

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

# **Report of the Inter-laboratory Comparison Project 2016**

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

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

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

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

**on Inland Aquatic Environment**

December 2017  
Network Center for EANET



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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) programs 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.

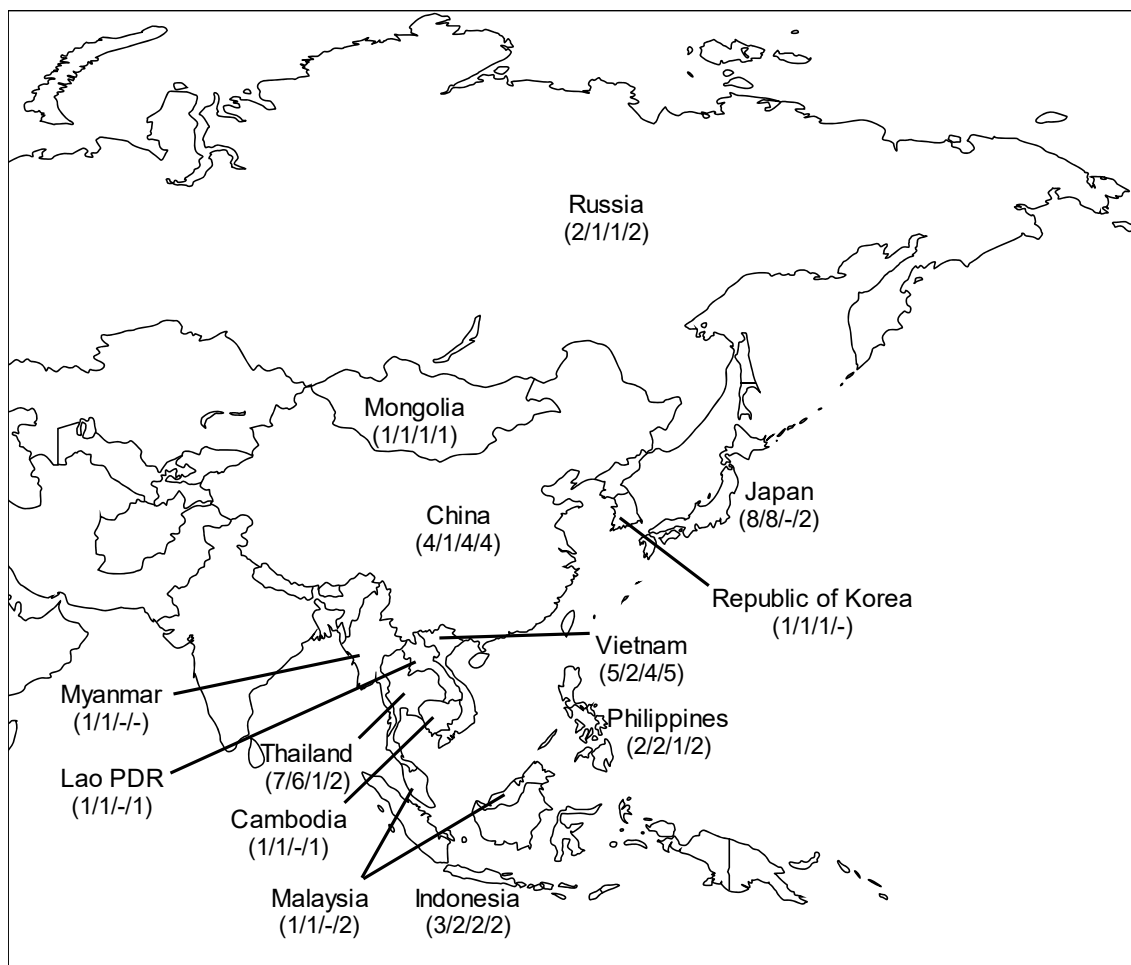
The Inter-laboratory Comparison Project is implemented by the Network Center (NC) of EANET annually for the following items:

- a. wet deposition
- b. dry deposition
- c. soil
- d. inland aquatic environment

This report presented the results of the 19<sup>th</sup> Inter-laboratory Comparison Project on wet deposition, 12<sup>th</sup> Inter-laboratory Comparison Project on dry deposition, 18<sup>th</sup> Inter-laboratory Comparison Project on soil, and 17<sup>th</sup> Inter-laboratory Comparison Project on inland aquatic environment.

The number of participating laboratories from each country by project is shown in Figure 1.1.

Table 1.1 shows the name and code of participating laboratories and data submission status. A check-mark(✓) indicates the analytical results were submitted by individual laboratories.



**Figure 1.1 Number of participating laboratories in 2016**

\* The values in parentheses show the number of participating laboratories from each country.  
(wet/dry/soil/inland aquatic environment)

**Table 1.1 Participating laboratories and data submission status**

Participating laboratories	Code	Data submission			
		Wet	Dry	Soil	IAE
<b><u>Cambodia</u></b> Department of Environment Pollution Control, Ministry of Environment	KH01				
<b><u>China</u></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><u>Indonesia</u></b> Environmental Management Center (EMC), Environmental Impact Management Agency (BAPEDAL)	ID01	✓	✓	✓	✓
Climatology, Meteorological and Geophysical Agency (BMKG)	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 Works	ID05				✓
<b><u>Japan</u></b> Institute of Environmental Sciences, Hokkaido Research Organization	JP01	✓	✓		
Niigata Prefectural Institute of Public Health and Environmental Sciences	JP02		✓		
Nagano Environmental Conservation Research Institute	JP03	✓	✓		
Gifu Prefectural Research Institute for Health and Environmental Sciences	JP04	✓	✓		✓
Kochi Prefectural Environmental Research Center	JP07	✓			
Okinawa Prefectural Institute of Health and Environment	JP08	✓	✓		
Asia Center for Air Pollution Research (ACAP)	JP09	✓	✓		
Japan Environmental Sanitation Center (JESC)	JP10	✓	✓		
Japan Environmental Sanitation Center West Japan Branch	JP11	✓	✓		
Public Corporation of Shimane Environmental and Health	JP12				✓
<b><u>Lao PDR</u></b> Environment Quality Monitoring Center(EQMC), Natural Resources and Environment Institute(NREI), Ministry of Natural Resources and Environment(MONRE)	LA01				
<b><u>Malaysia</u></b> Division of Environmental Health, Department of Chemistry (DOC)	MY01	✓	✓		✓
Faculty of Applied Science, University Technology Mara (UiTM)	MY03				
<b><u>Mongolia</u></b> Central Laboratory of Environment and Metrology	MN01	✓		✓	✓
<b><u>Myanmar</u></b> Department of Meteorology and Hydrology (DMH)	MM01	✓	✓		
<b><u>Philippines</u></b> Environmental Management Bureau - Central Office (EMB-CO)	PH01	✓	✓		✓
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	PH02	✓	✓		✓
University of the Philippines Los Baños (UPLB)	PH03				
<b><u>Republic of Korea</u></b> National Institute of Environment Research (NIER)	KR01	✓	✓		
<b><u>Russia</u></b> Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	RU01	✓	✓	✓	✓
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU02	✓			✓
<b><u>Thailand</u></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 Promotion	TH02	✓	✓		✓
Chemistry Department, Science Faculty, Chiangmai University (CMU)	TH04	✓	✓		
Khon Kaen University (KKU)	TH05	✓	✓		
King Mongkut's University of Technology Thonburi (KMUTT)	TH06	✓	✓		
Kasetsart University	TH07				
Songkla University	TH08	✓			
<b><u>Vietnam</u></b> Environmental Laboratory - Center for Environmental Research - Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE	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), MoNRE	VN04	✓		✓	✓
Southern Region Hydro-Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN05	✓		✓	✓
Total number of submitted data :		34	24	13	21





## 2. 19<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

### 2.1 Introduction

In the 19<sup>th</sup> Inter-laboratory Comparison Project on wet deposition, artificial rainwater samples containing known amounts 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 in the beginning of October 2016. Their analytical results were required to be submitted to the NC by 28 February 2017.

### 2.2 Procedures

#### 2.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 37 laboratories in charge of chemical analysis in 13 countries of EANET. 34 of the participating laboratories submitted their analytical results to the NC. All participating laboratories and their codes and data submission status are listed in Table 1.1 of Chapter 1.

#### 2.2.2 Description of samples

Two kinds of artificial rainwater samples were distributed to the laboratories. A description of the samples is given in Table 2.1.

**Table 2.1 Description of artificial rainwater samples**

Artificial rain-water sample	Quantity of sample	Container	Number of samples	Note
No. 161w No. 162w	100mL each	Polypropylene bottle 100mL	One bottle each	- Fixed quantity of reagents are dissolved in deionized water - Samples do not include other ions than shown in Table 2.2

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

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

	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
	-	mS m <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>	μmol L <sup>-1</sup>
No. 161w	4.85	2.39	44.5	21.0	32.3	31.5	18.3	6.9	28.8	7.0
No. 162w	5.30	0.67	10.2	8.4	8.5	13.0	6.5	1.7	3.7	1.8

\* 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 pure 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>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>.

The laboratories were required to apply the analytical methods and data checking procedures that were specified in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. Analytical methods specified in the Technical Manual are listed in Table 2.3.

**Table 2.3 Analytical methods specified in the Technical 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
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography Spectrophotometry (Indophenol Blue Method)
Na <sup>+</sup> K <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup>	Ion Chromatography Atomic Absorption Spectrometry Atomic Emission Spectrometry

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<sup>-1</sup>]) was calculated by summing the concentrations of all anions (c [μmol L<sup>-1</sup>]).

$$A [\mu\text{eq L}^{-1}] = \sum n c_{Ai} [\mu\text{mol L}^{-1}] = 2c (\text{SO}_4^{2-}) + c (\text{NO}_3^-) + c (\text{Cl}^-)$$

n, c<sub>Ai</sub> : electric charge and concentration [μmol L<sup>-1</sup>] of anion “i”.

- (2) Total cation equivalent concentration (C [μeq L<sup>-1</sup>]) was calculated by summing the concentrations of all cations (c [μmol L<sup>-1</sup>]).

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

n, c<sub>Ci</sub> : electric charge 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> calculated by the above equation was compared with allowable ranges specified in *Technical Manual for Wet Deposition Monitoring in East Asia -2010* which are shown 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 <sup>-1</sup> ]	R <sub>1</sub> [%]
< 50	± 30
50 – 100	± 15
> 100	± 8

## Comparison between calculated and measured values of electrical conductivity (R<sub>2</sub>)

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

$$\begin{aligned}\Lambda \text{ calc } [\text{mS m}^{-1}] = & \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2c(\text{SO}_4^{2-}) + 71.4 \times c(\text{NO}_3^-) \\ & + 76.3 \times c(\text{Cl}^-) + 73.5 \times c(\text{NH}_4^+) + 50.1 \times c(\text{Na}^+) + 73.5 \times c(\text{K}^+) \\ & + 59.5 \times 2c(\text{Ca}^{2+}) + 53.0 \times 2c(\text{Mg}^{2+})\} / 10000\end{aligned}$$

c : Molar concentrations [ $\mu\text{mol L}^{-1}$ ] of ions in the parenthesis; each constant value was ionic equivalent conductance at 25 degrees centigrade.

(2) Electrical conductivity comparison (R<sub>2</sub>) was calculated as follows;

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

$\Lambda$  meas : measured conductivity

(3) R<sub>2</sub> calculated by the above equation was compared with allowable ranges specified in the Technical Manual which are shown 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 [ $\text{mS m}^{-1}$ ]	R <sub>2</sub> [%]
< 0.5	$\pm 20$
0.5 – 3	$\pm 13$
> 3	$\pm 9$

## 2.3 Results

The NC received the analytical results from 34 laboratories in the participating countries of EANET. The original data submitted by the laboratories are shown in Appendix 2.2.

Basic statistics of submitted data summarized in Table 2.6 was 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, exceeding three standard deviations, were excluded from the calculation. As shown in Table 2.6, difference of Va from prepared value (Vp) was slightly large. The range of  $\Delta V/Vp$  was between -3.8% to 3.0% for sample No. 161w, and -3.3% to 16.4% for sample No. 162w.

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

Sample No. 161w							
Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp^{*1}$ %	S.D.	N	Min.	Max.
pH	4.85	4.92	1.4	0.15	33	4.53	5.44
EC [mS m <sup>-1</sup> ]	2.39	2.30	-3.8	0.17	33	1.67	2.92
SO <sub>4</sub> <sup>2-</sup> [μmol L <sup>-1</sup> ]	44.5	44.1	-0.9	1.71	32	38.8	48.6
NO <sub>3</sub> <sup>-</sup> [μmol L <sup>-1</sup> ]	21.0	20.6	-1.8	1.76	32	17.2	27.4
Cl <sup>-</sup> [μmol L <sup>-1</sup> ]	32.3	31.7	-1.9	1.39	32	29.1	35.3
NH <sub>4</sub> <sup>+</sup> [μmol L <sup>-1</sup> ]	31.5	31.6	0.2	2.95	32	25.6	39.2
Na <sup>+</sup> [μmol L <sup>-1</sup> ]	18.3	18.8	3.0	1.74	31	15.9	24.4
K <sup>+</sup> [μmol L <sup>-1</sup> ]	6.9	6.8	-0.9	0.73	32	5.3	9.0
Ca <sup>2+</sup> [μmol L <sup>-1</sup> ]	28.8	29.3	1.7	2.39	31	25.2	35.1
Mg <sup>2+</sup> [μmol L <sup>-1</sup> ]	7.0	6.9	-0.8	0.74	32	5.5	9.0
Sample No. 162w							
Constituents	Prepared (Vp)	Average (Va)	$\Delta V/Vp^{*1}$ %	S.D.	N	Min.	Max.
pH	5.30	5.33	0.6	0.19	34	4.87	5.73
EC [mS m <sup>-1</sup> ]	0.67	0.70	4.7	0.05	33	0.61	0.85
SO <sub>4</sub> <sup>2-</sup> [μmol L <sup>-1</sup> ]	10.2	10.0	-2.0	0.55	32	8.7	11.4
NO <sub>3</sub> <sup>-</sup> [μmol L <sup>-1</sup> ]	8.4	8.2	-2.4	0.83	33	6.2	10.6
Cl <sup>-</sup> [μmol L <sup>-1</sup> ]	8.5	8.4	-0.7	0.79	31	6.7	11.3
NH <sub>4</sub> <sup>+</sup> [μmol L <sup>-1</sup> ]	13.0	12.8	-1.9	1.29	32	10.8	16.1
Na <sup>+</sup> [μmol L <sup>-1</sup> ]	6.5	6.3	-3.3	1.10	31	3.3	8.5
K <sup>+</sup> [μmol L <sup>-1</sup> ]	1.7	1.7	2.8	0.29	31	1.2	2.5
Ca <sup>2+</sup> [μmol L <sup>-1</sup> ]	3.7	4.3	16.4	1.01	31	2.7	6.0
Mg <sup>2+</sup> [μmol L <sup>-1</sup> ]	1.8	2.0	10.8	0.47	32	1.3	3.3

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

The Data Quality Objective for accuracy (hereafter referred to as DQO) is specified in the QA/QC program of 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. The flag “E” indicates that the deviation from  $V_p$  exceeds  $\pm 15\%$  but not  $\pm 30\%$ , and the flag “X” indicates that the deviation from  $V_p$  exceeds  $\pm 30\%$ .

A set of data for each sample was evaluated by the data checking procedures described in section 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. 161w and No. 162w,
- ii) Comparison of individual parameters,
- iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both sample No. 161w and No. 162w is presented in “2.3.1 Evaluation of laboratories’ performance (by sample)”, evaluation of analytical data for each constituent is presented in 2.3.2 Evaluation of laboratories’ performance (by analytical parameter), 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 are presented in 2.3.4 Information on laboratories.

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

#### 1) Sample No. 161w

The number and percentage of the flagged data for sample No. 161w are shown in Table 2.7. 22 analytical data out of 326 were flagged by "E". And 8 analytical data out of 326 were flagged by "X". Data flagged by "E" and "X" shared 9.2 percent of all the submitted data for sample No. 161w.

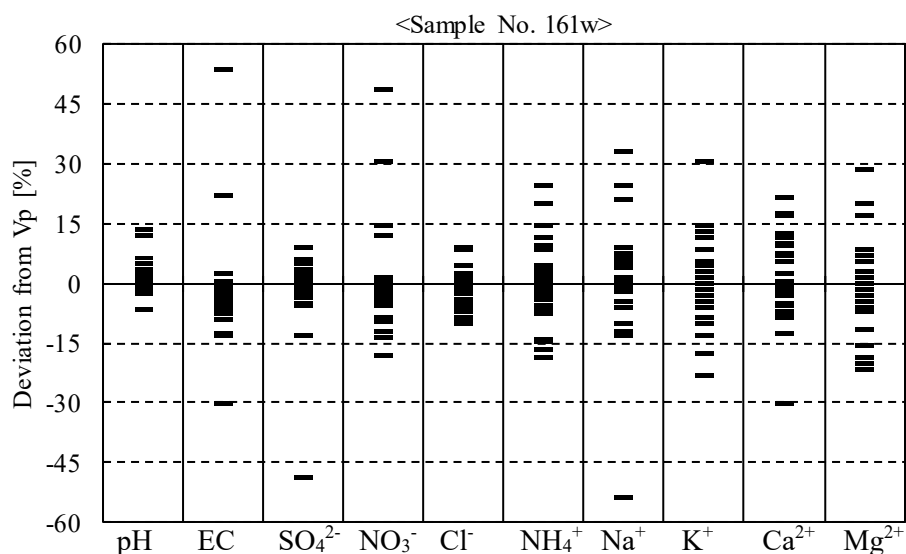
The data normalized by prepared value in each parameter are shown in Figure 2.1.

**Table 2.7 Number of flagged data for the Sample No. 161w**

Characterization of data	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Total
Data within DQO	34	31	32	30	32	28	28	28	28	25	296
Data with flag E <sup>*1</sup>	0	1	0	1	0	4	2	3	4	7	22
Data with flag X <sup>*2</sup>	0	2	1	2	0	0	2	1	0	0	8
Flagged data [%]	0.0	8.8	3.0	9.1	0.0	12.5	12.5	12.5	12.5	21.9	9.2

( Total data = 326 )

Note: \*1, flag E: 15%<| Deviation |≤30% \*2, flag X: 30%<| Deviation |



**Figure 2.1 Distribution of the data normalized by prepared value in each parameter for sample No. 161w**

The parameter which had the most flags was Mg<sup>2+</sup>. The analytical data submitted by the participating laboratories are shown in Table 2.8 with flags.

**Table 2.8 Analytical Results of Sample No. 161w**

Lab. ID <sup>*1</sup>	pH	EC mS m <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> μmol L <sup>-1</sup>	NO <sub>3</sub> <sup>-</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>	Na <sup>+</sup> μmol L <sup>-1</sup>	K <sup>+</sup> μmol L <sup>-1</sup>	Ca <sup>2+</sup> μmol L <sup>-1</sup>	Mg <sup>2+</sup> μmol L <sup>-1</sup>	R <sub>1</sub> %	R <sub>2</sub> %
CN01	4.98	2.32	43.1	19.0	29.4	32.3	16.1	7.7	27.3	7.5	0.6	-2.8
CN02	4.86	2.34	43.1	20.6	32.1	31.3	18.4	7.1	28.0	7.0	0.6	0.1
CN03	4.96	2.25	44.5	21.1	31.0	32.1	8.5 X	7.2	28.0	7.1	-4.5	-0.6
CN04	4.92	2.28	45.5	21.0	32.8	31.8	18.6	7.0	28.6	7.0	-1.5	1.3
ID01	4.94	2.25	42.4	19.9	30.9	27.0	18.0	7.9	30.4	6.5	0.9	-0.3
ID02	4.97	2.08	42.1	20.6	30.9	29.7	18.2	6.0	26.5	7.2	-1.4	2.3
ID03	5.03	2.25	44.6	20.8	32.0	30.9	19.7	7.8	28.8	7.6	-0.5	-0.2
JP01	4.90	2.38	43.0	20.0	31.0	32.3	17.5	6.7	28.1	7.0	0.8	-1.9
JP03	4.89	2.31	45.6	21.2	32.4	32.7	18.3	6.9	28.6	6.6	-1.3	1.3
JP04	4.90	2.34	43.9	20.5	31.8	30.5	17.9	6.7	28.1	6.5	-1.2	-0.9
JP07	4.85	2.40	44.0	20.2	32.1	29.2	18.4	6.5	26.8	6.5	-2.0	-1.5
JP08	4.88	2.27	44.6	20.6	32.3	31.2	19.1	6.8	30.8	6.8	1.2	2.4
JP09	4.98	2.27	43.9	20.6	32.2	31.7	18.5	6.9	28.6	7.1	-0.6	-0.4
JP10	4.89	2.35	43.2	20.5	31.7	32.0	18.6	7.0	28.4	7.0	1.0	-0.6
JP11	5.16	2.21	44.5	20.3	32.5	34.2	19.6	7.5	28.9	7.6	-0.2	-0.8
MY01	4.88	2.37	43.4	18.2	29.1	30.8	18.0	6.2	29.6	5.7 E	1.7	-1.9
MN01	4.53	2.33	48.6	20.3	29.5	---	---	---	---	---	---	---
MM01	4.74	3.67 X	43.8	19.2	31.9	29.8	16.5	6.3	28.3	5.9 E	0.2	-19.6 C
PH01	4.83	2.17	43.6	19.1	30.7	32.8	19.2	7.0	31.6	6.9	4.8	5.5
PH02	4.91	2.33	43.4	18.5	30.7	33.0	19.6	6.5	31.7	6.8	4.4	0.0
KR01	4.98	2.31	42.3	20.2	30.9	36.1	19.0	6.5	27.4	5.6 E	0.9	-2.1
RU01	4.85	2.36	43.1	20.6	31.5	27.1	18.5	6.9	25.2	6.2	-3.3	-1.7
RU02	5.52	1.67 X	22.8 X	27.4 X	35.3	25.6 E	24.4 X	9.0 X	20.2 E	8.2 E	4.6	-0.9
TH01	4.89	2.35	46.7	20.1	35.1	37.8 E	17.2	6.3	29.0	6.9	-0.9	1.8
TH02	4.97	2.33	44.6	20.6	31.6	31.3	18.5	7.3	27.9	6.9	-1.4	-1.6
TH04	4.78	2.35	46.2	20.9	33.1	30.2	17.5	6.6	32.1	7.1	1.0	3.8
TH05	4.91	2.30	44.7	17.2 E	30.4	35.1	15.9	5.3 E	33.9 E	7.4	4.9	1.3
TH06	4.86	2.38	44.5	21.2	31.6	31.3	19.0	6.9	26.4	9.0 E	0.0	-0.2
TH08	4.82	2.22	---	---	---	---	---	---	---	---	0.5 *2	4.3 *2
VN01	4.73	2.36	45.2	20.8	32.8	34.6	19.4	7.1	26.4	7.2	1.0	4.2
VN02	5.17	2.09	43.8	21.3	31.1	30.5	20.0	6.0	31.0	6.7	-0.5	1.1
VN03	4.83	2.92 E	43.4	31.2 X	---	29.4	22.2 E	5.7 E	33.8 E	6.9	---	---
VN04	5.10	2.45	47.2	24.1	33.7	39.2 E	22.8 E	7.8	35.1 E	8.4 E	4.0	-0.4
VN05	5.44	2.28	38.8	23.5	30.0	26.3 E	19.7	5.7 E	32.4	5.5 E	0.0	-8.5
Vp	4.85	2.39	44.5	21.0	32.3	31.5	18.3	6.9	28.8	7.0	0.0	0.1
N of data	34	34	33	33	32	32	32	32	32	32		
Within DQO	34	31	32	30	32	28	28	28	28	25		
Flag E	0	1	0	1	0	4	2	3	4	7		
Flag X	0	2	1	2	0	0	2	1	0	0		

Note: "E", 15%<| Deviation |≤30%; "X", 30%<| Deviation |

"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: R<sub>1</sub> and R<sub>2</sub> for TH08 were calculated with results of ion concentration from TH06.



## 2) Sample No. 162w

The number and percentage of the flagged data for sample No. 162w are shown in Table 2.9. 43 analytical data out of 326 were flagged by "E". 35 analytical data out of 326 were flagged by "X". Data marked with flags shared up to 23.9 percent of all the submitted data for sample No. 162w.

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

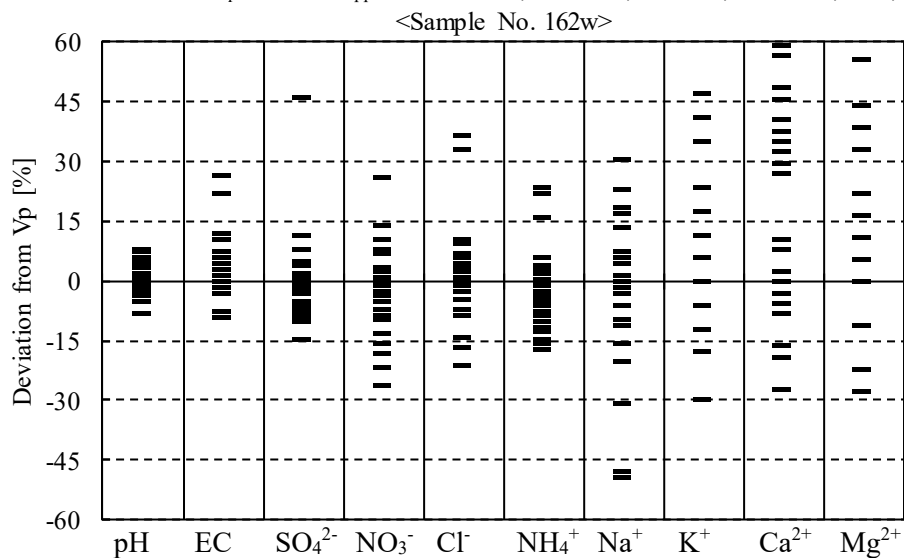
**Table 2.9 Number of flagged data for the sample No. 162w**

Characterization of data	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Total
Data within DQO	34	31	32	28	28	26	22	21	12	14	248
Data with flag E <sup>*1</sup>	0	2	0	5	2	6	5	7	7	9	43
Data with flag X <sup>*2</sup>	0	1	1	0	2	0	5	4	13	9	35
Flagged data [%]	0.0	8.8	3.0	15.2	12.5	18.8	31.3	34.4	62.5	56.3	23.9

( Total data = 326 )

Note: \*1, flag E: 15%<| Deviation |≤30% \*2, flag X: 30%<| Deviation |

Six plots are out of upper scale. EC: 65.7%, Na<sup>+</sup>: 227.7%, K<sup>+</sup>: 352.9%, Ca<sup>2+</sup>: 124.3%, 62.2%, Mg<sup>2+</sup>: 83.3%



**Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 162w**

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

**Table 2.10 Analytical Results of Sample No. 162w**

Lab. ID <sup>*1</sup>	pH	EC mS/m	SO <sub>4</sub> <sup>2-</sup> μmol L <sup>-1</sup>	NO <sub>3</sub> <sup>-</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>	Na <sup>+</sup> μmol L <sup>-1</sup>	K <sup>+</sup> μmol L <sup>-1</sup>	Ca <sup>2+</sup> μmol L <sup>-1</sup>	Mg <sup>2+</sup> μmol L <sup>-1</sup>	R <sub>1</sub> %	R <sub>2</sub> %
CN01	5.13	0.69	10.2	8.1	9.3	13.5	3.3 X	2.4 X	4.1	3.3 X	4.6	5.4
CN02	5.24	0.69	10.2	8.3	9.1	11.7	6.1	1.8	4.0	2.1 E	-0.3	0.2
CN03	5.27	0.69	10.1	8.1	8.7	11.7	3.4 X	1.8	4.1	2.1 E	-3.3	-2.2
CN04	5.27	0.69	10.4	8.1	9.0	12.7	5.8	1.5	4.1	2.1 E	-0.2	-0.4
ID01	5.73	0.66	10.1	6.9 E	9.4	11.7	4.5 X	1.5	5.9 X	1.6	-2.7	-8.7
ID02	5.34	0.62	9.9	8.6	7.9	13.4	6.6	2.1 E	8.3 X	2.5 X	14.2	6.9
ID03	5.49	0.65	10.7	8.6	8.9	13.5	7.6 E	2.5 X	5.8 X	2.6 X	5.7	1.2
JP01	5.30	0.75	10.2	8.3	8.3	12.3	5.8	1.7	3.4	1.6	-3.0	-7.1
JP03	5.28	0.70	10.3	8.6	8.5	13.4	6.4	1.5	3.7	2.0	0.3	-1.3
JP04	5.29	0.68	10.2	8.1	8.4	12.6	6.3	1.7	3.6	1.6	-1.1	-1.4
JP07	5.29	0.75	10.0	8.2	8.5	13.1	6.1	1.5	3.4	1.6	-1.2	-6.5
JP08	5.57	0.68	10.2	8.2	8.5	13.1	6.6	1.7	5.1 X	1.8	1.1	-6.1
JP09	5.37	0.68	10.1	8.6	8.6	13.3	6.5	1.7	3.7	2.0	-0.3	-2.6
JP10	5.25	0.72	9.9	8.2	8.3	13.4	6.8	1.8	3.6	1.9	3.1	-2.4
JP11	5.70	0.65	9.9	7.8	8.3	12.0	6.5	2.3 X	2.7 E	2.0	-5.4	-9.4
MY01	5.21	0.75	8.7	6.6 E	6.7 E	12.9	5.9	1.4 E	3.1 E	1.3 E	6.8	-8.0
MN01	4.87	0.71	10.4	7.8	7.1 E	---	---	---	---	---	---	---
MM01	5.25	1.11 X	9.4	7.6	7.3	11.5	5.5 E	1.5	3.0 E	1.4 E	-1.2	-27.5 C
PH01	5.31	0.65	9.6	7.7	7.9	15.1 E	7.0	1.8	5.4 X	1.3 E	9.6	2.1
PH02	5.31	0.72	9.3	7.3	7.9	12.5	6.9	1.6	4.9 X	1.3 E	6.2	-5.7
KR01	5.59	0.72	9.2	8.6	7.9	16.1 E	6.6	1.4 E	5.4 X	1.3 E	6.9	-9.2
RU01	5.20	0.69	10.1	8.2	8.4	11.0 E	6.1	1.7	2.7 E	1.6	-4.4	-0.9
RU02	5.63	0.82 E	14.9 X	10.6 E	11.6 X	11.4	21.3 X	7.7 X	4.7 E	2.4 X	4.5	-0.4
TH01	5.55	0.66	9.5	7.1 E	8.3	15.9 E	5.9	1.4 E	3.5	1.8	3.1	-6.3
TH02	5.30	0.70	9.5	8.0	8.1	13.5	6.5	2.0 E	3.8	1.9	4.5	-3.1
TH04	5.42	0.69	10.6	8.5	8.4	13.5	6.3	1.8	6.0 X	2.5 X	5.3	-1.5
TH05	5.33	0.67	9.7	6.2 E	7.8	12.4	5.2 E	1.2 E	2.7 E	2.2 E	-0.2	-5.2
TH06	5.25	0.74	10.6	9.1	11.3 X	12.2	6.6	2.0 E	4.8 E	2.8 X	0.0	0.1
TH08	5.17	0.72	---	---	---	---	---	---	---	---	1.4 *2	4.1 *2
VN01	5.05	0.75	11.0	8.0	8.8	10.8 E	6.4	1.8	5.0 X	2.0	3.9	4.3
VN02	5.41	0.61	9.4	8.7	8.3	11.0 E	8.0 E	1.6	5.2 X	2.4 X	5.2	1.8
VN03	5.24	0.72	9.4	9.3	---	11.9	8.5 X	1.8	5.5 X	2.4 X	---	---
VN04	5.12	0.85 E	11.4	9.6	9.1	13.8	7.7 E	1.8	5.1 X	2.4 X	5.0	-1.5
VN05	5.62	0.68	9.6	9.0	8.7	11.1	7.4	1.9	5.5 X	2.0	1.2	-7.3
Vp	5.30	0.67	10.2	8.4	8.5	13.0	6.5	1.7	3.7	1.8	-0.1	-0.2
N of data	34	34	33	33	32	32	32	32	32	32		
Within DQO	34	31	32	28	28	26	22	21	12	14		
Flag E	0	2	0	5	2	6	5	7	7	9		
Flag X	0	1	1	0	2	0	5	4	13	9		

Note: "E", 15%<| Deviation |≤30%; "X", 30%<| Deviation |

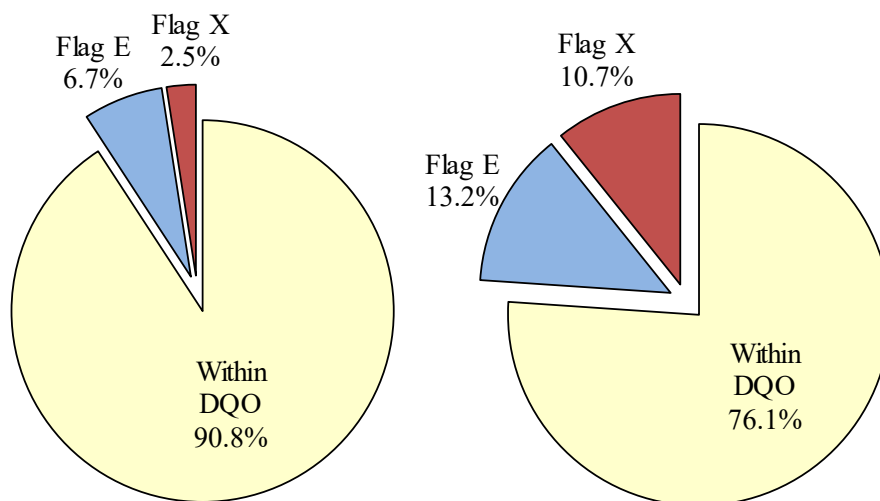
"I", Poor ion balance (R<sub>1</sub>); "C", Poor conductivity agreement (R<sub>2</sub>); "—", Not measured; "Vp", Prepared values of parameters;

\*1: The abbreviated name and code are given in Chapter 1

\*2: R<sub>1</sub> and R<sub>2</sub> for TH08 were calculated with results of ion concentration from TH06.

