the data sets by measuring EC, pH and all other chemical parameters.

5) Calibration of analytical instruments

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

2.5.2 Evaluation of reliability

1) Sensitivity fluctuation of analytical instruments

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

For example, in Ion chromatography

- ►A new calibration should be performed not more than 30-sample measurements.
- ►Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration.

- ►Control charts should be applied for the measurement of the reference materials.
- ►Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent.
- ►If the results of the control solutions are outside of 3 standard deviations, or out of 15 % from the expected value, the reasons should be found and corrections should be made, and reference solution should be measured again.
- ►If the retention time changes slowly while the separator column is deteriorating, then adequate actions should be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.

2.5.3 Data control

1) Data checks by the analytical laboratories

- ►When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the percentage of a theoretical value to that for determined data in ion balances and electrical conductivity is significantly different from 1.0, measurement should be repeated since reliability is low.
- ►When samples seem to be obviously contaminated, these data should be treated as unrecorded data.
- ►Abnormal or unrecorded data can corrupt research results. So, careful checks are needed to avoid data of questionable quality. When abnormal or unrecorded data is detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

References

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

2) Technical Documents for Wet Deposition Monitoring in East Asia
- Technical Manual for Wet Deposition Monitoring in East Asia
- Quality Assurance / Quality Control (QA/QC) Program for the Preparatory-Phase Wet Deposition Monitoring in East Asia adopted at Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, March 2000.

3) Report of the Inter-laboratory Comparison Project 1998
(Round robin analysis survey 1st Attempt) November 1999.

4) Report of the Inter-laboratory Comparison Project 1999
(Round robin analysis survey 2nd Attempt) October 2000

5) Report of the Inter-laboratory Comparison Project 2000 on Wet Deposition (3rd Attempt) October 2001

6) Report of the Inter-laboratory Comparison Project 2001 on Wet Deposition (4th Attempt) November 2002

7) Report of the Inter-laboratory Comparison Project 2002 on Wet Deposition (5th Attempt) November 2003

8) Report of the Inter-laboratory Comparison Project 2003 on Wet Deposition (6th Attempt) November 2004

9) Report of the Inter-laboratory Comparison Project 2004 on Wet Deposition (7th Attempt) November 2005

10) Report of the Inter-laboratory Comparison Project 2005 on Wet Deposition (8th Attempt) November 2006

Appendix 2-1 List of Participating laboratories

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

PHILIPPINES

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

REPUBLIC OF KOREA

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

RUSSIA

23) Limnological Institute of the Russian Academy of Sciences/Siberian Branch (RAS/SB)	**(RU01)**
24) Primorskii Environmental Monitoring Center of Roshydromet (Laboratory for Monitoring of Atmosphere and Soil Pollution)	**(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) Institute of Meteorology and Hydrology (IMH), Hydrometeorological Service of Viet Nam (HMS)	**(VN01)**
31) Middle of Central Regional Hydro-Meteorological Observatory National Hydro -Meteorological Center (NHMS)	**(VN02)**

OTHER LABORATORIES

32) Indian Institute of Chemical Technology (IICT)	**(IN01)**
33) Institute of Minerals & Materials Technology (formerly RRL) Bhubaneswar (IIMT)	**(IN03)**
34) Stockholm University	**(SE01)**

Appendix 2-2 Results submitted by the laboratories

Sample No.061 (high concentrations)

	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	2.20	48.0	38.0	59.3	43.6	6.7	23.7	11.6	44.2
CN01	4.70	2.90	46.6	35.3	62.5	41.7	6.4	26.4	11.7	38.3
CN02	4.73	2.97	47.5	38.0	60.8	45.0	6.0	30.2	12.2	38.6
CN03	4.74	2.96	47.9	36.5	58.4	44.7	6.6	25.8	11.2	42.9
CN04	4.87	2.82	46.5	36.9	58.7	42.9	7.0	27.4	12.0	42.9
ID01	4.65	3.00	44.3	34.2	56.0	48.0	7.1	26.1	12.9	44.9
ID02	4.76	2.90	49.9	26.6	56.9	45.6	9.8	21.8	11.4	45.0
ID03	5.04	2.60	41.2	32.5	56.5	46.9	6.2	23.8	11.7	56.4
JP01	4.73	3.00	46.4	36.9	58.8	46.2	7.3	24.1	11.4	45.7
JP02	4.73	3.10	45.2	35.0	56.4	43.5	6.9	24.0	11.5	42.7
JP03	4.80	3.02	45.8	35.8	57.2	44.0	6.8	23.6	11.8	44.0
JP04	4.76	3.01	46.9	37.0	58.2	41.8	6.4	23.5	11.4	42.9
JP05	4.81	2.94	42.8	34.7	50.8	43.6	6.7	23.4	11.7	43.4
JP06	4.78	3.05	45.5	36.8	56.2	45.8	7.1	24.5	11.9	41.5
JP07	4.83	2.96	48.7	38.1	59.3	46.0	6.9	24.8	11.8	45.4
LA01	5.10	2.72	32.5	24.9	37.2	48.0	8.1	26.9	12.8	55.1
MY01	4.62	2.77	47.7	38.3	60.6	42.8	6.4	23.4	11.0	43.7
MN01	4.92	2.94	44.9	34.5	54.6	46.2	10.6	26.6	13.9	49.7
MM01	4.71	2.74								
PH01	4.81	2.99	44.7	35.3	55.2	43.9	5.8	25.0	10.8	40.8
PH02	4.69	2.84								
KR01	4.51	3.00	45.8	30.7	59.7	42.3	6.1	21.1	10.6	44.9
RU01	4.62	3.11	45.8	36.3	57.5	45.2	7.0	23.4	11.6	42.8
RU02	4.74	3.14	46.0	39.0	56.0	48.0	6.9	23.5	11.0	43.8
TH01	4.77	3.04	46.2	35.7	56.8	45.0	7.0	24.9	12.0	44.7
TH02	4.72	3.05	43.6	35.2	55.6	44.9	6.5	23.8	11.5	43.4
TH04	4.75	3.14								
TH05	4.76	2.92	44.5	35.9	57.0	40.2	6.4	23.7	10.5	37.5
TH06	4.75	3.08	44.3	34.6	54.3	42.7	5.4	25.0	12.3	53.5
VN01	4.70	3.11	49.0	37.2	64.3	44.5	6.7	22.6	10.9	44.8
VN02	4.72	2.99	45.2	32.9	55.1	33.9	5.8	21.9	11.0	41.6
IN01	4.80	2.89	46.8	43.9	50.9	41.6	7.5	26.6	8.9	35.6
IN03	4.57	2.88	40.4	31.7	55.2	54.5	9.0	28.1	12.5	45.0
SE01	4.69	2.88	45.2	35.8	57.2	44.1	7.2	23.0	11.4	42.9
Prepared value	**4.72**	**3.10**	**45.8**	**36.3**	**57.5**	**44.5**	**6.9**	**23.8**	**11.7**	**43.9**
Data count	34	34	31	31	31	31	31	31	31	31
Average	4.77	2.93	45.3	35.3	56.6	44.4	7.0	24.6	11.6	44.1
Minimum	4.51	2.20	32.5	24.9	37.2	33.9	5.4	21.1	8.9	35.6
Maximum	5.21	3.14	49.9	43.9	64.3	54.5	10.6	30.2	13.9	56.4
Standard deviation	0.14	0.18	3.11	3.46	4.51	3.25	1.08	1.94	0.85	4.45

Sample No.062 (low concentrations)

	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	5.48	1.74	17.6	15.7	25.1	20.4	4.8	9.3	3.5	16.9
CN01	5.20	1.20	17.6	16.2	27.8	21.7	4.3	12.5	4.1	11.5
CN02	5.15	1.20	19.2	17.1	27.1	24.3	4.8	19.2	4.7	13.5
CN03	5.15	1.28	20.3	15.9	27.0	23.2	4.9	12.5	3.7	14.0
CN04	5.12	1.20	17.0	15.2	26.0	20.9	4.9	11.8	3.6	14.9
ID01	5.07	1.34	16.3	14.4	22.4	24.6	5.2	11.6	3.9	16.7
ID02	5.26	1.15	18.3	9.6	18.9	18.8	5.9	7.7	3.6	11.4
ID03	5.38	1.05	15.0	13.1	23.3	20.9	4.9	9.1	3.4	20.4
JP01	5.22	1.20	16.9	15.0	24.9	21.3	4.7	8.0	2.9	15.8
JP02	5.07	1.22	17.2	15.1	24.9	20.2	4.9	10.3	3.7	14.6
JP03	5.21	1.21	16.8	14.6	24.4	20.2	4.9	9.4	3.5	15.5
JP04	5.13	1.23	17.1	15.1	24.2	19.5	4.6	9.7	3.3	15.2
JP05	5.23	1.22	16.7	14.8	24.9	22.6	4.9	9.2	3.4	15.2
JP06	5.20	1.23	16.5	14.8	24.2	21.1	5.0	9.5	3.6	15.2
JP07	5.25	1.18	17.8	15.6	24.9	21.4	5.1	10.0	3.5	15.2
LA01	5.70	1.15	12.0	10.1	16.0	23.9	5.7	11.3	4.2	20.0
MY01	4.97	1.11	17.7	16.3	27.6	19.9	4.7	9.2	3.1	15.4
MN01	5.16	1.21	17.0	14.7	25.0	21.0	5.6	11.9	4.4	17.6
MM01	5.11	1.18								
PH01	5.26	1.17	16.1	14.0	23.7	19.9	3.9	11.5	3.3	12.8
PH02	5.10	1.12								
KR01	5.21	1.04	15.0	12.2	19.9	20.0	2.6	8.0	3.1	15.5
RU01	5.00	1.25	16.7	14.4	25.2	20.6	4.7	9.2	3.2	15.1
RU02	5.07	1.25	17.0	15.2	23.0	19.6	4.5	9.6	3.1	16.1
TH01	5.18	1.22	15.8	14.0	23.6	21.2	5.2	10.0	3.8	15.6
TH02	5.13	1.17	16.0	14.2	23.7	20.8	4.6	9.0	3.3	16.9
TH04	5.12	1.24								
TH05	5.31	1.18	16.3	15.1	24.6	19.2	4.5	10.7	3.6	12.1
TH06	5.10	1.29	16.2	14.0	23.0	18.6	3.7	10.1	4.1	17.1
VN01	5.13	1.24	18.2	15.6	28.9	20.8	5.4	10.8	3.8	14.6
VN02	5.16	1.18	13.8	11.7	22.5	13.8	3.5	9.0	3.4	14.8
IN01	5.25	1.47	17.9	17.3	20.4	25.4	5.1	11.2	3.1	9.2
IN03	4.96	1.19	14.5	12.8	24.2	28.3	6.1	13.4	3.9	15.5
SE01	5.05	1.16	16.5	14.7	24.1	20.1	4.8	9.1	3.4	15.2
Prepared value	**5.15**	**1.21**	**16.9**	**15.0**	**24.5**	**20.5**	**4.9**	**9.3**	**3.5**	**15.1**
Data count	34	34	31	31	31	31	31	31	31	31
Average	5.18	1.22	16.7	14.5	24.0	21.1	4.8	10.4	3.6	15.1
Minimum	4.96	1.04	12.0	9.6	16.0	13.8	2.6	7.7	2.9	9.2
Maximum	5.70	1.74	20.3	17.3	28.9	28.3	6.1	19.2	4.7	20.4
Standard deviation	0.14	0.12	1.54	1.72	2.59	2.47	0.68	2.12	0.41	2.23

Appendix 2-3 Normalized Data

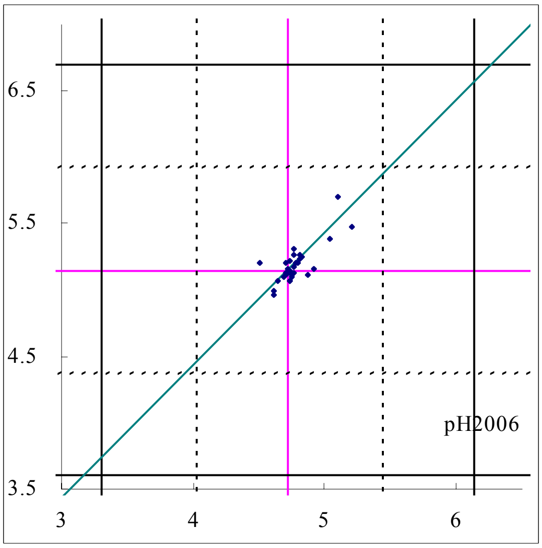
Deviation from prepared value (Va/Vp): {Average (Va) / Prepared value (Vp) - 1} x 100 (%)

Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	110.4	71.0	104.8	104.7	103.1	98.0	97.1	99.6	99.1	100.7
CN01	99.6	93.5	101.7	97.2	108.7	93.7	92.8	110.9	100.0	87.2
CN02	100.2	95.8	103.7	104.7	105.7	101.1	87.0	126.9	104.3	87.9
CN03	100.4	95.5	104.6	100.6	101.6	100.4	95.7	108.4	95.7	97.7
CN04	103.2	91.0	101.5	101.7	102.1	96.4	101.4	115.1	102.6	97.7
ID01	98.5	96.8	96.7	94.2	97.4	107.9	102.9	109.7	110.3	102.3
ID02	100.8	93.5	109.0	73.3	99.0	102.5	142.0	91.6	97.4	102.5
ID03	106.8	83.9	90.0	89.5	98.3	105.4	89.9	100.0	100.0	128.5
JP01	100.2	96.8	101.3	101.7	102.3	103.8	105.8	101.3	97.4	104.1
JP02	100.2	100.0	98.7	96.4	98.1	97.8	100.0	100.8	98.3	97.3
JP03	101.7	97.4	100.0	98.6	99.5	98.9	98.6	99.2	100.9	100.2
JP04	100.8	97.1	102.4	101.9	101.2	93.9	92.8	98.7	97.4	97.7
JP05	101.9	94.8	93.4	95.6	88.3	98.0	97.0	98.3	100.0	98.9
JP06	101.3	98.4	99.3	101.4	97.7	102.9	102.9	102.9	101.7	94.5
JP07	102.3	95.5	106.3	105.0	103.1	103.4	100.0	104.2	100.9	103.4
LA01	108.1	87.7	71.0	68.6	64.7	107.9	117.4	113.0	109.4	125.5
MY01	97.9	89.4	104.1	105.5	105.4	96.2	92.8	98.3	94.0	99.5
MN01	104.2	94.8	98.0	95.0	95.0	103.8	153.6	111.8	118.8	113.2
MM01	99.8	88.4								
PH01	101.9	96.5	97.6	97.2	96.0	98.7	84.1	105.0	92.3	92.9
PH02	99.4	91.6								
KR01	95.6	96.8	100.0	84.6	103.8	95.1	88.0	88.7	90.6	102.3
RU01	97.9	100.3	100.0	100.0	100.0	101.6	101.4	98.3	99.1	97.5
RU02	100.4	101.3	100.4	107.4	97.4	107.9	100.0	98.7	94.0	99.8
TH01	101.1	98.1	100.9	98.3	98.8	101.1	101.4	104.6	102.6	101.8
TH02	100.0	98.4	95.2	97.0	96.7	100.9	94.2	100.0	98.3	98.9
TH04	100.6	101.3								
TH05	100.8	94.2	97.2	98.9	99.1	90.3	92.8	99.6	89.7	85.4
TH06	100.6	99.4	96.7	95.3	94.4	96.0	78.3	105.0	105.1	121.9
VN01	99.6	100.3	107.0	102.5	111.8	100.0	97.1	95.0	93.2	102.1
VN02	100.0	96.5	98.7	90.6	95.8	76.2	84.1	92.0	94.0	94.8
IN01	101.7	93.2	102.3	120.9	88.5	93.5	107.9	111.5	76.4	81.0
IN03	96.7	93.0	88.4	87.3	96.0	122.6	129.6	117.8	106.9	102.5
SE01	99.3	92.9	98.8	98.6	99.5	99.1	104.0	96.6	97.4	97.7
Minimum	95.6	71.0	71.0	68.6	64.7	76.2	78.3	88.7	76.4	81.0
Maximum	110.4	101.3	109.0	120.9	111.8	122.6	153.6	126.9	118.8	128.5
Average	101.0	94.6	99.0	97.2	98.4	99.8	101.0	103.3	99.0	100.6

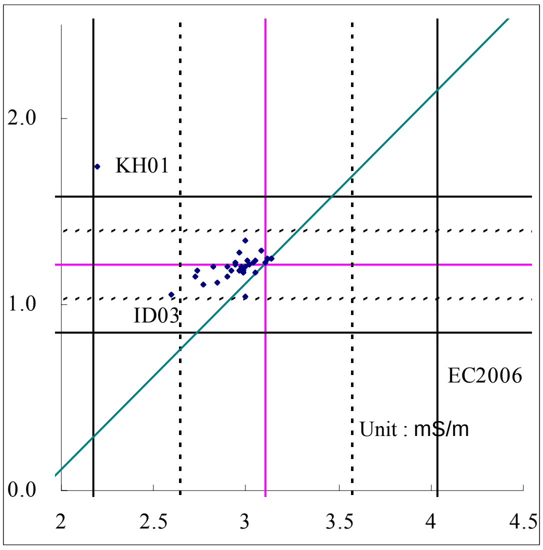
Lab. ID	pH	EC	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
KH01	106.4	143.8	104.1	104.7	102.4	99.5	98.0	100.0	100.0	111.9
CN01	101.0	99.2	104.1	108.0	113.5	105.9	87.8	134.4	117.1	76.2
CN02	100.0	99.2	113.6	114.0	110.6	118.5	98.0	206.5	134.3	89.4
CN03	100.0	105.8	120.1	106.0	110.2	113.2	100.0	134.4	105.7	92.7
CN04	99.4	99.2	100.6	101.3	106.1	102.0	100.0	126.9	102.9	98.7
ID01	98.4	110.7	96.4	96.0	91.4	120.0	106.1	124.7	111.4	110.6
ID02	102.1	95.0	108.3	64.0	77.1	91.7	120.4	82.8	102.9	75.5
ID03	104.5	86.8	88.8	87.3	95.1	102.0	100.0	97.8	97.1	135.1
JP01	101.4	99.2	100.0	100.0	101.6	103.9	95.9	86.0	82.9	104.6
JP02	98.4	100.8	101.8	100.7	101.6	98.5	100.0	110.8	105.7	96.7
JP03	101.2	100.0	99.4	97.3	99.6	98.5	100.0	101.1	100.0	102.6
JP04	99.6	101.7	101.2	100.7	98.8	95.1	93.9	104.3	94.3	100.7
JP05	101.6	100.8	98.8	98.7	101.6	110.2	99.2	98.9	97.1	100.7
JP06	101.0	101.7	97.6	98.7	98.8	102.9	102.0	102.2	102.9	100.7
JP07	101.9	97.5	105.3	104.0	101.6	104.4	104.1	107.5	100.0	100.7
LA01	110.7	95.0	71.0	67.3	65.3	116.6	116.3	121.5	120.0	132.5
MY01	96.5	91.7	104.7	108.7	112.7	97.1	95.9	98.9	88.6	102.0
MN01	100.2	100.0	100.6	98.0	102.0	102.4	114.3	128.0	125.7	116.6
MM01	99.2	97.5								
PH01	102.1	96.7	95.3	93.3	96.7	97.1	79.6	123.7	94.3	84.8
PH02	99.0	92.6								
KR01	101.2	86.0	88.8	81.3	81.2	97.6	53.1	85.7	88.6	102.6
RU01	97.1	103.3	98.8	96.0	102.9	100.5	95.9	98.9	91.4	100.0
RU02	98.4	103.3	100.6	101.3	93.9	95.6	91.8	103.2	88.6	106.6
TH01	100.6	100.8	93.5	93.3	96.3	103.4	106.1	107.5	108.6	103.3
TH02	99.6	96.7	94.7	94.7	96.7	101.5	93.9	96.8	94.3	111.9
TH04	99.4	102.5								
TH05	103.1	97.5	96.4	100.7	100.4	93.7	91.8	115.1	102.9	80.1
TH06	99.0	106.6	95.9	93.3	93.9	90.7	75.5	108.6	117.1	113.2
VN01	99.6	102.5	107.7	104.0	118.0	101.5	110.2	116.1	108.6	96.7
VN02	100.2	97.5	81.7	78.0	91.8	67.3	71.4	96.8	97.1	98.0
IN01	101.9	121.8	106.1	115.4	83.3	123.7	103.8	120.6	89.0	60.6
IN03	96.4	98.2	85.8	85.3	98.6	138.1	124.6	143.6	111.4	102.5
SE01	98.1	95.9	97.6	98.0	98.4	98.0	98.0	97.8	97.1	100.7
Minimum	96.4	86.0	71.0	64.0	65.3	67.3	53.1	82.8	82.9	60.6
Maximum	110.7	143.8	120.1	115.4	118.0	138.1	124.6	206.5	134.3	135.1
Average	100.6	100.8	98.7	96.5	98.1	102.9	97.7	112.3	102.5	100.3

Appendix 2-4 Scatter Diagrams

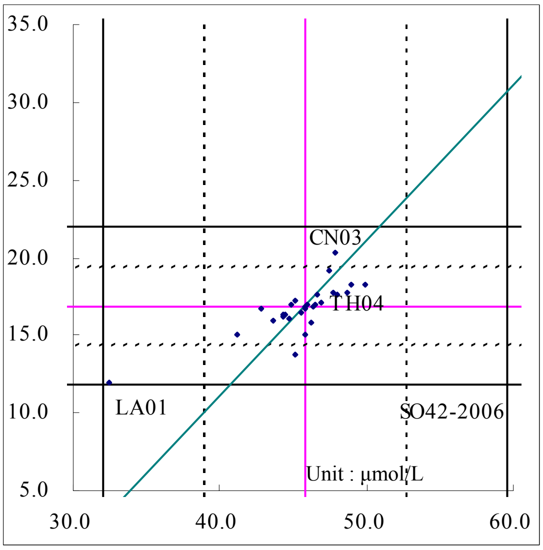
Dotted line depicts the concentration value of DQOs (15%) and solid line depicts the concentration value, which are twice the DQOs in each sample.



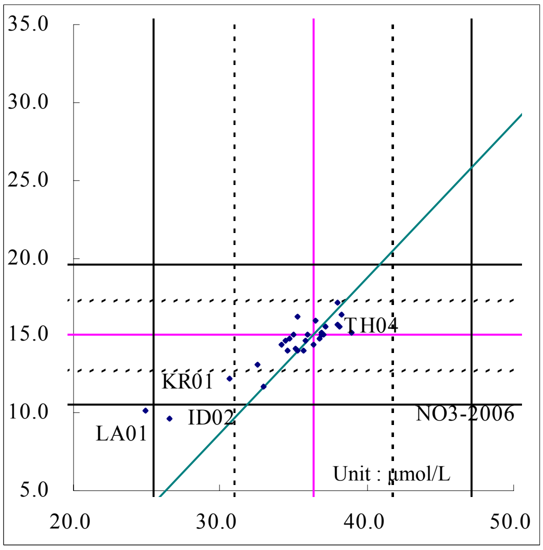
(i) Scatter diagram for pH



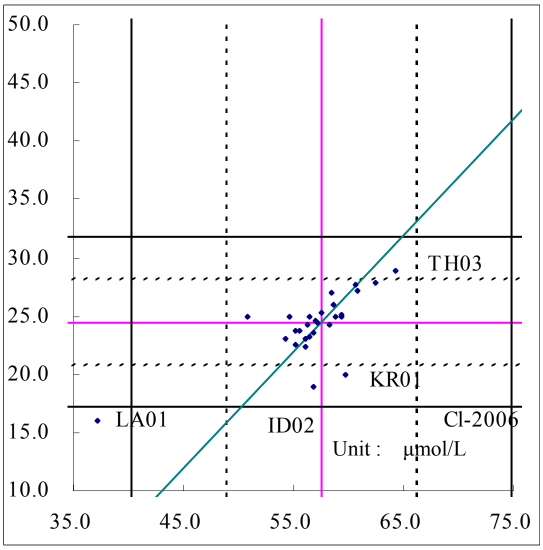
(ii) Scatter diagram for EC



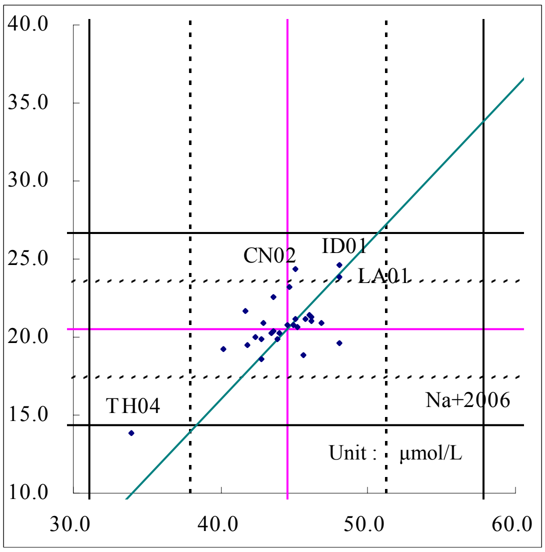
(iii) Scatter diagram for SO_4^{2-}



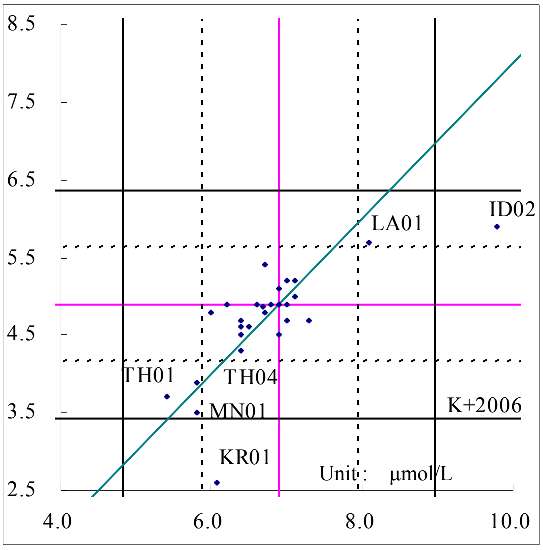
(iv)Scatter diagram for NO_3^-

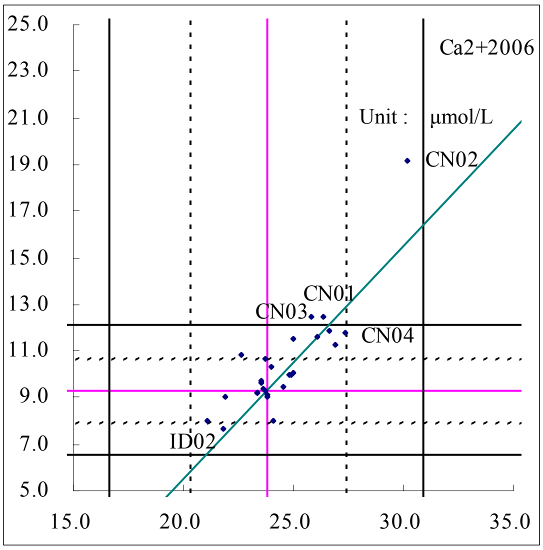


(v) Scatter diagram for Cl$^-$



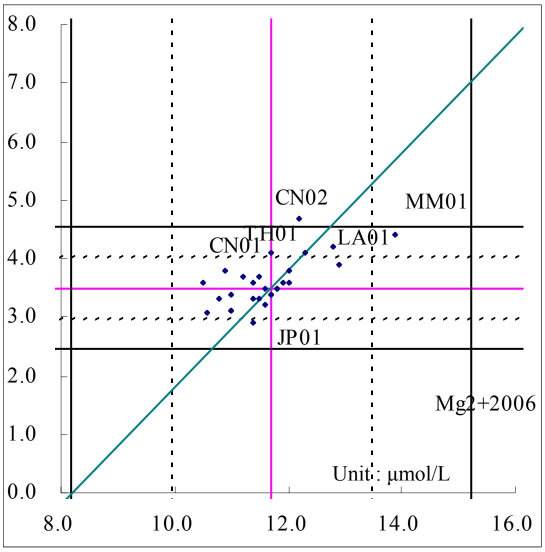
(vi) Scatter diagram for Na$^+$

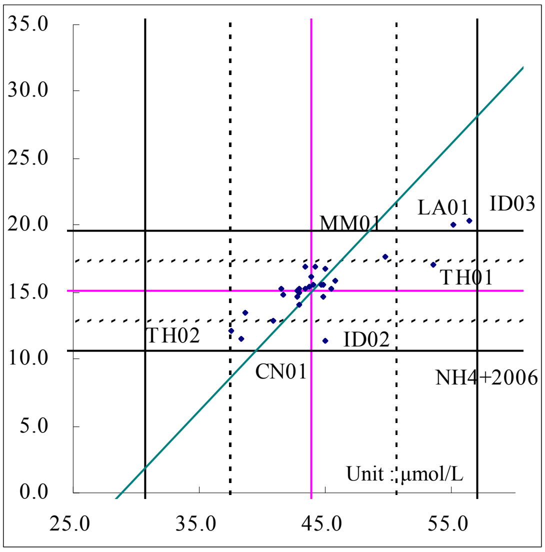




(vii) Scatter diagram for K$^+$

(viii) Scatter diagram for Ca^{2+}





(ix) Scatter diagram for Mg^{2+}

(x)Scatter diagram for NH$_4^+$

Appendix 2-5   Youden Diagrams

Method

The formula for Z-score calculations is as follows:

$$Z = (X - Q_2) / NIQR$$

where   X :   result obtained by the laboratory

Q2 :   Median result

NIQR (normalized inter quartile range) = IQR * 0.7413

IQR (inter quartile range) = (Q3 - Q1)

where   Q1: The result corresponding to the first quartile.

