

**Acid Deposition Monitoring Network  
in East Asia ( EANET )**

**Report of the Inter-laboratory Comparison  
Project 2010**

**13<sup>th</sup> Inter-laboratory Comparison Project on Wet Deposition**

**6<sup>th</sup> Inter-laboratory Comparison Project on Dry Deposition**

**12<sup>th</sup> Inter-laboratory Comparison Project on Soil**

**11<sup>th</sup> Inter-laboratory Comparison Project**

**on Inland Aquatic Environment**

November 2011  
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## 1. INTRODUCTION

The inter-laboratory comparison project 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 this project are, through the evaluation of analytical results, analytical equipment and its operating condition and other practices,

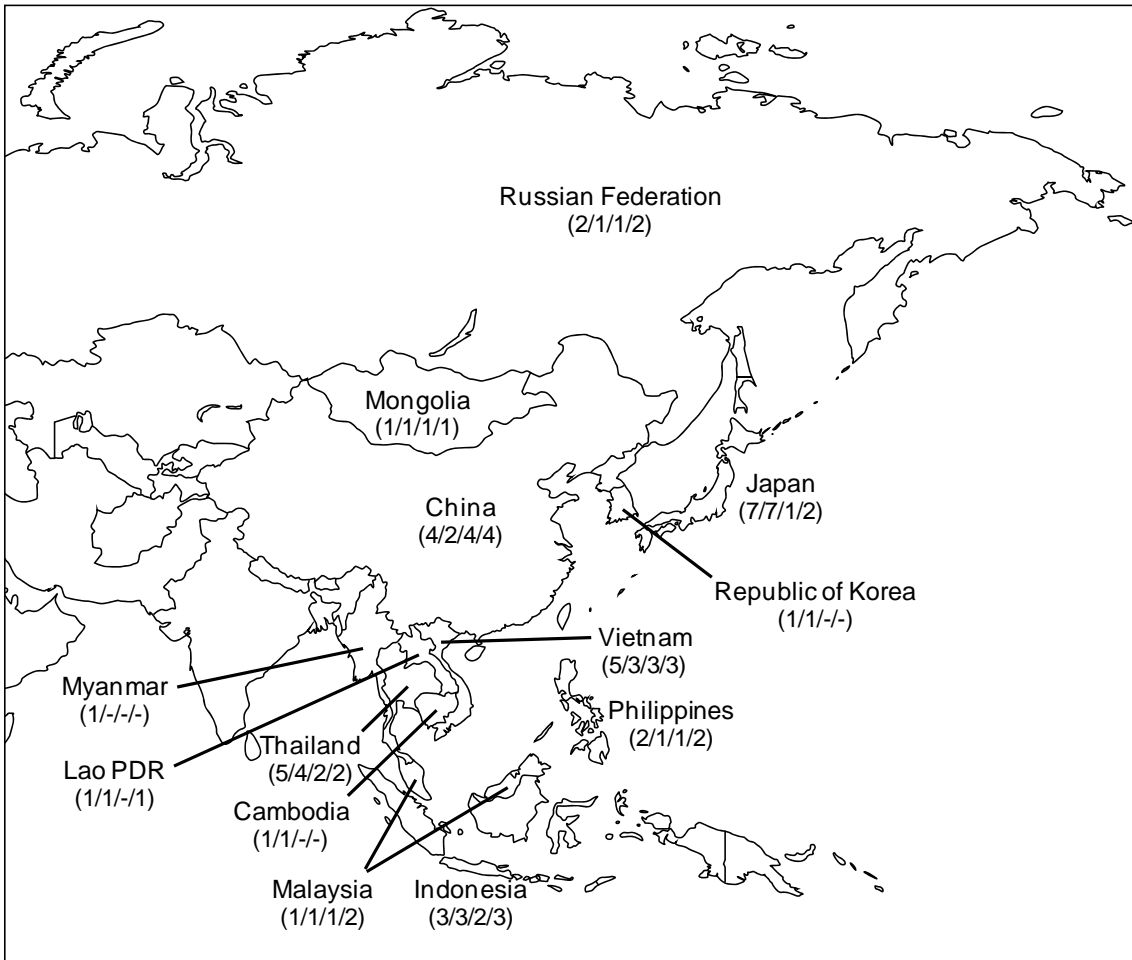
- (i) to recognize the analytical precision and accuracy of the measurement in each participating laboratory,
- (ii) to give further opportunities to improve the quality of the analysis on wet deposition, dry deposition (filter pack method), soil and inland aquatic monitoring of EANET,
- (iii) to improve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

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

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

This report presented the results of the 13<sup>th</sup> inter-laboratory comparison project on wet deposition, 6<sup>th</sup> inter-laboratory comparison project on dry deposition, 12<sup>th</sup> inter-laboratory comparison project on soil, and 11<sup>th</sup> inter-laboratory comparison project on inland aquatic environment.

The number of participating laboratories from each country by project was shown in Figure 1.1, and all participating laboratories and their codes were listed in Table 1.1.



**Figure 1.1 Number of participating laboratories in 2010**

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

**Table 1.1 Participating laboratories**

<b>Laboratories</b>	<b>Code</b>	<b>Wet</b>	<b>Dry</b>	<b>Soil</b>	<b>IAE</b>
<b>Cambodia</b> Department of Pollution Control, Ministry of Environment	KH01	✓	✓		
<b>China</b> Zhuhai Environmental Monitoring Center Station	CN01	✓		✓	✓
Xiamen Environmental Monitoring Station	CN02	✓	✓	✓	✓
Xi'an Environmental Monitoring Center Station	CN03	✓		✓	✓
Chongqing Institute of Environmental Science	CN04	✓	✓	✓	✓
<b>Indonesia</b> Environmental Management Center (EMC), Environmenta Impact Management Agency (BAPEDAL)	ID01	✓	✓	✓	✓
Analysis Division, Meteorological and Geophysical Agency (BMG)	ID02	✓	✓		
Indonesian National Institute of Aeronautic and Space (LAPAN)	ID03	✓	✓		
Indonesian Soil Research Institute (ISRI)	ID04			✓	
Research Center for Water Resources (RCWR), Agency for Research and Development, Ministry of Public	ID05				✓
Research Center for Limnology (RCL), Indonesian Institute of Sciences (LIPI) Cibinong Sciences Center	ID06				✓
<b>Japan</b> Institute of Environmental Sciences, Hokkaido Research Organization	JP01	✓	✓		
Niigata Prefectural Institute of Public Health and Environmental Sciences	JP02		✓		
Nagano Research Institute for Health and Pollution	JP03	✓	✓		
Gifu Prefectural Research Institute of Health and Environmental Science	JP04	✓	✓		✓
Shimane Prefectural Institute of Public Health and Environmental Science	JP05	✓	✓		✓
Shimane Agricultural Technology Center	JP06			✓	
Kochi Prefectural Environmental Research Center	JP07	✓			
Okinawa Research Institute of Health and Environment	JP08	✓	✓		
Asia Center for Air Pollution Research (ACAP)	JP09	✓	✓		
<b>Lao PDR</b> Environment Quality Monitoring Center, Environment Research Institute, Science technology and Environment	LA01	✓	✓		✓
<b>Malaysia</b> Division of Environmental Health, Department of Chemistry (DOC)	MY01	✓	✓		✓
Faculty of Applied Science, University Technology Mara (UiTM)	MY03				✓
Universiti Putra Malaysia, Campus Bintulu (UPMKB)	MY04			✓	
<b>Mongolia</b> Central Laboratory of Environmental Monitoring	MN01	✓	✓	✓	✓
<b>Myanmar</b> Department of Meteorology and Hydrology (DMH)	MM01	✓			
<b>Philippines</b> Environmental Management Bureau - Central Office (EMB-CO)	PH01	✓	✓		✓
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	PH02	✓			✓
University of the Philippines, Los Baños	PH03			✓	
<b>Republic of Korea</b> National Institute of Environment Research (NIER)	KR01	✓	✓		
<b>Russia</b> Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	RU01	✓	✓	✓	✓
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU02	✓			✓
<b>Thailand</b> Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE)	TH01	✓	✓	✓	✓
Environmental Research and Training Centre (ERTC), Department of Research and Environmental Quality	TH02	✓	✓		✓
Meteorological Observation Division, Thailand Meteorological Department (TMD)	TH03	✓			
Chemistry Department, Science Faculty, Chiangmai University (CMU)	TH04	✓	✓		
Khon Kaen University (KKU)	TH05	✓	✓		
King Mongkut's University of Technology Thonburi	TH06			✓	
<b>Vietnam</b> Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment	VN01	✓	✓	✓	✓
Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN02	✓	✓	✓	✓
Sub-Institute of HydroMeteorology and Environment of South Vietnam (SIHYMETE)	VN03	✓	✓	✓	✓
Center for Hydro-Meteorological and Environmental Networks, National Hydro-Meteorological Service of Vietnam (NHMS),	VN04	✓			
Southern Region Hydro-Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS).	VN05	✓			
<b>Total :</b>		<b>34</b>	<b>26</b>	<b>16</b>	<b>22</b>



## 2. 13<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

### 2.1 Introduction

In the 13<sup>th</sup> 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 measured values of pH, Electric Conductivity (EC) and concentrations of major ions submitted by the participating countries were compared with the prepared values and were treated statistically.

The NC shipped the artificial rainwater samples to laboratories in charge of chemical analysis in EANET on 1 October 2010. Their analytical results were required to be submitted to the NC by 28 February 2011.

### 2.2 Procedures

#### 2.2.1 Participating Laboratories

The NC distributed the artificial rainwater samples to 34 laboratories in charge of chemical analysis in 13 countries of EANET. 33 of the participating laboratories submitted their analytical results to the NC. A list of the participating laboratories and their codes were shown in Table 1.1.

#### 2.2.2 Description of samples

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

**Table 2.1 Description of artificial rainwater samples**

Artificial rainwater sample	Quantity of sample	Container	Number of samples	Note
No. 101w (high concentration sample) No. 102w (low concentration sample)	100mL each	Polypropylene bottle 100mL	One bottle each	Fixed quantity of reagents are dissolved in deionized water

The prepared values of analytical parameters in the artificial rainwater samples were described in Table 2.2.

**Table 2.2 Prepared values/concentrations of analytical parameters\***

	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
	-	mS/m	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
No. 101w (high concentration)	4.54	3.97	52.0	47.0	77.0	60.0	8.9	26.0	13.0	52.1
No. 102w (low concentration)	5.05	1.25	16.6	14.4	24.7	20.7	2.8	8.1	3.3	17.0

\* For 100 times diluted samples.

### 2.2.3 Analytical Methods and Data Checking Procedures

Before the measurement, the samples have to be diluted 100 times accurately with deionized water in each laboratory according to the specified procedure.

All participating laboratories were expected to analyze the diluted samples for the following 10 parameters; pH, EC, concentrations of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>.

The laboratories were required to apply the analytic methods and data checking procedures that were 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 were listed in Table 2.3.

**Table 2.3 Analytical methods specified in the manual**

Parameter	Analytical method
pH	Glass Electrode Method (preferably with the Electrode of non-leak inner cell)
EC	Conductivity Cell Method
SO <sub>4</sub> <sup>2-</sup> NO <sub>3</sub> <sup>-</sup> Cl <sup>-</sup>	Ion Chromatography (preferably with suppressor) Spectrophotometry
Na <sup>+</sup> K <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup>	Ion Chromatography Atomic Absorption Spectrometry Atomic Emission Spectrometry
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography Spectrophotometry (Indophenol Blue Method)

Checking analytical results was performed using the calculation of ion balance (R<sub>1</sub>) and total electric conductivity agreement (R<sub>2</sub>).

### Calculation of ion balance (R<sub>1</sub>)

(1) Total anion equivalent concentration (A [μeq /L]) was calculated by summing the concentrations of all anions (C [μmol /L]).

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

n, C<sub>Ai</sub>: electric charge of ion and concentration [μmol /L] of anion “i”.

(2) Total cation equivalent concentration (C [μeq /L]) was calculated by summing the concentrations of all cations (C [μmol /L]).

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

n, C<sub>Ci</sub>: electric charge of ion and concentration [μmol /L] of cation “i”.

(3) Calculation of ion balance (R<sub>1</sub>)

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

(4) R<sub>1</sub> calculated by the above equation was compared with allowable ranges in Table 2.4. If R<sub>1</sub> was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

**Table 2.4 Allowable ranges for R<sub>1</sub> in different concentration ranges**

C+A [μeq/L]	R <sub>1</sub> [%]
< 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<sub>2</sub>)

(1) Total electric conductivity ( $\Lambda$  calc) was calculated as follows;

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

C: Molar concentrations [ $\mu\text{mol/L}$ ] of ions in the parenthesis; each constant value was ionic equivalent conductance at 25 degrees centigrade.

(2) Ratio (R<sub>2</sub>) of calculations ( $\Lambda$  calc) to measurements ( $\Lambda$  meas) in electric conductivity was calculated as follows;

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

(3) R<sub>2</sub> calculated by the above equation was compared with allowable ranges in Table 2.5. If R<sub>2</sub> was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

**Table 2.5 Allowable ranges for R<sub>2</sub> in different ranges of EC**

$\Lambda$ meas [mS/m]	R <sub>2</sub> [%]
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9

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

## 2.3 Results

The NC received the analytical results from 32 laboratories in the participating countries of EANET. The original data submitted by the laboratories were shown in Appendix 2.1 and 2.2. Basic statistics of submitted data summarized in Table 2.6 were calculated for each parameter of the artificial rainwater samples such as: Average (Va), Minimum (Min.), Maximum (Max.), Standard deviation (S.D.), and Number of data (N). The outliers which are apart from the average greater than a factor of 3 of S.D. were not included for the statistics calculation. As shown in Table 2.6, Va agreed with prepared value (Vp) fairly well. The range of Va/Vp was between -4.6% to 1.3% for the sample No. 101w, and -3.3% to 4.6% for the sample No. 102w.

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

Sample No. 101w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp$ *1 %	S.D.	N	Min.	Max.
pH	4.54	4.55	0.3	0.10	32	4.32	4.81
EC [mS m <sup>-1</sup> ]	3.97	3.88	-2.2	0.15	32	3.64	4.39
SO <sub>4</sub> <sup>2-</sup> [μmol L <sup>-1</sup> ]	52.0	52.2	0.3	2.93	33	44.8	59.8
NO <sub>3</sub> <sup>-</sup> [μmol L <sup>-1</sup> ]	47.0	46.9	-0.3	3.10	31	39.4	58.1
Cl <sup>-</sup> [μmol L <sup>-1</sup> ]	77.0	76.5	-0.6	3.59	32	70.7	87.1
Na <sup>+</sup> [μmol L <sup>-1</sup> ]	60.0	59.7	-0.5	1.80	32	54.8	62.9
K <sup>+</sup> [μmol L <sup>-1</sup> ]	8.9	8.8	-0.6	0.79	33	7.2	10.3
Ca <sup>2+</sup> [μmol L <sup>-1</sup> ]	26.0	25.8	-0.6	1.77	33	22.5	31.0
Mg <sup>2+</sup> [μmol L <sup>-1</sup> ]	13.0	13.1	0.4	0.96	33	10.6	15.3
NH <sub>4</sub> <sup>+</sup> [μmol L <sup>-1</sup> ]	52.1	52.1	0.0	2.11	32	47.9	55.9

Sample No. 102w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp$ *1 %	S.D.	N	Min.	Max.
pH	5.05	5.10	1.1	0.11	32	4.93	5.35
EC [mS m <sup>-1</sup> ]	1.25	1.25	0.1	0.07	33	1.14	1.45
SO <sub>4</sub> <sup>2-</sup> [μmol L <sup>-1</sup> ]	16.6	16.3	-1.5	0.70	32	14.6	17.8
NO <sub>3</sub> <sup>-</sup> [μmol L <sup>-1</sup> ]	14.4	14.4	0.2	1.53	32	10.3	18.2
Cl <sup>-</sup> [μmol L <sup>-1</sup> ]	24.7	24.1	-2.5	1.51	32	20.8	28.3
Na <sup>+</sup> [μmol L <sup>-1</sup> ]	20.7	20.5	-1.1	0.94	32	18.6	22.3
K <sup>+</sup> [μmol L <sup>-1</sup> ]	2.8	2.8	-0.8	0.37	32	1.9	3.9
Ca <sup>2+</sup> [μmol L <sup>-1</sup> ]	8.1	8.3	2.9	0.88	32	6.8	10.3
Mg <sup>2+</sup> [μmol L <sup>-1</sup> ]	3.3	3.4	2.3	0.64	33	1.6	4.8
NH <sub>4</sub> <sup>+</sup> [μmol L <sup>-1</sup> ]	17.0	17.4	2.3	1.03	33	15.0	19.8

Note: \*1, (Va-Vp)/Vp x 100

The Data Quality Objective for accuracy (hereafter referred to as DQO) was specified in the QA/QC program of the EANET for every parameter to be within  $\pm 15\%$  of deviation from  $V_p$ . In this report, analytical data of the artificial rainwater samples were compared with  $V_p$ , and the data exceed DQO were marked with flags. Flag “E” was put to the data exceed DQO within a factor of 2 ( $\pm 15\%$  to  $\pm 30\%$ ), and flag “X” was put to the data exceed DQO more than a factor of 2 (over  $\pm 30\%$ ).

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 put to the data sets with poor ion balance and poor conductivity agreement, respectively.

The results were evaluated by the following three aspects:

- i) Comparison of concentration dependence on level of their concentration  
– sample No. 101w (high concentrations) and No. 102w (low concentrations),
- ii) Comparison of individual parameters,
- iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both the sample No. 101w and No. 102w was presented in “2.3.1 Evaluation of laboratories’ performance (by sample)”, evaluation of analytical data for each constituent was presented in “2.3.2 Evaluation of laboratories’ performance (by analytical parameters)”, and evaluation of analytical data by the circumstances of chemical analysis such as analytical method used, experience of personnel in charge, and other analytical condition were presented in “2.3.4 Information on Laboratories”.

### 2.3.1 Evaluation of laboratories' performance (by sample)

#### 1) High Concentration Sample No. 101w

The number and percentage of flagged data for the high concentration sample No. 101w were shown in Table 2.7. Fourteen analytical data out of 328 exceeded DQO within a factor of 2 and were flagged by "E". One analytical data out of 328 exceeded DQO more than a factor of 2 flagged by "X". Data flagged by "E" and "X" shared about 4.6 percent of all the submitted data for sample No. 101w.

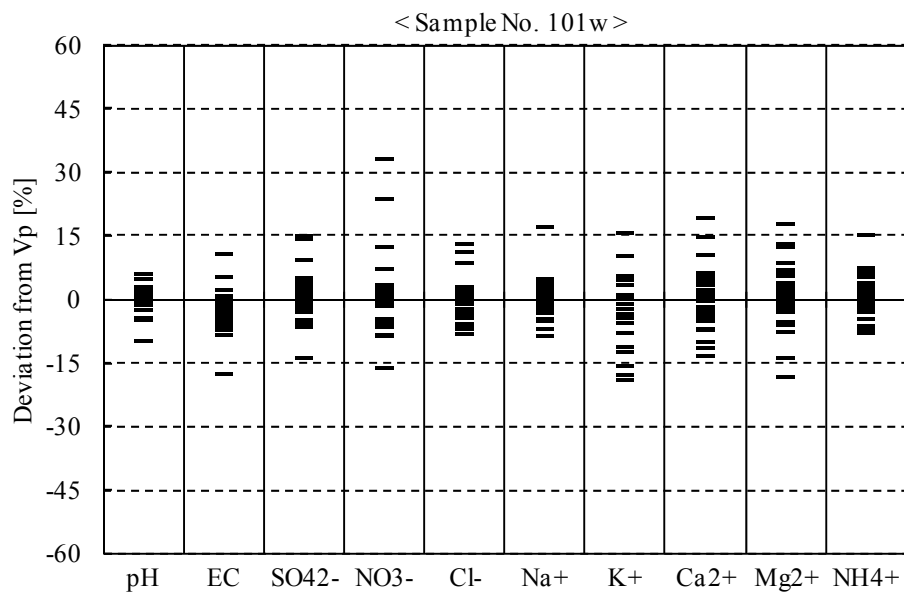
The data normalized by prepared value in each parameter were shown in Figure 2.1.

**Table 2.7 Number of flagged data for the Sample No. 101w (High concentrations)**

Characterization of data	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Data within DQO	33	32	33	29	32	32	27	32	31	32	313
Data with flag E <sup>*1</sup>	0	1	0	2	0	1	6	1	2	1	14
Data with flag X <sup>*2</sup>	0	0	0	1	0	0	0	0	0	0	1
Flagged data [%]	0.0	3.0	0.0	9.4	0.0	3.0	18.2	3.0	6.1	3.0	4.6

( Total data = 328 )

Note: \*1, Data exceeded DQO within a factor of 2; \*2, Data exceeded DQO more than a factor of 2



**Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 101w**

The parameter which had most flags was K<sup>+</sup>. The analytical data submitted by the participating laboratories were shown in Table 2.8 with flags.

**Table 2.8 Analytical Results of Sample No. 101w**

Lab. ID*1	pH	EC mS/m	SO <sub>4</sub> <sup>2-</sup> µmol/L	NO <sub>3</sub> <sup>-</sup> µmol/L	Cl <sup>-</sup> µmol/L	Na <sup>+</sup> µmol/L	K <sup>+</sup> µmol/L	Ca <sup>2+</sup> µmol/L	Mg <sup>2+</sup> µmol/L	NH <sub>4</sub> <sup>+</sup> µmol/L	R <sub>1</sub> %	R <sub>2</sub> %
KH01	4.34	3.68	59.4	X 62.6	85.6	59.3	8.5	25.9	13.2	48.4	-5.3	C 13.4
CN01	4.55	3.71	53.6	46.8	78.8	61.3	9.2	28.7	13.8	55.9	1.4	4.4
CN02	4.54	3.76	54.3	44.3	74.6	60.0	9.0	25.2	13.7	53.3	0.3	2.7
CN03	4.50	3.77	53.7	46.9	76.1	58.2	8.9	27.6	13.8	53.8	1.1	4.3
CN04	4.51	3.93	56.8	46.7	74.7	60.1	9.4	27.4	13.7	52.6	0.0	2.4
ID01	4.55	3.85	53.4	47.1	79.3	60.5	9.4	25.3	12.9	55.6	-0.7	1.9
ID02	4.59	3.64	48.9	E 39.4	74.4	62.0	9.0	27.2	13.2	50.7	3.8	1.4
ID03	4.43	4.39	54.6	46.2	70.7	62.9	9.8	26.3	13.3	53.4	3.5	-1.3
JP01	4.61	3.93	52.5	47.2	77.3	59.7	7.8	25.1	12.0	54.1	-2.0	-1.6
JP03	4.58	4.00	51.7	46.6	78.3	59.8	8.8	26.1	13.0	52.1	-0.7	-1.6
JP04	4.63	3.94	51.4	46.5	76.3	59.4	9.0	25.1	12.3	51.9	-1.6	-2.7
JP05	4.60	3.75	49.1	44.4	72.6	58.8	8.4	26.9	12.8	51.8	1.9	-0.3
JP07	4.55	3.97	50.9	46.4	76.6	57.2	8.4	25.4	12.6	52.9	-0.5	-1.0
JP08	4.59	3.88	49.2	46.2	74.9	57.0	8.2	25.9	12.3	50.9	-0.3	-1.7
JP09	4.59	4.00	51.8	47.4	77.2	58.6	8.8	25.0	12.7	52.2	-1.7	-2.1
LA01	4.55	3.69	52.5	42.9	75.3	62.3	8.4	25.4	11.2	53.2	0.5	2.7
MY01	4.60	3.90	53.7	48.6	83.6	61.6	8.4	24.8	12.2	52.2	-4.0	0.0
MN01	4.09	3.84	52.5	47.3	73.6	58.1	9.3	27.4	13.9	54.1	I 11.6	C 20.5
MM01	4.81	4.18	59.8	52.8	87.1	60.1	E 10.3	26.6	13.0	54.8	I -8.3	-5.1
PH01	4.56	3.79	51.3	46.2	77.9	59.0	8.6	24.2	13.1	55.2	-0.4	1.5
PH02	4.32	3.95	51.8	48.3	74.6	58.6	8.4	24.1	13.7	48.8	2.7	7.2
KR01	4.48	4.06	51.4	48.0	78.0	61.2	8.9	23.4	13.5	52.1	0.1	0.5
RU01	4.53	3.93	48.6	E 58.1	73.9	61.2	8.7	25.5	E 15.3	51.5	0.7	1.0
RU02	4.62	3.80	51.3	50.4	71.6	E 70.2	9.0	23.0	14.1	E 60.0	2.8	0.7
TH01	4.57	3.81	48.8	43.9	72.4	60.1	7.9	24.7	E 10.6	51.1	0.6	-1.0
TH02	4.57	3.84	50.5	44.8	74.8	60.4	9.2	27.1	12.6	51.9	1.6	0.1
TH04	4.49	3.84	49.5	43.0	73.8	55.8	E 7.5	24.2	12.0	48.0	0.1	0.8
TH05	4.54	3.86	54.3	47.0	74.9	58.3	E 7.2	25.1	12.0	55.0	-1.5	1.3
VN01	4.53	3.99	52.1	48.2	79.1	60.8	E 10.3	25.5	12.9	50.5	-0.8	0.2
VN02	4.76	3.68	52.9	47.2	76.6	61.2	E 10.3	25.5	12.8	49.7	-3.2	-1.6
VN03	4.67	E 3.27	44.8	---	---	60.3	9.8	29.8	13.4	51.2	---	---
VN04	4.63	3.89	53.9	47.7	77.6	60.9	9.8	E 31.0	14.6	50.9	0.7	0.0
VN05	4.33	3.94	50.8	46.2	77.1	54.8	E 7.3	22.5	14.7	47.9	1.4	6.3
Vp	4.54	3.97	52.0	47.0	77.0	60.0	8.9	26.0	13.0	52.1	0.0	-0.1
N of data	33	33	33	32	32	33	33	33	33	33		
Within DQO	33	32	33	29	32	32	27	32	31	32		
Flag E	0	1	0	2	0	1	6	1	2	1		
Flag X	0	0	0	1	0	0	0	0	0	0		

Note: "E", Value exceeded the DQO (Accuracy, ±15); "X", Value exceeded the DQO (Accuracy, ±15) more than a factor of 2;  
 "I", Poor ion balance (R<sub>1</sub>); "C", Poor conductivity agreement (R<sub>2</sub>); "---", Not measured; "Vp", Prepared values of parameters;  
 \*1. The abbreviated name and code are given in Chapter 1

## 2) Low Concentration Sample No. 102w

The number and percentage of flagged data for the low concentration sample No. 102w were shown in Table 2.9. Thirty analytical data out of 328 exceeded the DQO within a factor of 2 and were flagged by "E". Eight analytical data out of 328 exceeded the DQO more than a factor of 2 and were flagged by "X". Data marked with flags shared up to 11.6 percent of all the submitted data for sample No. 102w.

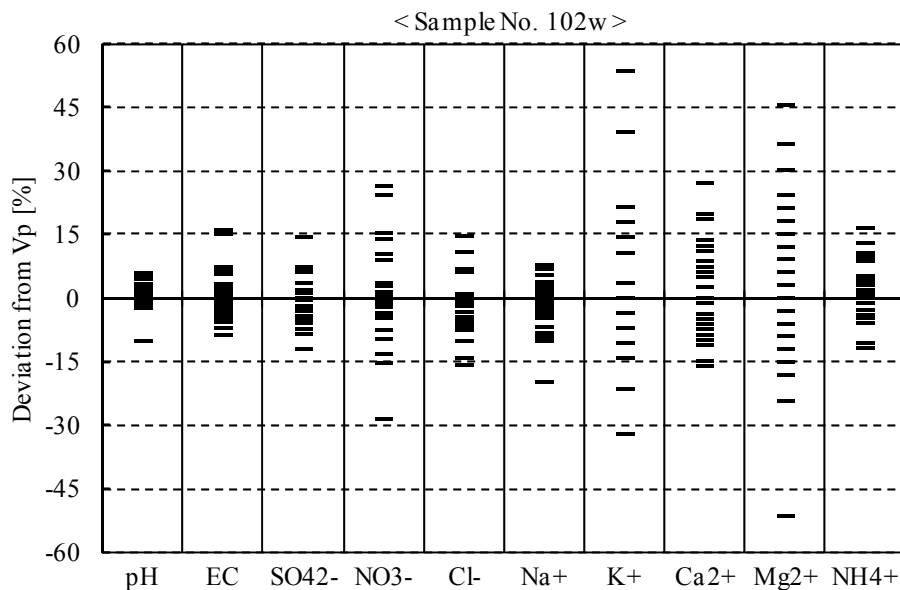
The normalized data by prepared value in each parameter were shown in Figure 2.2.

**Table 2.9 Number of flagged data for the Sample No. 102w (low concentrations)**

Characterization of data	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Data within DQO	33	31	33	27	31	32	26	27	18	32	290
Data with flag E <sup>*1</sup>	0	2	0	5	1	1	4	5	11	1	30
Data with flag X <sup>*2</sup>	0	0	0	0	0	0	3	1	4	0	8
Flagged data [%]	0.0	6.1	0.0	15.6	3.1	3.0	21.2	18.2	45.5	3.0	11.6

( Total data = 328 )

Note: \*1, Data exceeded DQO within a factor of 2; \*2, Data exceeded DQO more than a factor of 2



**Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 102w**

Analytical data of Cations had a tendency to be marked with flags in comparison with anions. The analytical data submitted by the participating laboratories were shown in Table 2.10 with flags.

**Table 2.10 Analytical Results of Sample No. 102w**

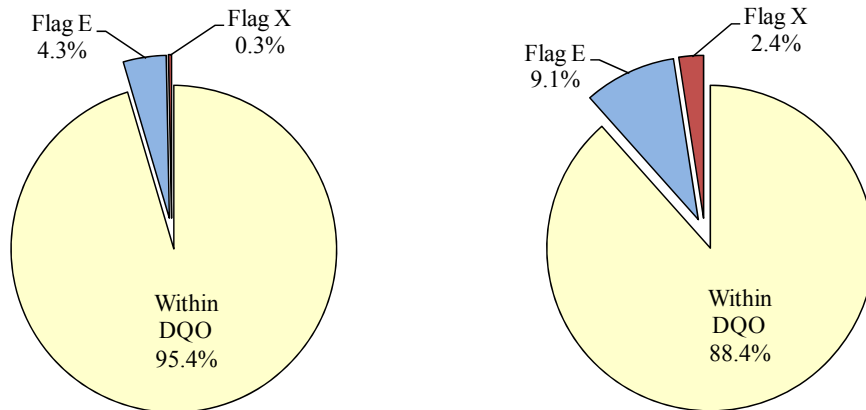
Lab. ID*1	pH	EC mS/m	SO <sub>4</sub> <sup>2-</sup> μmol/L	NO <sub>3</sub> <sup>-</sup> μmol/L	Cl <sup>-</sup> μmol/L	Na <sup>+</sup> μmol/L	K <sup>+</sup> μmol/L	Ca <sup>2+</sup> μmol/L	Mg <sup>2+</sup> μmol/L	NH <sub>4</sub> <sup>+</sup> μmol/L	R <sub>1</sub> %	R <sub>2</sub> %
KH01	5.35	1.22	17.8	E 18.2	26.2	21.2	2.8	8.8	E 3.9	17.2	-5.9	-2.0
CN01	5.04	1.20	16.6	14.2	24.2	21.1	E 3.4	E 10.3	E 4.1	17.6	5.6	3.9
CN02	5.02	1.22	16.8	14.4	23.6	20.0	2.7	7.6	3.4	17.8	0.3	1.8
CN03	5.00	1.21	16.2	14.5	23.9	20.0	2.9	8.8	X 4.3	17.1	3.7	3.3
CN04	5.00	1.28	17.6	14.3	23.6	20.8	E 3.3	9.1	E 4.0	17.2	2.9	1.5
ID01	5.16	1.25	17.7	14.9	27.4	20.1	2.7	7.6	3.4	E 19.8	-4.1	-0.6
ID02	5.10	1.18	16.6	E 10.3	E 20.8	21.1	E 3.3	9.1	E 3.9	17.3	I 8.1	0.1
ID03	5.10	E 1.44	16.8	13.3	21.2	21.8	X 3.9	9.0	3.6	18.6	6.4	-8.1
JP01	5.11	1.28	15.8	13.8	24.6	20.5	2.6	E 6.8	3.1	17.6	-1.3	-4.2
JP03	5.06	1.23	16.5	14.1	24.3	20.4	2.8	8.1	3.1	16.8	-0.2	0.0
JP04	5.09	1.27	16.5	14.3	24.5	20.1	2.9	8.7	3.2	16.2	-0.5	-2.1
JP05	5.12	1.20	16.6	14.4	24.7	19.7	2.4	8.3	3.1	17.5	-1.6	0.0
JP07	5.01	1.32	16.2	14.1	23.6	18.6	2.4	7.6	3.1	17.5	-0.3	-2.9
JP08	5.01	1.25	15.8	13.9	23.0	19.0	2.5	7.7	3.1	15.2	-0.3	-1.2
JP09	5.09	1.29	16.1	14.4	23.5	20.4	2.8	8.6	3.3	16.5	1.1	-3.4
LA01	4.98	1.21	15.7	12.5	23.0	21.5	E 2.2	7.2	X 1.6	17.3	1.6	1.1
MY01	5.05	1.24	16.5	14.6	26.4	20.5	2.5	6.9	E 2.7	17.6	-3.7	0.1
MN01	4.54	1.26	16.6	14.5	22.2	E 16.6	2.6	9.2	E 2.5	17.6	I 12.0	C 20.6
MM01	5.28	E 1.45	19.0	15.9	28.3	21.3	X 4.3	E 9.7	3.5	18.7	-4.0	-7.6
PH01	5.22	1.21	16.5	14.8	24.9	19.9	2.8	7.7	E 3.8	17.8	-2.2	-2.4
PH02	5.18	1.26	17.2	15.7	24.3	20.9	2.6	X 13.6	X 4.5	16.0	5.0	-0.2
KR01	4.93	1.23	16.3	14.4	23.4	19.3	2.8	7.8	X 4.8	18.8	5.0	4.8
RU01	4.96	1.29	15.9	E 17.9	24.9	20.9	2.8	8.0	3.7	17.5	0.6	2.1
RU02	5.30	1.16	14.6	16.4	24.5	22.3	3.1	8.5	3.5	19.2	2.4	-1.4
TH01	5.09	1.14	15.4	13.0	23.0	20.3	2.5	7.6	E 2.5	17.1	1.1	1.0
TH02	5.05	1.27	15.2	13.0	23.3	20.9	3.2	E 9.6	3.4	17.3	6.7	-1.5
TH04	5.00	1.25	15.7	E 12.2	23.1	19.9	2.5	7.5	3.1	16.0	2.1	-1.1
TH05	5.04	1.26	16.2	13.3	22.8	18.8	X 1.9	7.4	E 2.8	18.5	0.2	-2.0
VN01	5.03	1.33	16.6	14.6	24.9	20.6	2.8	E 9.7	3.0	17.9	2.2	-1.5
VN02	5.22	1.22	16.9	15.7	24.5	21.2	2.6	8.8	E 2.7	17.7	-2.4	-2.1
VN03	5.32	1.16	15.6	---	---	22.1	3.1	8.5	3.7	16.3	---	---
VN04	5.31	1.19	16.8	E 16.6	24.3	21.5	2.7	9.1	2.9	17.5	-2.7	-2.1
VN05	5.11	1.34	15.7	13.7	23.9	18.7	2.8	7.3	E 4.1	15.0	-1.4	-7.3
Vp	5.05	1.25	16.6	14.4	24.7	20.7	2.8	8.1	3.3	17.0	-0.1	0.0
N of data	33	33	33	32	32	33	33	33	33	33		
Within DQO	33	31	33	27	31	32	26	27	18	32		
Flag E	0	2	0	5	1	1	4	5	11	1		
Flag X	0	0	0	0	0	0	3	1	4	0		

Note: "E", Value exceeded the DQO (Accuracy, ±15); "X", Value exceeded the DQO (Accuracy, ±15) more than a factor of 2;  
 "I", Poor ion balance (R<sub>1</sub>); "C", Poor conductivity agreement (R<sub>2</sub>); "---", Not measured; "Vp", Prepared values of parameters;  
 \*1. The abbreviated name and code are given in Chapter 1

### 3) Comparison of High and Low Concentration Sample

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

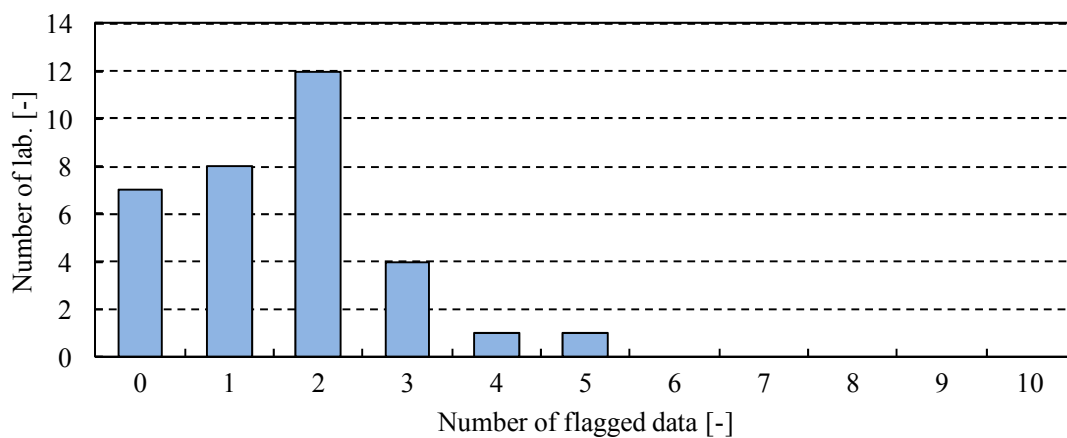
The percentage of the data within the DQO for the sample No. 101w and 102w were 95.4% and 88.4% respectively. The difference between both samples was 7.0%. In this project, the total number of flagged data was 53 (E: 44, X: 9) among the whole set of 656 data.



**Figure 2.3 Percentage of flagged data for Sample No. 101w and No. 102w (Left: No. 101w, Right: No. 102w)**

### 4) The number of laboratory (by number of flags)

The number of laboratory by number of flags was shown in Figure 2.4. The number of laboratory without flagged data was 7, which corresponds to 21.2% of all the analytical data submitted by participating laboratories.



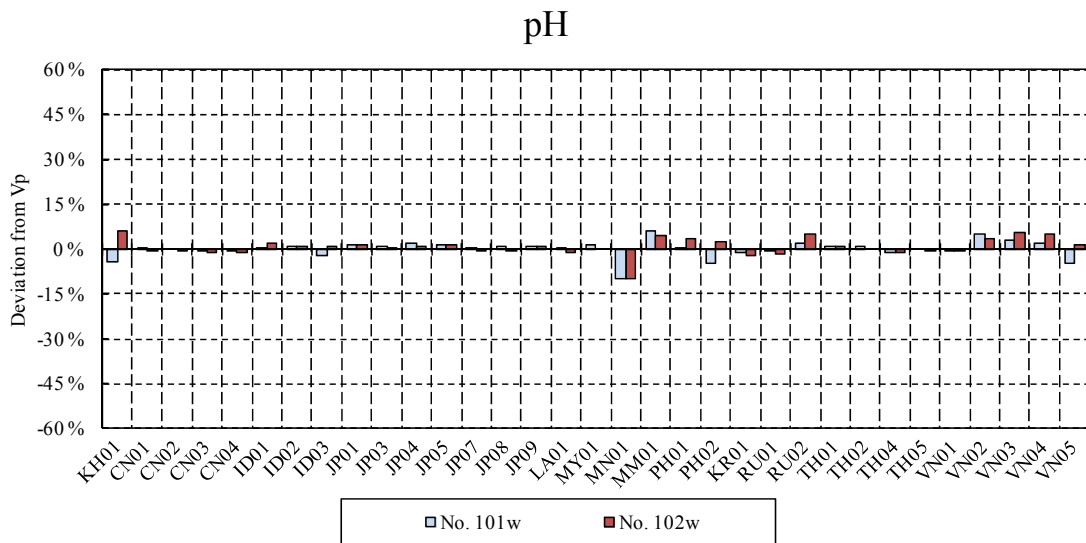
**Figure 2.4 Distribution of the number of laboratory (by number of flags)**

### 2.3.2 Evaluation of laboratories' performance (by analytical parameter)

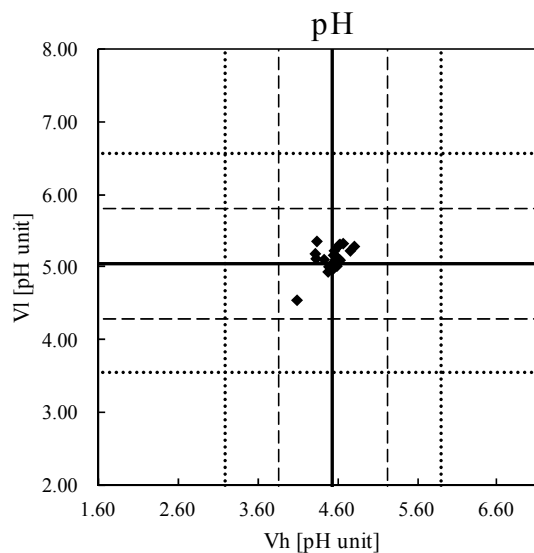
The data normalized by  $V_p$  were shown in Figures 2.5 through 2.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 101w and 102w, broken lines and dotted lines showed the values of  $V_p \pm 15\%$  and  $V_p \pm 30\%$  respectively.