### 3) Comparison of high and low concentration sample

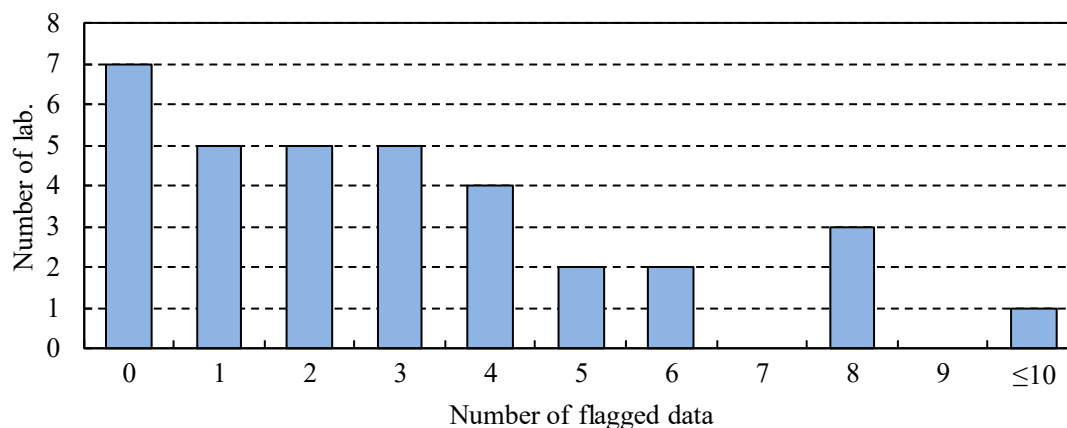
The percentage of the flagged data for sample No. 161w and 162w are shown in Figure 2.3. The percentage of the data within the DQO for sample No. 161w and 162w were 90.8% and 76.1% respectively. The difference between both samples was 14.7%. In this project, the total number of flagged data was 108 (E: 65, X: 43) among the whole set of 652 data.



**Figure 2.3 Percentage of flagged data for sample No. 161w and No. 162w (Left: No. 161w, Right: No. 162w)**

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

The number of laboratory by number of flags is shown in Figure 2.4. The number of laboratory without flagged data was 7, which corresponds to 20.6% of all the participating laboratories.



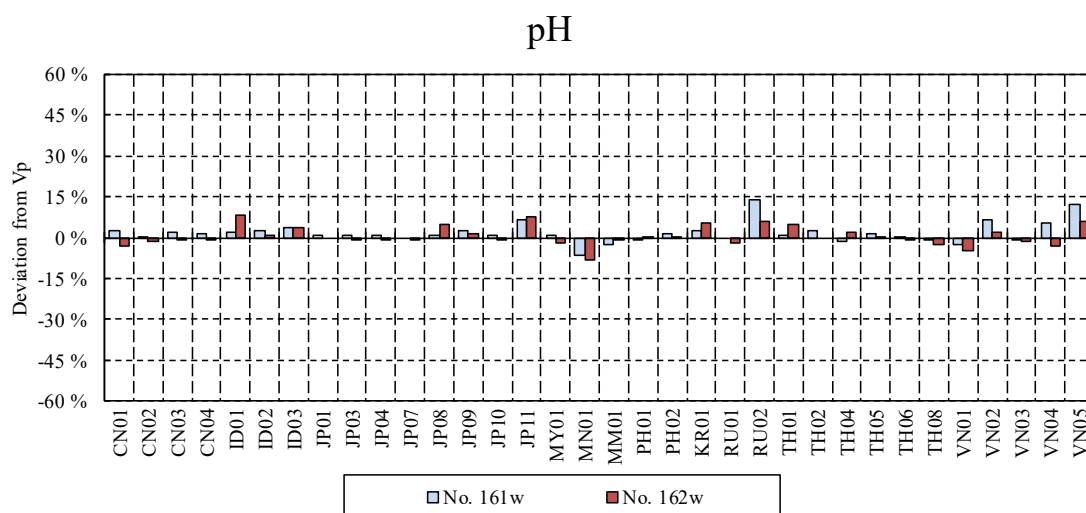
**Figure 2.4 Distribution of the number of laboratory (by number of flags)**

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

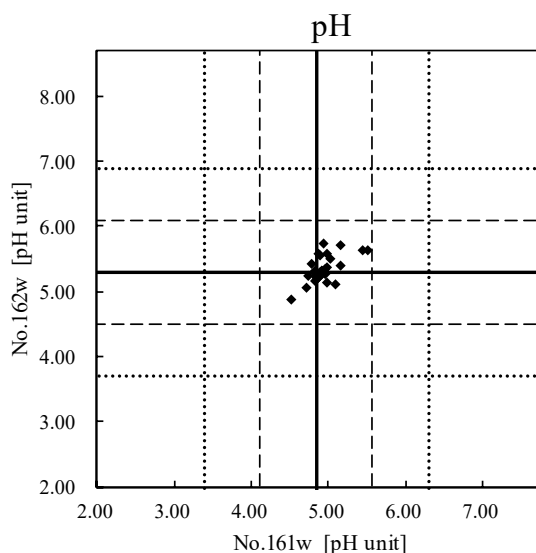
The data normalized by Vp are shown in Figures 2.5 through 2.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 161w and 162w, broken lines and dotted lines showed the values of  $V_p \pm 15\%$  and  $V_p \pm 30\%$  respectively.

#### 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.



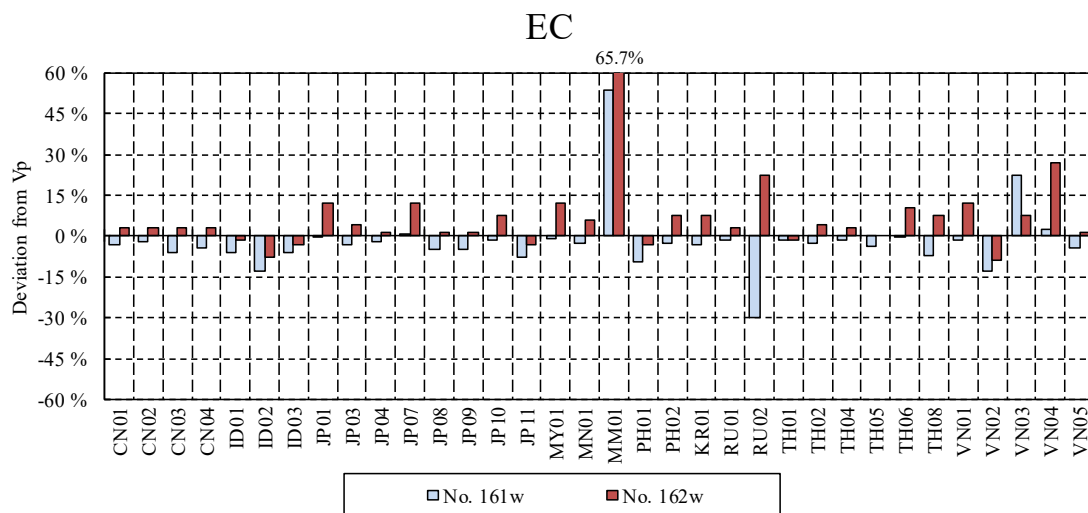
**Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)**



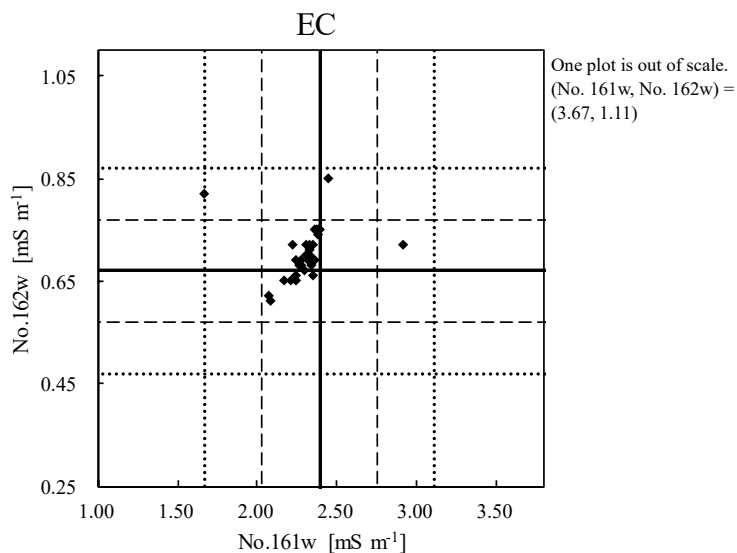
**Figure 2.6 Scatter diagram for pH**

## 2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No.161w from VN03 and the data of sample No.162w from 2 laboratories (RU02 and VN04) were marked with flag “E”. Additionally, the data of sample No.161w from 2 laboratories (MM01 and RU02) and the data of sample No.162w from MM01 were marked with flag “X”.



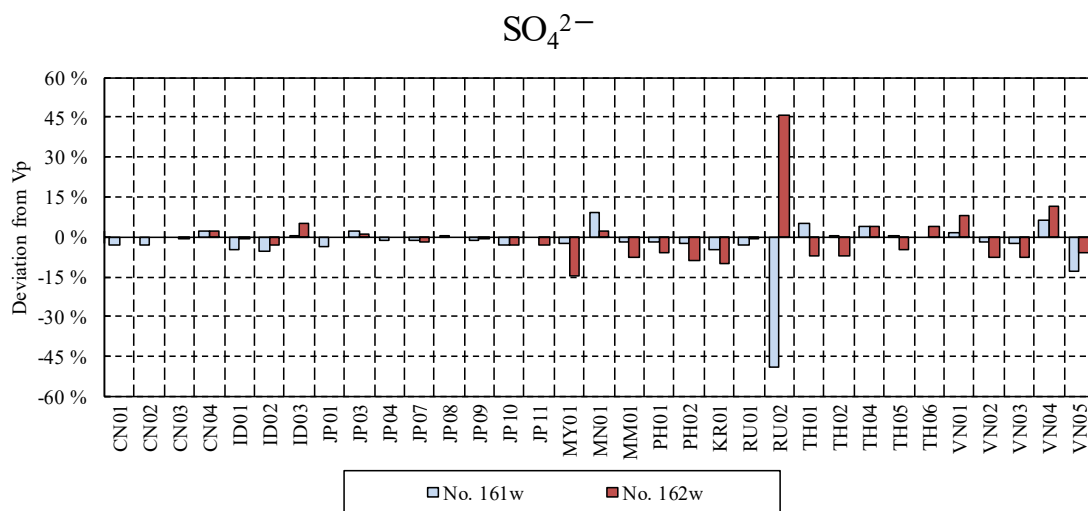
**Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)**



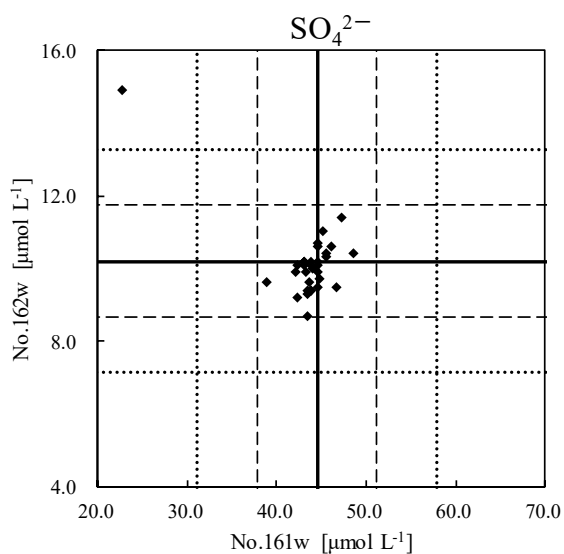
**Figure 2.8 Scatter diagram for EC**

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

The data of sample No.161w and No.162w from RU02 were marked with flag “X”. There were no data marked with flag “E”.



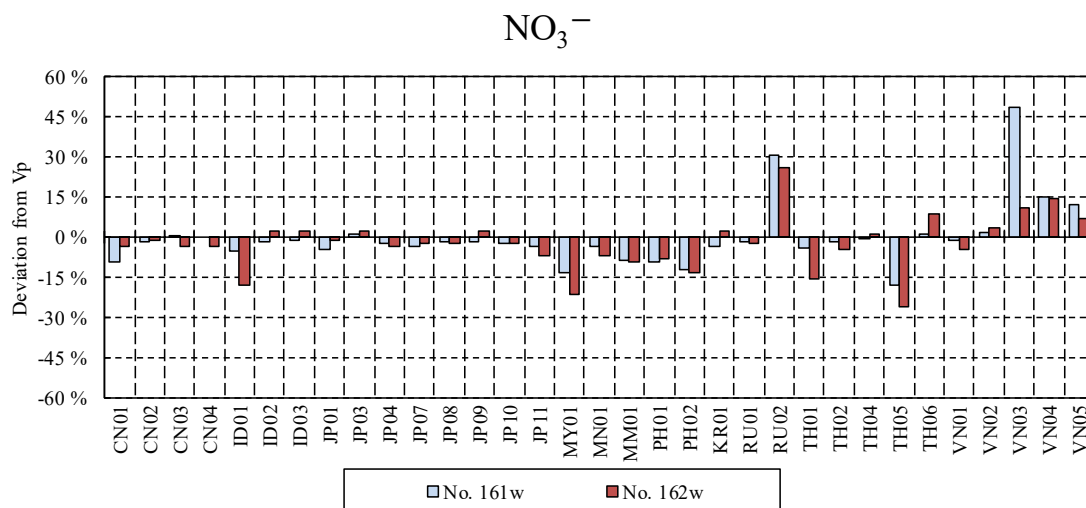
**Figure 2.9 Deviation from prepared value for  $\text{SO}_4^{2-}$  (normalized by prepared value)**



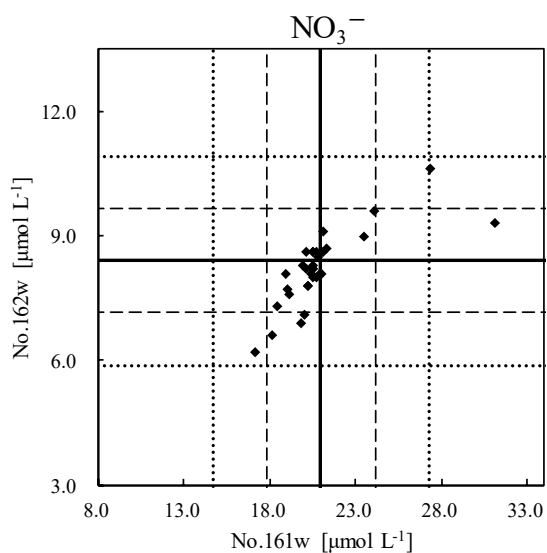
**Figure 2.10 Scatter diagram for  $\text{SO}_4^{2-}$**

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

The data of sample No. 161w from TH05 and the data of sample No. 162w from 5 laboratories (ID01, MY01, RU02, TH01 and TH05) were marked with flag “E”. Additionally, the data of sample No. 161w from 2 laboratories (RU02 and VN03) were marked with flag “X”.



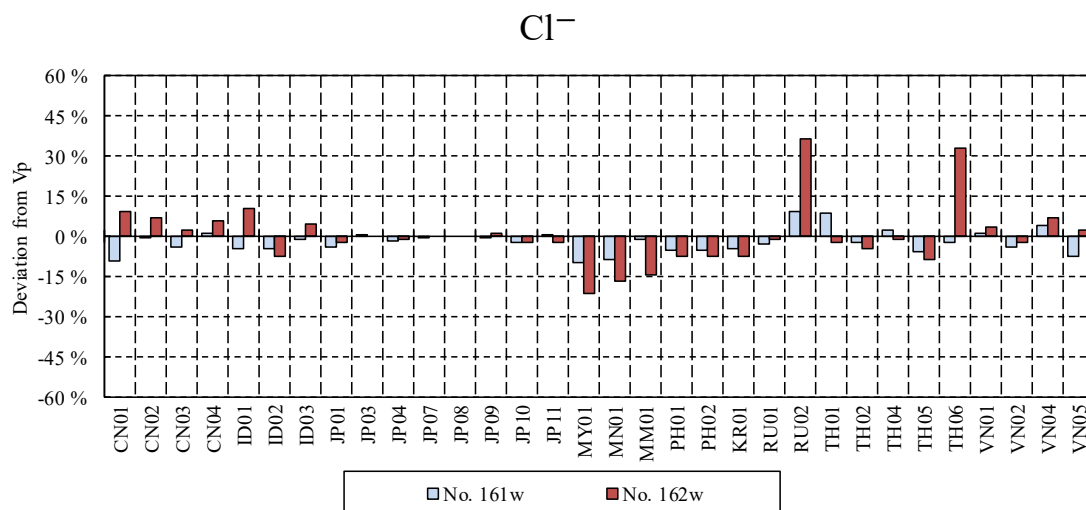
**Figure 2.11 Deviation from prepared value for  $\text{NO}_3^-$  (normalized by prepared value)**



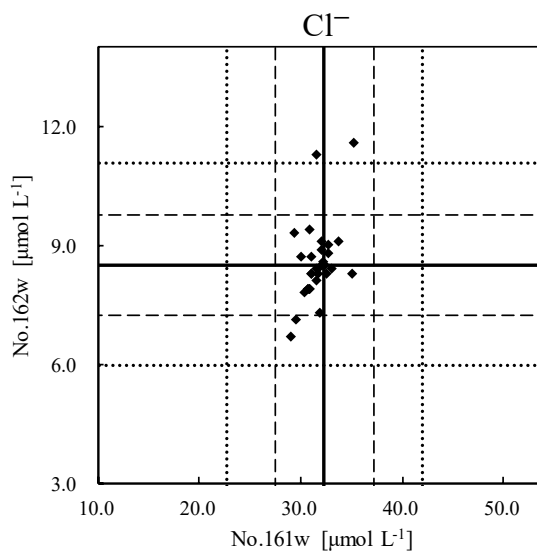
**Figure 2.12 Scatter diagram for  $\text{NO}_3^-$**

## 5) $\text{Cl}^-$

The data of sample No.162w from 2 laboratories (MY01 and MN01) were marked with flag “E”. Additionally, the data of sample No.162w from 2 laboratories (RU02 and TH06) were marked with flag “X”.



**Figure 2.13 Deviation from prepared value for  $\text{Cl}^-$  (normalized by prepared value)**

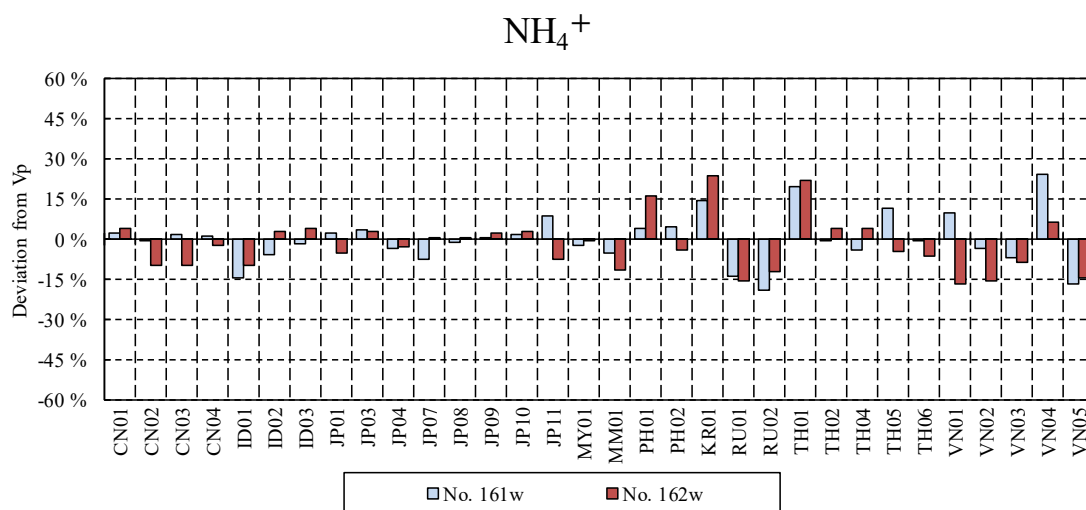


**Figure 2.14 Scatter diagram for  $\text{Cl}^-$**

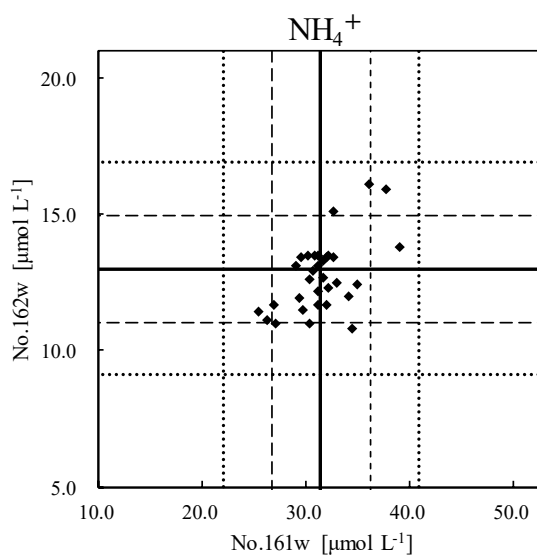


## 6) $\text{NH}_4^+$

The data of sample No. 161w from 4 laboratories (RU02, TH01, VN04 and VN05) and the data of sample No.162w from 6 laboratories (PH01, KR01, RU01, TH01, VN01 and VN02) were marked with flag “E”.



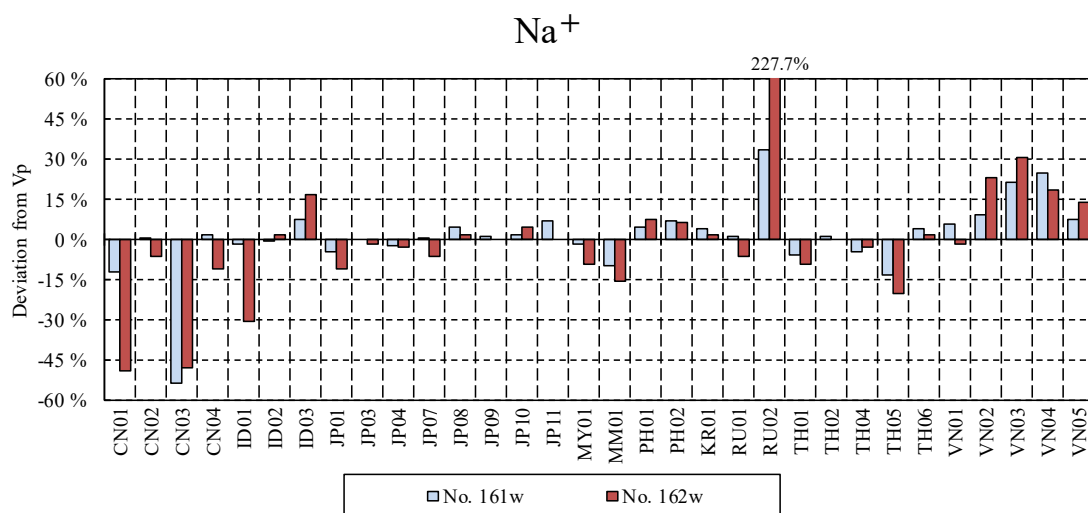
**Figure 2.15 Deviation from prepared value for  $\text{NH}_4^+$  (normalized by prepared value)**



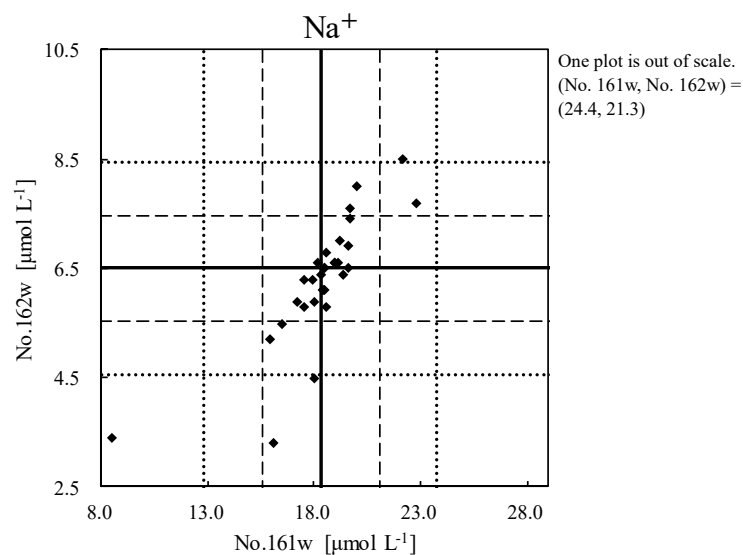
**Figure 2.16 Scatter diagram for  $\text{NH}_4^+$**

## 7) Na<sup>+</sup>

The data of sample No. 161w from 2 laboratories (VN03 and VN04) and the data of sample No. 162w from 5 laboratories (ID03, MM01, TH05, VN02 and VN04) were marked with flag “E”. Additionally, the data of sample No. 161w from 2 laboratories (CN03 and RU02) and the data of sample No. 162w from 5 laboratories (CN01, CN03, ID01, RU02 and VN03) were marked with flag “X”.



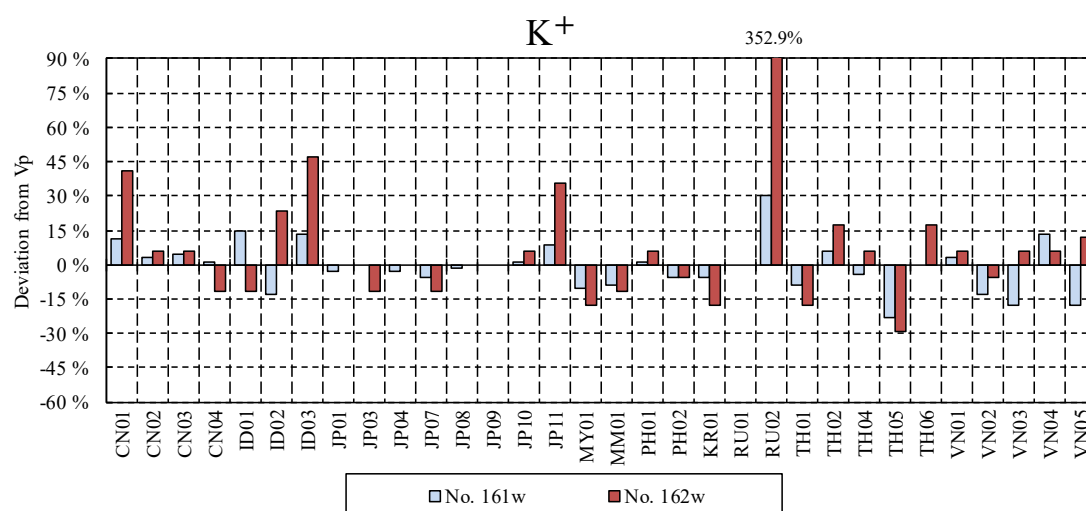
**Figure 2.17 Deviation from prepared value for Na<sup>+</sup> (normalized by prepared value)**



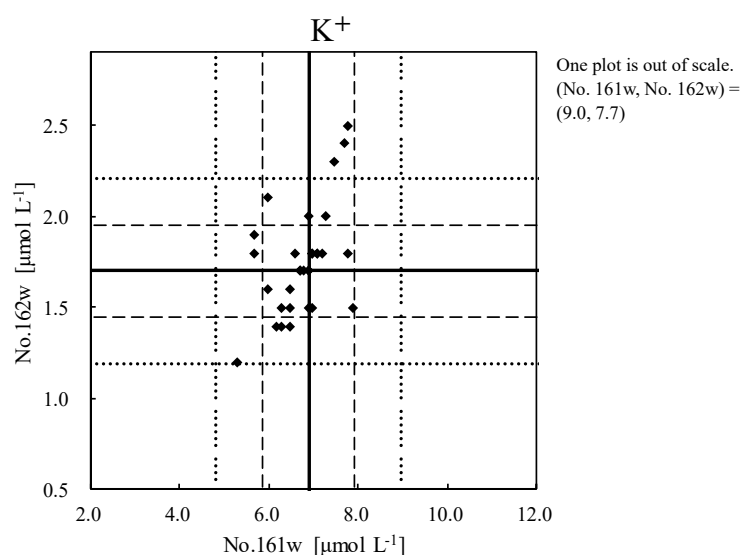
**Figure 2.18 Scatter diagram for Na<sup>+</sup>**

## 8) $K^+$

The data of sample No. 161w from 3 laboratories (TH05, VN03 and VN05) and the data of sample No. 162w from 7 laboratories (ID02, MY01, KR01, TH01, TH02, TH05 and TH06) were marked with flag “E”. Additionally, the data of sample No. 161w from RU02 and the data of sample No. 162w from 4 laboratories (CN01, ID03, JP11 and RU02) were marked with flag “X”.



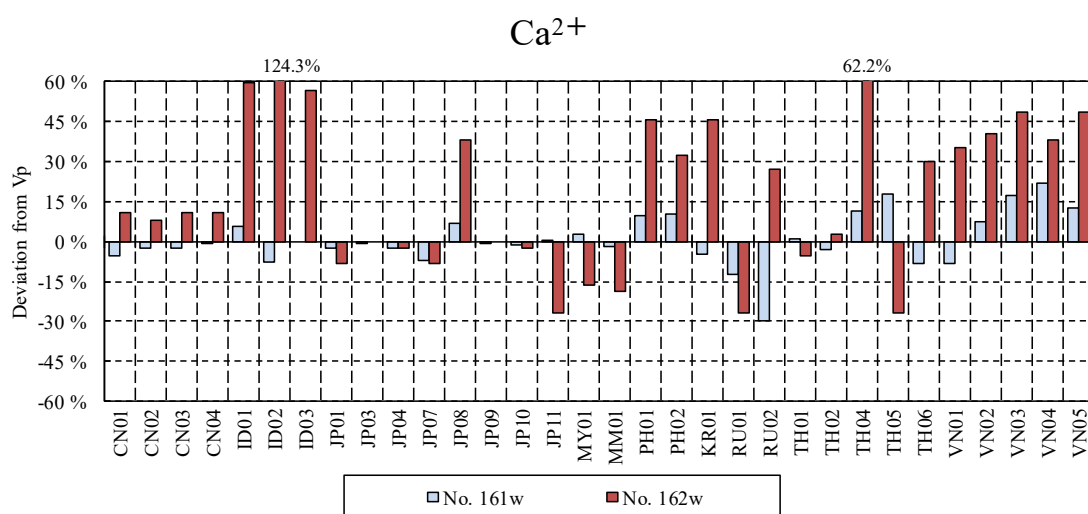
**Figure 2.19 Deviation from prepared value for  $K^+$  (normalized by prepared value)**



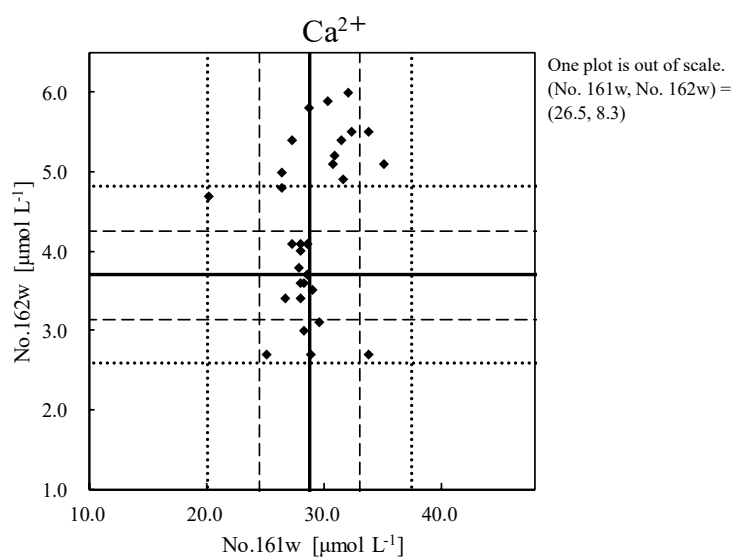
**Figure 2.20 Scatter diagram for  $K^+$**

## 9) $\text{Ca}^{2+}$

The data of sample No. 161w from 4 laboratories (RU02, TH05, VN03 and VN04) and the data of sample No. 162w from 7 laboratories (JP11, MY01, MM01, RU01, RU02, TH05 and TH06) were marked with flag “E”. Additionally, the data of sample No.162w from 13 laboratories (ID01, ID02, ID03, JP08, PH01, PH02, KR01, TH04, VN01, VN02, VN03, VN04 and VN05) were marked with flag “X”.



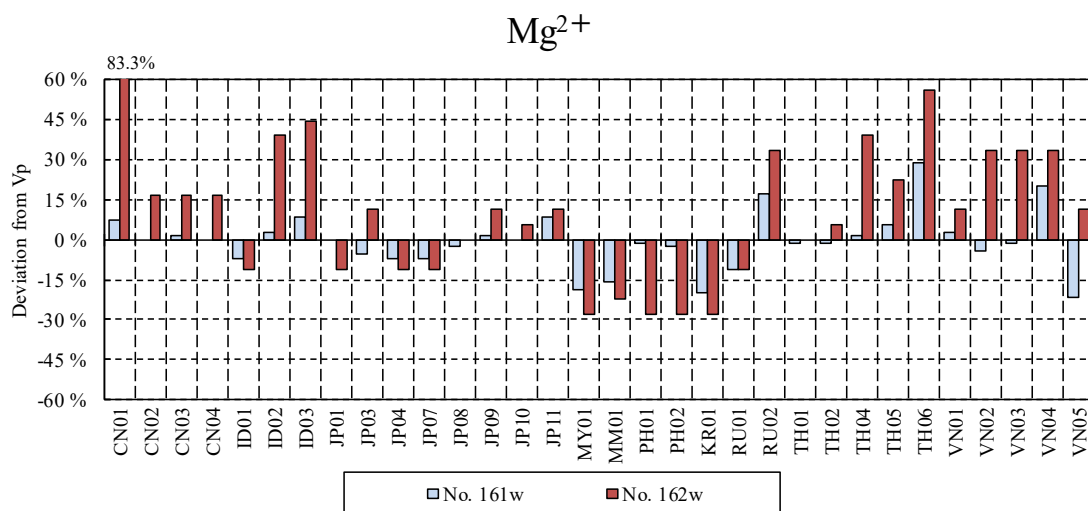
**Figure 2.21 Deviation from prepared value for  $\text{Ca}^{2+}$  (normalized by prepared value)**



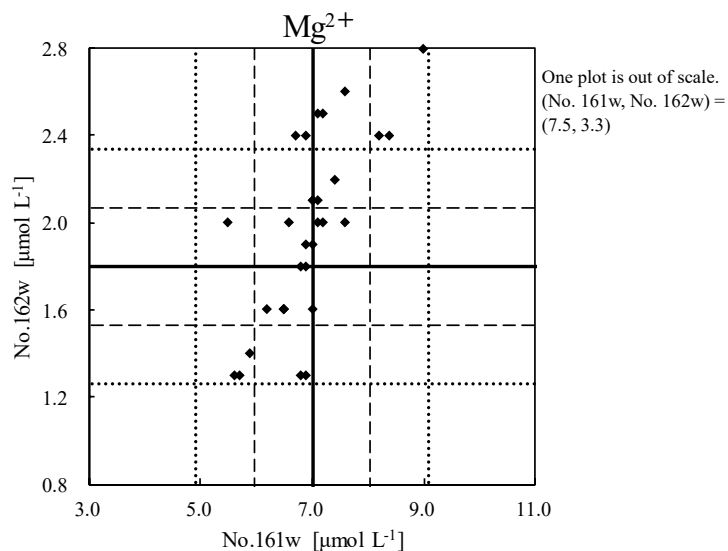
**Figure 2.22 Scatter diagram for  $\text{Ca}^{2+}$**

## 10) $\text{Mg}^{2+}$

The data of sample No. 161w from 7 laboratories (MY01, MM01, KR01, RU02, TH06, VN04 and VN05) and the data of sample No. 162w from 9 laboratories (CN02, CN03, CN04, MY01, MM01, PH01, PH02, KR01 and TH05) were marked with flag “E”. Additionally, the data of sample No. 162w from 9 laboratories (CN01, ID02, ID03, RU02, TH04, TH06, VN02, VN03 and VN04) were marked with flag “X”.