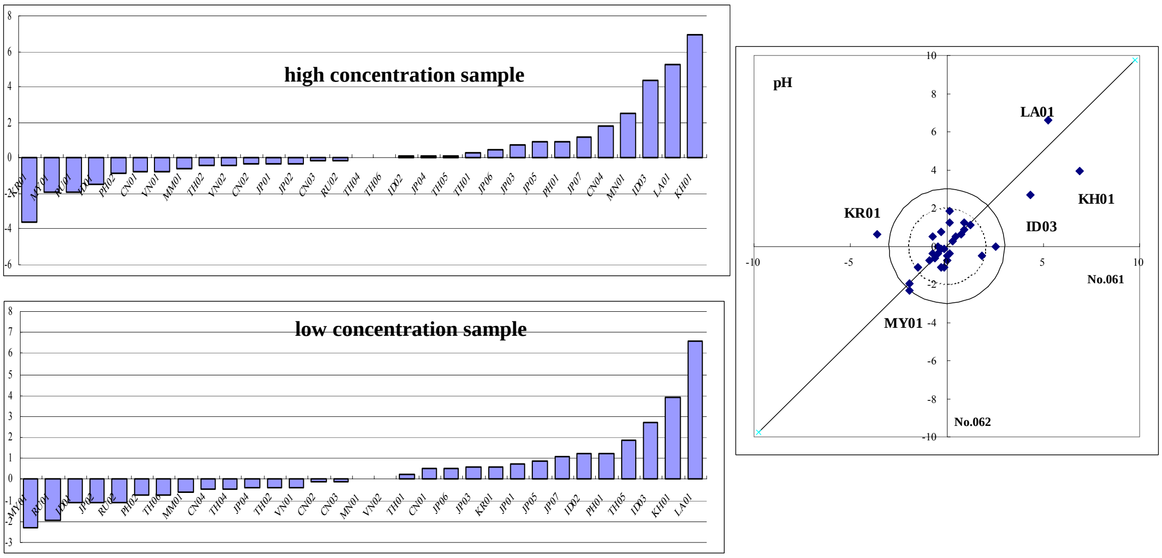
(First 25% when ranked in order)

Q3: The result corresponding to the 3rd quartile.

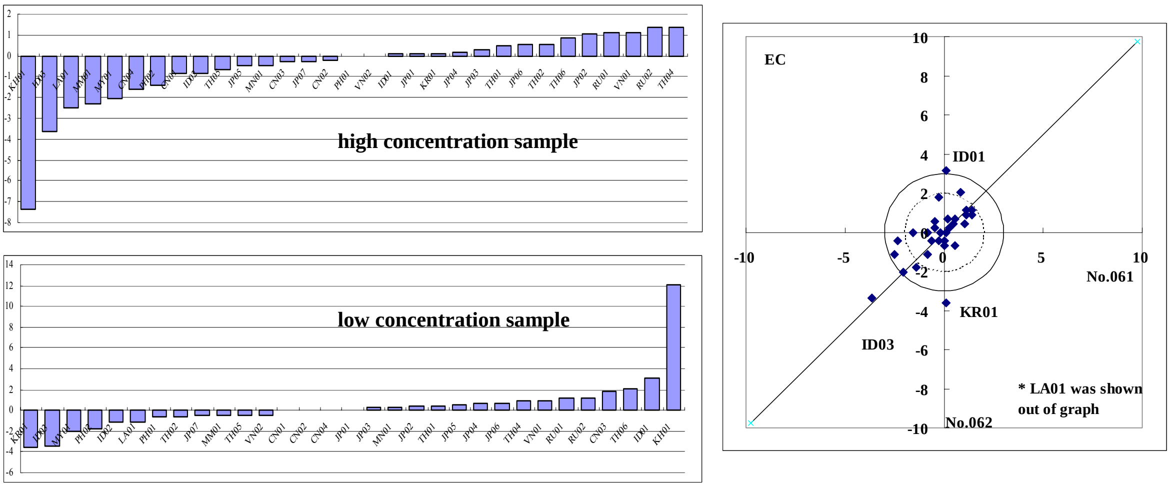
(First 75% when ranked in order)

A score is given to each laboratory which describes how close it is to the consensus result. The best Z-score is zero. The further from zero the Z-score is, the worse the result.

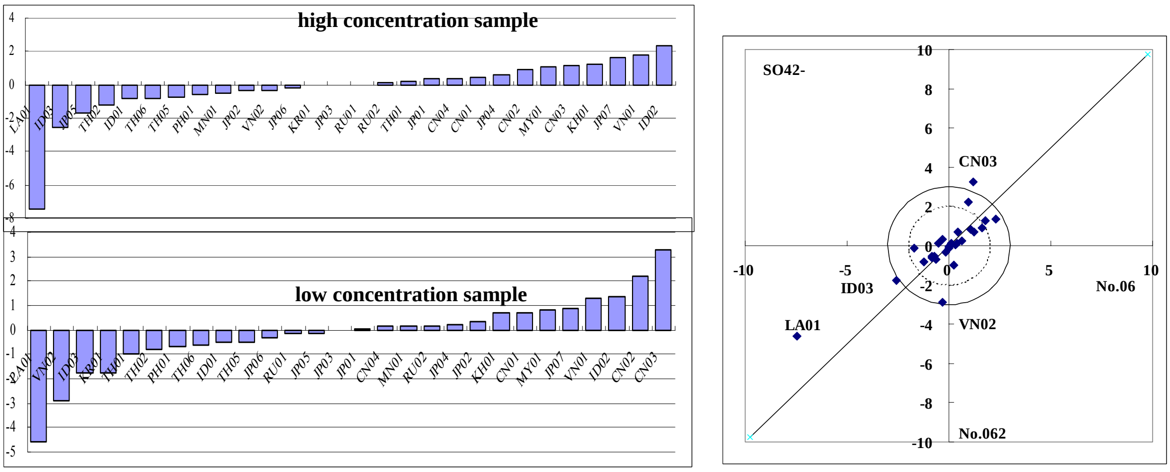
Generally, a Z-score less than 1.0 from zero is excellent, up to 2.0 is acceptable. Z-scores greater than 3.0 from zero are considered to be unacceptable and corrective action should be taken.



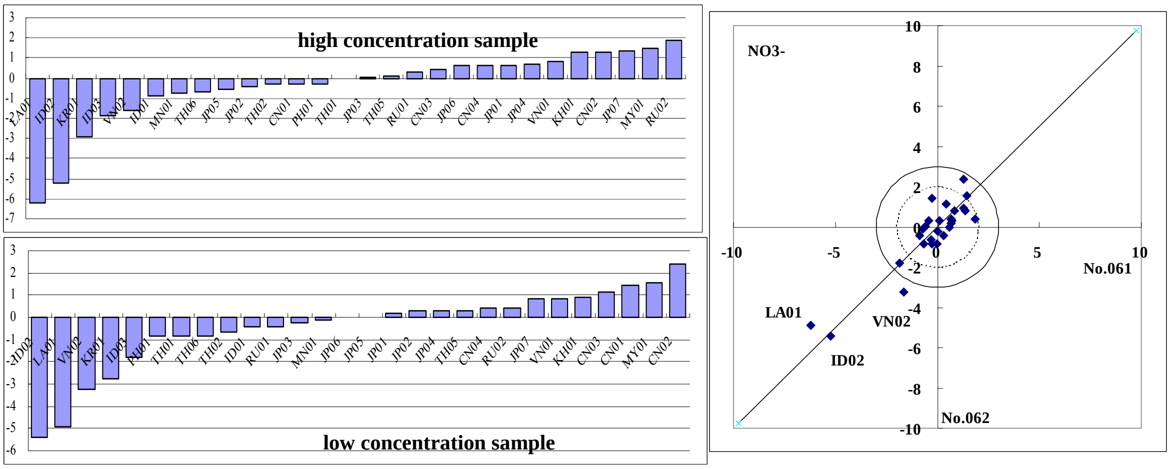
(a)   Distribution of Z-score and Youden diagram for pH



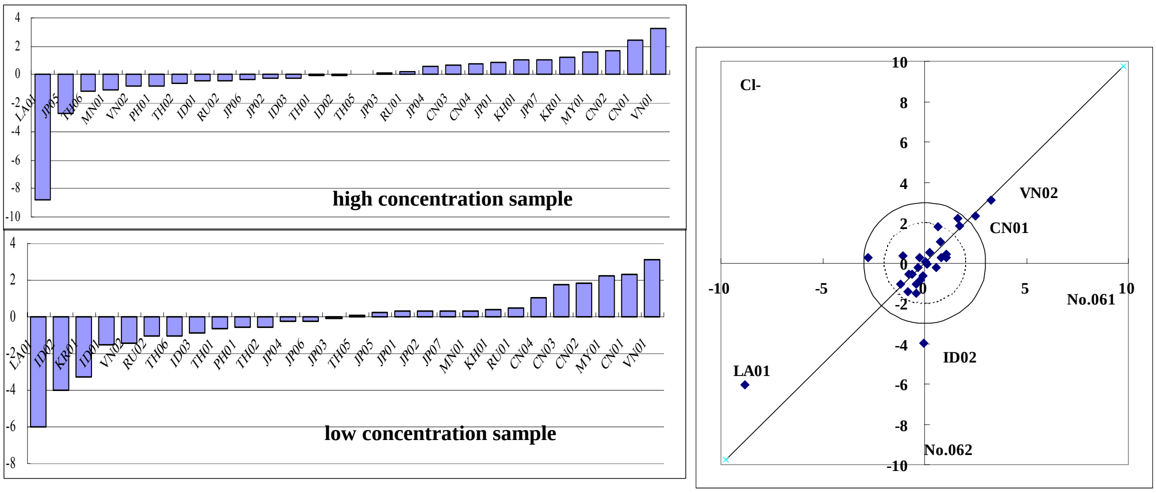
(b) Distribution of Z-score and Youden diagram for EC



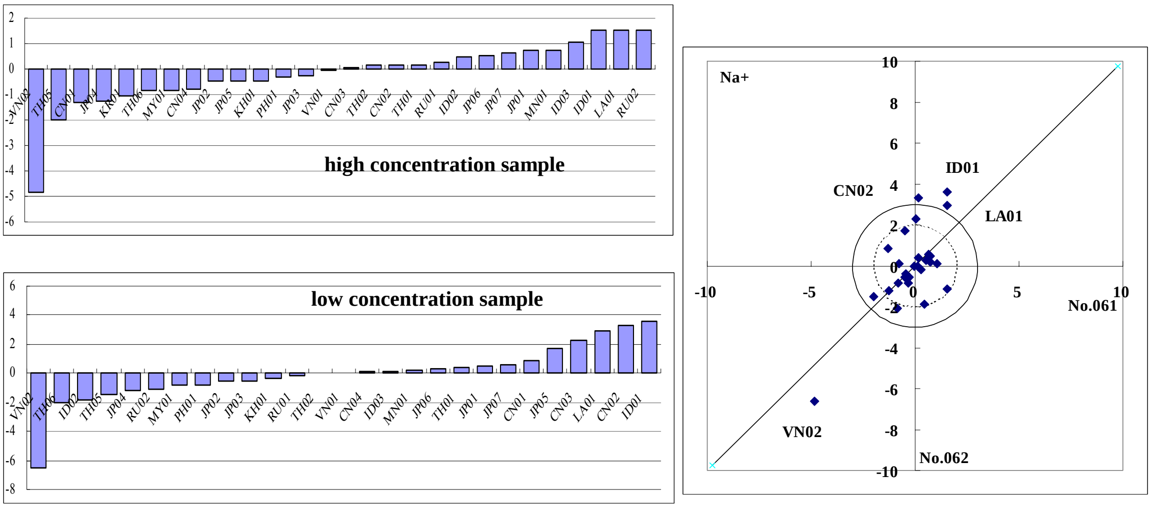
(c) Distribution of Z-score and Youden diagram for SO_4^{2-}



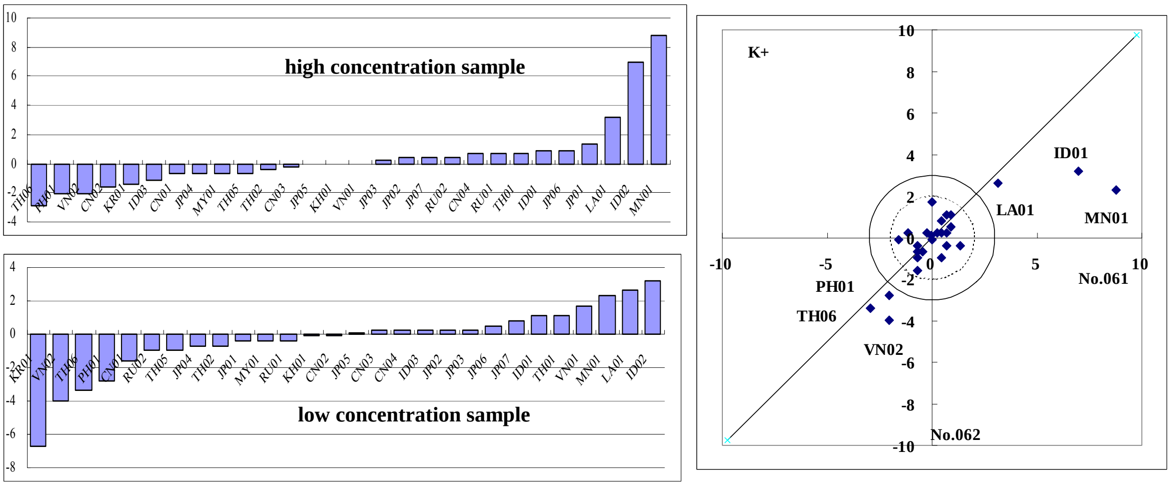
(d) Distribution of Z-score and Youden diagram for NO_3^-



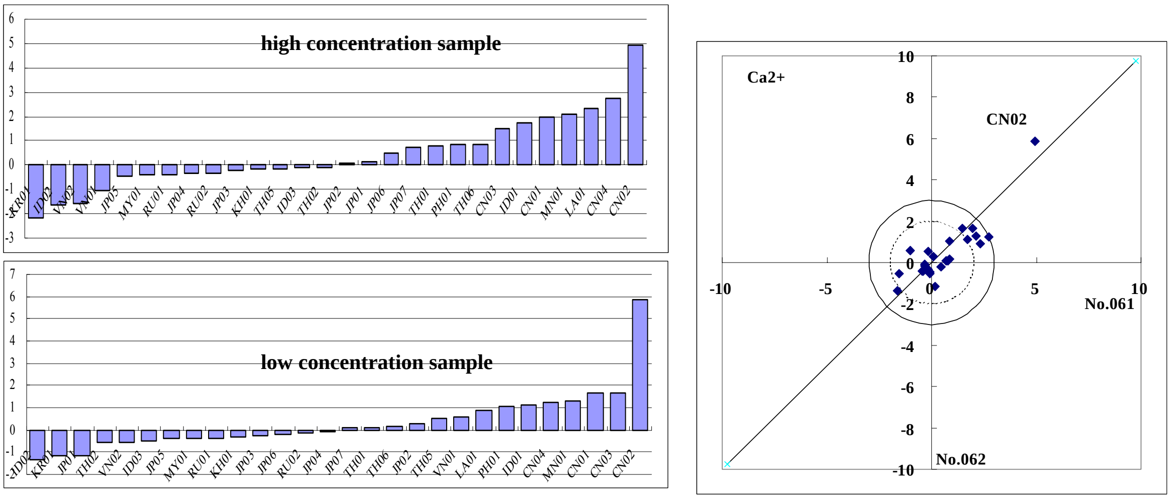
(e) Distribution of Z-score and Youden diagram for Cl^-



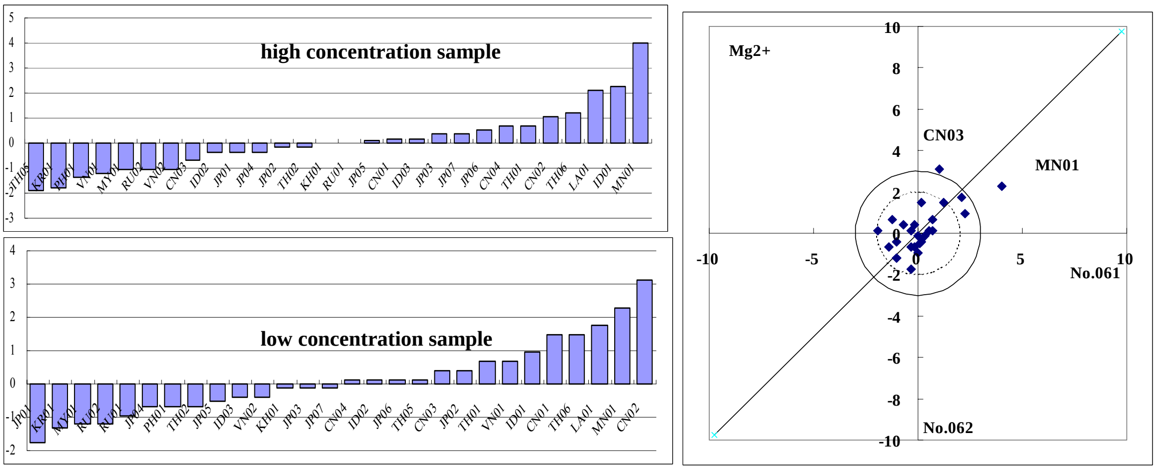
(f) Distribution of Z-score and Youden diagram for Na^+



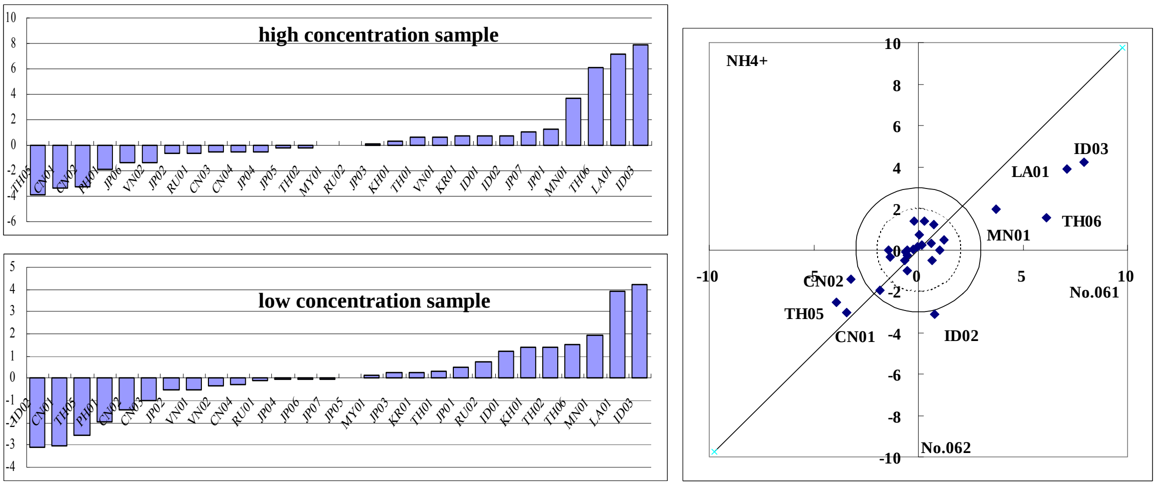
(g) Distribution of Z-score and Youden diagram for K^+



(h) Distribution of Z-score and Youden diagram for Ca^{2+}



(i) Distribution of Z-score and Youden diagram for Mg^{2+}



(j) Distribution of Z-score and Youden diagram for NH_4^+

3. 2nd INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

3.1 Introduction

In the 2nd inter-laboratory comparison for dry deposition, impregnated filters which contain three ions, SO_4^{2-}, Cl^-, and NH_4^+, were prepared and distributed to the participating laboratories by the Network Center (NC) in November 2006. Most of the laboratories participating in EANET activities joined this activity and submitted their analytical results to NC. Obtained results for the amount of SO_4^{2-}, Cl^-, and NH_4^+ on the distributed filters were compared with the prepared values and statistically treated.

3.2 Procedures

3.2.1 Participating Laboratories

Nineteen laboratories in charge of chemical analysis in 10 countries of EANET participated in the second attempt. NC shipped the sample filters to all of these laboratories in 10 countries, and almost all of them submitted their analytical results to NC. 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.061-1	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.061-2	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.062-1	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.062-2	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.063-1	Alkali-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by K_2CO_3
No.063-2	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.061-1, No.062-1, No.063-1, 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.061-2, No.062-2, No.063-2, pour exactly 20 mL deionized water into the centrifuging tube, then shake or vibrate the tubes during 20 minutes for the extractions using shaker or ultrasonic bath.
(3) Filter the insoluble matters out of the extracted solutions using a membrane filter (pore size 0.45μm) previously well washed by pure water (more than 100mL).

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

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

Table 3.2 Analytical methods specified in the Technical Document

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

3.2.5 Data Checking Procedures

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

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

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

The net values of absolute amount should be calculated by:

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

where $M_{sol,\ Sample}$: the net amount (μg) of each component in the extracting solution from the sample filters, No.061-1,No.061-2,No.062-1 and No.062-2;
$M_{sol,\ Blank}$: the averaged net amount (μg) in the extracting solutions from the blank filters, No.063-1 and No.063-2.

3.3 Results

NC distributed the sample filters to 19 laboratories in the participating countries of EANET, and received the data on analytical results. Outline of the submitted results are summarized in Table 3.3. Statistics such as Average, Minimum (Min.), Maximum (Max.), Standard deviation (S.D.) and Number of data (N) were calculated for each analyzed ion. Outlying result which was apart from the average greater than a factor of 3 of S.D. was not included for this statistical calculation. Statistics summary of every result is described in *Appendix 3.2*. As shown in Table 3.3, averages of submitted results were fairly well agreed with the prepared values within a range from -8.1% (SO_4^{2-}) to -1.8% (Cl^-) for Sample No.061 (low amount), and from -4.5% (Cl^-) to 0.9% (NH_4^+) for Sample No.062 (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.061 (low amount) and No.062 (high amount); ii) Individual parameters; iii) Circumstances of analysis in each participating laboratory. The evaluation of results on both of Sample No.061 and No.062 is presented in “3.3.1 Comparison by Sample”. The evaluation of results for each constituent is presented in “3.3.2 Analytical Parameters”. And the evaluation of results by the circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is presented in “3.3.3 Circumstances of Sample Analysis”.