#### 1) pH

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



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



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

**Figure 2.6 Scatter diagram for pH**

2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No. 101w from VN03 and the data of sample No. 102w from 2 laboratories (ID03 and MM01) exceeded the DQO and were marked with flag “E”.

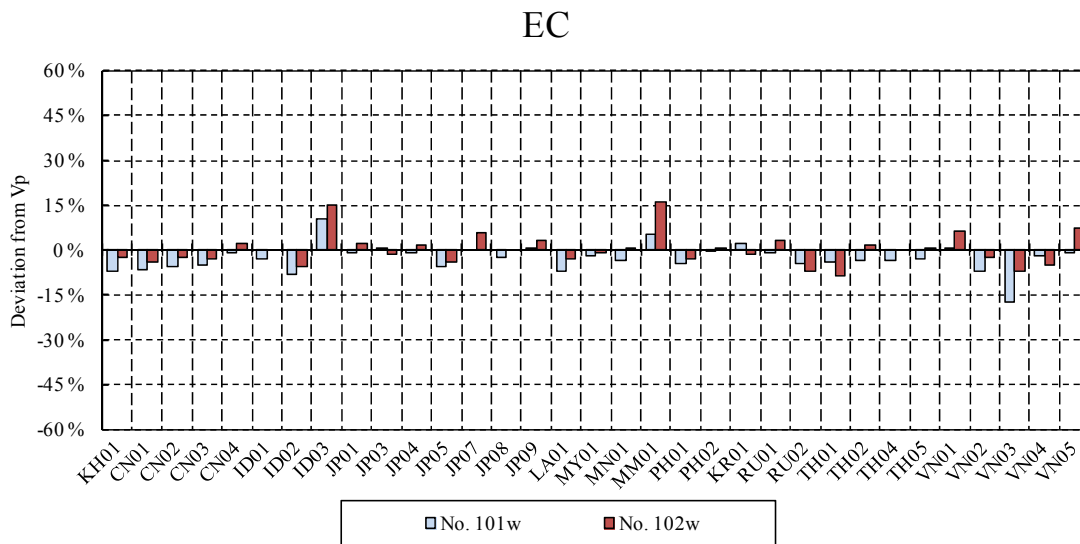
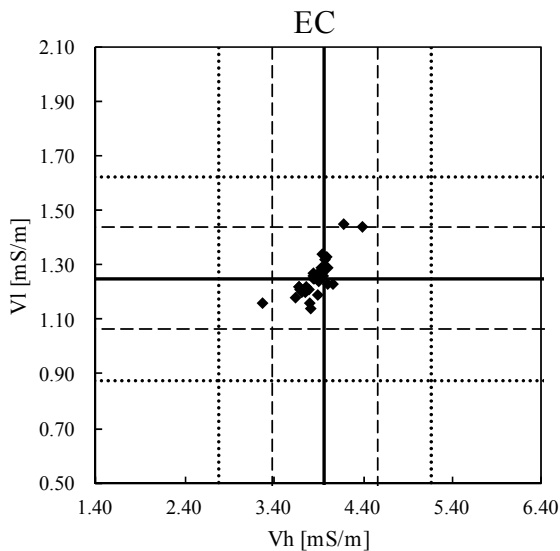


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

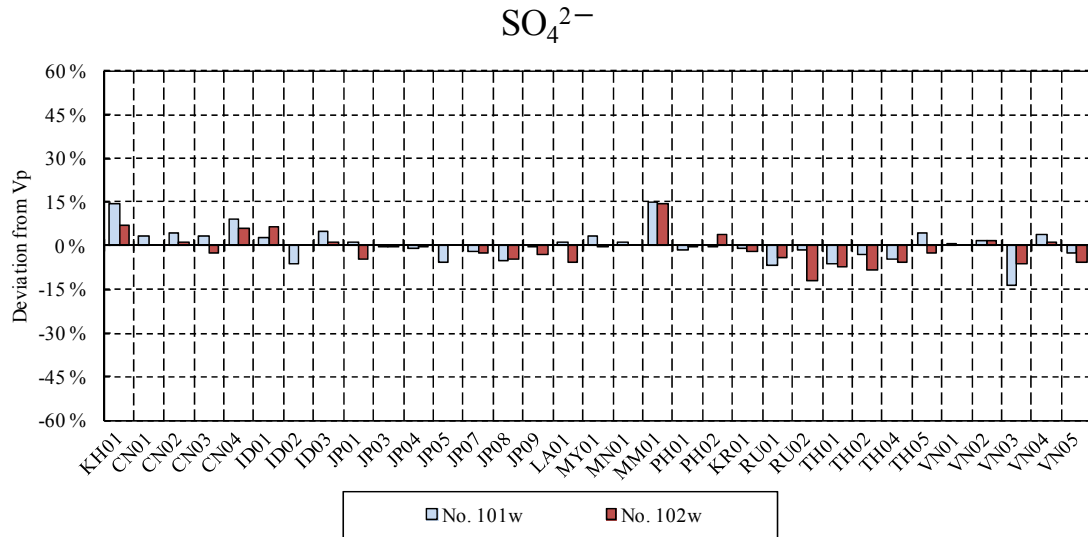


(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

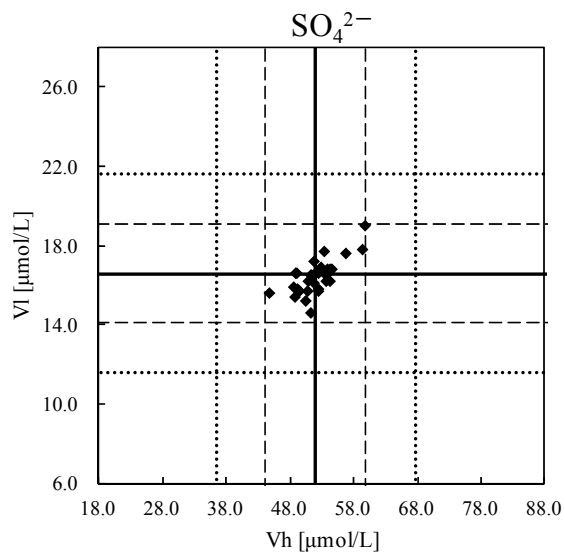
Figure 2.8 Scatter diagram for EC

### 3) $\text{SO}_4^{2-}$

All the obtained data satisfied the DQO.



**Figure 2.9 Deviation from prepared value for  $\text{SO}_4^{2-}$  (normalized by prepared value)**



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

**Figure 2.10 Scatter diagram for  $\text{SO}_4^{2-}$**

#### 4) $\text{NO}_3^-$

The data of sample No. 101w from 2 laboratories (ID02 and RU01) and the data of sample No. 102w from 5 laboratories (KH01, ID02, RU01, TH04 and VN04) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 101w from KH01 exceeded the DQO more than a factor of 2 and was marked with flag “X”.

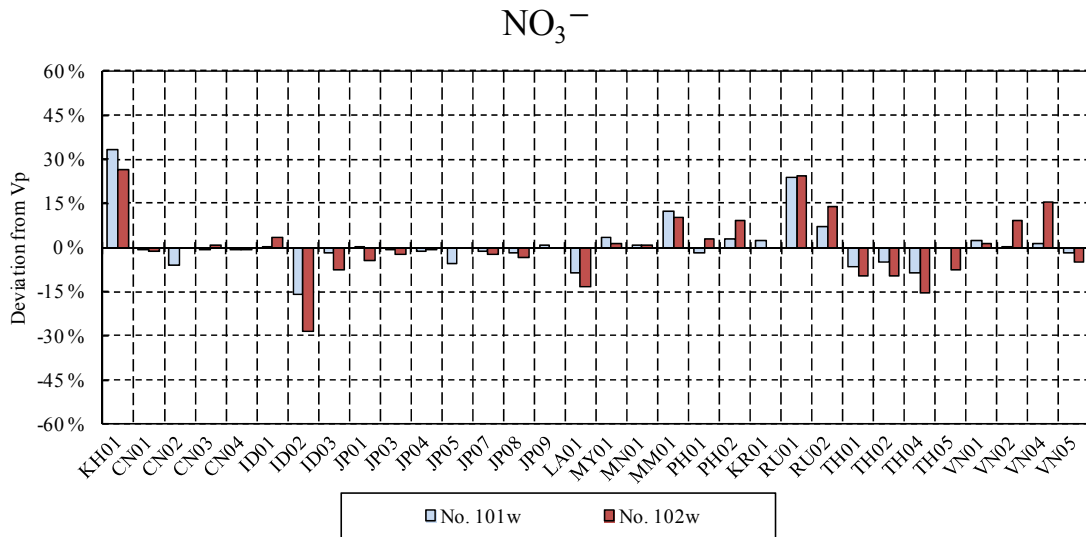
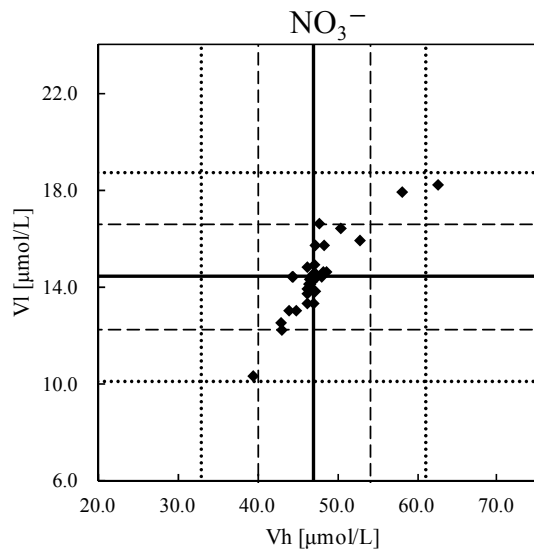


Figure 2.11 Deviation from prepared value for  $\text{NO}_3^-$  (normalized by prepared value)



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

Figure 2.12 Scatter diagram for  $\text{NO}_3^-$

5) Cl<sup>-</sup>

All data of sample No. 101w satisfied the DQO. The data of sample No. 102w from ID02 exceeded the DQO and was marked with flag “E”.

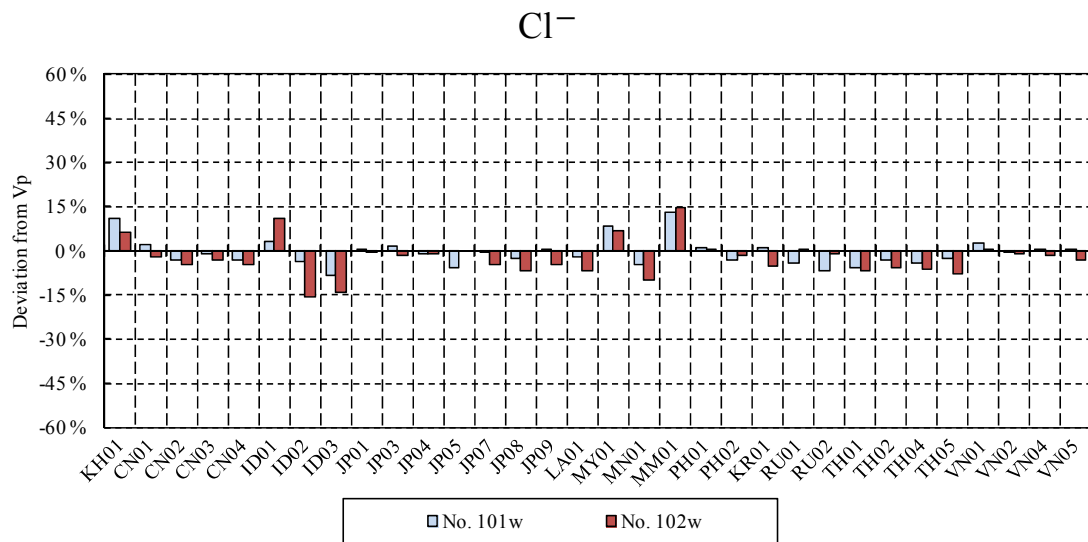
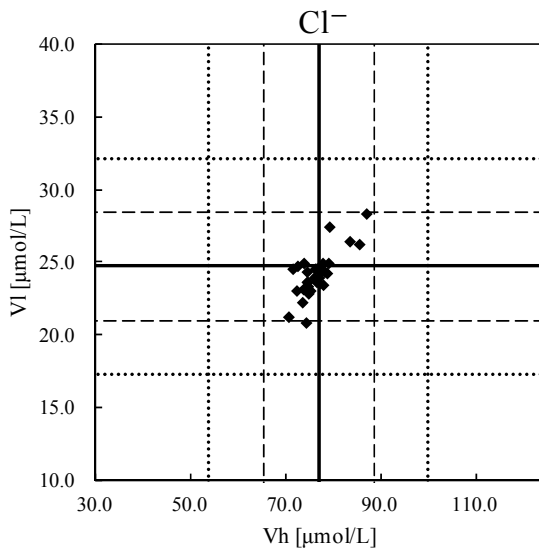


Figure 2.13 Deviation from prepared value for Cl<sup>-</sup> (normalized by prepared value)



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

Figure 2.14 Scatter diagram for Cl<sup>-</sup>

6) Na<sup>+</sup>

The data of sample No. 101w from RU02 and the data of sample No. 102w from MN01 exceeded the DQO and were marked with flag “E”.

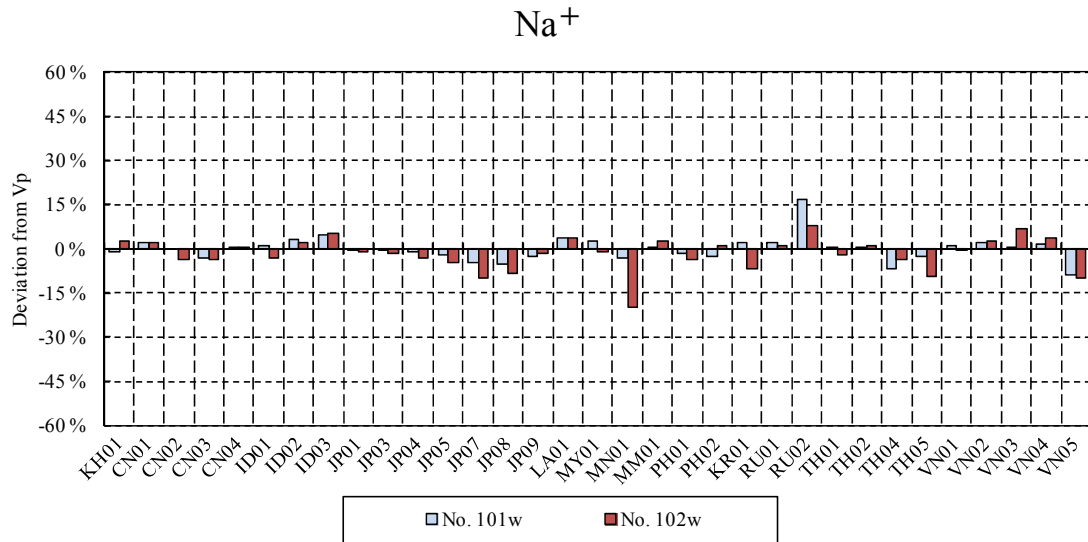
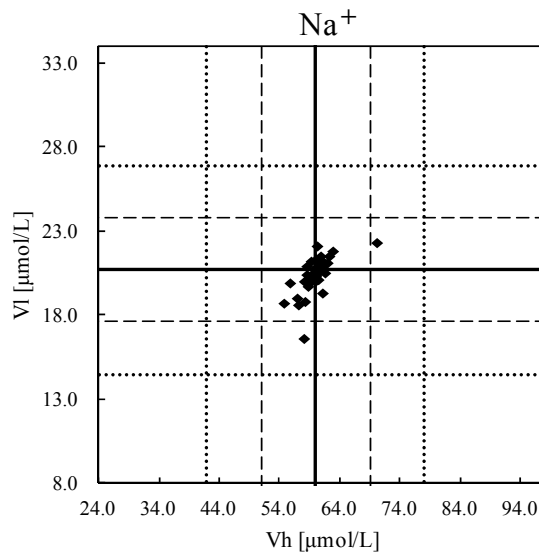


Figure 2.15 Deviation from prepared value for Na<sup>+</sup> (normalized by prepared value)



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

Figure 2.16 Scatter diagram for Na<sup>+</sup>

7)  $K^+$

The data of sample No. 101w from 6 laboratories (MM01, TH04, TH05, VN01, VN02 and VN05) and the data of sample No. 102w from 4 laboratories (CN01, CN04, ID02 and LA01) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 102w from 3 laboratories (ID03, MM01 and TH05) exceeded the DQO more than a factor of 2 and was marked with flag “X”.

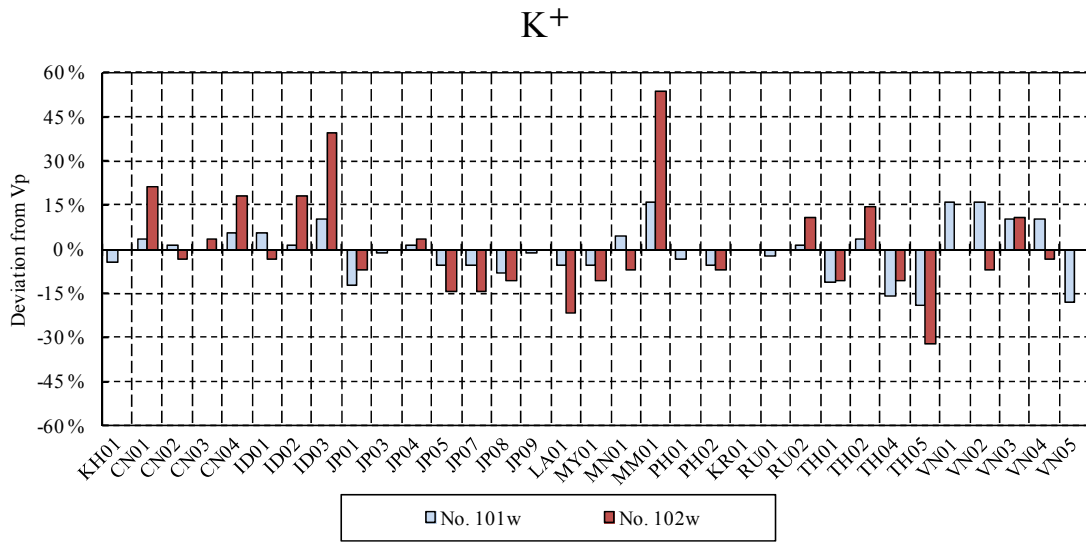
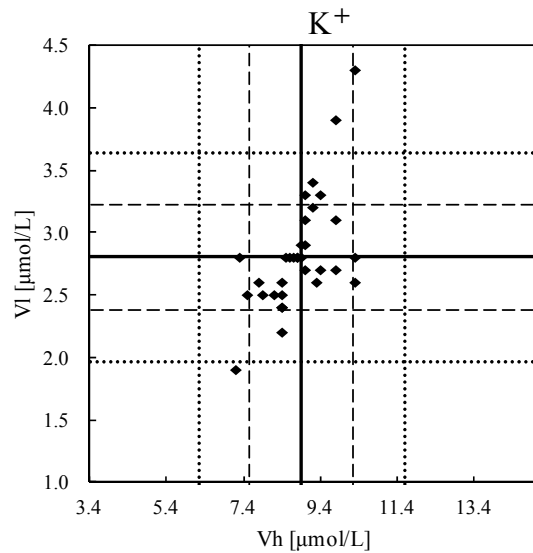


Figure 2.17 Deviation from prepared value for  $K^+$  (normalized by prepared value)

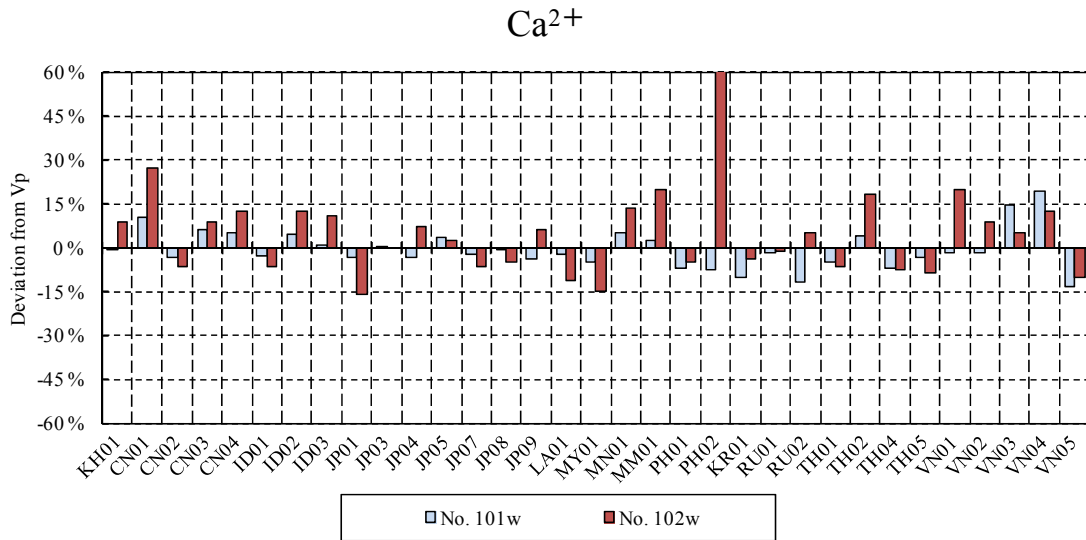


(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

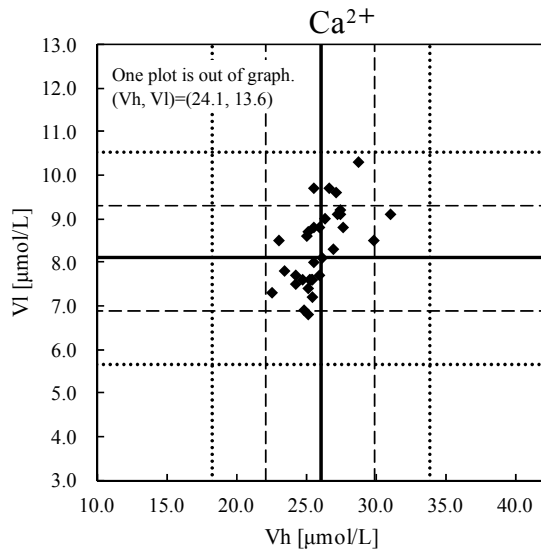
Figure 2.18 Scatter diagram for  $K^+$

### 8) Ca<sup>2+</sup>

The data of sample No. 101w from VN04 and the data of sample No. 102w from 5 laboratories (CN01, JP01, MM01, TH02 and VN01) exceeded the DQO and were marked with flag “E”. Additionally, the data of sample No. 102w from PH02 exceeded the DQO more than a factor of 2 and were marked with flag “X”.



**Figure 2.19 Deviation from prepared value for Ca<sup>2+</sup> (normalized by prepared value)**

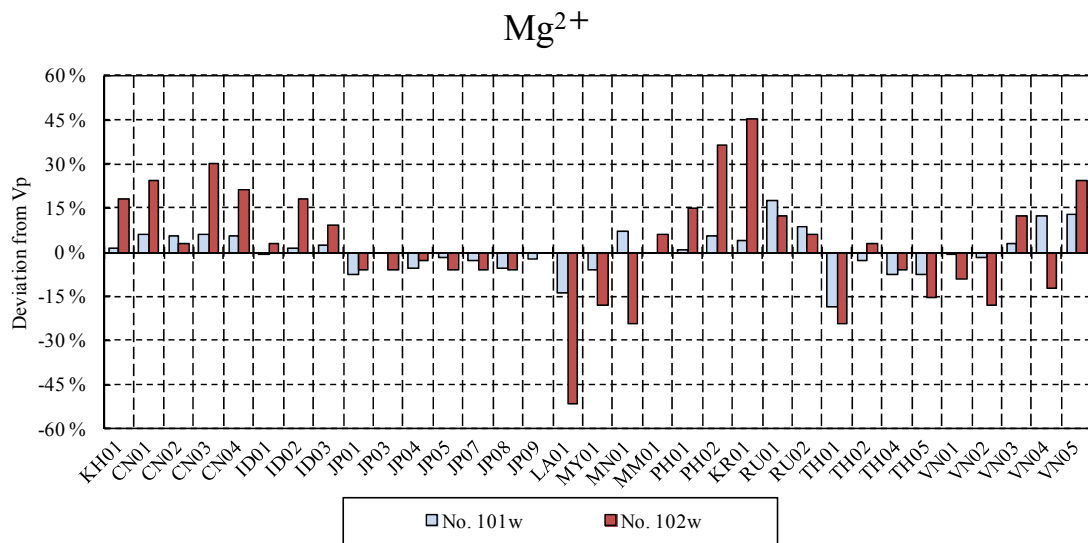


(Vh: Values for high conc. sample, Vl: Values for low conc. sample)

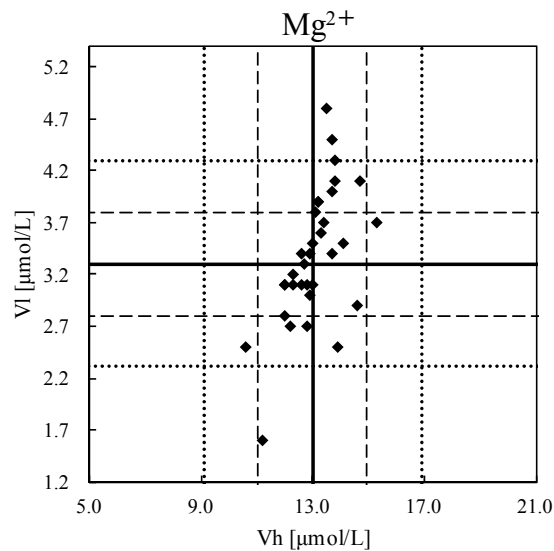
**Figure 2.20 Scatter diagram for Ca<sup>2+</sup>**

### 9) Mg<sup>2+</sup>

The data of sample No. 101w from 2 laboratories (RU01 and TH01) and the data of sample No. 102w from 11 laboratories (KH01, CN01, CN04, ID02, MY01, MN01, PH01, TH01, TH05, VN02 and VN05) exceeded the DQO and marked with flag “E”. Additionally, the data of sample No. 102w from 4 laboratories (CN03, LA01, PH02 and KR01) exceeded the DQO more than a factor of 2 and was marked with flag “X”.



**Figure 2.21 Deviation from prepared value for Mg<sup>2+</sup> (normalized by prepared value)**



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

**Figure 2.22 Scatter diagram for Mg<sup>2+</sup>**

10)  $\text{NH}_4^+$

The data of sample No. 101w from RU02 and the data of sample No. 102w from ID01 exceeded the DQO and marked with flag “E”.

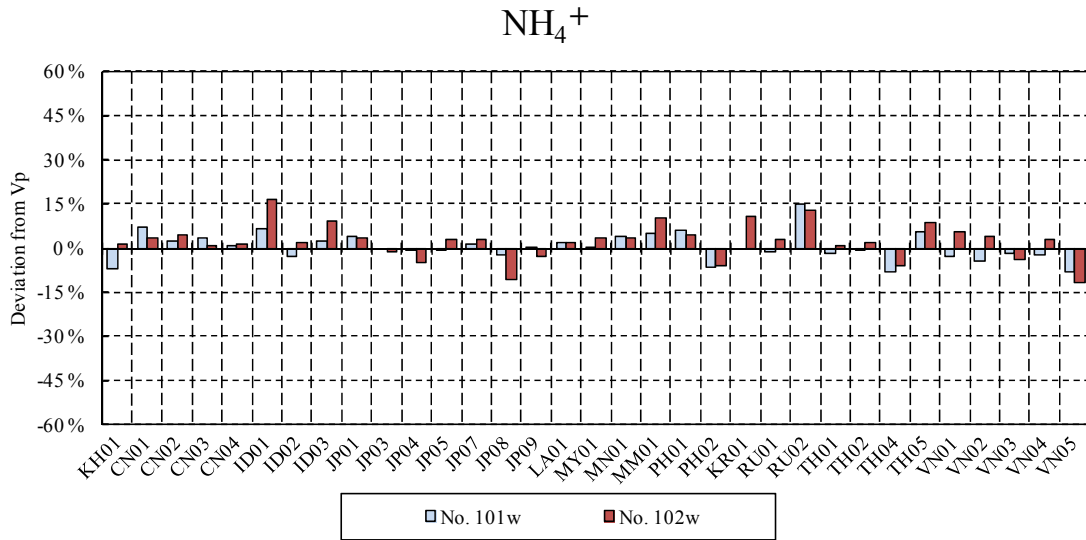
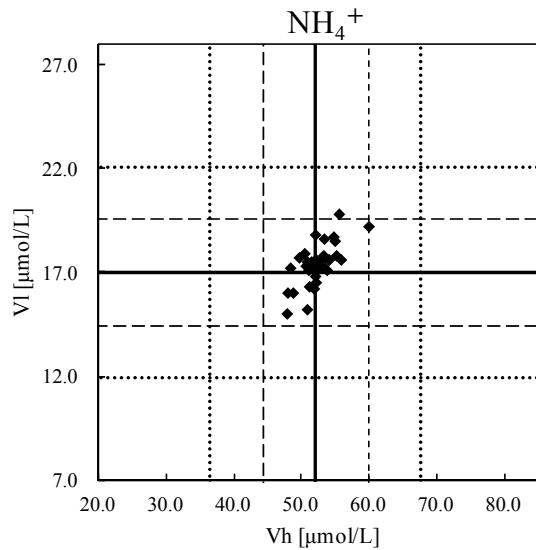


Figure 2.23 Deviation from prepared value for  $\text{NH}_4^+$  (normalized by prepared value)



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

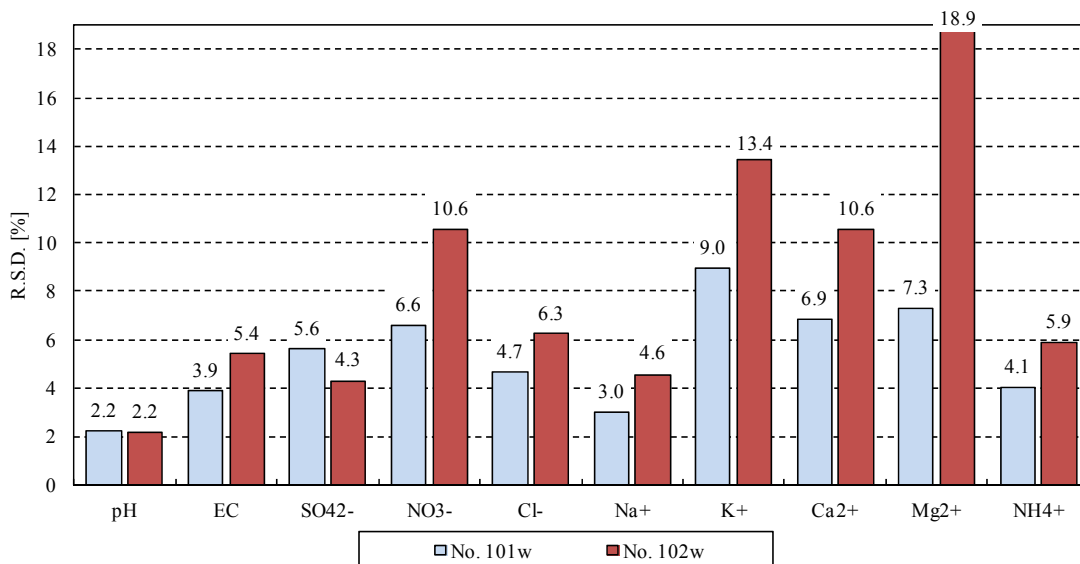
Figure 2.24 Scatter diagram for  $\text{NH}_4^+$

### 2.3.3 Overall Evaluation

The concentrations of the analytical parameters in the samples for this survey were fixed on the basis of the statistics of monitoring data on wet deposition in EANET. Compared to the samples for the survey in 2009, concentrations of ions in the sample No. 101w and 102w were lower. Especially, concentration of  $Mg^{2+}$  in the sample No. 102w was almost half of that of the survey in 2009. This low concentration of  $Mg^{2+}$  is estimated to have caused the low ratio of the number of data within DQO, which was 54.5%.

The relative standard deviations (R.S.D.) of each parameter for the sample No. 101w and No. 102w were shown in the Figure 2.25. The R.S.D. of  $Mg^{2+}$  for sample No. 102w was the highest in this survey. The R.S.D. values for sample No. 102w were higher than those for sample No. 101w except for pH and  $SO_4^{2-}$ .

(Relative standard deviation (%) = (Standard deviation / Average) x 100; Reported data after removing the outliers)



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

Some laboratories had problems in calibration curves for the determination of ion concentrations in this project as same as past projects. The person in charge of analysis needs to confirm that the calibration curves were suitable for accurate determination analysis. The reliability of the calibration curves have to be examined before the analysis of the samples by analyzing the Standard Reference Materials (SRMs) to avoid the acquisition of low quality data. In addition, the staffs in charge of analysis have to take care to prepare and save a portion of the standard solution for drawing the calibration curves.

### 2.3.4 Information on Laboratories

#### 1) Number of analysts and their experience

Number of analysts and years of their experience were shown in Table 2.11 and Table 2.12 respectively. In the Table 2.11, the letters of “A”, “B” and “C” mean individuals of analysts in each laboratory who carried out analyses. In 17 laboratories, same analyst carried out the analyses for all parameters. Clear relationship between the number of analysts and flagged data was not suggested.

**Table 2.11 Number of analysts**

Lab. ID	Total	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
KH01	1	A	A	A	A	A	A	A	A	A	A
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	2	A	A	B	B	B	B	B	B	B	B
CN04	2	A	A	B	B	B	B	B	B	B	B
ID01	1	A	A	A	A	A	A	A	A	A	A
ID02	2	A	A	A	A	A	B	B	B	B	B
ID03	2	A	B	B	B	B	B	B	B	B	B
JP01	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
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
JP09	1	A	A	A	A	A	A	A	A	A	A
LA01	2	A	B	B	B	B	B	B	B	B	B
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B	B	B	B	B	B	B	B
MM01	1	A	A	A	A	A	A	A	A	A	A
PH01	1	A	A	A	A	A	A	A	A	A	A
PH02	2	A	A	B	B	B	B	B	B	B	B
KR01	1	A	A	A	A	A	A	A	A	A	A
RU01	3	A	A	B	B	B	C	C	C	C	A
RU02	2	A	A	A	A	A	B	B	B	B	A
TH01	1	A	A	A	A	A	A	A	A	A	A
TH02	2	A	B	B	B	B	A	A	A	A	A
TH04	3	A	A	B	B	B	C	C	C	C	C
TH05	2	A	A	B	B	B	B	B	B	B	B
VN01	2	A	A	B	B	B	B	B	B	B	B
VN02	2	A	A	B	B	B	B	B	B	B	B
VN03	3	A	A	B	--	--	C	C	C	C	B
VN04	2	A	A	B	B	B	B	B	B	B	B
VN05	2	A	A	B	B	B	B	B	B	B	B

Note: Light mesh, Analytic data of sample No. 101w or No. 102w was marked with flag "E" or "X";

Dark mesh, Analytic data of both samples were marked with flag "E" or "X";

"--", Not measured

Total of 171 data out of 317 were analyzed by the analysts whose experience was less than 5 years. The number corresponds to 53.9% of all the submitted data. Clear relationship between the years of experience and flagged data was not suggested.

**Table 2.12 Years of experience**

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
KH01	2	2	2	2	2	2	2	2	2	2
CN01	19	19	19	19	19	19	19	19	19	19
CN02	12	12	2	2	2	2	2	2	2	2
CN03	2	2	12	12	12	12	12	12	12	12
CN04	2	2	15	15	15	15	15	15	15	15
ID01	9	9	9	9	9	9	9	9	9	9
ID02	11	11	11	11	11	11	11	11	11	11
ID03	1	2	2	2	2	2	2	2	2	2
JP01	7	7	7	7	7	7	7	7	7	7
JP03	4	4	4	4	4	4	4	4	4	4
JP04	3	3	3	3	3	3	3	3	3	3
JP05	1	1	1	1	1	1	1	1	1	1
JP07	3	3	3	3	3	3	3	3	3	3
JP08	4	4	4	4	4	4	4	4	4	4
JP09	2	2	2	2	2	2	2	2	2	2
LA01	3	4	4	4	4	4	4	4	4	
MY01	4	4	1	1	1	5	5	5	5	5
MN01	3	3	5	5	5	5	5	5	5	5
MM01	5	5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
PH01	<1	<1	3	3	3	13	13	13	13	5
PH02	3	3	3	3	3	3	3	3	3	3
KR01	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.	n. i.
RU01	7	7	12	12	12	13	13	13	13	7
RU02	1	1	1	1	1	19	19	19	19	1
TH01	1	1	1	1	1	1	1	1	1	1
TH02	13	8	8	8	8	13	13	13	13	13
TH04	7	7	4	4	4	1	1	1	1	1
TH05	9	9	7	7	7	7	7	7	7	7
VN01	2	2	17	17	17	17	17	17	17	17
VN02	1	1	6	6	6	6	6	6	6	6
VN03	4	4	5	--	--	7	7	7	7	5
VN04	5	5	6	6	6	6	6	6	6	6
VN05	2	2	4	4	4	4	4	4	4	4

Note: Light mesh, Analytic data of sample No. 101w or No. 102w was marked with flag "E" or "X";

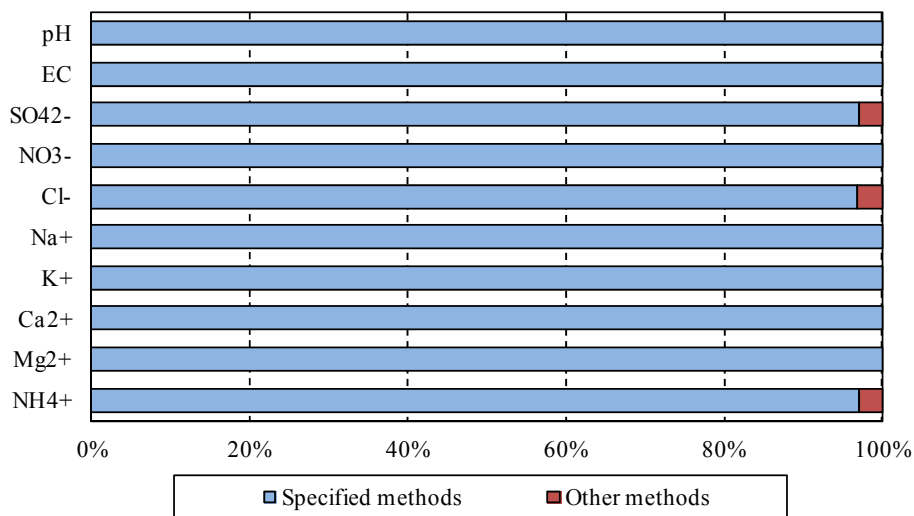
Dark mesh, Analytic data of both samples were marked with flag "E" or "X";

--- Not measured; "n.i.", No information

## 2) Analytical instruments

As shown in Figure 2.26, most of the participating laboratories used the specified methods described in the “Technical Manual for Wet Deposition Monitoring in East Asia”. Laboratory of RU02 did not used the specified methods for the analyses of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$ . ( $\text{SO}_4^{2-}$ : Nephelometry,  $\text{Cl}^-$ : Titrimetry,  $\text{NH}_4^+$ : Spectrophotometry without Indophenol) The specified methods were shown in Table 2.3.

Analytical methods used for the measurement in the participating laboratories were shown in Table 2.13.