**Figure 2.23 Deviation from prepared value for  $\text{Mg}^{2+}$  (normalized by prepared value)**



**Figure 2.24 Scatter diagram for  $\text{Mg}^{2+}$**

## 11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 161w and 162w. It suggested that systematic deviation could be the reason for the deviation of results in many of laboratories.

### 2.3.3 Sample and analysis evaluation

The concentrations of the analytical parameters in the samples for this survey were fixed on the basis of the reference to monitoring data on wet deposition in EANET. Two samples were not distinguished as high or low concentration samples when they were distributed to participating laboratories. Ions (including pH as  $H^+$ ) concentrations of sample No. 161w were higher than those of No. 162w.

The relative standard deviations (R.S.D.) of each parameter for sample No. 161w and No. 162w are shown in the Figure 2.25. The R.S.D. values for sample No. 162w were almost equal to those for sample No.161w or higher than those values. Especially, the difference between the R.S.D. values for sample No.161w and sample No. 162w were high in  $Ca^{2+}$  and  $Mg^{2+}$ . The R.S.D. of  $Mg^{2+}$  for sample No. 162w was the highest in this survey.

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

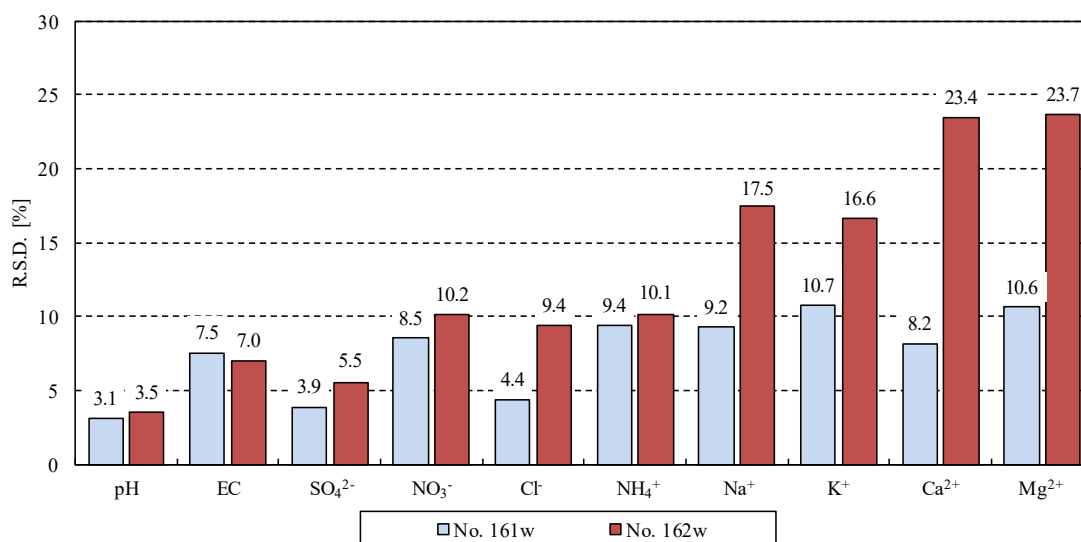


Figure 2.25 Relative standard deviations (R.S.D.) of each constituent

### 2.3.4 Information on laboratories

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

Number of analysts and years of their experience are shown in Table 2.11 and Table 2.12 respectively. In Table 2.11, the letters of “A”, “B” and “C” mean individuals of analysts in each laboratory who carried out analyses. In 16 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>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
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	1	A	A	A	A	A	A	A	A	A	A
ID01	2	A	A	B	B	B	B	B	B	B	B
ID02	4	A	B	C	C	C	D	D	D	D	D
ID03	1	A	A	A	A	A	A	A	A	A	A
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
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
JP10	1	A	A	A	A	A	A	A	A	A	A
JP11	2	A	A	B	B	B	B	B	B	B	B
MY01	4	A	A	B	B	C	D	D	D	D	D
MN01	2	A	A	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	A	C	C	C	C
RU02	2	A	A	A	A	A	A	B	B	B	B
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	2	A	A	B	B	B	B	B	B	B	B
TH05	2	A	A	B	B	B	B	B	B	B	B
TH06	1	A	A	A	A	A	A	A	A	A	A
TH08	1	A	A	---	---	---	---	---	---	---	---
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	A	---	A	C	C	A	C
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. 161w or No. 162w was marked with flag "E" or "X";

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

"---", Not measured

\*: For TH08, ions were analyzed by TH06.

Total of 152 data out of 326 were analyzed by the analysts whose experience was less than 5 years. The number corresponds to 46.6% 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>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
CN01	2	2	2	2	2	2	2	2	2	2
CN02	4	4	8	8	8	8	8	8	8	8
CN03	18	18	6	6	6	6	6	6	6	6
CN04	8	8	8	8	8	8	8	8	8	8
ID01	3	3	14	14	14	14	14	14	14	14
ID02	10	3	16	16	16	9	9	9	9	9
ID03	8	8	8	8	8	8	8	8	8	8
JP01	13	13	13	13	13	13	13	13	13	13
JP03	3	3	3	3	3	3	3	3	3	3
JP04	2	2	2	2	2	2	2	2	2	2
JP07	2	2	2	2	2	2	2	2	2	2
JP08	3	3	3	3	3	3	3	3	3	3
JP09	1	1	1	1	1	1	1	1	1	1
JP10	1	1	1	1	1	1	1	1	1	1
JP11	1	1	1	1	1	1	1	1	1	1
MY01	3	3	3	3	3	10	10	10	10	10
MN01	9	9	13	13	13	---	---	---	---	---
MM01	11	11	11	11	11	11	11	11	11	11
PH01	2	2	2	2	2	2	2	2	2	2
PH02	2	2	2	2	2	2	2	2	2	2
KR01	15	15	15	15	15	15	15	15	15	15
RU01	17	17	18	18	18	18	18	18	18	18
RU02	2	2	2	2	2	2	25	25	25	25
TH01	7	7	6	6	6	6	6	6	6	6
TH02	19	13	13	13	13	19	19	19	19	19
TH04	13	13	2	2	2	2	2	2	2	2
TH05	15	15	2	2	2	2	2	2	2	2
TH06	11	11	11	11	11	11	11	11	11	11
TH08	6	6	---	---	---	---	---	---	---	---
VN01	3	3	23	23	23	23	23	23	23	23
VN02	7	7	3	3	3	3	3	3	3	3
VN03	2	2	8	2	---	2	4	4	2	4
VN04	12	12	10	10	10	10	10	10	10	10
VN05	3	3	10	10	10	10	10	10	10	10

Note: Light mesh, Analytic data of sample No. 161w or No. 162w was marked with flag "E" or "X";

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

"---", Not measured

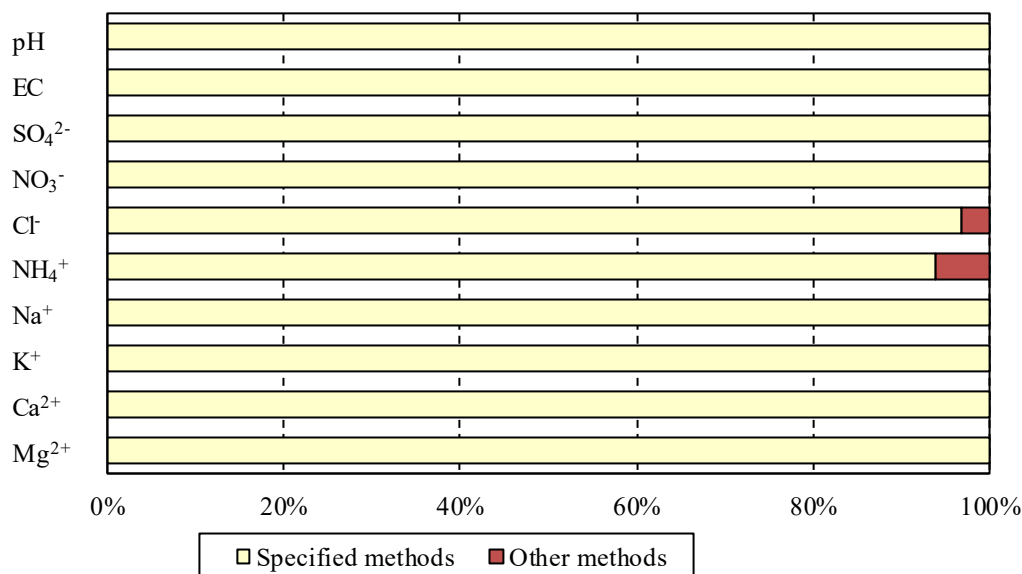
\*: For TH08, ions were analyzed by TH06.



## 2) Analytical instruments

As shown in Figure 2.26, most of the participating laboratories used the specified methods described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. RU01 and RU02 did not use the specified methods for the analyses of  $\text{NH}_4^+$  (Spectrophotometry without Indophenol). In addition, RU02 did not use the specified methods for the analyses of  $\text{Cl}^-$  (Titrimetry). The specified methods are shown in Table 2.3.

Analytical methods used for the measurement in the participating laboratories are shown in Table 2.13. Clear relationship between analytical methods and flagged data was not suggested.



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

**Table 2.13 Analytical method used for the measurement in the participating laboratories**

Lab. ID	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
KH01	---	---	---	---	---	---	---	---
CN01	IC	IC	IC	IC	IC	IC	IC	IC
CN02	IC	IC	IC	IC	IC	IC	IC	IC
CN03	IC	IC	IC	IC	IC	IC	IC	IC
CN04	IC	IC	IC	IC	IC	IC	IC	IC
ID01	IC	IC	IC	IC	IC	IC	IC	IC
ID02	IC	IC	IC	IC	IC	IC	IC	IC
ID03	IC	IC	IC	IC	IC	IC	IC	IC
JP01	IC	IC	IC	IC	IC	IC	IC	IC
JP03	IC	IC	IC	IC	IC	IC	IC	IC
JP04	IC	IC	IC	IC	IC	IC	IC	IC
JP07	IC	IC	IC	IC	IC	IC	IC	IC
JP08	IC	IC	IC	IC	IC	IC	IC	IC
JP09	IC	IC	IC	IC	IC	IC	IC	IC
JP10	IC	IC	IC	IC	IC	IC	IC	IC
JP11	IC	IC	IC	IC	IC	IC	IC	IC
LA01	---	---	---	---	---	---	---	---
MY01	IC	IC	IC	IC	IC	IC	IC	IC
MN01	IC	IC	IC	---	---	---	---	---
MM01	IC	IC	IC	IC	IC	IC	IC	IC
PH01	IC	IC	IC	IC	IC	IC	IC	IC
PH02	IC	IC	IC	IC	IC	IC	IC	IC
KR01	IC	IC	IC	IC	IC	IC	IC	IC
RU01	IC	IC	IC	SP	AES	AES	AAS	AAS
RU02	SP	SP	TI	SP	AES	AES	AAS	AAS
TH01	IC	IC	IC	IC	IC	IC	IC	IC
TH02	IC	IC	IC	IC	IC	IC	IC	IC
TH04	IC	IC	IC	IC	IC	IC	IC	IC
TH05	IC	IC	IC	IC	IC	IC	IC	IC
TH06	IC	IC	IC	IC	IC	IC	IC	IC
TH08	---	---	---	---	---	---	---	---
VN01	IC	IC	IC	IC	IC	IC	IC	IC
VN02	IC	IC	IC	IC	IC	IC	IC	IC
VN03	SP	SP	---	SP	AES	AES	AES	AES
VN04	IC	IC	IC	IC	IC	IC	IC	IC
VN05	IC	SP	IC	IC	IC	IC	IC	IC

Note: "---" Not measured

\*: For TH08, ions were analyzed by TH06.

IC: Ion Chromatography

AAS: Atomic Absorption Spectrometry

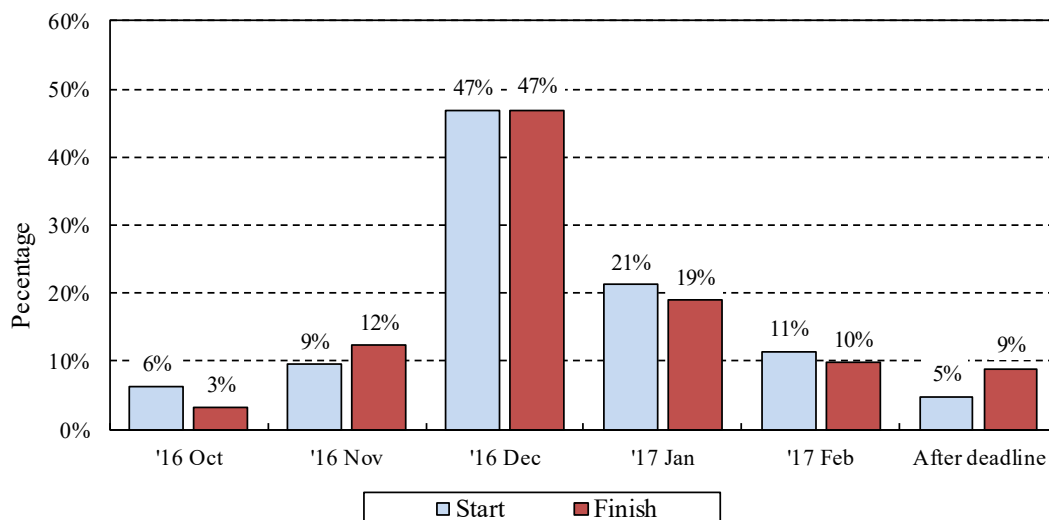
AES: Atomic Emission Spectrometry

SP: Spectrophotometry

TI: Titrimetry

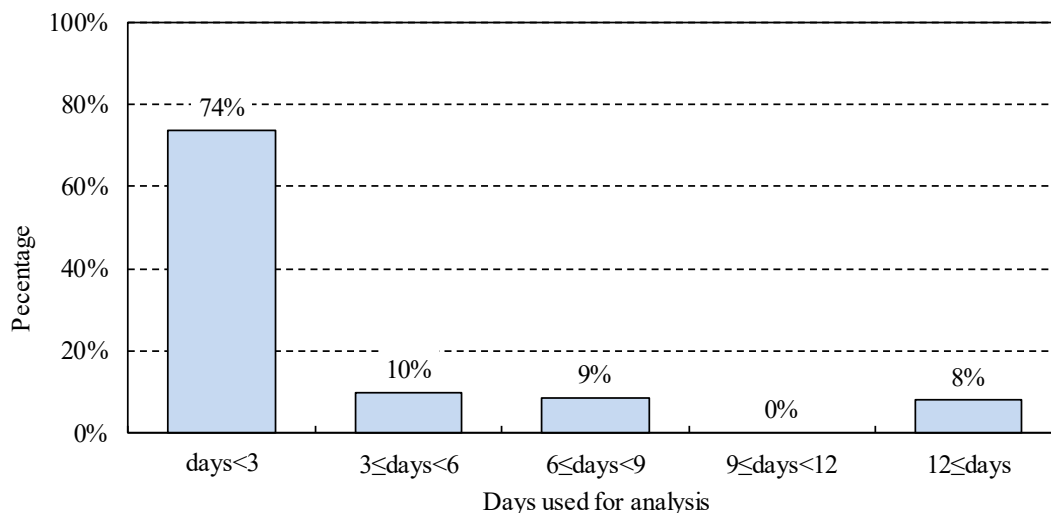
### 3) Date of analysis

Figure 2.27 shows the distribution of “Start date” and “Finish date” of analysis in the participating laboratories. In total, 62% of all the submitted data was determined within the year of 2016, and 9% was finished 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.



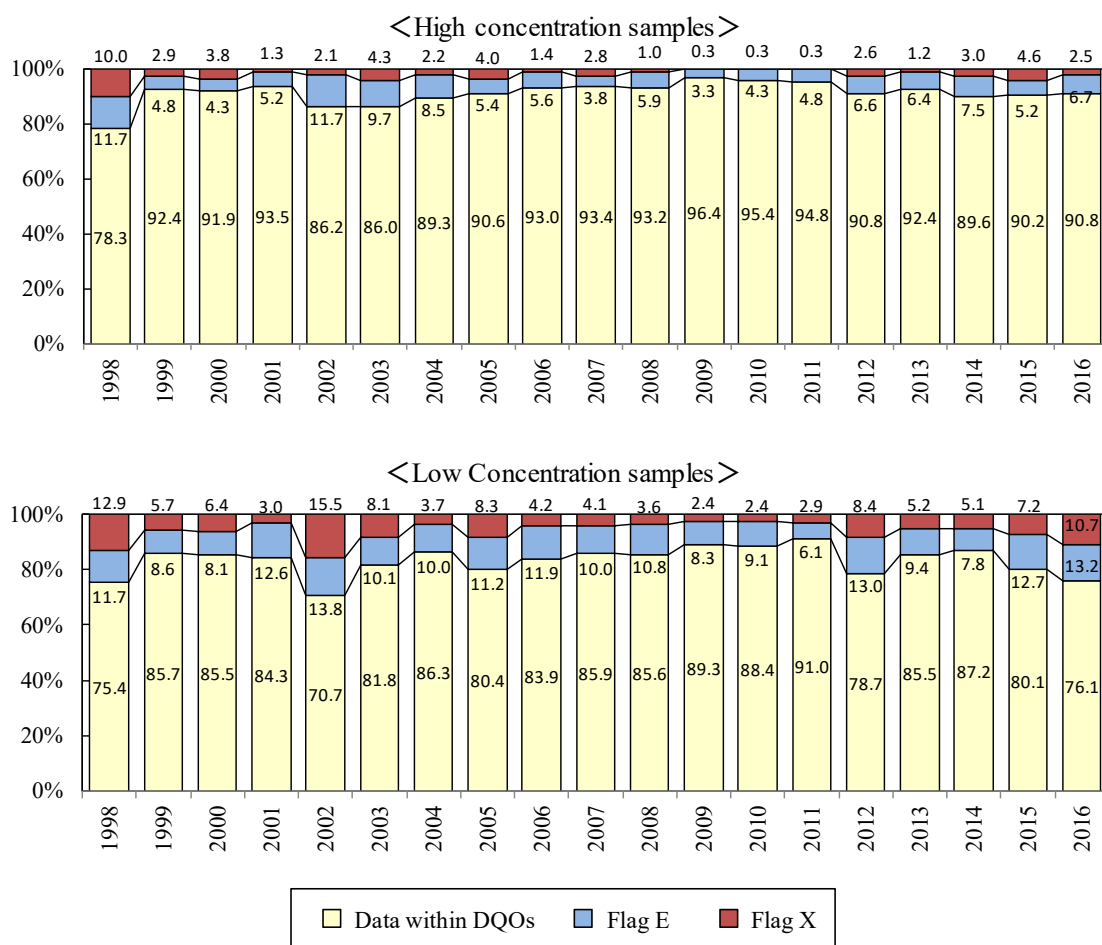
**Figure 2.28 Distribution of days used for analysis**

Clear relationship between date of analysis and flagged data was not suggested, however, it was encouraged to analyze samples as soon as possible if the samples were distributed.

## 2.4 Comparison with past surveys

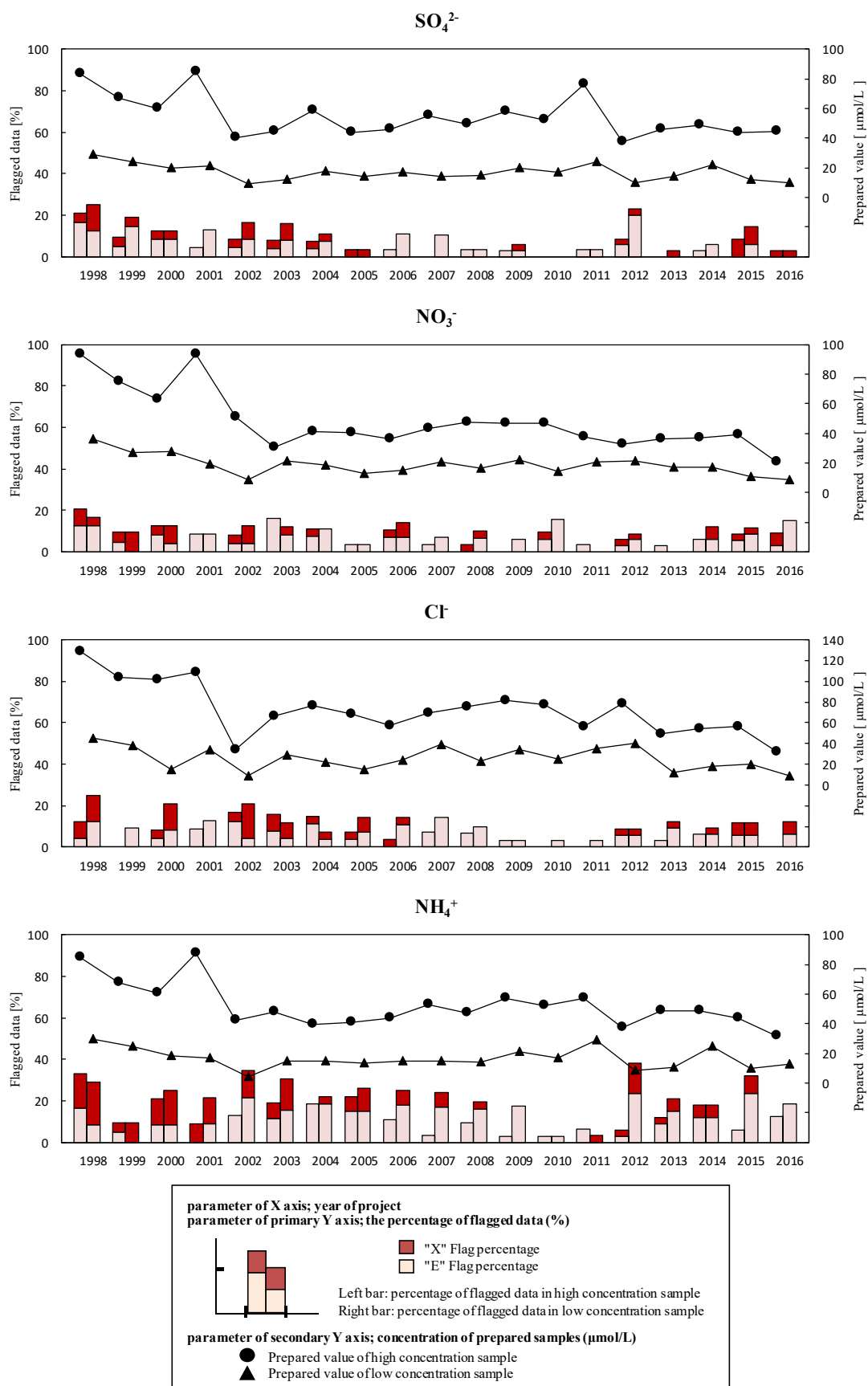
Since the beginning of EANET, inter-laboratory comparison on wet deposition reached the 19<sup>th</sup> survey. The results showing the percentages of flagged data and percentage of data that satisfied the DQO are shown in Figure 2.29. Hereafter, sample No. 161w and sample No. 162w were treated as high and low concentration samples respectively.

The percentages of data within DQO for the sample No. 161w and No. 162w were 90.8% and 76.1% respectively. Compared to previous survey, the percentage of data within DQO was slightly increased in high concentration samples and decreased in low concentration samples.



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

Figure 2.30 shows the trend of the prepared values and the percentage of the flagged data. The percentages of the flagged data were relatively high in cations than anions through the series of surveys. It is suggested that the concentration of ions affect to the percentage of flagged data. For example, while the prepared value of  $\text{Ca}^{2+}$  in low concentration samples was gradually decreased from 2014 to 2016, the percentage of flagged data of  $\text{Ca}^{2+}$  was increased from 27.3% to 62.5% .



**Figure 2.30 Comparison for each parameter in inter-laboratory comparison (ILC) project**

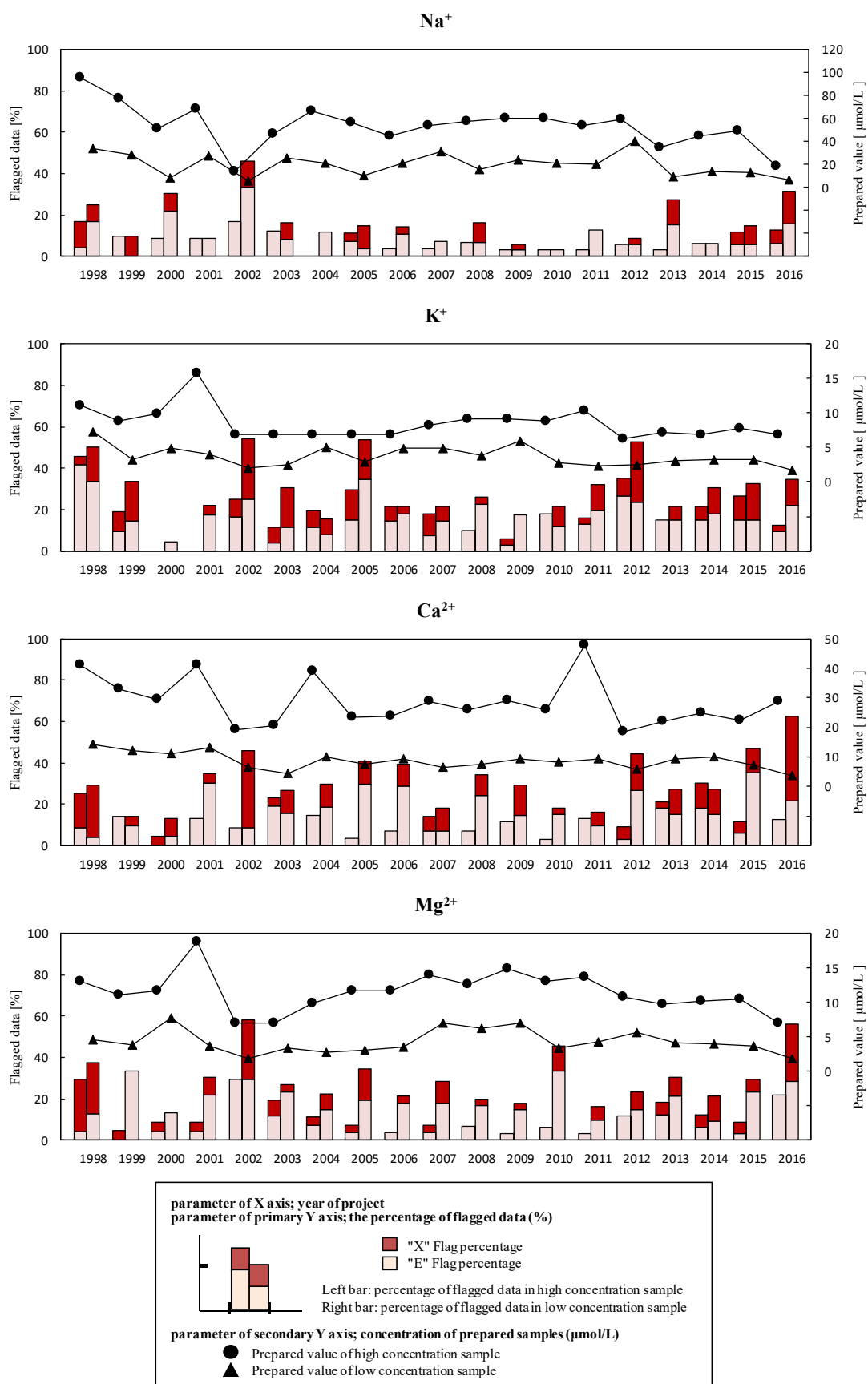
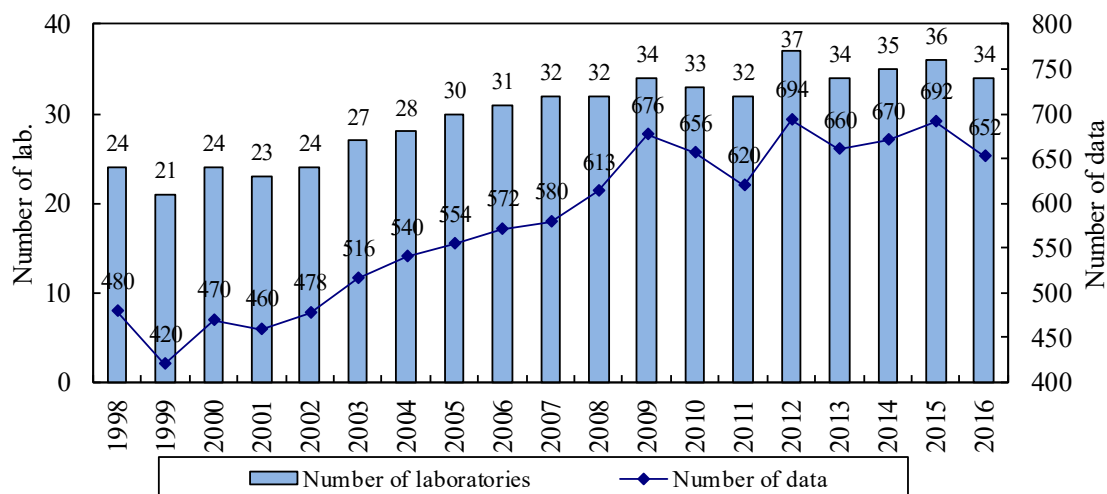


Figure 2.30 Comparison for each parameter in ILC project (continued)

As shown in figure 2.31, the total number of data in this survey was 652.



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

## 2.5 Recommendations for improvement

The fundamental matters for QA/QC on measurements and analyses of samples are described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*.

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

### 2.5.1 Measurement and Analysis

► *Technical Manual for Wet Deposition Monitoring in East Asia -2010* defined EANET DQO values for Detection limits and Determination limits. But both limits exceed the DQO in some laboratories. Both limits depend on the standard deviation from five times analysis of the standard solution which has concentration levels near determination limit of the analytical method. The standard deviation can be improved by method such as use of more purified water. Then Detection limits and Determination limits would be improved.

### 2.5.2 Data control

► After determining all the analytical parameters, the data check by calculating  $R_1$  and  $R_2$  values is important. Especially,  $R_1$  and  $R_2$  have to meet allowable ranges according to *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. 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.

► Participating laboratories are encouraged to check precision of results in prior to submission.

It should be noted that precision is greatly affected by concentration. To grasp the state of precision, drawing correlation curve between concentration and precision is effective.

► After ILC was done, artificial samples can be used as Standard Reference Material as described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. The concentration of artificial samples will be stable until next ILC when they are preserved in the refrigerator. Each laboratory should measure Standard Reference Materials in the analytical sample stream.

## References

EANET (2010). *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. Asia Center for Air Pollution Research, Niigata, Japan, 113p.



## Appendix 2.1 Data precision of submitted data

Data precision is one of the most important factors of data quality. Relative standard deviation (R.S.D.), which is one of the parameter to indicate precision, is defined by the equation below.

$$\text{R.S.D.} = \sigma / \text{Va} \times 100\%$$

$\sigma$ : standard deviation of result

$\text{Va}$ : average of result

In Appendix Table 2.1.1 and Appendix Table 2.1.2, data precisions calculated from the submitted results are shown. Sample No. 161w of higher concentration had a tendency to show better R.S.D. than sample No. 162w of lower concentration in each constituent. It was suggested that R.S.D. was greatly affected by sample concentration.

Participating laboratories are encouraged to check the precision of data in prior to submission. Correlation between sample concentration and precision should be also noted, because sample concentration could be the greatest factor to determine precision. Therefore, it is important to grasp the state of data quality during daily analysis. For example, drawing a correlation curve between concentration of standard solutions and R.S.D. of repeat analysis is effective.

