

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

# **Report of the Inter-laboratory Comparison Project 2024**

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

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

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

**25<sup>th</sup> Inter-laboratory Comparison Project on Inland Aquatic Environment**

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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.

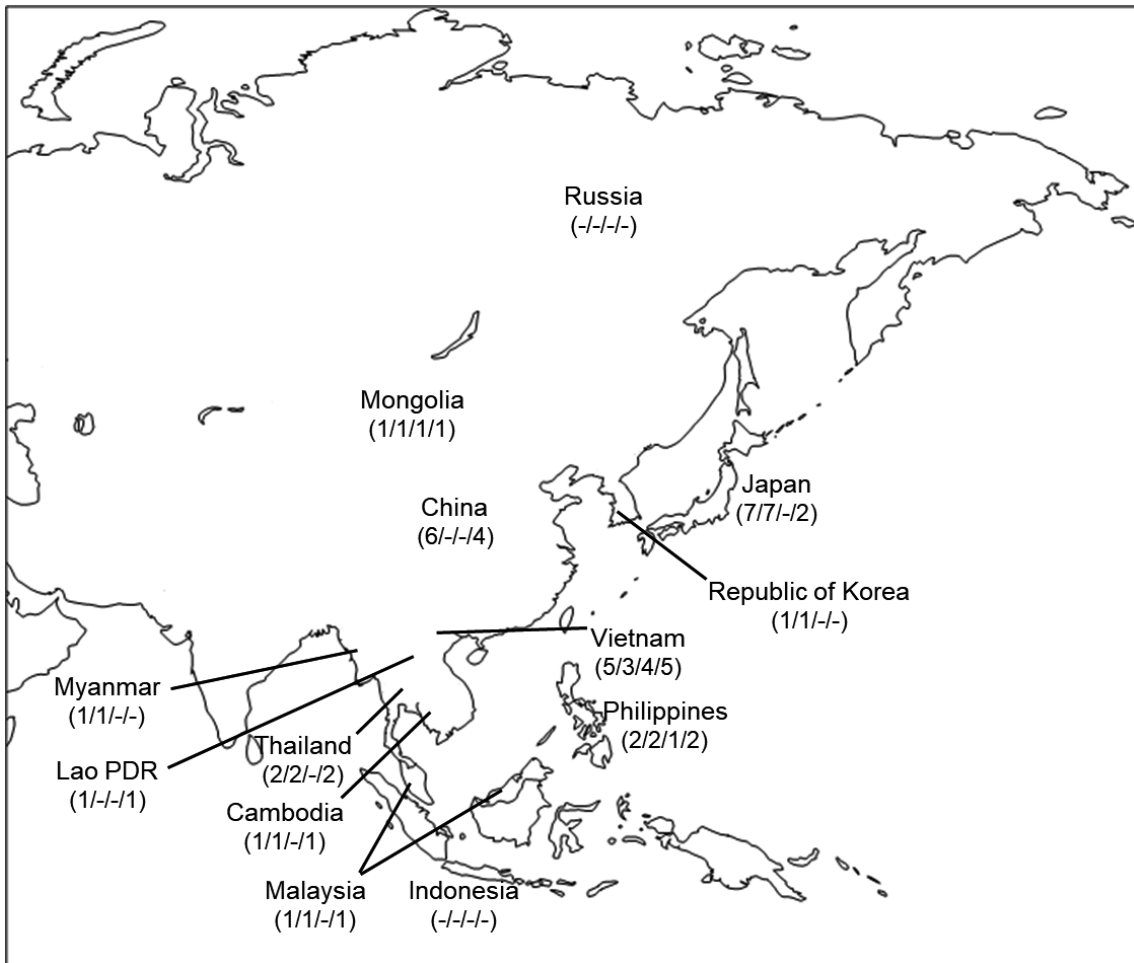
The Inter-laboratory Comparison Project is implemented by the Network Center (NC) of EANET annually for the following items:

- a. Wet deposition
- b. Dry deposition
- c. Soil
- d. Inland aquatic environment

This report presented the results of the 27<sup>th</sup> Inter-laboratory Comparison Project on wet deposition, 20<sup>th</sup> Inter-laboratory Comparison Project on dry deposition, 26<sup>th</sup> Inter-laboratory Comparison Project on soil, and 25<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. In addition, laboratories in charge of the analysis of each monitoring site in EANET are listed in Table 1.2.



**Figure 1.1 Number of participating laboratories in 2024**

\* The values in parentheses show the number of participating laboratories in 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>Cambodia</b>					
General Directorate of Environmental Protection (GDEP), Ministry of Environment	KH01				
<b>China</b>					
Zhuhai Environmental Monitoring Center Station	CN01	✓			✓
Xiamen Environmental Monitoring Station	CN02	✓			✓
Xi'an Environmental Monitoring Center Station	CN03	✓			✓
Chongqing Ecological and Environmental Monitoring Center	CN04	✓			✓
Wuzhishan City Ecological Environment Protection Monitoring Station	CN05				
The Ecological and Environmental Monitoring Station of DEEY in Lijiang	CN06	✓			
<b>Indonesia</b>					
Center for Standardization of Environmental Quality Instrument (PSIKLH)	ID01				
Climatology, Meteorological and Geophysical Agency (BMKG)	ID02				
Research Organization of Aeronautics and Space - National Research and Innovation Agency (LAPAN-BRIN)	ID03				
Indonesian Soil Research Institute (ISRI)	ID04				
<b>Japan</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	✓	✓		
Lake Suwa Environmental Research Center	JP15				✓
Gifu Prefectural Research Institute for Health and Environmental Sciences	JP04	✓	✓		✓
Okinawa Prefectural Institute of Health and Environment	JP08	✓	✓		
Asia Center for Air Pollution Research (ACAP)	JP09	✓	✓		
Japan Environmental Sanitation Center (JESC)	JP10	✓	✓		
Nagasaki Prefectural Institute of Environment and Public Health	JP14	✓			
<b>Lao PDR</b>					
Environmental Laboratory (EL), Natural Resource and Environment Research Institute (NRERI), Ministry of Natural Resource and Environment (MoNRE)	LA01				
<b>Malaysia</b>					
Environmental Quality Division, Department of Chemistry Malaysia (DOC)	MY01	✓	✓		✓
<b>Mongolia</b>					
Central Laboratory of Environment and Metrology (CLEM)	MN01	✓	✓	✓	✓
<b>Myanmar</b>					
Department of Meteorology and Hydrology (DMH)	MM01	✓	✓		
<b>Philippines</b>					
Environmental Management Bureau - Central Office (EMB-CO)	PH01	✓	✓	✓	✓
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	PH02	✓	✓		✓
<b>Republic of Korea</b>					
Aerosol research Lab. in National Institute of Environment Research	KR01	✓	✓		
<b>Russia</b>					
Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	RU01				
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU02				
<b>Thailand</b>					
Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE)	TH01	✓	✓		✓
Environmental Research and Training Center (ERTC), Department of Environmental Quality Promotion	TH02	✓	✓		✓
<b>Vietnam</b>					
Environmental Laboratory - Center for Environmental Research	VN01	✓	✓	✓	✓
- Vietnam Institute of Meteorology, Hydrology and Environment (IMHEN)- MoNRE					
Mid- Central Regional Hydro Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN02	✓		✓	✓
Sub-Institute of HydroMeteorology and Climate Change(SIHMECC)	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	✓		✓	✓
<b>Total number of submitted data :</b>		<b>25</b>	<b>17</b>	<b>6</b>	<b>17</b>