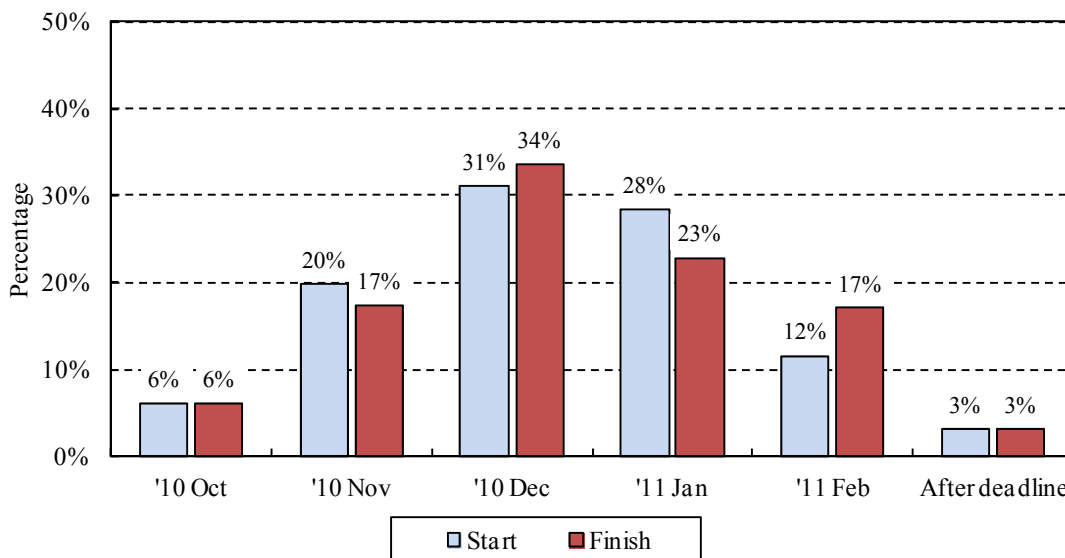


**Figure 2.26 Percentage of laboratories that used the specified methods**



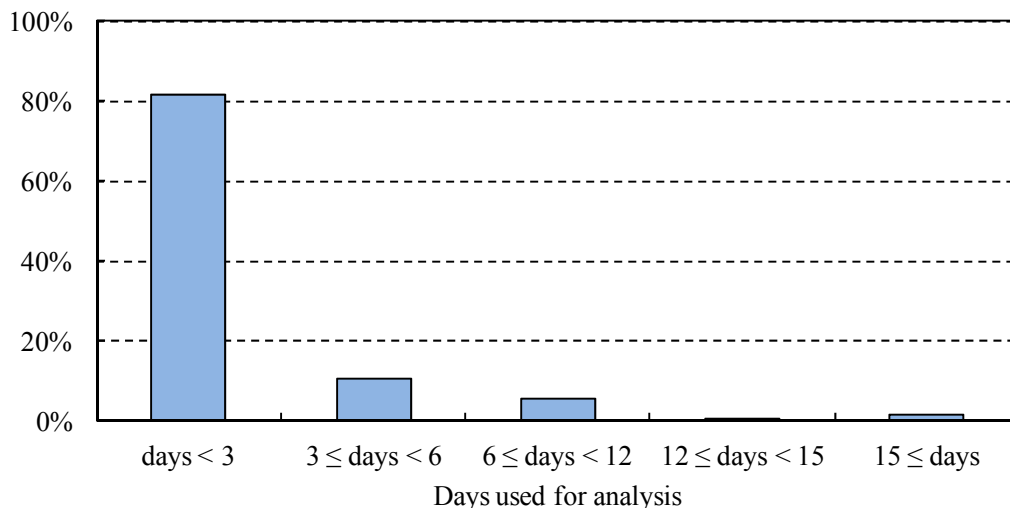
### 3) Date of Analysis

Figure 2.27 shows the Distribution of “Start date” and “Finish date” of analysis in the participating laboratories. In total, 57% of all the submitted data was determined within the year of 2010, and 3% was determined after the deadline of data submission in this project.



**Figure 2.27 Distribution of Start date and Finish date of analysis**

Figure 2.28 shows how many days were needed to determine the analytical data in the participating laboratories. Most analytical data were obtained within less than 3 days.



**Figure 2.28 Distribution of Days used for analysis**

## 2.4 Comparison with past surveys

Since the beginning of EANET, inter-laboratory comparison on wet deposition reached the 13<sup>th</sup> survey. The results showing the percentages of flagged data and percentage of data that satisfied the DQO were shown in Figure 2.29.

The percentages of data within DQO for the sample No. 101w and No. 102w were 95.4% and 88.4% respectively. These were the second highest percentages since the beginning and were slightly lower than the survey of 2009 which marked the highest percentages. The accuracy of the measurement on wet deposition monitoring might have improved due to the continuous efforts and experiences in participating laboratories.

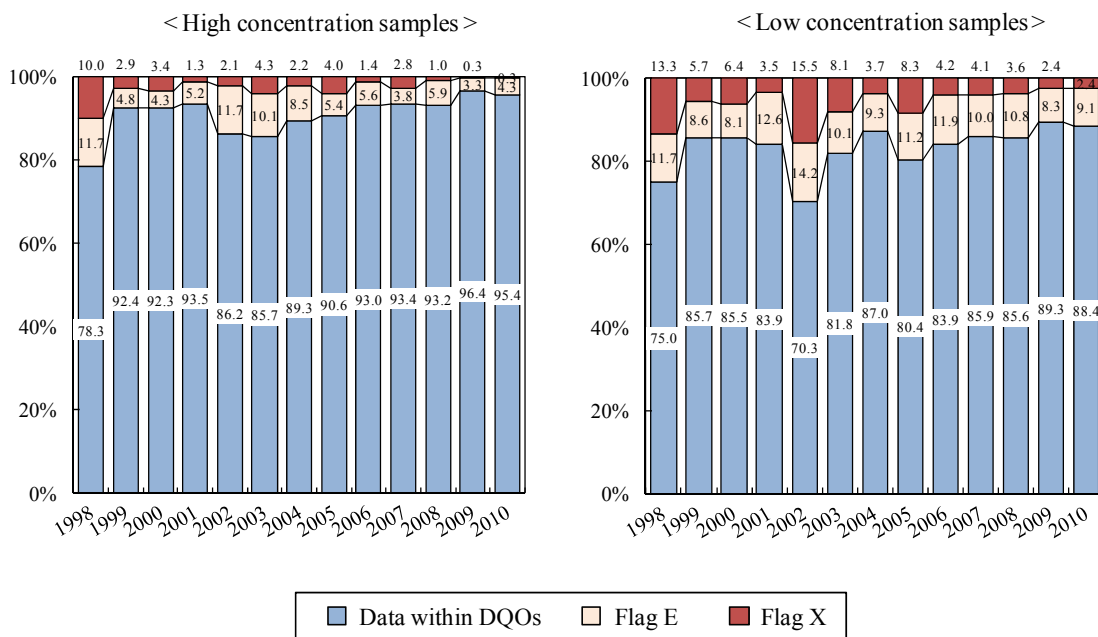


Figure 2.29 Comparison of results from the inter-laboratory comparison projects

Figure 2.30 showed the trend of the prepared values and the percentage of flagged data. Although the percentages of data marked with flags “E” and “X” decreased in most parameters compared with past surveys, the percentages were relatively high in cations as ever.

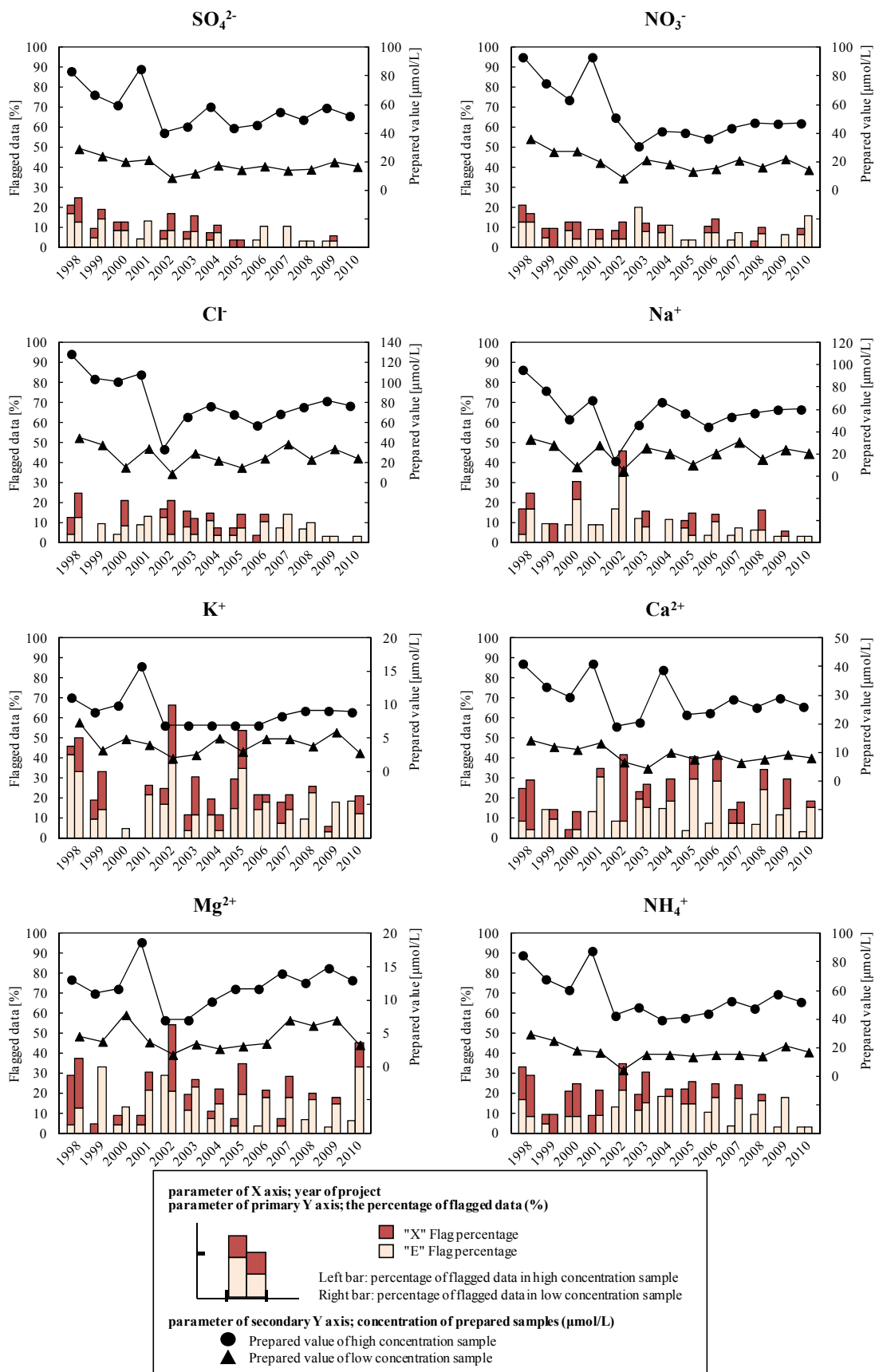
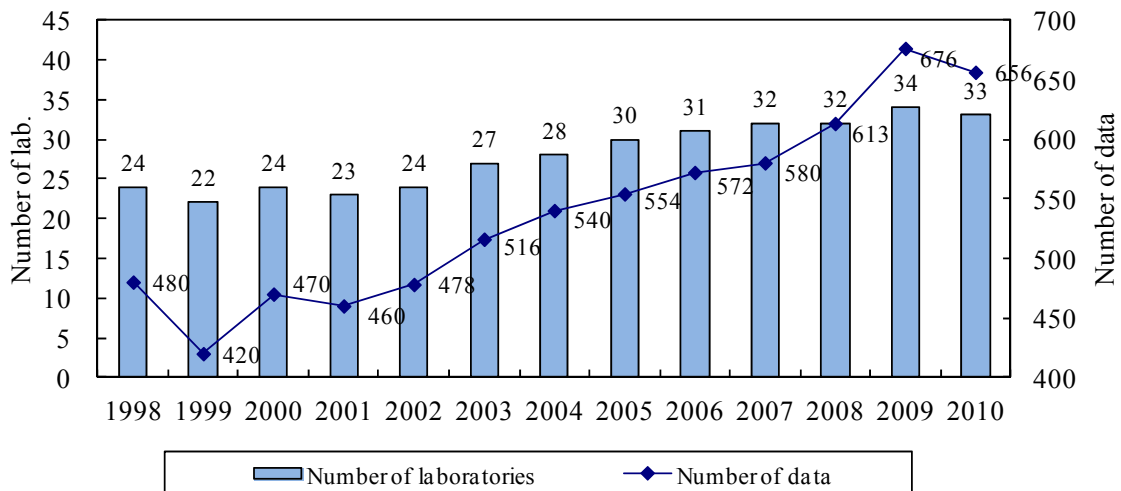


Figure 2.30 Comparison for each parameter in inter-laboratory comparison project

As shown in the figure 2.31, the number of data was decreased from the survey in last year. The total number of data was 656 in this survey because some participating laboratories did not submit analytical data.



**Figure 2.31 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition**

## 2.5 Recommendations for improvements

The fundamental matters for QA/QC on measurements and analyses of samples were described on the page 22 through 29 of the “Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia”.

Additionally, the NC showed the following matters for the improvement of data accuracy.

### 2.5.1 Measurement and Analysis

- ▶ After drawing calibration curves for the determination of ion concentrations, accuracy check by analyzing Reference Materials is recommended.
- ▶ Ranges of calibration curves need to cover the concentrations of the samples.

### 2.5.2 Data control

- ▶ After determining all the analytical parameters, data check by calculating  $R_1$  and  $R_2$  values is important. Especially,  $R_1$  and  $R_2$  values of artificial samples used for this survey are theoretically zero because they don't contain other extra ion species. If the values exceed their allowable ranges, the data set is doubtful and reanalysis shall be carried out after rechecking analytical instruments and analytical procedures.

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Appendix 2.1 Analytical Results submitted by the laboratories

**Appendix Table 2.1.1 Analytical data concerning high conc. sample No. 101w**

**Sample No. 101w (High concentrations)**

Lab. ID	pH	EC mS/m	SO <sub>4</sub> <sup>2-</sup> µmol/L	NO <sub>3</sub> <sup>-</sup> µmol/L	Cl <sup>-</sup> µmol/L	Na <sup>+</sup> µmol/L	K <sup>+</sup> µmol/L	Ca <sup>2+</sup> µmol/L	Mg <sup>2+</sup> µmol/L	NH <sub>4</sub> <sup>+</sup> µmol/L
KH01	4.34	3.68	59.4	62.6	85.6	59.3	8.5	25.9	13.2	48.4
CN01	4.55	3.71	53.6	46.8	78.8	61.3	9.2	28.7	13.8	55.9
CN02	4.54	3.76	54.3	44.3	74.6	60.0	9.0	25.2	13.7	53.3
CN03	4.50	3.77	53.7	46.9	76.1	58.2	8.9	27.6	13.8	53.8
CN04	4.51	3.93	56.8	46.7	74.7	60.1	9.4	27.4	13.7	52.6
ID01	4.55	3.85	53.4	47.1	79.3	60.5	9.4	25.3	12.9	55.6
ID02	4.59	3.64	48.9	39.4	74.4	62.0	9.0	27.2	13.2	50.7
ID03	4.43	4.39	54.6	46.2	70.7	62.9	9.8	26.3	13.3	53.4
JP01	4.61	3.93	52.5	47.2	77.3	59.7	7.8	25.1	12.0	54.1
JP03	4.58	4.00	51.7	46.6	78.3	59.8	8.8	26.1	13.0	52.1
JP04	4.63	3.94	51.4	46.5	76.3	59.4	9.0	25.1	12.3	51.9
JP05	4.60	3.75	49.1	44.4	72.6	58.8	8.4	26.9	12.8	51.8
JP07	4.55	3.97	50.9	46.4	76.6	57.2	8.4	25.4	12.6	52.9
JP08	4.59	3.88	49.2	46.2	74.9	57.0	8.2	25.9	12.3	50.9
JP09	4.59	4.00	51.8	47.4	77.2	58.6	8.8	25.0	12.7	52.2
LA01	4.55	3.69	52.5	42.9	75.3	62.3	8.4	25.4	11.2	53.2
MY01	4.60	3.90	53.7	48.6	83.6	61.6	8.4	24.8	12.2	52.2
MN01	4.09	3.84	52.5	47.3	73.6	58.1	9.3	27.4	13.9	54.1
MM01	4.81	4.18	59.8	52.8	87.1	60.1	10.3	26.6	13.0	54.8
PH01	4.56	3.79	51.3	46.2	77.9	59.0	8.6	24.2	13.1	55.2
PH02	4.32	3.95	51.8	48.3	74.6	58.6	8.4	24.1	13.7	48.8
KR01	4.48	4.06	51.4	48.0	78.0	61.2	8.9	23.4	13.5	52.1
RU01	4.53	3.93	48.6	58.1	73.9	61.2	8.7	25.5	15.3	51.5
RU02	4.62	3.80	51.3	50.4	71.6	70.2	9.0	23.0	14.1	60.0
TH01	4.57	3.81	48.8	43.9	72.4	60.1	7.9	24.7	10.6	51.1
TH02	4.57	3.84	50.5	44.8	74.8	60.4	9.2	27.1	12.6	51.9
TH04	4.49	3.84	49.5	43.0	73.8	55.8	7.5	24.2	12.0	48.0
TH05	4.54	3.86	54.3	47.0	74.9	58.3	7.2	25.1	12.0	55.0
VN01	4.53	3.99	52.1	48.2	79.1	60.8	10.3	25.5	12.9	50.5
VN02	4.76	3.68	52.9	47.2	76.6	61.2	10.3	25.5	12.8	49.7
VN03	4.67	3.27	44.8	---	---	60.3	9.8	29.8	13.4	51.2
VN04	4.63	3.89	53.9	47.7	77.6	60.9	9.8	31.0	14.6	50.9
VN05	4.33	3.94	50.8	46.2	77.1	54.8	7.3	22.5	14.7	47.9
<b>Prepared value</b>	<b>4.54</b>	<b>3.97</b>	<b>52.0</b>	<b>47.0</b>	<b>77.0</b>	<b>60.0</b>	<b>8.9</b>	<b>26.0</b>	<b>13.0</b>	<b>52.1</b>
Number of data	32	32	33	31	32	32	33	33	33	32
Average	4.55	3.88	52.2	46.9	76.5	59.7	8.8	25.8	13.1	52.1
Minimum	4.32	3.64	44.8	39.4	70.7	54.8	7.2	22.5	10.6	47.9
Maximum	4.81	4.39	59.8	58.1	87.1	62.9	10.3	31.0	15.3	55.9
Standard deviation	0.10	0.15	2.93	3.10	3.59	1.80	0.79	1.77	0.96	2.11

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

"---", Not measured

**Appendix Table 2.1.2 Analytical data concerning low conc. sample No. 102w**

**Sample No. 102w (Low concentrations)**

Lab. ID	pH	EC mS/m	SO <sub>4</sub> <sup>2-</sup> μmol/L	NO <sub>3</sub> <sup>-</sup> μmol/L	Cl <sup>-</sup> μmol/L	Na <sup>+</sup> μmol/L	K <sup>+</sup> μmol/L	Ca <sup>2+</sup> μmol/L	Mg <sup>2+</sup> μmol/L	NH <sub>4</sub> <sup>+</sup> μmol/L
KH01	5.35	1.22	17.8	18.2	26.2	21.2	2.8	8.8	3.9	17.2
CN01	5.04	1.20	16.6	14.2	24.2	21.1	3.4	10.3	4.1	17.6
CN02	5.02	1.22	16.8	14.4	23.6	20.0	2.7	7.6	3.4	17.8
CN03	5.00	1.21	16.2	14.5	23.9	20.0	2.9	8.8	4.3	17.1
CN04	5.00	1.28	17.6	14.3	23.6	20.8	3.3	9.1	4.0	17.2
ID01	5.16	1.25	17.7	14.9	27.4	20.1	2.7	7.6	3.4	19.8
ID02	5.10	1.18	16.6	10.3	20.8	21.1	3.3	9.1	3.9	17.3
ID03	5.10	1.44	16.8	13.3	21.2	21.8	3.9	9.0	3.6	18.6
JP01	5.11	1.28	15.8	13.8	24.6	20.5	2.6	6.8	3.1	17.6
JP03	5.06	1.23	16.5	14.1	24.3	20.4	2.8	8.1	3.1	16.8
JP04	5.09	1.27	16.5	14.3	24.5	20.1	2.9	8.7	3.2	16.2
JP05	5.12	1.20	16.6	14.4	24.7	19.7	2.4	8.3	3.1	17.5
JP07	5.01	1.32	16.2	14.1	23.6	18.6	2.4	7.6	3.1	17.5
JP08	5.01	1.25	15.8	13.9	23.0	19.0	2.5	7.7	3.1	15.2
JP09	5.09	1.29	16.1	14.4	23.5	20.4	2.8	8.6	3.3	16.5
LA01	4.98	1.21	15.7	12.5	23.0	21.5	2.2	7.2	1.6	17.3
MY01	5.05	1.24	16.5	14.6	26.4	20.5	2.5	6.9	2.7	17.6
MN01	4.54	1.26	16.6	14.5	22.2	16.6	2.6	9.2	2.5	17.6
MM01	5.28	1.45	19.0	15.9	28.3	21.3	4.3	9.7	3.5	18.7
PH01	5.22	1.21	16.5	14.8	24.9	19.9	2.8	7.7	3.8	17.8
PH02	5.18	1.26	17.2	15.7	24.3	20.9	2.6	13.6	4.5	16.0
KR01	4.93	1.23	16.3	14.4	23.4	19.3	2.8	7.8	4.8	18.8
RU01	4.96	1.29	15.9	17.9	24.9	20.9	2.8	8.0	3.7	17.5
RU02	5.30	1.16	14.6	16.4	24.5	22.3	3.1	8.5	3.5	19.2
TH01	5.09	1.14	15.4	13.0	23.0	20.3	2.5	7.6	2.5	17.1
TH02	5.05	1.27	15.2	13.0	23.3	20.9	3.2	9.6	3.4	17.3
TH04	5.00	1.25	15.7	12.2	23.1	19.9	2.5	7.5	3.1	16.0
TH05	5.04	1.26	16.2	13.3	22.8	18.8	1.9	7.4	2.8	18.5
VN01	5.03	1.33	16.6	14.6	24.9	20.6	2.8	9.7	3.0	17.9
VN02	5.22	1.22	16.9	15.7	24.5	21.2	2.6	8.8	2.7	17.7
VN03	5.32	1.16	15.6	---	---	22.1	3.1	8.5	3.7	16.3
VN04	5.31	1.19	16.8	16.6	24.3	21.5	2.7	9.1	2.9	17.5
VN05	5.11	1.34	15.7	13.7	23.9	18.7	2.8	7.3	4.1	15.0
<b>Prepared value</b>	<b>5.05</b>	<b>1.25</b>	<b>16.6</b>	<b>14.4</b>	<b>24.7</b>	<b>20.7</b>	<b>2.8</b>	<b>8.1</b>	<b>3.3</b>	<b>17.0</b>
Number of data	32	33	32	32	32	32	32	32	33	33
Average	5.10	1.25	16.3	14.4	24.1	20.5	2.8	8.3	3.4	17.4
Minimum	4.93	1.14	14.6	10.3	20.8	18.6	1.9	6.8	1.6	15.0
Maximum	5.35	1.45	17.8	18.2	28.3	22.3	3.9	10.3	4.8	19.8
Standard deviation	0.11	0.07	0.70	1.53	1.51	0.94	0.37	0.88	0.64	1.03

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

"---", Not measured

## Appendix 2.2 Normalized Data

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

**Appendix Table 2.2.1 Deviation% from prepared values of high conc. sample No. 101w**

**Sample No. 101w (High concentrations)**

Lab. ID	pH %	EC %	SO <sub>4</sub> <sup>2-</sup> %	NO <sub>3</sub> <sup>-</sup> %	Cl <sup>-</sup> %	Na <sup>+</sup> %	K <sup>+</sup> %	Ca <sup>2+</sup> %	Mg <sup>2+</sup> %	NH <sub>4</sub> <sup>+</sup> %
KH01	-4.4	-7.3	14.2	33.2	11.2	-1.2	-4.5	-0.4	1.5	-7.1
CN01	0.2	-6.5	3.1	-0.4	2.3	2.2	3.4	10.4	6.2	7.3
CN02	0.0	-5.3	4.4	-5.7	-3.1	0.0	1.1	-3.1	5.4	2.3
CN03	-0.9	-5.0	3.3	-0.2	-1.2	-3.0	0.0	6.2	6.2	3.3
CN04	-0.7	-1.0	9.2	-0.6	-3.0	0.2	5.6	5.4	5.4	1.0
ID01	0.2	-3.0	2.7	0.2	3.0	0.8	5.6	-2.7	-0.8	6.7
ID02	1.1	-8.3	-6.0	-16.2	-3.4	3.3	1.1	4.6	1.5	-2.7
ID03	-2.4	10.6	5.0	-1.7	-8.2	4.8	10.1	1.2	2.3	2.5
JP01	1.5	-1.0	1.0	0.4	0.4	-0.5	-12.4	-3.5	-7.7	3.8
JP03	0.9	0.8	-0.6	-0.9	1.7	-0.3	-1.1	0.4	0.0	0.0
JP04	2.0	-0.8	-1.2	-1.1	-0.9	-1.0	1.1	-3.5	-5.4	-0.4
JP05	1.3	-5.5	-5.6	-5.5	-5.7	-2.0	-5.6	3.5	-1.5	-0.6
JP07	0.2	0.0	-2.1	-1.3	-0.5	-4.7	-5.6	-2.3	-3.1	1.5
JP08	1.1	-2.3	-5.4	-1.7	-2.7	-5.0	-7.9	-0.4	-5.4	-2.3
JP09	1.1	0.8	-0.4	0.9	0.3	-2.3	-1.1	-3.8	-2.3	0.2
LA01	0.2	-7.1	1.0	-8.7	-2.2	3.8	-5.6	-2.3	-13.8	2.1
MY01	1.3	-1.8	3.3	3.4	8.6	2.7	-5.6	-4.6	-6.2	0.2
MN01	-9.9	-3.3	1.0	0.6	-4.4	-3.2	4.5	5.4	6.9	3.8
MM01	5.9	5.3	15.0	12.3	13.1	0.2	15.7	2.3	0.0	5.2
PH01	0.4	-4.5	-1.3	-1.7	1.2	-1.7	-3.4	-6.9	0.8	6.0
PH02	-4.8	-0.5	-0.4	2.8	-3.1	-2.3	-5.6	-7.3	5.4	-6.3
KR01	-1.3	2.3	-1.2	2.1	1.3	2.0	0.0	-10.0	3.8	0.0
RU01	-0.2	-1.0	-6.5	23.6	-4.0	2.0	-2.2	-1.9	17.7	-1.2
RU02	1.8	-4.3	-1.3	7.2	-7.0	17.0	1.1	-11.5	8.5	15.2
TH01	0.7	-4.0	-6.2	-6.6	-6.0	0.2	-11.2	-5.0	-18.5	-1.9
TH02	0.7	-3.3	-2.9	-4.7	-2.9	0.7	3.4	4.2	-3.1	-0.4
TH04	-1.1	-3.3	-4.8	-8.5	-4.2	-7.0	-15.7	-6.9	-7.7	-7.9
TH05	0.0	-2.8	4.4	0.0	-2.7	-2.8	-19.1	-3.5	-7.7	5.6
VN01	-0.2	0.5	0.2	2.6	2.7	1.3	15.7	-1.9	-0.8	-3.1
VN02	4.8	-7.3	1.7	0.4	-0.5	2.0	15.7	-1.9	-1.5	-4.6
VN03	2.9	-17.6	-13.8	---	---	0.5	10.1	14.6	3.1	-1.7
VN04	2.0	-2.0	3.7	1.5	0.8	1.5	10.1	19.2	12.3	-2.3
VN05	-4.6	-0.8	-2.3	-1.7	0.1	-8.7	-18.0	-13.5	13.1	-8.1
Number of data	33	33	33	32	32	33	33	33	33	33
Average	0.0	-2.7	0.3	0.8	-0.6	0.0	-0.6	-0.6	0.4	0.5
Minimum	-9.9	-17.6	-13.8	-16.2	-8.2	-8.7	-19.1	-13.5	-18.5	-8.1
Maximum	5.9	10.6	15.0	33.2	13.1	17.0	15.7	19.2	17.7	15.2

Note: "---", Not measured

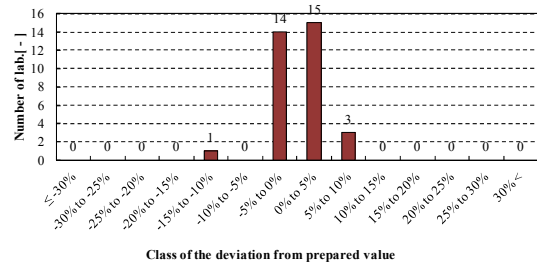
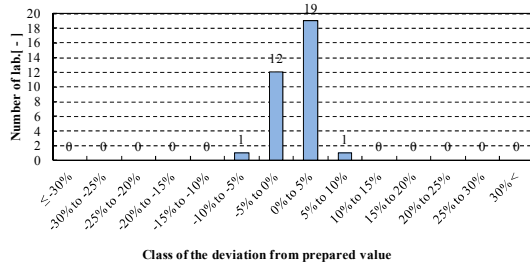
**Appendix Table 2.2.2 Deviation% from prepared values of low conc. sample No. 102w**

**Sample No. 102w (Low concentrations)**

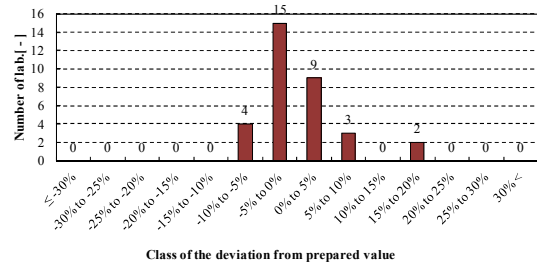
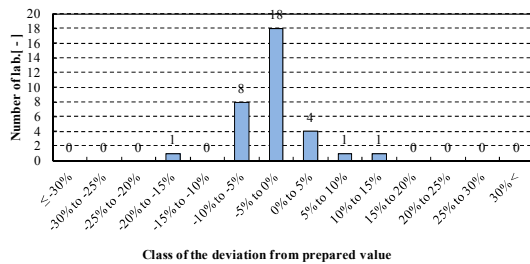
Lab. ID	pH %	EC %	SO <sub>4</sub> <sup>2-</sup> %	NO <sub>3</sub> <sup>-</sup> %	Cl <sup>-</sup> %	Na <sup>+</sup> %	K <sup>+</sup> %	Ca <sup>2+</sup> %	Mg <sup>2+</sup> %	NH <sub>4</sub> <sup>+</sup> %
KH01	5.9	-2.4	7.2	26.4	6.1	2.4	0.0	8.6	18.2	1.2
CN01	-0.2	-4.0	0.0	-1.4	-2.0	1.9	21.4	27.2	24.2	3.5
CN02	-0.6	-2.4	1.2	0.0	-4.5	-3.4	-3.6	-6.2	3.0	4.7
CN03	-1.0	-3.2	-2.4	0.7	-3.2	-3.4	3.6	8.6	30.3	0.6
CN04	-1.0	2.4	6.0	-0.7	-4.5	0.5	17.9	12.3	21.2	1.2
ID01	2.2	0.0	6.6	3.5	10.9	-2.9	-3.6	-6.2	3.0	16.5
ID02	1.0	-5.6	0.0	-28.5	-15.8	1.9	17.9	12.3	18.2	1.8
ID03	1.0	15.2	1.2	-7.6	-14.2	5.3	39.3	11.1	9.1	9.4
JP01	1.2	2.4	-4.8	-4.2	-0.4	-1.0	-7.1	-16.0	-6.1	3.5
JP03	0.2	-1.6	-0.6	-2.1	-1.6	-1.4	0.0	0.0	-6.1	-1.2
JP04	0.8	1.6	-0.6	-0.7	-0.8	-2.9	3.6	7.4	-3.0	-4.7
JP05	1.4	-4.0	0.0	0.0	0.0	-4.8	-14.3	2.5	-6.1	2.9
JP07	-0.8	5.6	-2.4	-2.1	-4.5	-10.1	-14.3	-6.2	-6.1	2.9
JP08	-0.8	0.0	-4.8	-3.5	-6.9	-8.2	-10.7	-4.9	-6.1	-10.6
JP09	0.8	3.2	-3.0	0.0	-4.9	-1.4	0.0	6.2	0.0	-2.9
LA01	-1.4	-3.2	-5.4	-13.2	-6.9	3.9	-21.4	-11.1	-51.5	1.8
MY01	0.0	-0.8	-0.6	1.4	6.9	-1.0	-10.7	-14.8	-18.2	3.5
MN01	-10.1	0.8	0.0	0.7	-10.1	-19.8	-7.1	13.6	-24.2	3.5
MM01	4.6	16.0	14.5	10.4	14.6	2.9	53.6	19.8	6.1	10.0
PH01	3.4	-3.2	-0.6	2.8	0.8	-3.9	0.0	-4.9	15.2	4.7
PH02	2.6	0.8	3.6	9.0	-1.6	1.0	-7.1	67.9	36.4	-5.9
KR01	-2.4	-1.6	-1.8	0.0	-5.3	-6.8	0.0	-3.7	45.5	10.6
RU01	-1.8	3.2	-4.2	24.3	0.8	1.0	0.0	-1.2	12.1	2.9
RU02	5.0	-7.2	-12.0	13.9	-0.8	7.7	10.7	4.9	6.1	12.9
TH01	0.8	-8.8	-7.2	-9.7	-6.9	-1.9	-10.7	-6.2	-24.2	0.6
TH02	0.0	1.6	-8.4	-9.7	-5.7	1.0	14.3	18.5	3.0	1.8
TH04	-1.0	0.0	-5.4	-15.3	-6.5	-3.9	-10.7	-7.4	-6.1	-5.9
TH05	-0.2	0.8	-2.4	-7.6	-7.7	-9.2	-32.1	-8.6	-15.2	8.8
VN01	-0.4	6.4	0.0	1.4	0.8	-0.5	0.0	19.8	-9.1	5.3
VN02	3.4	-2.4	1.8	9.0	-0.8	2.4	-7.1	8.6	-18.2	4.1
VN03	5.3	-7.2	-6.0	---	---	6.8	10.7	4.9	12.1	-4.1
VN04	5.1	-4.8	1.2	15.3	-1.6	3.9	-3.6	12.3	-12.1	2.9
VN05	1.2	7.2	-5.4	-4.9	-3.2	-9.7	0.0	-9.9	24.2	-11.8
Number of data	33	33	33	32	32	33	33	33	33	33
Average	0.7	0.1	-1.1	0.2	-2.5	-1.6	0.9	4.8	2.3	2.3
Minimum	-10.1	-8.8	-12.0	-28.5	-15.8	-19.8	-32.1	-16.0	-51.5	-11.8
Maximum	5.9	16.0	14.5	26.4	14.6	7.7	53.6	67.9	45.5	16.5

Note: "---", Not measured

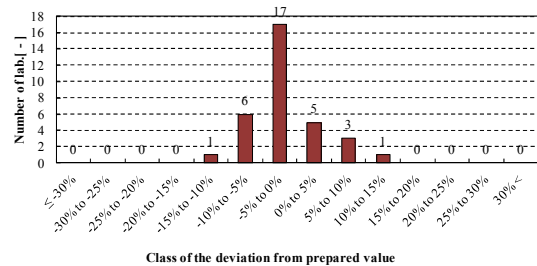
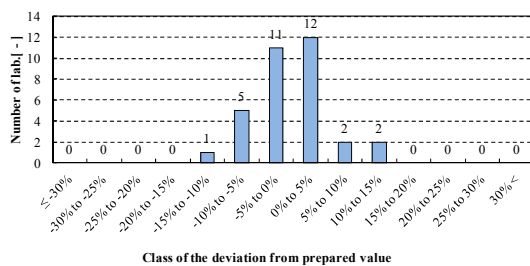
## Appendix 2.3 Data Distribution



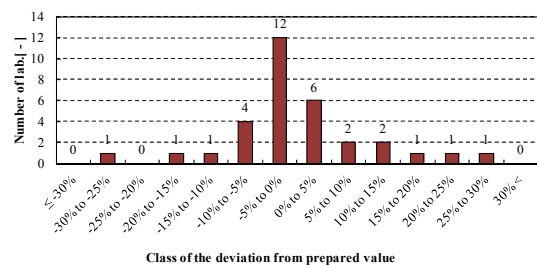
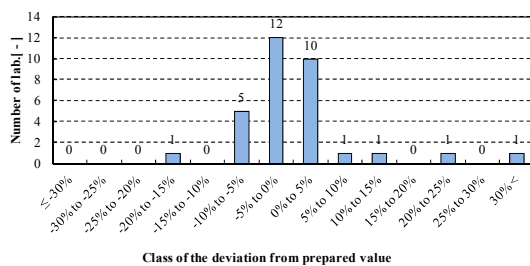
Appendix Figure 2.3.1 Data Distribution for pH (Left: 101w, Right: 102w)



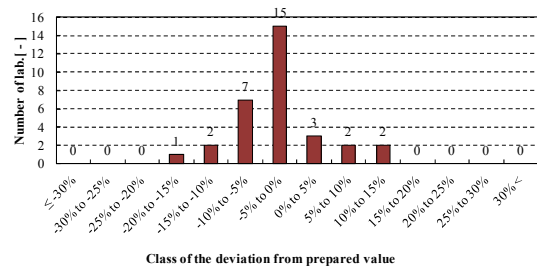
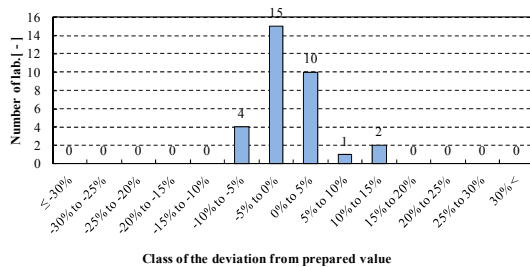
Appendix Figure 2.3.2 Data Distribution for EC (Left: 101w, Right: 102w)



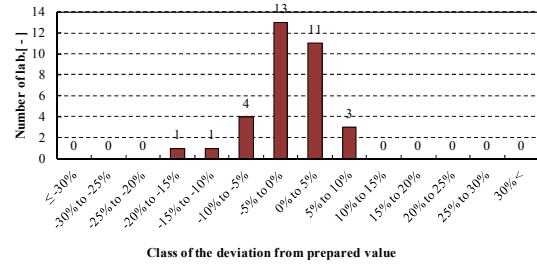
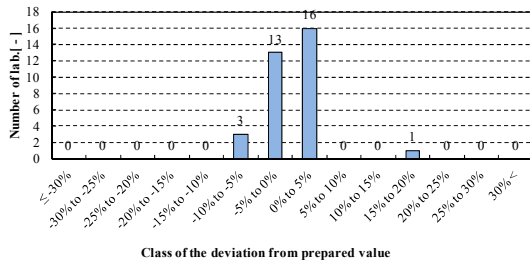
Appendix Figure 2.3.3 Data Distribution for  $\text{SO}_4^{2-}$  (Left: 101w, Right: 102w)



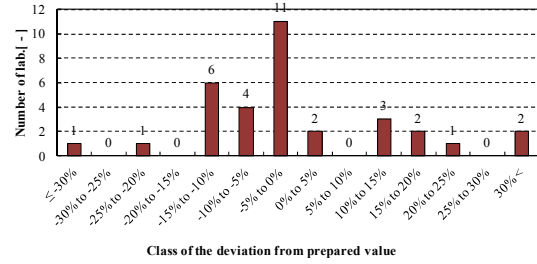
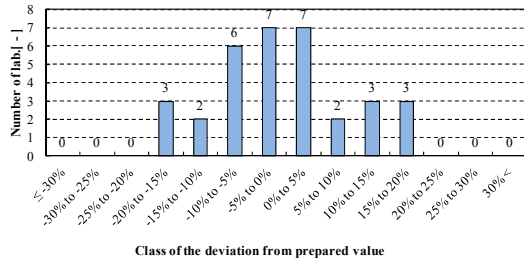
Appendix Figure 2.3.4 Data Distribution for  $\text{NO}_3^-$  (Left: 101w, Right: 102w)



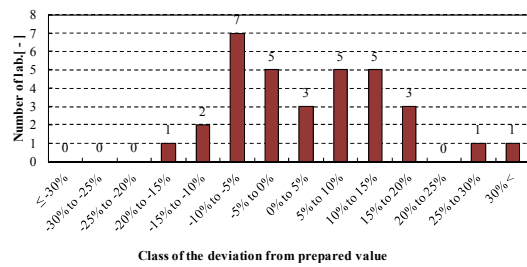
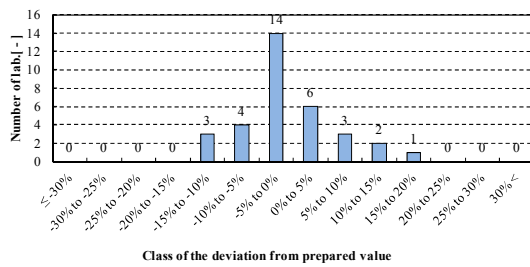
Appendix Figure 2.3.5 Data Distribution for  $\text{Cl}^-$  (Left: 101w, Right: 102w)



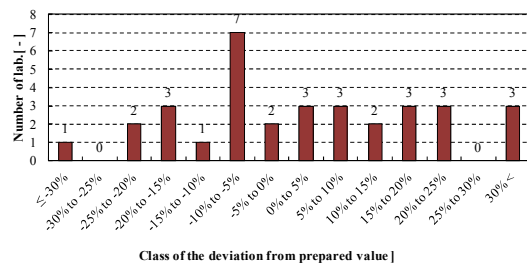
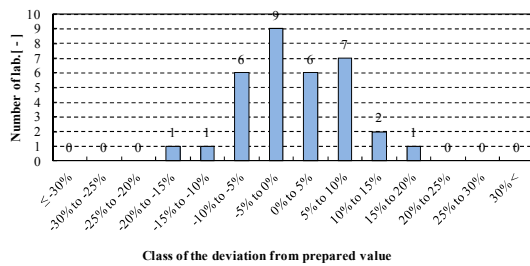
Appendix Figure 2.3.6 Data Distribution for Na<sup>+</sup> (Left: 101w, Right: 102w)



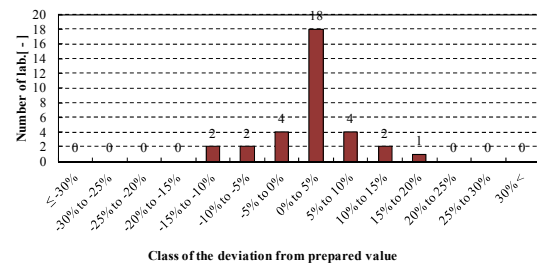
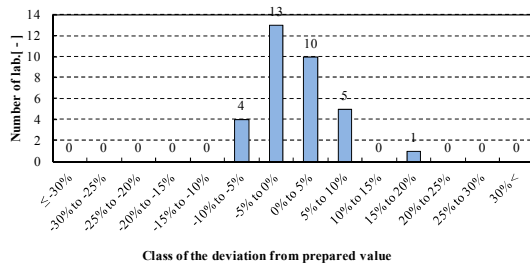
Appendix Figure 2.3.7 Data Distribution for K<sup>+</sup> (Left: 101w, Right: 102w)



Appendix Figure 2.3.8 Data Distribution for Ca<sup>2+</sup> (Left: 101w, Right: 102w)



Appendix Figure 2.3.9 Data Distribution for Mg<sup>2+</sup> (Left: 101w, Right: 102w)



Appendix Figure 2.3.10 Data Distribution for NH<sub>4</sub><sup>+</sup> (Left: 101w, Right: 102w)



### 3. 6<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

#### 3.1 Introduction

In the Inter-laboratory Comparison for dry deposition, impregnated filters which contained either  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , or  $\text{NH}_4^+$  were prepared and distributed to the participating laboratories by the Network Center (NC) in October 2010. Most of the laboratories participating in EANET joined this activity and submitted their analytical results to the NC. These results for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NH}_4^+$  on the filter were compared with the corresponding prepared value and statistically analyzed.