**Appendix Table 2.1.1 Data precision (R.S.D.) of sample No. 161w**

Lab. ID	pH as H <sup>+</sup> %	EC %	SO <sub>4</sub> <sup>2-</sup> %	NO <sub>3</sub> <sup>-</sup> %	Cl <sup>-</sup> %	NH <sub>4</sub> <sup>+</sup> %	Na <sup>+</sup> %	K <sup>+</sup> %	Ca <sup>2+</sup> %	Mg <sup>2+</sup> %
CN01	16.7	0.2	0.3	0.6	0.5	0.2	1.9	1.6	4.7	2.8
CN02	1.9	0.5	0.1	0.2	0.2	0.2	0.4	0.0	0.2	0.0
CN03	1.5	0.3	0.8	0.3	1.5	0.4	1.2	1.5	1.8	1.0
CN04	8.8	1.2	0.6	0.9	1.4	0.9	1.1	2.1	1.0	1.6
ID01	8.4	1.3	0.8	3.2	2.2	4.9	7.2	7.2	2.6	1.9
ID02	5.4	0.2	0.7	0.7	0.4	0.2	0.4	2.9	3.7	1.1
ID03	15.6	1.8	0.6	1.4	2.0	2.3	2.7	2.0	4.6	3.9
JP01	2.1	2.1	1.2	2.0	1.4	1.4	1.7	2.6	1.3	1.2
JP03	1.0	0.2	0.3	0.9	0.8	1.1	0.3	0.6	0.3	0.8
JP04	3.5	0.6	0.2	0.0	0.2	0.6	2.8	2.0	1.2	1.5
JP07	8.1	0.9	0.1	0.0	0.4	1.5	0.3	1.0	0.7	0.9
JP08	7.9	1.5	0.2	0.2	0.4	1.0	2.9	2.4	0.4	1.1
JP09	6.1	1.0	0.2	0.4	0.2	0.3	0.3	0.5	0.2	0.9
JP10	1.8	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.5	0.8
JP11	3.7	0.9	0.3	0.2	0.3	3.8	2.2	1.3	2.9	2.8
MY01	5.0	0.2	0.4	0.3	1.1	0.4	0.9	1.3	0.9	1.2
MN01	6.8	1.8	0.4	1.7	2.0	--	--	--	--	--
MM01	16.4	2.0	2.1	6.5	3.7	1.0	1.6	6.3	7.4	7.2
PH01	11.0	1.5	0.6	1.0	0.8	3.6	0.9	3.2	8.6	5.0
PH02	7.4	0.7	0.3	0.4	0.3	6.1	6.4	4.7	4.4	2.3
KR01	17.4	0.2	0.9	1.6	0.7	0.2	5.3	5.5	0.9	1.6
RU01	3.1	0.6	0.1	0.5	0.3	0.8	0.2	0.0	0.0	0.8
RU02	3.2	11.5	0.5	0.5	0.7	1.8	1.5	1.6	0.5	1.4
TH01	1.8	0.7	1.5	1.1	4.4	0.7	0.7	1.1	0.6	0.9
TH02	2.3	0.4	0.4	0.3	0.4	0.5	0.6	1.8	0.3	0.0
TH04	4.0	0.2	1.3	1.5	0.6	0.8	5.0	4.7	2.5	3.4
TH05	7.2	0.8	0.3	2.4	0.4	1.7	2.5	5.1	3.4	8.4
TH06	1.5	0.6	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.5
TH08	2.5	0.2	--	--	--	--	--	--	--	--
VN01	3.5	2.6	0.2	0.2	0.5	1.2	1.4	2.6	1.8	0.9
VN02	2.0	0.4	0.7	1.4	1.2	1.3	3.3	4.9	1.5	5.0
VN03	1.2	0.5	0.3	0.2	--	0.1	0.9	0.0	0.0	0.0
VN04	2.2	0.3	0.1	0.2	0.1	2.2	0.4	1.1	0.1	0.6
VN05	11.6	0.2	1.6	0.0	4.3	0.0	0.0	2.2	3.8	1.7
Number of data	34	34	33	33	32	32	32	32	32	32
Minimum	1.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25% value	2.1	0.3	0.2	0.2	0.3	0.4	0.4	1.0	0.3	0.9
Median	3.8	0.6	0.4	0.5	0.6	0.9	1.1	1.9	1.1	1.2
75% value	8.1	1.2	0.7	1.4	1.4	1.5	2.5	3.0	3.0	2.4
Maximum	17.4	11.5	2.1	6.5	4.4	6.1	7.2	7.2	8.6	8.4

Note: R.S.D for "pH as H<sup>+</sup>" was calculated after pH value was converted to H<sup>+</sup> concentration;  
"--", Not measured

**Appendix Table 2.1.2 Data precision (R.S.D.) of sample No. 162w**

Lab. ID	pH as H <sup>+</sup> %	EC %	SO <sub>4</sub> <sup>2-</sup> %	NO <sub>3</sub> <sup>-</sup> %	Cl <sup>-</sup> %	NH <sub>4</sub> <sup>+</sup> %	Na <sup>+</sup> %	K <sup>+</sup> %	Ca <sup>2+</sup> %	Mg <sup>2+</sup> %
CN01	4.1	0.0	1.2	1.8	1.1	0.7	9.1	4.2	6.3	3.0
CN02	1.7	0.9	0.5	0.0	0.0	0.5	0.0	0.0	0.0	0.0
CN03	1.7	0.9	0.7	0.8	1.0	0.9	3.3	4.3	1.3	3.7
CN04	5.2	1.5	1.3	1.8	1.2	2.2	3.0	6.1	2.4	2.1
ID01	34.5	4.7	2.1	1.4	5.1	1.0	11.7	25.3	23.3	2.1
ID02	4.3	0.8	2.0	2.3	1.9	0.4	0.8	0.0	5.7	3.4
ID03	14.9	1.7	3.8	2.8	3.1	6.2	7.6	21.6	6.6	9.8
JP01	3.9	2.9	0.5	1.4	0.9	0.4	0.0	2.6	1.3	0.0
JP03	1.0	0.5	0.8	1.7	1.0	0.8	0.0	3.3	2.1	0.0
JP04	6.0	0.7	0.0	0.0	0.6	1.0	4.0	8.1	5.9	7.1
JP07	6.2	0.9	0.5	1.1	0.4	0.4	0.0	7.2	2.3	2.8
JP08	33.9	2.9	0.0	0.6	0.6	0.3	0.8	2.9	1.0	2.9
JP09	16.2	2.2	0.5	0.5	0.7	0.5	0.0	2.9	0.0	0.0
JP10	1.4	0.5	0.3	0.5	0.4	0.4	0.7	1.9	0.0	0.0
JP11	2.5	0.5	0.4	0.6	0.4	10.7	15.1	5.7	35.3	9.5
MY01	4.1	1.3	0.4	0.8	0.9	0.7	0.7	5.4	2.1	4.2
MN01	6.6	1.5	1.5	1.9	2.1	--	--	--	--	--
MM01	31.5	2.4	18.7	16.7	17.6	3.3	5.2	7.6	28.4	18.0
PH01	34.2	4.2	1.7	1.1	1.7	4.2	1.7	9.7	8.4	25.8
PH02	6.6	1.2	1.3	4.2	1.2	3.3	1.8	13.1	4.4	7.2
KR01	58.1	0.6	11.0	2.2	1.5	4.9	4.9	15.5	35.3	8.6
RU01	2.9	1.0	0.4	0.0	0.4	1.0	0.7	2.6	0.0	0.0
RU02	3.7	4.3	1.5	2.1	1.6	2.1	1.0	1.9	3.3	6.5
TH01	3.1	0.8	0.9	0.8	1.2	0.8	0.8	2.4	3.1	2.8
TH02	4.9	0.0	0.0	0.4	0.0	0.9	0.7	2.5	1.4	1.8
TH04	34.7	0.8	0.8	0.9	7.4	7.5	9.8	7.2	6.3	9.1
TH05	23.1	2.5	0.0	0.7	0.6	4.1	10.2	51.0	12.8	7.0
TH06	1.4	0.0	0.0	0.0	0.0	0.4	0.0	1.7	0.0	0.0
TH08	1.8	1.1	--	--	--	--	--	--	--	--
VN01	3.8	2.2	1.0	0.6	0.6	2.8	0.8	2.4	1.1	2.2
VN02	2.6	0.9	1.9	2.5	1.9	3.4	6.1	7.4	4.0	7.4
VN03	1.4	0.6	0.0	0.0	--	0.4	0.0	0.0	0.0	0.0
VN04	2.9	0.9	0.5	0.6	0.9	0.6	1.5	2.9	1.0	2.8
VN05	6.8	1.0	3.3	0.0	3.3	0.0	1.5	4.1	4.5	4.2
Number of data	34	34	33	33	32	32	32	32	32	32
Minimum	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25% value	2.7	0.7	0.4	0.5	0.6	0.4	0.7	2.5	1.1	1.3
Median	4.2	1.0	0.8	0.8	1.0	0.9	1.3	4.2	2.7	2.9
75% value	12.9	2.1	1.5	1.8	1.7	3.3	5.0	7.5	6.3	7.2
Maximum	58.1	4.7	18.7	16.7	17.6	10.7	15.1	51.0	35.3	25.8

Note: R.S.D for "pH as H<sup>+</sup>" was calculated after pH value was converted to H<sup>+</sup> concentration;  
"--", Not measured

## Appendix 2.2 Analytical results submitted by the laboratories

**Appendix Table 2.2.1 Analytical data concerning sample No. 161w**

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	NH <sub>4</sub> <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
CN01	4.98	2.32	43.1	19.0	29.4	32.3	16.1	7.7	27.3	7.5
CN02	4.86	2.34	43.1	20.6	32.1	31.3	18.4	7.1	28.0	7.0
CN03	4.96	2.25	44.5	21.1	31.0	32.1	8.5	7.2	28.0	7.1
CN04	4.92	2.28	45.5	21.0	32.8	31.8	18.6	7.0	28.6	7.0
ID01	4.94	2.25	42.4	19.9	30.9	27.0	18.0	7.9	30.4	6.5
ID02	4.97	2.08	42.1	20.6	30.9	29.7	18.2	6.0	26.5	7.2
ID03	5.03	2.25	44.6	20.8	32.0	30.9	19.7	7.8	28.8	7.6
JP01	4.90	2.38	43.0	20.0	31.0	32.3	17.5	6.7	28.1	7.0
JP03	4.89	2.31	45.6	21.2	32.4	32.7	18.3	6.9	28.6	6.6
JP04	4.90	2.34	43.9	20.5	31.8	30.5	17.9	6.7	28.1	6.5
JP07	4.85	2.40	44.0	20.2	32.1	29.2	18.4	6.5	26.8	6.5
JP08	4.88	2.27	44.6	20.6	32.3	31.2	19.1	6.8	30.8	6.8
JP09	4.98	2.27	43.9	20.6	32.2	31.7	18.5	6.9	28.6	7.1
JP10	4.89	2.35	43.2	20.5	31.7	32.0	18.6	7.0	28.4	7.0
JP11	5.16	2.21	44.5	20.3	32.5	34.2	19.6	7.5	28.9	7.6
MY01	4.88	2.37	43.4	18.2	29.1	30.8	18.0	6.2	29.6	5.7
MN01	4.53	2.33	48.6	20.3	29.5	---	---	---	---	---
MM01	4.74	3.67	43.8	19.2	31.9	29.8	16.5	6.3	28.3	5.9
PH01	4.83	2.17	43.6	19.1	30.7	32.8	19.2	7.0	31.6	6.9
PH02	4.91	2.33	43.4	18.5	30.7	33.0	19.6	6.5	31.7	6.8
KR01	4.98	2.31	42.3	20.2	30.9	36.1	19.0	6.5	27.4	5.6
RU01	4.85	2.36	43.1	20.6	31.5	27.1	18.5	6.9	25.2	6.2
RU02	5.52	1.67	22.8	27.4	35.3	25.6	24.4	9.0	20.2	8.2
TH01	4.89	2.35	46.7	20.1	35.1	37.8	17.2	6.3	29.0	6.9
TH02	4.97	2.33	44.6	20.6	31.6	31.3	18.5	7.3	27.9	6.9
TH04	4.78	2.35	46.2	20.9	33.1	30.2	17.5	6.6	32.1	7.1
TH05	4.91	2.30	44.7	17.2	30.4	35.1	15.9	5.3	33.9	7.4
TH06	4.86	2.38	44.5	21.2	31.6	31.3	19.0	6.9	26.4	9.0
TH08	4.82	2.22	---	---	---	---	---	---	---	---
VN01	4.73	2.36	45.2	20.8	32.8	34.6	19.4	7.1	26.4	7.2
VN02	5.17	2.09	43.8	21.3	31.1	30.5	20.0	6.0	31.0	6.7
VN03	4.83	2.92	43.4	31.2	---	29.4	22.2	5.7	33.8	6.9
VN04	5.10	2.45	47.2	24.1	33.7	39.2	22.8	7.8	35.1	8.4
VN05	5.44	2.28	38.8	23.5	30.0	26.3	19.7	5.7	32.4	5.5
<b>Prepared value</b>	<b>4.85</b>	<b>2.39</b>	<b>44.5</b>	<b>21.0</b>	<b>32.3</b>	<b>31.5</b>	<b>18.3</b>	<b>6.9</b>	<b>28.8</b>	<b>7.0</b>
Number of data	33	33	32	32	32	32	31	32	31	32
Average	4.92	2.30	44.1	20.6	31.7	31.6	18.8	6.8	29.3	6.9
Minimum	4.53	1.67	38.8	17.2	29.1	25.6	15.9	5.3	25.2	5.5
Maximum	5.44	2.92	48.6	27.4	35.3	39.2	24.4	9.0	35.1	9.0
Standard deviation	0.15	0.17	1.71	1.76	1.39	2.95	1.74	0.73	2.39	0.74

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

"---", Not measured

**Appendix Table 2.2.2 Analytical data concerning sample No. 162w**

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
		mS/m	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
CN01	5.13	0.69	10.2	8.1	9.3	13.5	3.3	2.4	4.1	3.3
CN02	5.24	0.69	10.2	8.3	9.1	11.7	6.1	1.8	4.0	2.1
CN03	5.27	0.69	10.1	8.1	8.7	11.7	3.4	1.8	4.1	2.1
CN04	5.27	0.69	10.4	8.1	9.0	12.7	5.8	1.5	4.1	2.1
ID01	5.73	0.66	10.1	6.9	9.4	11.7	4.5	1.5	5.9	1.6
ID02	5.34	0.62	9.9	8.6	7.9	13.4	6.6	2.1	8.3	2.5
ID03	5.49	0.65	10.7	8.6	8.9	13.5	7.6	2.5	5.8	2.6
JP01	5.30	0.75	10.2	8.3	8.3	12.3	5.8	1.7	3.4	1.6
JP03	5.28	0.70	10.3	8.6	8.5	13.4	6.4	1.5	3.7	2.0
JP04	5.29	0.68	10.2	8.1	8.4	12.6	6.3	1.7	3.6	1.6
JP07	5.29	0.75	10.0	8.2	8.5	13.1	6.1	1.5	3.4	1.6
JP08	5.57	0.68	10.2	8.2	8.5	13.1	6.6	1.7	5.1	1.8
JP09	5.37	0.68	10.1	8.6	8.6	13.3	6.5	1.7	3.7	2.0
JP10	5.25	0.72	9.9	8.2	8.3	13.4	6.8	1.8	3.6	1.9
JP11	5.70	0.65	9.9	7.8	8.3	12.0	6.5	2.3	2.7	2.0
MY01	5.21	0.75	8.7	6.6	6.7	12.9	5.9	1.4	3.1	1.3
MN01	4.87	0.71	10.4	7.8	7.1	---	---	---	---	---
MM01	5.25	1.11	9.4	7.6	7.3	11.5	5.5	1.5	3.0	1.4
PH01	5.31	0.65	9.6	7.7	7.9	15.1	7.0	1.8	5.4	1.3
PH02	5.31	0.72	9.3	7.3	7.9	12.5	6.9	1.6	4.9	1.3
KR01	5.59	0.72	9.2	8.6	7.9	16.1	6.6	1.4	5.4	1.3
RU01	5.20	0.69	10.1	8.2	8.4	11.0	6.1	1.7	2.7	1.6
RU02	5.63	0.82	14.9	10.6	11.6	11.4	21.3	7.7	4.7	2.4
TH01	5.55	0.66	9.5	7.1	8.3	15.9	5.9	1.4	3.5	1.8
TH02	5.30	0.70	9.5	8.0	8.1	13.5	6.5	2.0	3.8	1.9
TH04	5.42	0.69	10.6	8.5	8.4	13.5	6.3	1.8	6.0	2.5
TH05	5.33	0.67	9.7	6.2	7.8	12.4	5.2	1.2	2.7	2.2
TH06	5.25	0.74	10.6	9.1	11.3	12.2	6.6	2.0	4.8	2.8
TH08	5.17	0.72	---	---	---	---	---	---	---	---
VN01	5.05	0.75	11.0	8.0	8.8	10.8	6.4	1.8	5.0	2.0
VN02	5.41	0.61	9.4	8.7	8.3	11.0	8.0	1.6	5.2	2.4
VN03	5.24	0.72	9.4	9.3	---	11.9	8.5	1.8	5.5	2.4
VN04	5.12	0.85	11.4	9.6	9.1	13.8	7.7	1.8	5.1	2.4
VN05	5.62	0.68	9.6	9.0	8.7	11.1	7.4	1.9	5.5	2.0
<b>Prepared value</b>	<b>5.30</b>	<b>0.67</b>	<b>10.2</b>	<b>8.4</b>	<b>8.5</b>	<b>13.0</b>	<b>6.5</b>	<b>1.7</b>	<b>3.7</b>	<b>1.8</b>
Number of data	34	33	32	33	31	32	31	31	31	32
Average	5.33	0.70	10.0	8.2	8.4	12.8	6.3	1.7	4.3	2.0
Minimum	4.87	0.61	8.7	6.2	6.7	10.8	3.3	1.2	2.7	1.3
Maximum	5.73	0.85	11.4	10.6	11.3	16.1	8.5	2.5	6.0	3.3
Standard deviation	0.19	0.05	0.55	0.83	0.79	1.29	1.10	0.29	1.01	0.47

Note: The outliers judged by 3S.D. method were painted with light mesh and were excluded from statistics;  
 "---", Not measured

## Appendix 2.3 Normalized data

**Appendix Table 2.3.1 Deviation% from prepared values of sample No. 161w**

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
	%	%	%	%	%	%	%	%	%	%
CN01	2.7	-2.9	-3.1	-9.5	-9.0	2.5	-12.0	11.6	-5.2	7.1
CN02	0.2	-2.1	-3.1	-1.9	-0.6	-0.6	0.5	2.9	-2.8	0.0
CN03	2.3	-5.9	0.0	0.5	-4.0	1.9	-53.6	4.3	-2.8	1.4
CN04	1.4	-4.6	2.2	0.0	1.5	1.0	1.6	1.4	-0.7	0.0
ID01	1.9	-5.9	-4.7	-5.2	-4.3	-14.3	-1.6	14.5	5.6	-7.1
ID02	2.5	-13.0	-5.4	-1.9	-4.3	-5.7	-0.5	-13.0	-8.0	2.9
ID03	3.7	-5.9	0.2	-1.0	-0.9	-1.9	7.7	13.0	0.0	8.6
JP01	1.0	-0.4	-3.4	-4.8	-4.0	2.5	-4.4	-2.9	-2.4	0.0
JP03	0.8	-3.3	2.5	1.0	0.3	3.8	0.0	0.0	-0.7	-5.7
JP04	1.0	-2.1	-1.3	-2.4	-1.5	-3.2	-2.2	-2.9	-2.4	-7.1
JP07	0.0	0.4	-1.1	-3.8	-0.6	-7.3	0.5	-5.8	-6.9	-7.1
JP08	0.6	-5.0	0.2	-1.9	0.0	-1.0	4.4	-1.4	6.9	-2.9
JP09	2.7	-5.0	-1.3	-1.9	-0.3	0.6	1.1	0.0	-0.7	1.4
JP10	0.8	-1.7	-2.9	-2.4	-1.9	1.6	1.6	1.4	-1.4	0.0
JP11	6.4	-7.5	0.0	-3.3	0.6	8.6	7.1	8.7	0.3	8.6
MY01	0.6	-0.8	-2.5	-13.3	-9.9	-2.2	-1.6	-10.1	2.8	-18.6
MN01	-6.6	-2.5	9.2	-3.3	-8.7	---	---	---	---	---
MM01	-2.3	53.6	-1.6	-8.6	-1.2	-5.4	-9.8	-8.7	-1.7	-15.7
PH01	-0.4	-9.2	-2.0	-9.0	-5.0	4.1	4.9	1.4	9.7	-1.4
PH02	1.2	-2.5	-2.5	-11.9	-5.0	4.8	7.1	-5.8	10.1	-2.9
KR01	2.7	-3.3	-4.9	-3.8	-4.3	14.6	3.8	-5.8	-4.9	-20.0
RU01	0.0	-1.3	-3.1	-1.9	-2.5	-14.0	1.1	0.0	-12.5	-11.4
RU02	13.8	-30.1	-48.8	30.5	9.3	-18.7	33.3	30.4	-29.9	17.1
TH01	0.8	-1.7	4.9	-4.3	8.7	20.0	-6.0	-8.7	0.7	-1.4
TH02	2.5	-2.5	0.2	-1.9	-2.2	-0.6	1.1	5.8	-3.1	-1.4
TH04	-1.4	-1.7	3.8	-0.5	2.5	-4.1	-4.4	-4.3	11.5	1.4
TH05	1.2	-3.8	0.4	-18.1	-5.9	11.4	-13.1	-23.2	17.7	5.7
TH06	0.2	-0.4	0.0	1.0	-2.2	-0.6	3.8	0.0	-8.3	28.6
TH08	-0.6	-7.1	---	---	---	---	---	---	---	---
VN01	-2.5	-1.3	1.6	-1.0	1.5	9.8	6.0	2.9	-8.3	2.9
VN02	6.6	-12.6	-1.6	1.4	-3.7	-3.2	9.3	-13.0	7.6	-4.3
VN03	-0.4	22.2	-2.5	48.6	---	-6.7	21.3	-17.4	17.4	-1.4
VN04	5.2	2.5	6.1	14.8	4.3	24.4	24.6	13.0	21.9	20.0
VN05	12.2	-4.6	-12.8	11.9	-7.1	-16.5	7.7	-17.4	12.5	-21.4
Number of data	34	34	33	33	32	32	32	32	32	32
Average	1.8	-2.1	-2.3	-0.2	-1.9	0.2	1.2	-0.9	0.7	-0.8
Minimum	-6.6	-30.1	-48.8	-18.1	-9.9	-18.7	-53.6	-23.2	-29.9	-21.4
Maximum	13.8	53.6	9.2	48.6	9.3	24.4	33.3	30.4	21.9	28.6

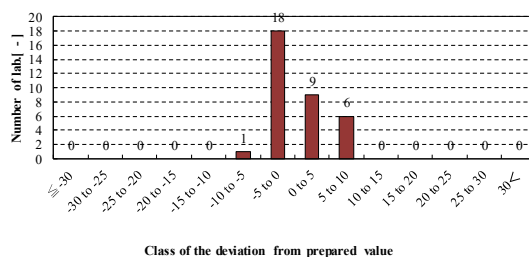
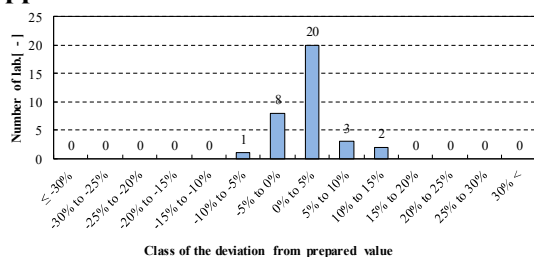
Note: "---", Not measured

**Appendix Table 2.3.2 Deviation% from prepared values of sample No. 162w**

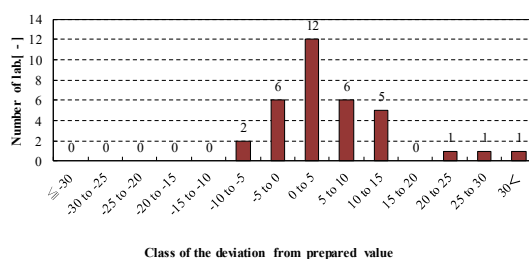
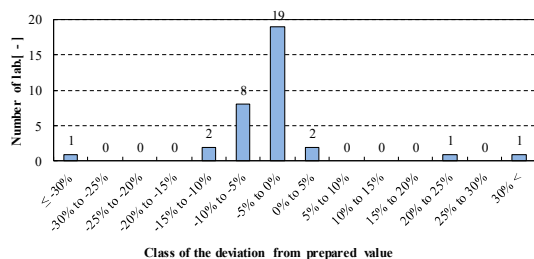
Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
	%	%	%	%	%	%	%	%	%	%
CN01	-3.2	3.0	0.0	-3.6	9.4	3.8	-49.2	41.2	10.8	83.3
CN02	-1.1	3.0	0.0	-1.2	7.1	-10.0	-6.2	5.9	8.1	16.7
CN03	-0.6	3.0	-1.0	-3.6	2.4	-10.0	-47.7	5.9	10.8	16.7
CN04	-0.6	3.0	2.0	-3.6	5.9	-2.3	-10.8	-11.8	10.8	16.7
ID01	8.1	-1.5	-1.0	-17.9	10.6	-10.0	-30.8	-11.8	59.5	-11.1
ID02	0.8	-7.5	-2.9	2.4	-7.1	3.1	1.5	23.5	124.3	38.9
ID03	3.6	-3.0	4.9	2.4	4.7	3.8	16.9	47.1	56.8	44.4
JP01	0.0	11.9	0.0	-1.2	-2.4	-5.4	-10.8	0.0	-8.1	-11.1
JP03	-0.4	4.5	1.0	2.4	0.0	3.1	-1.5	-11.8	0.0	11.1
JP04	-0.2	1.5	0.0	-3.6	-1.2	-3.1	-3.1	0.0	-2.7	-11.1
JP07	-0.2	11.9	-2.0	-2.4	0.0	0.8	-6.2	-11.8	-8.1	-11.1
JP08	5.1	1.5	0.0	-2.4	0.0	0.8	1.5	0.0	37.8	0.0
JP09	1.3	1.5	-1.0	2.4	1.2	2.3	0.0	0.0	0.0	11.1
JP10	-0.9	7.5	-2.9	-2.4	-2.4	3.1	4.6	5.9	-2.7	5.6
JP11	7.5	-3.0	-2.9	-7.1	-2.4	-7.7	0.0	35.3	-27.0	11.1
MY01	-1.7	11.9	-14.7	-21.4	-21.2	-0.8	-9.2	-17.6	-16.2	-27.8
MN01	-8.1	6.0	2.0	-7.1	-16.5	---	---	---	---	---
MM01	-0.9	65.7	-7.8	-9.5	-14.1	-11.5	-15.4	-11.8	-18.9	-22.2
PH01	0.2	-3.0	-5.9	-8.3	-7.1	16.2	7.7	5.9	45.9	-27.8
PH02	0.2	7.5	-8.8	-13.1	-7.1	-3.8	6.2	-5.9	32.4	-27.8
KR01	5.5	7.5	-9.8	2.4	-7.1	23.8	1.5	-17.6	45.9	-27.8
RU01	-1.9	3.0	-1.0	-2.4	-1.2	-15.4	-6.2	0.0	-27.0	-11.1
RU02	6.2	22.4	46.1	26.2	36.5	-12.3	227.7	352.9	27.0	33.3
TH01	4.7	-1.5	-6.9	-15.5	-2.4	22.3	-9.2	-17.6	-5.4	0.0
TH02	0.0	4.5	-6.9	-4.8	-4.7	3.8	0.0	17.6	2.7	5.6
TH04	2.3	3.0	3.9	1.2	-1.2	3.8	-3.1	5.9	62.2	38.9
TH05	0.6	0.0	-4.9	-26.2	-8.2	-4.6	-20.0	-29.4	-27.0	22.2
TH06	-0.9	10.4	3.9	8.3	32.9	-6.2	1.5	17.6	29.7	55.6
TH08	-2.5	7.5	---	---	---	---	---	---	---	---
VN01	-4.7	11.9	7.8	-4.8	3.5	-16.9	-1.5	5.9	35.1	11.1
VN02	2.1	-9.0	-7.8	3.6	-2.4	-15.4	23.1	-5.9	40.5	33.3
VN03	-1.1	7.5	-7.8	10.7	---	-8.5	30.8	5.9	48.6	33.3
VN04	-3.4	26.9	11.8	14.3	7.1	6.2	18.5	5.9	37.8	33.3
VN05	6.0	1.5	-5.9	7.1	2.4	-14.6	13.8	11.8	48.6	11.1
Number of data	34	34	33	33	32	32	32	32	32	32
Average	0.6	6.5	-0.6	-2.4	0.5	-1.9	3.9	13.8	19.8	10.8
Minimum	-8.1	-9.0	-14.7	-26.2	-21.2	-16.9	-49.2	-29.4	-27.0	-27.8
Maximum	8.1	65.7	46.1	26.2	36.5	23.8	227.7	352.9	124.3	83.3

Note: "---", Not measured

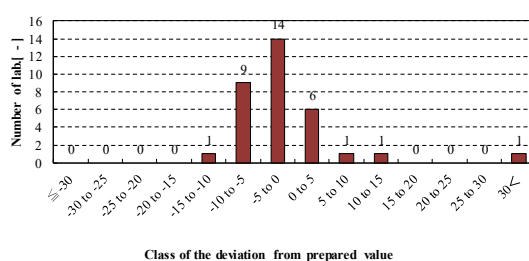
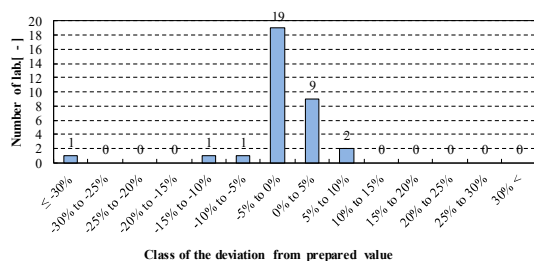
## Appendix 2.4 Data distribution



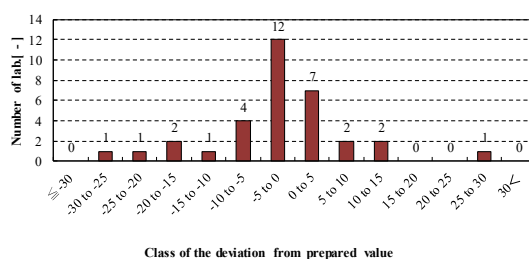
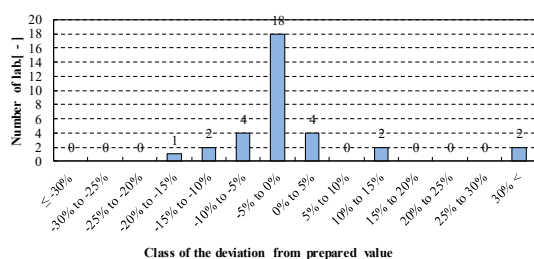
Appendix Figure 2.4.1 Data distribution for pH (Left: 161w, Right: 162w)



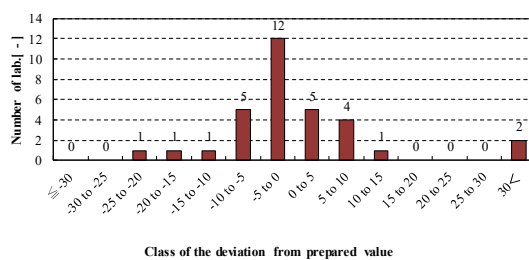
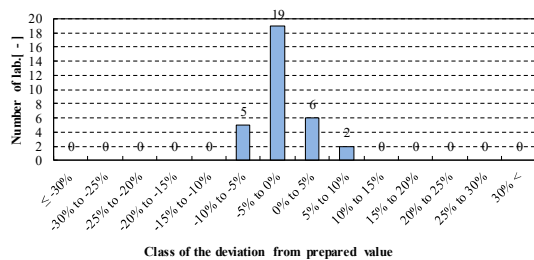
Appendix Figure 2.4.2 Data distribution for EC (Left: 161w, Right: 162w)



Appendix Figure 2.4.3 Data distribution for  $\text{SO}_4^{2-}$  (Left: 161w, Right: 162w)

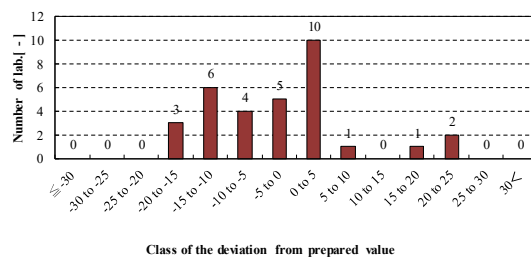
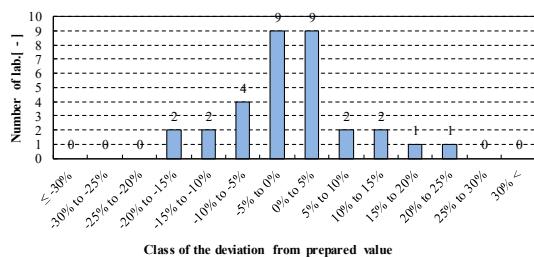


Appendix Figure 2.4.4 Data distribution for  $\text{NO}_3^-$  (Left: 161w, Right: 162w)

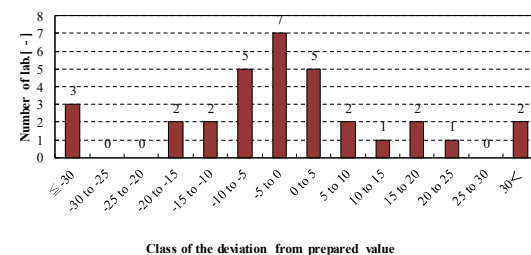
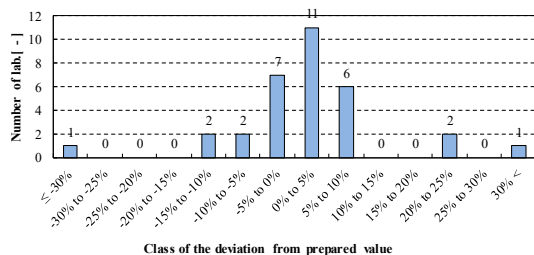


Appendix Figure 2.4.5 Data distribution for  $\text{Cl}^-$  (Left: 161w, Right: 162w)

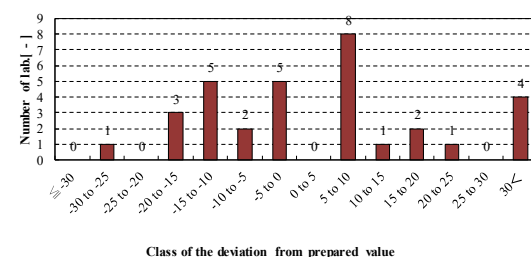
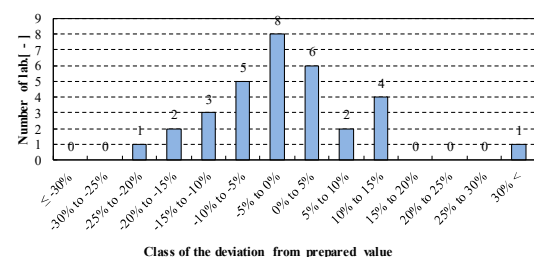




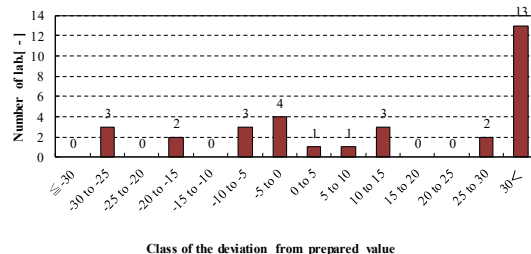
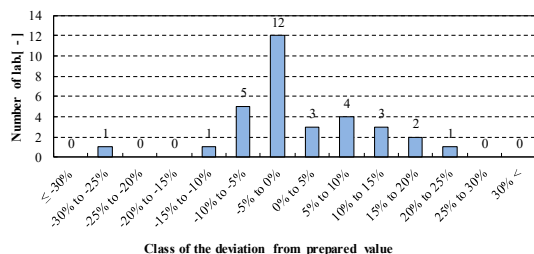
**Appendix Figure 2.4.6 Data distribution for  $\text{NH}_4^+$  (Left: 161w, Right: 162w)**



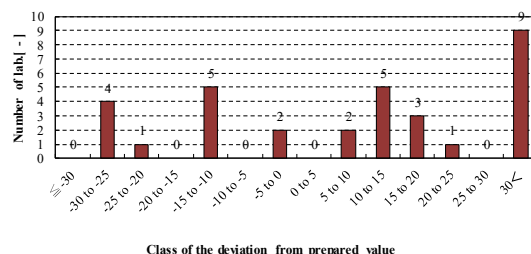
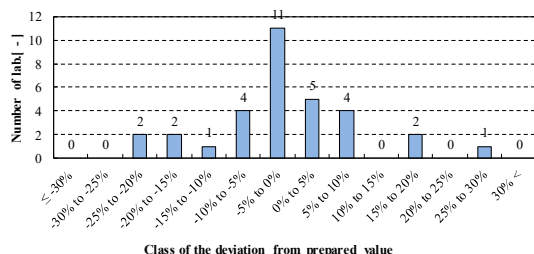
**Appendix Figure 2.4.7 Data distribution for  $\text{Na}^+$  (Left: 161w, Right: 162w)**



**Appendix Figure 2.4.8 Data distribution for  $\text{K}^+$  (Left: 161w, Right: 162w)**



**Appendix Figure 2.4.9 Data distribution for  $\text{Ca}^{2+}$  (Left: 161w, Right: 162w)**



**Appendix Figure 2.4.10 Data distribution for  $\text{Mg}^{2+}$  (Left: 161w, Right: 162w)**



### 3. 12<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

#### 3.1 Introduction

In the Inter-laboratory Comparison on 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 2016. Most of the laboratories which monitor with the filter pack method in EANET joined this activity and submitted their analytical results to the NC. These results were compared with the corresponding prepared value and statistically analyzed.