**Table 1.2 Laboratories in charge of the analysis of each monitoring site in EANET (2024)**

Country	Site for deposition monitoring	Code	Plot for soil and vegetation monitoring	Code	Site for monitoring on inland aquatic environment	Code	Laboratory code						
							Wet	Dry (FP*)	Soil	IAE			
<b>Cambodia</b>	Phnom Penh	<i>KHA001</i>			Sras Srang Lake	<i>KHI002</i>	KH01	KH01					KH01
<b>China</b>	Chingqing Xi'an Xiamen Zhuhai Wuzhishan Lijiang	<i>CNA003</i> <i>CNA004</i> <i>CNA005</i> <i>CNA007</i> <i>CNA008</i> <i>CNA009</i> <i>CNA010</i> <i>CNA011</i> <i>CNA012</i> <i>CNA013</i> <i>CNA014</i>	Jinyunshan Dabagou Xiaoping Zhuxiandong	<i>CNS004</i> <i>CNS007</i> <i>CNS009</i> <i>CNS011</i>	Jinyunshan Lake Jiwozi River Xiaoping Dam Zhuxiandong Stream	<i>CNI004</i> <i>CNI007</i> <i>CNI209</i> <i>CNI111</i>	CN04 CN04 CN03 CN02 CN01 CN01 CN05 CN06		CN04 CN03 CN02 CN02 CN01			CN04 CN03 CN02 CN01	CN04 CN03 CN02 CN01
<b>Indonesia</b>	Jakarta Serpong Kototabang Bandung Maros Jembrana Lombok	<i>IDA001</i> <i>IDA002</i> <i>IDA003</i> <i>IDA004</i> <i>IDA005</i> <i>IDA006</i> <i>IDA007</i>	Bogor Research Forest	<i>IDS002</i>	Patengang Lake Gunung Lake	<i>IDI004</i> <i>IDI006</i>	ID02 ID01 ID02 ID03 ID02 ID02 ID02	ID02 ID01	ID01			ID01 ID01	ID01 ID01
<b>Japan</b>	Rishiri Ochiishi Sado-seki Happo Ijira Okii Yusuhara Hedo Ogasawara Tokyo Niigata-maki Tsushima	<i>JPA001</i> <i>JPA002</i> <i>JPA004</i> <i>JPA005</i> <i>JPA006</i> <i>JPA007</i> <i>JPA009</i> <i>JPA010</i> <i>JPA011</i> <i>JPA012</i> <i>JPA013</i> <i>JPA014</i>	Sekido-san Horyu-zan Ijira Yamato	<i>JPS005</i> <i>JPS105</i> <i>JPS006</i> <i>JPS106</i>	Futago-ike Lake Ijira Lake	<i>IPI005</i> <i>JP1006</i>	JP01 JP09 JP09 JP03 JP09 JP07 JP08 JP10 JP10 JP02 JP14	JP01 JP09 JP02 JP03 JP04 JP09 JP09 JP08 JP10 JP10 JP09	JP13 JP13 JP04 JP04			JP15 JP04	JP15 JP04
<b>Lao PDR</b>	Vientiane	<i>LAA001</i>			Nam Houm Lake	<i>LAI001</i>	LA01	LA01					LA01
<b>Malaysia</b>	Petaling Jaya Tanah Rata Danum Valley Kuching Gunung Brinchang	<i>MYA001</i> <i>MYA002</i> <i>MYA003</i> <i>MYA004</i> <i>MYA005</i>	Pasoh Reserve Forest 1 / 2 Pasoh TEAM Plot 1 / 8 UPMKB Rehabilitated Forest Planted in 1991 / 2008	<i>MYS001</i> <i>MYS101</i> <i>MYS201</i> <i>MYS202</i> <i>MYS005</i> <i>MYS105</i>	Baru River Kuala Tahan	<i>MY1103</i> <i>MY1006</i>	MY01 MY01 MY01 MY01	MY01 MY01				MY01	MY01 MY01
<b>Mongolia</b>	Ulaanbaatar Terej	<i>MNA001</i> <i>MNA002</i>	Bogdkhan Mountain Terej Mountain	<i>MNS001</i> <i>MNS002</i>	Terej River	<i>MNI002</i>	MN01 MN01	MN01 MN01	MN01 MN01				MN01 MN01
<b>Myanmar</b>	Yangon Mandalay	<i>MMA001</i> <i>MMA002</i>					MM01	MM01					
<b>Philippines</b>	Manila Observatory Los Baños Mt. Sto. Tomas	<i>PHA001</i> <i>PHA002</i> <i>PHA003</i>	La Mesa Watershed Mt. Makiling UP Quezon, Land Grant Boneco Long Term Ecological	<i>PHS001</i> <i>PHS002</i> <i>PHS102</i> <i>PHS003</i>	Pandin Lake Ambulalakaw River	<i>PHI102</i> <i>PHI003</i>	PH01 PH01 PH02	PH01 PH01				PH01 PH02	PH01 PH02
<b>Republic of Korea</b>	Kanghwa Cheju (Kosan) Imsil	<i>KRA003</i>	Mt. Naejang	<i>KRS003</i>			KR01 KR01 KR01	KR01 KR01 KR01				KR01	
<b>Russia</b>	Mondy Listvyanka Irkutsk Primorskaya	<i>RUA001</i> <i>RUA002</i> <i>RUA003</i> <i>RUA004</i>	Ilchir Lake Okinskoe Lake Solar Observatory Bolshie Koty Pereemnya river Catchment Irkutsk Primorskaya	<i>RUS001</i> <i>RUS101</i> <i>RUS201</i> <i>RUS002</i> <i>RUS102</i> <i>RUS003</i> <i>RUS004</i>	Pereemnya River Komarovka River	<i>RUI102</i> <i>RUI004</i>	RU01 RU01 RU01 RU01 RU01 RU02	RU01 RU01	RU01 RU01 RU01 RU01			RU01 RU01 RU01 RU01	RU01 RU02
<b>Thailand</b>	Bangkok Samutprakarn Pathumthani Khanchanaburi	<i>THA001</i> <i>THA002</i> <i>THA003</i> <i>THA004</i>	Vachiralongkorn Dam Vachiralongkorn Puye	<i>THS004</i> <i>THS104</i>	Vachiralongkorn Dam	<i>THI004</i>	TH01 TH01 TH02 TH01	TH01 TH01				TH01	TH01
<b>Vietnam</b>	Hanoi Hoa Binh Cuc Phuong Da Nang Can Tho Ho Chi Minh Yen Bai	<i>VNA001</i> <i>VNA002</i> <i>VNA003</i> <i>VNA004</i> <i>VNA005</i> <i>VNA006</i> <i>VNA007</i>	Cave of Heaven Thang Ranh	<i>VNS002</i> <i>VNS102</i>	Hoa Binh Reservoir	<i>VNI002</i>	VN01 VN01 VN04 VN02 VN03 VN03 VN01	VN01 VN01	VN01 VN01 VN03 VN03 VN01			VN01 VN01 VN01	VN01 VN01