#### 3.2 Procedures

##### 3.2.1 Participating Laboratories

A total of 26 laboratories in charge of EANET monitoring in 12 countries of EANET participated in this sixth activity. All participating laboratories and their codes are listed in Table 1.1.

##### 3.2.2 Description of Samples

Two kinds of filter samples, one contained two ions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ), the other contained one ion ( $\text{NH}_4^+$ ), were prepared and distributed to the laboratories. The blank filters, which were impregnated with  $\text{K}_2\text{CO}_3$  or  $\text{H}_3\text{PO}_4$  but did not contain any  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , or  $\text{NH}_4^+$ , were also prepared and distributed. The details of the filter samples were described in Table 3.1. The analytical precision and accuracy on the individual analyte were summarized through statistical calculations of the submitted analytical results from each participating laboratory.

**Table 3.1 Outline of filter samples**

Name	Details	Container	Number of filters	Note
No.101d-1	Alkali-Impregnated filter (small quantity)	Polyethylene centrifuge tube	3	The $\text{K}_2\text{CO}_3$ impregnated filter contains two ions ( $\text{SO}_4^{2-}$ and $\text{Cl}^-$ ).
No.101d-2	Acid-Impregnated filter (small quantity)	Polyethylene centrifuge tube	3	The $\text{H}_3\text{PO}_4$ impregnated filter contains one ion ( $\text{NH}_4^+$ ).

No.102d-1	Alkali-Impregnated filter (large quantity)	Polyethylene centrifuge tube	3	The K <sub>2</sub> CO <sub>3</sub> impregnated filter contains two ions (SO <sub>4</sub> <sup>2-</sup> and Cl <sup>-</sup> ).
No.102d-2	Acid-Impregnated filter (large quantity)	Polyethylene centrifuge tube	3	The H <sub>3</sub> PO <sub>4</sub> impregnated filter contains one ion (NH <sub>4</sub> <sup>+</sup> ).
No.103d-1	Alkali-Impregnated filter (blank)	Polyethylene centrifuge tube	3	The filter impregnated with K <sub>2</sub> CO <sub>3</sub> .
No.103d-2	Acid-Impregnated filter (blank)	Polyethylene centrifuge tube	3	The filter impregnated with H <sub>3</sub> PO <sub>4</sub> .

### 3.2.3 Analytes

All participating laboratories were expected to analyze these filter samples and to submit their values as the net quantity of each ion (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup>) in micrograms (μg).

### 3.2.4 Analytical Methodologies

The recommended procedure for sampling and analyzing by the filter pack method is described in EANET Document, “Technical Document for Filter Pack Method in EAST Asia” (The NC, 2003). Each filter sample was put in a centrifuge tube, a solvent was directly poured into the tube for extraction. The extraction procedure is as follows;

(1) Sample No.101d-1, No.102d-1, No.103d-1

Add 20 mL of H<sub>2</sub>O<sub>2</sub> solution (0.05 %-v/v) as an extracting solvent into each centrifuge tube, then shake or agitate them for 20 minutes using a shaker or an ultrasonic bath for extraction.

(2) Sample No.101d-2, No.102d-2, No.103d-2

Add 20 mL of deionized water as an extracting solvent into each centrifuge tube, then shake or agitate them for 20 minutes using a shaker or an ultrasonic bath for extraction.

(3) Filtration

Remove insoluble matter from the solution using a membrane filter (pore size 0.45 μm). The membrane filter must be prewashed with pure water (more than 100 mL) before filtration. After filtration, those filtrates are assigned identification numbers and sealed tightly.

Note 1) Carry out the analysis immediately after extraction.

Note 2) In principle, it is strongly recommended that the filtrates be analyzed immediately after extraction, however, in the case that they need to be kept for certain reasons, store them in a refrigerator at 4°C.

The participating laboratories were expected to use the same analytical methods. Analytical methods specified in the Technical Document are shown in Table 3.2.

**Table 3.2 Analytical methods specified in the Technical Document**

Analyte	Analytical method
SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup>	Ion Chromatography Spectrophotometry
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography Spectrophotometry (Indophenol Blue)

### 3.2.5 Data Check Procedures

All participating laboratories were requested to report as the net quantity of each ion (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup>) in the filter sample.

Each quantity (M<sub>sol</sub>) is calculated as follows:

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

where M<sub>sol</sub>: quantity of each component in the filtrate (µg);

C<sub>sol</sub>: concentration of each component in the filtrate (mg L<sup>-1</sup>);

V<sub>sol</sub>: volume of the solvent (20 mL).

The net quantity of each ion (netM<sub>sol</sub>) is calculated as follows :

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

where netM<sub>sol</sub>: net quantity of each ion on the filter.

M<sub>sol, Sample</sub>: quantity (µg) of each component in the filtrate from sample No.101d-1, No.101d-2, No.102d-1 and No.102d-2;

M<sub>sol, Blank</sub>: the average quantity (µg) in the filtrate from blank sample No.103d-1 and No.103d-2.

Note 3) netM<sub>sol</sub> was automatically calculated by entering their values of M<sub>sol, sample</sub> and M<sub>sol, blank</sub> on Excell file. (File name : 2010Dry\_report1\_6\_format.xls.)

### 3.3 Results

The NC distributed the filter samples to 26 laboratories in the participating countries of EANET, and received the data from 24 laboratories. The summary of the results compared to the prepared value is summarized in Table 3.3. The average, minimum (Min.), maximum (Max.), standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion. Analytical results of Samples No.101d and No.102d are shown in *Appendix 3-1*.

Note 4 : Outliers exceeding 3 sigma S.D. were rejected before calculation.

As shown in Table 3.3, the deviation for  $\text{SO}_4^{2-}$  in Sample No.101d was -5.1 % and for  $\text{Cl}^-$  in Sample No.101d was -5.9 %. The other deviations were within  $\pm 5$  %.

The Data Quality Objectives (DQOs) of EANET is specified on the QA/QC program of EANET that determined values are expected to fall within  $\pm 15$  % deviation from the prepared value. Each laboratory analyzed each sample 3 times, averaged the values, and these average values were compared with the corresponding prepared value for this report. The flag "E" indicates that the deviation exceeds  $\pm 15$  % but not over  $\pm 30$  %, and the flag "X" indicates that the deviation exceeds more than  $\pm 30$ %.

$$\text{Deviation (\%)} = (\text{Determined value} - \text{Prepared value}) / \text{Prepared value} \times 100 (\%) \quad (3)$$

Flag E:  $15 \% < |\text{Deviation}| \leq 30 \%$

Flag X:  $30 \% < |\text{Deviation}|$

The evaluation of the results on both Samples No.101d and No.102d is described in "3.3.1 Evaluation of Laboratories' Performance (by sample)". The comparison of the results for each analyte is described in "3.3.2 Comparison of Laboratories' Performance (by analyte)". The evaluation of their analytical circumstance, such as analytical method, experience of personnel, and other analytical conditions is described in "3.3.3 Information on Laboratories".

**Table 3.3 Summary of analytical results of the filter samples  
(The results do not include outliers.)**

Analyte	Prepared* (V <sub>p</sub> )	Average (V <sub>a</sub> )	$\Delta V/V_p^*$ (%)	S.D.	Number (N)	Min.	Max.
<i>Sample No. 101d (Small)</i>							
SO <sub>4</sub> <sup>2-</sup>	( $\mu$ g) 30	28.5	-5.1	2.71	22	22.7	33.5
Cl <sup>-</sup>	( $\mu$ g) 6.0	5.65	-5.9	0.67	22	3.56	7.32
NH <sub>4</sub> <sup>+</sup>	( $\mu$ g) 5.8	5.88	1.3	0.64	24	4.96	7.32
<i>Sample No. 102d (Large)</i>							
SO <sub>4</sub> <sup>2-</sup>	( $\mu$ g) 90	89.6	-0.4	5.97	23	78.7	102
Cl <sup>-</sup>	( $\mu$ g) 27	26.1	-3.3	1.79	22	21.1	29.1
NH <sub>4</sub> <sup>+</sup>	( $\mu$ g) 45	44.5	-1.2	3.63	24	37.5	53.3

\* Prepared: Prepared values

\*  $\Delta V/V_p$ : (Average result (V<sub>a</sub>) - Prepared value (V<sub>p</sub>)) / Prepared value (V<sub>p</sub>)  $\times$  100 (%)

### 3.3.1 Evaluation of Laboratories' Performance (by sample)

#### Small quantity samples (No. 101d-1, No.101d-2)

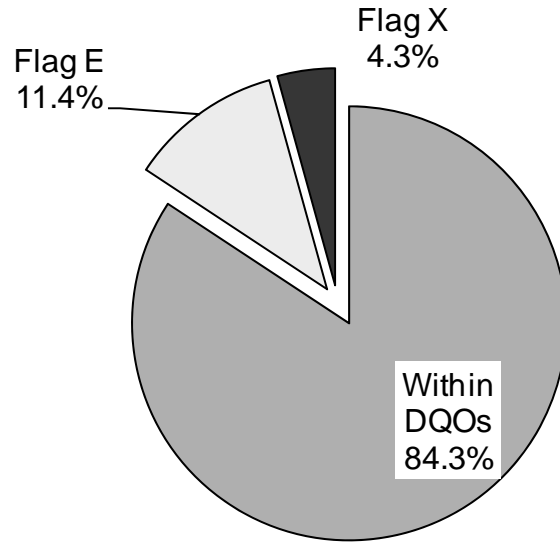
For Sample No.101d, 8 analytical data in 70 results exceeded the DQOs by  $\pm 15$  %, but did not exceed DQOs by  $\pm 30$  %, thus, they were flagged E. Also 3 analytical data exceeded the DQOs by  $\pm 30$  %, so they were flagged X. 11 data points were flagged, which was 15.7 % of the total for Sample No.101d (Figure 3.2, Table 3.4 and 3.5).

**Table 3.4 Number of flagged data for Sample No.101d (Small Quantity)**

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Flag E *	3	1	4	8
Flag X *	1	2	0	3
Data within DQOs	19	20	20	59
Ratio of Flagged (%)	17.4	13.0	16.7	15.7

\* E : Values exceeding the DQOs by  $\pm 15$  %, but not over  $\pm 30$ %.

\* X : Values exceeding the DQOs by  $\pm 30$  %.



**Figure 3.2** Percentage of flagged data for Sample No.101d (Small Quantity)

**Table 3.5** Average analytical results of Sample No.101d (Small Quantity)

Lab. Code		SO <sub>4</sub> <sup>2-</sup> (µg)	Cl <sup>-</sup> (µg)	NH <sub>4</sub> <sup>+</sup> (µg)
KH01	X	3.36	5.79	6.09
CN02	E	25.1	5.20	5.90
CN04	E	22.7	5.35	5.35
ID01		30.9	6.01	E 7.32
ID03		30.1	X 3.56	5.39
JP01		30.0	6.12	5.52
JP02		29.7	5.55	5.64
JP03		29.3	5.33	5.57
JP04		30.1	5.98	5.67
JP05		30.1	5.55	5.76
JP08		28.2	5.76	4.96
JP09		29.3	6.26	5.50
MY01		25.7	6.13	5.58
MN01		33.5	6.33	5.00
PH01		28.5	5.31	6.33
KR01		31.4	5.94	5.78
RU01		26.2	5.40	E 7.24
TH01	E	24.9	5.35	5.49
TH02		26.4	5.38	6.27

TH04	27.6		5.10	E	6.70
TH05	25.9		5.53	E	6.93
VN01	27.4	X	12.4		6.22
VN02	33.5	E	7.32		5.06
VN03	–		–		5.77

\* E : Values exceeding the DQOs by  $\pm 15\%$ , but not over  $\pm 30\%$ .

\* X : Values exceeding the DQOs by  $\pm 30\%$ .

**Large quantity samples (No. 102d-1, No.102d-2)**

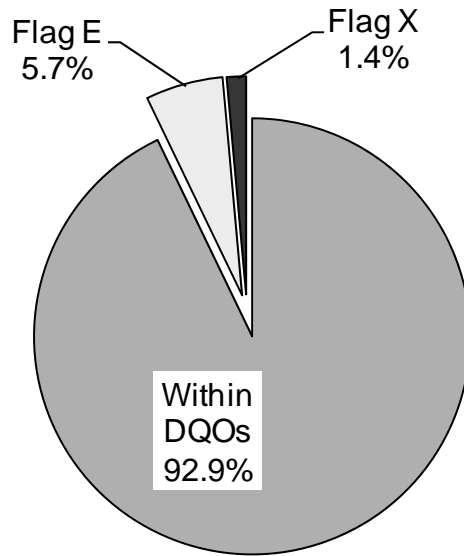
For Sample No.102d, 4 analytical data in 70 results exceeded the DQOs by  $\pm 15\%$ , but did not exceed DQOs by  $\pm 30\%$ , thus, they were flagged E. Also 1 analytical datum exceeded the DQOs by  $\pm 30\%$ , so that they were flagged X. 5 data points were flagged, which was 7.1 % of the total for Sample No.102d (Figure 3.3, Table 3.6 and 3.7).

**Table 3.6 Number of flagged data for Sample No.102d  
(Large Quantity)**

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Flag E *	0	1	3	4
Flag X *	0	1	0	1
Data within DQOs	23	21	21	65
Ratio of Flagged (%)	0.0	8.7	12.5	7.1

\* E : Values exceeding the DQOs by  $\pm 15\%$ , but not over  $\pm 30\%$ .

\* X : Values exceeding the DQOs by  $\pm 30\%$ .



**Figure 3.3** Percentage of flagged data for Sample No.102d (Large Quantity)

**Table 3.7** Average analytical results of Sample No.102d (large quantity)

Lab. Code	SO <sub>4</sub> <sup>2-</sup> (µg)	Cl <sup>-</sup> (µg)	NH <sub>4</sub> <sup>+</sup> (µg)
KH01	99.0	27.7	46.3
CN02	78.7	29.1	43.8
CN04	78.7	25.4	47.2
ID01	98.5	28.6	E 53.3
ID03	91.5	E 21.1	40.8
JP01	90.3	26.8	45.1
JP02	90.3	26.2	44.2
JP03	88.3	25.8	44.1
JP04	91.0	27.1	44.6
JP05	92.2	26.9	45.4
JP08	87.8	24.9	41.4
JP09	89.9	26.6	43.8
MY01	85.7	27.0	47.7
MN01	102.0	28.7	51.4
PH01	89.4	25.1	44.5
KR01	94.8	27.7	38.9
RU01	83.9	23.3	E 37.5
TH01	82.2	25.2	42.7
TH02	88.0	26.1	45.3

TH04	85.7		24.8	45.9
TH05	91.3		24.9	46.1
VN01	84.1	X	35.4	46.7
VN02	97.5		25.6	43.0
VN03	–		–	E 37.5

\* E : Values exceeding the DQOs by  $\pm 15\%$ , but not over  $\pm 30\%$ .

\*X : Values exceeding the DQOs by  $\pm 30\%$ .

### **Blank Sample (No.103d)**

Each quantity of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NH}_4^+$  was determined for blank sample No.103d-1 and No.103d-2. Their obtained values are shown in Table 3.8. Blank values were detected in a wide range, including 0  $\mu\text{g}$ . Table 3.9 showed the ratio of the blank value to analytical results by laboratory. Light gray color cells indicate that the sample is flagged E and dark gray color cells indicate that the sample is flagged X. At some laboratories, results were not flagged, even though some blank values were high.

**Table 3.8 Analytical results of Sample No.103d (blank)**

Lab. Code	$\text{SO}_4^{2-}$ ( $\mu\text{g}$ )	$\text{Cl}^-$ ( $\mu\text{g}$ )	$\text{NH}_4^+$ ( $\mu\text{g}$ )
KH01	30.1	0.95	0.16
CN02	0.15	0.24	0.47
CN04	2.50	0.54	0.34
ID01	0.00	0.71	1.45
ID03	1.09	1.03	1.34
JP01	0.09	0.46	0.20
JP02	0.10	0.92	0.33
JP03	0.00	1.22	0.17
JP04	0.79	0.42	0.09
JP05	0.00	0.54	0.31
JP08	0.00	0.33	0.24
JP09	0.36	1.68	0.85
MY01	0.04	0.63	0.34
MN01	2.07	0.00	2.40
PH01	0.00	0.99	0.22
KR01	0.00	0.83	1.38
RU01	0.96	1.48	0.49

TH01	0.06	0.36	0.28
TH02	1.00	0.45	0.29
TH04	0.00	0.00	0.00
TH05	3.80	1.67	0.00
VN01	1.27	0.05	0.73
VN02	0.00	0.00	1.04
VN03	–	–	5.45
Average	1.93	0.67	0.77
Median	0.10	0.54	0.33
Minimum	0.00	0.00	0.00
Maximum	30.1	1.68	5.45
Standard deviation	6.08	0.50	1.13

**Table 3.9 Ratio of blank value to analytical value ( $M_{\text{sol,blank}}/M_{\text{sol,sample}}$ ) (%)**

Lab. Code	Small Quantity (No.101d)			Large Quantity (No.102d)		
	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
KH01	90.1	14.1	2.5	23.3	3.3	0.3
CN02	0.6	4.4	7.4	0.2	0.8	1.1
CN04	9.9	9.2	6.0	3.1	2.1	0.7
ID01	0.0	10.6	16.5	0.0	2.4	2.6
ID03	3.5	22.5	19.9	1.2	4.7	3.2
JP01	0.3	7.0	3.4	0.1	1.7	0.4
JP02	0.3	14.2	5.5	0.1	3.4	0.7
JP03	0.0	18.6	2.9	0.0	4.5	0.4
JP04	2.5	6.6	1.5	0.9	1.5	0.2
JP05	0.0	8.9	5.1	0.0	2.0	0.7
JP08	0.0	5.4	4.7	0.0	1.3	0.6
JP09	1.2	21.1	13.4	0.4	5.9	1.9
MY01	0.2	9.3	5.7	0.1	2.3	0.7
MN01	5.8	0.0	32.4	2.0	0.0	4.5
PH01	0.0	15.7	3.4	0.0	3.8	0.5
KR01	0.0	12.3	19.2	0.0	2.9	3.4
RU01	3.5	21.5	6.4	1.1	6.0	1.3
TH01	0.2	6.2	4.9	0.1	1.4	0.7

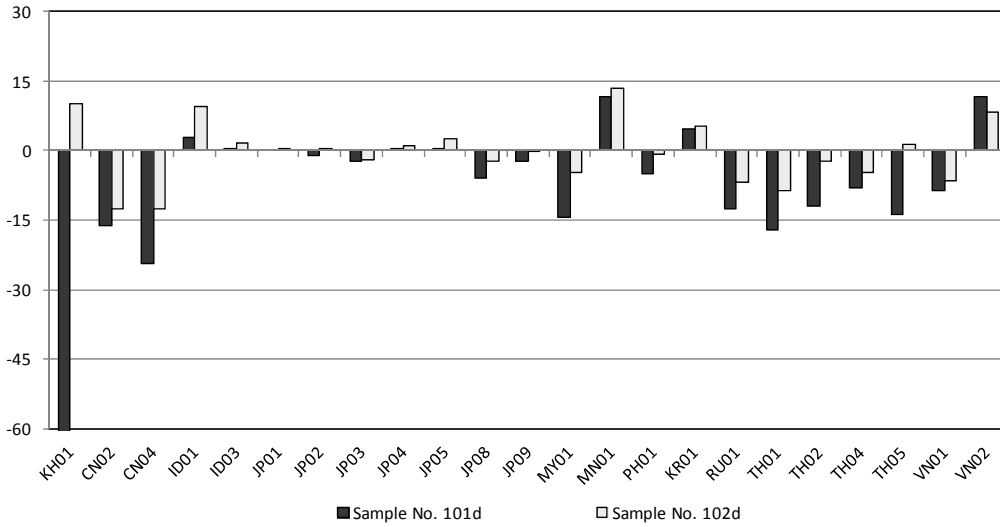
TH02	3.7	7.8	4.5	1.1	1.7	0.6
TH04	0.0	0.0	0.0	0.0	0.0	0.0
TH05	12.8	23.1	0.0	4.0	6.3	0.0
VN01	4.4	0.4	10.5	1.5	0.2	1.5
VN02	0.0	0.0	17.1	0.0	0.0	2.4
VN03	–	–	48.6	–	–	12.7

: Data flagged E  
 : Data flagged X

### 3.3.2 Comparison of Laboratories' Performance (by Analyte)

The overview of the results is shown in the following Figures and Tables for each analyte ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$ ). The obtained values from each laboratory were evaluated for their deviations. The number of flagged data is shown in Table 3.4 and 3.6 for each analyte.

**SO<sub>4</sub><sup>2-</sup> (Sulfate)**



**Figure 3.4 Deviation for SO<sub>4</sub><sup>2-</sup>**

$$\text{Deviation (\%)} = (\text{Determined value} - \text{Prepared value}) / \text{Prepared value} \times 100 (\%)$$

**Table 3.10.1 Analytical method of SO<sub>4</sub><sup>2-</sup>**

Analytical Method

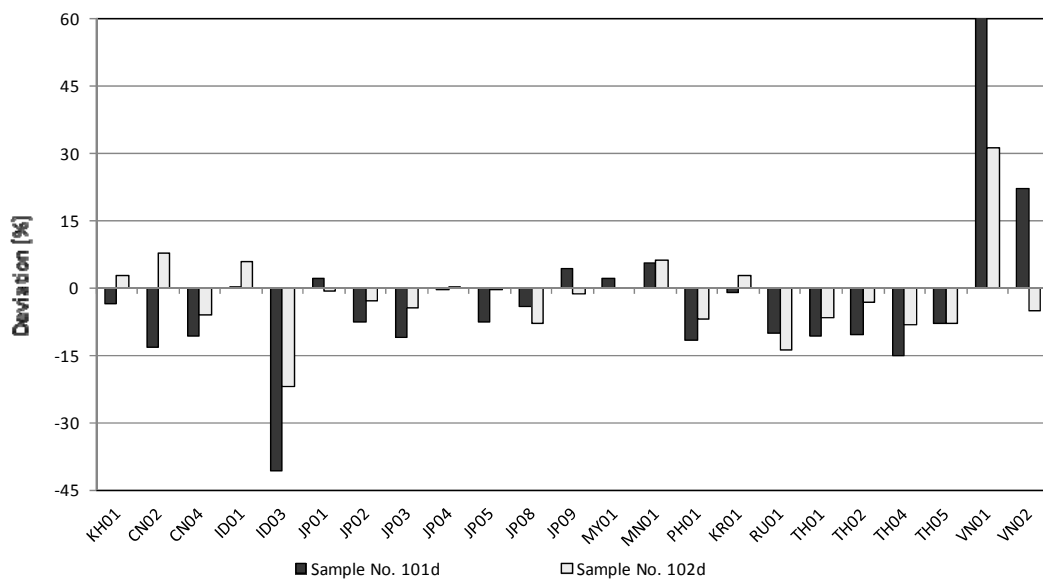
Ion Chromatography	23/23
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**Table 3.10.2 Flagged data of SO<sub>4</sub><sup>2-</sup>**

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.101d	3	1	17.4
Sample No.102d	0	0	0.0

All participating laboratories used Ion Chromatography for the determination of SO<sub>4</sub><sup>2-</sup>. Three laboratories were flagged E and 1 laboratory was flagged X.

**Cl<sup>-</sup> (Chloride)**



**Figure 3.5 Deviation for Cl<sup>-</sup>**

**Table 3.11.1 Analytical method of Cl<sup>-</sup>**

Analytical Method

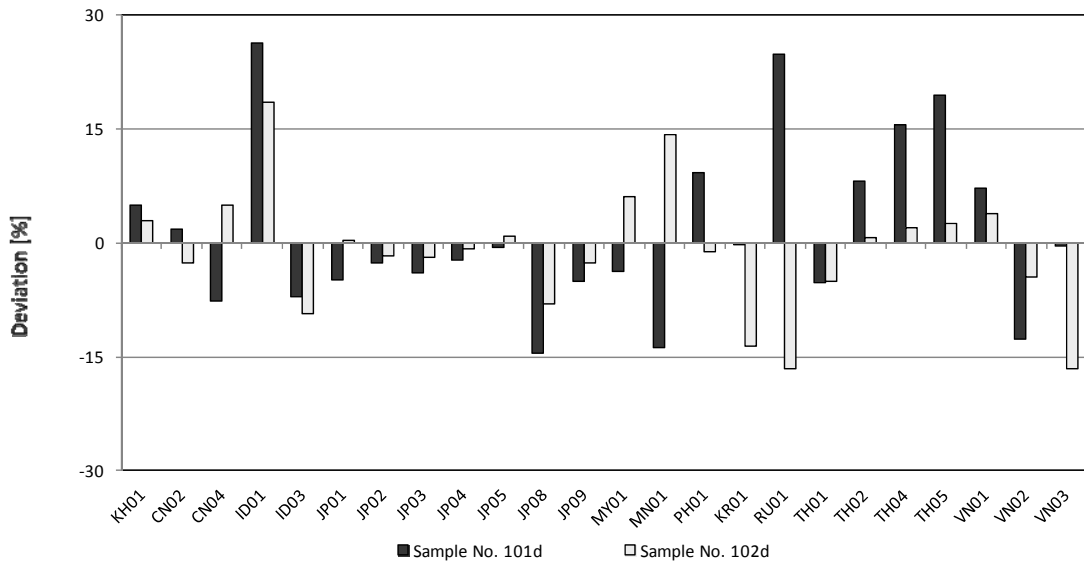
Ion Chromatography 23/23

**Table 3.11.2 Flagged data of Cl<sup>-</sup>**

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.101d	1	2	13.0
Sample No.102d	1	1	8.7

As with the analysis of SO<sub>4</sub><sup>2-</sup>, all laboratories used Ion Chromatography for the determination of Cl<sup>-</sup>. E flag appeared at 1 laboratory and X flags appeared at 2 laboratories for Sample No.101d. One flag of each (E and X) appeared at 2 laboratories for Sample No. 102d.

**NH<sub>4</sub><sup>+</sup> (Ammonium)**



**Figure 3.6 Deviation for NH<sub>4</sub><sup>+</sup>**

**Table 3.12.1 Analytical method of NH<sub>4</sub><sup>+</sup>**

Analytical Method

Ion Chromatography	23/24
Spectrophotometry (Indophenol blue)	1/24

**Table 3.12.2 Flagged data of NH<sub>4</sub><sup>+</sup>**

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.101d	4	0	16.7
Sample No.102d	3	0	12.5

Twenty-three laboratories used Ion Chromatography and 1 laboratory used Spectrophotometry (Indophenol Blue). There were 4 E flags for Sample No.101d, and 3 E flags for Sample No.102d.

### 3.3.3 Information on Laboratories

#### Methodologies Used

As shown in Table 3.13, most participating laboratories used the recommended methods of EANET and all laboratories used Ion Chromatography for the determination of anions. As for the determination of  $\text{NH}_4^+$ , 23 of 24 laboratories used Ion Chromatography and 1 laboratory used Spectrophotometry (Indophenol Blue).

**Table 3.13 Analytical methods used for sample analysis**

Lab. Code	$\text{SO}_4^{2-}, \text{Cl}^-$	$\text{NH}_4^+$
KH01		Ion Chromatography
CN02		Ion Chromatography
CN04		Ion Chromatography
ID01		Ion Chromatography
ID03		Ion Chromatography
JP01		Ion Chromatography
JP02		Ion Chromatography
JP03		Ion Chromatography
JP04		Ion Chromatography
JP05		Ion Chromatography
JP08		Ion Chromatography
JP09		Ion Chromatography
MY01		Ion Chromatography
MN01		Ion Chromatography
PH01		Ion Chromatography
KR01		Ion Chromatography
RU01		Ion Chromatography
TH01		Ion Chromatography
TH02		Ion Chromatography
TH04		Ion Chromatography
TH05		Ion Chromatography
VN01		Ion Chromatography
VN02		Ion Chromatography
VN03	–	Spectrophotometry (Indophenol Blue)

#### Years of staff experience

Years of staff experience are summarized in Table 3.14. Data in light gray color cells indicate

that there is a flag for Sample No.101d or 102d. Data in dark gray color cells indicate flagged data in both Sample No.101d and No.102d.

**Table 3.14 Years of staff experience (unit: year)**

Lab. Code	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
KH01	2	2	2
CN02	2	2	2
CN04	15	15	15
ID01	9	9	9
ID03 <sup>1)</sup>	2/1	2/1	2/1
JP01	26	26	26
JP02	12	12	12
JP03	4	4	4
JP04	3	3	3
JP05 <sup>1)</sup>	1/1	1/1	1/1
JP08	4	4	4
JP09 <sup>1)</sup>	3/2	3/2	3/2
MY01	1	1	5
MN01	5	5	5
PH01	7	7	<1
KR01 <sup>2)</sup>	*	*	*
RU01	12	12	12
TH01	1	1	1
TH02	13	13	13
TH04	4	4	4
TH05	7	7	7
VN01	17	17	17
VN02	6	6	6
VN03 <sup>3)</sup>	-	-	5

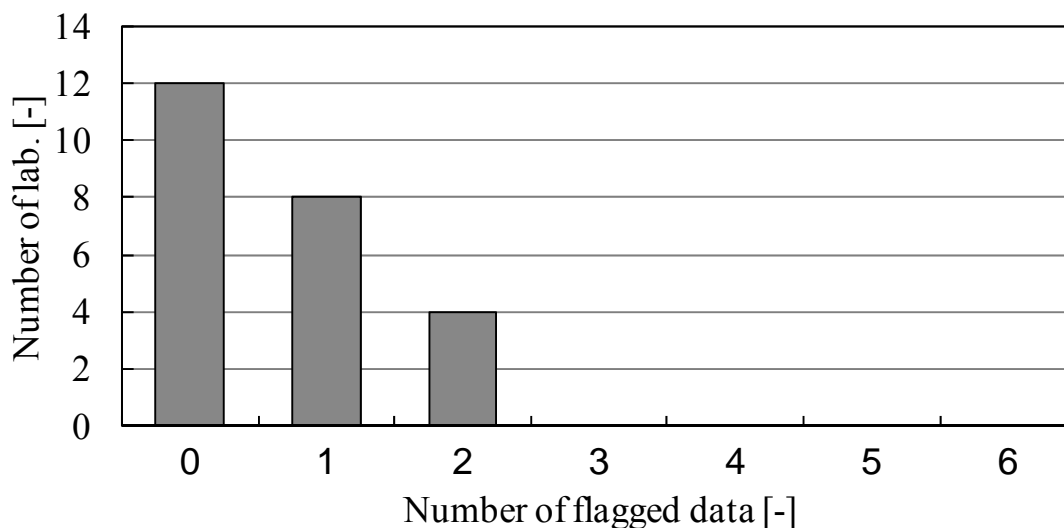
: 1 datum (either small or large quantity sample) is flagged.

: 2 data (both small and large quantity samples) are flagged.

- 1) Two analysts performed these analyses.
- 2) No information
- 3) Only ammonium analysis was carried out.

### **Flagged Data**

In the results of Sample No.101d and 102d, the total number of flagged data was 16 (E: 12, X: 4) in the whole values (140). The number of flagged data in each laboratory is shown in Figure 3.8. Twelve laboratories met DQOs (50 %).



**Figure 3.8** Number of flagged data and laboratories

### **Calibration standard solution**

Table 3.15 shows the lowest (except for zero) and highest concentrations of their calibration standard solutions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ) used in each laboratory, and also shows their concentrations of the prepared values in  $\mu\text{mol L}^{-1}$ . The concentrations of the standard solutions in some laboratories were not in the appropriate range. A boldfaced number in Table 3.15 indicates that the concentration value of standard solution is lower than that of the prepared value or higher than that of the prepared value.

Each concentration of prepared value was expected within the range of both concentrations of lowest and highest standard solutions. However, some laboratories used inappropriate solution ranges. If the concentrations of their obtained values were not in the range of the calibration standard, laboratories should have analyzed again with the appropriate concentration range of standard solution.

**Table 3.15 Ranges of the calibration standard solution in each laboratory**

Lab Code.	SO <sub>4</sub> <sup>2-</sup> (μmol L <sup>-1</sup> )		Cl <sup>-</sup> (μmol L <sup>-1</sup> )		NH <sub>4</sub> <sup>+</sup> (μmol L <sup>-1</sup> )	
	Lowest	Highest	Lowest	Highest	Lowest	Highest
KH01	0	52.1	0.282	141	0.0554	277
CN02	0	208	0	225	0	214
CN04	0	104	0	113	0	446
ID01	0	52.1	0	141	0	167
ID03	0	100	0	101	0	111
JP01	0	105	0	282	0	278
JP02	0	52.1	0	141	0	133
JP03	0	156	0	84.6	0	166
JP04	0	104	0	141	0	277
JP05	0	521	0	705	0	1386
JP08	0	83.5	0	226	0	222
JP09	0	104	0	282	0	554
MY01	0	62.5	0	113	0	166
MN01	0	125	0	96.8	0	111
PH01	0	104	0	282	0	554
KR01	0	52.1	0	141	0	277
RU01	0	10.4	0	28.5	0	139
TH01	0	104	0	141	0	166
TH02	0.104	62.5	0.282	169	1.11	139
TH04	0	62.5	0	56.4	0	222
TH05	0	62.5	0	56.4	0	111
VN01	0	104	0	141	0	277
VN02	0	52.1	0	56.4	0	139
VN03	–	–	–	–	5.56	66.7
Sample No. 101d	15.6		8.46		16.1	
Sample No. 102d		46.8		38.1		125

Gray Cell : The measured value was out of the calibration range.

Lowest and Highest : lowest/highest concentrations in the calibration standard solutions.

### 3.3.4 Comparison with past surveys

This Inter-Laboratory Comparison on dry deposition has been implemented since 2005. The results showing the percentages of flagged data and percentages of data that were satisfied the DQOs were shown in Figure 3.9.

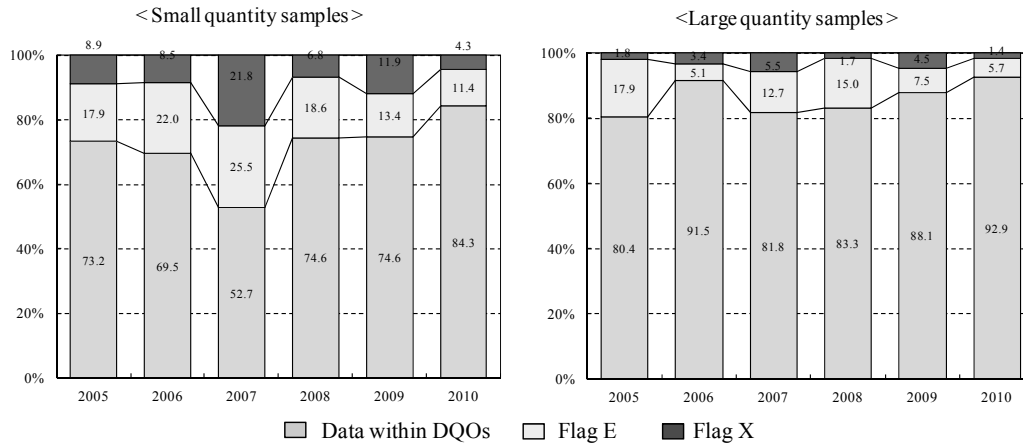


Figure 3.9 Comparison of DQOs' results for the past 5 years

The comparison for each analyte in Inter-Laboratory Comparison on dry deposition year-by-year is shown in Figure 3.10.

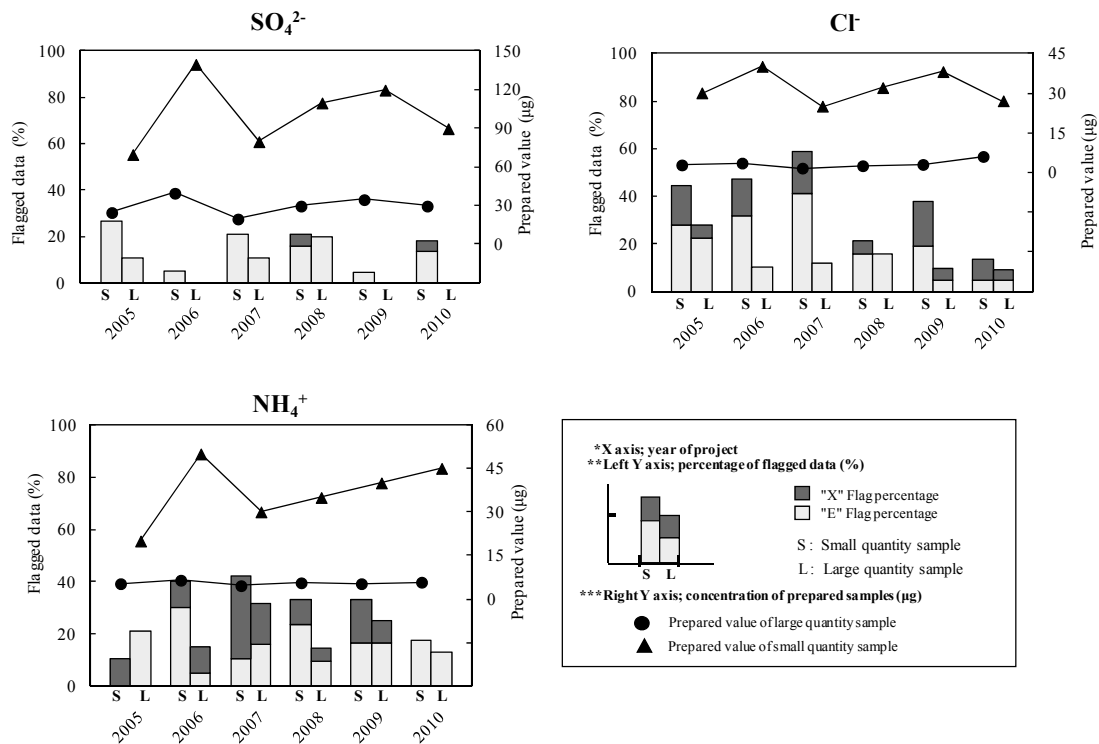


Figure 3.10 Comparison for each parameter in inter-laboratory comparison project

## References

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- Second ISAG Meeting of Acid Deposition Monitoring Network in East Asia (2000). *Technical Documents for Wet Deposition Monitoring in East Asia*. Niigata.
- Third Session of the Scientific Advisory Committee (SAC3) (2003). *Technical Document for Filter Pack Method in East Asia*. Niigata.