#### 3.2 Procedures

##### 3.2.1 Participating Laboratories

A total of 28 laboratories in charge of EANET dry monitoring participated in this 12<sup>th</sup> activity and 24 laboratories submitted the results to the NC. The participating laboratories and data submission status are shown 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. 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 are 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.161d-1	Alkali ( $\text{K}_2\text{CO}_3$ ) impregnated filter	Polyethylene centrifuge tube	3	Two kinds of the standard solutions which contained known concentration of sulfate or chloride ion were added.
No.161d-2	Acid ( $\text{H}_3\text{PO}_4$ ) impregnated filter	Polyethylene centrifuge tube	3	One kind of the standard solution which contained known concentration of ammonium ion was added.

No.162d-1	Alkali (K <sub>2</sub> CO <sub>3</sub> ) impregnated filter	Polyethylene centrifuge tube	3	Two kinds of the standard solutions which contained known concentration of sulfate or chloride ion were added.
No.162d-2	Acid (H <sub>3</sub> PO <sub>4</sub> ) impregnated filter	Polyethylene centrifuge tube	3	One kind of the standard solution which contained known concentration of ammonium ion was added.
No.163d-1	Alkali (K <sub>2</sub> CO <sub>3</sub> ) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.163d-2	Acid (H <sub>3</sub> PO <sub>4</sub> ) impregnated filter	Polyethylene centrifuge tube	3	Blank

### 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 sample analyses on the filter pack method is described in "*Technical Manual for Air Concentration Monitoring in East Asia*" (EANET, 2013). As 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.161d-1, No.162d-1, No.163d-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 them for 20 minutes.

#### (2) Sample No.161d-2, No.162d-2, No.163d-2

Add 20 mL of pure water (EC<0.15 mS L<sup>-1</sup>) as an extracting solvent into each centrifuge tube, then shake or agitate them for 20 minutes.

#### (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 analyses immediately after extraction.

Note 2) In principle, it is strongly recommended that the filtrate 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 analytical methods specified in “*Technical Manual for Wet Deposition Monitoring in East Asia – 2010*” (EANET, 2010) in Table 3.2.

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

Analyte	Analytical method
$\text{SO}_4^{2-}, \text{Cl}^-$	Ion Chromatography (preferably with suppressor) Spectrophotometry
$\text{NH}_4^+$	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 ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$ ) in the filter sample.

Each quantity ( $M_{\text{sol}}$ ) is calculated as follows:

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

where  $M_{\text{sol}}$  : quantity of each component in the filtrate ( $\mu\text{g}$ );

$C_{\text{sol}}$  : concentration of each component in the filtrate ( $\text{mg L}^{-1}$ );

$V_{\text{sol}}$  : volume of the solvent (20 mL);

The net quantity of each ion ( $\text{net}M_{\text{sol}}$ ) is calculated as follows :

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

where  $\text{net}M_{\text{sol}}$  : net quantity of each ion on the filter.

$M_{\text{sol, Sample}}$ : quantity ( $\mu\text{g}$ ) of each component in the filtrate from sample No.161d-1, No.161d-2, No.162d-1 and No.162d-2;

$M_{\text{sol, Blank}}$ : the median quantity ( $\mu\text{g}$ ) in the filtrate from blank sample No.163d-1 and No.163d-2.

## 3.3 Results

The NC distributed the filter samples to 28 laboratories in the participating countries of EANET, and received their results from 24 laboratories. The results compared to the prepared values are

summarized in Table 3.3. The average, minimum, maximum, standard deviation (S.D.) and number of data (N) were calculated from each analyzed ion quantity. Analytical results of Samples No.161d and No.162d are shown in Table 3.5 and Table 3.7.

Outliers, defined as those results exceeding three standard deviations, should be rejected before their calculation and this time one result was rejected.

As shown in Table 3.3, the deviations ( $\Delta V/V_p$ ) for  $\text{SO}_4^{2-}$  in Sample No. 161d and Sample No.162d were -12.9% and -8.6%. The deviations for  $\text{Cl}^-$  in Sample No. 161d and Sample No.162d were -6.9% and -5.5%. The deviations for  $\text{NH}_4^+$  in Sample No. 161d and Sample No.162d were -1.0% and -4.5%.

The Data Quality Objectives (DQOs) of EANET are specified that determined values are expected to fall within  $\pm 15\%$  deviation from the prepared values in *Technical Manual for Air Concentration Monitoring in East Asia* (2013). Each laboratory analyzed each sample 3 times, averaged the values, and these average values were compared with the corresponding prepared values for this report. A flag "E" indicates that its deviation exceeds  $\pm 15\%$  but not  $\pm 30\%$ , and a flag "X" indicates that its deviation exceeds  $\pm 30\%$ .

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

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

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

The evaluation of the results on both Samples No.161d and No.162d 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**

Analyte		Prepared* (V <sub>p</sub> )	Average (V <sub>a</sub> )	$\Delta V/V_p^*$ (%)	S.D.	Number (N)	Minimum	Maximum
<u>Sample No. 161d</u>								
SO <sub>4</sub> <sup>2-</sup>	(µg)	15	13.1	-12.9	2.26	24	7.31	15.7
Cl <sup>-</sup>	(µg)	4.0	3.73	-6.9	0.69	24	2.09	5.41
NH <sub>4</sub> <sup>+</sup>	(µg)	8.8	8.72	-1.0	1.78	24	4.15	13.4
<u>Sample No. 162d</u>								
SO <sub>4</sub> <sup>2-</sup>	(µg)	54	49.4	-8.6	4.4	24	39.9	55.6
Cl <sup>-</sup>	(µg)	15	14.2	-5.5	0.97	23	11.8	16.6
NH <sub>4</sub> <sup>+</sup>	(µg)	46	43.9	-4.5	7.64	24	21.8	59.0

\* 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>) × 100 (%)

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

#### Samples No. 161d-1, No.161d-2

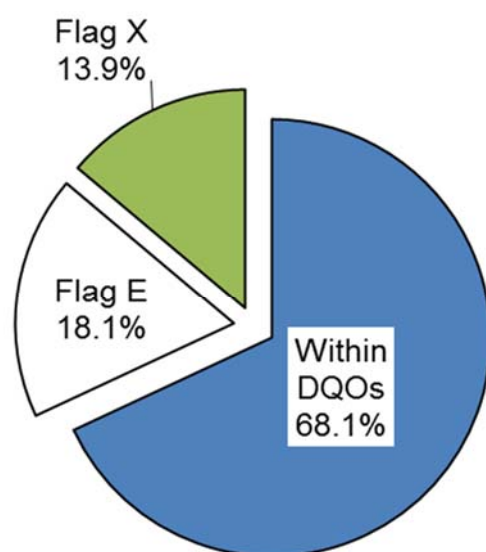
For Sample No.161d , 13 analytical data in 72 results were flagged E, and 10 analytical data were flagged X. The total percentage of the flagged samples was 31.9%. (Figure 3.1, Table 3.4 and 3.5).

**Table 3.4 Number of flagged data for Sample No.151d**

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Flag E *	5	4	4	13
Flag X *	4	3	3	10
Data within DQOs	15	17	17	49
Ratio of Flagged (%)	37.5	29.2	29.2	31.9

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

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



**Figure 3.1** Percentage of flagged data for Sample No.161d

**Table 3.5** Average analytical results of Sample No.161d

Lab. Code	SO <sub>4</sub> <sup>2-</sup> (µg)		Cl <sup>-</sup> (µg)		NH <sub>4</sub> <sup>+</sup> (µg)
CN02	7.31	X	2.45	X	8.59
ID01	13.1		3.30	E	7.99
ID03	14.0		3.52		8.52
JP01	14.2		3.61		4.15 X
JP02	15.7		3.94		8.63
JP03	15.6		3.77		9.21
JP04	14.6		3.81		7.99
JP08	15.4		3.97		9.44
JP09	14.9		3.82		8.95
JP10	13.2		3.70		8.73
JP11	9.11	X	3.72		8.51
MY01	10.3	X	3.67		8.66
MM01	10.6	E	4.92	E	6.27 E
PH01	15.0		3.75		8.25
PH02	12.0	E	2.09	X	6.05 X
KR01	9.71	X	2.92	E	10.8 E
RU01	15.5		5.41	X	9.00
TH01	13.7		3.82		11.2 E
TH02	12.3	E	3.40		8.08



TH04	14.5		3.52		8.99
TH05	11.4	E	3.68		13.4 X
TH06	15.4		4.99 E		8.89
VN01	13.3		4.15		11.1 E
VN02	12.6	E	3.47		7.76

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

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

### **Samples No. 162d-1, No.162d-2**

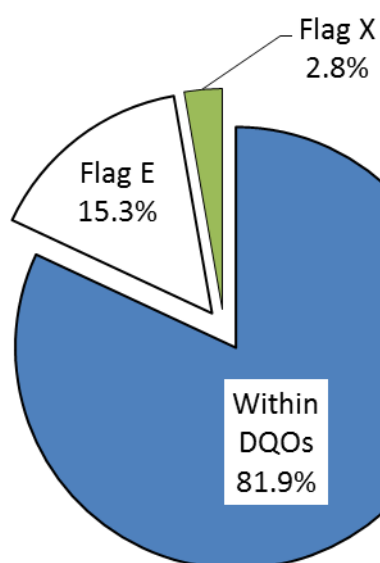
For Sample No.162d, 11 analytical data in 72 results were flagged E, and 2 analytical data were flagged X. The total percentage of the flagged samples was 18.1%. (Figure 3.2, Table 3.6 and 3.7).

**Table 3.6 Number of flagged data for Sample No.162d**

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Flag E *	4	2	5	11
Flag X *	0	1	1	2
Data within DQOs	20	21	18	59
Ratio of Flagged (%)	16.7	12.5	25.0	18.1

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

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



**Figure 3.2 Percentage of flagged data for Sample No.162d**

**Table 3.7 Average analytical results of Sample No.162d**

Lab. Code	SO <sub>4</sub> <sup>2-</sup> (µg)	Cl <sup>-</sup> (µg)	NH <sub>4</sub> <sup>+</sup> (µg)
CN02	40.8 E	11.8 E	42.6
ID01	50.8	12.2 E	34.0 E
ID03	51.9	13.8	35.0 E
JP01	48.2	14.4	21.8 X
JP02	54.1	14.8	43.4
JP03	53.9	14.6	48.7
JP04	53.1	14.6	42.2
JP08	55.6	14.9	47.3
JP09	52.0	14.4	44.6
JP10	50.0	14.3	45.4
JP11	40.9 E	14.8	44.7
MY01	47.9	15.1	45.5
MM01	44.3 E	13.8	41.0
PH01	54.4	14.0	45.4
PH02	39.9 E	8.72 X	41.6
KR01	46.1	13.4	43.5
RU01	54.2	16.6	43.7
TH01	47.8	14.9	58.9 E
TH02	47.8	13.5	40.6
TH04	54.1	15.0	39.6
TH05	49.4	13.3	57.7 E
TH06	50.4	13.9	44.8
VN01	47.4	14.1	59.0 E
VN02	49.7	13.9	42.8

\*Flag E: 15% < | Deviation | ≤ 30%

\*Flag X: 30% < | Deviation |

### **Blank Sample (No.163d)**

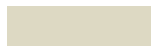
Each quantity of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and NH<sub>4</sub><sup>+</sup> was determined for blank sample No.163d-1 and No.163d-2. Their obtained values are shown in Table 3.8. Blank values were detected in a wide range, including 0 µg. Table 3.9 shows the ratio of the blank value to analytical results by laboratory. At some laboratories, results were not flagged even though some blank values were high.

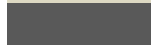
**Table 3.8 Analytical results of Sample No.163d (blank)**

Lab. Code	SO <sub>4</sub> <sup>2-</sup> (μg)	Cl <sup>-</sup> (μg)	NH <sub>4</sub> <sup>+</sup> (μg)
CN02	4.37	5.00	0.00
ID01	0.00	2.46	0.00
ID03	0.09	1.90	1.43
JP01	0.12	1.02	0.08
JP02	0.00	1.04	0.68
JP03	0.00	0.99	0.13
JP04	0.98	1.86	0.74
JP08	0.00	1.48	0.00
JP09	0.08	1.83	0.28
JP10	0.15	1.21	0.20
JP11	0.00	1.60	0.03
MY01	0.40	1.42	0.71
MM01	0.66	3.05	8.14
PH01	0.00	1.40	0.60
PH02	0.00	4.38	2.88
KR01	0.59	1.26	0.28
RU01	0.00	0.00	0.04
TH01	1.24	1.82	0.90
TH02	0.42	1.61	0.81
TH04	1.54	1.16	1.06
TH05	3.64	3.04	0.00
TH06	0.11	0.20	0.49
VN01	0.43	1.13	0.47
VN02	0.00	2.10	0.31
Average	0.62	1.79	0.84
Median	0.11	1.54	0.39
Minimum	0.00	0.00	0.00
Maximum	4.37	5.00	8.14
Standard deviation	1.11	1.12	1.64

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

Lab. Code	Sample No.161d			Sample No.162d		
	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>
CN02	37.3	67.1	0	9.7	29.6	0
ID01	0	42.7	0	0	16.7	0
ID03	0.7	35.1	14.3	0.2	12.1	3.9
JP01	0.8	28.3	1.9	0.2	7.1	0.4
JP02	0	20.9	7.3	0	6.6	1.5
JP03	0	20.8	1.4	0	6.3	0.3
JP04	6.3	32.8	8.5	1.8	11.3	1.7
JP08	0	27.2	0	0	9.0	0
JP09	0.5	32.4	3.0	0.2	11.2	0.6
JP10	1.1	24.6	2.2	0.3	7.8	0.4
JP11	0	30.0	0.4	0	9.8	0.1
MY01	3.7	27.9	7.6	0.8	8.6	1.5
MM01	5.9	38.3	56.6	1.5	18.1	16.6
PH01	0	27.2	6.8	0	9.1	1.3
PH02	0	67.7	32.3	0	33.4	6.5
KR01	5.8	30.2	2.5	1.3	8.6	0.6
RU01	0	0	0.5	0	0	0.1
TH01	8.3	32.3	7.4	2.5	10.9	1.5
TH02	3.3	32.0	9.2	0.9	10.6	2.0
TH04	9.6	24.8	10.5	2.8	7.2	2.6
TH05	24.1	45.2	0	6.9	18.7	0
TH06	0.7	3.8	5.2	0.2	1.4	1.1
VN01	3.2	21.4	4.1	0.9	7.4	0.8
VN02	0	37.7	3.8	0	13.1	0.7

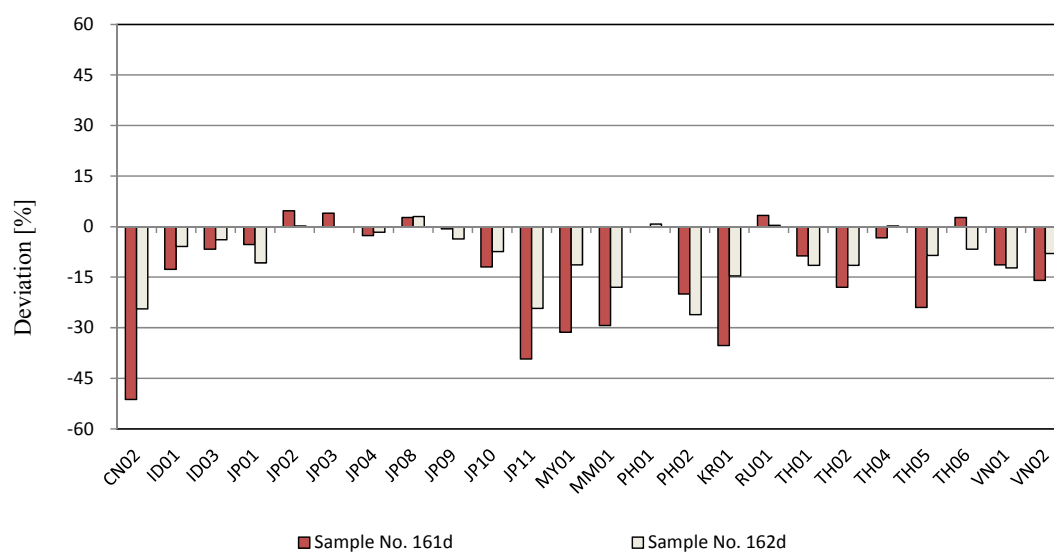
 : Data Flagged E

 : 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 (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup>). The obtained values from each laboratory were evaluated for their deviations. The number of the flagged data is shown in Table 3.4 and 3.6 for each analyte.

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



**Figure 3.3 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>**

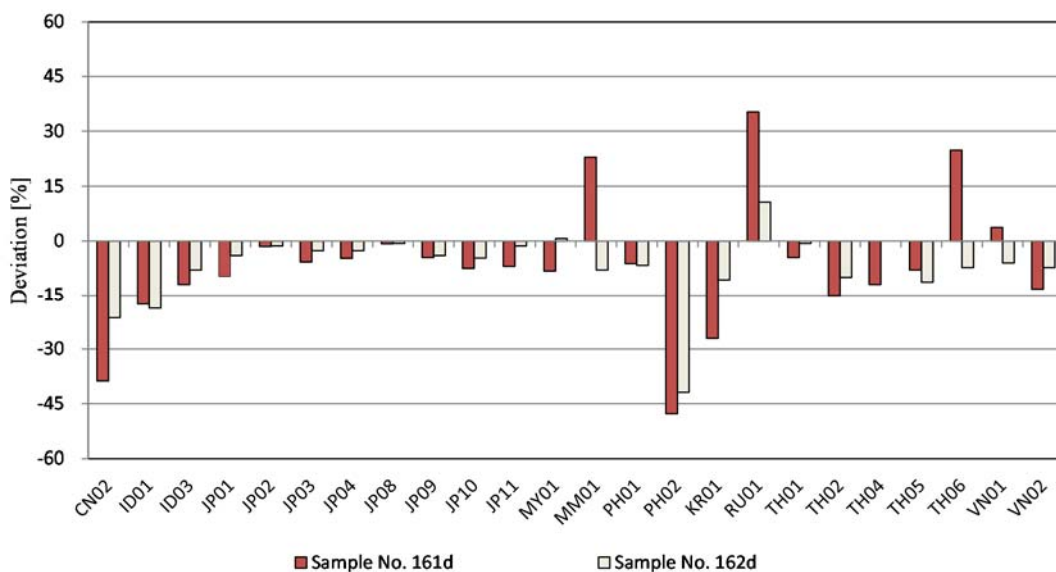
<u>Analytical Method</u>	
Ion Chromatography	24/24

**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.161d	5	4	37.5
Sample No.162d	4	0	16.7

All laboratories used Ion Chromatography for the determination of SO<sub>4</sub><sup>2-</sup>. E flag appeared at 9 laboratories for Sample No.161d and No. 162d. X flag appeared at 4 laboratories for Sample No.161d and No. 162d.

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



**Figure 3.4 Deviation for Cl<sup>-</sup>**

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

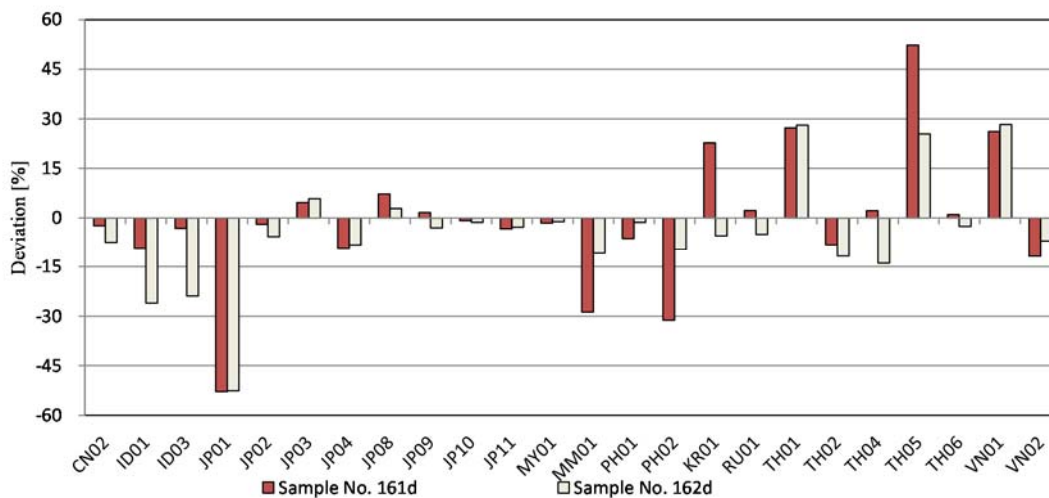
<u>Analytical Method</u>	
Ion Chromatography	24/24

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

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.161d	4	3	29.2
Sample No.162d	2	1	12.5

As with the analysis of Cl<sup>-</sup>, all laboratories used Ion Chromatography for the determination of Cl<sup>-</sup>. E flag appeared at 6 laboratories for Sample No.161d and No. 162d. X flag appeared at 4 laboratories for Sample No. 161d and No. 162d.

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



**Figure 3.5 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 24/24

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

<u>Flagged Data</u>	Flag E	Flag X	Flagged (%)
Sample No.161d	4	3	29.2
Sample No.162d	5	1	25.0

All laboratories used Ion Chromatography for the determination of NH<sub>4</sub><sup>+</sup>. E flag appeared at 9 laboratories for Sample No.161d and No.162d. X flag appeared at 4 laboratories.

### **3.3.3 Information on Laboratories**

#### **Methodologies used**

As shown in Table 3.13, all laboratories used Ion Chromatography which is recommended by EANET.

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

Lab. Code	SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
CN02		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
JP10		Ion Chromatography
MY01		Ion Chromatography
MM01		Ion Chromatography
PH01		Ion Chromatography
PH02		Ion Chromatography
KR01		Ion Chromatography
RU01		Ion Chromatography
TH01		Ion Chromatography
TH02		Ion Chromatography
TH04		Ion Chromatography
TH05		Ion Chromatography
TH06		Ion Chromatography
VN01		Ion Chromatography
VN02		Ion Chromatography

**Years of staff experience**

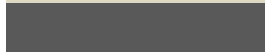
Years of staff experience are summarized in Table 3.14. A light gray color cell indicates that there is a flag for Sample No.161d or 162d. A dark gray color cell indicates the flagged data in both Sample No.161d and No.162d.

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



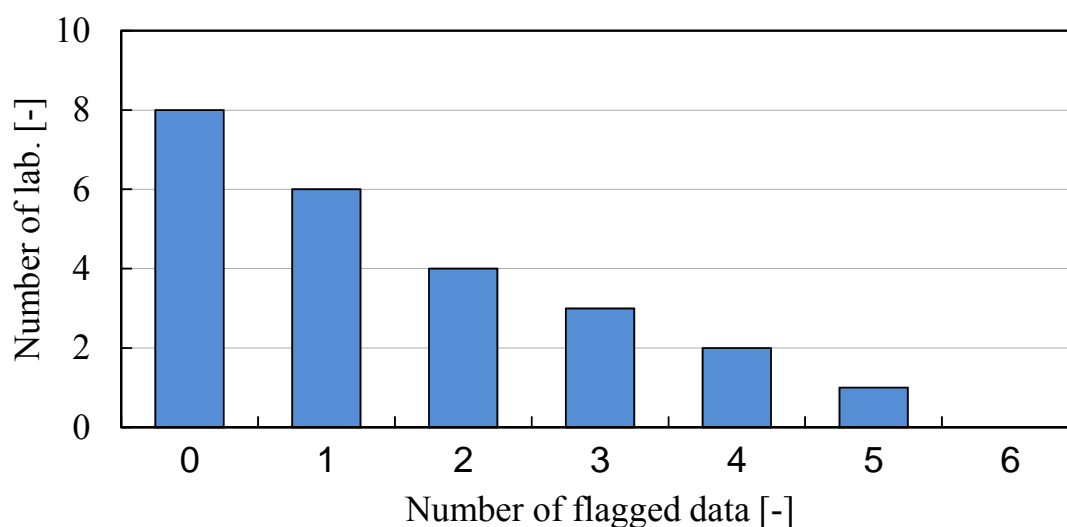
Lab. Code	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
CN02	8	8	8
ID01	14	14	14
ID03	6	6	6
JP01	13	13	13
JP02	12	12	12
JP03	3	3	3
JP04	2	2	2
JP08	3	3	3
JP09	1	1	1
JP10	5	5	5
JP11	1	1	1
MY01	3	3	10
MM01	5	5	5
PH01	11	11	11
PH02	2	2	2
KR01	15	15	15
RU01	18	18	18
TH01	6	6	6
TH02	13	13	13
TH04	2	2	2
TH05	16	16	16
TH06	11	11	11
VN01	23	23	23
VN02	3	3	3

 : One sample is flagged.

 : Two samples are flagged.

### **Flagged Data**

In the results of Sample No.161d and 162d, the total number of the flagged data was 36 (E: 24, X: 12) in the whole values (144). The number of the flagged data in each laboratory is shown in Figure 3.6. Eight laboratories met DQOs (33.3%).



**Figure 3.6** Number of flagged data and laboratories

### Calibration standard solution


Table 3.15 shows the lowest 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 gray highlighted value in Table 3.15 indicates that the concentration value of standard solution is lower than that of the prepared value. In contrast, some laboratories used extremely high concentration standards comparing with samples concentrations.

Each concentration of the prepared values 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.	$\text{SO}_4^{2-}$ ( $\mu\text{mol L}^{-1}$ )		$\text{Cl}^-$ ( $\mu\text{mol L}^{-1}$ )		$\text{NH}_4^+$ ( $\mu\text{mol L}^{-1}$ )	
	Lowest	Highest	Lowest	Highest	Lowest	Highest
CN02	0	81.6	0	225	0	111
ID01	0	52.1	0	84.5	0	66.7
ID03	0	104	0	113	0	111
JP01	0	208	0	564	0	554

JP02	0	52.1	0	141	0	277
JP03	0	52.1	0	28.2	0	166
JP04	0	52.1	0	141	0	277
JP08	0	104	0	283	0	277
JP09	0.3	104	0.9	28.2	1.7	166
JP10	0	52.1	0	28.2	0	277
JP11	0	260	0	280	0	55.0
MY01	0.1	64.1	0	85.4	0	139
MM01	0.1	104	1.2	26.4	0.3	168
PH01	0	52.1	0	56.3	0	277
PH02	0	104	0	290	1.6	557
KR01	0.9	104	2.6	282	7.6	282
RU01	0	46.8	0	25.4	0	333
TH01	0	104	0	283	0	557
TH02	0.2	41.7	0.5	113	1.1	111
TH04	0	19.4	0	55.4	0	54.9
TH05	0	62.5	0	56.4	0	222
TH06	0	93.7	0	254	0	188
VN01	0	104	0	141	0	277
VN02	0	83.3	0	35.2	0	140
<hr/>						
*Sample No. 161d	7.81		5.64		24.4	
*Sample No. 162d	28.1		21.2		127	

 The measured value was out of the calibration range.

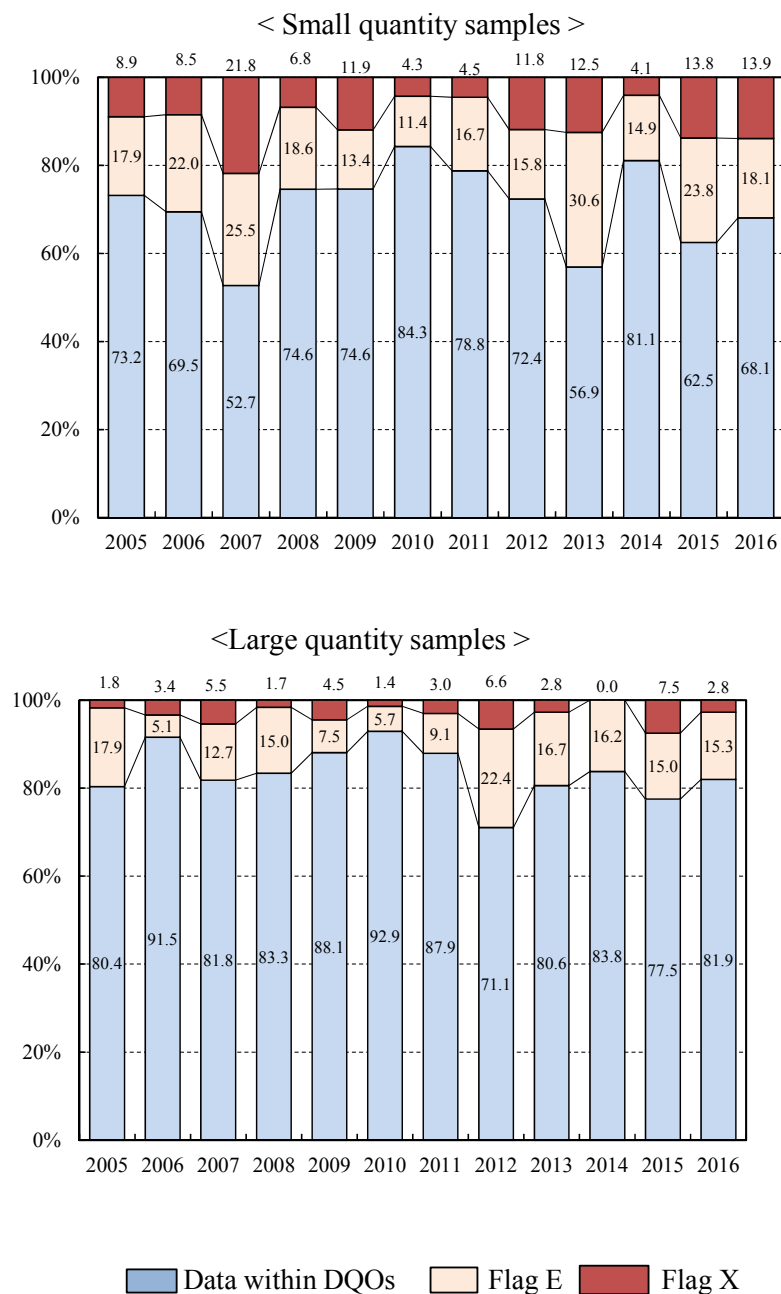
Lowest and Highest: lowest/highest concentrations in the calibration standard solutions.

\*Sample concentration ( $\mu\text{mol L}^{-1}$ ) = Prepared value ( $\mu\text{g}$ ) / Solvent (mL) / MW

MW: molecular weight

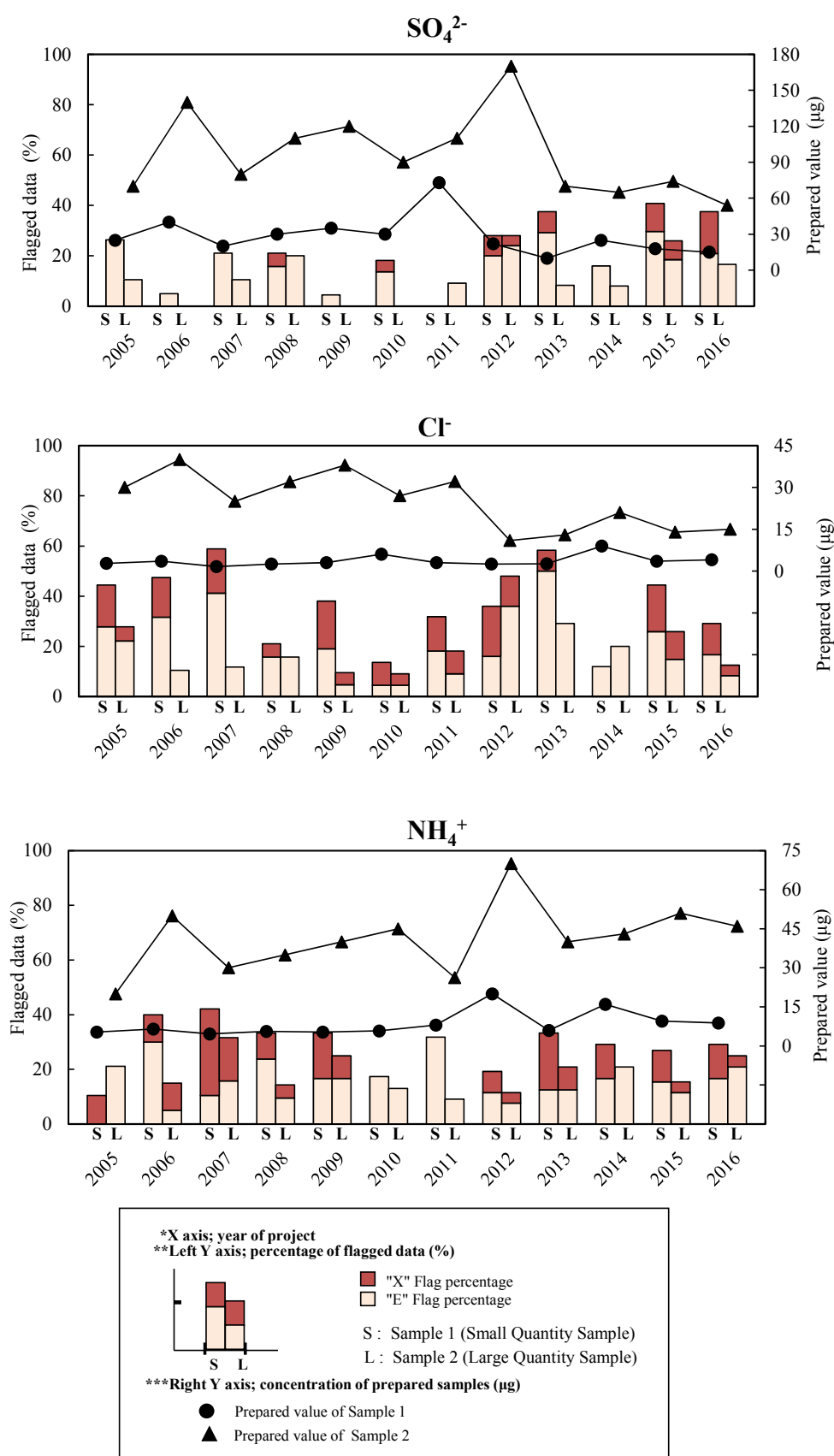
### 3.4 Comparison with past surveys

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 3.7.



**Figure 3.7 Comparison of DQOs' results for the past years**

The comparison for each analyte in Inter-laboratory Comparison on dry deposition year-by-year is shown in Figure 3.8.