\* FP: Filter pack method

## 2. 27<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

### 2.1 Introduction

In the 27<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 December 2024. Their analytical results were required to be submitted to the NC by 28 February 2025.

### 2.2 Procedures

#### 2.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 28 laboratories in charge of chemical analysis in 13 countries of EANET. 25 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. 241w No. 242w	100 mL each	Polypropylene bottle 100 mL	One bottle each	- Fixed quantity of reagents are dissolved in pure water ( $EC < 0.15 \text{ mS m}^{-1}$ ) - Ions other than shown in Table 2.2 are not added

The prepared values of analytical parameters in the artificial rainwater samples are described in Table 2.2. These parameters are calculated based on the quantity of reagents.

**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. 241w	4.70	2.72	34.2	40.4	47.8	34.8	42.8	5.9	16.8	9.8
No. 242w	5.10	1.16	11.7	15.6	29.7	10.6	25.7	3.8	6.4	3.9

\* For 100 times diluted samples.

### 2.2.3 Analytical methods and data checking procedures

Before the measurement, the samples must be diluted 100 times accurately with pure water (EC < 0.15 mS m<sup>-1</sup>) 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 recommended in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. Analytical methods recommended in the Technical Manual are listed in Table 2.3.

**Table 2.3 Analytical methods recommended 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 [ $\mu\text{eq L}^{-1}$ ]) was calculated by summing the concentrations of all anions (c [ $\mu\text{mol L}^{-1}$ ]).

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

n, c<sub>Ai</sub> : electric charge and concentration [ $\mu\text{mol L}^{-1}$ ] of anion “i”.

(2) Total cation equivalent concentration (C [ $\mu\text{eq L}^{-1}$ ]) was calculated by summing the concentrations of all cations (c [ $\mu\text{mol L}^{-1}$ ]).

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

n, c<sub>Ci</sub> : electric charge and concentration [ $\mu\text{mol L}^{-1}$ ] of cation “i”.

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

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

(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 [ $\mu\text{eq L}^{-1}$ ]	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	± 20
0.5 – 3	± 13
> 3	± 9

## 2.3 Results

The NC received the analytical results from 25 laboratories in the participating countries of EANET.

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, the range of  $\Delta V/V_p$  was between -3.3% to 2.1% for sample No. 241w, and -9.4% to 6.9% for sample No. 242w.

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

Sample No. 241w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/V_p$ *1 %	S.D.	N	Min.	Max.
pH	4.70	4.80	2.1	0.11	25	4.65	5.08
EC [mS m <sup>-1</sup> ]	2.72	2.63	-3.3	0.07	24	2.50	2.75
SO <sub>4</sub> <sup>2-</sup> [μmol L <sup>-1</sup> ]	34.2	34.3	0.4	0.83	23	33.1	37.3
NO <sub>3</sub> <sup>-</sup> [μmol L <sup>-1</sup> ]	40.4	39.9	-1.2	0.74	23	38.3	41.2
Cl <sup>-</sup> [μmol L <sup>-1</sup> ]	47.8	47.7	-0.2	1.14	23	45.1	49.7
NH <sub>4</sub> <sup>+</sup> [μmol L <sup>-1</sup> ]	34.8	35.0	0.6	1.16	24	32.7	37.8
Na <sup>+</sup> [μmol L <sup>-1</sup> ]	42.8	41.8	-2.3	3.46	23	34.3	53.8
K <sup>+</sup> [μmol L <sup>-1</sup> ]	5.9	5.7	-3.0	0.70	24	4.2	7.3
Ca <sup>2+</sup> [μmol L <sup>-1</sup> ]	16.8	16.9	0.8	1.04	23	15.0	19.8
Mg <sup>2+</sup> [μmol L <sup>-1</sup> ]	9.8	9.8	0.0	0.46	24	8.9	10.8

Sample No. 242w

Constituents	Prepared (Vp)	Average (Va)	$\Delta V/V_p$ *1 %	S.D.	N	Min.	Max.
pH	5.10	5.20	1.9	0.11	25	4.90	5.50
EC [mS m <sup>-1</sup> ]	1.16	1.13	-2.4	0.04	24	1.01	1.19
SO <sub>4</sub> <sup>2-</sup> [μmol L <sup>-1</sup> ]	11.7	12.0	2.9	0.65	23	11.0	13.6
NO <sub>3</sub> <sup>-</sup> [μmol L <sup>-1</sup> ]	15.6	15.4	-1.5	0.46	24	14.6	16.4
Cl <sup>-</sup> [μmol L <sup>-1</sup> ]	29.7	29.5	-0.5	0.97	23	27.7	31.4
NH <sub>4</sub> <sup>+</sup> [μmol L <sup>-1</sup> ]	10.6	10.8	1.6	0.45	24	9.9	11.8
Na <sup>+</sup> [μmol L <sup>-1</sup> ]	25.7	25.6	-0.6	0.98	22	21.7	27.0
K <sup>+</sup> [μmol L <sup>-1</sup> ]	3.8	3.4	-9.4	0.58	24	2.3	4.6
Ca <sup>2+</sup> [μmol L <sup>-1</sup> ]	6.4	6.5	1.1	0.74	23	5.3	8.3
Mg <sup>2+</sup> [μmol L <sup>-1</sup> ]	3.9	4.2	6.9	0.71	24	3.1	5.7

Note: \*1,  $(V_a - V_p)/V_p \times 100$

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  $\pm 30\%$ .