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

Constituents	Prepared * (Vp)	Average (Va)	ΔV/Vp * (%)	S.D.	Number (N)	Min.	Max.
Sample No.061 (Low)							
SO_4^{2-} (μg)	40.0	38.1	-4.8	2.76	20	33.4	44.9
Cl^-(μg)	3.50	3.07	-12.3	0.84	19	0.85	5.22
NH_4^+(μg)	6.50	6.54	0.6	1.19	20	5.07	9.58
Sample No.062 (High)							
SO_4^{2-}(μg)	140	137	-2.2	4.11	20	129.9	144.6
Cl^-(μg)	40.0	38.2	-4.6	3.55	19	29.2	48.7
NH_4^+(μg)	50.0	49.5	-0.9	9.53	20	19.3	70.9

* 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.061 (low amount), 13 analytical data in 59 submitted results exceeded the DQOs (±15%) by a factor of 2 (±30%) and were flagged by "E". Also 5 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". A number of flagged data was 18 and the ratio of the flagged data was about 30.5 percents in total for Sample No.061 (Figure 3.2). Result of SO_4^{2-} has no flags of "X". (Table 3.4 and 3.5)

Table 3.4 Number of flagged data for Sample No.061 (low amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	1	6	6	13
Flag X *	0	3	2	5
Data within DQOs	19	10	12	41
Ratio of Flagged (%)	5.0	47.4	40.0	30.5

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

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

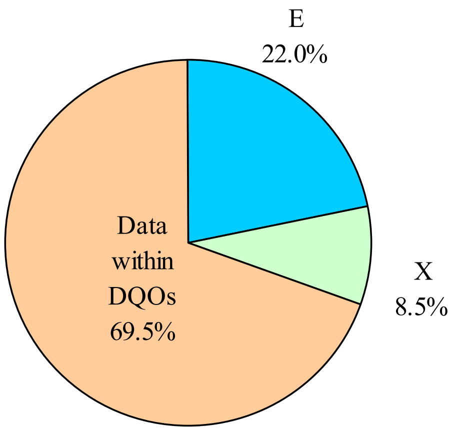


Figure 3.2 Percentage of flagged data for Sample No.061 (low amount)

Table 3.5 Averaged analytical results of Sample No.061 (low amount)

Lab. Code		SO_4^{2-} (μg)		Cl^- (μg)		NH_4^+ (μg)
CN01		37.5		3.34	X	9.58
ID01		38.3	E	2.57	E	5.07
JP01		36.5	E	2.92	E	7.56
JP02		39.7		3.24		6.01
JP03		38.6	E	2.95		6.10
JP04		40.3		3.42		6.51
JP06		38.6		3.46		6.35
JP07		39.0		3.10		6.03
JP08		35.6		3.25		5.97
KR01		39.3		3.30		5.82
MY01		37.4	E	2.62		6.85
MN01		37.9	E	2.57	E	5.37
PH01		34.8		3.99	E	5.51
RU01		36.8		-		7.23
TH01	E	33.4	E	2.78		7.45
TH02		37.7	X	2.20	X	8.87
TH03		36.9	X	5.22	E	7.51
TH04		34.5		3.09		6.04
VN01		43.5		3.49		5.62
VN02		44.9	X	0.85	E	5.30

(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.062 (high amount), 3 analytical data in 59 submitted results exceeded the DQOs (±15%) by a factor of 2 (±30%) and were flagged by "E". Also 2 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". A number of flagged data was 5 and the ratio of the flagged data was about 8.5 percents in total for Sample No.062 (Fig.3). Results of SO_4^{2-} have no flags of “E”and “X”, and results of Cl^- have no flags of “X”. (Table 3.6 and 3.7)

Table 3.6 Number of flagged data for Sample No.062 (high amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	0	2	1	3
Flag X *	0	0	2	2
Data within DQOs	20	17	17	54
Ratio of Flagged (%)	0	10.5	15.0	8.5

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

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

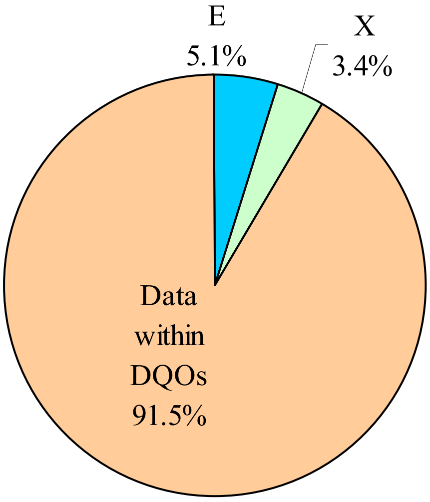


Figure 3.3 Percentage of flagged data for Sample No.062 (high amount)

Table 3.7 Averaged analytical results of Sample No.062 (high amount)

Lab. Code	SO_4^{2-} (µg)	Cl^- (µg)		NH_4^+ (µg)	
CN01	135		38.7	X	70.9
ID01	142		35.7		43.0
JP01	135		37.7		51.6
JP02	138		38.0		48.4
JP03	136		37.6		54.0
JP04	140		39.6		50.0
JP06	130		34.7		51.2
JP07	138		39.1		49.5
JP08	137		37.6		48.4
KR01	138		39.0		47.5
MY01	144		39.3		51.1
MN01	133	E	29.2		52.2
PH01	134		40.6		42.6
RU01	141			X	19.3
TH01	134		38.6		44.3
TH02	134		36.3		51.9
TH03	131		39.1	E	62.9
TH04	136		38.7		52.4
VN01	145	E	48.7		50.4
VN02	140		37.2		49.3

(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.063 (No.063-1 and No.063-2) 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 0.30 µg, 0.61 µg, and 0.40 µg, respectively. Blank values were detected in wide range including 0 µg. Table 9 shows the ratio of blank value to analytical result. Reverse mesh indicates that there was a flag for Sample No.061 or 062. 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.063 (blank)

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	2.48	1.07	0.47
ID01	1.12	0.61	0.47
JP01	0.13	0.46	0.38
JP02	0.08	1.14	0.56
JP03	0.00	1.15	0.18
JP04	0.92	0.63	0.26
JP06	0.15	0.46	0.46
JP07	0.00	0.84	0.40
JP08	0.63	0.56	0.35
KR01	0.00	1.08	4.26
MY01	0.28	0.46	0.25
MN01	1.47	1.57	0.40
PH01	1.22	1.43	0.00
RU01	0.00	-	0.00
TH01	0.00	0.48	0.91
TH02	1.53	1.87	0.07
TH03	1.65	0.00	0.10
TH04	0.31	0.45	0.49
VN01	0.03	0.34	0.46
VN02	6.37	0.00	1.67
Average	0.92	0.77	0.61
Median	0.30	0.61	0.40
Minimum	0.00	0.00	0.00
Maximum	6.37	1.87	4.26
Standard deviation	1.47	0.51	0.93

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

Lab. Code	High amount			Low amount		
	SO_4^{2-}	Cl^-	NH_4^+	SO_4^{2-}	Cl^-	NH_4^+
CN01	0.02	0.03	🟧 0.01	0.07	0.32	🟧 0.05
ID01	0.01	0.02	0.01	0.03	🟨 0.24	🟨 0.09
JP01	0.00	0.01	0.01	0.00	🟨 0.16	🟨 0.05
JP02	0.00	0.03	0.01	0.00	0.35	0.09
JP03	0.00	0.03	0.00	0.00	🟨 0.39	0.03
JP04	0.01	0.02	0.01	0.02	0.18	0.04
JP06	0.00	0.01	0.01	0.00	0.13	0.07
JP07	0.00	0.02	0.01	0.00	0.27	0.07
JP08	0.00	0.01	0.01	0.02	0.17	0.06
KR01	0.00	0.03	0.09	0.00	0.33	0.73
MY01	0.00	0.01	0.00	0.01	🟨 0.18	0.04
MN01	0.01	🟨 0.05	0.01	0.04	🟨 0.61	🟨 0.07
PH01	0.01	0.04	0.00	0.04	0.36	🟨 0.00
RU01	0.00		🟧 0.00	0.00		0.00
TH01	0.00	0.01	0.02	🟨 0.00	🟨 0.17	0.12
TH02	0.01	0.05	0.00	0.04	🟧 0.85	🟧 0.01
TH03	0.01	0.00	🟨 0.00	0.04	🟧 0.00	🟨 0.01
TH04	0.00	0.01	0.01	0.01	0.15	0.08
VN01	0.00	🟨 0.01	0.01	0.00	0.10	0.08
VN02	0.05	0.00	0.03	0.14	🟧 0.00	🟨 0.32

🟧 : Flagged data of “E” for Sample No.061 or No.062

🟨 : Flagged data of “X” for Sample No.061 or No.062

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)

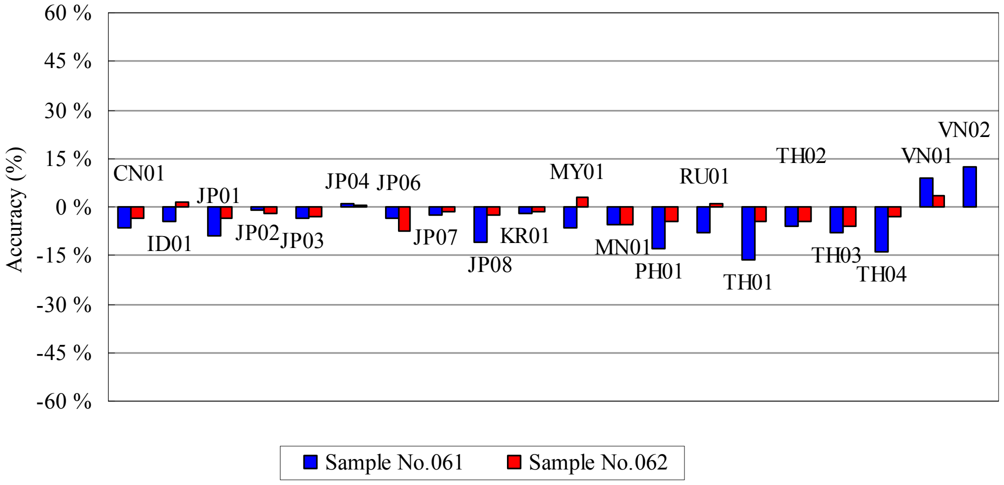


Figure 3.4 Distribution of results for SO_4^{2-} (normalized by prepared value)

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.061	1	0	5.0
Sample No.062	0	0	0

All of the participating laboratories used Ion Chromatography for the determination of SO_4^{2-}. “E” flags appeared at only 1 laboratories for Sample No.061. On the other hand, “X” flag did not appear for both samples. Flagged data were lower than the prepared value.

Cl^- (Chloride)

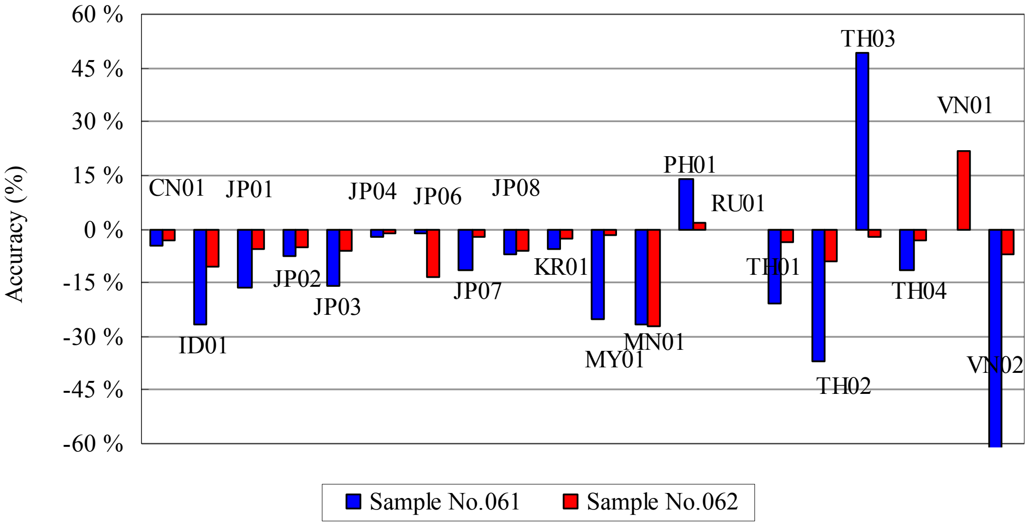


Figure 3.5 Distribution of results for Cl^- (normalized by prepared value)

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.061	6	3	47.4
Sample No.062	2	0	10.5

As same with the analysis of SO_4^{2-}, all laboratories used Ion Chromatography for the determination of Cl^-. Almost half of the data for Sample No.061 marked “E” and “X” flags. Results of MN01 had the flagged data for both of samples. Particularly the data of TH03 and VN02 exceeded “prepared value” about 50% and more than 60% for Sample No.061. The ratio of the flagged data for Sample No.061, which had low amount, was higher than that for Sample No.062 which had high amount.

NH_4^+ (Ammonium)

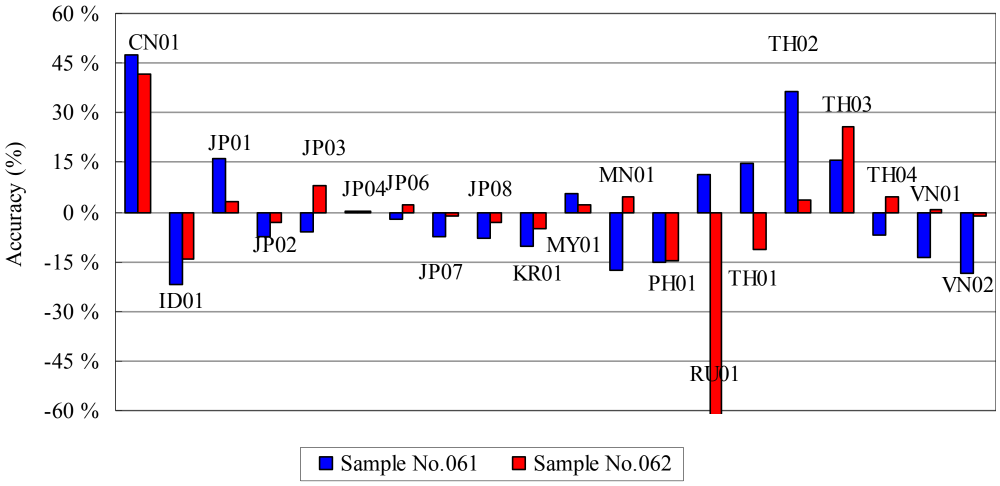


Figure 3.6 Distribution of results for NH_4^+ (normalized by prepared value)

Table 3.12 Analytical method and flagged data of NH_4^+

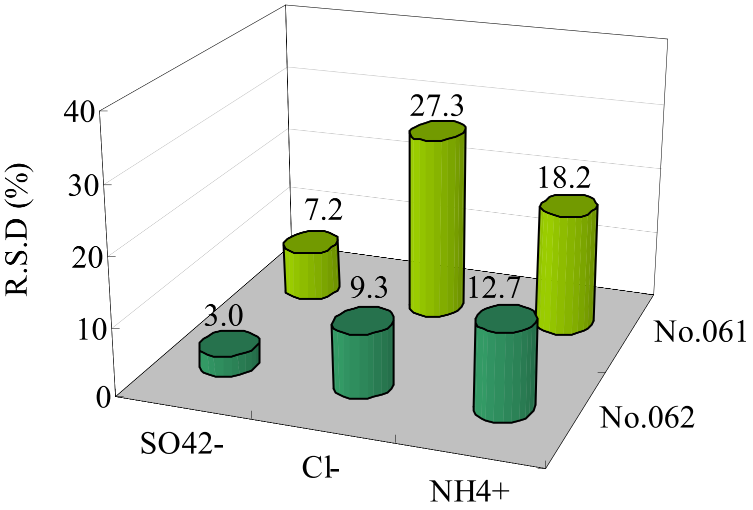
Analytical Method			
Ion Chromatography	18/20		
Spectrometry (Indophenol blue)	1/19		
Spectrometry (Nessler)	1/19		
Flagged Data	Flag E	Flag X	Flagged (%)
Sample No.061	6	2	40.0
Sample No.062	1	2	15.0

19 laboratories used recommended analytical method of EANET for the determination of NH_4^+; 18 laboratories used Ion Chromatography and 1 laboratory used Indophenol Spectrophotometry. 1 laboratory used Spectrophotometry other than Indophenol blue method. The ratio of the flagged data for Sample No.061, which had low amount, was higher than that for Sample No.062 which had high amount. There were 6 “E” flags and 2 “X” flags for Sample No.061.

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.061 and No.062 are shown in Figure 3.7. The values of R.S.D for Sample No.061 were highr than those for Sample No.062. Especially, R.S.D. of Cl^- for Sample No.061 showed relatively higher value compared with the others, which was the same as the first attempt, 2005. The use of inappropriate range for the calibration standard solution can be pointed out as one of the reasons for unsatisfied result of Cl^-. 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^+, 18 of 20 laboratories used Ion Chromatography and 1 laboratory used Indophenol Spectrophotometry. However, 1 laboratory used the Spectrophotometry other than Indophenol blue method.

Table 3.13 Analytical methods used for sample analysis

Lab. Code	SO_4^{2-},Cl^-	NH_4^+
CN01	Ion Chromatography	
ID01	Ion Chromatography	
JP01	Ion Chromatography	
JP02	Ion Chromatography	
JP03	Ion Chromatography	
JP04	Ion Chromatography	
JP06	Ion Chromatography	
JP07	Ion Chromatography	
JP08	Ion Chromatography	
KR01	Ion Chromatography	
MY01	Ion Chromatography	
MN01	Ion Chromatography	
PH01	Ion Chromatography	Indophenol Spectrophotometry
RU01	Ion Chromatography	Spectrophotometry(Nessler)
TH01	Ion Chromatography	
TH02	Ion Chromatography	
TH03	Ion Chromatography	
TH04	Ion Chromatography	
VN01	Ion Chromatography	
VN02	Ion Chromatography	

Staff (number and years of experience)

According to the information about “years of experience for staff in charge” obtained through this project, clear evidence for the relationship with data quality was not found. The average of the years of experience was 7.3 years, and this project was the first experience for the staff of MY01 to conduct the analysis of filter pack samples. 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.061 and/or 062. Reverse mesh with dark color indicate flagged data in both of Sample No.061 and No.062.

Table 3.14 Years of experience (unit: year)

Lab. Code	SO_4^{2-}	Cl^-	NH_4^+
CN01	14	14	14
ID01	5	5	5
JP01	22	22	22
JP02	7	7	7
JP03	2	2	2
JP04	11	11	11
JP06	3	3	3
JP07	2	2	2
JP08	1.8	1.8	1.8
KR01	4	4	4
MY01	2	2	1
MN01	8	8	8
PH01	5.5	5.7	7
RU01	16	16	26
TH01	10	10	10
TH02	7	7	3
TH03	3	3	3
TH04	4	4	9
VN01	13	13	13
VN02	2	2	2

(Note) Reverse mesh: Flagged data in Sample No.061 and/or No.062 (Dark color: Flagged data in both of Sample No.061 and No.062)

Flagged Data

In the results of Sample No.061 and 062, the total number of flagged data was 23 (E: 16, X: 7) among the whole of 118 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 7 (35%). The number of laboratories that submitted data with less than 2 flagged values were 12 (60%) in this attempt. There was one laboratory 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.

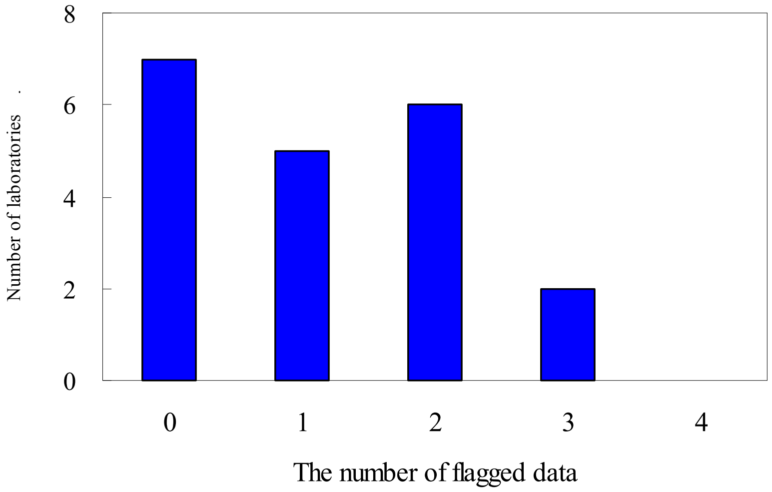


Figure 3.8 Distribution of laboratories with the number of flagged data

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

Lab. Code	SO_4^{2-} (µmol/L)		Cl^- (µmol/L)		NH_4^+ (µmol/L)	
	Lowest	Highest	Lowest	Highest	Lowest	Highest
CN01	29.2	293	**38.4**	384	13.9	139
ID01	5.21	**31.2**	**14.1**	84.5	11.1	**88.9**
JP01	5.21	208	**14.1**	565	11.2	558
JP02	0.50	208	1.40	141	1.40	141
JP03	5.21	156	2.82	84.3	5.54	166
JP04	1.04	104	2.82	141	2.77	277
JP06	1.04	520	1.41	705	1.39	1390
JP07	0.52	521	2.84	2840	1.44	1440
JP08	0.21	104	1.41	141	3.33	332
KR01	10.4	83.3	2.82	141	11.1	277
MY01	5.20	83.3	2.82	113	11.9	166
MN01	4.16	125	**5.64**	170	11.1	**111**
PH01	2.08	208	**5.64**	564		
RU01	5.21	104	-	-	5.56	**111**
TH01	0.1	104	0.28	282	0.55	554
TH02	2.08	72.9	**5.64**	113	4.43	166
TH03	2.30	**62.4**	3.01	64.7	4.43	221
TH04	0.21	83.3	0.56	226	1.11	277
VN01	2.08	104	2.82	141	5.54	277
VN02	20.8	104	2.82	56.4	11.1	277
Sample No.061	20.8		4.30		18.0	
Sample No.062		72.9		56.4		139

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

Reverse mesh: Flagged data in Sample No.061 and/or No.062 (Dark color: Flagged data "X")

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

References

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

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

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

Appendix 3-1 Participating Laboratories

Countries / Laboratories	**Code**
1. China	
1) Xiamen Environmental Monitoring Central Station	**(CN01)**
1. INDONESIA	
2) Environmental Management Center (PUSARPEDAL)	**(ID01)**
2. JAPAN	
3) Hokkaido Institute of Environmental Sciences	**(JP01)**
4) Niigata Prefectural Institute of Public Health and Environmental Sciences	**(JP02)**
5) Nagano Environmental Conservation Research Institute	**(JP03)**
6) Gifu Prefectural Institute of Health and Environmental Science	**(JP04)**
7) Shimane Prefectural Institute of Public Health and Environmental Science	**(JP06)**
8) Okinawa Prefectural Institute of Health and Environment	**(JP07)**
9) Acid Deposition and Oxidant Research Center (ADORC)	**(JP08)**
3. MALAYSIA	
10) Department of Chemistry	**(MY01)**
4. MONGOLIA	
11) Central Laboratory of Environmental Monitoring	**(MN01)**
5. PHILIPPINES	
12) Environmental Management Bureau (EMB)	**(PH01)**
6. REPUBLIC OF KOREA	
13) National Institute of Environmental Research (NIER)	**(KR01)**
7. RUSSIA	
14) Limnological Institute, Russian Academy of Sciences/Siberian Branch	**(RU01)**
8. 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)**
9.VIET NAM	
19) Center for Environmental research, Institute of Meteorology and Hydrology	**(VN01)**
20) Mid-central Regional Hydro Meteorological Center	**(VN02)**

Appendix 3-2 Summary of Results

Analytical results of Sample No.061 (low amount)

Lab. ID	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	37.5	3.34	9.58
ID01	38.3	2.57	5.07
JP01	36.5	2.92	7.56
JP02	39.7	3.24	6.01
JP03	38.6	2.95	6.10
JP04	40.3	3.42	6.51
JP06	38.6	3.46	6.35
JP07	39.0	3.10	6.03
JP08	35.6	3.25	5.97
KR01	39.3	3.30	5.82
MY01	37.4	2.62	6.85
MN01	37.9	2.57	5.37
PH01	34.8	3.99	5.51
RU01	36.8	-	7.23
TH01	33.4	2.78	7.45
TH02	37.7	2.20	8.87
TH03	36.9	5.22	7.51
TH04	34.5	3.09	6.04
VN01	43.5	3.49	5.62
VN02	44.9	0.85	5.30
Prepared value	40.0	3.50	6.50
Number of data	20	19	20
Average	38.1	3.07	6.54
Minimum	33.4	0.85	5.07
Maximum	44.9	5.22	9.58
Standard deviation	2.76	0.84	1.19

Analytical results of Sample No.062 (high amount)

Lab. ID	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
CN01	135	38.7	70.9
ID01	142	35.7	43.0
JP01	135	37.7	51.6
JP02	138	38.0	48.4
JP03	136	37.6	54.0
JP04	140	39.6	50.0
JP06	130	34.7	51.2
JP07	138	39.1	49.5
JP08	137	37.6	48.4
KR01	138	39.0	47.5
MY01	144	39.3	51.1
MN01	133	29.2	52.2
PH01	134	40.6	42.6
RU01	141	-	19.3
TH01	134	38.6	44.3
TH02	134	36.3	51.9
TH03	131	39.1	62.9
TH04	136	38.7	52.4
VN01	145	48.7	50.4
VN02	140	37.2	49.3
Prepared value	140	40.0	50.0
Number of data	20	19	20
Average	137	38.2	49.5
Minimum	130	29.2	19.3
Maximum	145	48.7	70.9
Standard deviation	4.11	3.55	9.53

4. 8th 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 among the participating laboratories 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

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 8th project, NC provided two soil samples (No.061 and 062) 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

Fourteen laboratories of 9 countries participated in the 8th 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. 061: Brown forest soil (Eutric Cambisols)
Sample No. 062: Brown forest soil (Dystric Cambisols)

Soils for Sample No. 061 and 062 were collected in Japanese cedar (*Cryptomeria japonica*) forests in Toyama Prefecture (Toyama City and Tateyama Town, respectively).

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

4.2.3 Parameters Analyzed

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

Table 4.1. Parameters to be measured

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

M: Mandatory items

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

4.2.4 Analytical Methodologies

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

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

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

4.2.4.1 Standardization of methods

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

In the 8th project,

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

4.2.4.2 Procedures for Ex-base cations

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

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

(3) Prepare three “prepared samples”.

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

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

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

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

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

(9) Calculation of content in the soil

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

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

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

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

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

Where

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

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

mcf = Moisture correction factor (Measured value)

S = Weight of air-dry sample (g)

V = Volume of extract (mL)

4.2.4.3 Procedures for Ex-acidity

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

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

(3) Repeat the procedure twice

(4) Calculation of content in the soil

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

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

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

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

Where

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

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

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

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

4.2.4.4 Reporting

(1) Preparation of the report

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

(2) Submission of the report

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

4.2.5 Data Checking Procedures

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

1) Verification of data

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

2) Analysis of variance and estimation of precision

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

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

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

3) Calculation of permissible tolerance

Permissible tolerances were calculated based on the above precisions.

4.3 Results

4.3.1 Outline of Laboratories' Performance

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

As for the entire data, the variations (CVs) among the participating laboratories were different in parameter. CVs were very small, 2.0 – 3.7%, in pH(H_2O) and pH(KCl) probably due to their simple analytical procedures and logarithmic values as discussed in the previous reports (ADORC, 2001a; 2000b). However, CVs in exchangeable cations were relatively large, and remarkably large CVs (larger than 100%) were observed especially in Ex-Ca of No. 062 and Ex-Na of both samples. On the other hand, variations in Ex-acidity and Al were relatively small, 15 – 21%, also probably due to their relatively simple titration procedures.

As for the verified data, the variations (CVs) of pH(H_2O) and pH(KCl) were also small, 1.5 – 3.7%. CVs for other parameters were improved after removing outliers. CVs of Ex-acidity and Al in No.062 were 3% and 15%, respectively. CVs of Ex-H were still relatively large, probably because the values calculated based on Ex-acidity and Ex-Al included errors of these parameters.