**Figure 3.8 Comparison for each parameter in inter-laboratory comparison project**

## **References**

EANET (2010). *Technical Manual for Wet Deposition Monitoring in East Asia-2010*. Asia Center for Air Pollution Research, Niigata, Japan, 113p.

EANET(2013). *Technical Manual for Air Concentration Monitoring in East Asia*. Asia Center for Air Pollution Research, Niigata, Japan, 155p.

## **4. 18th INTER-LABORATORY COMPARISON PROJECT ON SOIL**

### **4.1 Introduction**

The Inter-laboratory Comparison Project on Soil started in 1999 as one of 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. Possible factors affecting precisions 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 18th project, the Network Center (NC) provided two soil samples (No.161s and No.162s) 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 contribute to the assessment of the 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

Fifteen laboratories of 7 countries participated in the 18th project. The results submitted to the network center were analyzed statistically according to the QA/QC program. Names of the participating laboratories are listed in Table 1.1.

### 4.2.2 Description of Samples

The characteristics of the soil samples were as follows:

#### Sample No.161s: Cambisols

#### Sample No.162s: Cambisols

Soils for Sample No.161s and No.162s were collected in *Cryptomeria japonica* plantation in Toyama 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 400 - 500 g were weighed out, packed in 500 ml plastic bottles, and then, sterilized using radioisotope (20 kGy) 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.161s and 162s
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 *Technical Manual for Soil and Vegetation Monitoring in East Asia* (EANET, 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 *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 is not available, 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:

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

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

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

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

Where

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

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

$mcf$  = Moisture correction factor (Measured value)

$S$  = Weight of air-dry sample (g)

$V$  = Volume of extract (mL)

#### 4.2.4.3 Procedures for Ex-acidity

(1) Extraction and titration would be carried out according to *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:

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

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

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

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)

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

$bl_{\text{HCl}}$  = 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.

#### 4.2.4.5 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 plots 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 15 laboratories) were verified by Cochran and Grubbs methods, respectively. We also computed “verified” mean, median and other statistical summary from 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 variations. 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 changes in the same site or significant difference between two laboratories would be indicated if those changes or the 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 is shown in Table 4.2. On the 18th inter-laboratory project, pH(H<sub>2</sub>O), pH(KCl), Ex-base cations, and Ex-acidity were largely different between both samples. pH(H<sub>2</sub>O) and Ex-base cations were higher in No.162s than in No.161s, whereas Ex-acidity, Ex-Al<sup>3+</sup> and EX-H<sup>+</sup> were higher in No.161s than in No.162s. We observed the large variations in the analyzed data (CVs) of Ex-base cations, acidity and acid cations in both samples (> 15%). Meanwhile, in both samples, CVs were relatively small for both pH(H<sub>2</sub>O) and pH(KCl) (< 7%).

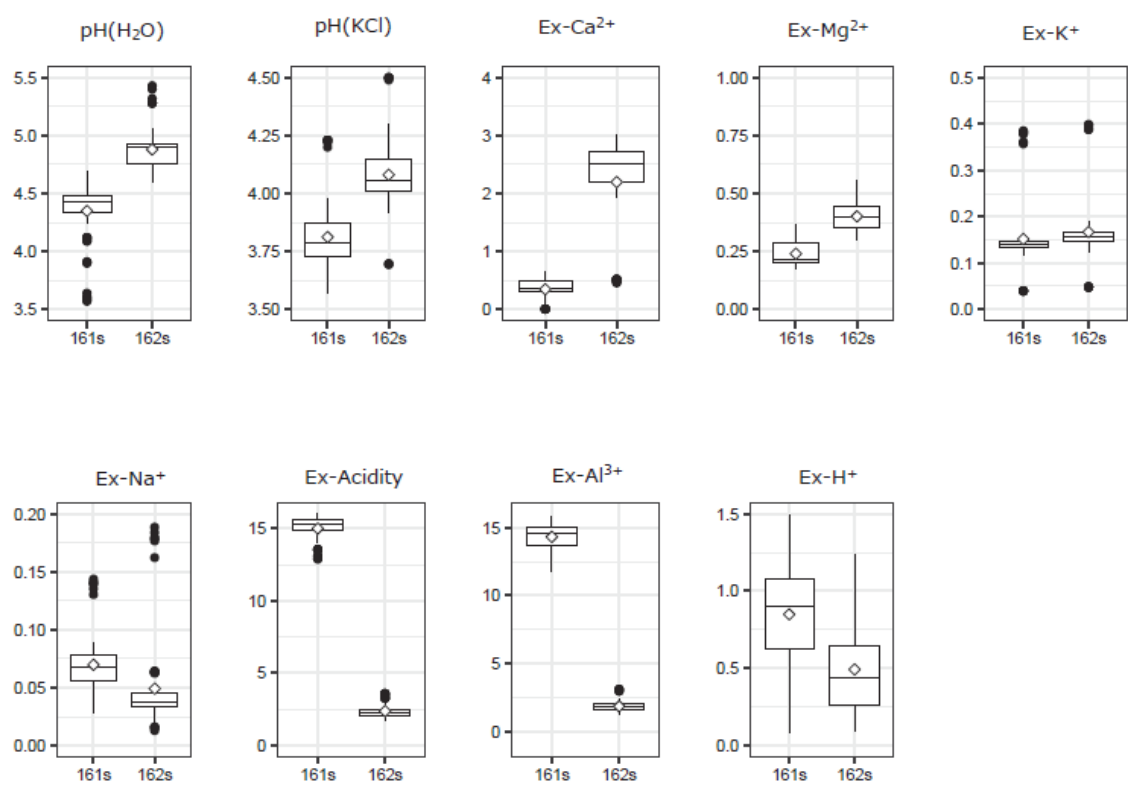
**Table 4.2 Statistical summary**

Statistics	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol <sub>c</sub> kg <sup>-1</sup>						
No. 161s									
Number of Laboratories	15	15	12	12	12	12	15	15	15
Total average	4.4	3.8	0.35	0.24	0.15	0.07	15.90	14.87	1.09
Median	4.4	3.8	0.35	0.21	0.14	0.06	15.57	14.73	1.02
Maximum	4.7	4.2	0.60	0.35	0.37	0.14	19.64	17.99	2.06
Minimum	3.6	3.6	0.01	0.19	0.04	0.03	13.38	12.28	0.13
Standard deviation	0.3	0.1	0.17	0.06	0.08	0.03	1.66	1.58	0.56
CV (%) <sup>*1</sup>	6.8	2.6	48.6	25.0	53.3	42.9	10.4	10.6	51.4
No. 162s									
Number of Laboratories	15	15	12	12	12	12	15	15	15
Total average	4.9	4.1	2.20	0.40	0.17	0.05	2.38	1.88	0.49
Median	4.9	4.1	2.52	0.40	0.16	0.04	2.25	1.85	0.44
Maximum	5.3	4.5	2.85	0.54	0.39	0.18	3.56	3.07	1.24
Minimum	4.6	3.9	0.49	0.31	0.05	0.02	1.77	1.39	0.13
Standard deviation	0.2	0.1	0.83	0.07	0.08	0.04	0.48	0.40	0.30
CV (%) <sup>*1</sup>	4.1	2.4	37.7	17.5	47.1	80.0	20.2	21.3	61.2

\*1: CV, Coefficient of variance (%) = (standard deviation/total average) \*100.

We also have an overview of the data by box-and-whisker plot (Figure 4.1) of No.161s and 162s analyzed by 15 laboratories. Box-and-whisker plot provides the six-number summaries; total average shown by an open argyle, lower quartile, median and upper quartile shown by a box and a bold line, and lowest and highest value within the range between the lower quartile minus 1.5 times the inter-quartile range and the upper quartile plus 1.5 times the inter-quartile range drawn by error bar. In addition, the values outside the error bar are shown as outliers, that is, non-parametrical outliers.

The plots showed several “non-parametrical” outliers in each property. Those outliers might be due to wrong calculation, procedure, irregular contamination, and so on because the values were 5-20 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.161s and No.162s**

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

**No. 161s**

Country	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
cmol <sub>c</sub> kg <sup>-1</sup>											
China	CN01	1st	4.4	3.8	0.32	0.20	0.12	0.03	14.95	14.75	0.20
		2nd	4.4	3.8	0.32	0.20	0.12	0.03	14.92	14.71	0.21
	CN02	1st	4.4	3.9	0.51	0.24	0.15	0.07	15.66	13.76	2.17
		2nd	4.4	3.8	0.50	0.24	0.15	0.07	15.48	13.80	1.95
	CN03	1st	4.5	3.9	0.51	0.21	0.15	0.09	13.53	12.51	1.02
		2nd	4.5	3.9	0.52	0.21	0.15	0.09	13.84	12.82	1.02
	CN04	1st	4.4	3.7	0.34	0.20	0.15 c	0.06	15.43	13.71	1.73
		2nd	4.4	3.7	0.35	0.20	0.14 c	0.06	15.11	13.55	1.58
Indonesia	ID01	1st	4.5	3.7	0.36	0.33	0.14	0.08	15.29	14.60	0.69
		2nd	4.5	3.7	0.35	0.31	0.14	0.07	15.77	14.92	0.84
	ID04	1st	4.4 c	3.9	0.61	0.35	0.37 g	0.14 g	13.47	12.38	1.09
		2nd	3.9 c	3.9	0.60	0.34	0.37 g	0.14 g	13.28	12.17	1.11
Japan	JP04	1st	4.6	3.8	0.30	0.18	0.14	0.05	16.41	15.78 c	0.63
		2nd	4.7	3.8	0.33	0.20	0.15	0.05	17.11	16.53 c	0.58
	JP10	1st	4.5	3.8	0.39	0.24	0.14 c	0.06	16.23	14.44	1.79
		2nd	4.5	3.8	0.43	0.23	0.15 c	0.06	16.49	14.49	2.00
Mongolia	MN01	1st	4.1 g	4.2 g	NA	NA	NA	NA	18.82	17.47	1.34
		2nd	4.1 g	4.2 g	NA	NA	NA	NA	18.82	17.47	1.34
Russia	RU01	1st	4.3	3.8	0.41	0.21	0.14	0.05	15.64	15.52	0.14
		2nd	4.3	3.8	0.39	0.20	0.14	0.05	15.76	15.64	0.12
Thailand	TH01	1st	4.5	3.8	0.34	0.21	0.13	0.06	15.43	14.97	1.57
		2nd	4.5	3.9	0.34	0.22	0.14	0.06	15.99	15.44	1.32
Vietnam	VN01	1st	4.3	3.8	0.01	0.19	0.15	0.07	14.83	14.01	0.82
		2nd	4.4	3.8	0.01	0.19	0.15	0.07	14.90	14.07	0.83
	VN02	1st	4.5	3.6	NA	NA	NA	NA	16.83	15.70	0.99
		2nd	4.5	3.6	NA	NA	NA	NA	16.83	15.70	0.99
	VN04	1st	3.6 g	3.6 c	0.08	0.32	0.04 g	0.08	15.44	14.56	0.88
		2nd	3.6 g	4.0 c	0.08	0.32	0.04 g	0.08	15.44	14.56	0.90
	VN05	3rd	4.5	3.7	NA	NA	NA	NA	19.64	17.99	1.50
		4th	4.5	3.7	NA	NA	NA	NA	19.64	17.99	1.50

**No. 162s**

Country	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
cmol <sub>c</sub> kg <sup>-1</sup>											
China	CN01	1st	4.8	4.1	2.54	0.36	0.13	0.02	1.98	1.85	0.13
		2nd	4.8	4.1	2.55	0.36	0.13	0.02	1.97	1.84	0.13
	CN02	1st	4.9	4.1	2.83	0.40	0.16	0.04	2.36	1.52	0.88
		2nd	4.9	4.1	2.87	0.39	0.16	0.04	2.50	1.62	0.91
	CN03	1st	5.0	4.2	2.51	0.31	0.18	0.04	2.63 c	1.96	0.68
		2nd	5.0	4.2	2.49	0.31	0.18	0.04	2.43 c	1.76	0.67
	CN04	1st	4.9	4.0	2.57	0.34	0.15	0.04	2.14	1.52	0.62
		2nd	4.9	3.9	2.50	0.34	0.16	0.04	2.14	1.51	0.64
Indonesia	ID01	1st	4.9	4.0	2.30	0.45	0.15	0.05	2.32	1.91	0.41
		2nd	4.9	4.0	2.26	0.45	0.15	0.04	2.29	1.97	0.32
	ID04	1st	4.7 c	4.2	2.85	0.54	0.39 g	0.17 g	1.83	1.50	0.33
		2nd	4.9 c	4.2	2.84	0.53	0.39 g	0.18 g	1.71	1.29	0.42
Japan	JP04	1st	5.0	4.1	1.94	0.30	0.17	0.03	2.17	1.69	0.48
		2nd	5.0	4.2	2.05	0.33	0.16	0.03	2.16	1.70	0.45
	JP10	1st	4.9	4.1	2.76	0.41	0.15 c	0.03	2.51	2.06	0.45
		2nd	4.9	4.1	2.79	0.44	0.16 c	0.04	2.47	2.05	0.43
Mongolia	MN01	1st	5.4 c	4.5 g	NA	NA	NA	NA	3.30 g	2.06	1.24 g
		2nd	5.3 c	4.5 g	NA	NA	NA	NA	3.30 g	2.06	1.24 g
Russia	RU01	1st	4.7	4.1	0.50	0.41 c	0.15	0.03	2.22	1.62	0.56
		2nd	4.7	4.1	0.49	0.37 c	0.14	0.03	2.27	1.67	0.61
Thailand	TH01	1st	5.0	4.2 c	2.32	0.37	0.15	0.03	2.12	1.60	0.71 c
		2nd	4.9	4.3 c	2.34	0.37	0.15	0.03	2.20	1.80	0.56 c
Vietnam	VN01	1st	4.7	4.0	0.51	0.41	0.17	0.04	2.00	1.78	0.23
		2nd	4.7	4.0	0.51	0.41	0.17	0.04	2.01	1.76	0.25
	VN02	1st	4.9	4.0	NA	NA	NA	NA	2.53	2.22	0.21
		2nd	4.9	4.0	NA	NA	NA	NA	2.53	2.22	0.21
	VN04	1st	4.9	4.0	2.72	0.51	0.05 g	0.06	2.07	1.89	0.16
		2nd	4.9	4.0	2.72	0.51	0.05 g	0.06	2.07	1.89	0.18
	VN05	3rd	4.6	3.7 c	NA	NA	NA	NA	3.55 g	3.09 g	0.35
		4th	4.6	4.1 c	NA	NA	NA	NA	3.57 g	3.05 g	0.35

The outliers were determined by Cochran and Grubbs tests, and were indicated by "c" and "g" signs, respectively.

### 4.3.2 Detection of outliers

Detection of outliers by Cochran-Grubbs methods is 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. “IN04” in pH(H<sub>2</sub>O), “CN04” in Ex-K of No.161s. 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. Cochran-Grubbs method detected the several outliers for each parameter. As a result of removing outliers, the “verified” dataset consisting of 12-13 laboratories in pH(H<sub>2</sub>O) and pH(KCl), 7-12 laboratories in Ex-base cations and 12-15 laboratories in Ex-acidity, Al and H were used for further analysis in the following section.

### 4.3.3 Statistical summary for verified data

The statistical summary for verified datasets in No.161s and No.162s is shown in Table 4.4. Although the chemical properties in both soils were not largely changed by verification, the data variability of almost all items decreased from the entire dataset. However, these variations were still too large to compare the regular monitoring data among the participating countries, accurately. The variation may include an 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 <sub>c</sub> kg <sup>-1</sup>						
No. 161s									
Number of Laboratories	12	13	12	12	7	11	15	13	15
Total average	4.5	3.8	0.35	0.24	0.14	0.06	15.90	14.70	1.09
Median	4.5	3.8	0.35	0.21	0.14	0.06	15.57	14.56	1.02
Maximum	4.7	3.9	0.60	0.35	0.15	0.09	19.64	17.99	2.06
Minimum	4.3	3.6	0.01	0.19	0.12	0.03	13.38	12.28	0.13
Standard deviation	0.1	0.1	0.17	0.06	0.01	0.02	1.66	1.64	0.56
CV (%) <sup>*1</sup>	2.2	2.6	48.6	25.0	7.1	33.3	10.4	11.2	51.4
No. 162s									
Number of Laboratories	12	12	12	11	9	11	12	14	13
Total average	4.9	4.1	2.20	0.40	0.16	0.04	2.19	1.80	0.42
Median	4.9	4.1	2.52	0.40	0.15	0.04	2.16	1.81	0.38
Maximum	5.0	4.2	2.85	0.54	0.18	0.06	2.53	2.22	0.89
Minimum	4.6	3.9	0.49	0.31	0.13	0.02	1.77	1.39	0.13
Standard deviation	0.1	0.1	0.83	0.07	0.02	0.01	0.22	0.23	0.22
CV (%) <sup>*1</sup>	2.0	2.4	37.7	17.5	12.5	25.0	10.0	12.8	52.4

<sup>\*1</sup>: CV, Coefficient of variance (%) = (standard deviation/average) \*100.

<sup>\*2</sup>: Dataset is verified removing outliers determined 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 (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 both pH(H<sub>2</sub>O) and pH(KCl), < 7% in Ex-base cations, Ex-acidity and Ex-Al, while it was almost 15% in Ex-H. The result suggests that triplicate analyses were carried out under the same condition. In general, the participating laboratories could analyze the parameters with their own standard procedures and stable instruments.

##### 2) Within-laboratory precision

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 3% in pH (H<sub>2</sub>O) and pH (KCl). However, the CVs of the rest of the items ranged from 8 to 53%. Thus, in this inter-laboratory comparison, almost all error in each parameter was produced by different laboratories. We discussed the possible factor of the relatively high 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 laboratories. 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. Meanwhile, the result about reproducibility limit (inter-laboratories reproducibility limit) suggested that participating laboratories can detect the significant difference between the monitoring sites if the differences are more than about 0.3 for pH(H<sub>2</sub>O), 0.2 for pH(KCl), 0.03-2.4 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-base cations, 0.7 or 5 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-acidity and Ex-Al, and 0.6 or 1.6 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-H.



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

Statistics	No. 161s								
	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	12	13	12	12	7	11	15	13	15
Total sum of square	100000	87000	630	300	35	18	200000	1300000	9700
ST/lmd	1400	1100	8.8	4.2	0.83	0.27	23000	17000	110
Number of Laboratories	12	13	12	12	7	11	15	13	15
Number of Data	72	78	72	72	42	66	90	78	90
Total sum	320	300	25	17	5.9	4.2	1400	1100	99
Total average	4.5	3.8	0.35	0.24	0.14	0.06	15.90	14.70	1.09
Sum of square inter-laboratories ( $S_R$ )	0.6	0.5	1.89	0.21	0.00	0.01	231.03	192.64	26.61
Sum of square within-laboratory ( $S_{RW}$ )	0.0	0.0	0.00	0.00	0.00	0.00	2.07	0.78	0.31
Sum of square repeatability ( $S_i$ )	0.0	0.0	0.01	0.00	0.00	0.00	3.05	2.99	0.27
Total sum of square ( $S_T$ )	0.7	0.5	1.91	0.22	0.00	0.02	236.15	196.41	27.19
Inter-laboratories degree of freedom ( $\phi_R$ )	11	12	11	11	6	10	14	12	14
Within-laboratory degree of freedom ( $\phi_{RW}$ )	12	13	12	12	7	11	15	13	15
Repeatability degree of freedom ( $\phi_i$ )	48	52	48	48	28	44	60	52	60
Total degree of freedom ( $\phi_T$ )	71	77	71	71	41	65	89	77	89
Inter-laboratories variance ( $V_R = S_R/\phi_R$ )	0.1	0.0	0.17	0.02	0.00	0.00	16.50	16.05	1.90
Within-laboratory variance ( $V_{RW} = S_{RW}/\phi_{RW}$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.14	0.06	0.02
Repeatability variance ( $V_i = S_i/\phi_i$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.05	0.06	0.00
Laboratory component of variance ( $s_b^2 = (V_R - V_{RW})/(2*3)$ )	0.0	0.0	0.03	0.00	0.00	0.00	2.73	2.67	0.31
Within-laboratory component of variance ( $s_c^2 = (V_{RW} - V_i)/3$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.03	0.00	0.01
Repeatability component of variance ( $s_t^2 = V_i$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.05	0.06	0.00
Inter-laboratories standard deviation ( $s_R = \text{SQRT}(s_b^2/(2*3) + s_c^2/2 + s_b^2)$ )	0.1	0.1	0.17	0.06	0.01	0.02	1.66	1.64	0.56
Within-laboratory standard deviation ( $s_{RW} = \text{SQRT}(s_t^2/3 + s_c^2)$ )	0.0	0.0	0.01	0.01	0.00	0.00	0.21	0.14	0.08
Repeatability standard deviation ( $s_i = \text{SQRT}(s_t^2)$ )	0.0	0.0	0.02	0.01	0.00	0.00	0.23	0.24	0.07
Inter-laboratories precision CV (%)	2.2	2.2	48.47	23.71	7.64	24.21	10.43	11.12	51.42
Within-laboratory precision CV (%)	0.4	0.6	3.23	2.63	1.38	3.62	1.35	0.96	7.53
Repeatability precision CV (%)	0.3	0.4	4.71	3.86	1.76	6.92	1.42	1.63	6.16
Reproducibility limit ( $R = D(2, 0.95)*s_R$ )	0.3	0.2	0.47	0.16	0.03	0.04	4.64	4.58	1.58
Within-laboratory-reproducibility limit ( $R_W = D(2, 0.95)*s_{RW}$ )	0.0	0.1	0.03	0.02	0.01	0.01	0.60	0.40	0.23
Repeatability limit ( $r = D(3, 0.95)*s_i$ )	0.0	0.0	0.05	0.03	0.01	0.01	0.74	0.79	0.22
Statistics	No. 162s								
	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	12	12	12	11	9	11	12	14	13
Total sum of square	120000	85000	25000	700	71	6.1	25000	23000	1100
ST/lmd	1700	1200	350	11	1.3	0.092	350	270	14
Number of Laboratories	12	12	12	11	9	11	12	14	13
Number of Data	72	72	72	66	54	66	72	84	78
Total sum	350	290	160	27	8.4	2.5	160	150	33
Total average	4.9	4.1	2.20	0.40	0.16	0.04	2.19	1.80	0.42
Sum of square inter-laboratories ( $S_R$ )	1.0	0.4	45.54	0.33	0.01	0.01	3.31	4.12	3.58
Sum of square within-laboratory ( $S_{RW}$ )	0.0	0.0	0.03	0.00	0.00	0.00	0.07	0.21	0.03
Sum of square repeatability ( $S_i$ )	0.0	0.0	0.22	0.00	0.00	0.00	0.12	0.61	0.08
Total sum of square ( $S_T$ )	1.0	0.4	45.79	0.33	0.01	0.01	3.50	4.93	3.70
Inter-laboratories degree of freedom ( $\phi_R$ )	11	11	11	10	8	10	11	13	12
Within-laboratory degree of freedom ( $\phi_{RW}$ )	12	12	12	11	9	11	12	14	13
Repeatability degree of freedom ( $\phi_i$ )	48	48	48	44	36	44	48	56	52
Total degree of freedom ( $\phi_T$ )	71	71	71	65	53	65	71	83	77
Inter-laboratories variance ( $V_R = S_R/\phi_R$ )	0.1	0.0	4.14	0.03	0.00	0.00	0.30	0.32	0.30
Within-laboratory variance ( $V_{RW} = S_{RW}/\phi_{RW}$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Repeatability variance ( $V_i = S_i/\phi_i$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Laboratory component of variance ( $s_b^2 = (V_R - V_{RW})/(2*3)$ )	0.0	0.0	0.69	0.01	0.00	0.00	0.05	0.05	0.05
Within-laboratory component of variance ( $s_c^2 = (V_{RW} - V_i)/3$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability component of variance ( $s_t^2 = V_i$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Inter-laboratories standard deviation ( $s_R = \text{SQRT}(s_b^2/(2*3) + s_c^2/2 + s_b^2)$ )	0.1	0.1	0.83	0.07	0.02	0.01	0.22	0.23	0.22
Within-laboratory standard deviation ( $s_{RW} = \text{SQRT}(s_t^2/3 + s_c^2)$ )	0.0	0.0	0.03	0.01	0.00	0.00	0.04	0.07	0.03
Repeatability standard deviation ( $s_i = \text{SQRT}(s_t^2)$ )	0.0	0.0	0.07	0.01	0.00	0.00	0.05	0.10	0.04
Inter-laboratories precision CV (%)	2.5	1.9	37.79	18.33	9.99	31.32	10.22	12.79	52.49
Within-laboratory precision CV (%)	0.3	0.3	1.39	1.96	1.08	6.95	1.95	3.91	6.89
Repeatability precision CV (%)	0.4	0.3	3.11	1.93	2.14	7.30	2.29	5.79	9.44
Reproducibility limit ( $R = D(2, 0.95)*s_R$ )	0.3	0.2	2.33	0.21	0.04	0.03	0.63	0.64	0.62
Within-laboratory-reproducibility limit ( $R_W = D(2, 0.95)*s_{RW}$ )	0.0	0.0	0.09	0.02	0.00	0.01	0.12	0.20	0.08
Repeatability limit ( $r = D(3, 0.95)*s_i$ )	0.1	0.0	0.23	0.03	0.01	0.01	0.17	0.34	0.13

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

To assess the precision in each laboratories and properties, we showed scatter plots between No.161s and No.162s with its “verified” mean indicated by solid line (Figure 4.2). As a guide for comparison, mean  $\pm$  standard deviation was added by dotted lines. The plot did not include extreme outliers for eye-friendly.

##### 1) pH

Linear correlation between No.161s and No.162s indicated the systematic errors of the inter-laboratory variation in pH(H<sub>2</sub>O) and pH(KCl). 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 mean  $\pm$  S.D. for No.161s and No.162s.

##### 2) Base cations

Linear correlation between the samples for Ex-base cations indicated the systematic error of the inter-laboratory variation, while most laboratories were included within the range of verified mean  $\pm$  S.D. The correlations were clear in Ex-K and Na. This might be caused by the condition of pure waters, standard solution and so on. The plots of Ex-Ca and Mg suggested random errors in a few laboratories. The errors might be caused by a calculation procedure, operation of the equipment, the contamination, and/or quality of ammonium acetate (extraction liquid). In the analysis of base cations, higher concentration or higher pH of extraction liquid may result in an increase of the base cations in the solution. To prepare appropriate standard solution from low to high concentrations is also important factor for reducing the error. Extraction liquid should be used for standard solution to minimize the matrix effect.

##### 3) Acidity

The plots of Ex-acidity seemed to indicate the systematic error of inter-laboratory variation. The error might be derived from the manipulation of titration by each analyst, which is easily affected by factor of volumetric solution or end-point detection. In the plots of Ex-Al and H, some more random errors were suggested probably because of their analytical steps. Participating laboratories should check the standard of procedure based on *Technical Manual for Soil and Vegetation Monitoring* (EANET, 2000).



### 4.3.6 Comparison with information on Laboratories

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

Number of analysts and years of their experience are 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 are shown in Table 4.7. Ex-base cations were analyzed either ICP-AES, ICP-OES or AAS. FEP was not used in the 18<sup>th</sup> inter-laboratory comparison. Years in use of instruments ranged from 1 to 31.

Five laboratories used percolation tube procedures for extraction of exchangeable base cations, while Buchner funnel procedures, centrifuge procedures and automatic extractor procedures were used in 4, 2 and 1 laboratories, respectively. No clear difference was observed among data by different procedures. As for the size of burette for titration of Ex-acidity, the capacities were varied from 5 to 50 ml while minimum graduates were 0.00125 to 0.1.

#### 3) Date of analysis

Dates of analysis in the respective laboratories and days used for the analysis are shown in Table 4.8. There was 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 50 days. It was suggested that repeat analyses would be carried out with several-day interval (three days or more) in order to estimate actual within-laboratory reproducibility, as a supplementary instruction for the project, based on the discussion at the third session of the Scientific Advisory Committee on EANET (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			Number of analyst	Ex-acidity		Analyst	
	Number of analyst	Years of experience			Number of analyst	Years of experience		
		Chemical	Soil			Chemical		Soil
CN01	2	6	6	2	6	6	s	
CN02	1	11	11	1	11	11	s	
CN03	1	6	6	1	21	18	d	
CN04	1	10	8	1	10	8	s	
ID01	1	12	9	1	12	9	s	
ID04	1	34	32	1	18	16	d	
JP04	1	1	1	1	1	1	s	
JP10	1	11	2	1	9	2	d	
MN01	-	-	-	1	15	15	-	
RU01	1	16	13	1	16	13	s	
TH01	1	13	13	1	23	6	d	
VN01	1	24	19	1	24	19	s	
VN02	-	-	-	1	12	8	-	
VN04	2	10	9	1	12	11	d	
VN05	-	-	-	1	12	3	-	

-, not analyzed; 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		Interference depressant for Ca and Mg	Ex-K		Ex-Na		Interference depressant for K and Na	Procedures for extraction of Ex-base cations	method	Ex-Acidity, Al and H Size of burette (ml)	
		Instrument	Years* <sup>1</sup>	Instrument	Years		Instrument	Years	Instrument	Years				Capacity	Minimum graduate
CN01	No.161	AAS	14	AAS	14	La	AAS	14	AAS	14	La	Centrifuge	Titration	10	0.1
	No.162	AAS	14	AAS	14	La	AAS	14	AAS	14	La			10	0.1
CN02	No.161	AAS	11	AAS	11	Sr	AAS	11	AAS	11	Sr	Percolation tube	Titration	25	0.1
	No.162	AAS	11	AAS	11	Sr	AAS	11	AAS	11	Sr			25	0.1
CN03	No.161	AAS	7	AAS	7	Sr	AAS	7	AAS	7	La	Automatic extractor	Titration	5	0.00125
	No.162	AAS	7	AAS	7	Sr	AAS	7	AAS	7	La			5	0.00125
CN04	No.161	ICP	7	ICP	7	+	ICP	7	ICP	7	+	Percolation tube	Titration	25	0.1
	No.162	ICP	7	ICP	7	+	ICP	7	ICP	7	+			25	0.1
ID01	No.161	AAS	12	AAS	12	La	AAS	12	AAS	12	La	Centrifuge	Titration	50	0.05
	No.162	AAS	12	AAS	12	La	AAS	12	AAS	12	La			50	0.05
ID04	No.161	AAS	2	AAS	1	+	AAS	1	AAS	1	+	Percolation tube	Titration	50	0.02
	No.162	AAS	2	AAS	1	+	AAS	1	AAS	1	+			50	0.02
JP04	No.161	ICP	5	ICP	5	Sr	ICP	5	ICP	5	Sr	Buchner funnel	Titration	25	0.1
	No.162	ICP	5	ICP	5	Sr	ICP	5	ICP	5	Sr			25	0.1
JP10	No.161	ICP	16	ICP	16	Sr	ICP	16	ICP	16	Sr	Percolation tube	Titration	10	0.05
	No.162	ICP	16	ICP	16	Sr	ICP	16	ICP	16	Sr			10	0.05
MN01	No.161												Titration	25	0.1
	No.162													25	0.1
RU01	No.161	AAS	31	AAS	31	+	AAS	31	AAS	31	na	Percolation tube	Titration	10	0.02
	No.162	AAS	31	AAS	31	+	AAS	31	AAS	31	na			10	0.02
TH01	No.161	ICP-OES	8	ICP-OES	8	na	ICP-OES	8	ICP-OES	8	na	Buchner funnel	Titration	25	0.05
	No.162	ICP-OES	8	ICP-OES	8	na	ICP-OES	8	ICP-OES	8	na			25	0.05
VN01	No.161	AAS	10	AAS	10	+	AAS	10	AAS	10	+	Buchner funnel	Titration	10	0.05
	No.162	AAS	10	AAS	10	+	AAS	10	AAS	10	+			10	0.05
VN02	No.161												Titration	10	0.05
	No.162													10	0.05
VN04	No.161	AAS	11	AAS	11	+	AAS	11	AAS	11	+	Buchner funnel	Titration	10	0.05
	No.162	AAS	11	AAS	11	+	AAS	11	AAS	11	+			10	0.05
VN05	No.161												Titration	10	0.05
	No.162													10	0.05

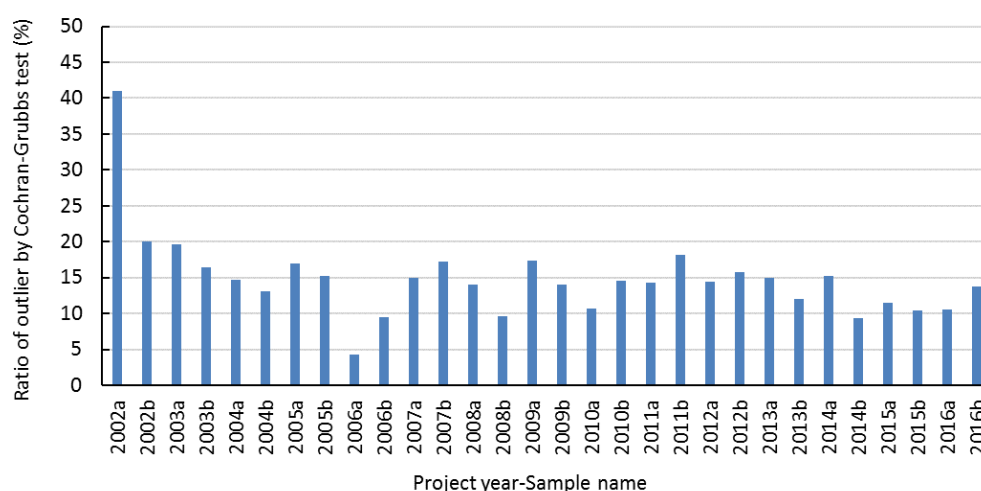
**Table 4.8 Date of analysis and days used for the analysis**

Lab.	Repeat	pH			Ex-Ca and Mg			Ex-K and Na			Ex-acidity, Al and H					
		Date* <sup>1</sup>	Analysis* <sup>2</sup> Interval* <sup>3</sup>		Date* <sup>1</sup>	Analysis* <sup>2</sup> Interval* <sup>3</sup>		Date* <sup>1</sup>	Analysis* <sup>2</sup> Interval* <sup>3</sup>		Date* <sup>1</sup>	Analysis* <sup>2</sup> Interval* <sup>3</sup>				
			Days			Days			Days			Days				
CN01	1st	2017/3/6	2	0	2017/3/17	5	0	2017/3/17	5	0	2017/3/16	4	1			
	2nd	2017/3/6	1		2017/3/17	3		2017/3/17	3		2017/3/17	3				
CN02	1st	2017/2/23	1	1	2017/2/24	2	1	2017/2/24	2	1	2017/2/27	1	1			
	2nd	2017/2/24	1		2017/2/25	2		2017/2/25	2		2017/2/28	1				
CN03	1st	2016/12/2	2	50	2017/1/18	3	2	2017/1/18	3	2	2017/1/14	2	14			
	2nd	2017/1/21	2		2017/1/20	3		2017/1/20	3		2017/1/28	3				
CN04	1st	2016/11/17	1	27	2017/2/13	8	0	2017/2/13	8	0	2016/12/16	7	0			
	2nd	2016/12/14	1		2017/2/13	5		2017/2/13	5		2016/12/16	3				
ID01	1st	2016/11/2	1	5	2016/11/25	4	20	2016/11/25	4	20	2016/11/8	2	1			
	2nd	2016/11/7	1		2016/12/15	3		2016/12/15	3		2016/11/9	2				
ID04	1st	2016/11/16	2	6	2016/11/23	9	7	2016/11/23	9	7	2016/11/18	4	7			
	2nd	2016/11/22	1		2016/11/30	7		2016/11/30	7		2016/11/25	4				
JP04	1st	2016/11/18	8	20	2017/1/24	1	1	2017/1/24	1	1	2016/11/25	10	10			
	2nd	2016/12/8	7		2017/1/25	1		2017/1/25	1		2016/12/5	4				
JP10	1st	2016/12/5	1	3	2017/2/23	50	0	2017/2/23	50	0	2016/12/13	1	1			
	2nd	2016/12/8	1		2017/2/23	49		2017/2/23	49		2016/12/14	1				
MN01	1st	2017/2/15	8	0		-			-		2017/2/15	8	0			
	2nd	2017/2/15	8								2017/2/15	8				
RU01	1st	2017/1/24	1	6	2017/1/24	2	8	2017/1/24	2	8	2017/1/25	1	8			
	2nd	2017/1/30	1		2017/2/1	2		2017/2/1	2		2017/2/2	1				
TH01	1st	2017/4/27	1	6	2017/4/28	2	10	2017/4/28	2	10	2017/4/26	2	6			
	2nd	2017/5/3	1		2017/5/8	2		2017/5/8	2		2017/5/2	2				
VN01	1st	2016/12/16	3	7	2016/12/16	3	7	2016/12/16	3	7	2016/12/16	3	7			
	2nd	2016/12/23	3		2016/12/23	3		2016/12/23	3		2016/12/23	3				
VN02	1st	2016/7/12	1	0		-			-		2016/7/12	31	0			
	2nd	2016/7/12	1								2016/7/12	31				
VN04	1st	2016/12/15	2	1	2016/12/14	1	1	2016/12/14	1	1	2016/12/14	1	1			
	2nd	2016/12/16	2		2016/12/15	1		2016/12/15	1		2016/12/15	1				
VN05	1st	2017/1/7	2	12		-			-		2017/1/7	2	12			
	2nd	2017/1/19	2								2017/1/19	2				

\*<sup>1</sup>, Finish date of 1st and 2nd analyses; \*<sup>2</sup>, Days used for analysis; \*<sup>3</sup>, Interval between the repeat analyses; +, not reported.