\*According to *Technical Manual for Wet Deposition Monitoring in East Asia -2010*, the deviation is calculated using the following formula:

$$\text{Deviation} = [(\text{analytical values}) - V_p] \times 100 / V_p$$

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. 241w and No. 242w,
- ii) Comparison of individual parameters,
- iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both sample No. 241w and No. 242w 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. 241w

The number and percentage of the flagged data for sample No. 241w are shown in Table 2.7. 9 analytical data out of 241 were flagged by "E". And 3 analytical data out of 241 were flagged by "X". Data flagged by "E" and "X" shared 5.0 percent of all the submitted data for sample No. 241w.

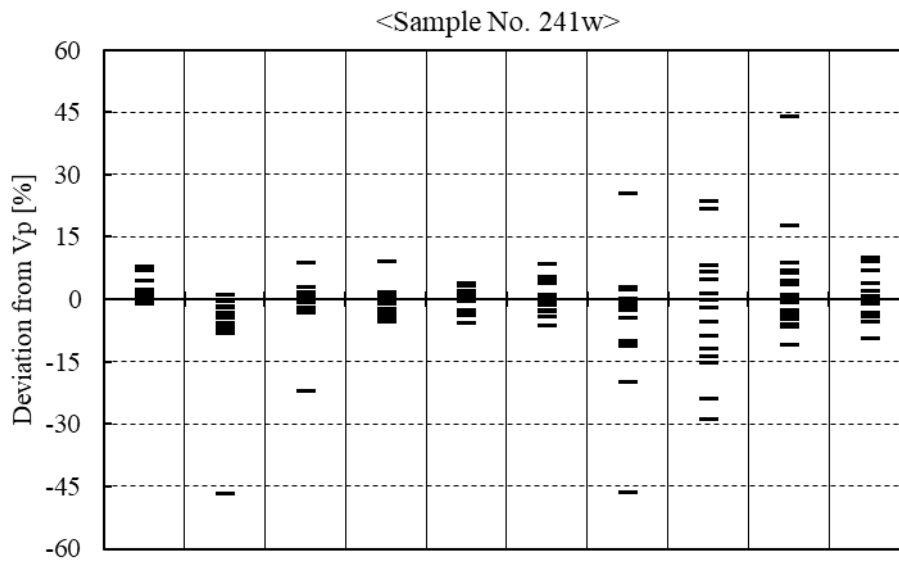
The data normalized by prepared value in each parameter are shown in Figure 2.1.

**Table 2.7 Number of flagged data for the Sample No. 241w**

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	25	24	23	24	23	24	21	19	22	24	229
Data with flag E* <sup>1</sup>	0	0	1	0	0	0	2	5	1	0	9
Data with flag X* <sup>2</sup>	0	1	0	0	0	0	1	0	1	0	3
Flagged data [%]	0.0	4.0	4.2	0.0	0.0	0.0	12.5	20.8	8.3	0.0	5.0

( Total data = 241 )

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. 241w**

The parameter which had the most flags was K<sup>+</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. 241w**

Lab. ID	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	4.65	2.60	34.5	40.4	47.7	36.4	44.1	5.8	17.6	9.8	2.0	4.3
CN02	4.73	2.68	34.7	40.2	48.2	34.4	43.0	6.4	16.3	10.0	-0.9	-0.1
CN03	4.71	2.55	35.3	40.2	49.4	36.7	42.1	5.1	15.7	10.0	-1.7	3.3
CN04	4.72	2.72	34.5	40.4	47.7	32.7	43.8	5.1	17.4	9.5	-0.8	-0.8
CN06	4.74	2.52	34.3	39.4	48.5	35.2	42.5	5.8	15.8	9.3	-1.5	2.3
JP01	4.75	2.71	34.8	40.4	47.9	34.5	42.6	6.3	16.2	9.7	-1.6	-1.3
JP03	4.71	2.68	34.3	40.3	48.0	34.7	42.3	5.6	16.7	9.4	-0.8	0.2
JP04	4.69	2.67	34.0	40.2	47.8	35.0	40.9	7.3 E	16.4	9.7	-0.1	1.0
JP08	4.77	2.53	34.1	40.4	48.3	34.6	42.8	5.8	16.9	9.7	-1.1	1.6
JP09	4.80	2.64	34.8	41.2	48.8	34.4	43.0	5.8	16.8	9.8	-2.4	-0.9
JP10	4.72	2.72	34.3	40.2	46.3	35.0	42.6	6.0	16.9	9.9	0.4	-0.8
JP14	4.78	2.67	34.7	40.8	47.9	34.5	43.0	6.0	17.0	9.7	-1.5	-1.1
MY01	4.76	2.71	34.7	40.7	49.5	35.0	42.5	6.2	16.9	8.9	-2.2	-1.3
MN01	4.92	2.54	37.3	44.1	49.7	37.8	42.7	5.6	18.0	9.8	-4.6	0.4
MM01	5.08	1.45 X	34.3	39.3	48.5	35.0	53.8 E	6.2	18.3	9.4	0.7	24.3 C
PH01	4.79	2.63	33.6	38.8	46.2	34.7	38.1	4.2 E	16.1	9.4	-2.7	-2.5
PH02	4.77	2.61	26.7 E	38.3	45.1	36.7	34.3 E	4.5 E	15.0	10.7	2.5	-4.1
KR01	4.67	2.63	33.5	39.3	46.1	35.2	41.8	5.6	16.0	9.5	0.8	1.6
TH01	4.76	2.57	---	---	---	---	---	---	---	---	---	---
TH02	5.03	2.50	33.4	39.5	46.7	33.4	41.7	5.4	16.1	9.3	-4.2	-4.5
VN01	4.92	2.64	34.2	40.1	47.7	33.9	38.6	5.4	17.9	10.5	-3.1	-4.3
VN02	4.80	2.75	34.2	40.0	47.7	33.8	38.5	5.0 E	17.9	10.2	-2.2	-3.8
VN03	4.81	2.61	33.1	38.4	---	36.2	23.0 X	7.2 E	24.2 X	9.7	---	---
VN04	5.03	2.55	34.3	40.2	47.6	33.8	38.5	5.9	17.9	10.8	-3.8	-4.3
VN05	4.81	2.68	33.1	39.1	46.3	36.2	38.5	5.2	19.8 E	10.5	1.4	-2.5
Vp	4.70	2.72	34.2	40.4	47.8	34.8	42.8	5.9	16.8	9.8	0.0	-0.1
N of data	25	25	24	24	23	24	24	24	24	24		
Within DQO	25	24	23	24	23	24	21	19	22	24		
Flag E	0	0	1	0	0	0	2	5	1	0		
Flag X	0	1	0	0	0	0	1	0	1	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;

The outliers judged by 3S.D. method were painted with light mesh and excluded from statistics in Table 2.6.