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

Three laboratories, “mn01”, “vn01”, 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. 061									
Number of Laboratories	14	14	11	11	12	12	14	14	14
Total average	4.4	3.9	0.20	0.17	0.21	0.16	6.76	5.95	0.83
Median	4.4	3.9	0.16	0.15	0.22	0.06	6.86	5.76	0.74
Maximum	4.5	4.0	0.49	0.43	0.42	1.30	8.39	8.08	1.93
Minimum	4.2	3.8	0.03	0.04	0.02	0.01	4.93	4.55	0.20
Standard deviation	0.1	0.1	0.12	0.10	0.09	0.36	1.01	1.00	0.47
CV (%)[*1]	2.0	2.0	62.3	61.0	44	229	15.0	16.9	56
No. 062									
Number of Laboratories	14	14	11	11	12	12	14	14	14
Total average	4.6	4.0	0.10	0.22	0.17	0.19	13.51	12.24	0.73
Median	4.7	4.0	0.08	0.21	0.16	0.08	14.09	12.90	0.40
Maximum	5.0	4.1	0.43	0.55	0.38	1.34	15.19	14.60	2.42
Minimum	4.3	3.8	0.00	0.06	0.10	0.03	7.79	6.81	0.00
Standard deviation	0.2	0.1	0.12	0.13	0.07	0.37	1.97	2.51	0.79
CV (%)[*1]	3.7	2.2	122.5	60.2	45	198	14.6	20.5	108

(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. 061									
Number of Laboratories	13	13	10	9	12	11	14	14	14
Total average	4.4	3.9	0.17	0.13	0.21	0.05	6.76	5.95	0.83
Median	4.4	3.9	0.16	0.13	0.22	0.05	6.86	5.76	0.74
Maximum	4.5	4.0	0.30	0.21	0.42	0.11	8.39	8.08	1.93
Minimum	4.3	3.8	0.03	0.04	0.02	0.01	4.93	4.55	0.20
Standard deviation	0.1	0.1	0.08	0.05	0.09	0.04	1.01	1.00	0.47
CV (%)[*1]	1.5	2.0	47.3	36.5	44.4	65.3	15.0	16.9	56.5
No. 062									
Number of Laboratories	14	14	10	9	11	10	10	13	14
Total average	4.6	4.0	0.06	0.18	0.15	0.07	14.24	12.22	0.73
Median	4.7	4.0	0.07	0.21	0.15	0.07	14.16	12.91	0.40
Maximum	5.0	4.1	0.12	0.27	0.21	0.10	15.13	14.60	2.42
Minimum	4.3	3.8	0.00	0.06	0.10	0.03	13.72	6.81	0.00
Standard deviation	0.2	0.1	0.04	0.08	0.03	0.02	0.42	2.61	0.79
CV (%)[*1]	3.7	2.2	69.0	44.0	22.9	35.0	3.0	21.3	108.3

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

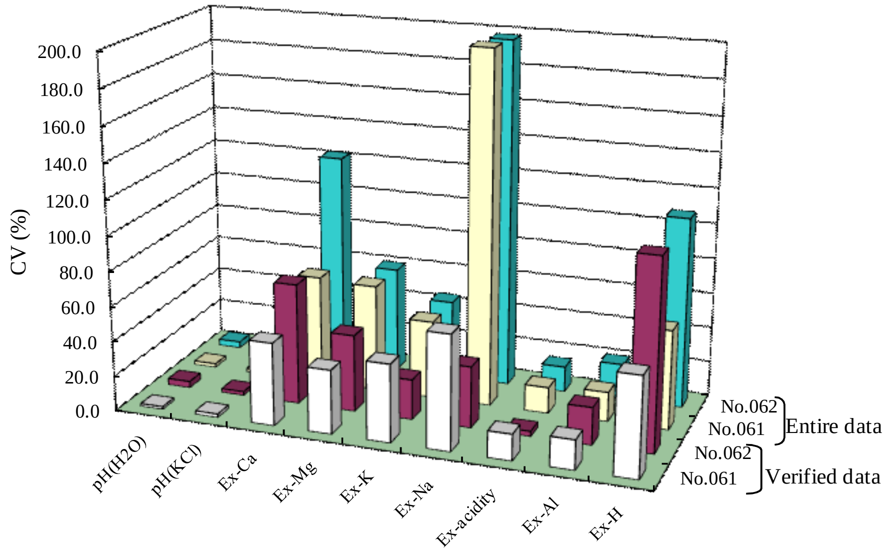


Figure 4.1. CV among laboratories

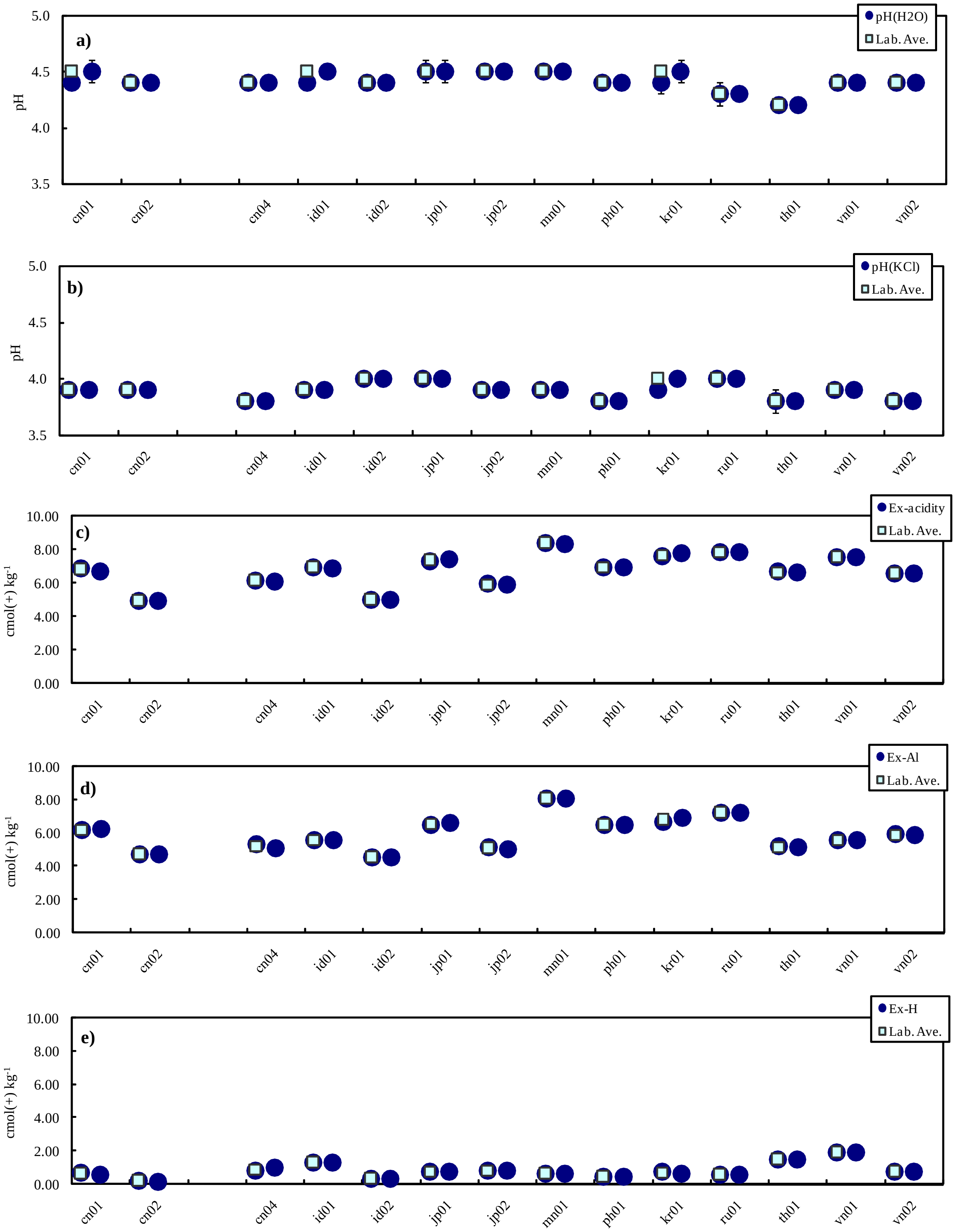


Figure 4.2-1 Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 061. Error bar shows standard deviation of triplicate analysis.

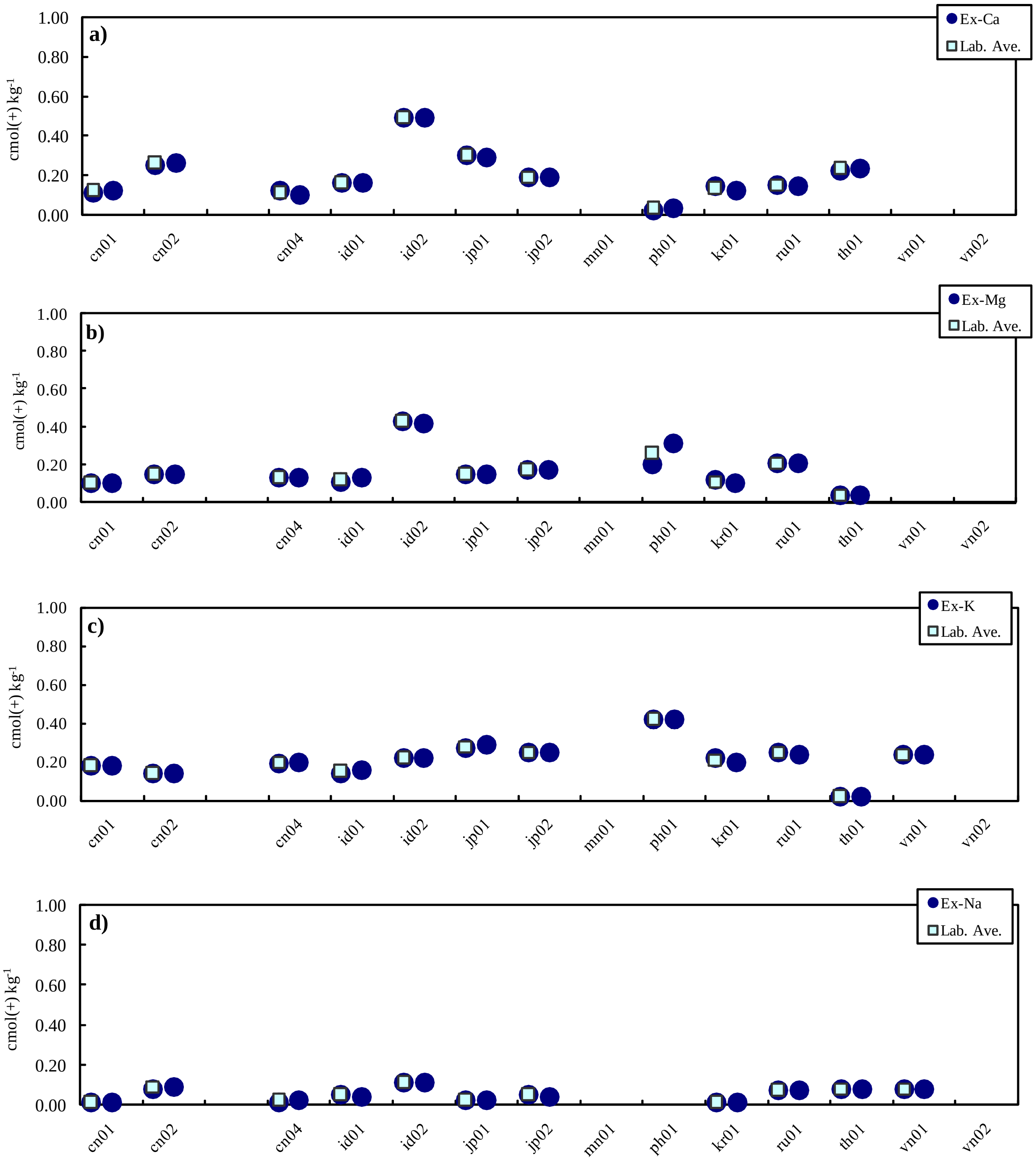


Figure 4.2-2 Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 061. Error bar shows standard deviation of triplicate analysis.

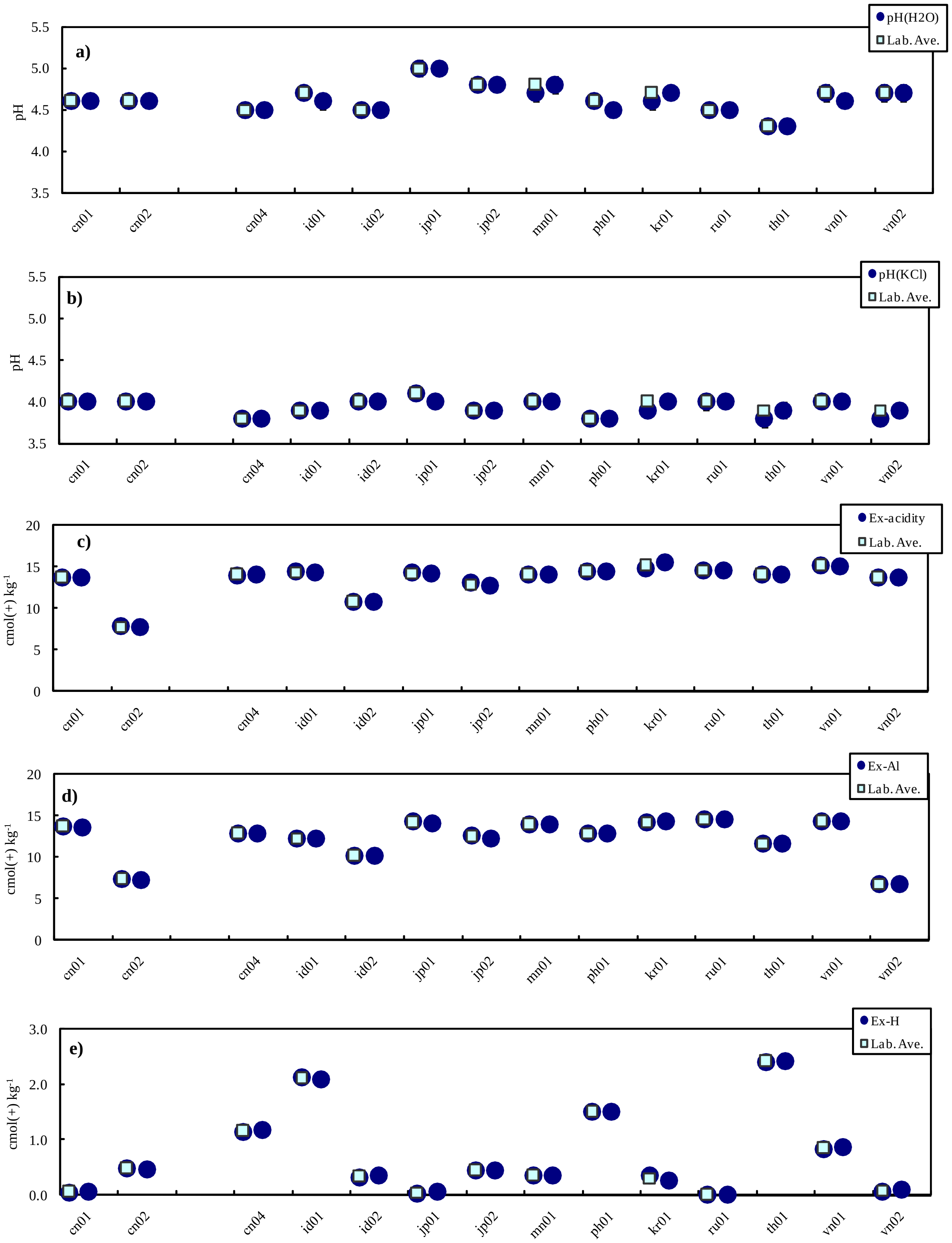


Figure 4.2-3 Averages of triplicate analysis and the laboratory average for a) pH(H_2O), b) pH(KCl), c) Ex-acidity, d) Ex-Al and e) Ex-H in Sample No. 062. Error bar shows standard deviation of triplicate analysis.

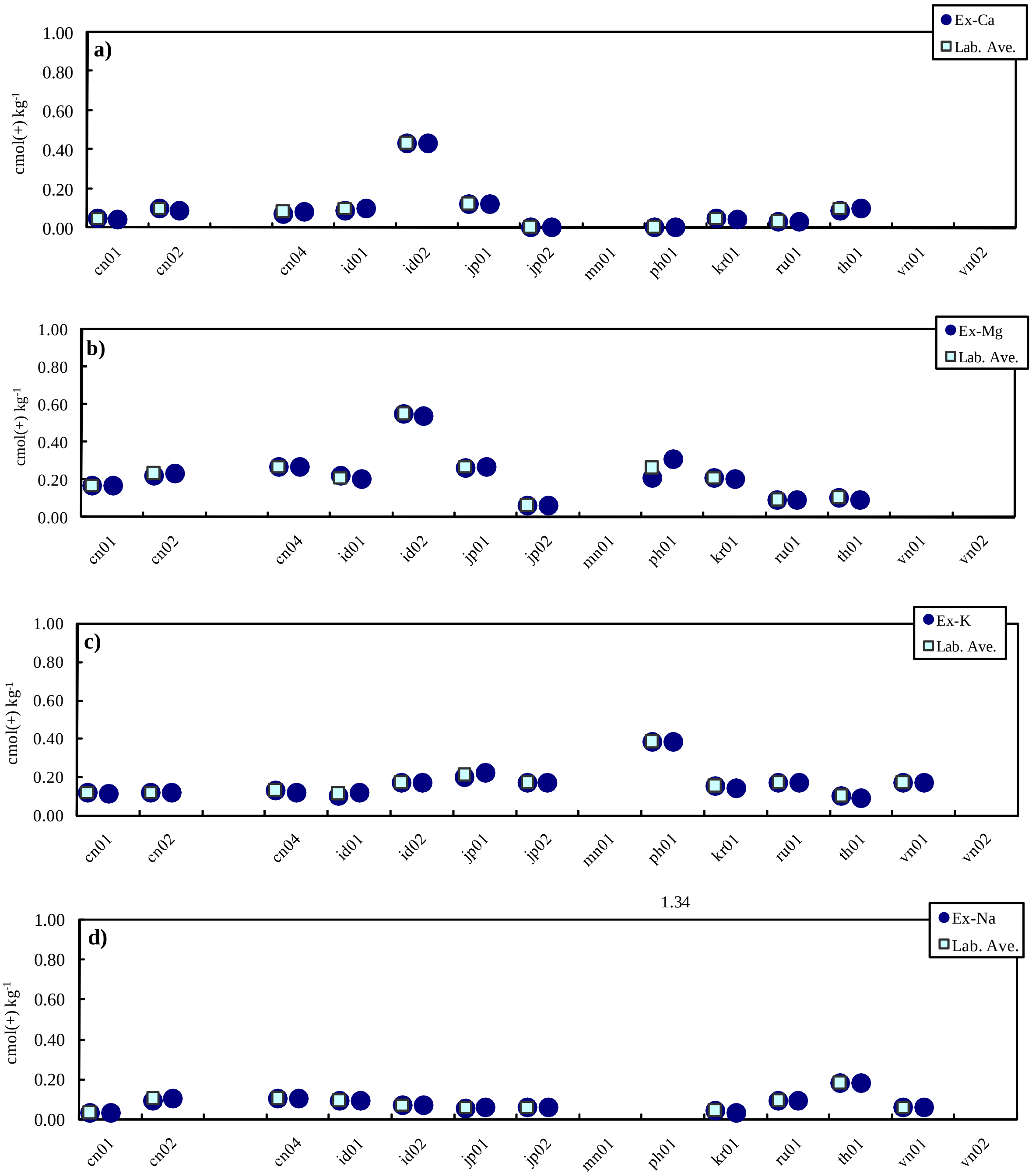


Figure 4.2-4 Averages of triplicate analysis and the laboratory average for a) Ex-Ca, b) Ex-Mg, c) Ex-K and d) Ex-Na in Sample No. 062. Error bar shows standard deviation of triplicate analysis.

4.3.2 Detection of outliers

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

Laboratories, which have large difference in repeat analyses, were judged as outliers by Cochran method (examination of the evenness of within-laboratory precision): e.g. “ph01” in Ex-Mg, “jp02” in Ex-acidity and Al of No. 062, etc. Then, the rest of data were tested, and laboratories, which have remarkably large or small average, were judged as outliers by Grubbs method (examination of the average value of each laboratory): e.g. “id02” in Ex-Ca and Mg, “ph01” in Ex-Na and Ex-K of No. 062, “th01” in Ex-Na of No. 062, etc.

In a few laboratories, more than three outliers were detected. It was suggested that some systematic errors in the analytical procedures might occur in such laboratories. No outlier was detected in pH (H_2O) and pH (KCl) of No. 062, Ex-acidity, Al, and H of No. 061, and Ex-H of No. 062. One to three outliers were detected in most parameters.

Table 4.3-1. Data verified by Cochran-Grubbs methods: No. 061

Lab.	Repeat analysis	$pH(H_2O)$	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
				cmol(+) kg^{-1}						
cn01	1st	4.4	3.9	0.11	0.10	0.18	0.01	6.88	6.18	0.69
	2nd	4.5	3.9	0.12	0.10	0.18	0.01	6.72	6.22	0.60
cn02	1st	4.4	3.9	0.25	0.15	0.14	0.08	4.93	4.71	0.22
	2nd	4.4	3.9	0.26	0.15	0.14	0.09	4.92	4.74	0.18
cn04	1st	4.4	3.8	0.12	0.13	0.19	0.01	6.16	5.34	0.82
	2nd	4.4	3.8	0.10	0.13	0.20	0.02	6.10	5.12	0.98
id01	1st	4.4	3.9	0.16	0.11	0.14	0.05	6.94	5.59	1.34
	2nd	4.5	3.9	0.16	0.13	0.16	0.04	6.90	5.59	1.30
id02	1st	4.4	4.0	0.49*g	0.43*g	0.22	0.11	4.97	4.54	0.35
	2nd	4.4	4.0	0.49*g	0.42*g	0.22	0.11	5.00	4.55	0.33
jp01	1st	4.5	4.0	0.30	0.15	0.27	0.02	7.30	6.52	0.78
	2nd	4.5	4.0	0.29	0.15	0.29	0.02	7.40	6.61	0.79
jp02	1st	4.5	3.9	0.19	0.17	0.25	0.05	5.95	5.13	0.82
	2nd	4.5	3.9	0.19	0.17	0.25	0.04	5.91	5.06	0.85
mn01	1st	4.5	3.9					8.41	8.08	0.61
	2nd	4.5	3.9					8.36	8.08	0.61
ph01	1st	4.4	3.8	0.02	0.20*c	0.42	1.30*g	6.94	6.48	0.46
	2nd	4.4	3.8	0.03	0.31*c	0.42	1.30*g	6.95	6.50	0.44
kr01	1st	4.4	3.9*c	0.14	0.12	0.22	0.01	7.59	6.69	0.79
	2nd	4.5	4.0*c	0.12	0.10	0.20	0.01	7.79	6.91	0.65
ru01	1st	4.3	4.0	0.15	0.21	0.25	0.07	7.87	7.21	0.57
	2nd	4.3	4.0	0.14	0.21	0.24	0.07	7.87	7.21	0.57
th01	1st	4.2*g	3.8	0.22	0.04	0.02	0.08	6.68	5.19	1.49
	2nd	4.2*g	3.8	0.23	0.04	0.02	0.08	6.64	5.17	1.47
vn01	1st	4.4	3.9			0.24	0.08	7.52	5.60	1.92
	2nd	4.4	3.9			0.24	0.08	7.52	5.59	1.93
vn02	1st	4.4	3.8					6.55	5.92	0.76
	2nd	4.4	3.8					6.55	5.90	0.76

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. 062

Lab.	Repeat analysis	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
				cmol(+) kg^{-1}						
cn01	1st	4.6	4.0	0.05	0.17	0.12	0.03	13.74	13.69	0.05
	2nd	4.6	4.0	0.04	0.17	0.11	0.03	13.69	13.63	0.06
cn02	1st	4.6	4.0	0.10	0.22	0.12	0.09	7.85*g	7.38	0.48
	2nd	4.6	4.0	0.09	0.23	0.12	0.10	7.73*g	7.26	0.47
cn04	1st	4.5	3.8	0.07	0.27	0.13	0.10	14.02	12.89	1.14
	2nd	4.5	3.8	0.08	0.27	0.12	0.10	14.04	12.86	1.18
id01	1st	4.7	3.9	0.09	0.22	0.10	0.09	14.41	12.28	2.13
	2nd	4.6	3.9	0.10	0.20	0.12	0.09	14.37	12.28	2.09
id02	1st	4.5	4.0	0.43*g	0.55*g	0.17	0.07	10.75*g	10.15	0.32
	2nd	4.5	4.0	0.43*g	0.54*g	0.17	0.07	10.77*g	10.15	0.35
jp01	1st	5.0	4.1	0.12	0.26	0.20	0.05	14.30	14.27	0.03
	2nd	5.0	4.0	0.12	0.27	0.22	0.06	14.15	14.09	0.06
jp02	1st	4.8	3.9	0.00	0.06	0.17	0.06	13.1*c	12.66*c	0.44
	2nd	4.8	3.9	0.00	0.06	0.17	0.06	12.72*c	12.28*c	0.44
mn01	1st	4.7	4.0					14.08	13.91	0.35
	2nd	4.8	4.0					14.08	13.91	0.35
ph01	1st	4.6	3.8	0.00	0.21*c	0.38*g	1.34*g	14.41	12.90	1.51
	2nd	4.5	3.8	0.00	0.31*c	0.38*g	1.34*g	14.43	12.92	1.51
kr01	1st	4.6	3.9	0.05	0.21	0.15	0.04	14.79*c	14.17	0.35
	2nd	4.7	4.0	0.04	0.20	0.14	0.03	15.59*c	14.31	0.27
ru01	1st	4.5	4.0	0.03	0.09	0.17	0.09	14.60	14.60	0.00
	2nd	4.5	4.0	0.03	0.09	0.17	0.09	14.60	14.60	0.00
th01	1st	4.3	3.8	0.09	0.10	0.10	0.18*g	14.05	11.65	2.41
	2nd	4.3	3.9	0.10	0.09	0.09	0.18*g	14.12	11.69	2.43
vn01	1st	4.7	4.0			0.17	0.06	15.13	14.31	0.83
	2nd	4.6	4.0			0.17	0.06	15.12	14.27	0.86
vn02	1st	4.7	3.8					13.74	6.81	0.07
	2nd	4.7	3.9					13.72	6.81	0.10

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

4.3.3 Overall analysis

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

1) Repeatability-precision

Repeatability standard deviations were relatively small for most of the parameters in the verified data, and CVs of most parameters were smaller than 10%. Especially CVs of pH(H_2O) and pH(KCl) in both samples were smaller than 0.7%, and those of Ex-acidity and Al were smaller 1.0%.