#### 4.4 Needs for improvement of soil analysis

Figure 4.3 shows the change of outlier ratio in all properties and laboratories from 2002 to 2016 (the ratio is calculated by  $\{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset})$ ). Although the ratio decreased from first experiment in 2002, this is still high (10-20% from 2003 to 2016). Outliers may disturb evaluation and understanding of actual monitoring data. For the inter-laboratory comparison project on soil, a decrease in the outliers is most important task in near future. Appropriate standard solution, extraction liquid, dilution rate and calculation should be checked to reduce extremely different values considered as outliers.



**Figure 4.3 Change of the outlier ratio in all properties and laboratories from 2002 to 2016 calculated by  $\{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset})$ . "a" and "b" show the 2 kinds of the samples in each year (e.g. 161s and 162s). The ratios from 2002 to 2015 were from *Report of Inter-Laboratory Comparison Project 2000-2015* (<http://www.eanet.asia/product/index.html>).**

#### 4.5 Recommendations

Reducing the outliers (about 15% of all data) in exchangeable base and acid cations will be considered firstly. In addition, the precision for the samples with low concentrations should be improved. The condition of standard solution, extraction liquid, dilution rate, calculation and operation of equipment will be checked. Analyst needs an effort to improve the standard of procedure in each laboratory. Not only analytical procedures but also reporting procedures should be checked carefully.

#### References

- EANET (2000). *Technical Documents for Soil and Vegetation Monitoring in East Asia: Acid Deposition and Oxidant Research Center*, Niigata, Japan.
- Japanese Standards Association (1991). *General rules for permissible tolerance of chemical analyses and physical tests (JIS Z-8402-1991)*: Japanese Standards Association, Tokyo, Japan.

**Appendix Table 4.1 Results submitted by the laboratories (sample No. 161s)**

Lab	pH(H <sub>2</sub> O)			pH(KCl)			Ex-Ca (cmol kg <sup>-1</sup> )			Ex-Mg (cmol kg <sup>-1</sup> )			Ex-K (cmol kg <sup>-1</sup> )			Ex-Na (cmol kg <sup>-1</sup> )			Ex-Acidity (cmol kg <sup>-1</sup> )			Ex-Al (cmol kg <sup>-1</sup> )			Ex-H (cmol kg <sup>-1</sup> )		
	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat
	(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.		(S.D.)	Ave.	
CN01	4.4 (0.0)	4.4 (0.0)	4.4 (0.0)	3.8 (0.0)	3.8 (0.0)	3.8 (0.0)	3.2 (0.01)	3.2 (0.01)	3.1 (0.01)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)	3.2 (0.00)
CN02	4.4 (0.0)	4.4 (0.0)	4.5 (0.0)	3.8 (0.0)	3.9 (0.0)	3.9 (0.0)	0.50 (0.01)	0.51 (0.00)	0.51 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)	0.24 (0.00)
CN03	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	0.51 (0.01)	0.51 (0.01)	0.51 (0.01)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)
CN04	4.4 (0.0)	4.4 (0.0)	4.4 (0.0)	3.7 (0.0)	3.7 (0.0)	3.7 (0.0)	0.35 (0.02)	0.34 (0.01)	0.35 (0.01)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)	0.20 (0.00)
ID01	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	3.7 (0.0)	3.7 (0.0)	3.7 (0.0)	0.35 (0.01)	0.36 (0.01)	0.36 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)	0.32 (0.01)
ID04	4.1 (0.3)	4.4 (0.0)	4.4 (0.0)	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	0.60 (0.02)	0.61 (0.02)	0.60 (0.02)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)	0.35 (0.01)
JP04	4.7 (0.0)	4.6 (0.0)	4.6 (0.0)	3.8 (0.0)	3.8 (0.0)	3.8 (0.0)	0.32 (0.02)	0.30 (0.01)	0.30 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)





**Appendix Table 4.2 Results submitted by the laboratories (sample No. 162s)**

Lab	pH(H <sub>2</sub> O)			pH(KCl)			Ex-Ca (cmol kg <sup>-1</sup> )			Ex-Mg (cmol kg <sup>-1</sup> )			Ex-K (cmol kg <sup>-1</sup> )			Ex-Na (cmol kg <sup>-1</sup> )			Ex-Acidity (cmol kg <sup>-1</sup> )			Ex-Al (cmol kg <sup>-1</sup> )			Ex-H (cmol kg <sup>-1</sup> )																																																																																																																																																																																																																																																																																																																																																																																																																																														
	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat	Lab Ave.		Repeat																																																																																																																																																																																																																																																																																																																																																																																																																																									
	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)	(S.D.)																																																																																																																																																																																																																																																																																																																																																																																																																																										
CN01	4.8 (0.0)	4.8 (0.0)	4.8 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	2.54 (0.03)	2.54 (0.04)	2.50 (0.01)	0.36 (0.01)	0.36 (0.01)	0.37 (0.01)	0.13 (0.00)	0.13 (0.01)	0.12 (0.00)	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)	1.97 (0.04)	1.98 (0.07)	2.01 (0.10)	1.85 (0.06)	1.85 (0.10)	1.93 (0.02)	1.85 (0.06)	1.85 (0.10)	1.87 (0.03)	1.74 (0.16)	1.74 (0.16)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.13)	1.85 (0.00)	1.85 (0.00)	1.84 (0.13)	1.84 (0.

Appendix Table 4.2 continued

Lab	pH(H <sub>2</sub> O)			pH(KCl)			Ex-Ca (cmol kg <sup>-1</sup> )			Ex-Mg (cmol kg <sup>-1</sup> )			Ex-K (cmol kg <sup>-1</sup> )			Ex-Na (cmol kg <sup>-1</sup> )			Ex-Activity (cmol kg <sup>-1</sup> )			Ex-Al (cmol kg <sup>-1</sup> )			Ex-H (cmol kg <sup>-1</sup> )			
	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	Lab Ave. (S.D.)	Ave. (S.D.)	Repeat	
JP10	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.1 (0.0)	4.1 (0.14)	4.1 (0.11)	2.78 (0.11)	2.76 (0.11)	2.87 (0.11)	0.42 (0.02)	0.41 (0.01)	0.41 (0.01)	0.16 (0.01)	0.15 (0.01)	0.15 (0.01)	0.03 (0.01)	0.03 (0.01)	0.03 (0.01)	2.49 (0.03)	2.51 (0.02)	2.52 (0.02)	2.05 (0.01)	2.06 (0.00)	2.06 (0.00)	2.06 (0.00)	0.44 (0.02)	0.45 (0.02)	0.46 (0.02)
	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.1 (0.0)	4.1 (0.19)	4.1 (0.19)	2.79 (0.19)	2.67 (0.19)	2.65 (0.19)	0.44 (0.03)	0.42 (0.03)	0.42 (0.03)	0.16 (0.00)	0.17 (0.00)	0.17 (0.00)	0.04 (0.00)	0.04 (0.00)	0.04 (0.00)	2.47 (0.00)	2.47 (0.00)	2.47 (0.00)	2.05 (0.01)	2.06 (0.00)	2.06 (0.00)	2.06 (0.00)	0.43 (0.00)	0.43 (0.00)	0.43 (0.00)
MN01	5.3 (0.1)	5.4 (0.1)	5.4 (0.1)	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.30 (0.00)	3.30 (0.00)	3.30 (0.00)	2.06 (0.00)	2.06 (0.00)	2.06 (0.00)	2.06 (0.00)	1.24 (0.00)	1.24 (0.00)	1.24 (0.00)
	5.3 (0.0)	5.3 (0.0)	5.3 (0.0)	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.30 (0.00)	3.30 (0.00)	3.30 (0.00)	2.06 (0.00)	2.06 (0.00)	2.06 (0.00)	2.06 (0.00)	1.24 (0.00)	1.24 (0.00)	1.24 (0.00)
RU01	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.1 (0.0)	4.1 (0.03)	4.1 (0.03)	0.50 (0.03)	0.52 (0.03)	0.46 (0.03)	0.39 (0.02)	0.41 (0.02)	0.43 (0.02)	0.14 (0.00)	0.15 (0.00)	0.15 (0.00)	0.03 (0.00)	0.03 (0.00)	0.04 (0.00)	2.25 (0.05)	2.22 (0.03)	2.21 (0.03)	1.65 (0.03)	1.62 (0.02)	1.61 (0.02)	1.61 (0.02)	0.58 (0.06)	0.56 (0.01)	0.57 (0.01)
	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.1 (0.0)	4.1 (0.03)	4.1 (0.03)	0.49 (0.02)	0.50 (0.02)	0.52 (0.02)	0.37 (0.02)	0.39 (0.02)	0.42 (0.02)	0.14 (0.00)	0.15 (0.00)	0.15 (0.00)	0.03 (0.00)	0.03 (0.00)	0.04 (0.00)	2.27 (0.05)	2.22 (0.03)	2.20 (0.03)	1.67 (0.01)	1.67 (0.01)	1.67 (0.01)	1.67 (0.01)	0.61 (0.08)	0.59 (0.08)	0.60 (0.08)
TH01	4.9 (0.0)	5.0 (0.0)	4.9 (0.0)	4.2 (0.1)	4.2 (0.02)	4.2 (0.02)	2.32 (0.03)	2.33 (0.03)	2.30 (0.03)	0.37 (0.00)	0.37 (0.00)	0.36 (0.00)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	0.03 (0.00)	0.03 (0.00)	0.04 (0.00)	2.16 (0.12)	2.12 (0.17)	2.31 (0.17)	1.70 (0.24)	1.60 (0.35)	2.00 (0.40)	1.60 (0.35)	0.64 (0.18)	0.71 (0.22)	0.84 (0.22)
	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.3 (0.0)	4.3 (0.02)	4.3 (0.02)	2.34 (0.02)	2.33 (0.02)	2.33 (0.02)	0.37 (0.00)	0.38 (0.00)	0.37 (0.00)	0.15 (0.00)	0.15 (0.00)	0.15 (0.00)	0.03 (0.00)	0.03 (0.00)	0.04 (0.00)	2.20 (0.03)	2.22 (0.03)	2.22 (0.03)	1.80 (0.00)	1.80 (0.00)	1.80 (0.00)	1.80 (0.00)	0.56 (0.13)	0.71 (0.13)	0.48 (0.13)
VN01	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.0 (0.0)	4.0 (0.01)	4.0 (0.01)	0.51 (0.01)	0.51 (0.01)	0.52 (0.01)	0.41 (0.00)	0.41 (0.00)	0.40 (0.00)	0.17 (0.00)	0.17 (0.00)	0.17 (0.00)	0.04 (0.00)	0.04 (0.00)	0.04 (0.00)	2.01 (0.03)	2.00 (0.03)	2.02 (0.03)	1.77 (0.02)	1.78 (0.01)	1.78 (0.01)	1.78 (0.01)	0.24 (0.02)	0.23 (0.02)	0.24 (0.02)
	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.0 (0.0)	4.0 (0.00)	4.0 (0.00)	0.51 (0.00)	0.51 (0.00)	0.51 (0.00)	0.41 (0.00)	0.41 (0.00)	0.41 (0.00)	0.17 (0.00)	0.17 (0.00)	0.17 (0.00)	0.04 (0.00)	0.04 (0.00)	0.04 (0.00)	2.01 (0.04)	2.02 (0.04)	2.02 (0.04)	1.76 (0.02)	1.76 (0.02)	1.76 (0.02)	1.76 (0.02)	0.25 (0.02)	0.26 (0.02)	0.26 (0.02)
VN02	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.53 (0.03)	2.53 (0.03)	2.56 (0.03)	2.22 (0.05)	2.22 (0.06)	2.26 (0.06)	2.26 (0.06)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)
	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.0 (0.0)	4.0 (0.0)	4.0 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.53 (0.03)	2.56 (0.03)	2.56 (0.03)	2.22 (0.06)	2.22 (0.06)	2.26 (0.06)	2.26 (0.06)	0.21 (0.00)	0.21 (0.00)	0.21 (0.00)
VN04	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.0 (0.0)	4.0 (0.01)	4.0 (0.01)	2.72 (0.02)	2.72 (0.02)	2.70 (0.02)	0.51 (0.00)	0.51 (0.00)	0.51 (0.00)	0.05 (0.00)	0.05 (0.00)	0.05 (0.00)	0.06 (0.00)	0.06 (0.00)	0.06 (0.00)	2.07 (0.00)	2.07 (0.00)	2.07 (0.00)	1.89 (0.00)	1.89 (0.00)	1.89 (0.00)	1.89 (0.00)	0.16 (0.00)	0.16 (0.00)	0.16 (0.00)
	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.0 (0.0)	4.0 (0.01)	4.0 (0.01)	2.71 (0.01)	2.71 (0.01)	2.71 (0.01)	0.51 (0.00)	0.51 (0.00)	0.51 (0.00)	0.05 (0.00)	0.05 (0.00)	0.05 (0.00)	0.06 (0.00)	0.06 (0.00)	0.06 (0.00)	2.07 (0.00)	2.07 (0.00)	2.07 (0.00)	1.89 (0.00)	1.89 (0.00)	1.89 (0.00)	1.89 (0.00)	0.18 (0.00)	0.18 (0.00)	0.18 (0.00)
VN05	4.6 (0.0)	4.6 (0.0)	4.6 (0.0)	3.9 (0.2)	3.7 (0.0)	3.7 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.56 (0.03)	3.55 (0.03)	3.54 (0.03)	3.07 (0.06)	3.09 (0.06)	3.12 (0.06)	3.12 (0.06)	0.35 (0.05)	0.35 (0.06)	0.31 (0.06)
	4.6 (0.0)	4.6 (0.0)	4.6 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.57 (0.03)	3.54 (0.03)	3.54 (0.03)	3.05 (0.06)	3.05 (0.06)	3.12 (0.06)	3.12 (0.06)	0.35 (0.06)	0.35 (0.06)	0.31 (0.06)
	4.6 (0.0)	4.6 (0.0)	4.6 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.59 (0.03)	3.59 (0.03)	3.59 (0.03)	3.02 (0.06)	3.02 (0.06)	3.02 (0.06)	3.02 (0.06)	0.31 (0.06)	0.31 (0.06)	0.31 (0.06)

## 5. 17<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON INLAND AQUATIC ENVIRONMENT

### 5.1 Introduction

In the Inter-laboratory Comparison Project on inland aquatic environment, an artificial inland water sample containing known concentrations of major ions was prepared and sent to the EANET participating countries by the Network Center (NC). The measured results 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  $\text{NH}_4^+$  in the participating laboratories were compared with the prepared values and the results were statistically analyzed.

### 5.2 Procedures

#### 5.2.1 Participating Laboratories

In the 17<sup>th</sup> Project, the NC shipped an artificial inland water sample to 24 laboratories involved in the EANET activities on October 18, 2016, and most of them submitted their analytical data to the NC by February 28, 2017. Participating laboratories and their identification codes are listed in Table 1.1. For this attempt, the laboratory MN01 submitted the data of 3 parameters, namely pH, EC and alkalinity.

#### 5.2.2 Description of Sample

A description of the sample is given in Table 5.1.

**Table 5.1 Description of the artificial inland water sample**

Name	Amount of the sample	Container	Number of samples	Note
Artificial inland water 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 water 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 mg L <sup>-1</sup>
Alkalinity	0.05 – 0.5 meq L <sup>-1</sup>	Ca <sup>2+</sup>	0.5 – 5 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 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 specified in the technical documents in EANET to the analysis. The methods and procedures applied were specified in Technical Manual for Inland Aquatic Environment Monitoring in East Asia (2010).

Analytical methods specified in the manual are described in Table 5.4.

**Table 5.4 Analytical methods specified in the Technical 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>	
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 ( $R_1$ )

- (1) Total anion ( $A$ ) equivalent concentration ( $\mu\text{eq L}^{-1}$ ) is calculated by sum up the concentration of anions ( $C$ :  $\mu\text{mol L}^{-1}$ ) and alkalinity ( $ALK$ :  $\mu\text{eq L}^{-1}$ ). Alkalinity considered to be corresponded to bicarbonate ions ( $\text{HCO}_3^-$ ).

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

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

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

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

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

- (3) Calculation of ion balance ( $R_1$ )

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

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

**Table 5.5 Allowable ranges for  $R_1$  in different concentration ranges**

$(C+A)$ [ $\mu\text{eq L}^{-1}$ ]	$R_1$ [%]
< 50	+30 ~ -30
50 ~ 100	+15 ~ -15
>100	+8 ~ -8

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

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

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

$C$ : 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 ( $R_2$ ) of calculations ( $A_{\text{calc}}$ ) to measurements ( $A_{\text{meas}}$ ) in electric conductivity is calculated as follows;

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

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

**Table 5.6 Allowable ranges for  $R_2$  in different concentration ranges**

$A_{\text{meas}} [\text{mS m}^{-1}]$	$R_2$ [%]
< 0.5	+20 ~ -20
0.5 ~ 3	+13 ~ -13
> 3	+9 ~ -9

## 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 the analytical results. The outliers, defined as those results exceeding three standard deviations, were excluded from calculations in Table 5.7. Each average of submitted data agreed well with the corresponding prepared value/concentration.

**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	6.76	6.72	0.18	21	6.40	7.01
EC (mS m <sup>-1</sup> )	3.07	2.94	0.09	21	2.79	3.13
Alkalinity (meq L <sup>-1</sup> )	0.094	0.097	0.01	20	0.061	0.116
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	3.89	3.76	0.16	20	3.49	4.18
NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	0.49	0.47	0.05	19	0.30	0.53
Cl <sup>-</sup> (mg L <sup>-1</sup> )	2.36	2.31	0.14	19	2.00	2.58
Na <sup>+</sup> (mg L <sup>-1</sup> )	2.38	2.39	0.12	20	2.20	2.65
K <sup>+</sup> (mg L <sup>-1</sup> )	0.58	0.54	0.05	20	0.40	0.59
Ca <sup>2+</sup> (mg L <sup>-1</sup> )	1.35	1.39	0.11	20	1.23	1.60
Mg <sup>2+</sup> (mg L <sup>-1</sup> )	0.60	0.57	0.05	20	0.45	0.65
NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	0.24	0.21	0.03	20	0.14	0.26

(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 the EANET are specified in Chapter 6 of the Technical Manual. In this report, analytical data were compared with the prepared values/concentrations and evaluated by the criteria : A flag E is given to the value in the case that its deviation exceeds  $\pm 15\%$  but not  $\pm 30\%$ , and the flag X is given to the value in the case that its deviation exceeds  $\pm 30\%$ .

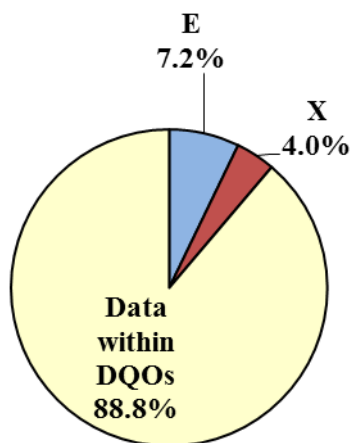
Table 5.8 shows the number of flagged data for each parameter and Figure 5.1 shows the percentage of flagged data.

**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	4	0	0	2	0	2	2	2	4	16	7.2%
X	0	0	2	0	2	0	0	1	0	0	4	9	4.0%
Data within DQOs	21	21	15	20	18	18	20	17	18	18	12	198	88.8%
Flagged(%)	0.0	0.0	28.6	0.0	10.0	10.0	0.0	15.0	10.0	10.0	40.0	11.2	

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

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

**Figure 5.1 Percentage of flagged data**

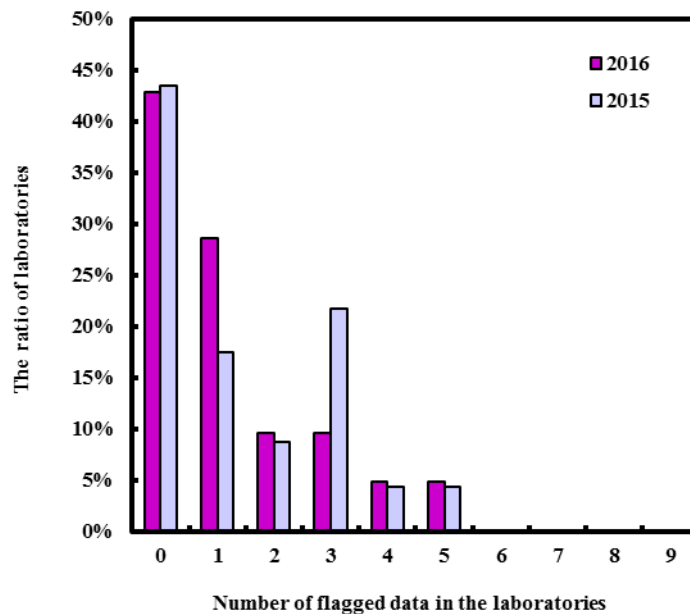
The data flagged by "E" shared 7.2% of all reported data, and the data flagged by "X" shared 4.0% of all reported data of samples. The NH<sub>4</sub><sup>+</sup> results were flagged most (E and X), and their percentage was 40.0%.

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	9	43%
1	6	29%
2	2	10%
3	2	10%
4	1	5%
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 43% in this attempt, while that in the last attempt (2015) was 43%. The maximum number of flagged data was five, which was submitted by one laboratory.

The Analytical data submitted by the participating laboratories are shown in Table 5.10 with flags.

**Table 5.10 Analytical Results of Sample No.161i (artificial inland aquatic environment sample : EANET in 2016)**

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	6.93	2.90	0.104	3.85	0.48	2.23	2.38	0.57	1.41	0.60	0.22	-1.04	-
CN02	6.81	2.92	0.101	3.75	0.48	2.21	2.35	0.59	1.38	0.58	0.20 E	-1.01	0.94
CN03	6.73	2.90	0.104	3.90	0.50	2.23	2.30	0.57	1.44	0.59	0.21	-1.96	2.35
CN04	6.71	2.93	0.103	3.72	0.50	2.24	2.36	0.56	1.45	0.60	0.21	-0.28	1.53
ID01	6.84	2.88	0.116 E	3.61	0.47	2.14	2.20	0.53	1.60 E	0.65	0.15 X	-1.49	2.67
ID05	6.50	2.95	0.108 E	3.65	0.30 X	2.00 E	2.20	0.53	1.32	0.57	0.18 E	-2.71	-1.54
JP04	6.82	2.90	0.105	3.81	0.49	2.35	2.34	0.57	1.31	0.61	0.24	-2.77	2.31
JP12	6.88	2.93	0.113 E	3.70	0.51	2.14	2.28	0.57	1.28	0.55	0.26	-4.28	0.78
MY01	6.71	2.96	0.099	3.61	0.46	2.35	2.36	0.57	1.38	0.57	0.22	-0.51	0.34
MN01	6.44	2.86	0.061 X									-	-
PH01	6.85	2.79	0.087	3.78	0.43	2.39	2.42	0.56	1.25	0.54	0.21	-0.40	2.20
PH02	6.89	2.91	0.100	3.82	0.42	2.42	2.43	0.57	1.23	0.52	0.22	-3.64	1.18
RU01	6.84	2.99	0.090	4.18	0.47	2.24	2.38	0.55	1.38	0.53	0.23	-0.99	0.13
RU02	6.81	2.92	0.096	3.60	0.50	2.48	2.50	0.54	1.30	0.59	0.26	0.31	1.72
TH01	7.01	2.82	0.108 E	3.60	0.43	2.28	2.35	0.56	1.39	0.60	0.21	-1.44	3.17
TH02	6.75	2.89	0.087	3.87	0.48	2.36	2.48	0.59	1.29	0.59	0.17 X	0.57	1.29
VN01	6.40	3.03	0.090	3.49	0.44	2.58	2.34	0.57	1.33	0.60	0.20 E	0.14	-1.14
VN02	6.70	2.94	0.088	3.80	0.48	2.30	2.55	0.45 E	1.50	0.63	0.17 X	3.57	1.30
VN03	6.56	3.13	0.160 X	3.70	0.50	2.93 E	2.65	0.44 E	1.52	0.45 E	0.20 E	-13.30 I	4.37
VN04	6.51	3.12	0.084	4.01	0.81 X	2.52	2.59	0.56	1.51	0.55	0.14 X	0.80	-0.26
VN05	6.45	3.06	0.095	3.74	0.53	2.34	2.25	0.40 X	1.59 E	0.45 E	0.21	-2.19	-1.97
Expected value	6.76	3.07	0.094	3.89	0.49	2.36	2.38	0.58	1.35	0.60	0.24	-	-

Flag E: 15% < |Deviation| ≤ 30%

Flag X: 30% < |Deviation|

I: Poor ion balance (R1)

C: Rich Conductivity agreement (R2)

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

The laboratories' performances are presented below in Figures from 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.

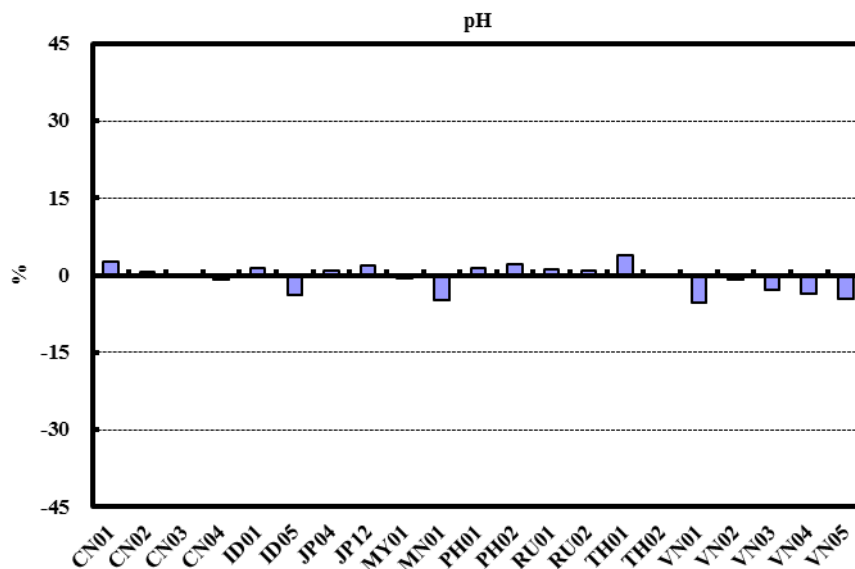


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

All the submitted data of pH were within DQO, 15%.

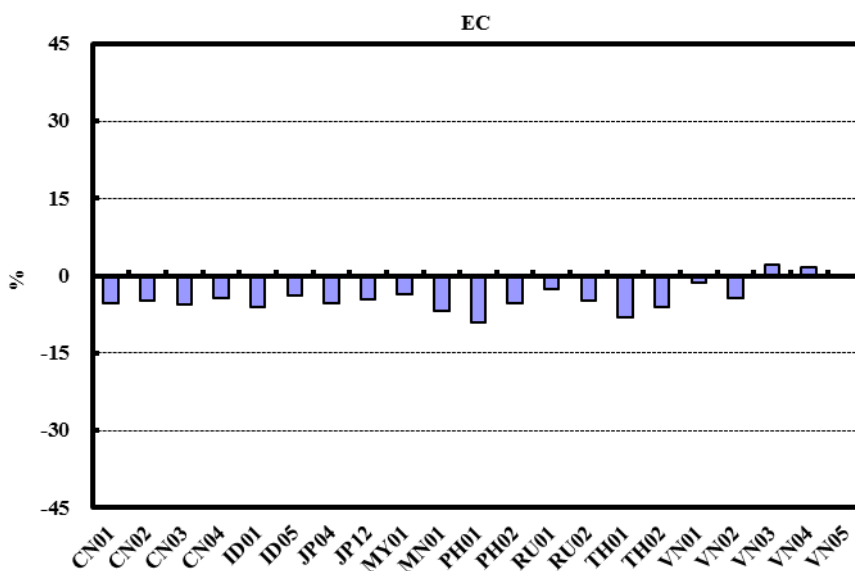
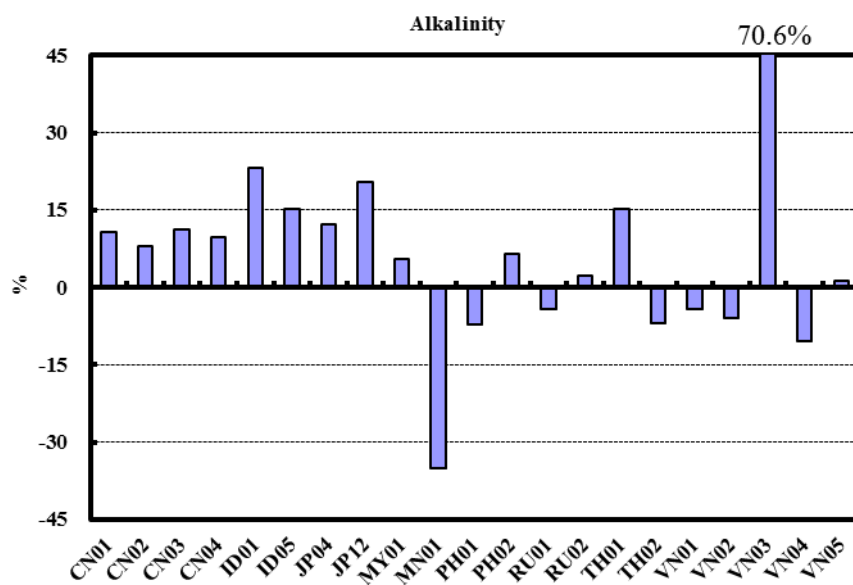


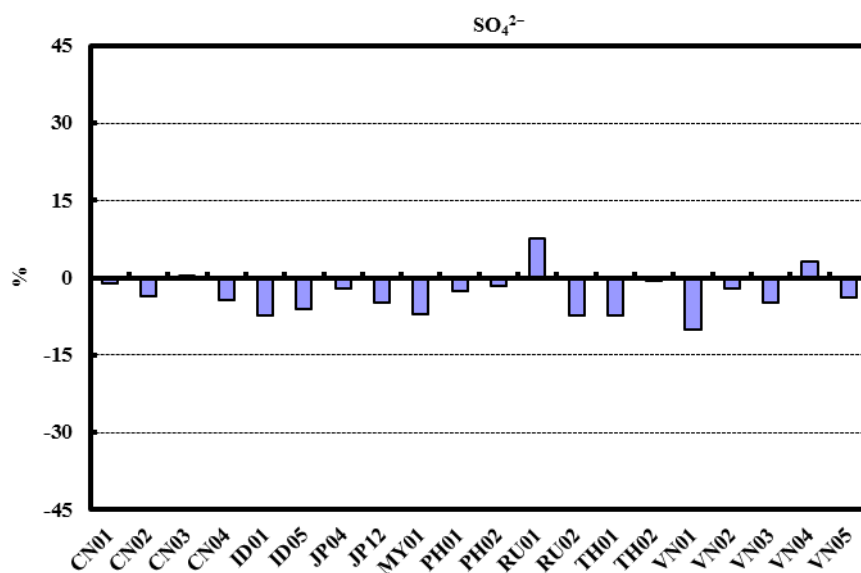
Figure 5.4 Distribution of results for EC (normalized by the prepared value)

All the submitted data of EC were within DQOs. Almost all of them were lower than the prepared value.



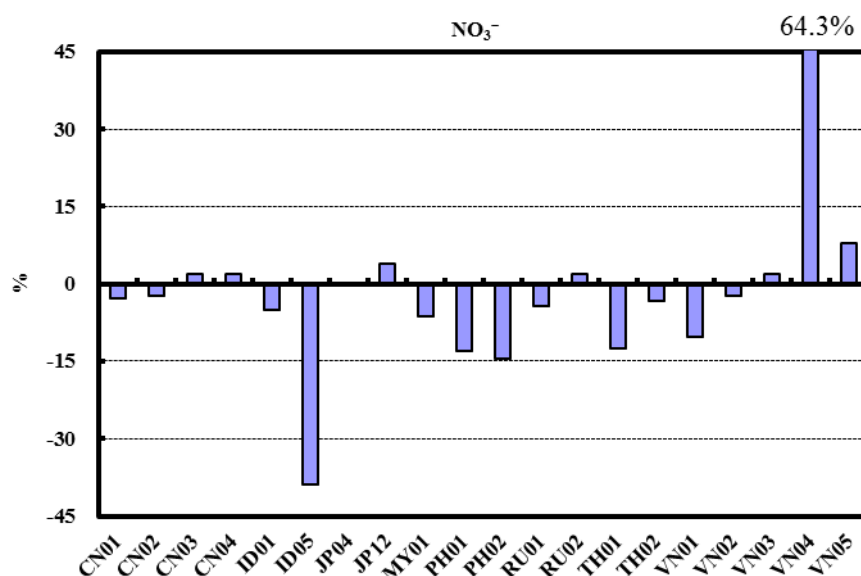
**Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)**

Data of alkalinity from six laboratories were flagged and two of them were deviated more than 30%. The number of flagged data of alkalinity was three in last attempt. The flagged data increased.