## Appendix 3.1 Summary of data

Appendix Table 3.1.1 Analytical results of Sample No. 101d (small quantity)

Lab. ID	SO <sub>4</sub> <sup>2-</sup> [μg]	Cl <sup>-</sup> [μg]	NH <sub>4</sub> <sup>+</sup> [μg]
KH01	3.36	5.79	6.09
CN02	25.1	5.20	5.90
CN04	22.7	5.35	5.35
ID01	30.9	6.01	7.32
ID03	30.1	3.56	5.39
JP01	30.0	6.12	5.52
JP02	29.7	5.55	5.64
JP03	29.3	5.33	5.57
JP04	30.1	5.98	5.67
JP05	30.1	5.55	5.76
JP08	28.2	5.76	4.96
JP09	29.3	6.26	5.50
MY01	25.7	6.13	5.58
MN01	33.5	6.33	5.00
PH01	28.5	5.31	6.33
KR01	31.4	5.94	5.78
RU01	26.2	5.40	7.24
TH01	24.9	5.35	5.49
TH02	26.4	5.38	6.27
TH04	27.6	5.10	6.70
TH05	25.9	5.53	6.93
VN01	27.4	12.4	6.22
VN02	33.5	7.32	5.06
VN03	–	–	5.77
Prepared value	30	6.0	5.8
Number of data	23	23	24
Average	27.4	5.94	5.88
Minimum	3.36	3.56	4.96
Maximum	33.5	12.4	7.32
Standard Deviation	5.77	1.52	0.64

**Appendix Table 3.1.2 Analytical results of Sample No. 102d (large quantity)**

Lab. ID	SO <sub>4</sub> <sup>2-</sup> [μg]	Cl <sup>-</sup> [μg]	NH <sub>4</sub> <sup>+</sup> [μg]
KH01	99.0	27.7	46.3
CN02	78.7	29.1	43.8
CN04	78.7	25.4	47.2
ID01	98.5	28.6	53.3
ID03	91.5	21.1	40.8
JP01	90.3	26.8	45.1
JP02	90.3	26.2	44.2
JP03	88.3	25.8	44.1
JP04	91.0	27.1	44.6
JP05	92.2	26.9	45.4
JP08	87.8	24.9	41.4
JP09	89.9	26.6	43.8
MY01	85.7	27.0	47.7
MN01	102	28.7	51.4
PH01	89.4	25.1	44.5
KR01	94.8	27.7	38.9
RU01	83.9	23.3	37.5
TH01	82.2	25.2	42.7
TH02	88.0	26.1	45.3
TH04	85.7	24.8	45.9
TH05	91.3	24.9	46.1
VN01	84.1	35.4	46.7
VN02	97.5	25.6	43.0
VN03	–	–	37.5
Prepared value	90	27	45
Number of data	23	23	24
Average	89.6	26.5	44.5
Minimum	78.7	21.1	37.5
Maximum	102	35.4	53.3
Standard Deviation	5.97	2.58	3.63

## **4. 12th INTER-LABORATORY COMPARISON PROJECT ON SOIL**

### **4.1 Introduction**

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

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

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

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

In the 12th project, NC provided two soil samples (No.101 and 102) to laboratories to improve the inter-laboratory precision further more by standardization of methods. In this report, the data from participating laboratories were evaluated statistically according to the QA/QC program for soil monitoring. The results may contribute to the assessment of inter-laboratory variation in soil monitoring and provide useful information to improve precision of soil analysis on EANET.

## 4.2 Procedures

### 4.2.1 Participating Laboratories

Sixteen laboratories of 9 countries participated in the 12th project. Names of the participating laboratories are listed in Table 1.1. Abbreviations for each laboratory are common with wet and dry deposition and inland aquatic monitoring.

### 4.2.2 Description of Samples

The characteristics of the soil samples were as follows:

#### Sample No. 101: Cambisols

#### Sample No. 102: Andosols

Soils for Sample No.101 and No.102 were collected in Japanese cypress (*Chamaecyparis obtusa*) plantation of Kochi prefecture, Japan. Both soils were collected from B-horizon composed chiefly of soil minerals. The soils were air-dried, sieved to separate the fine earth fraction (< 2 mm) and mixed well by the following procedures; 1) the bulk sample was divided into two parts, 2) each part was mixed well, 3) the parts were joined and mixed well and 4) the sample was divided again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of ca. 400 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 the parameters shown in Table 4.1.

**Table 4.1 Parameters to be measured**

Parameters	Unit	No.101 and 102
a) Moisture Content	wt %	M
b) pH (H <sub>2</sub> O)		M
c) pH (KCl)		M
d) Exchangeable Ca <sup>2+</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	M
e) Exchangeable Mg <sup>2+</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	M
f) Exchangeable K <sup>+</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	M
g) Exchangeable Na <sup>+</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	M
h) Exchangeable Acidity	cmol <sub>c</sub> kg <sup>-1</sup>	M
i) Exchangeable Al <sup>3+</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	M
j) Exchangeable H <sup>+</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	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” (2<sup>nd</sup> ISAG, 2000). In the respective laboratories, all the parameters were analyzed three times under the same conditions (as analyst, time, and instrument). Then, under within-laboratory-reproducibility condition (i.e. different analyst, time, and instrument), all the analytical procedures should be repeated twice.

##### 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)”. Additionally, the following analytical procedures were standardized;

- (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<sub>3</sub>COONH<sub>4</sub> (pH 7.0)** for analysis of Ex-Ca, Mg, K and Na. Then, 1M CH<sub>3</sub>COONH<sub>4</sub> (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 cannot be obtained, La is allowable.)

##### 4.2.4.2 Procedures for Ex-base cations

- (1) Extract from air-dry sample with 1M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0) solution.
- (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<sub>2</sub> solution eliminates the interference of the sample.) And then make to volume with 1M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0). This solution is named “Prepared sample”.
- (3) Prepare three “prepared samples”.
- (4) Prepare each standard solution with diluting 1M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0) solution.
- (5) Add 100g-Sr/L solution to each standard solution to be the same concentration SrCl<sub>2</sub> 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:

$$\text{Ex-Ca (cmol}_c \text{ kg}^{-1} \text{ soil)} = [A * B * V * \text{mcf}] / [10 * 20.04 * S]$$

$$\text{Ex-Mg (cmol}_c \text{ kg}^{-1} \text{ soil)} = [A * B * V * \text{mcf}] / [10 * 12.15 * S]$$

$$\text{Ex-K (cmol}_c \text{ kg}^{-1} \text{ soil)} = [A * B * V * \text{mcf}] / [10 * 39.10 * S]$$

$$\text{Ex-Na (cmol}_c \text{ kg}^{-1} \text{ soil)} = [A * B * V * \text{mcf}] / [10 * 23.00 * S]$$

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:

$$\text{Ex-Acidity (cmol}_c \text{ kg}^{-1} \text{ soil)} = [(A_{\text{NaOH}} - b_{\text{NaOH}}) * M_{\text{NaOH}} * c * 100 * \text{mcf}] / S$$

$$\text{Ex-Al (cmol}_c \text{ kg}^{-1} \text{ soil)} = [(A_{\text{HCl}} - b_{\text{HCl}}) * M_{\text{HCl}} * c * 100 * \text{mcf}] / S$$

$$\text{Ex-H (cmol}_c \text{ kg}^{-1} \text{ soil)} = [(A_{\text{NaOH}} - b_{\text{NaOH}}) * M_{\text{NaOH}} - (A_{\text{HCl}} - b_{\text{HCl}}) * M_{\text{HCl}}] * c * 100 * \text{mcf} / S$$

Where

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

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

$b_{\text{NaOH}}$  = Titration volume of 0.025M NaOH solution needed for blank (mL)

$b_{\text{HCl}}$  = Titration volume of 0.02M HCl solution needed for blank (mL)

$M_{\text{NaOH}}$  = Molarity of NaOH solution (mol/L)

$M_{\text{HCl}}$  = 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) were provided to the participating laboratories. Chemical

properties of soil sample were calculated automatically by the formula written in the formats.

(2) Submission of the report

Entered data in digital formats and other information (e.g. calibration curve) were submitted by E-mail.

#### 4.2.5 Data Checking Procedures

We statistically evaluated the data according to the following procedures described in the “Technical Manual for Soil and Vegetation Monitoring in East Asia” (2<sup>nd</sup> ISAG, 2000). Dataset with one decimal place for pH and two decimal places for Ex-cations concentrations and Ex-acidity were used for the statistical analysis.

1) General description of the data variability

Mean, median, variance and coefficient variation (CV) were calculated for entire dataset in inter-laboratory project. Box-and-whisker plot were also used for checking the data variability and detecting outliers in the dataset, visually.

2) Detection of outliers to prepare the verified dataset

Evenness of within-laboratory precision (variation in each laboratory) and inter-laboratory precision (variation between 16 laboratories) were verified by Cochran and Grubbs methods, respectively. Datasets were verified by removing outliers which were detected by Cochran-Grubs methods. We also computed “verified” mean, median and other statistical summary from those verified datasets. In inter-laboratory comparison project on soil, “verified” mean will be a good reference to assess the analyzed value of each laboratory.

3) Analysis of variance

Total variation among laboratories includes within-laboratory and inter-laboratory 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 precision was estimated.

4) Calculation of permissible tolerance

Permissible tolerances were calculated based on the above precision; 1) repeatability limit, 2) within-laboratory reproducibility limit and 3) inter-laboratory reproducibility limit. Permissible tolerances are meaningful to determine “5% significant difference” in actual monitoring data. For instance, significantly temporal change in the same site or significant difference between two laboratories would be indicated if those change or difference were more than “within-laboratory reproducibility limit” or “inter-laboratory reproducibility limit”.

## 4.3 Results

### 4.3.1 General description of the data variability

The statistical summary was shown in Table 4.2. Both samples in 12th inter-laboratory project had similar chemical properties which indicate low fertility and acidic soil; i.e. low pH, low exchangeable base cations and high acidity. We however observed the large variations in the analyzed data of exchangeable base cations (Ex-Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup>). CVs were much high in those properties (e.g. 61% and 177% in Ex-Ca of No.101 and No.102) whereas CVs were very low in pH (H<sub>2</sub>O) and pH (KCl) (less than 5 %). Ex-Acidity had moderately high CVs (less than 25%).

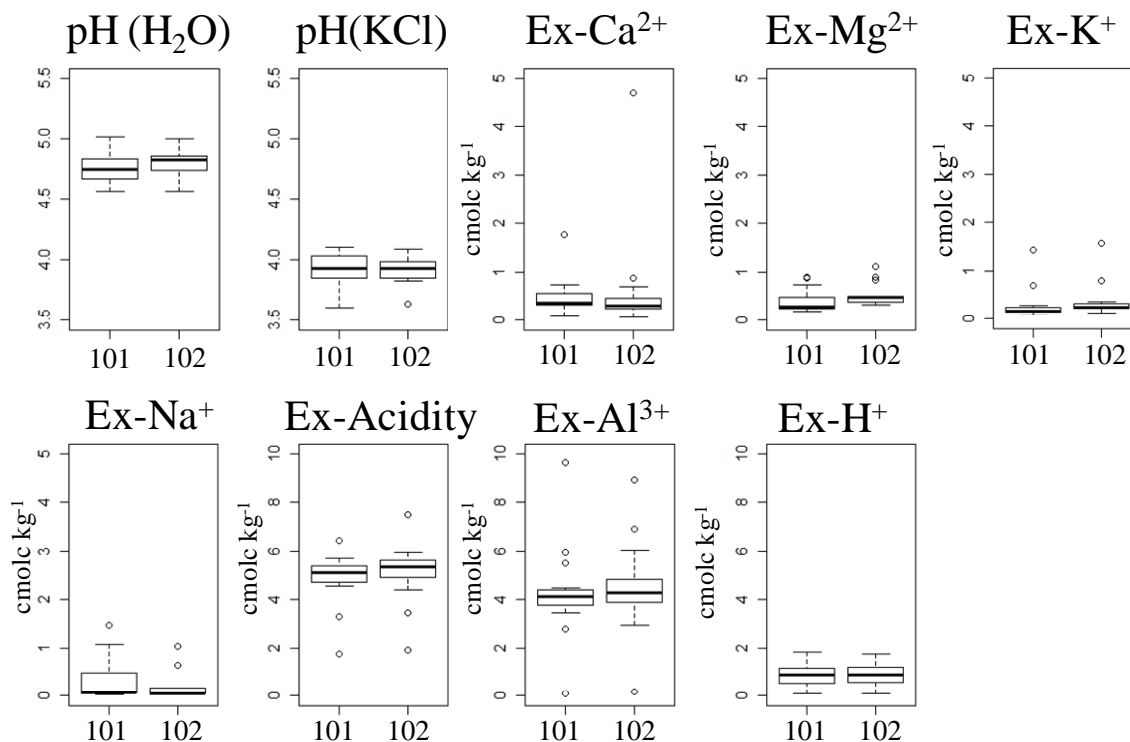
**Table 4.2 Statistical summary**

Statistics	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol(+) kg <sup>-1</sup>						
<b>No. 101</b>									
Number of Laboratories	16	16	13	13	12	12	16	16	16
Total average	4.8	3.9	0.42	0.31	0.16	0.34	4.92	4.35	0.84
Median	4.8	4.0	0.29	0.18	0.16	0.09	5.16	4.17	0.74
Maximum	5.0	4.1	0.90	1.43	0.23	1.47	6.43	9.67	1.81
Minimum	4.6	3.6	0.19	0.09	0.12	0.03	1.77	0.10	0.11
Standard deviation	0.1	0.1	0.25	0.37	0.03	0.49	1.07	1.92	0.51
CV (%) <sup>*1</sup>	2.4	3.6	60.7	118.0	20	143	21.7	44.1	60
<b>No. 102</b>									
Number of Laboratories	16	16	13	13	13	12	16	16	16
Total average	4.8	3.9	0.69	0.55	0.39	0.23	5.19	4.57	0.89
Median	4.8	3.9	0.32	0.48	0.25	0.09	5.44	4.38	0.87
Maximum	5.0	4.1	4.71	1.12	1.57	1.04	7.50	8.89	1.77
Minimum	4.6	3.7	0.06	0.32	0.12	0.02	1.93	0.16	0.09
Standard deviation	0.1	0.1	1.23	0.24	0.39	0.31	1.21	1.86	0.47
CV (%) <sup>*1</sup>	2.5	2.6	176.8	44.9	100	137	23.3	40.7	53

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

We also have an overview of the data by box-and-whisker plot (Figure 4.1) of No.101 and 102 analyzed by 16 laboratories. Box-and-whisker plot provides the five-number summaries: lower quartile, median and upper quartile shown by box and bold lines, and maximum and minimum values drawn by error bars. In addition, the values lower quartile minus 1.5 times the inter-quartile range, or larger than the upper quartile plus 1.5 times the inter-quartile range are shown as outliers, that is, non-parametrical outliers.

The ranges from lower quartile to upper quartile were around 0.5 in pH, 1.0 cmol<sub>c</sub> kg<sup>-1</sup> in exchangeable base cations and 2.0 in exchangeable acidity. Meanwhile, the plots showed one or two clear non-parametrical outliers in each parameter except pH (H<sub>2</sub>O) and Ex-H<sup>+</sup>. Those outliers might be produced by miss calculation, wrong procedure, irregular contamination, and so on because the values were 5-10 times higher or lower than average. Therefore, in following section, we removed these outliers by parametrically statistical method to calculate the good reference more close to true value.



**Figure 4.1 Data variability of No.101 and No.102 among 16 laboratories**

#### 4.3.2 Detection of outliers

Detection of outliers by Cochran-Grubbs methods were shown in Table 4.3. The laboratory which has a large difference in repeat analyses was judged as outlier by Cochran method (examination of the evenness of within-laboratory precision); e.g. “MY04” in Ex-Ca, CN03 in Ex-acidity of No.101. Then, the rest of data were tested by Grubbs method (examination of the average value of each laboratory). In this method, the laboratory which has remarkably large or small average was judged as outliers; e.g. MY04 and VN03 in Ex-Al of No.101. Cochran-Grubbs method detected the 2-5 outliers for exchangeable base cations or exchangeable acidity. Outliers by Cochran method were more observed in Ex-Al of No.101 than others whereas outliers by Grubbs method were widely detected in exchangeable base and acid cations. Any outliers were not detected in pH (H<sub>2</sub>O) and pH (KCl). As a result of removing outliers, the “verified” dataset consisting of 16 laboratories in pH, 9-12 laboratories in base cations and 11-15 laboratories in acid cations were used for further analysis in the following section.

**Table 4.3 Data verification by Cochran-Grubbs methods**

**No.101**

Lab.	Repeat analysis	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
CN01	1st	4.8	3.9	0.2	0.2	0.2	0.0	5.2	4.1	1.0
	2nd	4.8	3.9	0.3	0.2	0.2	0.0	5.2	4.1	1.1
CN02	1st	4.9	4.1	0.3	0.3	0.2	0.1	5.1	4.1	1.0
	2nd	4.9	4.1	0.3	0.3	0.2	0.1	5.1	4.0	1.1
CN03	1st	4.8	4.1	0.4	0.4	0.1	1.5*g	6.1*c	5.7	0.5
	2nd	4.8	4.1	0.4	0.3	0.1	1.5*g	6.7*c	6.3	0.5
CN04	1st	4.8	4.0	0.4	0.3	0.2	0.1	5.2	3.6	1.4
	2nd	4.8	4.0	0.4	0.2	0.2	0.1	5.1	3.8	1.3
ID01	1st	4.7	3.9	0.2	0.3	0.2	0.0	5.3	3.5	1.8
	2nd	4.7	3.8	0.2	0.3	0.2	0.0	5.3	3.5	1.8
ID04	1st	4.7	4.0	0.1	0.4	0.1	0.1	3.3*g	2.8	0.5
	2nd	4.6	4.0	0.1	0.4	0.1	0.1	3.3*g	2.8	0.5
JP06	1st	5.0	4.0	0.6	0.3	0.2	0.1	5.1	4.3	0.9
	2nd	5.0	3.9	0.6	0.3	0.2	0.1	5.2	4.3	0.8
MN01	1st	4.6	3.7					5.2	4.3	0.9
	2nd	4.6	3.7					5.2	4.3	0.9
MY04	1st	4.6	3.6	0.8*c	0.5*c	1.4*g	0.7*c	1.7*g	0.1*g	1.6
	2nd	4.5	3.6	0.6*c	1.0*c	1.4*g	0.8*c	1.8*g	0.1*g	1.8
PH03	1st	4.8	4.1	0.5	0.9	0.7*g	1.1*g	4.6	4.2	0.4
	2nd	4.7	4.1	0.5	0.9	0.7*g	1.0*g	4.7	4.2	0.4
RU01	1st	4.6	4.0	1.8*c	0.9	0.2	0.2	5.8	5.8	0.1
	2nd	4.6	4.0	1.7*c	0.9	0.2	0.2	5.6	5.3	0.1
TH01	1st	4.7	3.9	0.3	0.2	0.1		5.6	3.6	1.6*c
	2nd	4.7	4.0	0.3	0.2	0.1		5.7	4.0	1.0*c
TH06	1st	4.8	4.0	0.7	0.3	0.3	0.2	5.2	5.1	0.1
	2nd	4.8	3.9	0.6	0.3	0.3	0.2	5.3	5.1	0.2
VN01	1st	4.8	3.8					4.6	4.0	0.6
	2nd	4.8	3.8					4.6	4.0	0.6
VN02	1st	4.9	3.9					4.9	4.4	0.6
	2nd	4.9	3.9					4.9	4.5	0.6
VN03	1st	4.7	3.9	0.5	0.5	0.3	0.1	5.5	9.7*g	0.6
	2nd	4.7	3.9	0.6	0.5	0.3	0.1	5.5	9.7*g	0.6

**No.102**

Lab.	Repeat analysis	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
CN01	1st	4.9	3.9	0.2	0.3	0.2	0.0	5.8	4.7	1.1
	2nd	5.0	3.9	0.2	0.3	0.2	0.0	5.8	4.7	1.1
CN02	1st	4.9	4.1	0.2	0.4	0.2	0.1	6.0	4.5	1.4
	2nd	4.9	4.1	0.3	0.4	0.3	0.1	6.0	4.5	1.4
CN03	1st	4.9	4.0	0.3	0.4	0.3	0.2	7.2	6.6*c	0.6
	2nd	4.9	4.0	0.3	0.4	0.3	0.2	7.8	7.2*c	0.6
CN04	1st	4.7	4.0	0.3	0.4	0.2	0.0	5.7	4.2	1.4
	2nd	4.8	3.9	0.3	0.4	0.2	0.0	5.6	4.3	1.3
ID01	1st	4.8	3.9	0.1	0.5	0.2	0.0	5.3	3.7	1.6
	2nd	4.8	3.8	0.1	0.5	0.2	0.0	5.2	3.7	1.6
ID04	1st	4.6	4.0	0.1	0.5	0.1	0.1	3.5	2.9	0.5
	2nd	4.6	4.0	0.1	0.5	0.1	0.1	3.4	2.9	0.5
JP06	1st	5.0	3.9	0.5*c	0.5*c	0.3	0.1	5.5	4.5	0.9
	2nd	5.0	3.9	0.5*c	0.5*c	0.3	0.1	5.2	4.4	0.8
MN01	1st	4.7	3.9					4.4	3.5	0.0*c
	2nd	4.7	3.9					4.4	3.5	0.9*c
MY04	1st	4.6	3.6	0.7*c	1.2*c	1.5*c	0.5*c	2.0*g	0.1*g	1.9*c
	2nd	4.6	3.7	1.0*c	1.0*c	1.6*c	0.8*c	1.9*g	0.2*g	1.7*c
PH03	1st	4.8	4.0	0.4	0.9	0.8*c	1.0*g	4.8	4.3	0.5
	2nd	4.9	4.2	0.4	0.9	0.8*c	1.0*g	4.8	4.3	0.5
RU01	1st	4.7	4.0	0.4	0.5	0.3	0.2	5.4	5.8*c	0.1
	2nd	4.7	4.0	0.4	0.5	0.3	0.2	6.0	6.3*c	0.1
TH01	1st	4.8	3.9	0.3	0.3	0.1		5.3	4.0*c	1.1
	2nd	4.8	4.0	0.3	0.4	0.1		5.8	4.2*c	1.0
TH06	1st	4.9	3.9	0.7*g	0.5	0.4	0.4*g	5.8	5.4	0.4
	2nd	4.8	3.9	0.7*g	0.5	0.4	0.3*g	5.9	5.5	0.4
VN01	1st	4.8	3.8					5.1	4.2	1.0
	2nd	4.8	3.9					5.1	4.2	1.0
VN02	1st	4.9	3.9					5.5	5.0	0.6
	2nd	4.9	3.9					5.5	5.0	0.6
VN03	1st	4.8	3.8	4.7*g	0.8	0.4	0.0	5.2	8.9*g	0.5
	2nd	4.8	3.8	4.7*g	0.8	0.4	0.0	5.2	8.9*g	0.5

Note; The outliers judged by Cochran and Grubbs methods were marked with **c** and **g**, respectively

### 4.3.3 Statistical summary for verified data

The statistical summary for verified datasets in No.101 and No.102 were shown in Table 4.4. Although chemical properties in both soils were not largely changed by verification, the data variability of exchangeable cations decreased from entire dataset. Meanwhile, CVs were still high in Ex-Ca, Ex-Mg, Ex-Na and Ex-H (e.g. 58% and 45% in Ex-Ca in No.101 and No.102, respectively). The variation included the many kinds of error produced by same person (repetition), different person (within-laboratory) or different laboratories (inter-laboratory). We separated this variation in next section to detect the source of it.

**Table 4.4 Statistical summary of the “verified” dataset<sup>\*2</sup>**

Statistics	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol(+) kg <sup>-1</sup>						
<b>No. 101</b>									
Number of Laboratories	16	16	11	12	11	9	13	14	15
Total average	4.8	3.9	0.35	0.22	0.16	0.08	5.17	4.28	0.81
Median	4.8	4.0	0.29	0.18	0.16	0.07	5.16	4.17	0.61
Maximum	5.0	4.1	0.90	0.70	0.23	0.17	5.72	5.97	1.81
Minimum	4.6	3.6	0.19	0.09	0.12	0.03	4.56	2.79	0.11
Standard deviation	0.1	0.1	0.20	0.16	0.04	0.05	0.34	0.82	0.51
CV (%) <sup>*1</sup>	2.4	3.6	57.8	73.4	21.4	58.9	6.6	19.2	63.0
<b>No. 102</b>									
Number of Laboratories	16	16	9	11	11	9	15	11	14
Total average	4.8	3.9	0.25	0.50	0.25	0.08	5.41	4.27	0.82
Median	4.8	3.9	0.27	0.47	0.25	0.06	5.51	4.29	0.73
Maximum	5.0	4.1	0.39	0.89	0.38	0.17	7.50	5.48	1.61
Minimum	4.6	3.7	0.06	0.32	0.12	0.02	3.45	2.92	0.09
Standard deviation	0.1	0.1	0.11	0.19	0.08	0.06	0.87	0.71	0.44
CV (%) <sup>*1</sup>	2.5	2.6	44.6	38.0	31.9	71.3	16.1	16.6	53.5

Note: \*1. CV, Coefficient of variance (%) = (standard deviation/average)\*100, \*2.dataset is verified removing outliers judged by Cochran-Grubbs methods.

### 4.3.4 Analysis of variance for verified data

“Repeatability-precision”, “within-laboratory-precision” and “inter-laboratories-precision” were discussed using analysis of variance model (ANOVA) to detect the source of data variability (Table 4.5).

#### 1) Repeatability-precision

Repeatability-precision was enough high for all properties. The CVs were less than 1% in pH and 10% in Ex-cations. The result suggests that triplicate analyses were carried out under the same condition. Relatively low repeatability precision in Ex-H indicates that an operation of titration could lead to the error for the repeat analysis. In general, the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

#### 2) Within-laboratory precision

High within-laboratory precision was also observed for most parameters. CVs in within-laboratory precision for almost all parameters were smaller than CVs in 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. We assumed that participating laboratories could analyze the parameters with their own standard procedures.

### **3) Inter-laboratories precision**

The CVs in the inter-laboratories precision were less than 5% in pH (H<sub>2</sub>O) and pH (KCl). However, the CVs of exchangeable base and acid cations were large for both samples. CVs are 30-70% and 5-60% in exchangeable base cations and acid cations, respectively. We discussed the possible factor of the large CVs in inter-laboratory precision, in the following section.

### **4) Calculation of permissible tolerance**

The repeatability limit and within-laboratory reproducibility limit might be enough small to use as a reference value for the repeat analysis on the instrumental analysis in the respective laboratory. For assessment of temporal pH change of monitoring data at each site, participating laboratories can detect the significant change more than 0.1 pH units. The reproducibility limit (inter-laboratories reproducibility limit) is also small for pH. Participating laboratories can detect the significant difference between the monitoring sites if the differences are more than about 0.3 pH units. Meanwhile, the reproducibility limit in 12<sup>th</sup> inter-laboratory comparison project should be improved for exchangeable base and acid cations. For example, participating laboratories can detect the significant difference among the monitoring site if the differences are more than about 0.5 and 2.0 in Ex-Ca and Ex-Acidity, respectively.

**Table 4.5 Analysis of variance for “verified” dataset**

Statistics	No. 101								
	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	16	16	11	12	11	9	13	14	15
Total sum of square	208801	141419	618	787	134	20	162741	128749	5267
ST/lmd	2175	1473	9	11	2	0	2086	1533	59
Number of Data	96	96	66	72	66	54	78	84	90
Total sum	456.9	376.1	24.86	28.06	11.59	4.51	403.41	358.82	72.57
Total average	4.8	3.9	0.38	0.39	0.18	0.08	5.17	4.27	0.81
Sum of square inter-laboratories (S <sub>R</sub> )	1.3	1.7	1.83	4.01	0.21	0.11	8.42	52.70	21.82
Sum of square within-laboratory (S <sub>RW</sub> )	0.0	0.0	0.00	0.00	0.00	0.00	0.19	1.14	0.09
Sum of square repeatability (S <sub>r</sub> )	0.1	0.0	0.02	0.01	0.00	0.00	0.83	1.79	0.18
Total sum of square (S <sub>T</sub> )	1.4	1.7	1.85	4.02	0.22	0.12	9.45	55.62	22.10
Inter-laboratories degree of freedom (φ <sub>R</sub> )	15	15	10	11	10	8	12	13	14
Within-laboratory degree of freedom (φ <sub>RW</sub> )	16	16	11	12	11	9	13	14	15
Repeatability degree of freedom (φ <sub>r</sub> )	64	64	44	48	44	36	52	56	60
Total degree of freedom (φ <sub>T</sub> )	95	95	65	71	65	53	77	83	89
Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /φ <sub>R</sub> )	0.09	0.11	0.183	0.364	0.021	0.014	0.702	4.054	1.559
Within-laboratory variance (V <sub>RW</sub> = S <sub>RW</sub> /φ <sub>RW</sub> )	0.00	0.00	0.000	0.000	0.000	0.000	0.015	0.081	0.006
Repeatability variance (V <sub>r</sub> = S <sub>r</sub> /φ <sub>r</sub> )	0.00	0.00	0.001	0.000	0.000	0.000	0.016	0.032	0.003
Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> -V <sub>RW</sub> )/(2*3))	0.01	0.02	0.030	0.061	0.004	0.002	0.114	0.662	0.259
Within-laboratory component of variance (s <sub>c</sub> <sup>2</sup> = (V <sub>RW</sub> -V <sub>r</sub> )/3)	0.00	0.00	0.000	0.000	0.000	0.000	0.000	0.017	0.001
Repeatability component of variance (s <sub>t</sub> <sup>2</sup> = V <sub>r</sub> )	0.00	0.00	0.001	0.000	0.000	0.000	0.016	0.032	0.003
Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>b</sub> <sup>2</sup> /(2*3) + s <sub>c</sub> <sup>2</sup> /2)	0.1	0.1	0.17	0.25	0.06	0.05	0.34	0.82	0.51
Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(s <sub>t</sub> <sup>2</sup> /3 + s <sub>c</sub> <sup>2</sup> ))	0.0	0.0	0.01	0.01	0.01	0.01	0.07	0.16	0.05
Repeatability standard deviation (s <sub>r</sub> = SQRT(s <sub>t</sub> <sup>2</sup> ))	0.0	0.0	0.02	0.01	0.01	0.01	0.13	0.18	0.05
Inter-laboratories precision CV (%)	2.5	3.5	46.31	63.22	34.06	58.25	6.61	19.24	63.21
Within-laboratory precision CV (%)	0.3	0.7	3.25	2.81	3.64	9.51	1.36	3.86	5.68
Repeatability precision CV (%)	0.7	0.5	5.97	3.82	4.50	8.34	2.45	4.18	6.76
Reproducibility limit (R = D(2, 0.95)*s <sub>R</sub> )	0.34	0.38	0.489	0.690	0.167	0.136	0.958	2.301	1.427
Within-laboratory-reproducibility limit (R <sub>w</sub> = D(2, 0.95)*s <sub>RW</sub> )	0.04	0.08	0.034	0.031	0.018	0.022	0.197	0.461	0.128
Repeatability limit (r = D(3, 0.95)*s <sub>r</sub> )	0.11	0.07	0.074	0.049	0.026	0.023	0.418	0.590	0.180

**Table 4.5 (continued)**

Statistics	No. 102								
	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	16	16	9	11	11	9	15	11	14
Total sum of square	212784	141657	181	1079	264	17	236753	79432	4775
ST/lmd	2216	1476	3	16	4	0	2631	1204	57
Number of Data	96	96	54	66	66	54	90	66	84
Total sum	461.3	376.4	13.47	32.84	16.26	4.16	486.57	281.84	69.10
Total average	4.8	3.9	0.25	0.50	0.25	0.08	5.41	4.27	0.82
Sum of square inter-laboratories (S <sub>R</sub> )	1.1	1.1	0.59	2.17	0.36	0.14	63.89	30.14	15.12
Sum of square within-laboratory (S <sub>RW</sub> )	0.0	0.1	0.00	0.00	0.00	0.00	1.54	0.04	0.02
Sum of square repeatability (S <sub>r</sub> )	0.1	0.0	0.01	0.01	0.01	0.00	1.37	0.06	0.14
Total sum of square (S <sub>T</sub> )	1.2	1.1	0.61	2.18	0.37	0.15	66.80	30.24	15.29
Inter-laboratories degree of freedom (φ <sub>R</sub> )	15	15	8	10	10	8	14	10	13
Within-laboratory degree of freedom (φ <sub>RW</sub> )	16	16	9	11	11	9	15	11	14
Repeatability degree of freedom (φ <sub>r</sub> )	64	64	36	44	44	36	60	44	56
Total degree of freedom (φ <sub>T</sub> )	95	95	53	65	65	53	89	65	83
Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /φ <sub>R</sub> )	0.07	0.07	0.074	0.217	0.036	0.018	4.563	3.014	1.163
Within-laboratory variance (V <sub>RW</sub> = S <sub>RW</sub> /φ <sub>RW</sub> )	0.00	0.00	0.000	0.000	0.000	0.000	0.103	0.003	0.002
Repeatability variance (V <sub>r</sub> = S <sub>r</sub> /φ <sub>r</sub> )	0.00	0.00	0.000	0.000	0.000	0.000	0.023	0.001	0.002
Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> -V <sub>RW</sub> )/(2*3))	0.01	0.01	0.012	0.036	0.006	0.003	0.743	0.502	0.194
Within-laboratory component of variance (s <sub>c</sub> <sup>2</sup> = (V <sub>RW</sub> -V <sub>r</sub> )/3)	0.00	0.00	0.000	0.000	0.000	0.000	0.027	0.001	0.000
Repeatability component of variance (s <sub>t</sub> <sup>2</sup> = V <sub>r</sub> )	0.00	0.00	0.000	0.000	0.000	0.000	0.023	0.001	0.002
Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>b</sub> <sup>2</sup> /(2*3) + s <sub>c</sub> <sup>2</sup> /2)	0.1	0.1	0.11	0.19	0.08	0.05	0.87	0.71	0.44
Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(s <sub>t</sub> <sup>2</sup> /3 + s <sub>c</sub> <sup>2</sup> ))	0.0	0.0	0.01	0.01	0.01	0.01	0.18	0.03	0.02
Repeatability standard deviation (s <sub>r</sub> = SQRT(s <sub>t</sub> <sup>2</sup> ))	0.0	0.0	0.02	0.02	0.02	0.01	0.15	0.04	0.05
Inter-laboratories precision CV (%)	2.3	2.8	44.63	38.17	31.45	71.20	16.13	16.60	53.53
Within-laboratory precision CV (%)	0.4	0.9	4.93	1.95	2.26	7.16	3.42	0.76	2.96
Repeatability precision CV (%)	0.8	0.6	6.58	3.34	6.18	7.59	2.80	0.90	5.99
Reproducibility limit (R = D(2, 0.95)*s <sub>R</sub> )	0.31	0.30	0.312	0.532	0.217	0.154	2.442	1.985	1.233
Within-laboratory-reproducibility limit (R <sub>w</sub> = D(2, 0.95)*s <sub>RW</sub> )	0.06	0.09	0.034	0.027	0.016	0.015	0.518	0.091	0.068
Repeatability limit (r = D(3, 0.95)*s <sub>r</sub> )	0.13	0.08	0.054	0.055	0.050	0.019	0.499	0.126	0.163

#### **4.3.5 Inter-laboratory variations in each parameter**

To assess the precision in each laboratories and properties, we showed scatter plots between No.101 and No.102 with its “verified” mean indicated by solid line. As a guide for comparison, 20% of verified mean is added by dashed lines, while 0.2 units from the average are used for pH. Outliers selected by Cochran and Grubbs method (as mentioned above) were denoted by ¶ and §, respectively. Outliers within the 20 % total average are due to poor repeatability in each laboratory (i.e. large within-laboratory variation). The plot did not include extreme outliers for eye-friendly.

##### **1) pH**

Linear correlation between No.101 and No.102 indicated the systematic errors of the inter-laboratory variation in pH (Figure 4.2 and Figure 4.3). The systematic error might be caused by the condition of pure water, standard solution or glass electrode. In addition, measuring time to the stabilization of value may lead to the variation because a carbon dioxide pressure, leakage of KCl solution from the electrode or settling the clay particles in the sample tube change the ion balance in soil suspension.

Meanwhile, most laboratories were included within the range of 0.2 pH unit for No.101 and No.102. Any laboratories were not judged by outliers using Cochran-Grubbs method. The result indicates enough capacity of participating countries for analyzing soil pH.

##### **2) Base cations**

The plot of exchangeable base cations (Figure 4.4 to 4.7) suggested large systematic error of inter-laboratory variations. A few laboratories were included in the range of 20% of verified mean for exchangeable base cations. The systematic error led to the very large variation in the dataset and many outliers.

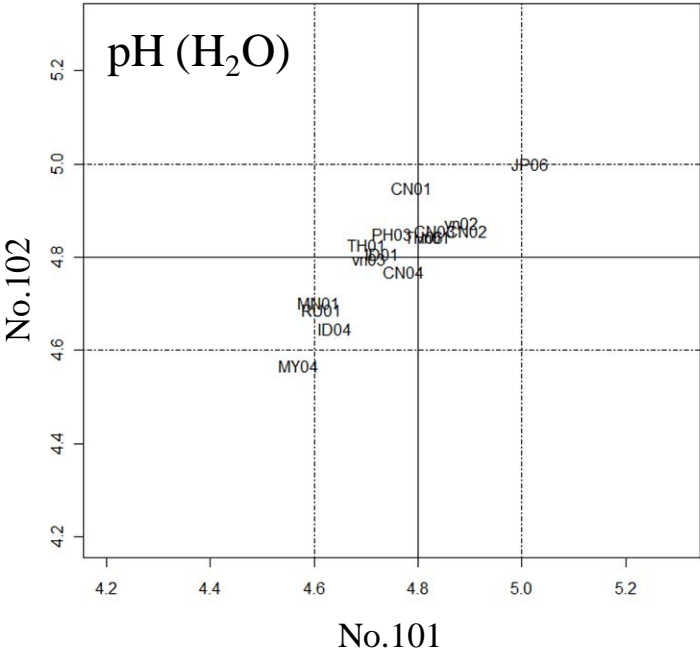
The systematic error might be caused by the condition of ammonium acetate (extraction liquid), standard solution or dilution rate. In this analysis, higher concentration or higher pH of extraction liquid may result in an increase of the base cations in the solution. Standard solution is also important factor for the systematic error. Extraction liquid should be used for standard solution to harmonize the background with that of the samples. Wrong dilution rate also may result in this kind of large systematic error.

##### **3) Acidity**

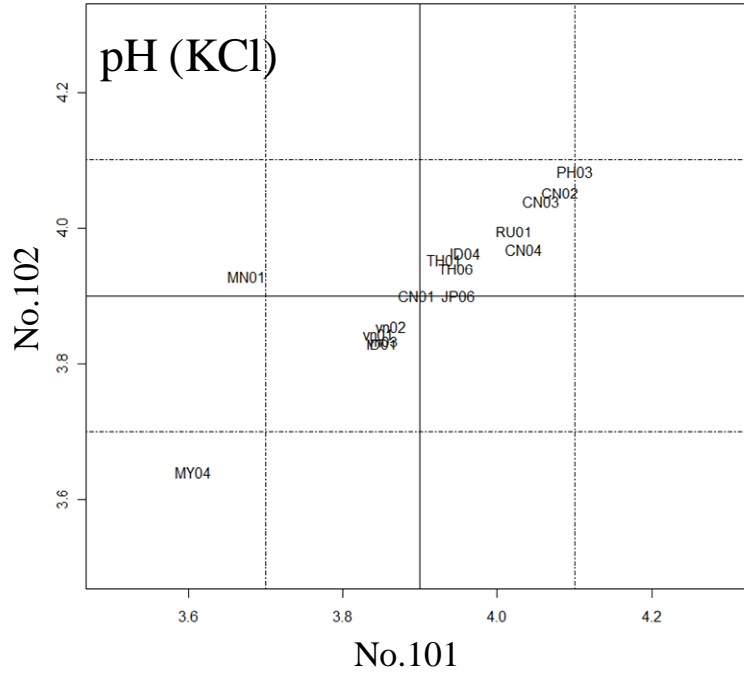
The plots of Ex-Acidity, Ex-Al and Ex-H indicated random error of inter-laboratory variation except the outliers (Figure 4.8 to 4.10). In Ex-acidity, almost all laboratories were included in the 20% range of verified mean of No.101 and No.102.