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 pH(H_2O), pH(KCl) and Ex-acidity in both samples were smaller than 1.0%. The CV of Ex-Al in No. 062 was also smaller than 0.5%.

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

3) Inter-laboratories precision

CVs of the inter-laboratories precision were smaller than 5% in pH(H_2O) and pH(KCl). On the other hand, CVs of exchangeable base cations were mostly larger than 40%, while those of Ex-acidity and Al were mostly smaller than 20%.

4) Calculation of permissible tolerance

As for the repeatability limit and within-laboratory reproducibility limit, values might be enough small, and it could be used as a reference value for the repeat analysis on the instrumental analysis in the respective laboratories.

As for the reproducibility limit, inter-laboratories precision should be improved for Ex-base cations, and then the discussion should be carried out.

Table 4.4-1 Analysis of variance for the entire data

Statistics	No. 061								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	14	11	11	12	12	14	14	14
Total sum of square	137270	107191	166	125	236	126	322499	249281	4800
ST/lmd	1634	1276	3	2	3	2	3839	2968	57
Number of Data	84	84	66	66	72	72	84	84	84
Total sum	370.5	327.4	12.87	11.19	15.36	11.22	567.89	499.28	69.28
Total average	4.4	3.9	0.20	0.17	0.21	0.16	6.76	5.94	0.82
Sum of square inter-laboratories (S_R)	0.5	0.4	0.92	0.63	0.59	8.64	80.15	78.84	16.90
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.02	0.00	0.00	0.13	0.17	0.09
Sum of square repeatablility (S_r)	0.0	0.0	0.00	0.00	0.01	0.01	0.15	0.17	0.39
Total sum of square (S_T)	0.6	0.4	0.92	0.65	0.60	8.65	80.43	79.18	17.38
Inter-laboratories degree of freedom (ϕ_R)	13	13	10	10	11	11	13	13	13
Within-laboratory degree of freedom (ϕ_{RW})	14	14	11	11	12	12	14	14	14
Repeatability degree of freedom (ϕ_r)	56	56	44	44	48	48	56	56	56
Total degree of freedom (ϕ_T)	83	83	65	65	71	71	83	83	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.04	0.03	0.092	0.063	0.054	0.786	6.165	6.065	1.300
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.002	0.000	0.000	0.009	0.012	0.006
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.003	0.003	0.007
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.01	0.01	0.015	0.010	0.009	0.131	1.026	1.009	0.216
Within-laboratory component of variance ($s_c^2 = (V_{RW}-V_r)/3$)	0.00	0.00	0.000	0.001	0.000	0.000	0.002	0.003	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.003	0.003	0.007
Inter-laboratories standard deviation (s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2))	0.1	0.1	0.12	0.10	0.09	0.36	1.01	1.01	0.47
Within-laboratory standard deviation (s_{RW} = SQRT(s_r^2/3 + s_c^2))	0.0	0.0	0.01	0.02	0.01	0.00	0.06	0.06	0.05
Repeatability standard deviation (s_r = SQRT(s_r^2))	0.0	0.0	0.01	0.01	0.01	0.01	0.05	0.06	0.08
Inter-laboratories precision CV (%)	1.9	1.9	63.45	60.44	44.35	232.20	14.99	16.91	56.44
Within-laboratory precision CV (%)	0.7	0.5	3.80	13.91	3.41	1.38	0.83	1.06	5.62
Repeatability precision CV (%)	0.6	0.3	4.37	2.99	5.27	7.21	0.76	0.94	10.09
Reproducibility limit (R = D(2, 0.95)*s_R)	0.23	0.20	0.346	0.287	0.265	1.013	2.838	2.815	1.303
Within-laboratory-reproducibility limit (R_W = D(2, 0.95)*s_{Rw})	0.08	0.06	0.021	0.066	0.020	0.006	0.156	0.177	0.130
Repeatability limit (r = D(3, 0.95)*s_r)	0.09	0.04	0.028	0.017	0.037	0.037	0.169	0.184	0.275

Statistics	No. 062								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	14	11	11	12	12	14	14	14
Total sum of square	151088	109362	38	206	141	175	1286636	1057216	3693
ST/lmd	1799	1302	1	3	2	2	15317	12586	44
Number of Data	84	84	66	66	72	72	84	84	84
Total sum	388.7	330.7	6.20	14.37	11.88	13.24	1134.30	1028.21	60.77
Total average	4.6	3.9	0.09	0.22	0.17	0.18	13.50	12.24	0.72
Sum of square inter-laboratories (S_R)	2.1	0.6	0.84	1.04	0.37	8.85	302.27	489.57	48.37
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.02	0.00	0.00	1.24	0.33	0.02
Sum of square repeatablility (S_r)	0.1	0.0	0.00	0.00	0.00	0.01	0.85	0.67	0.14
Total sum of square (S_T)	2.2	0.6	0.84	1.06	0.38	8.85	304.36	490.56	48.52
Inter-laboratories degree of freedom (ϕ_R)	13	13	10	10	11	11	13	13	13
Within-laboratory degree of freedom (ϕ_{RW})	14	14	11	11	12	12	14	14	14
Repeatability degree of freedom (ϕ_r)	56	56	44	44	48	48	56	56	56
Total degree of freedom (ϕ_T)	83	83	65	65	71	71	83	83	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.16	0.04	0.084	0.104	0.034	0.804	23.252	37.659	3.721
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.002	0.000	0.000	0.089	0.024	0.001
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.015	0.012	0.002
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.03	0.01	0.014	0.017	0.006	0.134	3.861	6.273	0.620
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	0.024	0.004	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.015	0.012	0.002
Inter-laboratories standard deviation (s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2))	0.2	0.1	0.12	0.13	0.07	0.37	1.97	2.51	0.79
Within-laboratory standard deviation (s_{RW} = SQRT(s_r^2/3 + s_c^2))	0.0	0.0	0.01	0.02	0.01	0.00	0.17	0.09	0.02
Repeatability standard deviation (s_r = SQRT(s_r^2))	0.0	0.0	0.01	0.01	0.01	0.01	0.12	0.11	0.05
Inter-laboratories precision CV (%)	3.5	2.2	126.08	60.60	45.43	199.09	14.58	20.47	108.85
Within-laboratory precision CV (%)	0.7	0.9	6.05	10.29	3.91	1.65	1.27	0.72	2.99
Repeatability precision CV (%)	0.7	0.5	6.93	3.34	5.30	6.01	0.91	0.89	6.82
Reproducibility limit (R = D(2, 0.95)*s_R)	0.46	0.24	0.332	0.369	0.210	1.025	5.512	7.015	2.205
Within-laboratory-reproducibility limit (R_W = D(2, 0.95)*s_{Rw})	0.08	0.09	0.016	0.063	0.018	0.009	0.481	0.248	0.061
Repeatability limit (r = D(3, 0.95)*s_r)	0.10	0.06	0.021	0.024	0.029	0.036	0.406	0.360	0.163

Table 4.4-2 Analysis of variance for the entire data

Statistics	No. 061								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	13	10	9	12	11	14	14	14
Total sum of square	137270	92234	98	50	236	12	322499	249281	4800
ST/lmd	1634	1182	2	1	3	0	3839	2968	57
Number of Data	84	78	60	54	72	66	84	84	84
Total sum	370.5	303.7	9.92	7.09	15.36	3.42	567.89	499.28	69.28
Total average	4.4	3.9	0.17	0.13	0.21	0.05	6.76	5.94	0.82
Sum of square inter-laboratories (S_R)	0.5	0.4	0.34	0.11	0.59	0.07	80.15	78.84	16.90
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.13	0.17	0.09
Sum of square repeatablility (S_r)	0.0	0.0	0.00	0.00	0.01	0.00	0.15	0.17	0.39
Total sum of square (S_T)	0.6	0.4	0.34	0.11	0.60	0.07	80.43	79.18	17.38
Inter-laboratories degree of freedom (ϕ_R)	13	12	9	8	11	10	13	13	13
Within-laboratory degree of freedom (ϕ_{RW})	14	13	10	9	12	11	14	14	14
Repeatability degree of freedom (ϕ_r)	56	52	40	36	48	44	56	56	56
Total degree of freedom (ϕ_T)	83	77	59	53	71	65	83	83	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.04	0.03	0.038	0.014	0.054	0.007	6.165	6.065	1.300
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.000	0.000	0.000	0.009	0.012	0.006
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.003	0.003	0.007
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.01	0.01	0.006	0.002	0.009	0.001	1.026	1.009	0.216
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	0.003	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.003	0.003	0.007
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.1	0.1	0.08	0.05	0.09	0.03	1.01	1.01	0.47
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	0.06	0.06	0.05
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.01	0.00	0.01	0.01	0.05	0.06	0.08
Inter-laboratories precision CV (%)	1.9	1.9	47.84	36.26	44.35	67.11	14.99	16.91	56.44
Within-laboratory precision CV (%)	0.7	0.2	4.69	5.11	3.41	4.34	0.83	1.06	5.62
Repeatability precision CV (%)	0.6	0.3	5.35	3.11	5.27	10.35	0.76	0.94	10.09
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.23	0.21	0.221	0.133	0.265	0.097	2.838	2.815	1.303
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.08	0.02	0.022	0.019	0.020	0.006	0.156	0.177	0.130
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.09	0.04	0.029	0.013	0.037	0.018	0.169	0.184	0.275

Statistics	No. 062								
	pH(H_2O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	14	14	10	9	11	10	10	13	14
Total sum of square	151088	109362	13	91	93	17	730051	908952	3693
ST/lmd	1799	1302	0	2	1	0	12168	11653	44
Number of Data	84	84	60	54	66	60	60	78	84
Total sum	388.7	330.7	3.62	9.53	9.62	4.13	854.43	953.39	60.77
Total average	4.6	3.9	0.06	0.18	0.15	0.07	14.24	12.22	0.72
Sum of square inter-laboratories (S_R)	2.1	0.6	0.10	0.29	0.08	0.03	9.61	489.23	48.37
Sum of square within-laboratory (S_{RW})	0.0	0.0	0.00	0.00	0.00	0.00	0.05	0.11	0.02
Sum of square repeatablility (S_r)	0.1	0.0	0.00	0.00	0.00	0.00	0.06	0.38	0.14
Total sum of square (S_T)	2.2	0.6	0.10	0.30	0.08	0.03	9.72	489.72	48.52
Inter-laboratories degree of freedom (ϕ_R)	13	13	9	8	10	9	9	12	13
Within-laboratory degree of freedom (ϕ_{RW})	14	14	10	9	11	10	10	13	14
Repeatability degree of freedom (ϕ_r)	56	56	40	36	44	40	40	52	56
Total degree of freedom (ϕ_T)	83	83	59	53	65	59	59	77	83
Inter-laboratories variance ($V_R = S_R/\phi_R$)	0.16	0.04	0.011	0.037	0.008	0.004	1.068	40.769	3.721
Within-laboratory variance ($V_{RW} = S_{RW}/\phi_{RW}$)	0.00	0.00	0.000	0.000	0.000	0.000	0.005	0.009	0.001
Repeatability variance ($V_r = S_r/\phi_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.002	0.007	0.002
Laboratory component of variance ($s_b^2 = (V_R-V_{RW})/(2*3)$)	0.03	0.01	0.002	0.006	0.001	0.001	0.177	6.793	0.620
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	0.001	0.000	0.000
Repeatability component of variance ($s_r^2 = V_r$)	0.00	0.00	0.000	0.000	0.000	0.000	0.002	0.007	0.002
Inter-laboratories standard deviation ($s_R = SQRT(s_r^2/(2*3) + s_c^2/2 + s_b^2)$)	0.2	0.1	0.04	0.08	0.04	0.02	0.42	2.61	0.79
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	0.04	0.05	0.02
Repeatability standard deviation ($s_r = SQRT(s_r^2)$)	0.0	0.0	0.01	0.01	0.01	0.00	0.04	0.09	0.05
Inter-laboratories precision CV (%)	3.5	2.2	69.98	44.25	24.67	35.31	2.96	21.33	108.85
Within-laboratory precision CV (%)	0.7	0.9	9.57	4.20	4.63	4.72	0.28	0.44	2.99
Repeatability precision CV (%)	0.7	0.5	10.91	3.86	4.05	7.26	0.27	0.70	6.82
Reproducibility limit ($R = D(2, 0.95)*s_R$)	0.46	0.24	0.118	0.219	0.101	0.068	1.181	7.299	2.205
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95)*s_{Rw}$)	0.08	0.09	0.016	0.021	0.019	0.009	0.112	0.151	0.061
Repeatability limit ($r = D(3, 0.95)*s_r$)	0.10	0.06	0.022	0.022	0.019	0.016	0.128	0.283	0.163

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 (11 laboratories) used AAS for measurement of Ex-Ca and Mg, and 7 laboratories used FEP for Ex-K and Na. Years in use of instruments were varied from 1 to 26 for AAS and from 1 to 37 for FEP. All the laboratories except “ru01” 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, 2 laboratories used Buchner funnel procedures, and one laboratory used centrifuge procedures and automatic extractor procedures, respectively. No clear difference was observed among data by different procedures. As for size of burette for titration of Ex-acidity, capacities were varied from 5 to 50 ml, but minimum graduates were 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 57 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. More than half of laboratories followed the recommendation.

Table 4.5. Number and experience of analyst

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of	Years of experience		
		Chemical	Soil		Chemical	Soil	
cn01	1	22	3	1	22	3	s
cn02	1	11	8	1	11	8	d
cn04	2	5/12	2/2	1	12	2	s
id01	1	9	4	1	9	4	s
id02	1	25	25	1	10	8	d
jp01	1	8	8	1	8	8	s
jp02	1	4	1	1	4	1	s
mn01	-	-	-	1	12	12	-
ph01	1	15	15	1	31	31	d
kr01	1	11	11	1	11	11	s
ru01	1	10	10	1	10	10	s
th01	2	2/1	0/0	2	2/1	0/0	s
vn01	1	14	9	1	14	9	s
vn02	-	-	-	1	4	1	-

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

Table 4.6 Analytical instruments and their conditions for exchangeable cations

Lab.	Sample	Ex-Ca		Ex-Mg			Ex-K		Ex-Na			Procedures for extraction of Ex-base cations	Ex-Acidity, Al and H		
													method	Size of burette (ml)	
		Instrument	Years[*1]	Instrument	Years		Instrument	Years	Instrument	Years				Capacity	Minimum graduate
cn01	No.061	AAS	1	AAS	1	Sr	FEP	1	FEP	1	Sr	Percolation tube	Titration	50	0.1
	No.062	AAS	1	AAS	1	Sr	FEP	1	FEP	1	Sr				
cn02	No.061	AAS	17	AAS	17	(Sr)	AAS	17	AAS	17	+	Automatic	Titration	5	0.00125
	No.062	AAS	17	AAS	17	(Sr)	AAS	17	AAS	17	+				
cn04	No.061	AAS	8	AAS	8	Sr	FEP	8	FEP	8	Cs	Centrifuge	Titration	25	0.1
	No.062	AAS	8	AAS	8	Sr	FEP	8	FEP	8	Cs				
id01	No.061	AAS	1	AAS	1	La	AAS	1	AAS	1	La	Percolation tube	Titration	25	0.05
	No.062	AAS	1	AAS	1	La	AAS	1	AAS	1	La				
id02	No.061	AAS	19	AAS	19	(Sr)	FEP	37	FEP	37	(Cs)	Percolation tube	Titration	50	0.01
	No.062	AAS	19	AAS	19	(Sr)	FEP	37	FEP	37	(Cs)				
jp01	No.061	AAS	21	AAS	21	Sr	FEP	21	FEP	21	na	Percolation tube	Titration	25/10	0.1/0.05
	No.062	AAS	21	AAS	21	Sr	FEP	21	FEP	21	na			(NaOH/HCl)	(NaOH/HCl)
jp02	No.061	AAS	15	AAS	15	La	AAS	15	AAS	15	na	Percolation tube	Titration	10	0.05
	No.062	AAS	15	AAS	15	La	AAS	15	AAS	15	na				
mn01	No.061	-	-	-	-	-	-	-	-	-	-	-	Titration	25	0.1
	No.062	-	-	-	-	-	-	-	-	-	-				
ph01	No.061	AAS	16	AAS	16	Sr	AAS	16	AAS	16	na	Buchner funnel	Titration	50	0.01
	No.062	AAS	16	AAS	16	Sr	AAS	16	AAS	16	na				
kr01	No.061	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Sr	Percolation tube	Titration	25	0.05
	No.062	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Sr				
ru01	No.061	AAS	26	AAS	26	na	FEP	26	FEP	26	na	Percolation tube	Titration		
	No.062	AAS	26	AAS	26	na	FEP	26	FEP	26	na			-25	0.13
th01	No.061	AAS	12	AAS	12	Sr	FEP	12	FEP	12	Sr	Percolation tube	Titration	50	0.05
	No.062	AAS	12	AAS	12	Sr	FEP	12	FEP	12	Sr				
vn01	No.061	-	-	-	-	-	FEP	8	FEP	8	na	Buchner funnel	Titration	10	0.02
	No.062	-	-	-	-	-	FEP	8	FEP	8	na				
vn02	No.061	-	-	-	-	-	-	-	-	-	-	-	Titration	10	0.05
	No.062	-	-	-	-	-	-	-	-	-	-				

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	24-Jan	1	1	13-Feb	6	0	13-Feb	6	0	7-Feb	3	7
	2nd	25-Jan	1		13-Feb	4		13-Feb	4		14-Feb	3	
cn02	1st	26-Jan	1	14	26-Jan	5	14	26-Jan	5	14	26-Jan	5	14
	2nd	9-Feb	1		9-Feb	5		9-Feb	5		9-Feb	5	
cn04	1st	17-Jan	1	19	23-Jan	2	17	23-Jan	2	17	26-Jan	2	18
	2nd	5-Feb	1		9-Feb	2		9-Feb	2		13-Feb	2	
id01	1st	26-Dec	1	57	15-Jan	12	15	15-Jan	12	15	3-Jan	8	0
	2nd	21-Feb	1		30-Jan	19		30-Jan	19		3-Jan	8	
id02	1st	2-Jan	1	6	2-Jan	1	6	2-Jan	1	6	2-Jan	1	6
	2nd	8-Jan	1		8-Jan	1		8-Jan	1		8-Jan	1	
jp01	1st	12-Jan	3	45	17-Jan	3	40	17-Jan	3	40	23-Jan	2	35
	2nd	26-Feb	1		26-Feb	7		26-Feb	7		27-Feb	2	
jp02	1st	18-Jan	2	7	30-Jan	2	9	31-Jan	2	8	12-Jan	2	17
	2nd	25-Jan	2		8-Feb	2		8-Feb	2		29-Jan	4	
mn01	1st	22-Feb	1	0	-	-	-	-	-	-	22-Feb	1	0
	2nd	23-Feb	1		-	-		-	-		22-Feb	1	
ph01	1st	5-Feb	1	7	28-Feb	1	7	28-Feb	1	7	19-Feb	1	7
	2nd	12-Feb	1		7-Mar	1		7-Mar	1		26-Feb	1	
kr01	1st	18-Jun	1	23	15-Jun	2	42	15-Jun	2	42	19-Jun	1	35
	2nd	11-Jul	1		27-Jul	2		27-Jul	2		24-Jul	1	
ru01	1st	10-Feb	1	3	20-Feb	1	3	20-Feb	1	3	20-Feb	1	3
	2nd	13-Feb	1		23-Feb	1		23-Feb	1		23-Feb	1	
th01	1st	18-Jan	1	12	1-Feb	1	4	1-Feb	1	4	24-Jan	1	6
	2nd	30-Jan	1		5-Feb	1		5-Feb	1		30-Jan	1	
vn01	1st	8-Jan	1	4	-	-	-	8-Jan	1	4	8-Jan	1	4
	2nd	12-Jan	1		-	-		12-Jan	1		12-Jan	1	
vn02	1st	2-Feb	1	3	-	-	-	-	-	-	18-Jan	1	1
	2nd	5-Feb	1		-	-		-	-		19-Jan	1	

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

4.4 Comparison with Past Surveys

By using digital formats, no obvious calculation mistake was found in the data. Moreover, most laboratories followed the standard procedures for the analysis. However, the inter-laboratories standard deviations (CV%) were still large compared with those of the past surveys, as shown in Figure 4.3. The precisions of Ex-acidity were probably improved compared with those of the past surveys but the precisions of Ex-base cations should be improved furthermore.

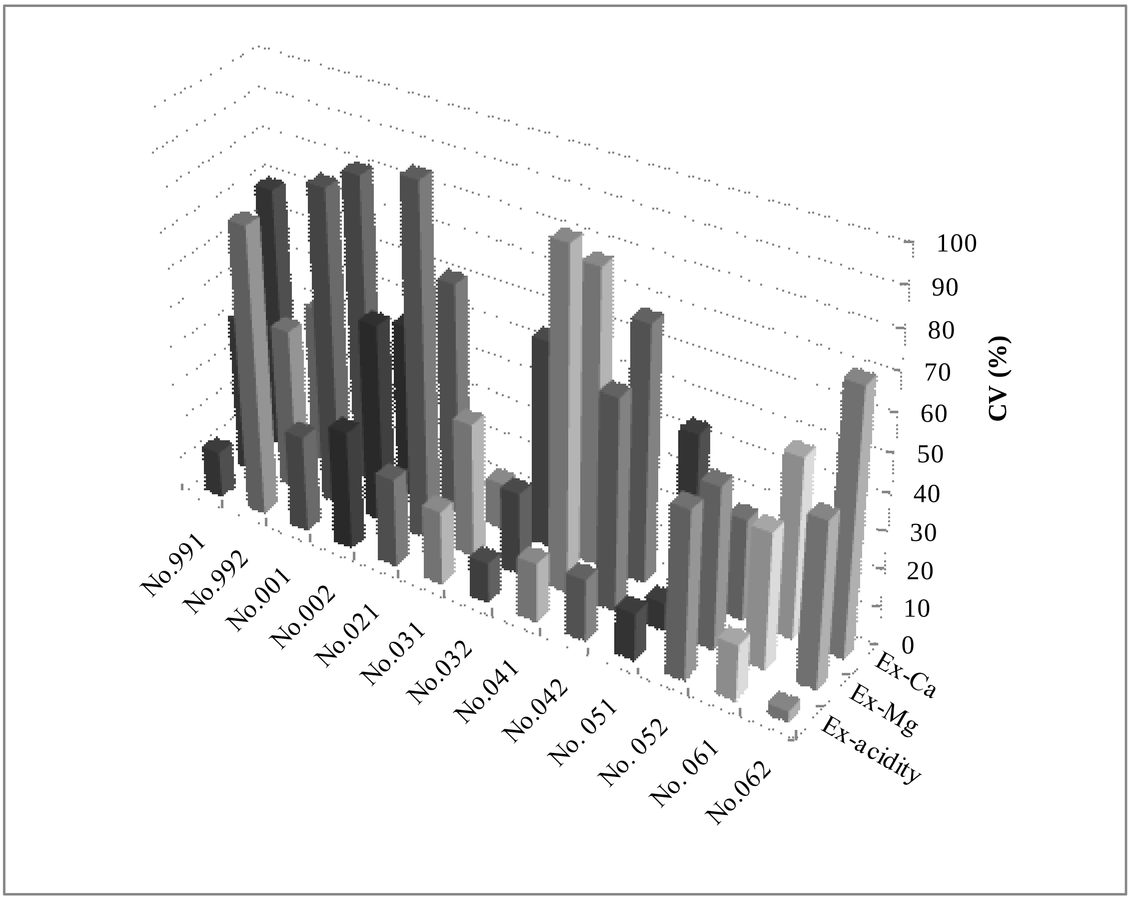


Figure 4.3 Comparison with inter-laboratories standard deviations (CV%) of the past surveys for Ex-Ca, Mg, and acidity

4.5 Recommendations for Improvement

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

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

References

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

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

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

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

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

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

Appendix 4.1 Participating laboratories

1. CHINA

1) Chongqing Institute of Environmental Science	**cn01**
2) Xi'an Environmental Monitoring Station	**cn02**
3) Xiamen Environmental Monitoring Central Station	Not Participated in 2006
4) Zhuhai Environmental Protected Monitoring Station	**cn04**

2. INDONESIA

Air Quality Laboratory, Environmental Management Center	**id01**
Soil Research Institute	**id02**

3. JAPAN

Shimane Agricultural Technology Center	**jp01**
Gifu Prefectural Research Institute of Health and Environment	**jp02**

5. MONGOLIA

Central Laboratory of Environmental Monitoring	**mn01**

6. PHILIPPINES

University of the Philippines, Los Baños	**ph01**

7. Republic of KOREA

Soil Environmental Division, National Institute of Environmental Research	**kr01**

8. RUSSIA

Limnological Institute Russian Academy of Science/Siberian Branch	**ru01**

9. THAILAND

King Mongkut’s University of Technology Thonburi	**th01**

10. VIET NAM

Center for Environmental Research, Institute of Meteorology and Hydrology, MoNRE	**vn01**
Highland and Mid-Central Environment Analysis Laboratory, Middle of Central regional Hydro-Meteorological Observatory, National Hydro-Meteorological Center, MoNRE	**vn02**

Appendix 4.2-1 Entire data of pH in Sample No.061

Lab.	pH(H_2O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	4.5	4.4 (0.0)	4.4	3.9	3.9 (0.0)	3.9
			4.4			3.9
			4.4			3.9
		4.5 (0.1)	4.5		3.9 (0.0)	3.9
			4.5			3.9
			4.4			3.9
cn02	4.4	4.4 (0.0)	4.4	3.9	3.9 (0.0)	3.9
			4.4			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
cn04	4.4	4.4 (0.0)	4.4	3.8	3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8
		4.4 (0.0)	4.4		3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8
id01	4.5	4.4 (0.0)	4.4	3.9	3.9 (0.0)	3.9
			4.4			3.9
			4.4			3.9
		4.5 (0.0)	4.5		3.9 (0.0)	3.9
			4.5			3.9
			4.5			3.9
id02	4.4	4.4 (0.0)	4.4	4.0	4.0 (0.0)	4.0
			4.4			4.0
			4.4			4.0
		4.4 (0.0)	4.4		4.0 (0.0)	4.0
			4.4			4.0
			4.4			4.0
jp01	4.5	4.5 (0.1)	4.5	4.0	4.0 (0.0)	4.0
			4.5			4.0
			4.6			4.0
		4.5 (0.1)	4.6		4.0 (0.0)	4.0
			4.5			4.0
			4.5			4.0
jp02	4.5	4.5 (0.0)	4.5	3.9	3.9 (0.0)	3.9
			4.5			3.9
			4.5			3.9
		4.5 (0.0)	4.5		3.9 (0.0)	3.9
			4.5			3.9
			4.5			3.9
mn01	4.5	4.5 (0.0)	4.5	3.9	3.9 (0.0)	3.9
			4.5			3.9
			4.5			3.9
		4.5 (0.0)	4.5		3.9 (0.0)	3.9
			4.5			3.9
			4.5			3.9
ph01	4.4	4.4 (0.0)	4.4	3.8	3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8
		4.4 (0.0)	4.4		3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8
kr01	4.5	4.4 (0.1)	4.3	4.0	3.9 (0.0)	3.9
			4.4			3.9
			4.4			3.9
		4.5 (0.1)	4.5		4.0 (0.0)	4.0
			4.4			4.0
			4.5			4.0
ru01	4.3	4.3 (0.1)	4.3	4.0	4.0 (0.0)	4.0
			4.3			4.0
			4.4			4.0
		4.3 (0.0)	4.3		4.0 (0.0)	4.0
			4.3			4.0
			4.3			4.0
th01	4.2	4.2 (0.0)	4.2	3.8	3.8 (0.1)	3.8
			4.2			3.8
			4.2			3.9
		4.2 (0.0)	4.2		3.8 (0.0)	3.8
			4.2			3.8
			4.2			3.8
vn01	4.4	4.4 (0.0)	4.4	3.9	3.9 (0.0)	3.9
			4.4			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
vn02	4.4	4.4 (0.0)	4.4	3.8	3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8
		4.4 (0.0)	4.4		3.8 (0.0)	3.8
			4.4			3.8
			4.4			3.8