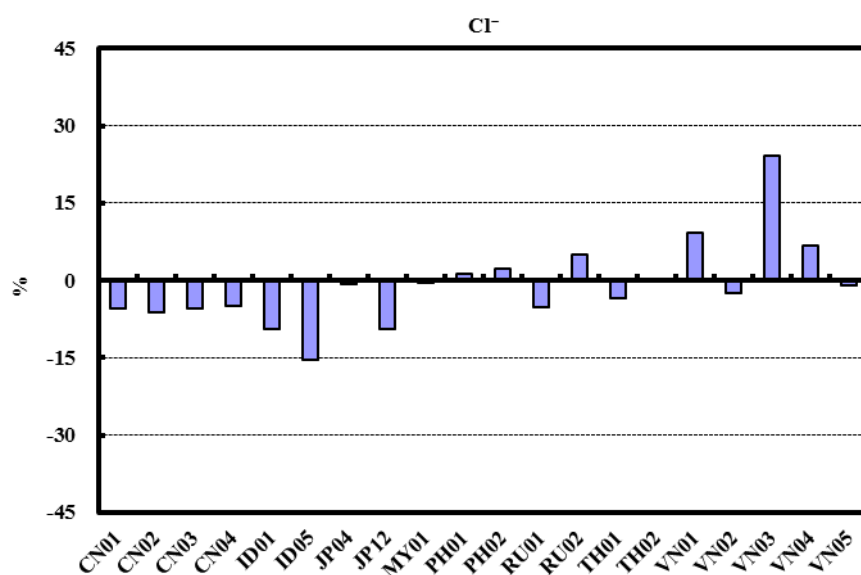
**Figure 5.6 Distribution of results for SO<sub>4</sub><sup>2-</sup> (normalized by prepared concentration)**

All the submitted data of  $\text{SO}_4^{2-}$  were within DQO, 15%. Almost all of them were lower than the prepared value.



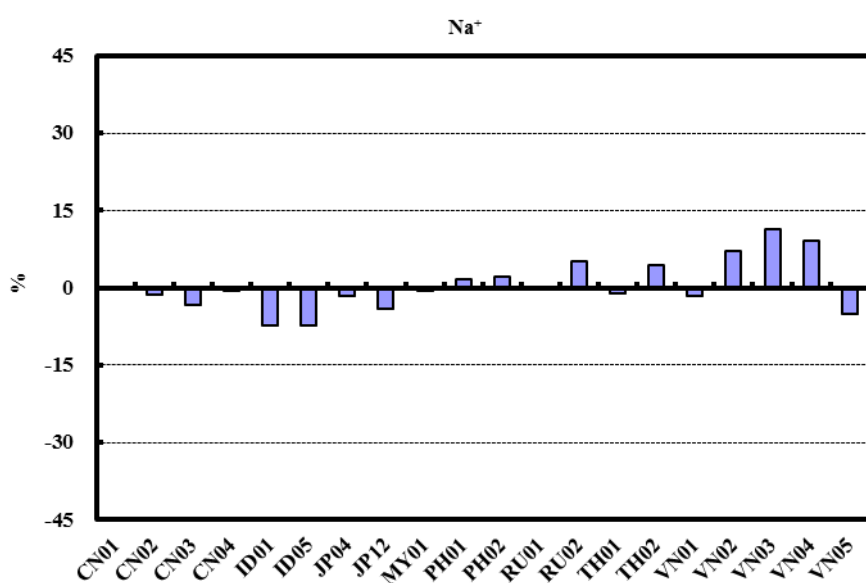
**Figure 5.7 Distribution of results for  $\text{NO}_3^-$  (normalized by prepared concentration)**

Except for ID05 and VN04, all the submitted data of  $\text{NO}_3^-$  were within DQO, 15%. All the flagged data were deviated more than 30%.



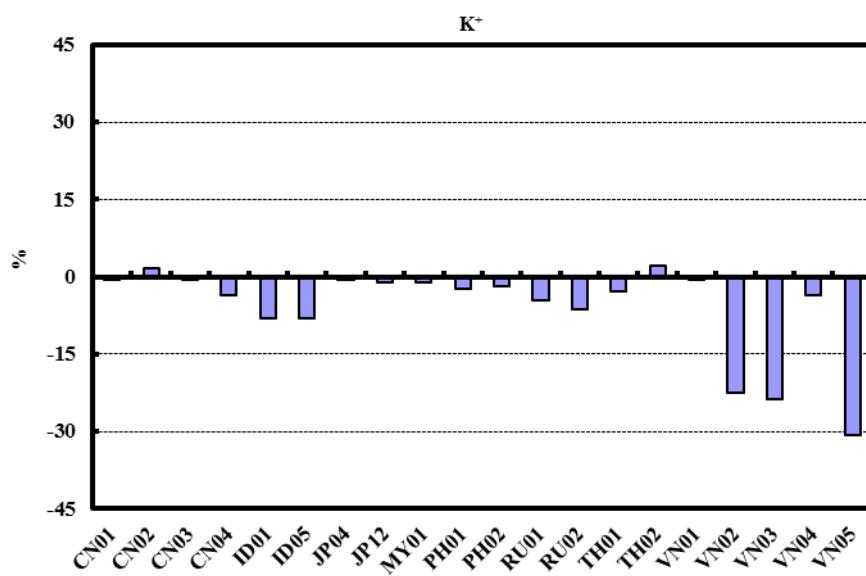
**Figure 5.8 Distribution of results for  $\text{Cl}^-$  (normalized by prepared concentration)**

Except for ID05 and VN03, all the submitted data of  $\text{Cl}^-$  were within DQOs.



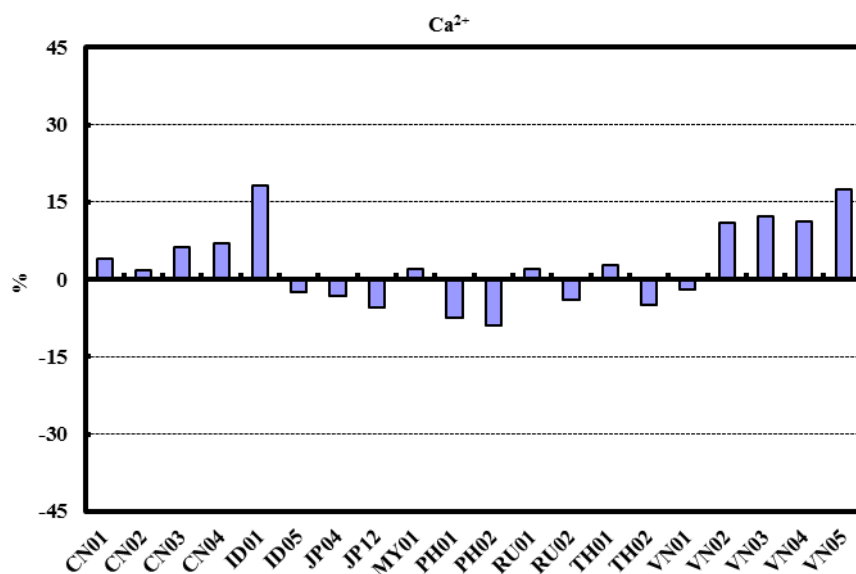
**Figure 5.9 Distribution of results for Na<sup>+</sup> (normalized by prepared concentration)**

All the submitted data of Na<sup>+</sup> were within DQOs.



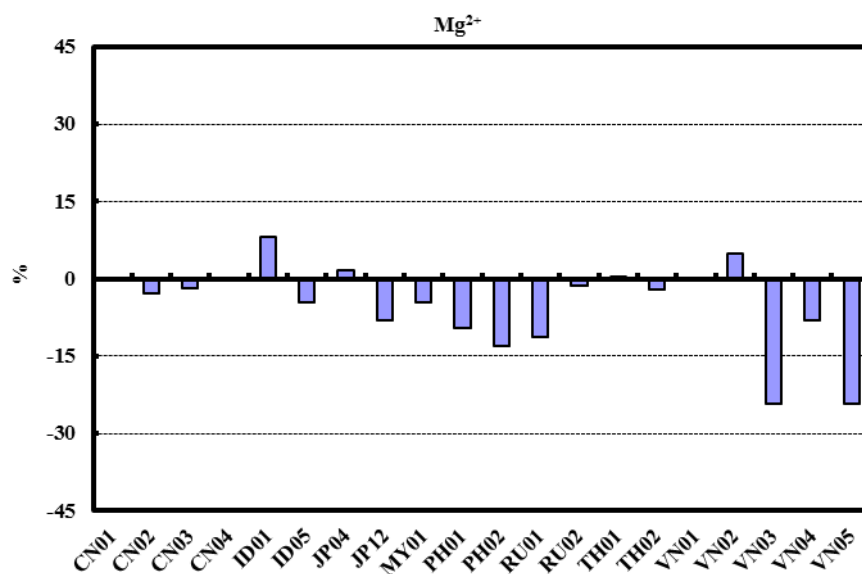
**Figure 5.10 Distribution of results for K<sup>+</sup> (normalized by prepared concentration)**

Except for VN02, VN03 and VN05, all the submitted data of K<sup>+</sup> were within DQOs. Almost all of them were lower than the prepared value.



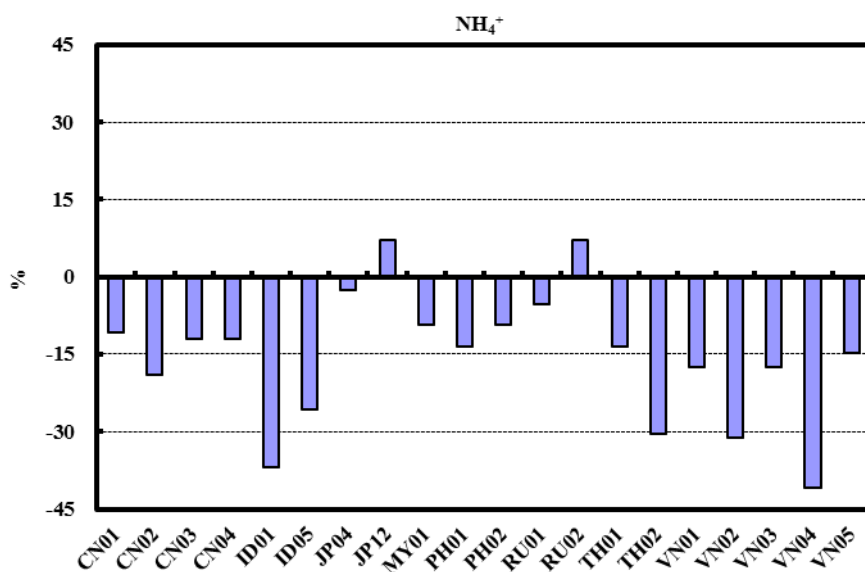
**Figure 5.11 Distribution of results for  $\text{Ca}^{2+}$  (normalized by prepared concentration)**

Except for ID03 and VN05, all the submitted data of  $\text{Ca}^{2+}$  were within DQOs. The number of flagged data of  $\text{Ca}^{2+}$  was five in last attempt. The flagged data decreased.



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

Except for VN03 and VN05, all the submitted data of  $\text{Mg}^{2+}$  were within DQOs. The number of flagged data of  $\text{Ca}^{2+}$  was six in last attempt. The flagged data decreased.



**Figure 5.13 Distribution of results for  $\text{NH}_4^+$  (normalized by prepared concentration)**

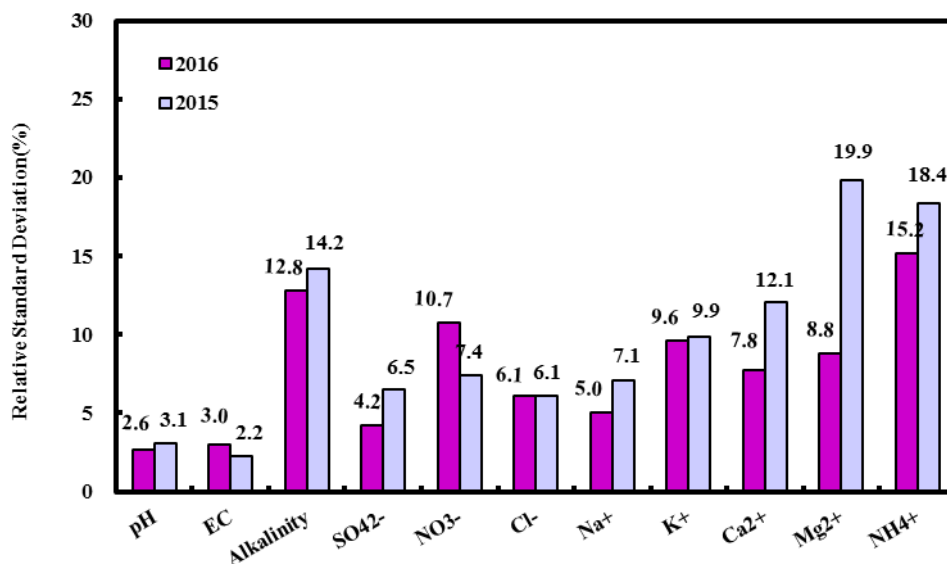
Data of  $\text{NH}_4^+$  from eight laboratories were flagged, and four of them were deviated more than 30%. Among 20 participating laboratories, 15 laboratories used ion chromatography, 4 laboratories used spectrophotometry (Indophenol) and 1 laboratory used spectrophotometry (other method) for the determination of  $\text{NH}_4^+$ . Six laboratories with flagged data used ion chromatography, and another two laboratory used spectrophotometry (Indophenol) methods.

$\text{NH}_4^+$  was the parameter that has the highest flagged percentage in this attempt.



### 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 (2015).



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

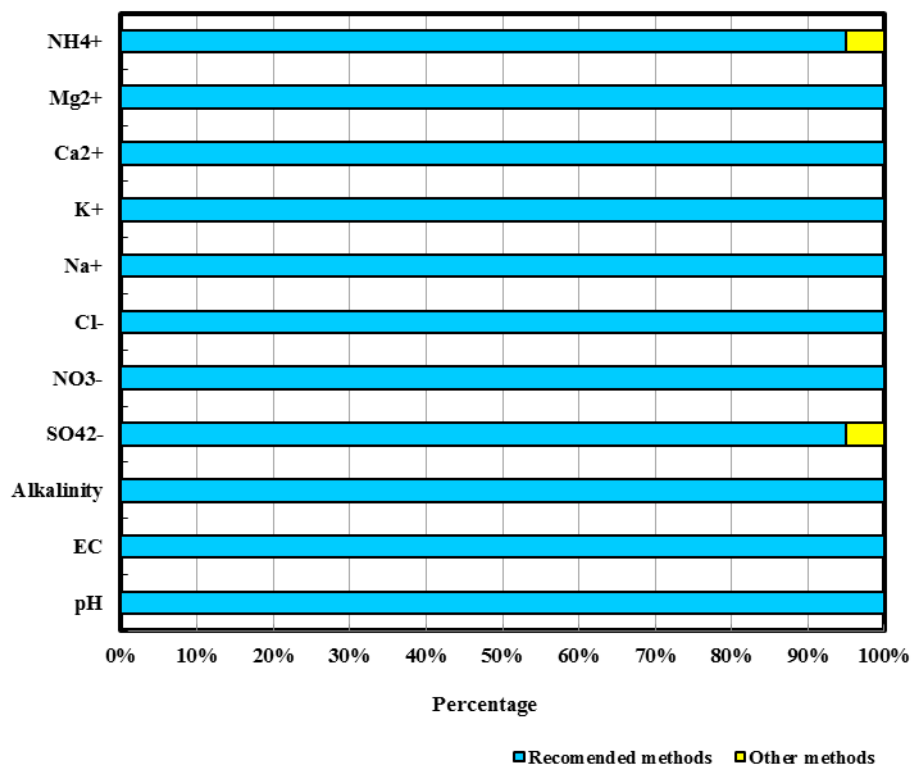
**Figure 5.14 Relative standard deviation of each constituent**

The relative standard deviation (RSD) of NO<sub>3</sub><sup>-</sup> in 2016 became high than the last attempt. On the other hand, almost all RSDs of major ions became lower, especially Mg<sup>2+</sup>.

### 5.3.4 Information on laboratories

#### Methodologies used

The percentages of laboratories using the recommended methods are shown in Figure 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(6)			3(2)					
3							5	5(1)	5	5(1)	
4				17	15(1)	17	15	15(2)	15(2)	15(1)	15(6)
5											
6											
7				2	5(1)						1
8											4(2)
9											
10											
11				1							
Flagged E	0	0	4	0	0	2	0	2	2	2	4
Flagged X	0	0	2	0	2	0	0	1	0	0	4

☒ Recommended methods
 ☐ Other methods  
 ( ) : Number of data, which flagged by "E" or "X"

The participating laboratories used recommended methods of the EANET except for measurement of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>.

For the determination of anions/cations, most of the participating laboratories used ion chromatography, while some of them used other methods. Either data of all anions/cations obtained through ion chromatography included some flagged data. As a conclusion, 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	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Unit : year	
												NH <sub>4</sub> <sup>+</sup>	
CN01	1	A	A	A	A	A	A	A	A	A	A	A	A
CN02	3	A	A	B	C	C	C	C	C	C	C	C	C
CN03	2	A	A	A	B	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A	A	A
ID01	2	A	A	A	B	B	B	B	B	B	B	B	B
ID05	5	A	A	B	A	C	C	D	D	E	E	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A	A	A
JP12	3	A	A	B	A	A	A	C	C	C	C	C	A
MY01	4	A	A	B	C	C	C	D	D	D	D	D	D
MN01	2	A	A	B									
PH01	1	A	A	A	A	A	A	A	A	A	A	A	A
PH02	2	A	A	A	B	B	B	B	B	B	B	B	B
RU01	3	A	A	A	B	B	B	C	C	C	C	C	A
RU02	5	A	B	A	C	D	A	E	E	E	E	E	C
TH01	1	A	A	A	A	A	A	A	A	A	A	A	A
TH02	2	A	B	A	B	B	B	A	A	A	A	A	A
VN01	2	A	A	B	B	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C	C
VN03	3	A	A	B	B	A	A	C	C	A	C	C	A
VN04	3	A	A	B	C	C	C	C	C	C	C	C	C
VN05	4	A	A	B	C	D	C	C	C	C	C	C	C

Letters represent individuals of staff in each laboratory who are in charge of measurement.

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

-: no information

blank: not analyzed

In many laboratories, 2 or 3 persons analyzed the sample, and usually they shared the works 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>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Unit : year	
											NH <sub>4</sub> <sup>+</sup>	
CN01	2	2	2	2	2	2	2	2	2	2	2	
CN02	19	11	11	11	11	11	11	11	11	11	11	
CN03	21	21	21	6	6	6	6	6	6	6	6	
CN04	10	10	10	10	10	10	10	10	10	10	10	
ID01	5	5	5	16	16	16	16	16	16	16	16	
ID05	10	10	12	10	3	3	8	8	8	8	10	
JP04	14	14	14	14	14	14	14	14	14	14	14	
JP12	4	4	5	4	4	4	16	16	16	16	4	
MY01	3	3	4	1	1	1	10	10	10	10	10	
MN01	15	15	18									
PH01	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	
PH02	2	2	2	6	6	6	6	6	6	6	6	
RU01	23	23	23	21	21	21	31	31	31	31	23	
RU02	56	38	56	31	2	56	25	25	25	25	31	
TH01	19	19	19	19	19	19	19	19	19	19	19	
TH02	19	13	19	13	13	13	19	19	19	19	19	
VN01	3	3	24	24	24	24	24	24	24	24	24	
VN02	10	10	12	12	12	12	12	12	12	12	12	
VN03	2	2	8	8	2	2	4	4	2	4	2	
VN04	13	13	13	11	11	11	11	11	11	11	11	
VN05	4	4	5	13	12	13	13	13	13	13	13	

Data were Flagged by "E" or "X" in sample

1 year means experienced with one year or less.

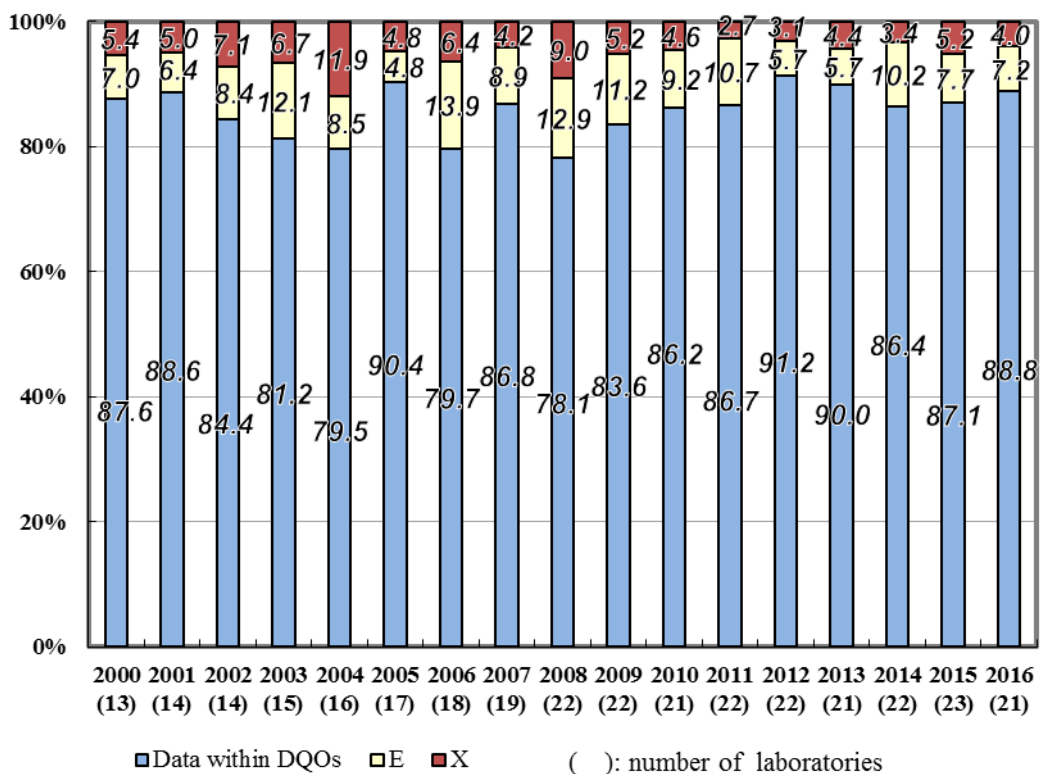
-: no information

blank: not analyzed

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

#### 5.4. Comparison with past surveys

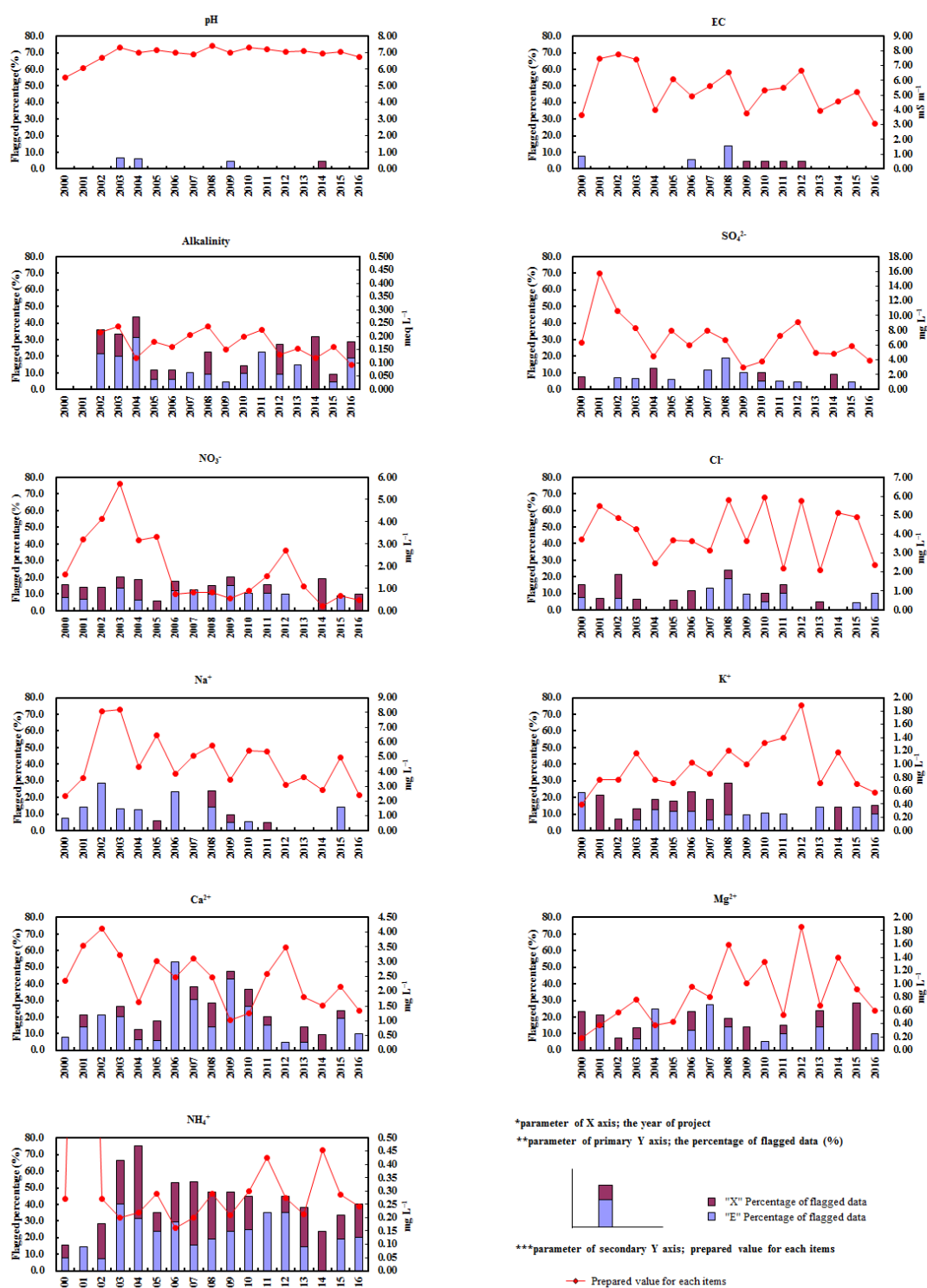
The inter-laboratory comparison projects of the EANET have been carried out 17 times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure 5.16.



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

The percentage of data satisfied the DQOs decreased from 2012 to 2014, but it increased slightly in this attempt. The percentage of each data in this attempt was almost same as the last attempt.

The values/concentrations for each parameter from the 1<sup>st</sup> to 17<sup>th</sup> project were compared with the percentage of flagged data in Figure 5.17.



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

There was no flagged data in pH, EC,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  in this attempt. The analyses of pH,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were improved. In this attempt, flagged percentages of alkalinity,  $\text{Cl}^-$  and  $\text{NH}_4^+$  became higher than the last attempt. It may be caused by low concentrations and condition of instrument, especially ion chromatography column.

Furthermore, the percentage of flagged data was larger in  $\text{NH}_4^+$  than for other parameters in every survey except for the 1<sup>st</sup>- 3<sup>rd</sup> project. The percentage of flagged  $\text{Ca}^{2+}$  in the 7<sup>th</sup> - 11<sup>th</sup> project was also comparatively high. Therefore, in the inland water analysis, it is necessary to pay more attention to  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ .



## **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, SOP (Standard Operating Procedures) 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 with 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 are detected, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

## References

EANET (2000). *Technical Manual for Monitoring on Inland Aquatic Environment in East Asia*. Acid Deposition and Oxidant Research Center, Niigata, Japan, 46p.

EANET (2000). *Quality Assurance/Quality Control (QA/QC) Program for Monitoring on Inland Aquatic Environment in East Asia*. Acid Deposition and Oxidant Research Center, Niigata, Japan, 22p.

EANET (2010). *Technical Manual for Inland Aquatic Environment Monitoring in East Asia -2010*. Asia Center for Air Pollution Research, Niigata, Japan, 124p.

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	6.93	2.90	0.104	3.85	0.48	2.23	2.38	0.57	1.41	0.60	0.22
CN02	6.81	2.92	0.101	3.75	0.48	2.21	2.35	0.59	1.38	0.58	0.20
CN03	6.73	2.90	0.104	3.90	0.50	2.23	2.30	0.57	1.44	0.59	0.21
CN04	6.71	2.93	0.103	3.72	0.50	2.24	2.36	0.56	1.45	0.60	0.21
ID01	6.84	2.88	0.116	3.61	0.47	2.14	2.20	0.53	1.60	0.65	0.15
ID05	6.50	2.95	0.108	3.65	0.30	2.00	2.20	0.53	1.32	0.57	0.18
JP04	6.82	2.90	0.105	3.81	0.49	2.35	2.34	0.57	1.31	0.61	0.24
JP12	6.88	2.93	0.113	3.70	0.51	2.14	2.28	0.57	1.28	0.55	0.26
MY01	6.71	2.96	0.099	3.61	0.46	2.35	2.36	0.57	1.38	0.57	0.22
MN01	6.44	2.86	0.061	0.00	0.00	0.00					
PH01	6.85	2.79	0.087	3.78	0.43	2.39	2.42	0.56	1.25	0.54	0.21
PH02	6.89	2.91	0.100	3.82	0.42	2.42	2.43	0.57	1.23	0.52	0.22
RU01	6.84	2.99	0.090	4.18	0.47	2.24	2.38	0.55	1.38	0.53	0.23
RU02	6.81	2.92	0.096	3.60	0.50	2.48	2.50	0.54	1.30	0.59	0.26
TH01	7.01	2.82	0.108	3.60	0.43	2.28	2.35	0.56	1.39	0.60	0.21
TH02	6.75	2.9	0.087	3.87	0.48	2.36	2.48	0.59	1.29	0.59	0.17
VN01	6.40	3.0	0.090	3.49	0.44	2.58	2.34	0.57	1.33	0.60	0.20
VN02	6.70	2.9	0.088	3.80	0.48	2.30	2.55	0.45	1.50	0.63	0.17
VN03	6.56	3.1	0.160	3.70	0.50	2.93	2.65	0.44	1.52	0.45	0.20
VN04	6.51	3.1	0.084	4.01	0.81	2.52	2.59	0.56	1.51	0.55	0.14
VN05	6.45	3.06	0.10	3.74	0.53	2.34	2.25	0.40	1.59	0.45	0.21
Expected value	6.76	3.07	0.094	3.89	0.49	2.36	2.38	0.58	1.35	0.60	0.24
Number of data	21	21	21	20	20	20	20	20	20	20	20
Average	6.72	2.94	0.10	3.76	0.48	2.34	2.39	0.54	1.39	0.57	0.21
Minimum	6.40	2.79	0.06	3.49	0.30	2.00	2.20	0.40	1.23	0.45	0.14
Maximum	7.01	3.13	0.16	4.18	0.81	2.93	2.65	0.59	1.60	0.65	0.26

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	2.6	-5.4	10.9	-1.1	-2.9	-5.5	0.0	-0.6	4.0	-0.1	-10.7	
CN02	0.8	-4.8	8.0	-3.6	-2.2	-6.2	-1.3	1.7	1.8	-2.9	-18.9	
CN03	-0.4	-5.5	11.2	0.3	1.8	-5.5	-3.2	-0.6	6.2	-1.8	-12.1	
CN04	-0.7	-4.5	9.8	-4.4	1.8	-5.0	-0.6	-3.5	6.9	-0.1	-12.1	
ID01	1.3	-6.2	23.3	-7.2	-4.9	-9.3	-7.3	-8.1	18.3	8.2	-36.8	
ID05	-3.8	-3.9	15.1	-6.1	-38.9	-15.3	-7.4	-8.1	-2.4	-4.6	-25.8	
JP04	0.9	-5.4	12.3	-2.0	-0.2	-0.6	-1.7	-0.6	-3.2	1.5	-2.4	
JP12	1.8	-4.6	20.5	-4.8	3.9	-9.3	-4.1	-1.2	-5.4	-8.0	7.2	
MY01	-0.7	-3.6	5.5	-7.2	-6.3	-0.5	-0.7	-1.2	2.0	-4.6	-9.3	
PH01	1.4	-9.1	-7.3	-2.7	-13.1	1.4	1.7	-2.3	-7.3	-9.6	-13.4	
PH02	2.0	-5.3	6.6	-1.7	-14.5	2.4	2.1	-1.8	-8.8	-13.0	-9.3	
RU01	1.2	-2.6	-4.1	7.5	-4.3	-5.1	0.1	-4.6	2.0	-11.3	-5.2	
RU02	0.8	-4.9	2.3	-7.4	1.8	5.1	5.2	-6.4	-3.9	-1.3	7.2	
TH01	3.8	-8.1	15.1	-7.4	-12.4	-3.4	-1.1	-2.9	2.8	0.4	-13.4	
TH02	-0.1	-6.0	-6.9	-0.6	-3.3	0.0	4.5	2.2	-5.0	-2.1	-30.3	
VN01	-5.3	-1.4	-4.1	-10.2	-10.4	9.1	-1.5	-0.6	-1.9	-0.1	-17.6	
VN02	-0.8	-4.3	-5.8	-2.2	-2.2	-2.4	7.1	-22.6	10.9	4.9	-31.3	
VN03	-2.9	2.1	70.6	-4.8	1.8	24.1	11.4	-23.7	12.4	-24.1	-17.6	
VN04	-3.6	1.7	-10.5	3.2	64.3	6.7	9.1	-3.5	11.4	-8.0	-40.9	
VN05	-4.5	-0.2	1.3	-3.9	8.0	-1.0	-5.2	-30.6	17.5	-24.1	-14.8	
Minimum	-5.3	-9.1	-35.0	-10.2	-38.9	-15.3	-7.4	-30.6	-8.8	-24.1	-40.9	
Maximum	3.8	2.1	70.6	7.5	64.3	24.1	11.4	2.2	18.3	8.2	7.2	
Average	-0.5	-4.2	6.6	-3.3	-1.6	-1.0	0.4	-5.9	2.9	-5.0	-15.4	

blank: not analyzed



## **6. ACKNOWLEDGEMENT**

ACAP wishes to thank Toyama Prefecture for their cooperation in the collection of soil samples used for the Inter-laboratory Comparison Project on soil.

## **7. CONTACT INFORMATION**

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