The random error might be caused by manipulation of titration, which is easily affected by factor of

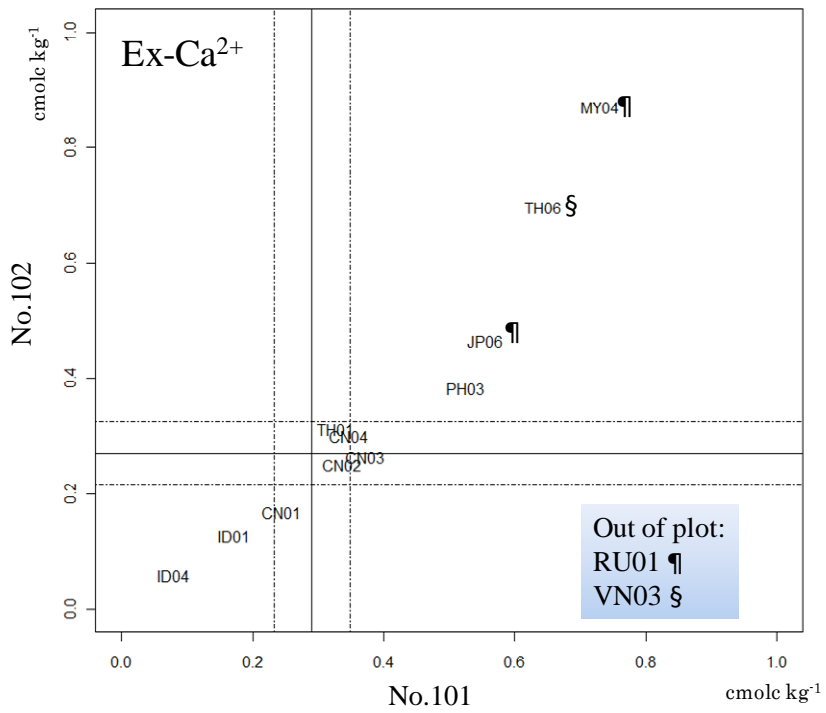
volumetric solution or end-point detection. Meanwhile, some outliers might be caused by the wrong kinds or concentrations of the reagent because Ex-AI was much higher than Ex-acidity in some laboratory (Ex-acidity is equivalent to sum of Ex-AI and Ex-H in this method). Participating laboratories should check the standard of procedure based on the Technical Manual for Soil and Vegetation Monitoring (EANET, 2000).



**Figure 4.2 Scatter diagram of pH (H<sub>2</sub>O) between No.101 and No.102 (Solid lines show mean of verified datasets and dashed lines show 0.2 pH units from the mean)**



**Figure 4.3 Scatter diagram of pH (KCl) between No.101 and No.102**



**Figure 4.4 Scatter plot of Ex-Ca between No.101 and No.102 (Solid lines show mean of verified datasets and dashed lines show 20% from the mean, ¶ shows outlier in No.101 or 102)**

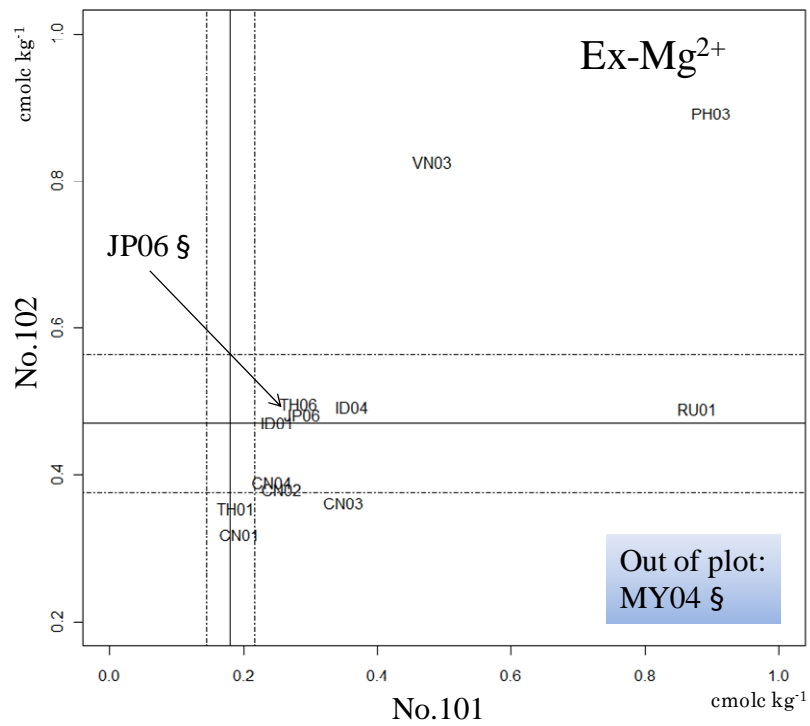


Figure 4.5 Scatter plot of Ex-Mg between No.101 and No.102

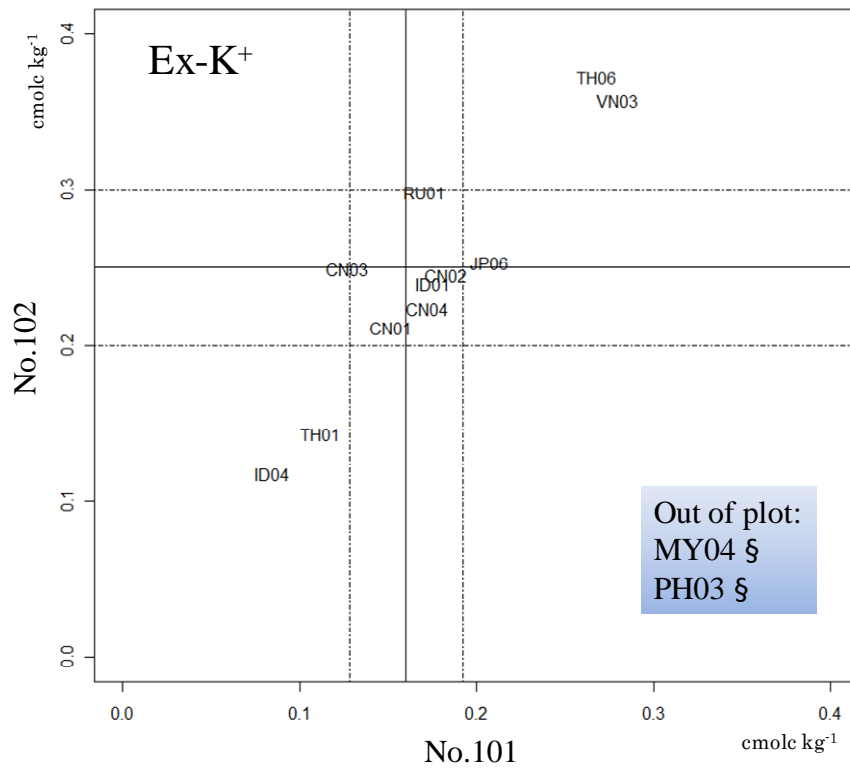


Figure 4.6 Scatter plot of Ex-K between No.101 and No.102

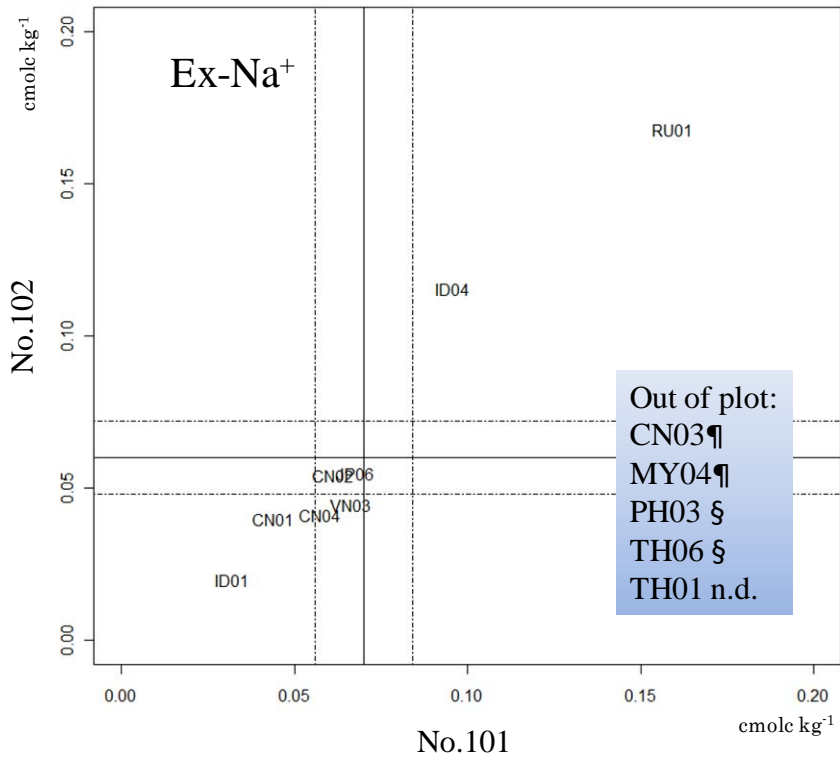


Figure 4.7 Scatter plot of Ex-Na between No.101 and No.102

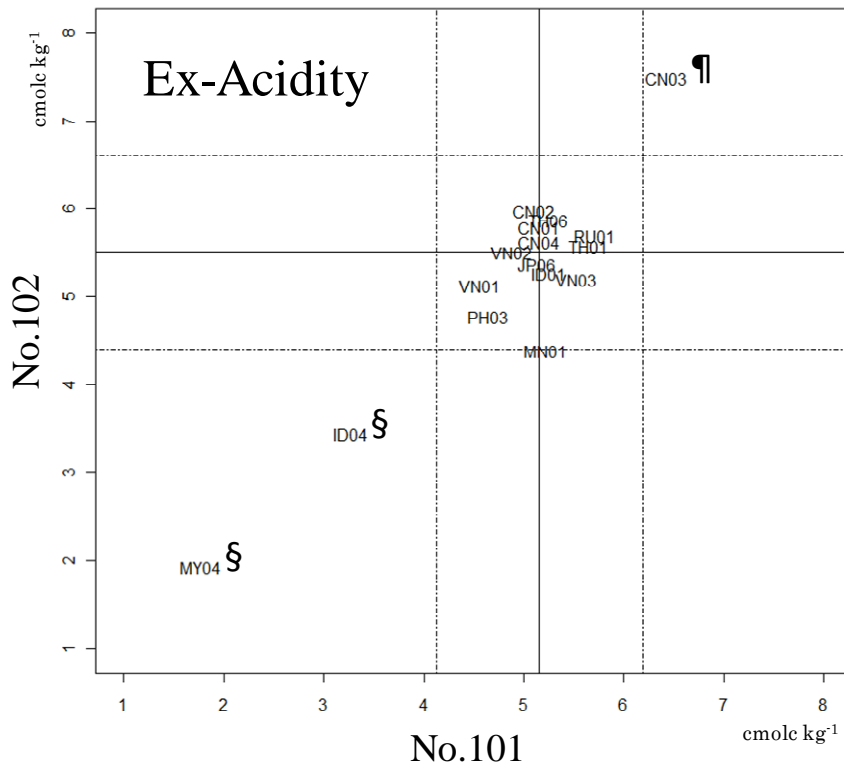


Figure 4.8 Scatter plot of Ex-Acidity between No.101 and No.102

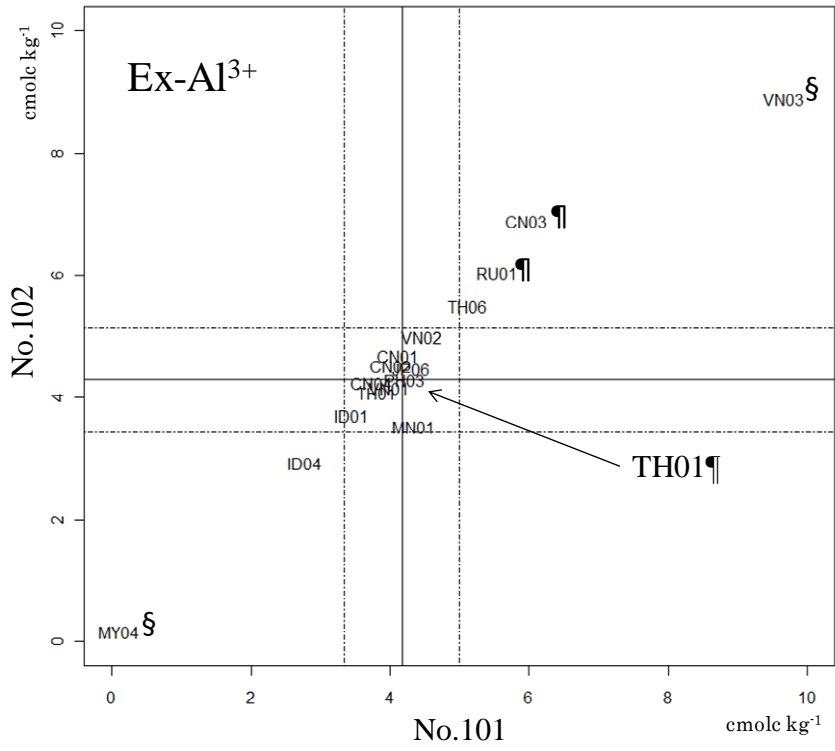


Figure 4.9 Scatter plot of Ex-Al between No.101 and No.102

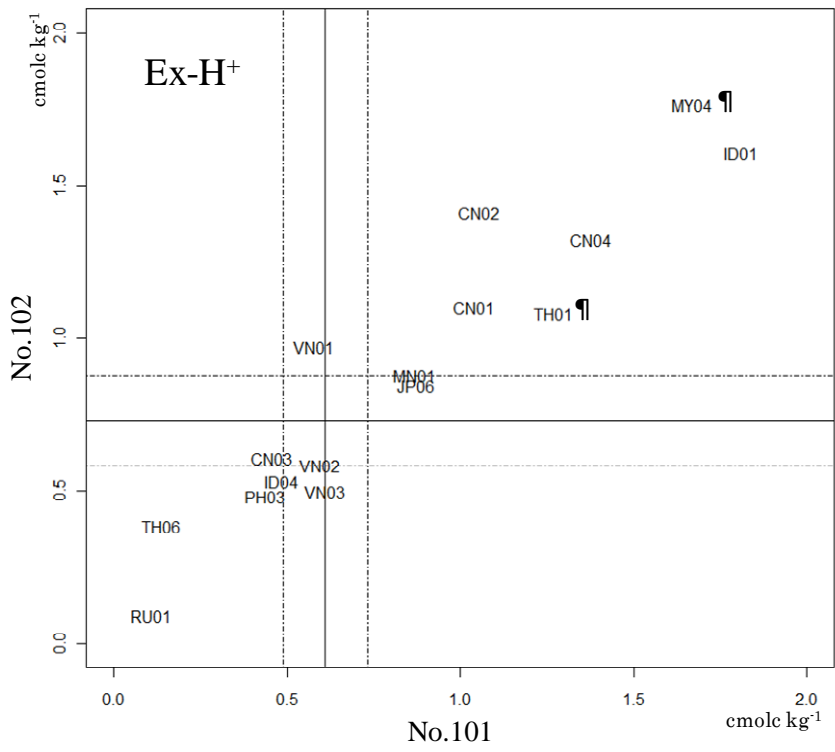


Figure 4.10 Scatter plot of Ex-H between No.101 and No.102

#### **4.3.6 Comparison with information on Laboratories**

##### **1) Number of analysts and their experience**

Number of analysts and years of their experience were shown in Table 4.6. The same analyst carried out the repeat analyses in some laboratories for all parameters. No relationship between the number of analyst, years of experience and the outliers was suggested.

##### **2) Analytical instruments and condition of instruments**

Analytical instruments used for the measurement, procedures for extraction of base cations, and size of burette used for the titration method in Ex-acidity were shown in Table 4.7. Almost all laboratories used AAS for measurement of Ex-Ca and Mg, and 3 laboratories used FEP for Ex-K and Na. One laboratory used ICP for measurement of Ex-Ca, Mg, K and Na. Years in use of instruments were varied from 1 to 25. All the laboratories except “MY04”, “RU01”, “TH01” and “VN03” applied Sr for measurement of Ex-Ca and Mg by AAS.

Seven laboratories used percolation tube procedures for extraction of exchangeable base cations, while Buchner funnel procedures, centrifuge procedures and automatic extractor procedures were used in 1, 3 and 2 laboratories, 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 3 to 50 ml while minimum graduates were 0.00125 to 0.1.

##### **3) Date of analysis**

Date of analysis in the respective laboratories and days used for the analysis were shown in Table 4.8. 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 about 2 months. It was suggested that repeat analyses would be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at SAC3. Mostly half of the laboratories followed the recommendation, although a few laboratories might conduct the instrumental analysis of both samples in a same day.

**Table 4.6 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	2	8	6	2	8	6	s
CN02	1	12	12	1	20	20	d
CN03	1	15	12	1	15	12	s
CN04	1	25	7	2	4	2	d
ID01	1	7	4	1	7	4	s
ID04	2	n	n	1	13	11	d
JP01	1	18	1	1	18	1	s
MY01	-	-	-	-	-	-	-
MY04	1	3	3	1	3	3	s
MN01	-	-	-	1	17	17	-
PH03	1	22	3	1	34	34	d
RU01	1	6	6	1	15	15	d
TH01	1	7	7	1	16	1	s
TH06	2	6	2	2	5/1	5/1	s
VN01	-	-	-	1	18	13	-
VN02	-	-	-	1	8	5	-
VN03	1	5	5	1	5	5	s

Note: -, Not measured; n, no information; s, Same analysts; d, Different analysts

**Table 4.7 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)	Capacity — Minimum graduate	
		Instrument	Years <sup>*1</sup>	Instrument	Years		Instrument	Years	Instrument	Years			Capacity	Minimum graduate
CN01	No.101	AAS	6	AAS	6	Sr	AAS	6	AAS	6	Centrifuge	Titration	10	0.05
	No.102	AAS	6	AAS	6	Sr	AAS	6	AAS	6				
CN02	No.101	AAS	12	AAS	12	Sr	AAS	12	AAS	12	Percolation tube	Titration	50	0.1
	No.102	AAS	12	AAS	12	Sr	AAS	12	AAS	12				
CN03	No.101	AAS	3	AAS	3	Sr	AAS	3	AAS	3	Automatic	Titration	5	0.00125
	No.102	AAS	3	AAS	3	Sr	AAS	3	AAS	3				
CN04	No.101	AAS	4	AAS	4	Sr	AAS	4	AAS	4	Automatic	Titration	3	0.02
	No.102	AAS	4	AAS	4	Sr	AAS	4	AAS	4				
ID01	No.101	AAS	6	AAS	4	Sr	AAS	6	AAS	4	Centrifuge	Titration	50	0.05
	No.102	AAS	6	AAS	4	Sr	AAS	6	AAS	4				
ID04	No.101	AAS	21	AAS	21	+	AAS	21	AAS	21	Percolation tube	Titration	50	0.02
	No.102	AAS	21	AAS	21	+	AAS	21	AAS	21				
JP06	No.101	AAS	25	AAS	25	Sr	FEP	25	FEP	25	Percolation tube	Titration	25	0.1
	No.102	AAS	25	AAS	25	Sr	FEP	25	FEP	25				
MY01	No.101	-	-	-	-	-	-	-	-	-				
	No.102	-	-	-	-	-	-	-	-	-				
MY04	No.101	AAS	5	AAS	5	na	AAS	5	AAS	5	Centrifuge	Titration	50	0.5
	No.102	AAS	5	AAS	5	na	AAS	5	AAS	5				
MN01	No.101	-	-	-	-	-	-	-	-	-	-	Titration	25	0.1
	No.102	-	-	-	-	-	-	-	-	-				
PH03	No.101	AAS	1	AAS	1	Sr	AAS	1	AAS	1	Buchner funnel	Titration	50	0.01
	No.102	AAS	1	AAS	1	Sr	AAS	1	AAS	1				
RU01	No.101	AAS	+	AAS	+	Sr/na	FEP	+	FEP	+	Percolation tube	Titration	50	0.05
	No.102	AAS	+	AAS	+	Sr/na	FEP	+	FEP	+				
TH01	No.101	ICP	3	ICP	3	na	ICP	3	ICP	3	Percolation tube	Titration	10	0.02
	No.102	ICP	3	ICP	3	na	ICP	3	ICP	3				
TH06	No.101	AAS	3	AAS	3	Sr	FEP	3	FEP	3	Percolation tube	Titration	25	0.05
	No.102	AAS	3	AAS	3	Sr	FEP	3	FEP	3				
VN01	No.101	-	-	-	-	-	-	-	-	-	-	Titration	10	0.02
	No.102	-	-	-	-	-	-	-	-	-				
VN02	No.101	-	-	-	-	-	-	-	-	-	-	Titration	10	0.05
	No.102	-	-	-	-	-	-	-	-	-				
VN03	No.101	AAS	5	AAS	5	na	AAS	5	AAS	5	Percolation tube	Titration	10	0.02
	No.102	AAS	5	AAS	5	na	AAS	5	AAS	5				

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

**Table 4.8 Date of analysis and days used for the 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
CN01	1st	8-Dec	1	1	9-Dec	2	2	9-Dec	2	2	10-Oct	1	1
	2nd	9-Dec	1		11-Dec	2		11-Dec	2		11-Oct	1	
CN02	1st	24-Jan	1	1	11-Jan	2	7	11-Jan	2	7	21-Jan	4	6
	2nd	25-Jan	1		18-Jan	2		18-Jan	2		27-Jan	4	
CN03	1st	1-Dec	10	15	1-Dec	10	15	1-Dec	10	15	1-Dec	10	15
	2nd	16-Dec	10		16-Dec	10		16-Dec	10		16-Dec	10	
CN04	1st	4-Jan	1	9	3-Mar	1	5	3-Mar	1	5	14-Jan	2	4
	2nd	13-Jan	1		8-Mar	3		8-Mar	3		18-Jan	2	
ID01	1st	4-Jan	1	3	8-Feb	1	0	8-Feb	1	0	4-Jan	1	4
	2nd	7-Jan	1		8-Feb	1		8-Feb	1		8-Jan	1	
ID04	1st	1-Mar	74	0	1-Mar	74	0	3-Jan	74	0	3-Jan	74	0
	2nd	1-Mar	74		1-Mar	74		3-Jan	74		3-Jan	74	
JP06	1st	24-Jan	1	3	28-Jan	5	6	28-Jan	5	6	28-Jan	4	6
	2nd	27-Jan	1		3-Feb	4		3-Feb	4		3-Feb	3	
MY01	1st		-			-			-			-	
	2nd												
MY04	1st	16-Feb	2	3	4-Dec	3	33	4-Dec	3	33	11-Mar	5	17
	2nd	19-Feb	2		6-Jan	4		6-Jan	4		28-Mar	9	
MN01	1st	1-Jun	1	30		-			-		10-Jan	1	1
	2nd	1-Jul	1								11-Jan	1	
PH01	1st	9-May	1	7	11-May	1	7	11-May	1	7	10-May	1	7
	2nd	16-May	1		18-May	1		18-May	1		17-May	1	
RU01	1st	2-Dec	2	3	2-Dec	2	3	2-Dec	2	3	2-Dec	2	2
	2nd	5-Dec	2		5-Dec	2		5-Dec	2		4-Dec	2	
TH01	1st	16-Feb	1	7	20-Feb	2	3	20-Feb	2	3	16-Feb	1	7
	2nd	23-Feb	1		23-Feb	2		23-Feb	2		23-Feb	1	
TH06	1st	17-Feb	1	4	22-Feb	2	4	22-Feb	2	4	16-Feb	1	7
	2nd	21-Feb	1		26-Feb	2		26-Feb	2		23-Feb	1	
VN01	1st	17-Dec	3	7		-			-		17-Dec	3	7
	2nd	24-Dec	3								24-Dec	3	
VN02	1st	24-Nov	1	1		-			-		16-Nov	1	1
	2nd	25-Nov	1								17-Nov	1	
VN03	1st	6-Jan	3	0	13-Jan	1	0	14-Jan	1	0	11-Jan	1	1
	2nd	6-Jan	3		13-Jan	1		14-Jan	1		12-Jan	1	

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

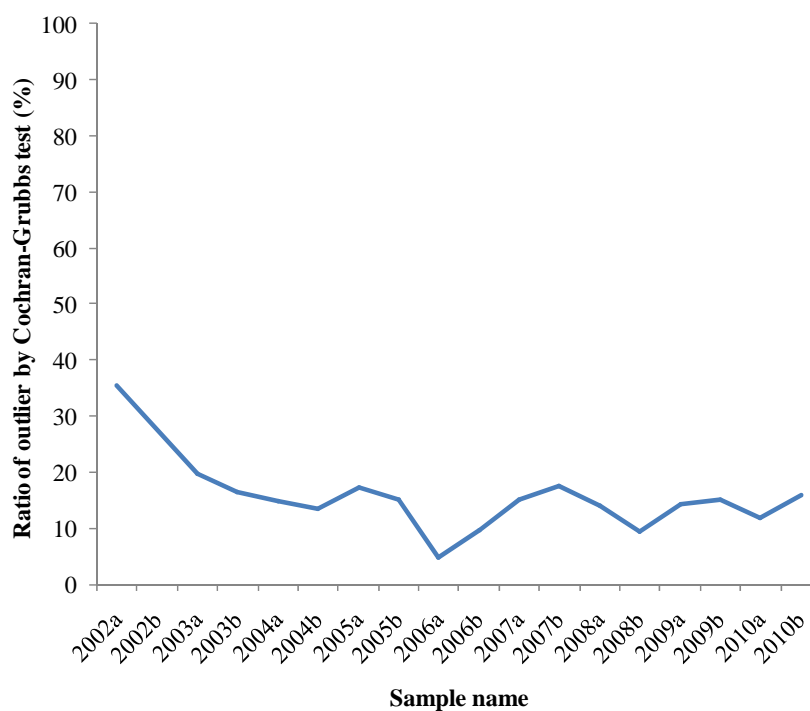
#### 4.4 Needs for improvement of soil analysis

Figure 4.11 shows the change of outlier ratio in all properties and laboratories from 2002 to 2010 (the ratio are calculated by N of outliers / N of all data). Although the ratio decreased from first experiment in 2002, this is still high (10-20% from 2003 to 2010). Outliers may disturb evaluation and understanding of actual monitoring data. For inter-laboratory comparison project on soil, a decrease in the ratio is most important task in near future. Appropriate standard solution, extraction liquid, dilution rate and calculation should be checked to decrease the extremely wrong value which is considered an outlier.

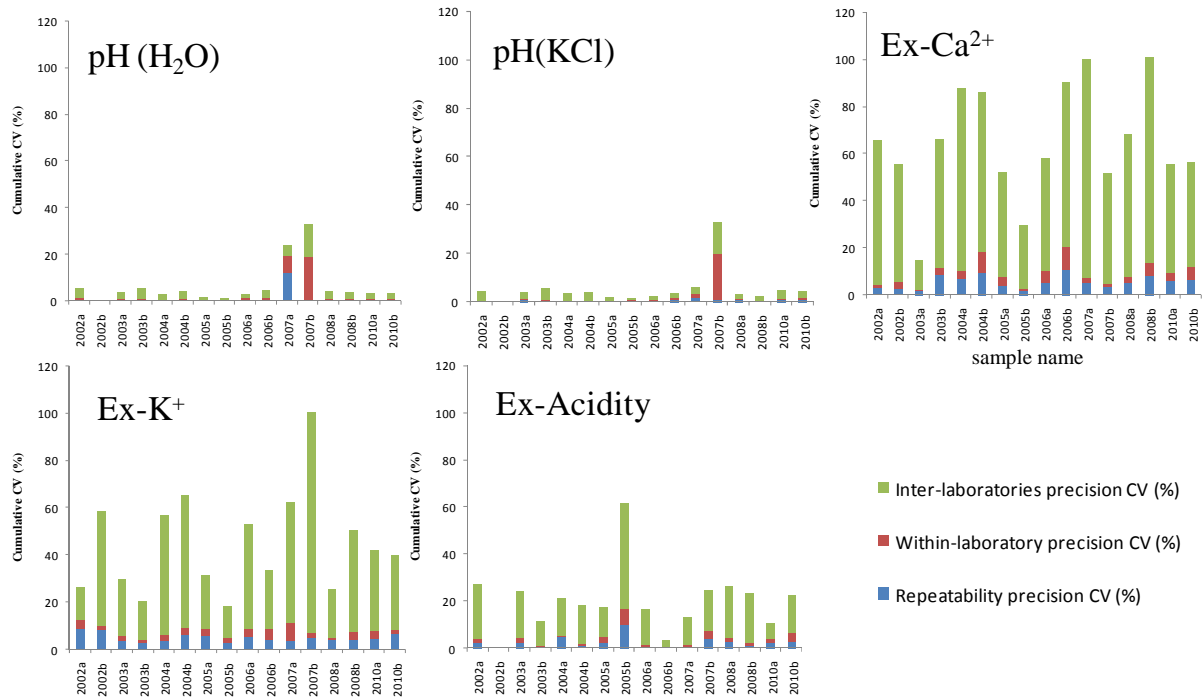
Figure 4.12 shows CV in inter-laboratories, within-laboratories and repeatability precision from 2002 to 2010, which were calculated from verified data. In most years and properties, inter-laboratory variations were much larger than within-laboratory and repeatability variations. We also found the fluctuation of cumulative variations (as shown in CV%) among the year and properties. Cumulative CV in pH (H<sub>2</sub>O) and pH (KCl) were less than 10% from 2002 to 2010 except 2007, where those in base cations were 20-100%. Cumulative CV in exchangeable acidity was around 20% from 2002 to 2010 except 2005. Therefore, from 2002 to 2010, the performance was better in the following order; pH > exchangeable acidity (acid cations) > exchangeable base cations, although the performances have not so improved in each parameters since 2002.

On the other hand, Figure 4.13 shows inter-laboratory reproducibility limit, within-laboratory

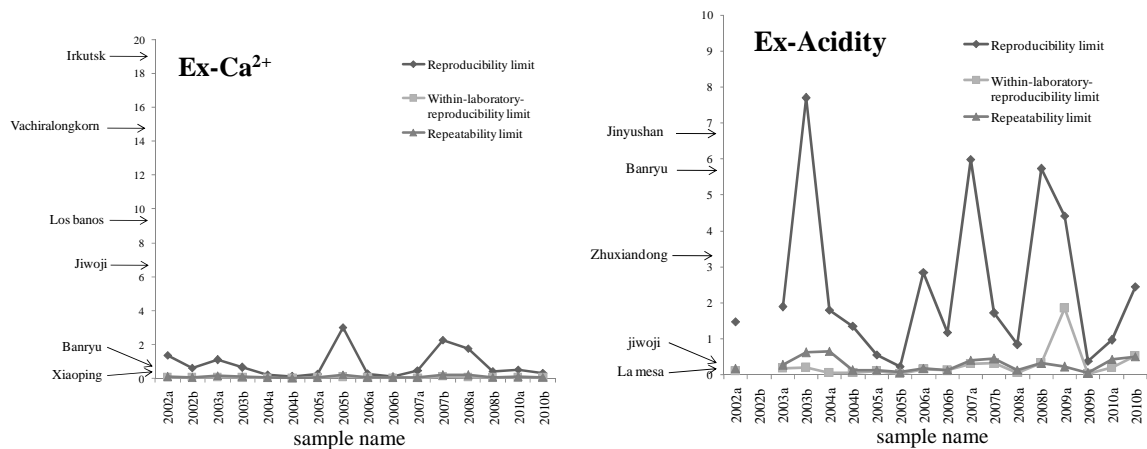
reproducibility limit and repeatability limit from 2002 to 2010. In addition, mean of the soil monitoring data (0-10 cm depth) from 2000 to 2009 in representative monitoring site were shown by arrows and site name. In case of Ex-Ca, inter-laboratory reproducibility limit were around  $1.0 \text{ cmol}_c \text{ kg}^{-1}$  from 2002 to 2010. This limit was enough small to detect the difference among the site where relatively high concentration was observed (e.g. Irkutsk, Los Banos or Jiwoji). In the case of Ex-acidity, the limit was around  $1.5 \text{ cmol}_c \text{ kg}^{-1}$ , which was not so different from Ex-Ca. However, the limit value might be too high to detect the difference among the monitoring sites because actual monitoring data ranged about 0 to  $7.0 \text{ cmol}_c \text{ kg}^{-1}$  in each site. Therefore, we need more precise data for Ex-acidity although data variation in Ex-acidity was not so large in comparison with exchangeable base cations.



**Figure 4.11** Change of the outlier ratio in all properties and laboratories from 2002 to 2010 ( $N$  of outliers /  $N$  of all data)



**Figure 4.12 Inter-laboratories, within-laboratories and repeatability precision (CV %) from 2002 to 2010, calculated from verified datasets**



**Figure 4.13 Inter-laboratory reproducibility limit, within-laboratory reproducibility limit and repeatability limit from 2002 to 2010, site name and arrows show mean of the soil monitoring data (0-10 cm depth) from 2000 to 2009 in representative monitoring site (unit: cmol<sub>c</sub> kg<sup>-1</sup>).**

#### 4.5 Recommendations

Reducing the outliers (about 20% of all data) in exchangeable base and acid cations will be considered firstly. The condition of standard solution, extraction needs a liquid (potassium chloride and ammonium acetate), dilution rate and calculation will be checked. Precision for exchangeable acidity should be more improved to evaluate the actual monitoring data. Analyst needs an effort to improve the manipulation of titration in terms of appropriate reagent concentration, volume and so on. Not only

analytical procedures but also reporting procedures should be checked carefully in the respective laboratories.

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### Appendix 4.1.1 Entire data of pH in Sample No.101

Lab.	pH(H <sub>2</sub> O)			pH(KCl)			
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	
CN01	4.8	4.8 (0.1)	4.8	3.9	3.9 (0.0)	3.9	
			4.9			3.9	
	4.8 (0.1)	4.8	3.9 (0.0)	3.9			
		4.7		3.9			
		4.8		3.9			
	CN02	4.9	4.9 (0.0)	4.9	4.1	4.1 (0.0)	4.1
				4.9			4.1
4.9 (0.0)		4.9	4.1 (0.0)	4.1			
		4.9		4.1			
CN03		4.8	4.8 (0.1)	4.9	4.1	4.1 (0.0)	4.1
				4.9			4.1
	4.8 (0.1)	4.8	4.1 (0.0)	4.1			
		4.9		4.1			
		4.9		4.1			
CN04	4.8	4.8 (0.0)	4.8	4.0	4.0 (0.0)	4.0	
			4.8			4.0	
	4.8 (0.0)	4.8	4.0 (0.0)	4.0			
		4.8		4.0			
	ID01	4.7	4.7 (0.0)	4.7	3.9	3.9 (0.0)	3.9
				4.7			3.9
4.7 (0.0)		4.7	3.8 (0.0)	3.8			
		4.7		3.8			
		4.7		3.8			
ID04	4.7	4.7 (0.0)	4.7	4.0	4.0 (0.0)	4.0	
			4.7			4.0	
	4.6 (0.0)	4.6	4.0 (0.0)	4.0			
		4.6		4.0			
	JP06	5.0	5.0 (0.1)	5.1	4.0	4.0 (0.0)	4.0
				5.0			4.0
5.0 (0.0)		5.0	3.9 (0.0)	3.9			
		5.0		3.9			
MN01		4.6	4.6 (0.0)	4.6	3.7	3.7 (0.0)	3.7
				4.6			3.6
	4.6 (0.0)	4.6	3.7 (0.0)	3.7			
		4.6		3.7			
		4.6		3.7			
MY04	4.6	4.6 (0.1)	4.6	3.6	3.6 (0.0)	3.6	
			4.5			3.6	
	4.5 (0.0)	4.7	3.6 (0.0)	3.7			
		4.6		3.5			
	PH03	4.8	4.8 (0.1)	4.7	4.1	4.1 (0.1)	4.2
				4.9			4.1
4.7 (0.1)		4.7	4.1 (0.0)	4.0			
		4.7		4.1			
		4.8		4.1			
RU01	4.6	4.6 (0.0)	4.6	4.0	4.0 (0.0)	4.0	
			4.6			4.0	
	4.6 (0.0)	4.6	4.0 (0.0)	4.0			
		4.6		4.0			
	TH01	4.7	4.7 (0.0)	4.7	4.0	3.9 (0.0)	3.9
				4.7			3.9
4.7 (0.0)		4.7	4.0 (0.0)	3.9			
		4.7		4.0			
TH06		4.8	4.8 (0.0)	4.7	4.0	4.0 (0.0)	4.0
				4.8			4.0
	4.8 (0.0)	4.8	3.9 (0.0)	3.9			
		4.8		3.9			
	VN01	4.8	4.8 (0.0)	4.8	3.8	3.8 (0.0)	3.8
				4.8			3.9
4.8 (0.0)		4.8	3.8 (0.0)	3.9			
		4.8		3.8			
VN02		4.9	4.9 (0.0)	4.9	3.9	3.9 (0.0)	3.9
				4.9			3.9
	4.9 (0.0)	4.9	3.9 (0.0)	3.9			
		4.9		3.9			
	VN03	4.7	4.7 (0.0)	4.7	3.9	3.9 (0.0)	3.8
				4.7			3.9
4.7 (0.0)		4.7	3.9 (0.0)	3.9			
		4.7		3.8			
				4.7			3.9
				4.7			3.9

Note: Value in parenthesis showed standard deviation of triplicate analyses

### Appendix 4.1.2 Entire data of exchangeable base cations in Sample No.101

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na			
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	
CN01	0.25	0.24 (0.02)	0.25	0.20	0.19 (0.00)	0.19	0.15	0.15 (0.00)	0.15	0.04	0.04 (0.00)	0.04	
			0.22			0.19			0.15			0.05	
			0.25			0.19			0.15			0.04	
	0.25 (0.01)	0.24	0.20 (0.00)	0.20	0.15 (0.00)	0.16	0.04 (0.00)	0.05					
		0.26		0.15		0.04							
		0.25		0.15		0.04							
	CN02	0.34	0.33 (0.02)	0.34	0.26	0.26 (0.01)	0.26	0.18	0.18 (0.01)	0.19	0.06	0.06 (0.00)	0.06
				0.35			0.26			0.18			0.06
				0.31			0.25			0.18			0.06
0.34 (0.02)		0.36	0.26 (0.01)	0.26	0.18 (0.00)	0.18	0.06 (0.01)	0.06					
		0.31		0.26		0.19		0.06					
		0.34		0.27		0.19		0.07					
CN03	0.37	0.35 (0.02)	0.37	0.35	0.37 (0.04)	0.41	0.13	0.12 (0.02)	0.10	1.47	1.46 (0.07)	1.54	
			0.33			0.35			0.12			1.43	
			0.35			0.34			0.13			1.42	
	0.39 (0.00)	0.40	0.33 (0.01)	0.34	0.14 (0.01)	0.13	1.48 (0.07)	1.50					
		0.39		0.32		0.14		1.53					
		0.40		0.32		0.14		1.41					
CN04	0.35	0.35 (0.01)	0.34	0.25	0.25 (0.01)	0.24	0.17	0.17 (0.00)	0.17	0.06	0.06 (0.00)	0.06	
			0.36			0.25			0.17			0.05	
			0.34			0.24			0.17			0.06	
	0.35 (0.00)	0.34	0.24 (0.01)	0.24	0.17 (0.00)	0.17	0.06 (0.00)	0.06					
		0.35		0.23		0.17		0.06					
		0.35		0.25		0.18		0.05					
ID01	0.17	0.17 (0.00)	0.17	0.25	0.25 (0.00)	0.25	0.18	0.18 (0.00)	0.17	0.03	0.03 (0.00)	0.03	
			0.17			0.25			0.18			0.03	
			0.17			0.25			0.18			0.03	
	0.17 (0.00)	0.17	0.25 (0.00)	0.25	0.18 (0.00)	0.18	0.03 (0.00)	0.03					
		0.17		0.25		0.17		0.03					
		0.17		0.25		0.18		0.03					
ID04	0.08	0.08 (0.01)	0.07	0.36	0.36 (0.01)	0.37	0.09	0.08 (0.00)	0.08	0.10	0.10 (0.01)	0.10	
			0.07			0.35			0.08			0.09	
			0.09			0.37			0.09			0.09	
	0.08 (0.01)	0.09	0.36 (0.01)	0.37	0.09 (0.00)	0.09	0.10 (0.01)	0.10					
		0.07		0.37		0.09		0.09					
		0.09		0.35		0.08		0.09					
JP06	0.56	0.56 (0.03)	0.54	0.29	0.29 (0.01)	0.29	0.21	0.21 (0.00)	0.22	0.07	0.07 (0.01)	0.07	
			0.59			0.29			0.22			0.07	
			0.54			0.28			0.21			0.08	
	0.55 (0.06)	0.58	0.29 (0.01)	0.30	0.20 (0.00)	0.20	0.06 (0.01)	0.07					
		0.49		0.28		0.20		0.07					
		0.60		0.29		0.20		0.05					
MY04	-	-	-	-	-	-	-	-	-	-	-		
MN01	0.73	0.83 (0.32)	0.60	0.74	0.47 (0.35)	0.50	1.43	1.43 (0.35)	1.80	0.78	0.73 (0.35)	0.70	
			1.20			0.80			1.10			1.10	
			0.70			0.10			1.40			0.40	
	0.63 (0.21)	0.40	1.00 (0.30)	0.70	1.43 (0.57)	1.60	0.83 (0.31)	0.50					
		0.80		1.00		1.90		0.90					
		0.68		1.30		0.80		1.10					
PH03	0.53	0.51 (0.02)	0.53	0.90	0.90 (0.01)	0.90	0.70	0.70 (0.02)	0.68	1.07	1.09 (0.01)	1.08	
			0.52			0.90			0.71			1.11	
			0.49			0.91			0.71			1.09	
	0.54 (0.04)	0.50	0.89 (0.03)	0.86	0.69 (0.02)	0.67	1.04 (0.01)	1.05					
		0.53		0.90		0.69		1.05					
		0.58		0.93		0.71		1.03					
RU01	1.76	1.84 (0.10)	1.89	0.88	0.89 (0.02)	0.92	0.17	0.18 (0.01)	0.19	0.16	0.17 (0.01)	0.15	
			1.72			0.88			0.18			0.18	
			1.90			0.88			0.17			0.17	
	1.67 (0.12)	1.74	0.86 (0.03)	0.89	0.16 (0.01)	0.18	0.15 (0.02)	0.13					
		1.54		0.88		0.16		0.16					
		1.75		0.83		0.15		0.15					
TH01	0.33	0.33 (0.04)	0.34	0.19	0.19 (0.00)	0.19	0.11	0.11 (0.01)	0.11	-	-	0.11	
			0.30			0.19			0.12			0.12	
			0.37			0.20			0.11			0.11	
	0.32 (0.00)	0.32	0.18 (0.02)	0.17	0.11 (0.01)	0.11	-	0.11					
		0.32		0.20		0.12		0.12					
		0.32		0.18		0.09		0.09					
TH06	0.65	0.65 (0.00)	0.64	0.29	0.29 (0.01)	0.30	0.27	0.27 (0.01)	0.27	0.17	0.16 (0.00)	0.15	
			0.65			0.28			0.26			0.16	
			0.65			0.29			0.27			0.16	
	0.64 (0.03)	0.67	0.28 (0.01)	0.29	0.27 (0.02)	0.29	0.18 (0.01)	0.18					
		0.63		0.28		0.26		0.18					
		0.61		0.27		0.26		0.17					
VN01	-	-	-	-	-	-	-	-	-	-	-		
VN02	-	-	-	-	-	-	-	-	-	-	-		
VN03	0.55	0.54 (0.02)	0.55	0.48	0.48 (0.01)	0.48	0.28	0.28 (0.00)	0.28	0.07	0.07 (0.00)	0.07	
			0.55			0.47			0.28			0.06	
			0.51			0.49			0.28			0.06	
	0.55 (0.00)	0.55	0.48 (0.01)	0.48	0.28 (0.00)	0.28	0.07 (0.00)	0.07					
		0.55		0.49		0.28		0.06					
		0.55		0.48		0.28		0.07					