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

Appendix 4.2-2 Entire data of exchangeable base cations in Sample No.061

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	0.12	0.11 (0.01)	0.11	0.10	0.10 (0.01)	0.10	0.18	0.18 (0.01)	0.18	0.01	0.01 (0.00)	0.01
			0.10			0.10			0.18			0.01
			0.11			0.11			0.19			0.01
		0.12 (0.02)	0.14		0.10 (0.01)	0.11		0.18 (0.01)	0.19		0.01 (0.00)	0.01
			0.10			0.10			0.18			0.01
			0.11			0.10			0.18			0.01
cn02	0.26	0.25 (0.02)	0.24	0.15	0.15 (0.00)	0.15	0.14	0.14 (0.01)	0.14	0.09	0.08 (0.01)	0.08
			0.24			0.15			0.14			0.08
			0.28			0.15			0.15			0.09
		0.26 (0.01)	0.26		0.15 (0.00)	0.15		0.14 (0.01)	0.14		0.09 (0.01)	0.08
			0.26			0.15			0.14			0.10
			0.27			0.15			0.15			0.09
cn04	0.11	0.12 (0.01)	0.12	0.13	0.13 (0.00)	0.13	0.20	0.19 (0.01)	0.19	0.02	0.01 (0.01)	0.01
			0.11			0.13			0.20			0.02
			0.12			0.13			0.19			0.01
		0.10 (0.01)	0.10		0.13 (0.00)	0.13		0.20 (0.01)	0.20		0.02 (0.01)	0.02
			0.11			0.13			0.20			0.02
			0.10			0.13			0.21			0.01
id01	0.16	0.16 (0.01)	0.17	0.12	0.11 (0.01)	0.11	0.15	0.14 (0.01)	0.13	0.05	0.05 (0.01)	0.04
			0.15			0.10			0.15			0.06
			0.15			0.11			0.14			0.04
		0.16 (0.01)	0.16		0.13 (0.00)	0.13		0.16 (0.00)	0.16		0.04 (0.01)	0.04
			0.16			0.13			0.16			0.05
			0.17			0.13			0.16			0.04
id02	0.49	0.49 (0.00)	0.49	0.43	0.43 (0.00)	0.43	0.22	0.22 (0.01)	0.22	0.11	0.11 (0.01)	0.11
			0.49			0.43			0.22			0.11
			0.49			0.43			0.23			0.10
		0.49 (0.01)	0.49		0.42 (0.01)	0.41		0.22 (0.01)	0.22		0.11 (0.00)	0.11
			0.50			0.43			0.23			0.11
			0.49			0.43			0.22			0.11
jp01	0.30	0.30 (0.01)	0.30	0.15	0.15 (0.00)	0.15	0.28	0.27 (0.01)	0.26	0.02	0.02 (0.00)	0.02
			0.29			0.15			0.27			0.02
			0.30			0.15			0.27			0.02
		0.29 (0.00)	0.29		0.15 (0.00)	0.15		0.29 (0.01)	0.29		0.02 (0.01)	0.02
			0.29			0.15			0.28			0.03
			0.29			0.15			0.29			0.02
jp02	0.19	0.19 (0.01)	0.20	0.17	0.17 (0.00)	0.17	0.25	0.25 (0.01)	0.25	0.05	0.05 (0.01)	0.04
			0.19			0.17			0.24			0.06
			0.19			0.17			0.25			0.04
		0.19 (0.01)	0.19		0.17 (0.00)	0.17		0.25 (0.00)	0.25		0.04 (0.01)	0.04
			0.20			0.17			0.25			0.05
			0.19			0.17			0.25			0.04
mn01												
ph01	0.03	0.02 (0.01)	0.02	0.26	0.20 (0.01)	0.20	0.42	0.42 (0.04)	0.39	1.30	1.30 (0.03)	1.26
			0.02			0.20			0.42			1.32
			0.03			0.21			0.46			1.32
		0.03 (0.00)	0.03		0.31 (0.01)	0.30		0.42 (0.04)	0.42		1.30 (0.03)	1.32
			0.03			0.31			0.39			1.26
			0.03			0.32			0.46			1.32
kr01	0.13	0.14 (0.00)	0.14	0.11	0.12 (0.01)	0.12	0.21	0.22 (0.01)	0.22	0.01	0.01 (0.00)	0.01
			0.14			0.12			0.22			0.01
			0.14			0.11			0.21			0.01
		0.12 (0.01)	0.11		0.10 (0.01)	0.10		0.20 (0.01)	0.21		0.01 (0.00)	0.01
			0.13			0.11			0.20			0.01
			0.11			0.10			0.20			0.01
ru01	0.15	0.15 (0.00)	0.15	0.21	0.21 (0.01)	0.21	0.25	0.25 (0.00)	0.25	0.07	0.07 (0.00)	0.07
			0.15			0.21			0.25			0.07
			0.15			0.22			0.25			0.07
		0.14 (0.01)	0.15		0.21 (0.01)	0.21		0.24 (0.01)	0.23		0.07 (0.00)	0.07
			0.14			0.20			0.24			0.07
			0.14			0.21			0.24			0.07
th01	0.23	0.22 (0.00)	0.22	0.04	0.04 (0.01)	0.04	0.02	0.02 (0.00)	0.02	0.08	0.08 (0.00)	0.08
			0.22			0.05			0.02			0.08
			0.22			0.04			0.02			0.08
		0.23 (0.00)	0.23		0.04 (0.01)	0.03		0.02 (0.00)	0.02		0.08 (0.01)	0.08
			0.23			0.04			0.02			0.08
			0.23			0.04			0.02			0.07
vn01							0.24	0.24 (0.00)	0.24	0.08	0.08 (0.00)	0.08
									0.24			0.08
									0.24			0.08
								0.24 (0.00)	0.24		0.08 (0.00)	0.08
									0.24			0.08
									0.24			0.08
vn02												

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

Appendix 4.2-3 Entire data of exchangeable acidity and acid cations in Sample No.061

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+) kg^{-1}								
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	6.80	6.88 (0.04)	6.91	6.20	6.18 (0.03)	6.14	0.65	0.69 (0.09)	0.76
			6.90			6.20			0.73
			6.84			6.20			0.59
		6.72 (0.08)	6.64		6.22 (0.06)	6.26		0.60 (0.02)	0.59
			6.74			6.24			0.59
			6.79			6.15			0.62
cn02	4.93	4.93 (0.04)	4.94	4.73	4.71 (0.03)	4.71	0.20	0.22 (0.02)	0.23
			4.96			4.74			0.23
			4.89			4.69			0.20
		4.92 (0.00)	4.92		4.74 (0.02)	4.75		0.18 (0.02)	0.17
			4.92			4.75			0.17
			4.92			4.72			0.20
cn04	6.13	6.16 (0.02)	6.18	5.23	5.34 (0.05)	5.37	0.90	0.82 (0.04)	0.81
			6.16			5.37			0.79
			6.14			5.28			0.86
		6.10 (0.01)	6.09		5.12 (0.03)	5.12		0.98 (0.02)	0.97
			6.11			5.15			0.97
			6.10			5.10			1.00
id01	6.92	6.94 (0.10)	6.91	5.59	5.59 (0.05)	5.56	1.32	1.34 (0.05)	1.35
			6.86			5.57			1.29
			7.05			5.65			1.39
		6.90 (0.03)	6.91		5.59 (0.05)	5.56		1.30 (0.04)	1.35
			6.86			5.57			1.29
			6.92			5.65			1.27
id02	4.99	4.97 (0.03)	4.94	4.55	4.54 (0.02)	4.52	0.34	0.35 (0.06)	0.42
			4.98			4.55			0.31
			5.00			4.55			0.33
		5.00 (0.03)	5.03		4.55 (0.02)	4.57		0.33 (0.00)	0.33
			5.00			4.55			0.33
			4.98			4.53			0.33
jp01	7.35	7.30 (0.05)	7.34	6.57	6.52 (0.04)	6.56	0.79	0.78 (0.07)	0.78
			7.32			6.48			0.85
			7.24			6.52			0.72
		7.40 (0.05)	7.40		6.61 (0.07)	6.64		0.79 (0.04)	0.75
			7.35			6.53			0.82
			7.45			6.65			0.80
jp02	5.93	5.95 (0.02)	5.96	5.10	5.13 (0.04)	5.09	0.84	0.82 (0.05)	0.88
			5.92			5.13			0.79
			5.96			5.17			0.79
		5.91 (0.11)	5.92		5.06 (0.13)	5.09		0.85 (0.03)	0.83
			5.79			4.91			0.88
			6.01			5.17			0.83
mn01	8.39	8.41 (0.06)	8.48	8.08	8.08 (0.00)	8.08	0.61	0.61 (0.00)	0.61
			8.37			8.08			0.61
			8.37			8.08			0.61
		8.36 (0.00)	8.36		8.08 (0.00)	8.08		0.61 (0.00)	0.61
			8.36			8.08			0.61
			8.36			8.08			0.61
ph01	6.95	6.94 (0.05)	6.92	6.49	6.48 (0.06)	6.47	0.45	0.46 (0.01)	0.45
			6.99			6.54			0.45
			6.90			6.43			0.47
		6.95 (0.05)	6.95		6.50 (0.06)	6.49		0.44 (0.01)	0.45
			6.99			6.56			0.43
			6.90			6.45			0.45
kr01	7.69	7.59 (0.09)	7.68	6.80	6.69 (0.13)	6.76	0.72	0.79 (0.33)	0.86
			7.51			6.76			1.08
			7.57			6.54			0.43
		7.79 (0.11)	7.79		6.91 (0.13)	6.76		0.65 (0.22)	0.65
			7.89			6.98			0.86
			7.68			6.98			0.43
ru01	7.87	7.87 (0.00)	7.87	7.21	7.21 (0.00)	7.21	0.57	0.57 (0.00)	0.57
			7.87			7.21			0.57
			7.87			7.21			0.57
		7.87 (0.00)	7.87		7.21 (0.00)	7.21		0.57 (0.00)	0.57
			7.87			7.21			0.57
			7.87			7.21			0.57
th01	6.66	6.68 (0.01)	6.67	5.18	5.19 (0.03)	5.17	1.48	1.49 (0.02)	1.50
			6.68			5.22			1.46
			6.68			5.17			1.50
		6.64 (0.03)	6.62		5.17 (0.04)	5.21		1.47 (0.05)	1.41
			6.68			5.18			1.50
			6.62			5.13			1.49
vn01	7.52	7.52 (0.08)	7.55	5.60	5.60 (0.02)	5.59	1.93	1.92 (0.06)	1.96
			7.57			5.62			1.95
			7.43			5.58			1.85
		7.52 (0.01)	7.52		5.59 (0.05)	5.59		1.93 (0.06)	1.93
			7.51			5.63			1.88
			7.52			5.54			1.99
vn02	6.55	6.55 (0.02)	6.56	5.91	5.92 (0.06)	5.98	0.76	0.76 (0.02)	0.75
			6.53			5.92			0.75
			6.56			5.87			0.79
		6.55 (0.02)	6.56		5.90 (0.03)	5.87		0.76 (0.02)	0.79
			6.56			5.92			0.75
			6.53			5.92			0.75

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

Appendix 4.3-1 Entire data of pH in Sample No.062

Lab.	pH(H_2O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	4.6	4.6 (0.0)	4.6	4.0	4.0 (0.0)	4.0
			4.6			4.0
			4.6			4.0
		4.6 (0.0)	4.6		4.0 (0.0)	4.0
			4.6			4.0
			4.6			4.0
cn02	4.6	4.6 (0.0)	4.6	4.0	4.0 (0.0)	4.0
			4.6			4.0
			4.6			4.0
		4.6 (0.0)	4.6		4.0 (0.0)	4.0
			4.6			4.0
			4.6			4.0
cn04	4.5	4.5 (0.0)	4.5	3.8	3.8 (0.0)	3.8
			4.5			3.8
			4.5			3.8
		4.5 (0.0)	4.5		3.8 (0.0)	3.8
			4.5			3.8
			4.5			3.8
id01	4.7	4.7 (0.0)	4.7	3.9	3.9 (0.0)	3.9
			4.7			3.9
			4.7			3.9
		4.6 (0.1)	4.7		3.9 (0.0)	3.9
			4.6			3.9
			4.6			3.9
id02	4.5	4.5 (0.0)	4.5	4.0	4.0 (0.0)	4.0
			4.5			4.0
			4.5			4.0
		4.5 (0.0)	4.5		4.0 (0.0)	4.0
			4.5			4.0
			4.5			4.0
jp01	5.0	5.0 (0.1)	4.9	4.1	4.1 (0.0)	4.1
			5.0			4.1
			5.0			4.1
		5.0 (0.0)	5.0		4.0 (0.0)	4.0
			5.0			4.0
			5.0			4.0
jp02	4.8	4.8 (0.0)	4.8	3.9	3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
		4.8 (0.0)	4.8		3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
mn01	4.8	4.7 (0.1)	4.7	4.0	4.0 (0.0)	4.0
			4.7			4.0
			4.8			4.0
		4.8 (0.1)	4.7		4.0 (0.0)	4.0
			4.8			4.0
			4.8			4.0
ph01	4.6	4.6 (0.0)	4.6	3.8	3.8 (0.0)	3.8
			4.6			3.8
			4.6			3.8
		4.5 (0.0)	4.5		3.8 (0.0)	3.8
			4.5			3.8
			4.5			3.8
kr01	4.7	4.6 (0.1)	4.6	4.0	3.9 (0.0)	3.9
			4.7			3.9
			4.6			3.9
		4.7 (0.0)	4.7		4.0 (0.0)	4.0
			4.7			4.0
			4.7			4.0
ru01	4.5	4.5 (0.0)	4.5	4.0	4.0 (0.1)	4.0
			4.5			4.0
			4.5			4.1
		4.5 (0.0)	4.5		4.0 (0.0)	4.0
			4.5			4.0
			4.5			4.0
th01	4.3	4.3 (0.0)	4.3	3.9	3.8 (0.1)	3.9
			4.3			3.8
			4.3			3.8
		4.3 (0.0)	4.3		3.9 (0.1)	3.8
			4.3			3.9
			4.3			3.9
vn01	4.7	4.7 (0.1)	4.7	4.0	4.0 (0.0)	4.0
			4.7			4.0
			4.6			4.0
		4.6 (0.0)	4.6		4.0 (0.0)	4.0
			4.6			4.0
			4.6			4.0
vn02	4.7	4.7 (0.1)	4.7	3.9	3.8 (0.0)	3.8
			4.7			3.8
			4.8			3.8
		4.7 (0.1)	4.7		3.9 (0.0)	3.9
			4.8			3.9
			4.7			3.9

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

Appendix 4.3-2 Entire data of exchangeable base cations in Sample No.062

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	0.05	0.05 (0.01)	0.06	0.17	0.17 (0.01)	0.17	0.12	0.12 (0.01)	0.13	0.03	0.03 (0.01)	0.03
			0.05			0.17			0.12			0.02
			0.04			0.16			0.11			0.03
		0.04 (0.01)	0.05		0.17 (0.00)	0.17		0.11 (0.00)	0.11		0.03 (0.00)	0.03
			0.04			0.17			0.11			0.03
			0.04			0.17			0.11			0.03
cn02	0.10	0.10 (0.01)	0.09	0.23	0.22 (0.01)	0.22	0.12	0.12 (0.00)	0.12	0.10	0.09 (0.01)	0.08
			0.10			0.21			0.12			0.10
			0.11			0.22			0.12			0.10
		0.09 (0.02)	0.08		0.23 (0.01)	0.23		0.12 (0.02)	0.10		0.10 (0.00)	0.10
			0.08			0.23			0.13			0.10
			0.11			0.22			0.13			0.10
cn04	0.08	0.07 (0.01)	0.07	0.27	0.27 (0.01)	0.27	0.13	0.13 (0.01)	0.13	0.10	0.10 (0.01)	0.10
			0.06			0.28			0.13			0.10
			0.07			0.27			0.12			0.09
		0.08 (0.01)	0.08		0.27 (0.00)	0.27		0.12 (0.01)	0.12		0.10 (0.01)	0.10
			0.09			0.27			0.12			0.10
			0.08			0.27			0.11			0.09
id01	0.10	0.09 (0.00)	0.09	0.21	0.22 (0.02)	0.23	0.11	0.10 (0.01)	0.10	0.09	0.09 (0.01)	0.09
			0.09			0.24			0.10			0.09
			0.09			0.20			0.11			0.10
		0.10 (0.01)	0.10		0.20 (0.01)	0.19		0.12 (0.00)	0.12		0.09 (0.01)	0.08
			0.11			0.20			0.12			0.09
			0.10			0.20			0.12			0.09
id02	0.43	0.43 (0.01)	0.43	0.55	0.55 (0.00)	0.55	0.17	0.17 (0.00)	0.17	0.07	0.07 (0.00)	0.07
			0.44			0.55			0.17			0.07
			0.43			0.55			0.17			0.07
		0.43 (0.01)	0.43		0.54 (0.01)	0.55		0.17 (0.00)	0.17		0.07 (0.01)	0.07
			0.43			0.53			0.17			0.08
			0.42			0.55			0.17			0.07
jp01	0.12	0.12 (0.01)	0.12	0.27	0.26 (0.01)	0.26	0.21	0.20 (0.01)	0.20	0.06	0.05 (0.01)	0.05
			0.12			0.27			0.21			0.06
			0.11			0.26			0.20			0.05
		0.12 (0.01)	0.12		0.27 (0.01)	0.27		0.22 (0.01)	0.22		0.06 (0.00)	0.06
			0.13			0.27			0.22			0.06
			0.11			0.26			0.23			0.06
jp02	0.00	0.00 (0.00)	0.00	0.06	0.06 (0.00)	0.06	0.17	0.17 (0.00)	0.17	0.06	0.06 (0.01)	0.06
			0.00			0.06			0.17			0.06
			0.00			0.06			0.17			0.07
		0.00 (0.00)	0.00		0.06 (0.00)	0.06		0.17 (0.00)	0.17		0.06 (0.01)	0.07
			0.00			0.06			0.17			0.06
			0.00			0.06			0.17			0.06
mn01												
ph01	0.00	0.00 (0.00)	0.00	0.26	0.21 (0.01)	0.20	0.38	0.38 (0.02)	0.39	1.34	1.34 (0.03)	1.32
			0.00			0.21			0.39			1.32
			0.00			0.22			0.35			1.38
		0.00 (0.00)	0.00		0.31 (0.01)	0.30		0.38 (0.02)	0.35		1.34 (0.03)	1.32
			0.00			0.32			0.39			1.32
			0.00			0.31			0.39			1.38
kr01	0.05	0.05 (0.01)	0.05	0.21	0.21 (0.00)	0.21	0.15	0.15 (0.00)	0.15	0.04	0.04 (0.00)	0.04
			0.05			0.21			0.15			0.04
			0.04			0.21			0.15			0.04
		0.04 (0.01)	0.05		0.20 (0.01)	0.20		0.14 (0.01)	0.15		0.03 (0.01)	0.03
			0.04			0.20			0.14			0.03
			0.04			0.21			0.13			0.04
ru01	0.03	0.03 (0.00)	0.03	0.09	0.09 (0.01)	0.09	0.17	0.17 (0.00)	0.17	0.09	0.09 (0.00)	0.09
			0.03			0.08			0.17			0.09
			0.03			0.09			0.17			0.09
		0.03 (0.00)	0.03		0.09 (0.01)	0.09		0.17 (0.01)	0.18		0.09 (0.01)	0.09
			0.03			0.08			0.17			0.08
			0.03			0.09			0.17			0.09
th01	0.10	0.09 (0.01)	0.09	0.10	0.10 (0.01)	0.10	0.10	0.10 (0.01)	0.09	0.18	0.18 (0.00)	0.18
			0.10			0.11			0.10			0.18
			0.09			0.10			0.10			0.18
		0.10 (0.00)	0.10		0.09 (0.01)	0.09		0.09 (0.01)	0.09		0.18 (0.01)	0.18
			0.10			0.09			0.09			0.17
			0.10			0.10			0.10			0.18
vn01							0.17	0.17 (0.00)	0.17	0.06	0.06 (0.00)	0.06
									0.17			0.06
									0.17			0.06
								0.17 (0.00)	0.17		0.06 (0.00)	0.06
									0.17			0.06
									0.17			0.06
vn02												

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

Appendix 4.3-3 Entire data of exchangeable acidity and acid cations in Sample No.062

Lab.	Ex-acidity			Ex-Al			Ex-H		
	cmol(+) kg^{-1}								
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
cn01	13.72	13.74 (0.07)	13.66	13.66	13.69 (0.07)	13.61	0.06	0.05 (0.01)	0.05
			13.79			13.74			0.06
			13.76			13.71			0.05
		13.69 (0.04)	13.69		13.63 (0.03)	13.62		0.06 (0.01)	0.07
			13.65			13.60			0.05
			13.73			13.66			0.06
cn02	7.79	7.85 (0.03)	7.87	7.32	7.38 (0.07)	7.45	0.48	0.48 (0.06)	0.43
			7.82			7.37			0.45
			7.87			7.32			0.55
		7.73 (0.01)	7.74		7.26 (0.08)	7.29		0.47 (0.07)	0.45
			7.72			7.17			0.55
			7.74			7.32			0.42
cn04	14.03	14.02 (0.03)	14.02	12.88	12.89 (0.03)	12.91	1.16	1.14 (0.02)	1.12
			13.99			12.86			1.13
			14.05			12.89			1.16
		14.04 (0.03)	14.02		12.86 (0.03)	12.84		1.18 (0.04)	1.18
			14.07			12.86			1.21
			14.03			12.89			1.14
id01	14.39	14.41 (0.08)	14.50	12.28	12.28 (0.01)	12.28	2.11	2.13 (0.08)	2.22
			14.37			12.28			2.09
			14.37			12.29			2.09
		14.37 (0.00)	14.37		12.28 (0.01)	12.29		2.09 (0.00)	2.09
			14.37			12.28			2.09
			14.37			12.28			2.09
id02	10.76	10.75 (0.01)	10.74	10.15	10.15 (0.02)	10.15	0.34	0.32 (0.02)	0.31
			10.74			10.13			0.34
			10.76			10.17			0.31
		10.77 (0.02)	10.78		10.15 (0.02)	10.17		0.35 (0.01)	0.34
			10.74			10.13			0.34
			10.78			10.15			0.36
jp01	14.23	14.30 (0.07)	14.29	14.18	14.27 (0.05)	14.23	0.05	0.03 (0.05)	0.06
			14.38			14.32			0.05
			14.24			14.27			-0.03
		14.15 (0.04)	14.12		14.09 (0.06)	14.10		0.06 (0.06)	0.01
			14.19			14.14			0.06
			14.15			14.03			0.12
jp02	12.91	13.10 (0.31)	12.75	12.47	12.66 (0.28)	12.35	0.44	0.44 (0.05)	0.39
			13.36			12.88			0.48
			13.18			12.75			0.44
		12.72 (0.29)	12.70		12.28 (0.26)	12.18		0.44 (0.09)	0.53
			13.01			12.57			0.44
			12.44			12.09			0.35
mn01	14.08	14.08 (0.00)	14.08	13.91	13.91 (0.00)	13.91	0.35	0.35 (0.00)	0.35
			14.08			13.91			0.35
			14.08			13.91			0.35
		14.08 (0.00)	14.08		13.91 (0.00)	13.91		0.35 (0.00)	0.35
			14.08			13.91			0.35
			14.08			13.91			0.35
ph01	14.42	14.41 (0.08)	14.48	12.91	12.90 (0.04)	12.94	1.51	1.51 (0.04)	1.54
			14.33			12.86			1.47
			14.42			12.90			1.52
		14.43 (0.03)	14.42		12.92 (0.02)	12.92		1.51 (0.01)	1.50
			14.40			12.90			1.50
			14.46			12.94			1.52
kr01	15.19	14.79 (0.08)	14.70	14.24	14.17 (0.22)	13.95	0.31	0.35 (0.13)	0.42
			14.86			14.39			0.42
			14.81			14.17			0.20
		15.59 (0.45)	15.35		14.31 (0.33)	13.95		0.27 (0.13)	0.42
			15.30			14.60			0.20
			16.11			14.39			0.20
ru01	14.60	14.60 (0.00)	14.60	14.60	14.60 (0.00)	14.60	0.00	0.00 (0.00)	0.00
			14.60			14.60			0.00
			14.60			14.60			0.00
		14.60 (0.00)	14.60		14.60 (0.00)	14.60		0.00 (0.00)	0.00
			14.60			14.60			0.00
			14.60			14.60			0.00
th01	14.09	14.05 (0.04)	14.10	11.67	11.65 (0.05)	11.70	2.42	2.41 (0.02)	2.40
			14.03			11.60			2.43
			14.03			11.65			2.39
		14.12 (0.03)	14.10		11.69 (0.03)	11.66		2.43 (0.03)	2.44
			14.11			11.71			2.40
			14.15			11.69			2.45
vn01	15.13	15.13 (0.01)	15.14	14.29	14.31 (0.03)	14.33	0.85	0.83 (0.02)	0.81
			15.13			14.31			0.82
			15.12			14.28			0.85
		15.12 (0.02)	15.14		14.27 (0.02)	14.28		0.86 (0.01)	0.86
			15.11			14.25			0.86
			15.12			14.28			0.85
vn02	13.73	13.74 (0.03)	13.72	6.81	6.81 (0.04)	6.86	0.09	0.07 (0.00)	0.07
			13.78			6.79			0.07
			13.72			6.79			0.07
		13.72 (0.00)	13.72		6.81 (0.04)	6.79		0.10 (0.02)	0.11
			13.72			6.79			0.11
			13.72			6.86			0.07

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

5. 7th INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

5.1 Introduction

In the 7th inter-laboratory comparison of inland aquatic environment, artificial inland aquatic environment samples containing known concentrations of major ions, were prepared and sent to the participating countries of EANET by the Network Center (NC) in November 2006. 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 18 laboratories on November 22 in 2006, and all laboratories submitted their analytical data to NC by February 28 in 2007. 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 Philippines (Lab.ID ph.02) participated for the first time in this inter-laboratory comparison project on inland aquatic environment. This laboratory submitted the data of only two parameters, pH and EC.