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

## 2) Sample No. 242w

The number and percentage of the flagged data for sample No. 242w are shown in Table 2.9. 12 analytical data out of 241 were flagged by "E". 13 analytical data out of 241 were flagged by "X". Data marked with flags shared up to 10.4 percent of all the submitted data for sample No. 242w.

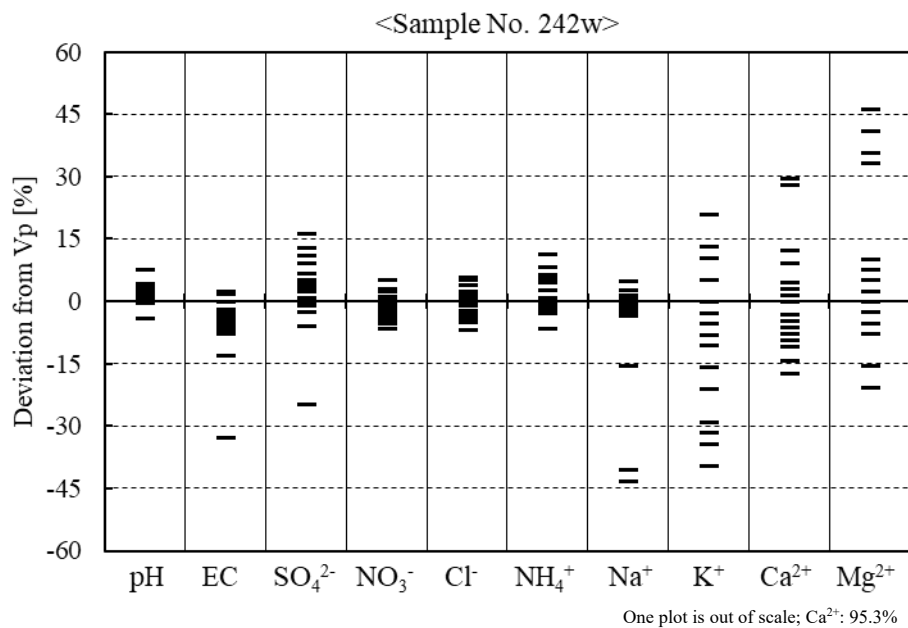
The normalized data by prepared value in each parameter are shown in Figure 2.2.

**Table 2.9 Number of flagged data for the sample No. 242w**

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	25	24	22	24	23	24	21	16	20	17	216
Data with flag E <sup>*1</sup>	0	0	2	0	0	0	1	4	3	2	12
Data with flag X <sup>*2</sup>	0	1	0	0	0	0	2	4	1	5	13
Flagged data [%]	0.0	4.0	8.3	0.0	0.0	0.0	12.5	33.3	16.7	29.2	10.4

( Total data = 241 )

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



**Figure 2.2 Distribution of the data normalized by prepared value for each parameter for sample No. 242w**

The parameter which had the most flags was K<sup>+</sup>, which is the same tendency as No.241w. The analytical data submitted by the participating laboratories are shown in Table 2.10 with flags.

**Table 2.10 Analytical Results of Sample No. 242w**

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	5.09	1.13	11.6	15.4	29.9	11.5	26.4	3.4	6.0	3.8	0.4	1.4
CN02	5.21	1.13	12.1	15.2	30.4	10.6	26.1	3.8	7.0	4.2	-0.5	-0.7
CN03	5.22	1.14	12.5	14.9	31.4	11.1	25.2	2.5 X	5.8	4.2	-4.8	-1.9
CN04	5.23	1.14	11.7	15.3	29.6	10.5	27.0	2.3 X	7.0	4.1	-0.3	-2.5
CN06	5.27	1.11	12.0	15.0	30.1	10.3	26.0	3.7	5.5	3.3 E	-4.6	-2.8
JP01	5.12	1.19	11.8	15.8	29.4	10.6	25.4	3.6	6.0	3.8	-1.5	-2.4
JP03	5.08	1.16	11.8	15.7	29.6	10.7	25.4	3.4	6.1	3.6	-1.2	0.0
JP04	5.08	1.16	11.6	15.4	29.6	10.5	25.3	4.3	6.7	4.0	1.2	0.4
JP08	5.17	1.01	13.6 E	15.6	29.9	10.3	25.7	3.7	6.5	3.8	-4.0	6.2
JP09	5.18	1.16	12.0	16.1	30.9	10.9	25.7	3.7	6.5	3.9	-2.4	-1.4
JP10	5.09	1.19	11.6	15.5	28.6	10.4	25.7	3.7	6.6	4.1	1.5	-1.6
JP14	5.22	1.14	12.1	15.7	30.4	10.4	26.4	4.2	6.2	3.7	-2.5	-1.7
MY01	5.15	1.19	11.4	15.2	31.3	11.5	25.8	3.5	6.2	3.1 E	-2.1	-2.9
MN01	5.26	1.13	12.5	16.4	30.3	10.5	26.0	3.5	8.2 E	4.3	-0.8	-0.6
MM01	5.27	0.78 X	11.6	15.0	29.6	11.2	26.4	4.0	8.3 E	4.0	2.7	16.6 C
PH01	5.24	1.08	11.6	16.0	28.3	11.2	21.7 E	3.0 E	5.7	3.7	-5.5	-2.0
PH02	5.26	1.14	8.8 E	16.1	27.7	9.9	15.3 X	2.7 E	5.3 E	3.9	-8.5 I	-10.0
KR01	4.90	1.18	11.0	14.8	28.2	10.6	25.0	3.5	6.0	3.8	4.6	4.0
TH01	5.20	1.07	---	---	---	---	---	---	---	---	---	---
TH02	5.19	1.09	11.0	15.1	29.4	10.9	24.8	3.4	5.9	3.6	-1.5	-0.8
VN01	5.32	1.10	13.0	15.1	28.9	10.6	25.7	3.2 E	6.7	5.5 X	-0.9	-1.3
VN02	5.23	1.18	12.8	14.9	28.7	10.7	25.5	2.5 X	7.0	5.3 X	0.0	-3.5
VN03	5.22	1.12	12.2	14.6	---	11.8	14.6 X	4.6 E	12.5 X	5.2 X	---	---
VN04	5.50	1.07	13.2	15.3	29.1	10.5	25.8	3.8	6.4	5.7 X	-2.4	-2.2
VN05	5.20	1.16	12.3	14.8	28.2	11.3	25.2	2.6 X	7.2	5.5 X	2.3	-2.2
Vp	5.10	1.16	11.7	15.6	29.7	10.6	25.7	3.8	6.4	3.9	0.0	-0.2
N of data	25	25	24	24	23	24	24	24	24	24		
Within DQO	25	24	22	24	23	24	21	16	20	17		
Flag E	0	0	2	0	0	0	1	4	3	2		
Flag X	0	1	0	0	0	0	2	4	1	5		