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

### Appendix 4.1.3 Entire data of exchangeable acidity and acid cations in Sample No.101

Lab.	Ex-acidity			Ex-AI			Ex-H		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
CN01	5.16	5.15 (0.05)	5.21	4.12	4.13 (0.06)	4.14	1.04	1.01 (0.06)	1.06
			5.10			4.07			1.03
			5.13			4.19			0.94
			5.19		4.10 (0.03)	4.11		1.07 (0.01)	1.08
			5.18			4.11			1.07
			5.11			4.06			1.05
									1.06
CN02	5.10	5.11 (0.04)	5.15	4.01	4.06 (0.02)	4.05	1.06	1.01 (0.05)	1.06
			5.10			4.08			0.98
			5.08			4.06			0.98
			5.10		3.95 (0.03)	3.97		1.10 (0.03)	1.09
			5.08			3.97			1.07
			5.10			3.92			1.14
									1.06
CN03	6.43	6.14 (0.39)	5.73	5.97	5.68 (0.30)	5.36	0.46	0.46 (0.09)	0.37
			6.17			5.71			0.46
			6.51			5.97			0.54
			6.25		6.26 (0.51)	5.88		0.46 (0.09)	0.37
			7.29			6.83			0.46
			6.60			6.05			0.54
									0.46
CN04	5.15	5.17 (0.02)	5.18	3.73	3.64 (0.02)	3.62	1.38	1.44 (0.03)	1.47
			5.19			3.66			1.43
			5.14			3.65			1.40
			5.13 (0.02)		3.82 (0.01)	3.81		1.32 (0.03)	1.33
			5.15			3.82			1.34
			5.12			3.84			1.29
									1.47
ID01	5.26	5.25 (0.00)	5.25	3.46	3.45 (0.05)	3.48	1.81	1.80 (0.05)	1.77
			5.25			3.39			1.86
			5.26			3.48			1.77
			5.27 (0.00)		3.46 (0.05)	3.49		1.82 (0.04)	1.78
			5.27			3.40			1.86
			5.27			3.49			1.82
									1.86
ID04	3.27	3.27 (0.01)	3.28	2.79	2.79 (0.01)	2.80	0.49	0.49 (0.00)	0.49
			3.26			2.77			0.49
			3.28			2.80			0.49
			3.27 (0.01)		2.78 (0.01)	2.77		0.49 (0.00)	0.49
			3.26			2.77			0.49
			3.26			2.80			0.49
			3.28			2.80			0.49
JP06	5.14	5.06 (0.03)	5.05	4.31	4.29 (0.06)	4.22	0.88	0.93 (0.06)	1.00
			5.04			4.33			0.89
			5.10			4.30			0.89
			5.22 (0.09)		4.32 (0.19)	4.53		0.82 (0.07)	0.76
			5.13			4.19			0.80
			5.21			4.23			0.90
									0.87
MY04	5.21	5.21 (0.00)	5.21	4.34	4.34 (0.00)	4.34	0.87	0.87 (0.00)	0.87
			5.21			4.34			0.87
			5.21			4.34			0.87
			5.21 (0.00)		4.34 (0.00)	4.34		0.87 (0.00)	0.87
			5.21			4.34			0.87
			5.21			4.34			0.87
									0.87
MN01	1.77	1.71 (0.07)	1.66	0.10	0.12 (0.01)	0.10	1.67	1.59 (0.07)	1.56
			1.79			0.12			1.66
			1.66			0.12			1.54
			1.83 (0.04)		0.08 (0.02)	0.10		1.75 (0.02)	1.77
			1.83			0.08			1.75
			1.79			0.06			1.73
									1.73
PH03	4.65	4.63 (0.06)	4.57	4.21	4.20 (0.05)	4.16	0.44	0.43 (0.01)	0.42
			4.63			4.19			0.44
			4.69			4.25			0.44
			4.66 (0.01)		4.21 (0.03)	4.24		0.44 (0.01)	0.42
			4.65			4.21			0.44
			4.65			4.19			0.44
									0.44
RU01	5.72	5.84 (0.41)	6.13	5.54	5.75 (0.57)	6.40	0.11	0.11 (0.00)	0.11
			5.37			5.32			0.11
			6.02			5.53			0.11
			5.59 (0.43)		5.32 (0.38)	5.53		0.11 (0.00)	0.11
			5.59			4.88			0.11
			5.15			5.53			0.11
									0.11
TH01	5.65	5.55 (0.18)	5.57	3.81	3.59 (0.05)	3.56	1.27	1.55 (0.16)	1.74
			5.71			3.56			1.45
			5.36			3.64			1.46
			5.74 (0.06)		4.02 (0.10)	4.08		0.99 (0.14)	1.12
			5.69			4.08			0.84
			5.81			3.91			1.01
									1.01
TH06	5.25	5.23 (0.00)	5.23	5.12	5.11 (0.02)	5.09	0.14	0.13 (0.02)	0.14
			5.23			5.09			0.14
			5.23			5.13			0.10
			5.27 (0.03)		5.12 (0.02)	5.14		0.15 (0.01)	0.15
			5.23			5.09			0.14
			5.28			5.13			0.15
									0.15
VN01	4.56	4.56 (0.01)	4.56	3.99	3.98 (0.04)	3.96	0.58	0.58 (0.03)	0.60
			4.55			3.96			0.59
			4.57			4.03			0.54
			4.56 (0.00)		3.99 (0.02)	4.00		0.58 (0.02)	0.57
			4.56			3.97			0.60
			4.57			4.00			0.57
									0.60
VN02	4.88	4.88 (0.03)	4.84	4.46	4.44 (0.06)	4.40	0.59	0.59 (0.00)	0.59
			4.89			4.51			0.60
			4.89			4.40			0.60
			4.88 (0.03)		4.47 (0.06)	4.40		0.59 (0.00)	0.59
			4.89			4.51			0.60
			4.84			4.51			0.60
									0.60
VN03	5.53	5.53 (0.04)	5.48	9.67	9.67 (0.43)	10.12	0.61	0.61 (0.15)	0.77
			5.55			9.61			0.47
			5.55			9.27			0.60
			5.52 (0.03)		9.67 (0.43)	10.12		0.61 (0.15)	0.77
			5.49			9.61			0.47
			5.55			9.27			0.60
			5.53			9.27			0.60

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

### Appendix 4.2.1 Entire data of pH in Sample No.102

Lab.	pH(H <sub>2</sub> O)			pH(KCl)		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
CN01	5.0	4.9 (0.0)	4.9	3.9	3.9 (0.0)	3.9
			5.0			3.9
			5.0			3.9
			4.9			3.9
			5.0			3.9
			5.0			3.9
CN02	4.9	4.9 (0.0)	4.9	4.1	4.1 (0.0)	4.1
			4.9			4.1
			4.9			4.1
			4.9			4.1
			4.9			4.1
			4.9			4.1
CN03	4.9	4.9 (0.0)	4.9	4.0	4.0 (0.0)	4.1
			4.9			4.0
			4.9			4.0
			4.9			4.1
			4.9			4.1
			4.9			4.0
CN04	4.8	4.7 (0.0)	4.7	4.0	4.0 (0.0)	4.0
			4.8			4.0
			4.7			4.0
			4.8			4.0
			4.8			3.9
			4.8			3.9
ID01	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			3.8
			4.8			3.8
			4.8			3.8
ID04	4.6	4.6 (0.0)	4.7	4.0	4.0 (0.0)	4.0
			4.6			4.0
			4.6			4.0
			4.6			4.0
			4.7			4.0
			4.7			4.0
JP06	5.0	5.0 (0.0)	5.0	3.9	3.9 (0.0)	3.9
			5.0			3.9
			5.0			3.9
			5.0			3.9
			5.0			3.9
			5.0			3.9
MN01	4.7	4.7 (0.0)	4.7	3.9	3.9 (0.0)	3.9
			4.7			3.9
			4.7			3.9
			4.7			3.9
			4.7			4.0
			4.7			4.0
MY04	4.6	4.6 (0.0)	4.6	3.7	3.6 (0.0)	3.6
			4.6			3.6
			4.6			3.6
			4.6			3.7
			4.5			3.7
			4.6			3.6
PH03	4.9	4.8 (0.2)	4.7	4.1	4.0 (0.1)	3.9
			4.7			4.0
			5.0			4.1
			5.0			4.2
			4.9			4.2
			4.8			4.2
RU01	4.7	4.7 (0.0)	4.7	4.0	4.0 (0.0)	4.0
			4.7			4.0
			4.7			4.0
			4.7			4.0
			4.7			4.0
			4.7			4.0
TH01	4.8	4.8 (0.0)	4.8	4.0	3.9 (0.0)	3.9
			4.8			3.9
			4.8			3.9
			4.8			4.0
			4.8			4.0
			4.9			4.0
TH06	4.9	4.9 (0.0)	4.9	3.9	3.9 (0.0)	4.0
			4.9			3.9
			4.9			4.0
			4.9			3.9
			4.8			3.9
			4.8			3.9
VN01	4.8	4.8 (0.0)	4.8	3.9	3.8 (0.0)	3.8
			4.8			3.8
			4.9			3.9
			4.8			3.9
			4.9			3.9
			4.9			3.9
VN02	4.9	4.9 (0.0)	4.9	3.9	3.9 (0.0)	3.9
			4.9			3.9
			4.9			3.9
			4.9			3.9
			4.9			3.9
			4.9			3.9
VN03	4.8	4.8 (0.0)	4.8	3.8	3.8 (0.0)	3.8
			4.8			3.8
			4.8			3.8
			4.8			3.8
			4.8			3.8
			4.8			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.102

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
CN01	0.17	0.17 (0.02)	0.15 0.16 0.19 0.17 0.19 0.16	0.32	0.32 (0.00)	0.31 0.31 0.32 0.32 0.32 0.33	0.21	0.21 (0.00)	0.21 0.21 0.21 0.21 0.22 0.22	0.04	0.04 (0.01)	0.03 0.04 0.04 0.05 0.04 0.04
CN02	0.25	0.23 (0.02)	0.22 0.25 0.23 0.27 0.27 0.28	0.38	0.37 (0.02)	0.38 0.39 0.35 0.37 0.39 0.41	0.25	0.24 (0.01)	0.23 0.25 0.23 0.26 0.26 0.25	0.06	0.05 (0.00)	0.05 0.05 0.05 0.05 0.06 0.06 0.07
CN03	0.27	0.28 (0.03)	0.31 0.26 0.26 0.25 0.25	0.37	0.35 (0.01)	0.34 0.36 0.35 0.37 0.38 0.38	0.25	0.25 (0.00)	0.24 0.25 0.25 0.24 0.26 0.26	0.16	0.15 (0.00)	0.16 0.15 0.16 0.16 0.15 0.16
CN04	0.30	0.30 (0.01)	0.30 0.31 0.29 0.30 0.31 0.31	0.39	0.39 (0.01)	0.39 0.40 0.38 0.39 0.39 0.39	0.23	0.23 (0.01)	0.23 0.23 0.22 0.22 0.21 0.22	0.04	0.04 (0.00)	0.04 0.04 0.05 0.04 0.04 0.03
ID01	0.13	0.13 (0.00)	0.13 0.13 0.13 0.12 0.13 0.13	0.47	0.47 (0.00)	0.48 0.47 0.47 0.48 0.47 0.46	0.24	0.24 (0.01)	0.24 0.25 0.24 0.24 0.24 0.23	0.02	0.02 (0.00)	0.02 0.02 0.02 0.02 0.02 0.02
ID04	0.06	0.06 (0.01)	0.06 0.05 0.05 0.06 0.06 0.05	0.50	0.50 (0.00)	0.50 0.50 0.50 0.50 0.48 0.50	0.12	0.12 (0.01)	0.11 0.12 0.12 0.12 0.12 0.12	0.12	0.12 (0.01)	0.11 0.11 0.12 0.12 0.11 0.11
JP06	0.47	0.45 (0.02)	0.44 0.47 0.43 0.48 0.40 0.51	0.48	0.47 (0.01)	0.46 0.48 0.48 0.61 0.38 0.48	0.25	0.25 (0.01)	0.24 0.26 0.26 0.26 0.23 0.27	0.06	0.06 (0.01)	0.08 0.05 0.06 0.03 0.06 0.05
MN01	-	-	-	-	-	-	-	-	-	-	-	-
MY04	0.87	0.73 (0.25)	0.50 1.00 0.70 0.90 0.73 1.40	1.12	1.23 (0.68)	2.00 1.00 0.70 1.20 1.30 0.50	1.57	1.53 (0.25)	1.80 1.50 1.30 1.90 1.40 1.50	0.64	0.47 (0.25)	0.20 0.70 0.50 0.90 1.10 0.40
PH03	0.39	0.38 (0.02)	0.37 0.37 0.40 0.39 0.39 0.41	0.89	0.89 (0.01)	0.88 0.91 0.89 0.86 0.90 0.92	0.79	0.80 (0.02)	0.82 0.77 0.80 0.80 0.76 0.79	1.04	1.03 (0.03)	1.06 1.00 1.02 1.05 1.03 1.04
RU01	0.38	0.37 (0.01)	0.37 0.37 0.38 0.39 0.42 0.38	0.49	0.49 (0.02)	0.47 0.50 0.51 0.45 0.48 0.45	0.30	0.30 (0.01)	0.31 0.31 0.29 0.31 0.29 0.29	0.17	0.17 (0.01)	0.18 0.17 0.18 0.17 0.15 0.17
TH01	0.32	0.31 (0.01)	0.31 0.32 0.29 0.32 0.33 0.34	0.35	0.34 (0.02)	0.33 0.36 0.34 0.34 0.38 0.37	0.14	0.14 (0.01)	0.14 0.15 0.14 0.10 0.18 0.16	-0.04	-0.03 (0.01)	-0.02 -0.04 -0.03 -0.10 -0.03 -0.03
TH06	0.70	0.71 (0.02)	0.72 0.72 0.69 0.69 0.69	0.50	0.49 (0.02)	0.50 0.50 0.46 0.51 0.50 0.51	0.38	0.37 (0.02)	0.34 0.38 0.38 0.34 0.41 0.39	0.35	0.36 (0.03)	0.33 0.38 0.37 0.33 0.35 0.35
VN01	-	-	-	-	-	-	-	-	-	-	-	-
VN02	-	-	-	-	-	-	-	-	-	-	-	-
VN03	4.71	4.71 (0.01)	4.71 4.69 4.72 4.70 4.72 4.72	0.83	0.83 (0.03)	0.80 0.82 0.86 0.81 0.82 0.84	0.36	0.36 (0.01)	0.35 0.36 0.37 0.35 0.36 0.36	0.04	0.04 (0.00)	0.04 0.04 0.05 0.04 0.04 0.05

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.102

Lab.	Ex-acidity			Ex-Al cmol(+) kg <sup>-1</sup>			Ex-H		
	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat	Lab. Ave.	Average	repeat
CN01	5.79	5.78 (0.10)	5.86	4.69	4.69 (0.05)	4.74	1.10	1.08 (0.09)	1.12
			5.80			4.65			1.15
			5.67			4.69			0.98
		5.80 (0.07)	5.73	4.68 (0.05)	4.62	1.12 (0.03)	1.12		
			5.79		4.69		1.09		
			5.87		4.71		1.16		
CN02	5.98	5.96 (0.02)	5.97	4.53	4.52 (0.03)	4.49	1.41	1.40 (0.04)	1.45
			5.94			4.53			1.37
			5.96			4.53			1.38
		6.00 (0.01)	6.01	4.54 (0.03)	4.56	1.42 (0.04)	1.40		
			6.01		4.50		1.47		
			5.99		4.55		1.40		
CN03	7.50	7.18 (0.22)	7.26	6.89	6.59 (0.25)	6.67	0.61	0.59 (0.03)	0.59
			7.35			6.79			0.56
			6.93			6.30			0.63
		7.81 (0.40)	8.04	7.19 (0.40)	7.42	0.63 (0.00)	0.63		
			7.35		6.72		0.63		
			8.04		7.42		0.63		
CN04	5.63	5.65 (0.02)	5.65	4.25	4.19 (0.06)	4.19	1.33	1.35 (0.04)	1.34
			5.66			4.24			1.32
			5.63			4.13			1.39
		5.60 (0.03)	5.61	4.30 (0.03)	4.27	1.30 (0.04)	1.33		
			5.62		4.32		1.30		
			5.56		4.31		1.25		
ID01	5.26	5.30 (0.00)	5.30	3.70	3.72 (0.05)	3.77	1.61	1.63 (0.05)	1.57
			5.30			3.69			1.66
			5.30			3.69			1.66
		5.22 (0.06)	5.30	3.68 (0.00)	3.68	1.58 (0.06)	1.66		
			5.18		3.68		1.55		
			5.19		3.68		1.55		
ID04	3.45	3.45 (0.01)	3.44	2.92	2.92 (0.01)	2.91	0.53	0.53 (0.00)	0.53
			3.46			2.93			0.53
			3.46			2.93			0.53
		3.44 (0.00)	3.44	2.91 (0.01)	2.91	0.53 (0.01)	0.53		
			3.44		2.91		0.53		
			3.44		2.93		0.51		
JP06	5.37	5.54 (0.09)	5.45	4.47	4.49 (0.02)	4.51	0.85	0.85 (0.09)	0.75
			5.55			4.47			0.87
			5.63			4.49			0.93
		5.19 (0.07)	5.23	4.44 (0.09)	4.47	0.84 (0.10)	0.79		
			5.11		4.34		0.95		
			5.24		4.52		0.78		
MN01	4.39	4.39 (0.00)	4.39	3.51	3.51 (0.00)	3.51	0.88	0.88 (0.00)	0.88
			4.39			3.51			0.88
			4.39			3.51			0.88
		4.39 (0.00)	4.39	3.51 (0.00)	3.51	0.88 (0.00)	0.88		
			4.39		3.51		0.88		
			4.39		3.51		0.88		
MY04	1.93	2.00 (0.09)	1.97	0.16	0.14 (0.03)	0.14	1.77	1.86 (0.06)	1.83
			2.09			0.16			1.93
			1.93			0.10			1.83
		1.85 (0.00)	1.85	0.18 (0.03)	0.14	1.67 (0.03)	1.70		
			1.85		0.21		1.64		
			1.85		0.20		1.66		
PH03	4.77	4.77 (0.02)	4.78	4.29	4.28 (0.01)	4.28	0.48	0.48 (0.02)	0.50
			4.75			4.29			0.46
			4.76			4.28			0.48
		4.77 (0.01)	4.77	4.29 (0.01)	4.29	0.48 (0.01)	0.48		
			4.76		4.28		0.48		
			4.77		4.30		0.47		
RU01	5.70	5.44 (0.56)	6.09	6.04	5.79 (0.38)	6.14	0.09	0.07 (0.06)	0.11
			5.12			5.82			0.11
			5.12			5.39			0.00
		5.95 (0.12)	6.09	6.29 (0.12)	6.36	0.11 (0.00)	0.11		
			5.88		6.14		0.11		
			5.88		6.29		0.11		
TH01	5.58	5.34 (0.05)	5.36	4.07	3.95 (0.05)	3.90	1.08	1.12 (0.10)	1.02
			5.29			3.98			1.22
			5.38			3.98			1.12
		5.82 (0.25)	6.10	4.19 (0.10)	4.25	1.04 (0.07)	0.98		
			5.62		4.08		1.02		
			5.74		4.25		1.12		
TH06	5.87	5.83 (0.00)	5.83	5.48	5.44 (0.02)	5.43	0.39	0.39 (0.02)	0.41
			5.83			5.43			0.41
			5.83			5.47			0.36
		5.90 (0.03)	5.88	5.52 (0.02)	5.51	0.38 (0.01)	0.37		
			5.88		5.51		0.37		
			5.93		5.55		0.38		
VN01	5.13	5.13 (0.02)	5.14	4.16	4.16 (0.03)	4.19	0.98	0.98 (0.03)	0.95
			5.14			4.13			1.00
			5.11			4.14			0.97
		5.13 (0.02)	5.12	4.16 (0.01)	4.17	0.97 (0.02)	0.94		
			5.15		4.17		0.98		
			5.12		4.15		0.97		
VN02	5.51	5.49 (0.03)	5.46	5.00	5.00 (0.06)	4.92	0.58	0.58 (0.00)	0.59
			5.51			5.03			0.59
			5.51			5.03			0.58
		5.53 (0.03)	5.51	5.00 (0.06)	5.03	0.58 (0.00)	0.59		
			5.51		4.92		0.58		
			5.56		5.03		0.59		
VN03	5.20	5.19 (0.16)	5.20	8.89	8.89 (0.31)	8.81	0.50	0.50 (0.05)	0.56
			5.34			9.24			0.47
			5.02			8.64			0.47
		5.20 (0.15)	5.20	8.89 (0.31)	8.81	0.50 (0.05)	0.56		
			5.34		9.24		0.47		
			5.05		8.64		0.47		

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



## 5. 11<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

### 5.1 Introduction

In the 11<sup>th</sup> inter-laboratory comparison of inland aquatic environment, artificial inland aquatic environment samples containing known concentrations of major ions, were prepared and sent to the participating countries of EANET by the Network Center (NC) in October 2010. Almost all the participating laboratories submitted their analytical data to NC. The measurement of pH, EC, Alkalinity and concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  from the participating countries were compared with the prepared values and the results were statistically analyzed.

### 5.2 Procedure

#### 5.2.1 Participating Laboratories

The Network Center (NC) shipped artificial inland aquatic environment samples to 22 laboratories which participate in EANET activities on October 6 in 2010, and almost all of them submitted their analytical data to NC by March 30 in 2011. All participating laboratories and their codes are listed in Table 1.1. For this attempt, the laboratory ID06 submitted the data of 7 parameters, pH, EC, Alkalinity and concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$ . The laboratory MY03 submitted the data of 3 parameters, pH, EC and Alkalinity. Furthermore, the laboratory VN03 submitted all the data except  $\text{NO}_3^-$ .

#### 5.2.2 Description Samples

A description of the samples is given in Table 5.1.

**Table 5.1 Description of the artificial inland aquatic environment sample**

Name	Amount of the sample	Container	Number of samples	Note
Artificial inland aquatic environment sample	Approximately 1L	Poly-ethylene 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 per meter	mS m <sup>-1</sup>
Alkalinity	milli equivalent per liter	meq L <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	milli gram per liter	mg L <sup>-1</sup>
NO <sub>3</sub> <sup>-</sup>	milli gram per liter	mg L <sup>-1</sup>
Cl <sup>-</sup>	milli gram per liter	mg L <sup>-1</sup>
Na <sup>+</sup>	milli gram per liter	mg L <sup>-1</sup>
K <sup>+</sup>	milli gram per liter	mg L <sup>-1</sup>
Ca <sup>2+</sup>	milli gram per liter	mg L <sup>-1</sup>
Mg <sup>2+</sup>	milli gram per liter	mg L <sup>-1</sup>
NH <sub>4</sub> <sup>+</sup>	milli gram per liter	mg L <sup>-1</sup>

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 <sup>+</sup>	1 – 10 mg L <sup>-1</sup>
EC	1.5 – 15 mS m <sup>-1</sup>	K <sup>+</sup>	0.2 – 2.0 mg L <sup>-1</sup>
Alkalinity	0.05 – 0.5 meq L <sup>-1</sup>	Ca <sup>2+</sup>	1 – 10 mg L <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	2 – 20 mg L <sup>-1</sup>	Mg <sup>2+</sup>	0.2 – 2.0 mg L <sup>-1</sup>
NO <sub>3</sub> <sup>-</sup>	0.5 – 5 mg L <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup>	0.05 – 0.5 mg L <sup>-1</sup>
Cl <sup>-</sup>	1 – 10 mg L <sup>-1</sup>		

### 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 <sub>4</sub> <sup>2-</sup> NO <sub>3</sub> <sup>-</sup>	Ion Chromatography or Spectrophotometry
Cl <sup>-</sup>	Ion Chromatography or Titration
Na <sup>+</sup> K <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup>	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography or Spectrophotometry (Indophenol blue)

#### 5.2.4 Data Checking Procedures

##### a) Calculation of ion balance (R<sub>1</sub>)

(1) Total anion (A) equivalent concentration (μeq L<sup>-1</sup>) is calculated by sum up the concentration of anions (C: μmol L<sup>-1</sup>) and Alkalinity (ALK: μeq L<sup>-1</sup>). Alkalinity considered to be corresponded to bicarbonate ions (HCO<sub>3</sub><sup>-</sup>).

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

C<sub>Ai</sub>: electric charge of ion and concentration (μmol L<sup>-1</sup>) of anion “i”.

(2) Total cation (C) equivalent concentration (μeq L<sup>-1</sup>) is calculated by sum up the concentration of all cations (C: μmol L<sup>-1</sup>).

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

C<sub>Ci</sub>: electric charge of ion and concentration (μmol L<sup>-1</sup>) of cation “i”.

(3) Calculation of ion balance (R<sub>1</sub>)

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

(4) R<sub>1</sub>, 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<sub>1</sub> is not within the range.

**Table 5.5 Allowable ranges for R<sub>1</sub> in different concentration ranges**

(C+A) [ $\mu\text{eq L}^{-1}$ ]	R <sub>1</sub> [%]
< 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<sub>2</sub>)

(1) Total electric conductivity ( $\Lambda_{\text{calc}}$ ) is calculated as follows;

$$\Lambda_{\text{calc}} (\text{mS m}^{-1}) = \{349.7 \times 10^{(3-\text{pH})} + 80.0 \times C (\text{SO}_4^{2-}) + 71.5 \times C (\text{NO}_3^-) + 76.3 \times C (\text{Cl}^-) + 73.5 \times C (\text{NH}_4^+) + 50.1 \times C (\text{Na}^+) + 73.5 \times C (\text{K}^+) + 59.8 \times C (\text{Ca}^{2+}) + 53.3 \times C (\text{Mg}^{2+}) + 44.5 \times (\text{ALK})\} / 10000$$

C: Molar concentrations ( $\mu\text{mol L}^{-1}$ ) of ions in the parenthesis; each constant value is ionic equivalent conductance at 25°C. Alkalinity considered to be corresponded to bicarbonate ions ( $\text{HCO}_3^-$ ).

(2) Ratio (R<sub>2</sub>) of calculations ( $\Lambda_{\text{calc}}$ ) to measurements ( $\Lambda_{\text{meas}}$ ) in electric conductivity is calculated as follows;

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

(3) R<sub>2</sub>, 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<sub>2</sub> is not within the range.

**Table 5.6 Allowable ranges for R<sub>2</sub> in different concentration ranges**

$\Lambda_{\text{meas}} [\text{mS m}^{-1}]$	R <sub>2</sub> [%]
< 0.5	+20 ~ -20
0.5 ~ 3	+13 ~ -13
> 3	+9 ~ -9

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

## 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. Outlying data that apart from the average three times greater than S.D. is not included for the calculation in Table 5.7. As shown in Table 5.7, average of submitted data agreed fairly well with the prepared value/concentration within a range of  $\pm 10\%$ .

**Table 5.7 Summary of analytical results of the artificial inland aquatic environment sample**  
(Reported data after outliers were removed)

Constituents	Prepared	Average	S.D.	N	Min.	Max.
pH	7.30	7.05	0.20	21	6.61	7.40
EC (mS m <sup>-1</sup> )	5.35	5.23	0.10	20	5.01	5.37
Alkalinity (meq L <sup>-1</sup> )	0.198	0.199	0.02	21	0.160	0.260
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	3.78	3.78	0.25	19	3.10	4.20
NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	0.89	0.91	0.07	19	0.84	1.09
Cl <sup>-</sup> (mg L <sup>-1</sup> )	5.92	5.93	0.31	19	4.93	6.51
Na <sup>+</sup> (mg L <sup>-1</sup> )	5.43	5.40	0.16	18	5.06	5.71
K <sup>+</sup> (mg L <sup>-1</sup> )	1.32	1.25	0.11	19	0.96	1.50
Ca <sup>2+</sup> (mg L <sup>-1</sup> )	1.24	1.36	0.23	19	1.01	2.01
Mg <sup>2+</sup> (mg L <sup>-1</sup> )	1.33	1.37	0.08	19	1.23	1.56
NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	0.30	0.32	0.09	20	0.18	0.57

(note) Prepared: value calculated from the amount of chemicals used for the preparation of samples. S.D.: standard deviation, N: number of data, Min: the minimum data, Max: the maximum data

The Data Quality Objectives (DQOs) of EANET is specified for every constituent as  $\pm 15\%$  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 ( $\pm 15\%$  -  $\pm 30\%$ ) 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”.

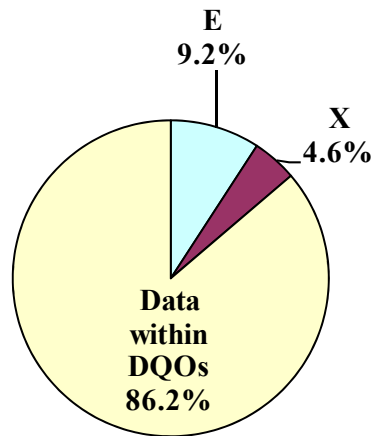
Table 5.8 shows the number of flagged data for each parameters and Figure 5.1 shows the percentage of flagged data.

**Table 5.8 Number of flagged data**

Flag *	pH	EC	Alkalinity	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Total	Ratio
E	0	0	2	1	2	1	1	2	5	1	5	20	9.2%
X	0	1	1	1	0	1	0	0	2	0	4	10	4.6%
Data within DQOs	21	20	18	18	17	18	18	17	12	18	11	188	86.2%
Flagged(%)	0.0	4.8	14.3	10.0	10.5	10.0	5.3	10.5	36.8	5.3	45.0	13.8	

\*E : Value exceeded the DQO by a factor of 2 of the DQO ( $\pm 15\%$  -  $\pm 30\%$ )

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



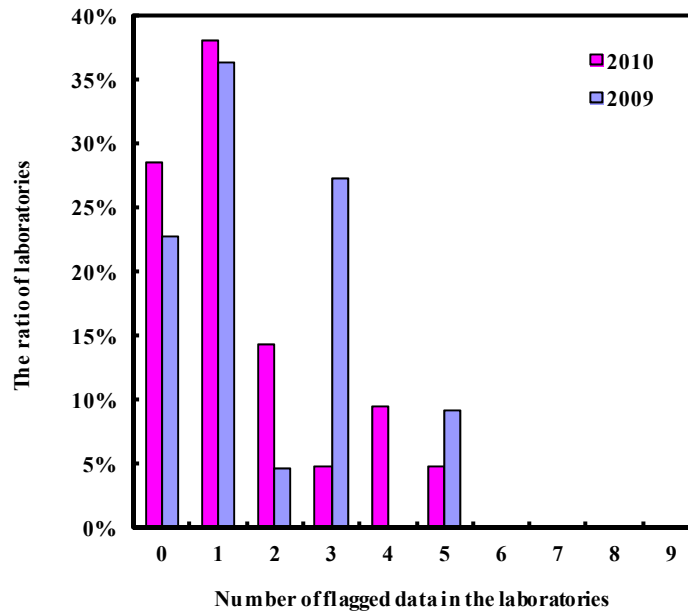
**Figure 5.1 Percentage of flagged data**

The data flagged by "E", which exceeded the DQOs within a factor of 2, shared 9.2% of all the reported data of samples. Furthermore, the data flagged by "X", which exceeded the DQOs more than a factor of 2, shared 4.6% of all the reported data of samples. Concerning respective parameters, the percentage of flagged Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> were comparatively high, more than 30%.

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

**Table 5.9 Number of flagged data in each laboratory**

Number of flagged data	Number of laboratories	Ratio
0	6	29%
1	8	38%
2	3	14%
3	1	5%
4	2	10%
5	1	5%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	21	100%



**Figure 5.2 Distribution of laboratories with the number of flagged data**

The percentage of the laboratories without flagged data was 23% in last attempt (2009), and that of this year was 29%. There was one laboratory that has five flagged data in this attempt.

**Table 5.10 Analytical Results of Sample No.101i (artificial inland aquatic environment sample : E/ANET in 2010)**

Lab. ID	pH	EC (mS m <sup>-1</sup> )	Alkalinity (meq L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	Cl <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	K <sup>+</sup> (mg L <sup>-1</sup> )	Ca <sup>2+</sup> (mg L <sup>-1</sup> )	Mg <sup>2+</sup> (mg L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	R1	R2
CN01	7.17	5.18	0.19	3.80	0.89	6.06	5.47	1.37	E 1.44	1.44	0.30	2.76	3.17
CN02	7.11	5.17	0.19	3.74	0.88	5.89	5.50	1.25	1.28	1.41	0.27	1.95	1.99
CN03	7.10	5.03	0.19	3.74	0.88	5.90	5.50	1.28	1.42	1.44	0.27	3.00	4.00
CN04	7.08	5.32	0.20	3.63	0.94	5.91	5.29	1.26	E 1.59	1.50	0.29	2.37	1.83
ID01	7.06	5.24	E 0.16	4.09	0.94	6.51	5.71	1.24	1.24	1.34	E 0.37	3.11	2.33
ID05	6.71	5.31	0.20	X 5.61	E 1.08	6.45	5.34	E 0.96	X 2.01	1.26	X 0.18	-4.68	5.42
ID06	7.00	5.37	E 0.23	4.20	E 1.09	E 4.93					E 0.35	-	-
JP04	7.15	5.36	0.21	3.70	0.86	5.99	5.24	1.29	1.21	1.28	0.31	-2.87	0.14
JP05	7.17	5.21	0.20	3.46	0.84	5.89	5.36	1.23	1.23	1.38	0.32	0.67	1.21
MN01	6.64	5.19	0.18	3.74	0.85	5.95	5.17	1.34	E 1.48	E 1.56	X 0.47	5.18	2.99
MY01	6.83	5.29	0.21	3.84	0.91	6.07	5.53	1.32	1.22	1.35	0.29	-1.14	1.94
MY03	6.99	X 52.60	X 0.26									-	-
PH01	7.07	5.09	0.18	3.85	0.89	5.89	5.39	1.26	1.24	1.35	0.31	1.85	2.16
PH02	6.98	5.30	0.20	3.78	0.93	5.71	5.26	1.23	X 1.70	1.36	0.29	1.61	1.57
RU01	7.23	5.21	0.18	3.86	0.91	6.00	5.41	1.25	1.12	1.31	E 0.36	0.63	0.97
RU02	7.20	5.30	0.19	4.20	0.91	5.85	5.50	1.50	E 1.01	1.24	E 0.36	-0.54	0.68
TH01	7.40	5.13	0.21	3.67	0.87	5.92	5.06	1.15	1.25	1.23	E 0.24	-4.93	1.28
TH02	6.61	5.01	0.18	3.81	0.85	5.98	5.39	1.29	E 1.44	1.41	0.29	3.28	3.83
VN01	7.18	5.34	0.20	3.61	0.88	5.93	5.64	1.20	1.30	1.35	X 0.20	0.70	0.49
VN02	7.22	5.24	0.21	4.02	0.87	5.87	5.46	1.21	1.35	1.40	X 0.57	1.07	3.69
VN03	7.21	5.23	0.21	E 3.10	X 0.87	X 8.14	E 4.19	E 1.05	1.25	1.33	0.33	-	-
Expected value	7.30	5.35	0.20	3.78	0.89	5.92	5.43	1.32	1.24	1.33	0.30	-	-

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

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

### 5.3.2 Evaluation of laboratories' performance (by analytical parameters)

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

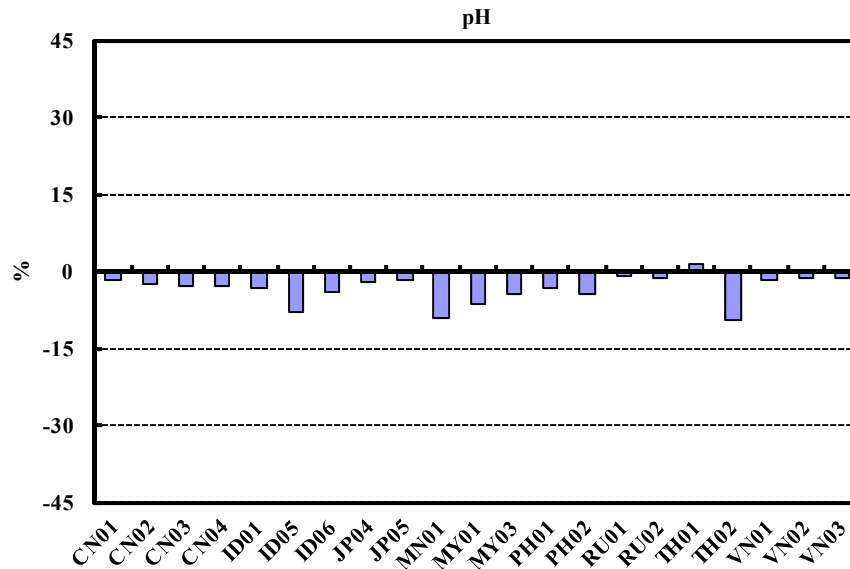


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

All the obtained data of pH were within DQOs.