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) $= 2C(SO_4^{2-}) + C(NO_3^-) + C(Cl^-) + (ALK)$

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) $= 10^{(6-pH)} + C(NH_4^+) + C(Na^+) + C(K^+)$

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

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

(3) Calculation of ion balance (R_1)

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

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

Table 5.5 Allowable ranges for R_1 in different concentration ranges

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

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

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

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

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

C: Molar concentrations (μmol/L) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C. Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

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

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

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

Table 5.6 Allowable ranges for R_2 in different concentration ranges

Λmeas[mS/m]	R_2 [%]
< 0.5	+ 20 ~ -20
0.5 ~ 3	+13 ~ -13
> 3	+9 ~ -9

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

5.3 Results

5.3.1 Outline of Results

Original data from the laboratories are shown in 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. As shown in Table 5.7, average of submitted data agreed fairly well with the prepared value/concentration within a range of ±10%.

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

Constituents		Prepared	Average	S.D	N	Min.	Max.
pH		7.01	6.99	0.24	18	6.3	7.26
EC	(mS/m)	4.91	4.68	0.12	17	4.45	4.89
Alkalinity	(meq/L)	0.159	0.154	0.018	17	0.106	0.180
SO_4^{2-}	(mg/L)	6.04	6.37	0.23	17	6.04	6.9
NO_3^-	(mg/L)	0.74	0.74	0.09	17	0.60	1.00
Cl^-	(mg/L)	3.65	3.64	0.50	17	2.48	4.99
Na^+	(mg/L)	3.85	3.98	0.40	17	3.22	4.69
K^+	(mg/L)	1.02	0.96	0.07	15	0.78	1.06
Ca^{2+}	(mg/L)	2.48	2.62	0.36	17	2.08	3.04
Mg^{2+}	(mg/L)	0.96	0.90	0.17	17	0.41	1.10
NH_4^+	(mg/L)	0.16	0.16	0.06	17	0.00	0.31

(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	1	1	0	2	0	4	2	9	2	5	26	13.9%
X	0	0	1	0	1	2	0	2	0	2	4	12	6.4%
Data within DQOs	17	16	15	17	14	15	13	13	8	13	8	149	79.7%
Flagged(%)	0.0	5.9	11.8	0.0	17.6	11.8	23.5	23.5	52.9	23.5	52.9	20.3	

*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%)

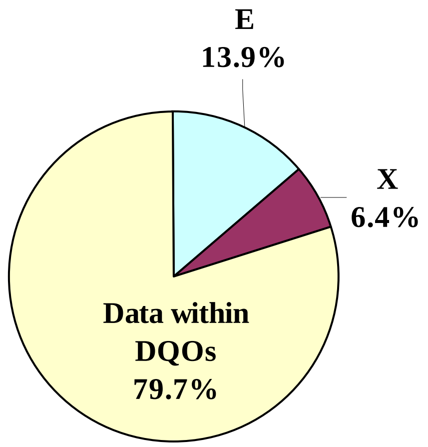


Figure 5.1 Percentage of flagged data

The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 13.9% of all reported data of samples. And the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 6.4% of all reported data of samples. And the percentage of flagged cations was larger than that of anions. Especially the percentage of flagged Ca^{2+} and NH_4^+ exceeded more than 50%.

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	2	12%
1	6	35%
2	4	24%
3	3	18%
4	2	12%
5	0	0%
6	0	0%
7	1	6%
Total	17	100%

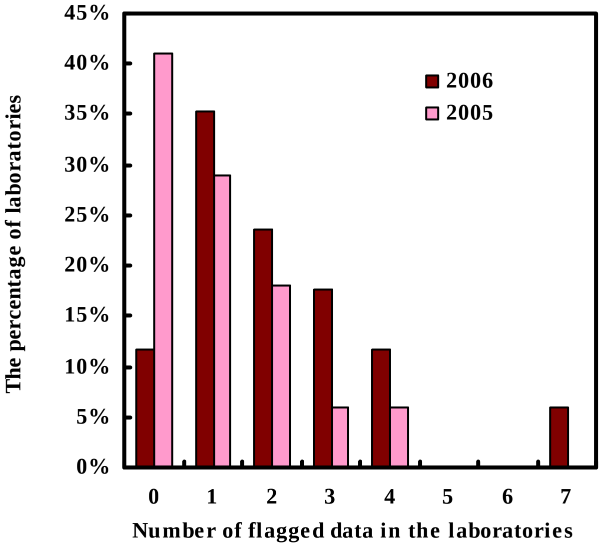


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 41% in last attempt (2005), but that of this year was only 12%. There was a laboratory that has seven flagged data in this attempt.

Table 5.9 Analytical Results of Sample No.061 (artificial inland aquatic environment sample : EANET in 2006)

Lab. ID	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	R1	R2
	-	(mS/m)	(meq/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	-	-
cn01	7.16	4.56	0.155	6.25	0.70	4.08	4.13	0.97	E 2.86	1.03	0.14	3.3	5.9
cn02	7.15	4.68	0.147	6.88	E 0.85	3.86	4.29	0.95	E 2.99	1.06	E 0.20	5.2	6.1
cn03	7.17	4.65	0.165	6.25	0.71	3.79	4.02	0.99	E 2.99	1.03	0.18	3.6	5.1
cn04	7.10	4.60	0.164	6.32	0.74	3.68	3.74	0.99	2.78	0.99	0.15	0.6	4.1
id01	6.76	4.57	0.155	6.90	0.82	X 2.48	E 3.22	X 0.50	E 3.04	0.85	0.17	0.3	0.5
id02	6.30	4.60	X 0.106	6.50	0.72	X 4.99	E 4.67	E 0.84	E 2.09	X 0.64	X 0.10	-0.8	2.6
jp01	6.91	4.70	0.166	6.29	0.71	3.56	3.80	1.01	2.45	0.93	0.17	-1.2	1.7
jp02	7.26	4.61	0.162	6.30	0.72	3.29	3.80	0.98	E 2.08	E 0.80	0.16	-3.7	0.0
mn01	6.98	4.65	E 0.131	6.10	0.74	3.44	E 4.69	0.95	E 2.98	1.10	X 0.00	I 12.1	3.6
my01	6.95	4.86	0.175	6.31	X 1.00	3.33	E 4.56	0.96	2.37	0.84	E 0.19	0.5	1.3
ph01	6.59	4.66	0.164	6.38	0.70	3.59	4.06	1.06	E 2.96	E 0.81	0.16	2.1	3.9
ph02	6.99	E 4.01											
ru01	7.07	4.83	0.139	6.23	0.74	3.73	3.74	0.96	2.17	0.95	X 0.24	0.1	-1.3
ru02	7.08	4.85	0.140	6.48	0.69	3.74	3.49	0.93	2.30	X 0.41	X 0.31	-6.8	-3.5
th01	6.85	4.45	0.141	6.25	0.66	3.54	3.87	X 1.99	2.21	0.95	E 0.12	4.1	4.3
th02	7.12	4.89	0.180	6.04	0.68	3.31	3.94	1.01	2.71	1.00	E 0.13	1.4	0.6
vn01	7.15	4.77	0.160	6.51	0.77	3.98	3.92	1.01	2.73	0.96	E 0.13	-0.2	3.1
vn02	7.14	4.71	0.166	6.30	E 0.60	3.52	3.70	E 0.78	E 2.91	0.96	0.17	1.0	2.3
Expected value	7.01	4.91	0.159	6.37	0.74	3.65	3.85	1.02	2.48	0.96	0.16	-	-

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)

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.

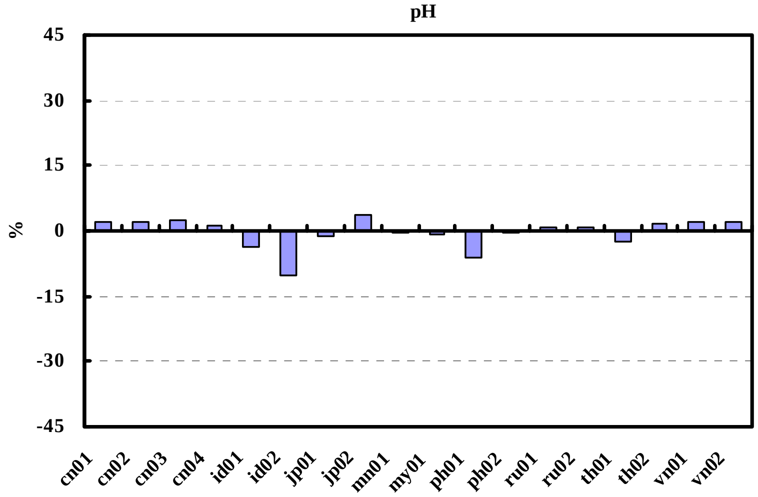


Figure 5.3 Distribution of results for pH (normalized by prepared value)

All obtained data of pH were within DQOs.

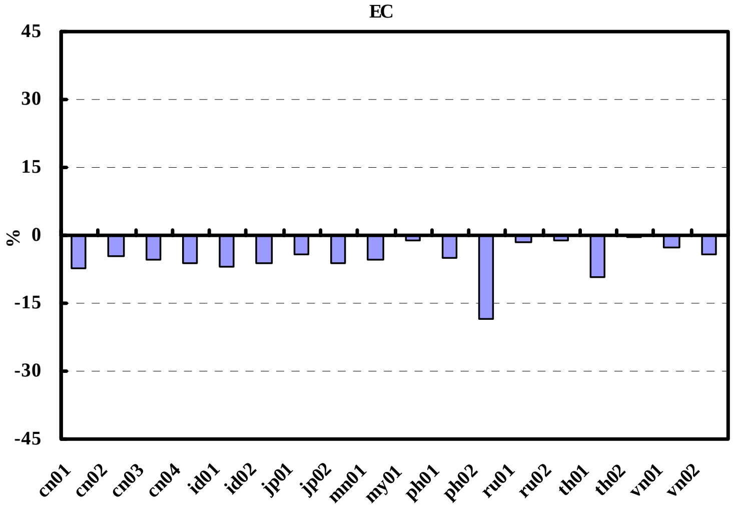


Figure 5.4 Distribution of results for EC (normalized by prepared value)

One data was flagged. The variation between laboratories was very small except the one flagged data.

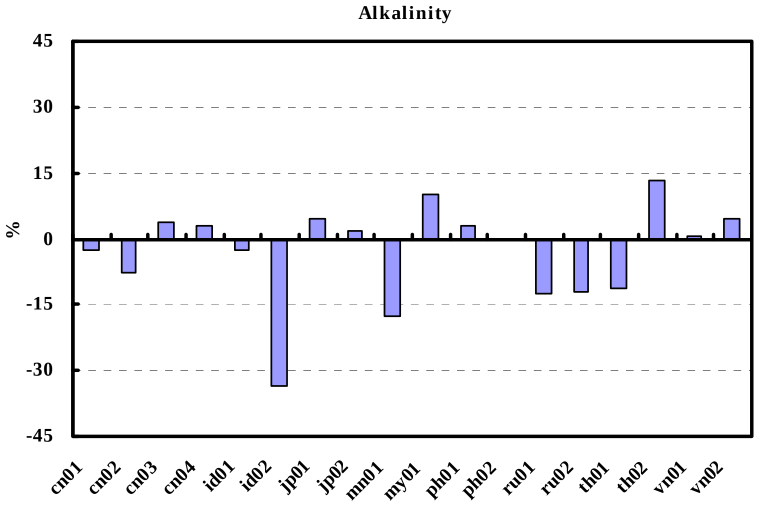


Figure 5.5 Distribution of results for Alkalinity (normalized by prepared concentration)

Data from two laboratories were flagged. Especially one data was significantly deviated from prepared value.

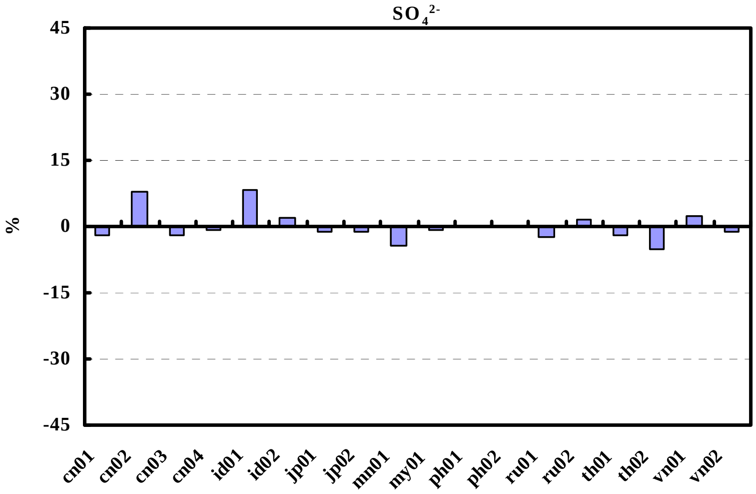


Figure 5.6 Distribution of results for SO_4^{2-} (normalized by prepared concentration)

Most of participating laboratories used ion chromatography for the determination of SO_4^{2-}, while two laboratories used spectrophotometry. All obtained data were close to the prepared value and the variation between laboratories was very small.

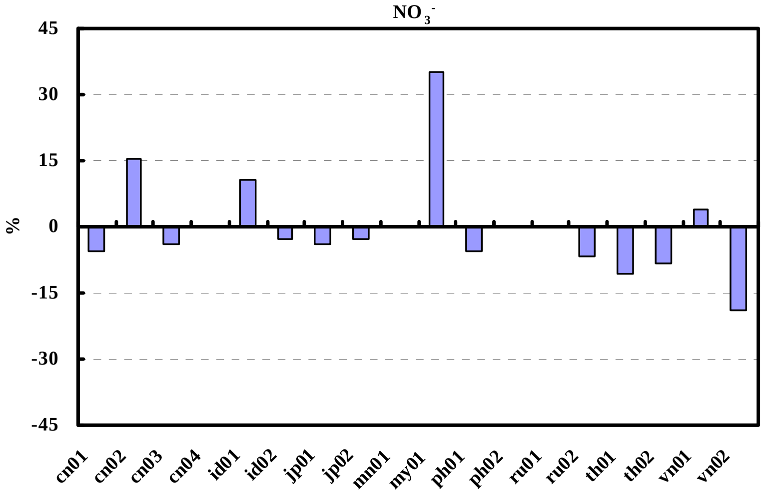


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

Most of the participating laboratories used ion chromatography for the determination of NO_3^-, while three laboratories used spectrophotometry. Data from three laboratories were flagged. Especially one data significantly deviated from the prepared value. The samples which had flagged data were analyzed with ion chromatography method.

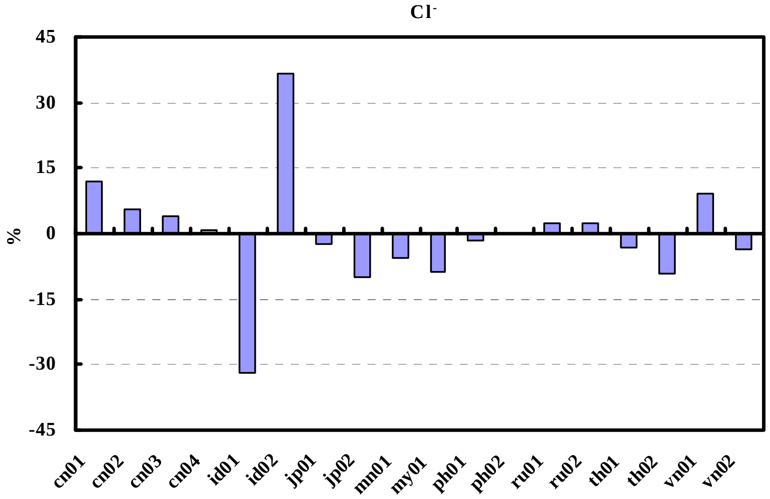


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

Most of participating laboratories used ion chromatography for the determination of Cl^- and two laboratories used titration method. Data from two laboratories were significantly deviated from prepared value. One of the samples which had flagged data was analyzed by ion chromatography method, and the other one was analyzed by titration method.

Concerning the data obtained by titration method, it was found that the values of both last attempt (2005) and this attempt were significantly higher than prepared value. There may be other factors causing this analytical problem in the laboratory.

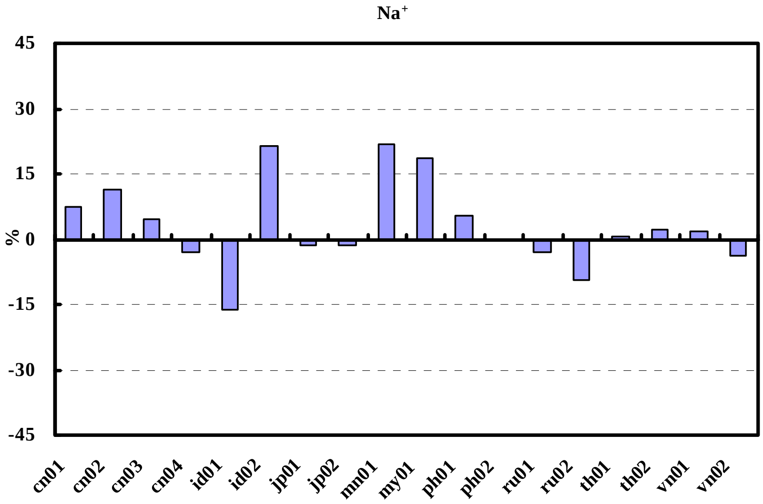


Figure 5.9 Distribution of results for Na^+ (normalized by prepared concentration)

Among 17 participating laboratories, 13 laboratories used ion chromatography, while 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Na^+. Data from four laboratories were flagged. Two flagged data were obtained from the use of ion chromatography method, and the other two data were from the used of atomic absorption/flame (emission) photometry method.

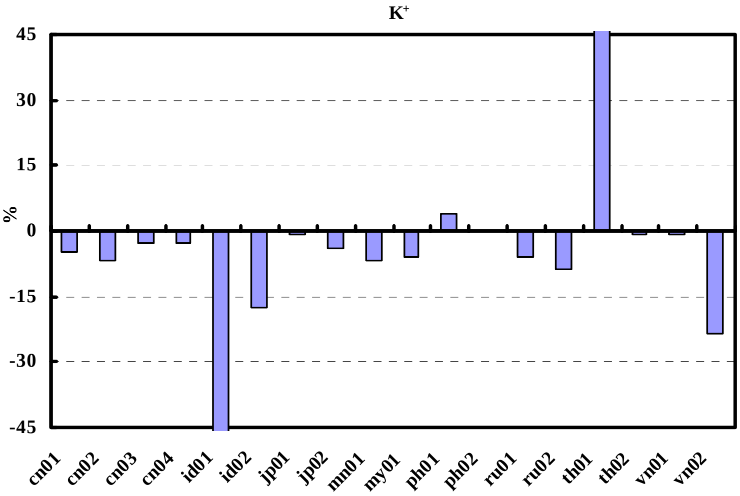


Figure 5.10 Distribution of results for K^+ (normalized by prepared concentration)

Among 17 participating laboratories, 14 laboratories used ion chromatography, and 3 laboratories used atomic absorption/flame (emission) photometry for the determination of K^+. Data from 4 laboratories were flagged. Especially two data were significantly deviated from prepared value. Three flagged data were obtained from the use of ion chromatography method, and one data was obtained from the use of atomic absorption/flame (emission) photometry method.

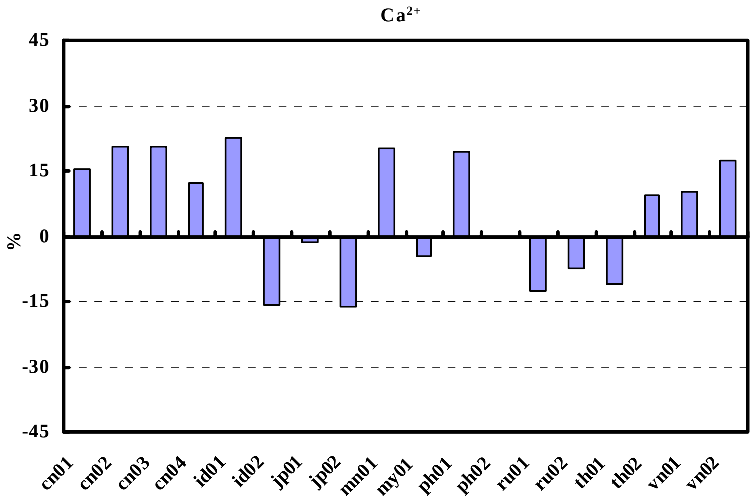


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Ca^{2+} was one of the parameters that have the highest flagged percentage in this attempt.

Among 17 participating laboratories, 13 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Ca^{2+}. Data from 9 laboratories were flagged. Seven flagged data were obtained from the use of ion chromatography method, and two data were obtained from the use of atomic absorption/flame (emission) photometry method.

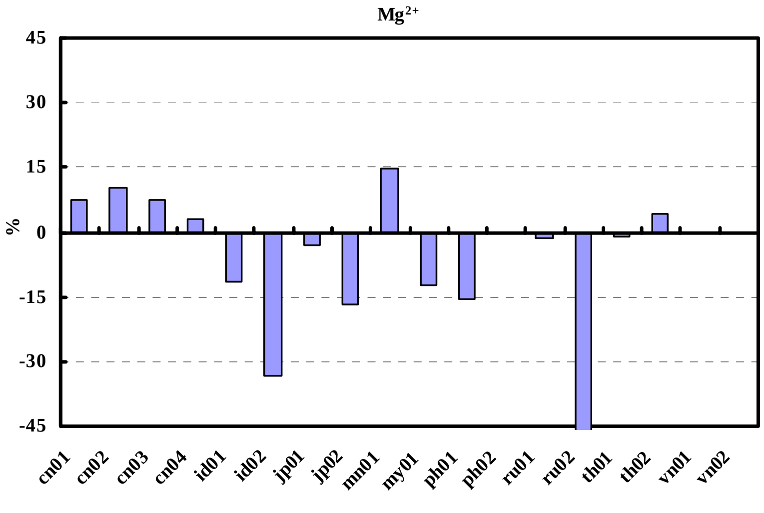


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Among 17 participating laboratories, 13 laboratories used ion chromatography and 4 laboratories used atomic absorption/flame (emission) photometry for the determination of Mg^{2+}. Data from 4 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 two data were obtained from the use of atomic absorption/flame (emission) photometry method.

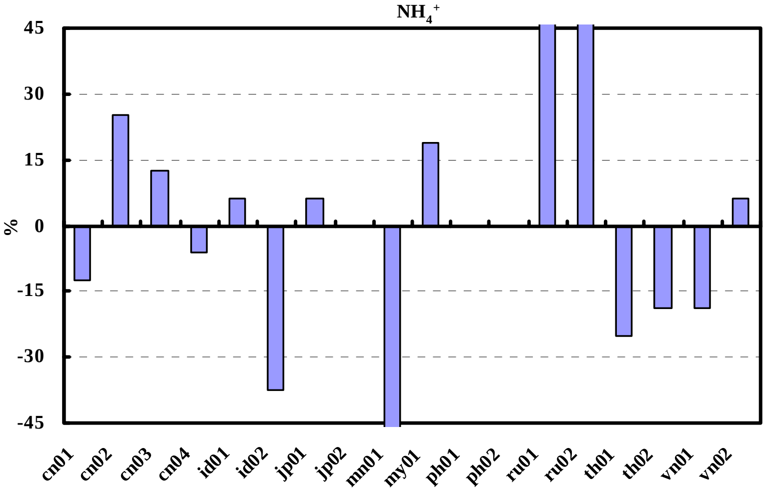


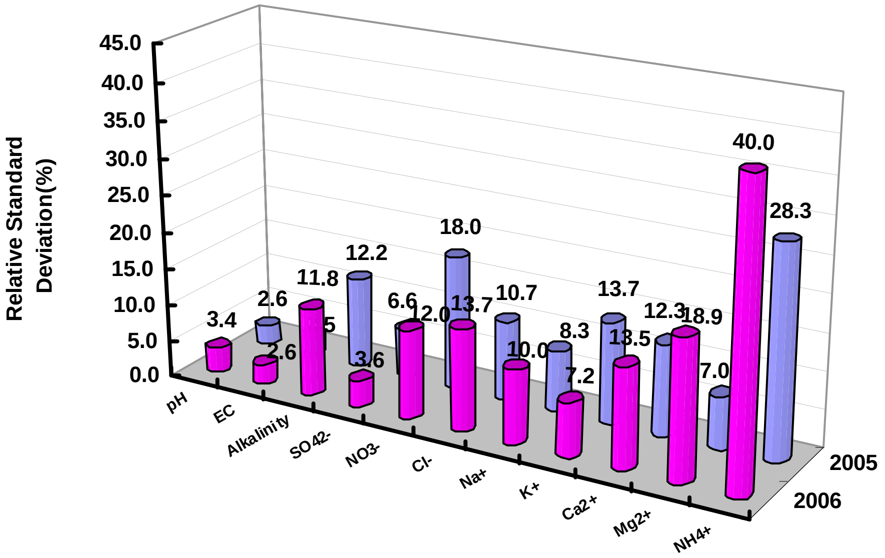
Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Among 17 participating laboratories, 13 laboratories used ion chromatography, 2 laboratories used spectrophotometry (Indophenol) and 2 laboratories used spectrophotometry (other method) for the determination of NH_4^+. Data from 9 laboratories were flagged. Especially four data were significantly deviated from prepared value. Six flagged data were obtained by ion chromatography method, one data was obtained by indophenol method, and two data was obtained by spectrophotometry except indophenol method.

NH_4^+ was one of the parameters that have the highest flagged percentage in this attempt. It had also the highest flagged percentage in the attempt in 2003-2005. 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 (2005).



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

Figure 5.14 Relative standard deviation of each constituent

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

5.3.4 Information on laboratories

Methodologies used

The percentage of laboratories using the recommended methods are is shown in Fig. 5.15, and the codes used for the various analytical methods are shown in Table 5.10 and 5.11.