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

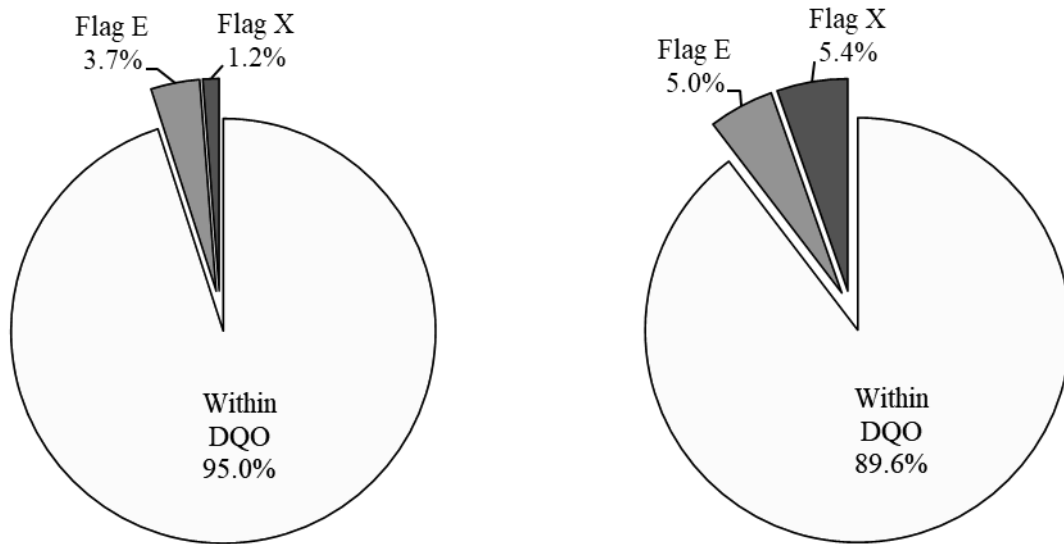
"I", Poor ion balance (R<sub>1</sub>); "C", Poor conductivity agreement (R<sub>2</sub>); "---", Not measured; "Vp", Prepared values of parameters;

The outliers judged by 3S.D. method were painted with light mesh and excluded from statistics in Table 2.6.

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

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

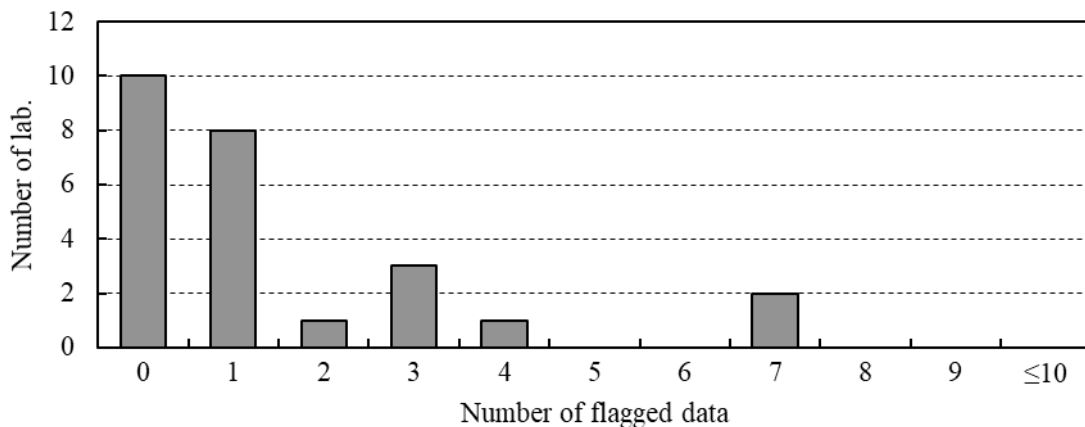
The percentage of the flagged data for sample No. 241w and 242w are shown in Figure 2.3. The percentage of the data within the DQO for sample No. 241w and 242w were 95.0% and 89.6%, respectively. The difference between both samples was 5.4%. In this project, the total number of flagged data was 37 (E: 21, X: 16) out of all the 482 data.



**Figure 2.3 Percentage of flagged data for sample No. 241w and No. 242w (Left: No. 241w, Right: No. 242w)**

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

The number of laboratories by number of flags is shown in Figure 2.4. The number of laboratories without flagged data was 10, which corresponds to 40.0% 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  $V_p$  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. 241w and 242w, 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. None of the data was marked with flag "E" nor "X".

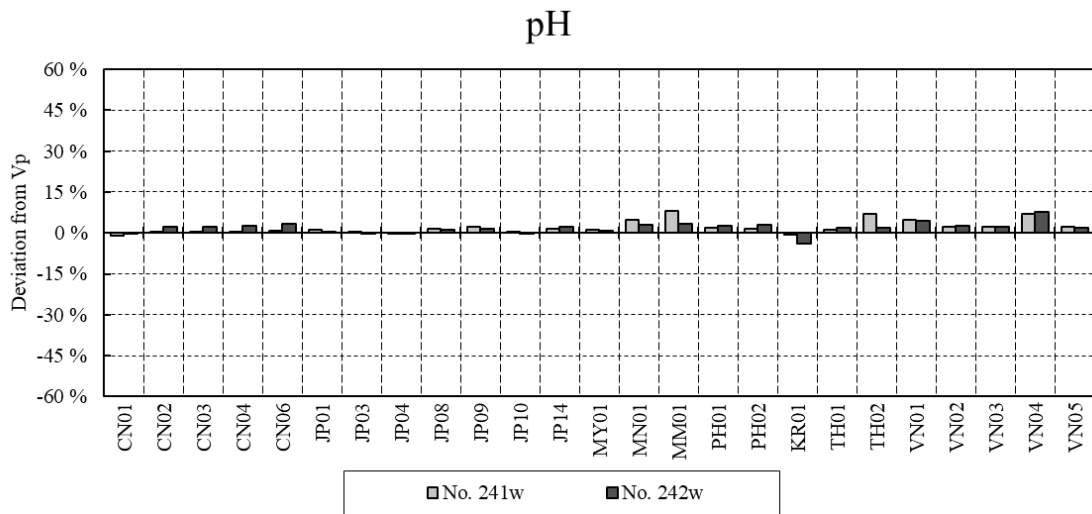


Figure 2.5 Deviation from prepared value for pH (normalized by prepared value)