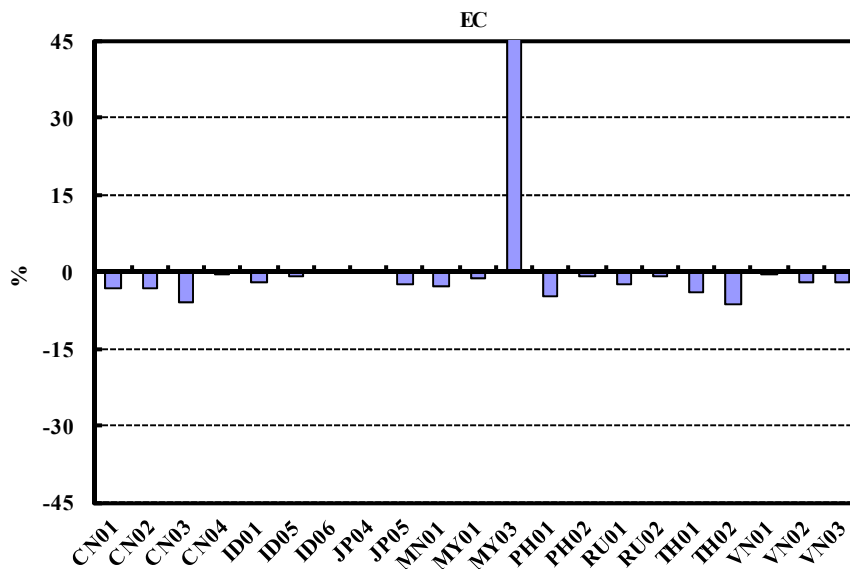
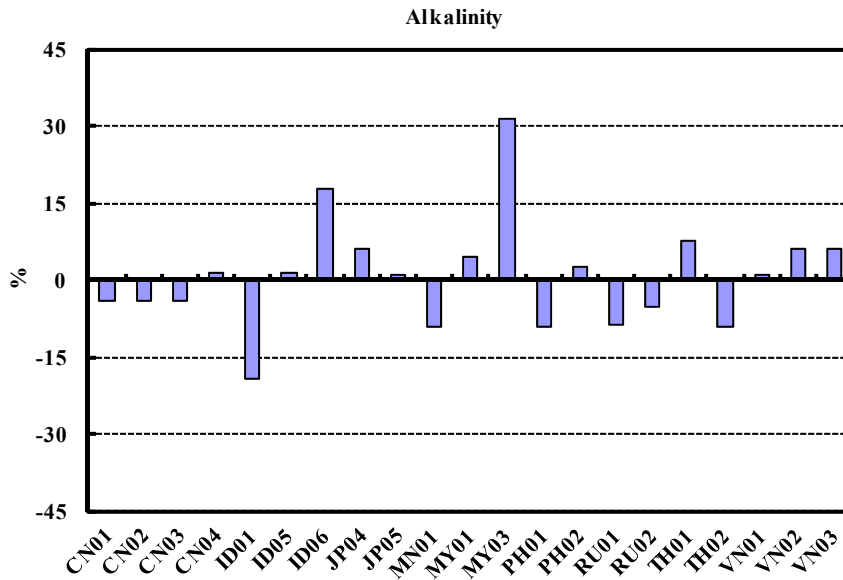


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

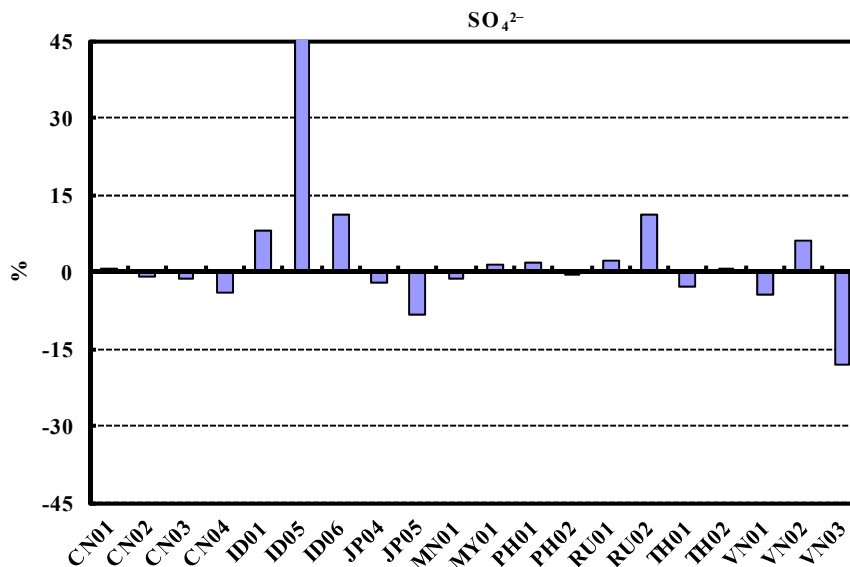
Except for MY03, all the obtained data of EC were within DQOs. They were close to the

prepared value and their differences between laboratories were small, although the data of MY03 exceeds DQOs extremely.



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

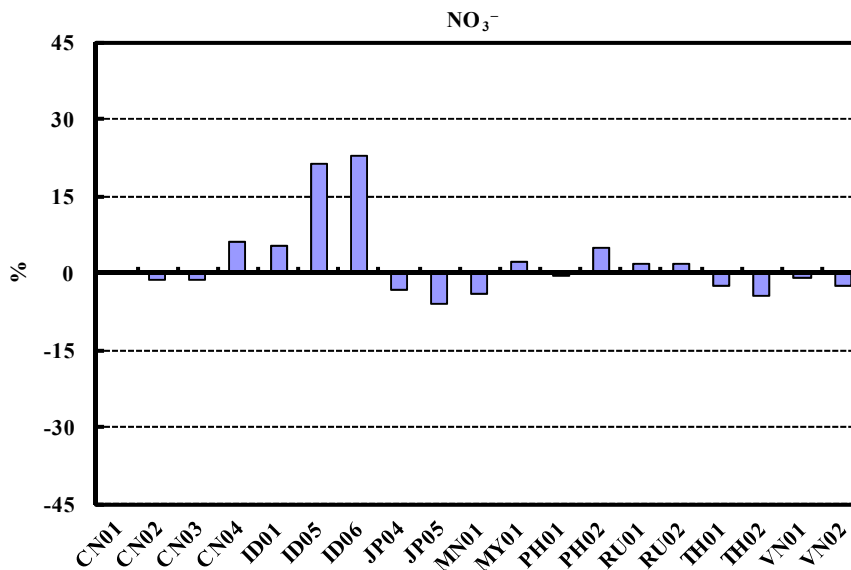
Data from three laboratories were flagged. Especially one of them was comparatively deviated from the prepared value.



**Figure 5.6 Distribution of results for SO<sub>4</sub><sup>2-</sup> (normalized by prepared concentration)**

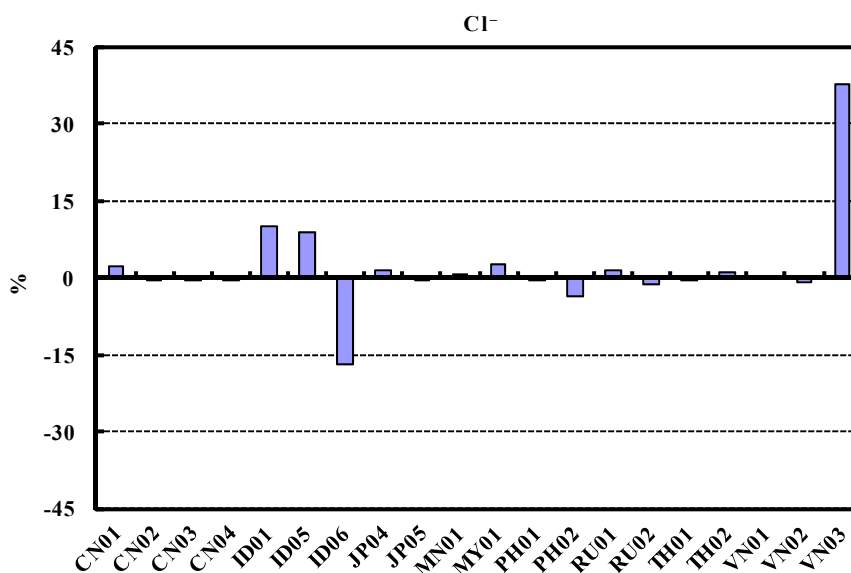
Data from two laboratories were flagged. Especially one of them was significantly deviated from the prepared value. Most of the participating laboratories used ion chromatography for the

determination of  $\text{SO}_4^{2-}$ , and there was no flagged data in these laboratories. Four laboratories used spectrophotometry and two of them were flagged.



**Figure 5.7 Distribution of results for  $\text{NO}_3^-$  (normalized by prepared concentration)**

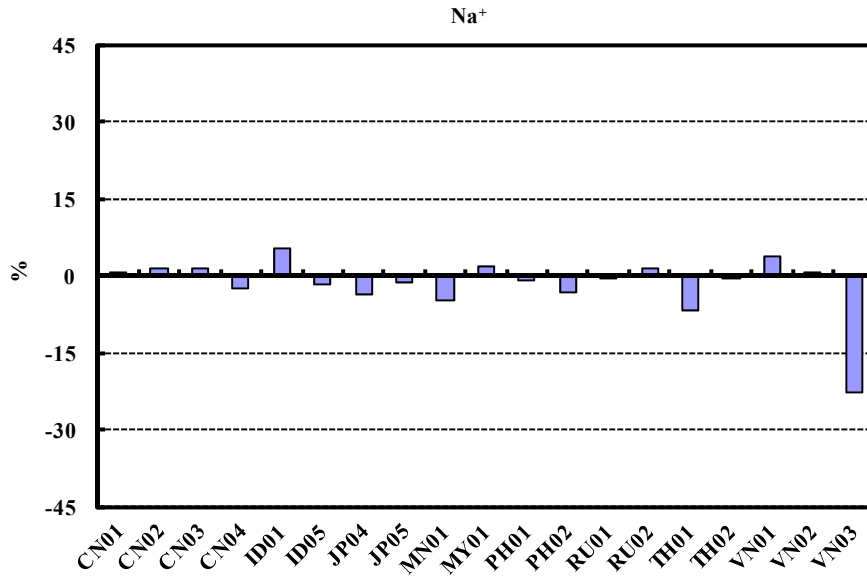
Data from two laboratories were flagged. Most of the participating laboratories used ion chromatography for the determination of  $\text{NO}_3^-$ , and there was no flagged data in these laboratories. Three laboratories used spectrophotometry and two of them were flagged.



**Figure 5.8 Distribution of results for  $\text{Cl}^-$  (normalized by prepared concentration)**

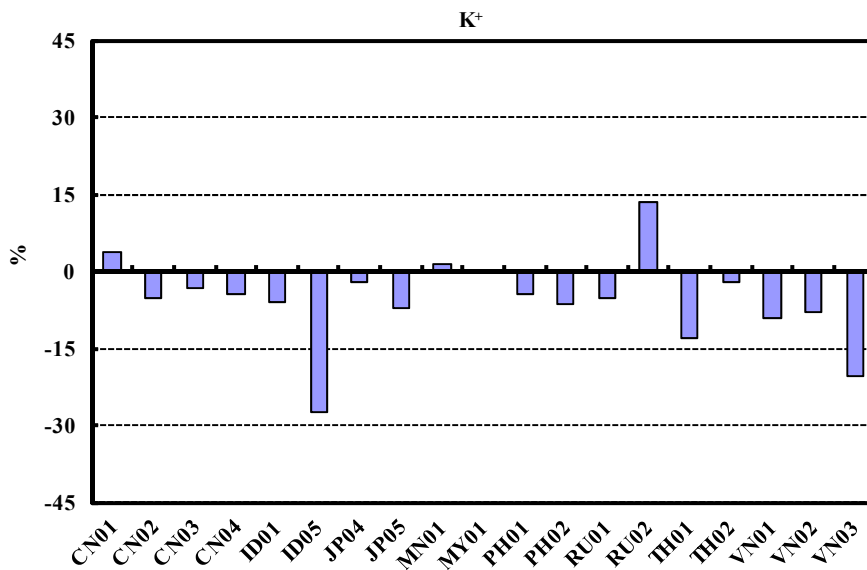
Data from two laboratories were flagged. Especially one of them was comparatively deviated

from the prepared value. Most of the participating laboratories used ion chromatography for the determination of  $\text{Cl}^-$ , while four laboratories used titration method. The two flagged data were analyzed by titration method.



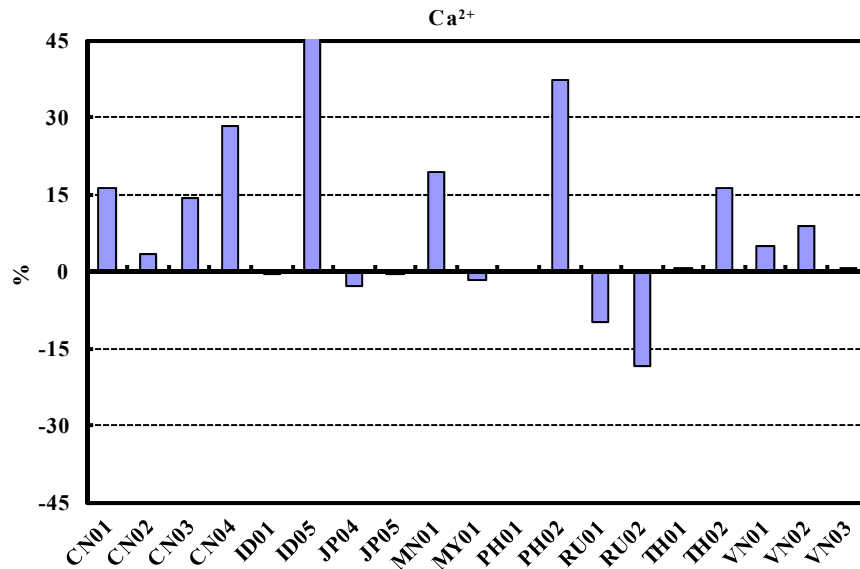
**Figure 5.9 Distribution of results for  $\text{Na}^+$  (normalized by prepared concentration)**

One data was flagged. Most of the participating laboratories used ion chromatography for the determination of  $\text{Na}^+$ , and there was no flagged data in these laboratories. Four laboratories used atomic absorption / flame (emission) photometry and one of them was flagged.



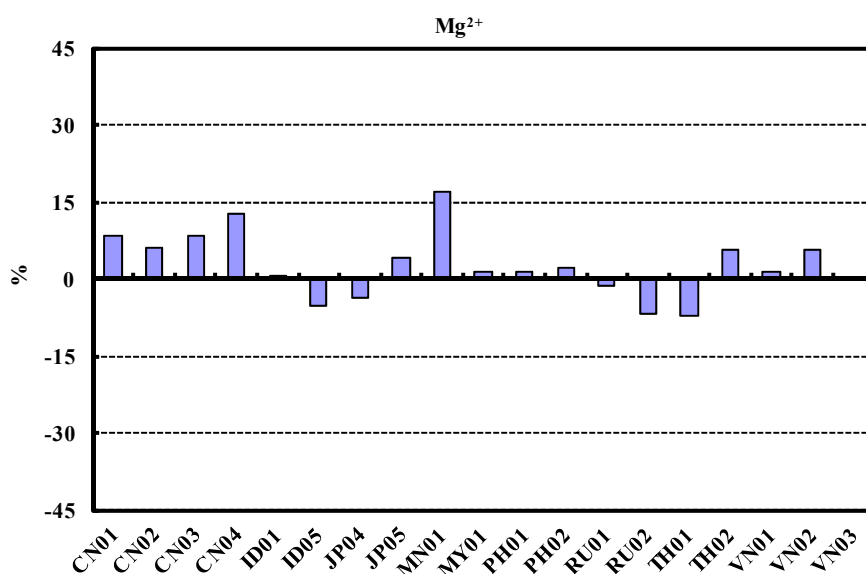
**Figure 5.10 Distribution of results for  $\text{K}^+$  (normalized by prepared concentration)**

Data from two laboratories were flagged. Most of the participating laboratories used ion chromatography for the determination of  $K^+$ , and there was no flagged data in these laboratories. Four laboratories used atomic absorption / flame (emission) photometry and two of them were flagged.



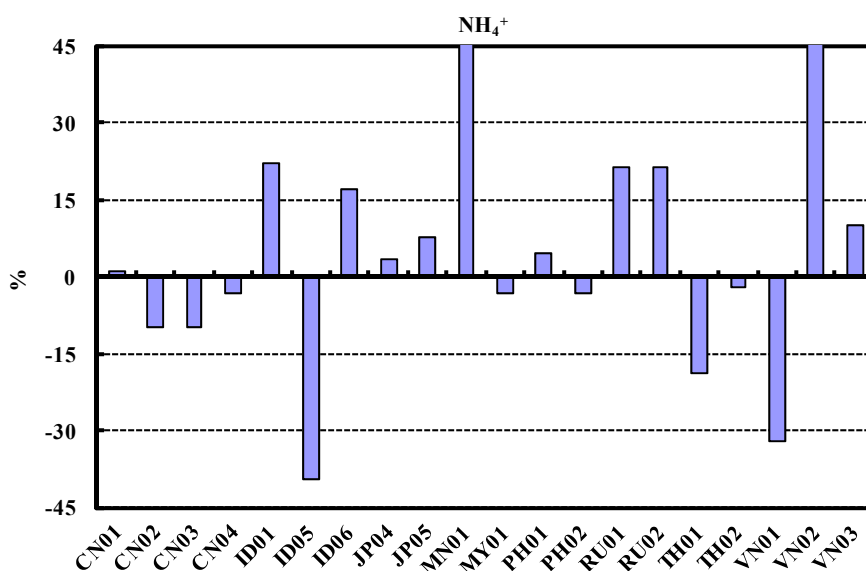
**Figure 5.11 Distribution of results for  $Ca^{2+}$  (normalized by prepared concentration)**

Data from seven laboratories were flagged. In particular, the laboratory ID05 was significantly deviated from the prepared value, and the laboratory PH02 was comparatively deviated from the prepared value. Among 19 participating laboratories, 15 laboratories used ion chromatography, 3 laboratories used atomic absorption / flame (emission) photometry and 1 laboratory used titration method for the determination of  $Ca^{2+}$ . The most deviant data of flagged ones was obtained by titration method. Other five flagged data were obtained by ion chromatography, and the other one was obtained by atomic absorption / flame (emission) photometry.



**Figure 5.12 Distribution of results for Mg<sup>2+</sup> (normalized by prepared concentration)**

One data was flagged. Most of the participating laboratories used ion chromatography for the determination of Mg<sup>2+</sup>, while four laboratories used atomic absorption / flame (emission) photometry. The flagged data was analyzed by ion chromatography.



**Figure 5.13 Distribution of results for NH<sub>4</sub><sup>+</sup> (normalized by prepared concentration)**

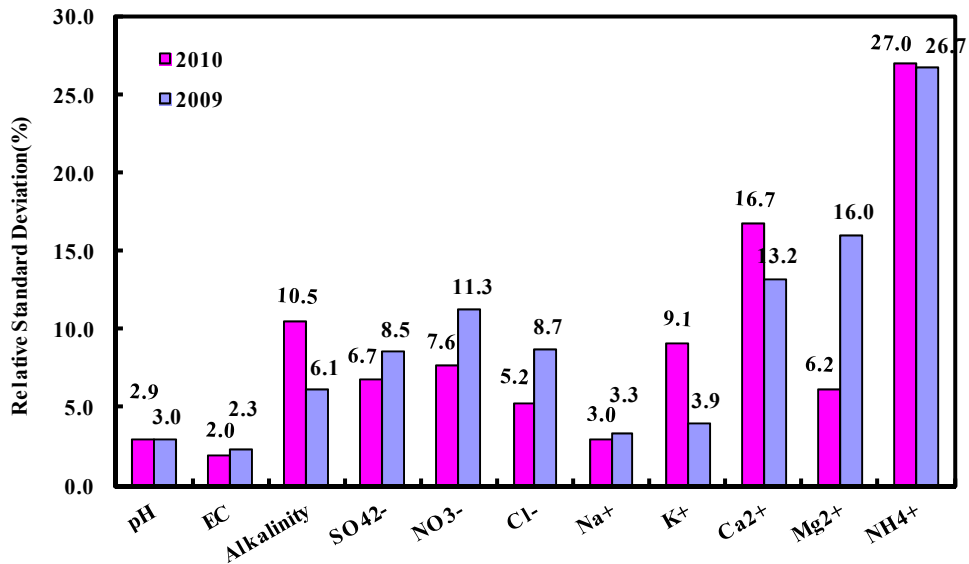
Data from nine laboratories were flagged. In particular, the laboratory MN01 and VN02 were deviated more than 50% from the prepared value respectively. Furthermore, the laboratory ID05 and VN01 were deviated more than 30% from the prepared value respectively. Among 20 participating laboratories, 15 laboratories used ion chromatography, 4 laboratories used

spectrophotometry (Indophenol) and 1 laboratory used spectrophotometry (other method) for the determination of  $\text{NH}_4^+$ . Five flagged data which include the two most deviant ones were obtained by ion chromatography. Other three flagged data were obtained by spectrophotometry (Indophenol), and the other one was obtained by spectrophotometry (other method).

$\text{NH}_4^+$  was the parameter that has the highest flagged percentage in this attempt, too. This parameter had also the highest flagged percentage in the attempts in 2003-2009. It may be necessary to pay more attention to the accuracy of  $\text{NH}_4^+$  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 (2009).



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

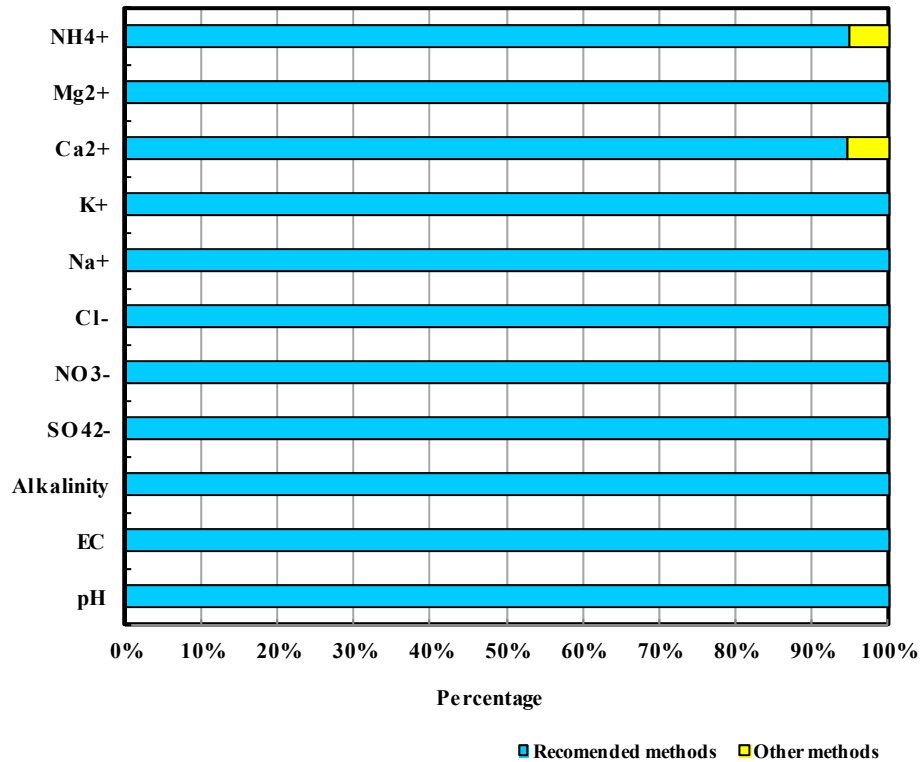
**Figure 5.14 Relative standard deviation of each constituent**

The relative standard deviation of NH<sub>4</sub><sup>+</sup> results from laboratories was larger than the other parameters comparatively. That of last attempt was also larger than the other ions. It may be necessary to pay more attention to the variation among the laboratories of NH<sub>4</sub><sup>+</sup> analysis in the inland water than other analytical parameters. In addition, the relative standard deviation of Ca<sup>2+</sup> results from laboratories was over 15 %. On the other hand, Mg<sup>2+</sup> of this attempt was smaller than that of last year.

### 5.3.4 Information on laboratories

#### Methodologies used

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



**Figure 5.15 Percentage of laboratories using the recommended methods**

**Table 5.11 List of methods**

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

**Table 5.12 Analytical methods**

Code	pH	EC	Alkalinity	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
0	21										
1		21									
2			21(3)			4(2)			1(1)		
3							4(1)	4(2)	3(1)	4	
4				16	16	16	15	15	15(5)	15(1)	15(5)
5											
6											
7				4(2)	3(2)						1(1)
8											4(3)
9											
10											
11											
Flagged E	0	0	2	1	2	1	1	2	5	1	5
Flagged X	0	1	1	1	0	1	0	0	2	0	4

Reverse mesh is a recommended method of EANET

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

The participating laboratories used recommended methods of EANET except measurement of Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>. One laboratory used titration method for Ca<sup>2+</sup> analysis, and another one laboratory used spectrophotometry without indophenol blue for NH<sub>4</sub><sup>+</sup> analysis. These data were both flagged.

For the determination of anions/cations, most of the participating laboratories used ion chromatography, while some of them used other methods. The data of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup> and K<sup>+</sup> analyzed by ion chromatography were not flagged at all. However, the data of Ca<sup>2+</sup>, Mg<sup>2+</sup>

and  $\text{NH}_4^+$  analyzed by it were partially flagged, and they included some data deviated from the prepared value significantly. There was no clear relationship between analytical methods and appearance of flagged data.

### Staff (numbers and years of experience)

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

**Table 5.13 Staff in charge of measurement**

Lab.ID	Total	pH	EC	Alkalinity	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NH}_4^+$
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	2	A	A	A	B	B	B	B	B	B	B	B
ID01	1	A	A	A	A	A	A	A	A	A	A	A
ID05	6	A	B	C	A	B	D	E	F	C	E	C
ID06	1	A	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A	A
JP05	2	A	A	A	B	B	B	B	B	B	B	B
MN01	2	A	A	B	B	B	B	B	B	B	B	B
MY01	3	A	A	A	B	B	B	C	C	C	C	C
MY03	1	A	A	A	A	A	A	A	A	A	A	A
PH01	2	A	A	B	A	A	A	A	A	A	A	A
PH02	3	A	A	B	C	C	C	C	C	C	C	C
RU01	3	A	A	A	B	B	B	C	C	C	C	A
RU02	3	A	A	A	B	B	A	C	C	C	C	B
TH01	1	A	A	A	A	A	A	A	A	A	A	A
TH02	2	A	B	A	B	B	B	A	A	A	A	A
VN01	2	A	A	B	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C
VN03	3	A	B	B	A	A	B	C	B	C	C	B

"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.

In many laboratories, 2 or 3 persons analyzed the sample, and usually their responsibilities were separated according to the methods such as pH, EC and ionic items.

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

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

**Table 5.14 Years of experience**

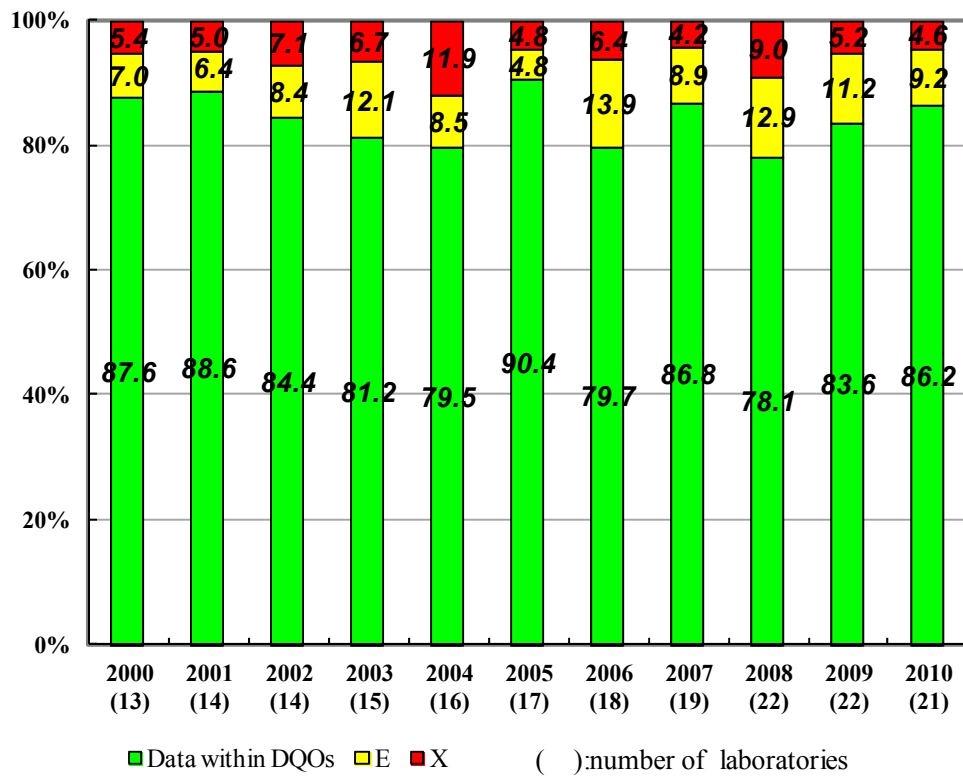
Lab.ID	pH	EC	Alkalinity	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Unit : year		
									Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
CN01	19	19	19	19	19	19	19	19	19	19	19
CN02	20	20	4	5	5	5	5	5	5	5	5
CN03	15	15	15	15	15	15	15	15	15	15	15
CN04	4	4	4	25	25	25	25	25	25	25	25
ID01	13	13	13	13	13	13	13	13	13	13	13
ID05	28	2	4	28	2	33	6	2	4	6	4
ID06	2	2	2	2	2	2					2
JP04	2	2	2	2	2	2	2	2	2	2	2
JP05	2	2	2	8	8	8	8	8	8	8	8
MN01	9	9	11	11	11	11	11	11	11	11	11
MY01	4	4	4	1	1	1	8	8	8	8	8
MY03	2	2	2								
PH01	1	1	10	3	3	3	13	13	13	13	5
PH02	19	19	6	19	19	19	19	19	19	19	19
RU01	17	17	17	15	15	15	25	25	25	25	17
RU02	50	50	50	16	16	50	19	19	19	19	16
TH01	6	6	6	10	10	10	10	10	10	10	10
TH02	13	8	13	8	8	8	13	13	13	13	13
VN01	2	2	18	18	18	18	18	18	18	18	18
VN02	4	4	6	18	18	18	18	18	18	18	18
VN03	4	5	5	4		5	7	5	7	7	5

Reverse mesh:Data were Flagged by “E” or “X” in sample  
 1 year means experienced with one year or less.

There was 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 11 times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure.5.16.



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

In this attempt, the number of laboratories was reduced a little bit, but the percentage of data that satisfied the DQOs still maintain high level.

The comparison for each parameter from 1<sup>st</sup> to 10<sup>th</sup> project with the percentage of flagged data is shown in Figure 5.17.

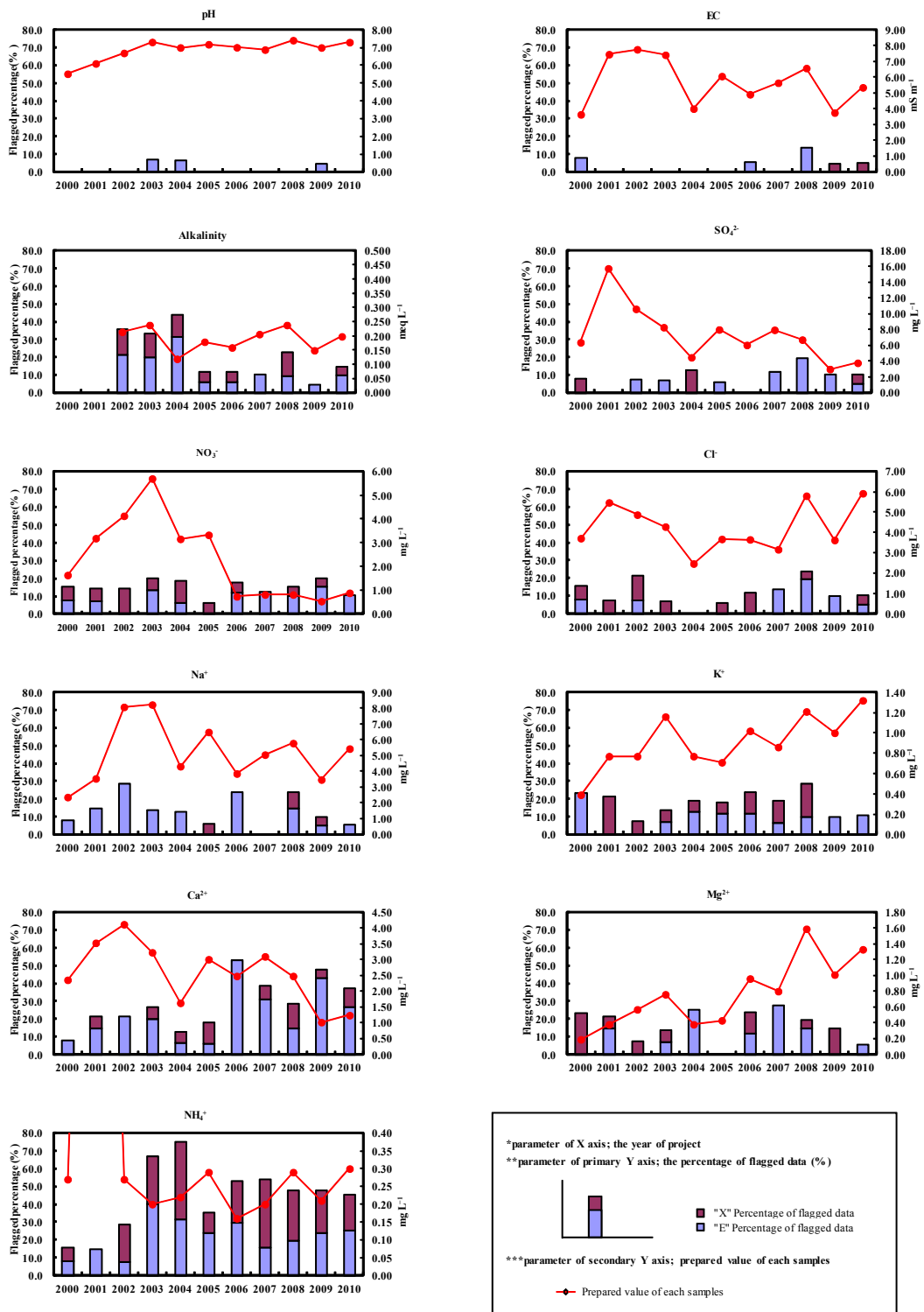


Figure 5.17 Comparison of the percentage of flagged data for each parameter in inter-laboratory comparison projects

The percentage of flagged data of  $\text{NH}_4^+$  has maintained high level since 2003 its concentration was prepared low. Concerning the other parameters, there was no clear relationship between the concentration and the percentage of flagged data.

The percentages of flagged cations' data seemed generally to be larger than those of anions throughout the projects. Furthermore, the percentage of flagged  $\text{NH}_4^+$  was larger than other parameters in every survey except 1<sup>st</sup>- 3<sup>rd</sup> project. The percentage of flagged  $\text{Ca}^{2+}$  of 7<sup>th</sup> - 10<sup>th</sup> project was also comparatively high. However, the reason for these parameters' state was not clear. Actually, concentration of  $\text{NH}_4^+$  is relatively low or under detection limit in inland aquatic environment samples in some monitoring sites. It might be important to detect the targeted level for evaluation of nitrogen cycle in the monitoring sites. Therefore, it is necessary to pay more attention to the analysis not only of  $\text{NH}_4^+$  but also of  $\text{Ca}^{2+}$  , in the inland water than the other analytical parameters.

## **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.

### **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  $0.15\text{mS m}^{-1}$  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

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EANET (2010). *Report of the Inter-laboratory Comparison Project 2009*. Niigata, Japan: Asia Center for Air Pollution Research.

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**Appendix Table 5.1 Results submitted by the laboratories**

Lab. ID	pH	EC (mS m <sup>-1</sup> )	Alkalinity (meq L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	Cl <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	K <sup>+</sup> (mg L <sup>-1</sup> )	Ca <sup>2+</sup> (mg L <sup>-1</sup> )	Mg <sup>2+</sup> (mg L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )
CN01	7.17	5.18	0.19	3.80	0.89	6.06	5.47	1.37	1.44	1.44	0.30
CN02	7.11	5.17	0.190	3.74	0.88	5.89	5.50	1.25	1.28	1.41	0.27
CN03	7.10	5.03	0.190	3.74	0.88	5.90	5.50	1.28	1.42	1.44	0.27
CN04	7.08	5.32	0.201	3.63	0.94	5.91	5.29	1.26	1.59	1.50	0.29
ID01	7.06	5.24	0.160	4.09	0.94	6.51	5.71	1.24	1.24	1.34	0.37
ID05	6.71	5.31	0.201	5.61	1.08	6.45	5.34	0.96	2.01	1.26	0.18
ID06	7.00	5.37	0.233	4.20	1.09	4.93					0.35
JP04	7.15	5.36	0.210	3.70	0.86	5.99	5.24	1.29	1.21	1.28	0.31
JP05	7.17	5.21	0.200	3.46	0.84	5.89	5.36	1.23	1.23	1.38	0.32
MN01	6.64	5.19	0.180	3.74	0.85	5.95	5.17	1.34	1.48	1.56	0.47
MY01	6.83	5.29	0.207	3.84	0.91	6.07	5.53	1.32	1.22	1.35	0.29
MY03	6.99	52.60	0.260								
PH01	7.07	5.09	0.180	3.85	0.89	5.89	5.39	1.26	1.24	1.35	0.31
PH02	6.98	5.30	0.203	3.78	0.93	5.71	5.26	1.23	1.70	1.36	0.29
RU01	7.23	5.21	0.181	3.86	0.91	6.00	5.41	1.25	1.12	1.31	0.36
RU02	7.20	5.30	0.188	4.20	0.91	5.85	5.50	1.50	1.01	1.24	0.36
TH01	7.40	5.13	0.213	3.67	0.87	5.92	5.06	1.15	1.25	1.23	0.24
TH02	6.61	5.01	0.180	3.81	0.85	5.98	5.39	1.29	1.44	1.41	0.29
VN01	7.18	5.34	0.200	3.61	0.88	5.93	5.64	1.20	1.30	1.35	0.20
VN02	7.22	5.24	0.210	4.02	0.87	5.87	5.46	1.21	1.35	1.40	0.57
VN03	7.21	5.23	0.210	3.10		8.14	4.19	1.05	1.25	1.33	0.33
Expected value	7.30	5.35	0.198	3.78	0.89	5.92	5.43	1.32	1.24	1.33	0.30
Number of data	21	21	21	20	19	20	19	19	19	19	20
Average	7.05	7.48	0.199	3.87	0.91	6.04	5.34	1.25	1.36	1.37	0.32
Minimum	6.61	5.01	0.160	3.10	0.84	4.93	4.19	0.96	1.01	1.23	0.18
Maximum	7.40	52.60	0.260	5.61	1.09	8.14	5.71	1.50	2.01	1.56	0.57

blank : not analyzed

Appendix Table 5.2 Data normalized by the prepared value

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

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO <sub>4</sub> <sup>2-</sup> (%)	NO <sub>3</sub> <sup>-</sup> (%)	Cl <sup>-</sup> (%)	Na <sup>+</sup> (%)	K <sup>+</sup> (%)	Ca <sup>2+</sup> (%)	Mg <sup>2+</sup> (%)	NH <sub>4</sub> <sup>+</sup> (%)
CN01	-1.7	-3.1	-4.0	0.6	0.4	2.3	0.8	3.8	16.1	8.3	1.1
CN02	-2.6	-3.3	-4.0	-1.1	-1.1	-0.5	1.3	-5.3	3.2	6.0	-10.0
CN03	-2.7	-6.0	-4.0	-1.1	-1.5	-0.3	1.2	-3.3	14.2	8.5	-10.0
CN04	-3.0	-0.5	1.5	-4.0	6.0	-0.1	-2.6	-4.3	28.2	12.5	-3.3
ID01	-3.3	-2.1	-19.2	8.2	5.2	10.0	5.2	-5.8	-0.3	0.8	22.2
ID05	-8.1	-0.7	1.5	48.4	21.3	9.0	-1.7	-27.3	62.1	-5.3	-39.7
ID06	-4.1	0.4	17.7	11.1	22.7	-16.8					16.9
JP04	-2.1	0.2	6.1	-2.1	-3.4	1.2	-3.5	-2.0	-2.7	-3.8	3.3
JP05	-1.8	-2.6	1.0	-8.5	-6.0	-0.5	-1.3	-7.1	-0.5	4.0	7.8
MN01	-9.0	-3.1	-9.1	-1.1	-4.1	0.6	-4.7	1.3	19.4	17.0	57.8
MY01	-6.5	-1.1	4.4	1.5	2.2	2.5	1.8	0.0	-1.9	1.3	-3.3
MY03	-4.2	883.2	31.3								
PH01	-3.2	-4.8	-9.1	1.9	-0.4	-0.5	-0.7	-4.3	0.3	1.5	4.4
PH02	-4.3	-0.9	2.7	-0.1	4.9	-3.5	-3.1	-6.6	37.1	2.0	-3.3
RU01	-0.9	-2.6	-8.6	2.0	1.9	1.4	-0.4	-5.1	-9.9	-1.5	21.1
RU02	-1.4	-0.9	-5.1	11.2	1.9	-1.2	1.4	13.4	-18.5	-6.8	21.1
TH01	1.3	-4.0	7.7	-2.9	-2.6	0.0	-6.9	-12.9	0.5	-7.3	-18.9
TH02	-9.5	-6.3	-9.1	0.7	-4.5	1.0	-0.7	-2.3	16.1	5.8	-2.2
VN01	-1.6	-0.2	1.0	-4.5	-0.7	0.2	3.9	-9.1	4.8	1.5	-32.2
VN02	-1.1	-2.1	6.1	6.3	-2.6	-0.9	0.6	-8.1	8.9	5.5	91.1
VN03	-1.2	-2.2	6.1	-18.0		37.5	-22.8	-20.5	0.8	0.0	10.0
Minimum	-9.5	-6.3	-19.2	-18.0	-6.0	-16.8	-22.8	-27.3	-18.5	-7.3	-39.7
Maximum	1.3	883.2	31.3	48.4	22.7	37.5	5.2	13.4	62.1	17.0	91.1
Average	-3.4	39.9	0.7	2.4	2.1	2.1	-1.7	-5.5	9.4	2.6	6.7

blank : not analyzed

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## 7. CONTACT INFORMATION

Please address all inquiries, comments and suggestions to:

Asia Center for Air Pollution Research (ACAP)

1182, Sowa, Nishi-ku, Niigata-shi, 950-2144, Japan

Tel: +81 25-263-0550

Fax: +81 25-263-0567

E-mail: [eanetdata@acap.asia](mailto:eanetdata@acap.asia)

URL: <http://www.eanet.cc>

Contact person:

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Name	Department & E-mail address
Dr. Takuya SHIOZAKI (EANET QA/QC Manager)	Dept. Head, Data Management Department E-mail: <a href="mailto:shiozaki@acap.asia">shiozaki@acap.asia</a>

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