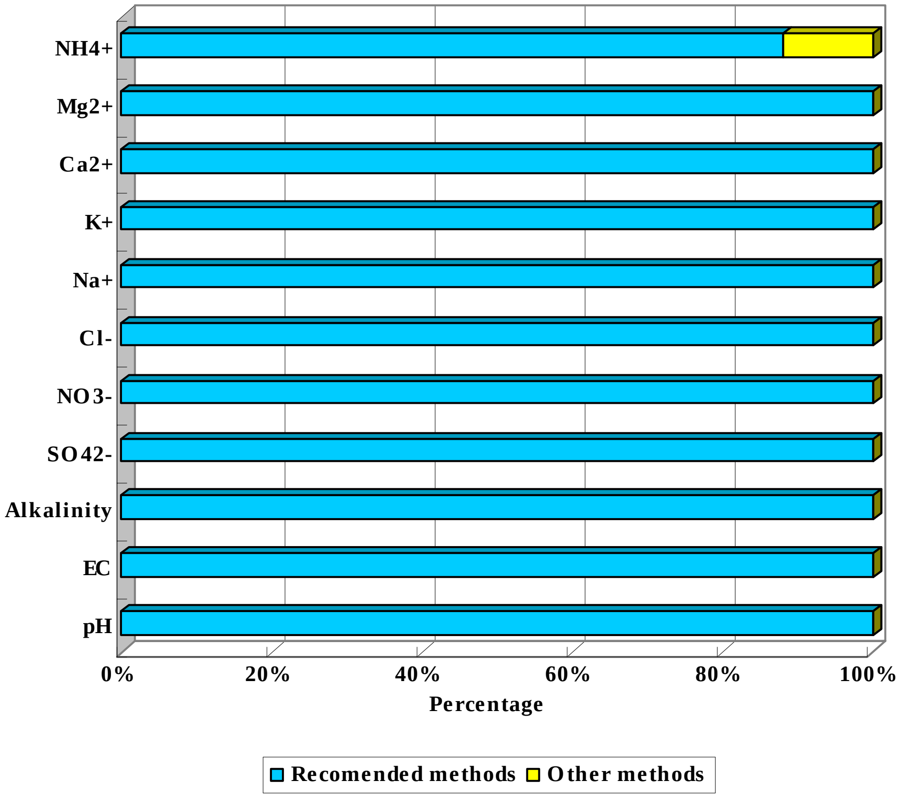


Figure 5.15 Percentage of laboratories using the recommended methods

Table 5.10 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 5.11 Analytical Method

Code	pH	EC	Alkalinity	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
0	17										
1		17(1)									
2			17(2)			2(1)					
3							4(2)	3(1)	4(2)	4(2)	
4				15	14(3)	15(1)	13(2)	14(3)	13(7)	13(2)	13(6)
5											
6											
7				2	3						2(2)
8											2(1)
9											
10											
11											
Flagged E	0	1	1	0	2	0	4	2	9	2	5
Flagged X	0	0	1	0	1	2	0	2	0	2	4

Reverse mesh is recommended method of EANET

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

The participating laboratories used recommended methods of EANET except measurement of NH_4^+. Two laboratories used spectrophotometry instead of indophenol blue for NH_4^+ analysis, and data from both two laboratories were flagged.

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

Staff (numbers and years of experience)

Number of staff in charge of measurement in each laboratory is shown in Table 5.12.

Table 5.12 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	A	A	A	A	B	A	B	A	A
id02	4	A	B	C	C	C	D	A	A	B	A	C
jp01	1	A	A	A	A	A	A	A	A	A	A	A
jp02	3	A	A	B	B	A	C	C	C	C	C	B
mn01	3	A	B	C	B	B	B	A	A	A	A	A
my01	1	A	A	A	A	A	A	A	A	A	A	A
ph01	3	A	A	A	B	B	B	C	C	C	C	A
ph02	1	A	A									
ru01	4	A	B	A	C	C	C	D	D	D	D	B
ru02	4	A	B	A	C	B	A	D	D	D	D	C
th01	2	A	A	A	B	B	B	B	B	B	B	B
th02	2	A	B	A	B	B	B	A	A	A	A	A
vn01	2	A	A	B	A	A	A	B	B	B	B	B
vn02	1	A	A	A	A	A	A	A	A	A	A	A

"A", "B", "C", and "D" represent individuals of staff in each laboratory who are in charge of measurement. Reverse mesh: "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 5.13.

Table 5.13 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	15	15	15	15	15	15	15	15	15	15	15
cn02	8	8	21	14	14	14	14	14	14	14	14
cn03	8	8	8	8	8	8	8	8	8	8	8
cn04	11	11	11	11	11	11	11	11	11	11	11
id01	5	5	5	5	5	5	3	5	3	5	5
id02	6	16	3	3	3	28	6	6	16	6	3
jp01	1	1	1	1	1	1	1	1	1	1	1
jp02	0.5	0.5	10	10	0.5	10	10	10	10	10	0.5
mn01	8	8	7	8	8	8	8	8	8	8	8
my01	3	3	3	3	3	3	3	3	3	3	3
ph01	7	7	7	5.5	5.5	5.5	10	10	10	10	2
ph02	0.3	0.3									
ru01	4	6	4	3	3	3	8	8	8	8	6
ru02	46	26	46	12	26	46	15	15	15	14	11
th01	2	2	2	9	9	9	9	9	9	9	9
th02	9	4	9	4	4	4	9	9	9	9	9
vn01	22	22	13	22	22	22	13	13	13	13	13
vn02	2	2	2	2	2	2	2	2	2	2	2

Reverse mesh: “E” or “X” flagged data in sample

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 seven times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure.5.15.

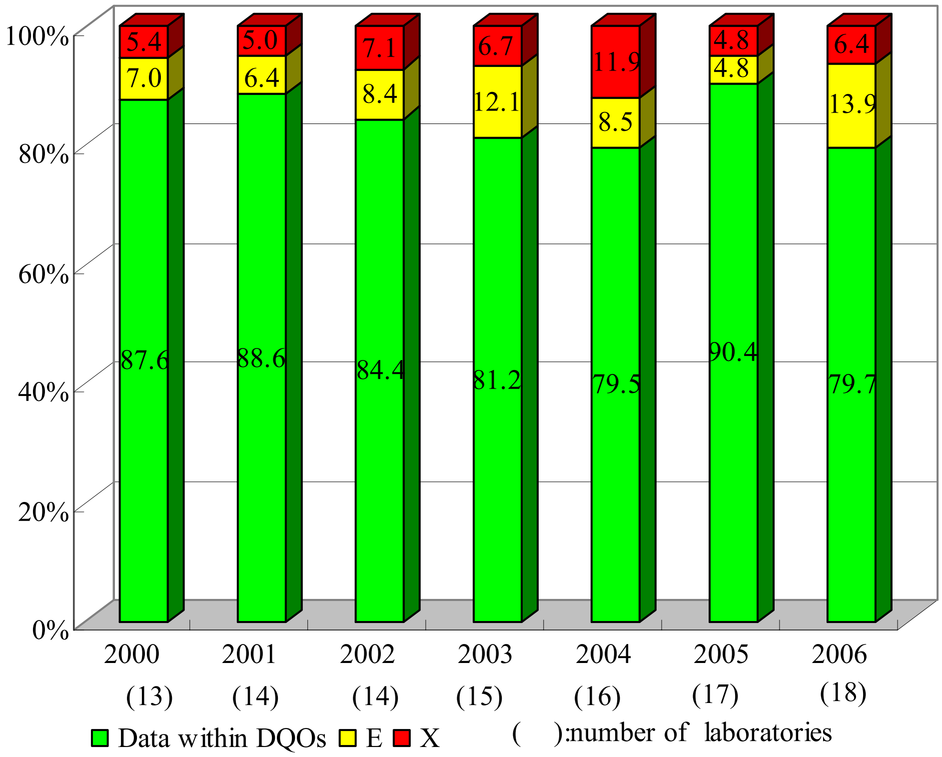
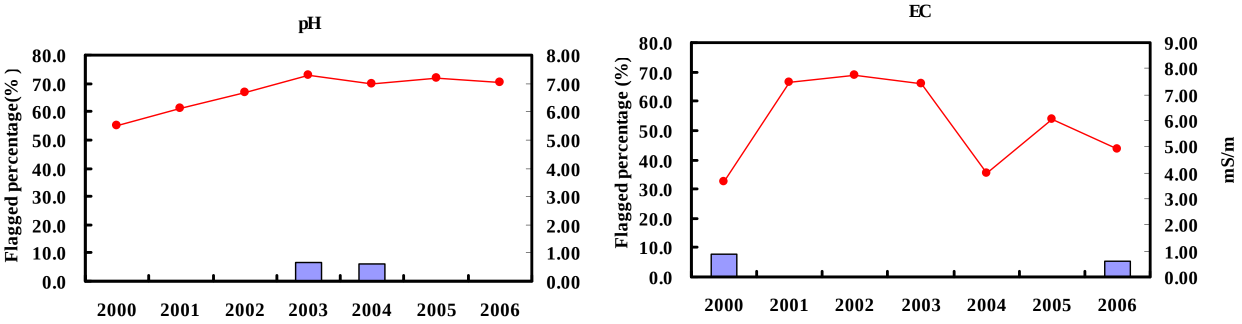
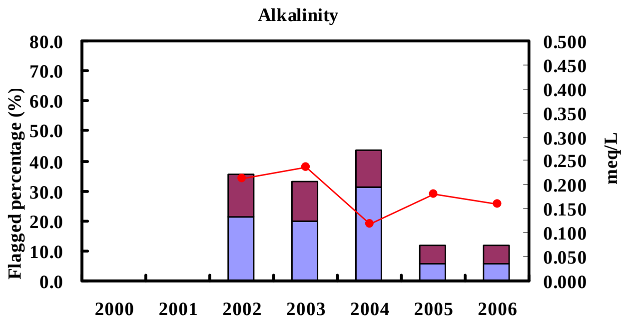


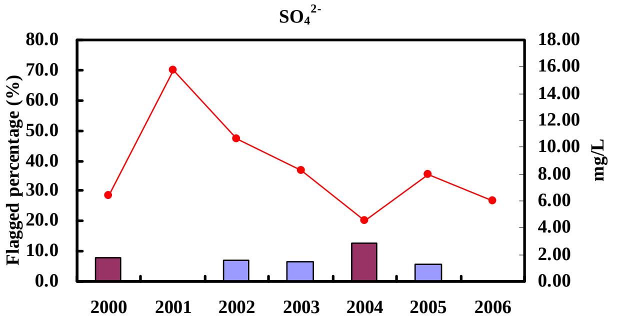
Figure 5. 16 Comparison of the results from the inter-laboratory comparison projects

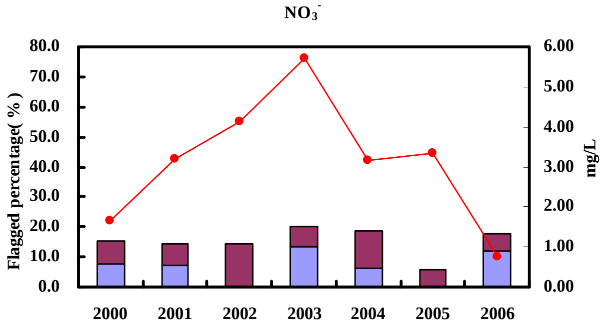
In this project, the percentage of data that satisfied the DQOs was lower than that of the last project. But it was almost the same as in 2003 and 2004.

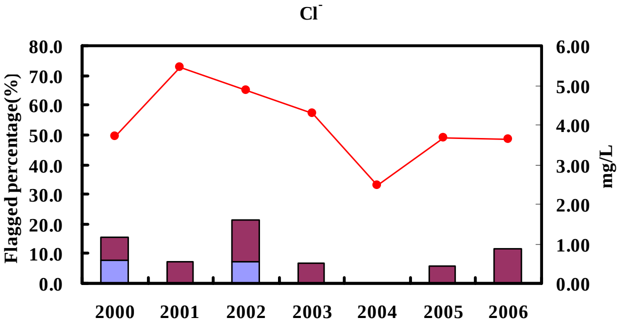
The comparison for each parameter from 1st to 7th project with the percentage of flagged data is shown in Figure 5.17.

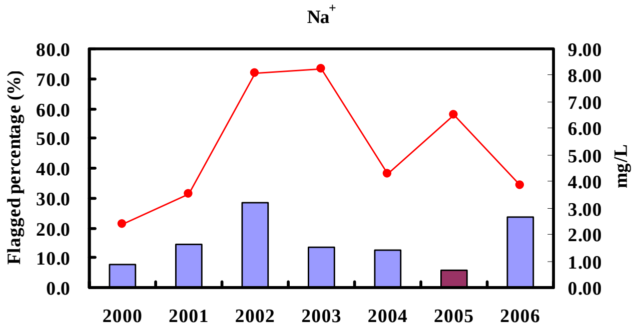


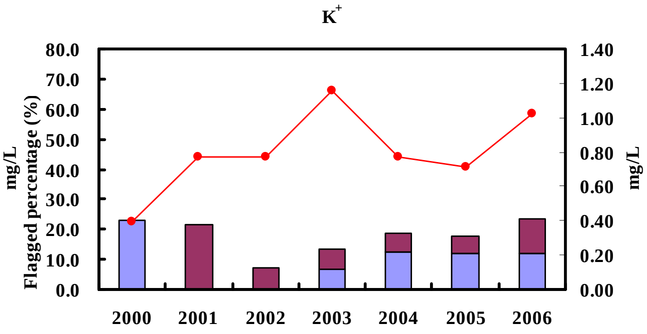

Alkalinity
Flagged percentage (%)
meq/L
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
2000
2001
2002
2003
2004
2005
2006


SO_4^{2-}
Flagged percentage (%)
mg/L
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
2000
2001
2002
2003
2004
2005
2006


NO_3^-
Flagged percentage(%)
mg/L
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
6.00
5.00
4.00
3.00
2.00
1.00
0.00
2000
2001
2002
2003
2004
2005
2006


Cl^-
Flagged percentage(%)
mg/L
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
6.00
5.00
4.00
3.00
2.00
1.00
0.00
2000
2001
2002
2003
2004
2005
2006


Na^+
Flagged percentage (%)
mg/L
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
2000
2001
2002
2003
2004
2005
2006


K^+
Flagged percentage (%)
mg/L
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2000
2001
2002
2003
2004
2005
2006

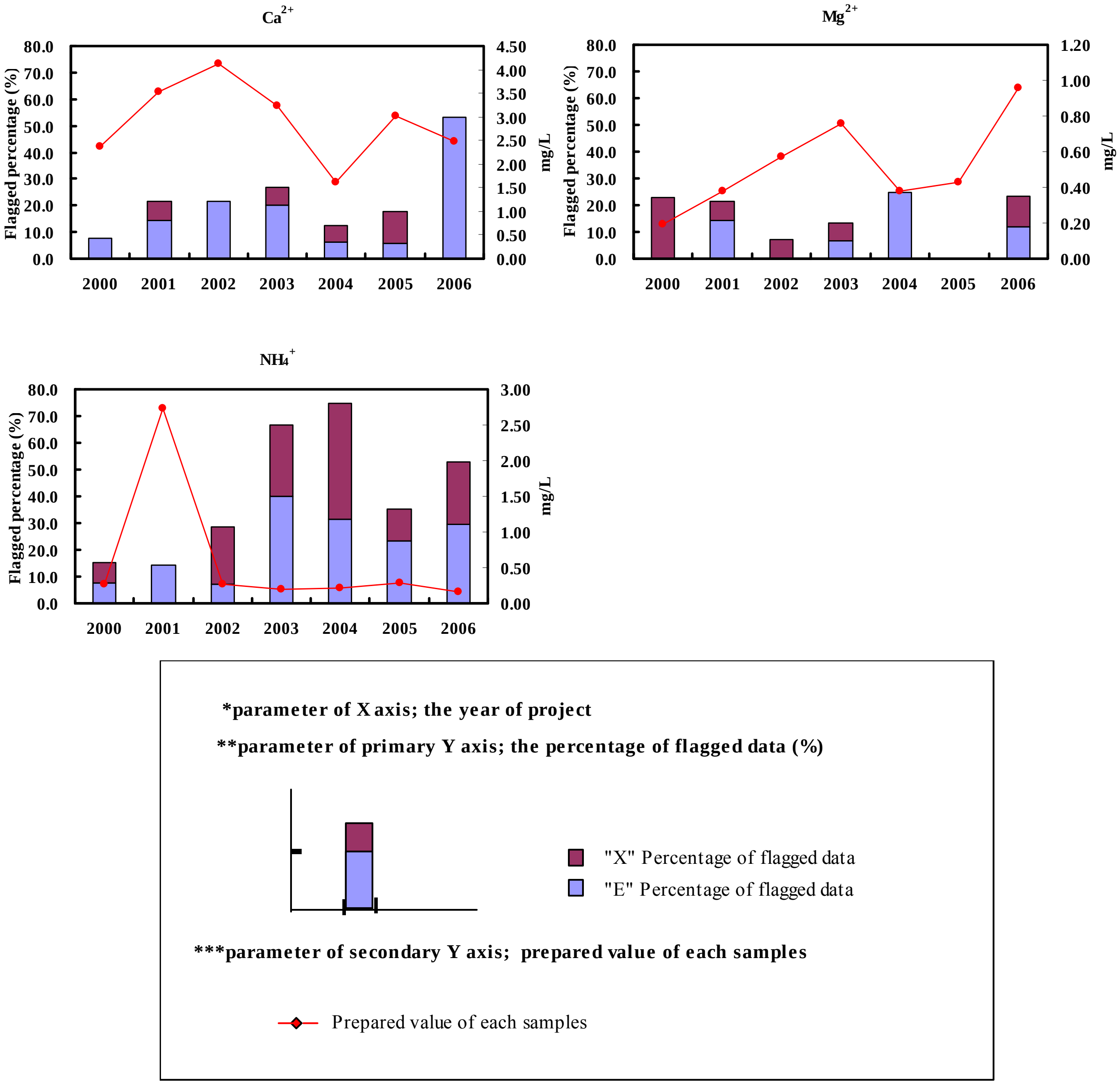


Figure 5.17 Comparison of the percentage of flagged data for each parameter in inter-laboratory comparison projects

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

The percentage of flagged cations was larger than that of anions in this project. Especially the percentage of flagged Ca^{2+} and NH_4^+ exceeded more than 50%. The percentage of flagged NH_4^+ was larger then other parameters in every survey except 1st and 2nd project. The percentage of flagged Ca^{2+} of 7th project was larger than that of 1st- 6th project. It was not clear why the number of flagged data for Ca^{2+} increased than previous years. But it seems that there is necessity to pay attention to the analysis of Ca^{2+} and NH_4^+ in inland water.

5.5. Recommendations for improvement

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

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

5.5.1 Measurement and Analysis

1) General

- ►Clearance from contamination of the apparatus, materials and reagents used for measurement and analysis must be confirmed beforehand.
- ►Blank values of target substances should be as low as possible.
- ►Measurement and analysis should be conducted by persons who are well trained.
- ►To maintain high analytical quality, **SOPs** must be prepared for the management of apparatus, reagents, and procedure of operation.

2) Deionized water

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

3) Certified materials and certified samples

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

4) Pretreatment of samples at analytical laboratory

- ►Conductivity and pH should be measured as soon as possible after sample receiving, and checking agreement of samples and sample list.
- ►Effort should be made to start analysis of the other parameters within a week of sample arrival in the laboratory and to complete the data sets by measuring EC, pH and all other chemical parameters.

5) Calibration of analytical instruments

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

5.5.2 Evaluation of reliability

1) Sensitivity fluctuation of analytical instruments

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

For example, in Ion chromatography

- ►A new calibration should be performed before the measurements are reached to over 30 samples.
- ►Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration.
- ►Control charts should be applied for the measurement of the reference materials.
- ►Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent.
- ►If the results of the control solutions are outside of 3 standard deviations, or out of 15 % from the expected value, the reasons should be found and corrections should be made, and reference solution should be measured again.
- ►If the retention time changes slowly while the separator column is deteriorating, then adequate actions should be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.

5.5.3 Data control

1) Data checks by the analytical laboratories

- ►When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the percentage of a theoretical value to that for determined data in ion balances and electrical conductivity is significantly different from 1.0, measurement should be repeated since reliability is low.
- ►When samples seem to be obviously contaminated, these data should be treated as unrecorded data.
- ►Abnormal or unrecorded data can corrupt research results. So, careful checks are needed to avoid data of questionable quality. When abnormal or unrecorded data is detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

References

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

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

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

Appendix 5.1 Participating laboratories

CHINA

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

INDONESIA

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

JAPAN

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

MALAYSIA

9) Faculty of Applied Science University Technology Mara	(my01)

MONGOLIA

10) Central Laboratory of Environmental Monitoring,	(mn01)

PHILIPPINES

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

RUSSIA

13) Limnologcal Institute of Russian Academy of Science/Siberian Branch(RAS/SB)	(ru01)
14) Laboratory for Monitoring of Atmosphere and Soil Pollution	(ru02)

THAILAND

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

VIET NAM

17) Institute of Meteorology and Hydrology (IMH) Hydrometeorological Service of Viet Nam (HMS)	(vn01)
18) Middle of Central regional Hydro-Meteorological Observatory National Hydro -Meteorological Center (NHMS)	(vn02)

Appendix 5.2

Results submitted by the laboratories

Lab. ID	pH -	EC (mS/m)	Alkalinity (meq/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)
cn01	7.16	4.56	0.155	6.25	0.70	4.08	4.13	0.97	2.86	1.03	0.14
cn02	7.15	4.68	0.147	6.88	0.85	3.86	4.29	0.95	2.99	1.06	0.20
cn03	7.17	4.65	0.165	6.25	0.71	3.79	4.02	0.99	2.99	1.03	0.18
cn04	7.10	4.60	0.164	6.32	0.74	3.68	3.74	0.99	2.78	0.99	0.15
id01	6.76	4.57	0.155	6.90	0.82	2.48	3.22	0.50	3.04	0.85	0.17
id02	6.30	4.60	0.106	6.50	0.72	4.99	4.67	0.84	2.09	0.64	0.10
jp01	6.91	4.70	0.166	6.29	0.71	3.56	3.80	1.01	2.45	0.93	0.17
jp02	7.26	4.61	0.162	6.30	0.72	3.29	3.80	0.98	2.08	0.80	0.16
mn01	6.98	4.65	0.131	6.10	0.74	3.44	4.69	0.95	2.98	1.10	0.00
my01	6.95	4.86	0.175	6.31	1.00	3.33	4.56	0.96	2.37	0.84	0.19
ph01	6.59	4.66	0.164	6.38	0.70	3.59	4.06	1.06	2.96	0.81	0.16
ph02	6.99	4.01									
ru01	7.07	4.83	0.139	6.23	0.74	3.73	3.74	0.96	2.17	0.95	0.24
ru02	7.08	4.85	0.140	6.48	0.69	3.74	3.49	0.93	2.30	0.41	0.31
th01	6.85	4.45	0.141	6.25	0.66	3.54	3.87	1.99	2.21	0.95	0.12
th02	7.12	4.89	0.180	6.04	0.68	3.31	3.94	1.01	2.71	1.00	0.13
vn01	7.15	4.77	0.160	6.51	0.77	3.98	3.92	1.01	2.73	0.96	0.13
vn02	7.14	4.71	0.166	6.30	0.60	3.52	3.70	0.78	2.91	0.96	0.17
Expected value	7.01	4.91	0.159	6.37	0.74	3.65	3.85	1.02	2.48	0.96	0.16
Number of data	18	18	17	17	17	17	17	17	17	17	17
Average	6.99	4.65	0.154	6.37	0.74	3.64	3.98	0.99	2.62	0.90	0.16
Minimum	6.30	4.01	0.106	6.04	0.60	2.48	3.22	0.50	2.08	0.41	0.00
Maximum	7.26	4.89	0.18	6.90	1.00	4.99	4.69	1.99	3.04	1.10	0.31

Appendix 5.3

Data normalized by prepared value

(Original data / Expected Value - 1) * 100 (%)

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO_4^{2-} (%)	NO_3^- (%)	Cl^- (%)	Na^+ (%)	K^+ (%)	Ca^{2+} (%)	Mg^{2+} (%)	NH_4^+ (%)
cn01	2.1	-7.1	-2.5	-1.9	-5.4	11.8	7.3	-4.9	15.3	7.3	-12.5
cn02	2.0	-4.7	-7.5	8.0	15.3	5.8	11.4	-6.9	20.6	10.4	25.0
cn03	2.3	-5.3	3.8	-1.9	-4.1	3.8	4.4	-2.9	20.6	7.3	12.5
cn04	1.3	-6.3	3.1	-0.8	0.0	0.8	-2.9	-2.9	12.1	3.1	-6.3
id01	-3.6	-6.9	-2.5	8.3	10.8	-32.1	-16.4	-51.0	22.6	-11.5	6.3
id02	-10.1	-6.3	-33.3	2.0	-2.7	36.7	21.3	-17.6	-15.7	-33.3	-37.5
jp01	-1.4	-4.3	4.4	-1.3	-4.1	-2.5	-1.3	-1.0	-1.2	-3.1	6.3
jp02	3.6	-6.1	1.9	-1.1	-2.7	-9.9	-1.3	-3.9	-16.1	-16.7	0.0
mn01	-0.4	-5.3	-17.6	-4.2	0.0	-5.8	21.8	-6.9	20.2	14.6	-100.0
my01	-0.9	-1.0	10.1	-0.9	35.1	-8.8	18.4	-5.9	-4.4	-12.5	18.8
ph01	-6.0	-5.1	3.1	0.2	-5.4	-1.6	5.5	3.9	19.4	-15.6	0.0
ph02	-0.3	-18.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ru01	0.9	-1.6	-12.6	-2.2	0.0	2.2	-2.9	-5.9	-12.5	-1.6	51.9
ru02	1.0	-1.2	-11.9	1.7	-6.8	2.5	-9.4	-8.8	-7.3	-57.3	93.8
th01	-2.3	-9.4	-11.3	-1.9	-10.8	-3.0	0.5	95.1	-10.9	-1.0	-25.0
th02	1.6	-0.4	13.2	-5.2	-8.1	-9.3	2.3	-1.0	9.3	4.2	-18.8
vn01	2.0	-2.9	0.6	2.2	4.1	9.0	1.8	-1.0	10.1	0.0	-18.8
vn02	1.9	-4.1	4.4	-1.1	-18.9	-3.6	-3.9	-23.5	17.3	0.0	6.3
Minimum	-10.1	-18.3	-33.3	-5.2	-18.9	-32.1	-16.4	-51.0	-16.1	-57.3	-100.0
Maximum	3.6	-0.4	13.2	8.3	35.1	36.7	21.8	95.1	22.6	14.6	93.8

6. ACKKNOWLEDGEMENT

ADORC wishes to thank Toyama Prefecture for their cooperation on collecting soil samples.

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