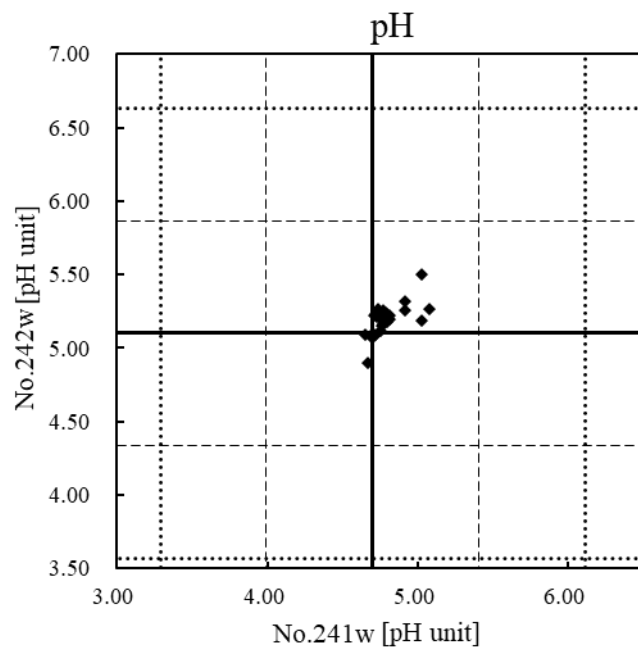


Figure 2.6 Scatter diagram for pH

## 2) EC

All participating laboratories used conductivity cell method for the measurement of EC. The data of sample No.241w and No.242w from MM01 was marked with flag “X”.

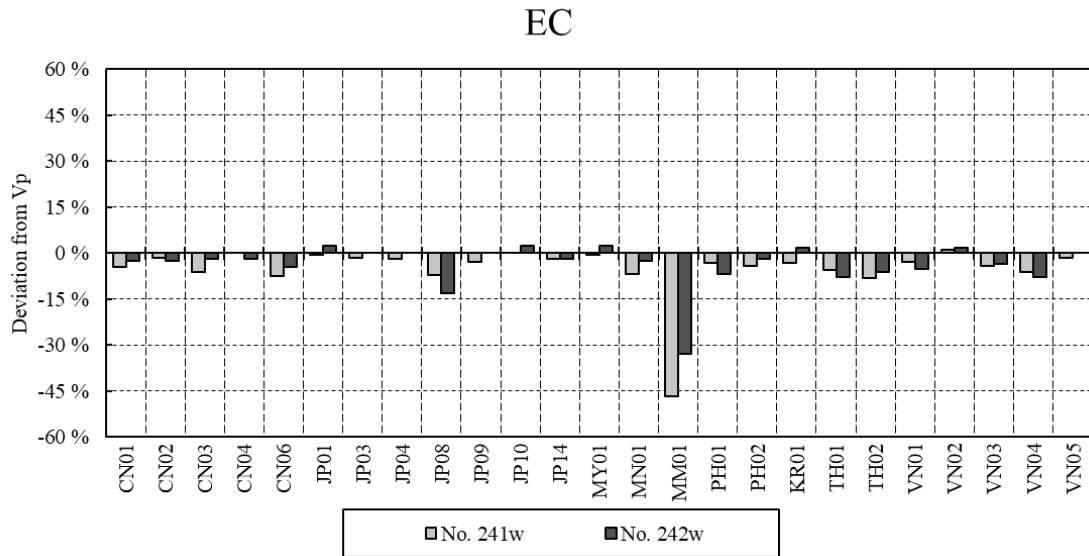


Figure 2.7 Deviation from prepared value for EC (normalized by prepared value)

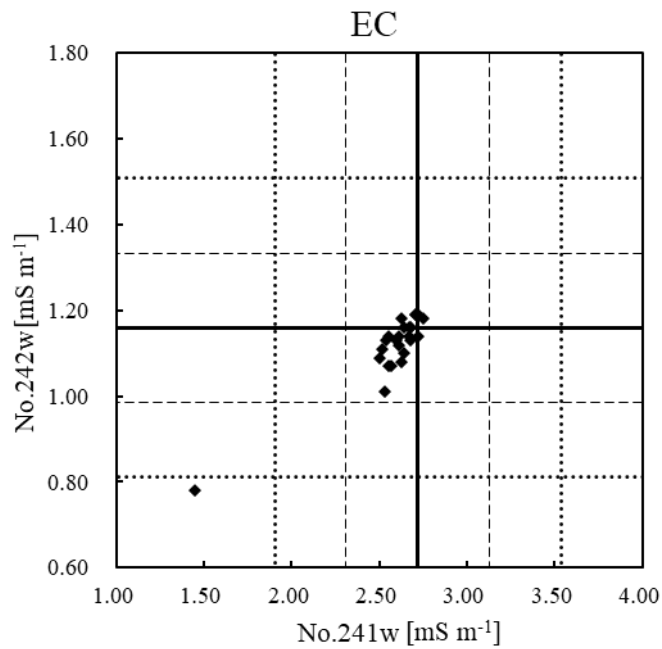
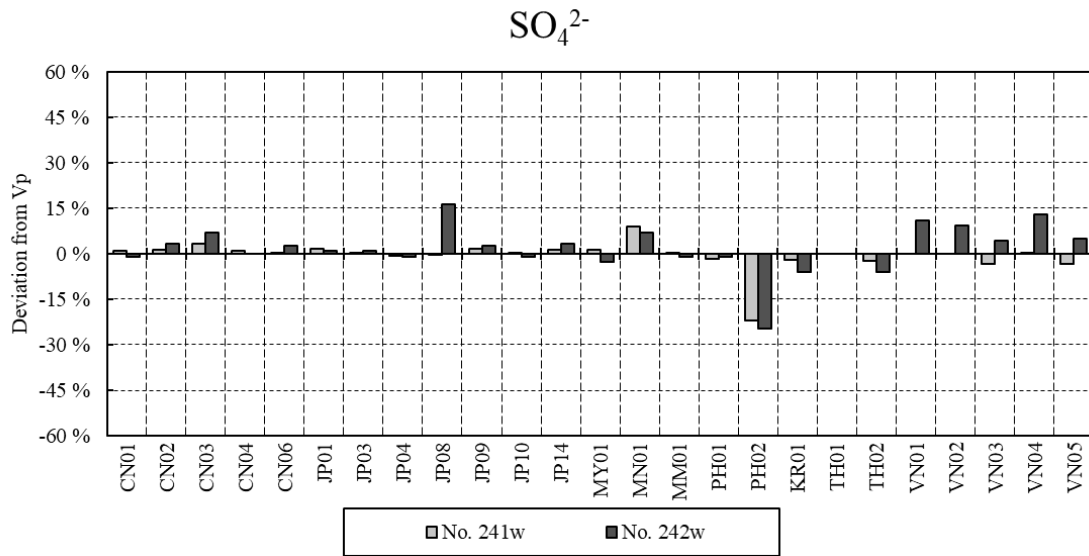


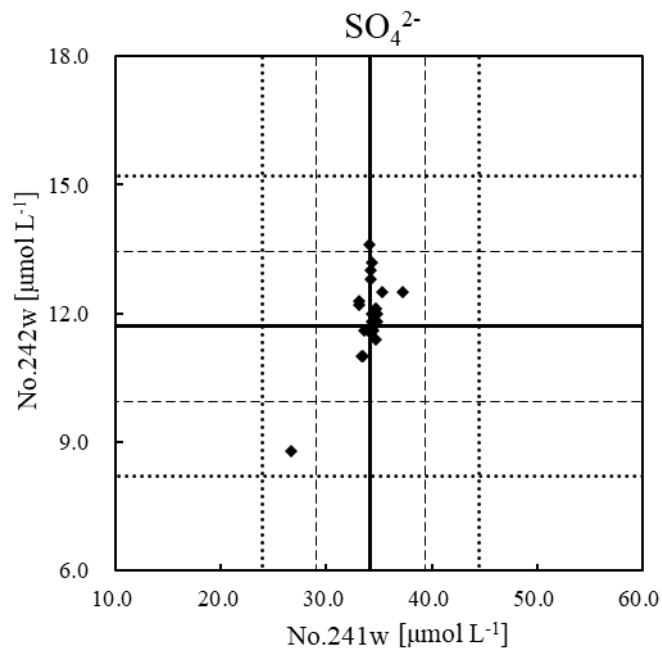
Figure 2.8 Scatter diagram for EC

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

The data of sample No.241w from PH02 and No.242w from 2 laboratories (JP08 and PH02) were 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) $\text{NO}_3^-$

None of the data was marked with flag “E” nor “X”.

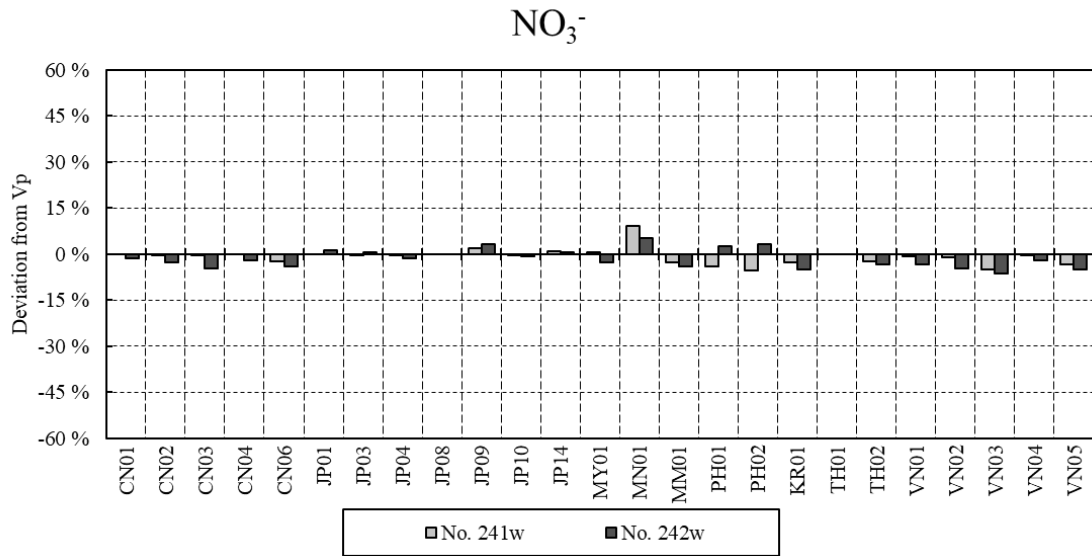


Figure 2.11 Deviation from prepared value for  $\text{NO}_3^-$  (normalized by prepared value)

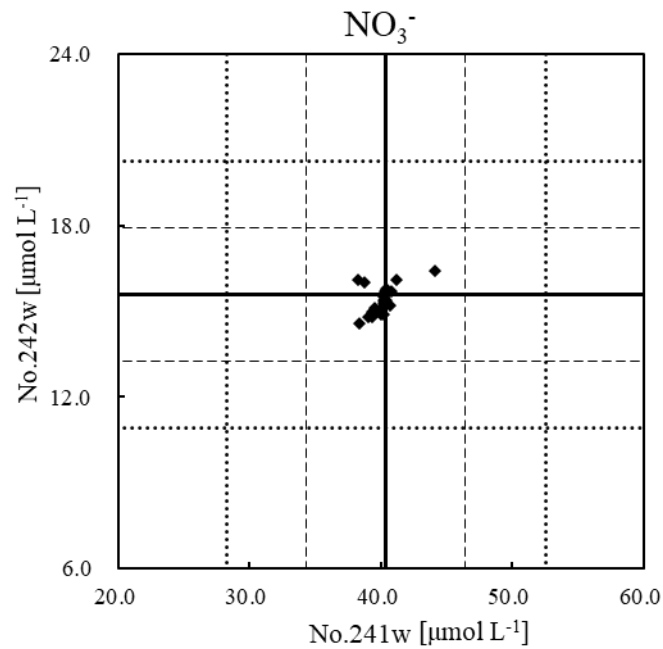
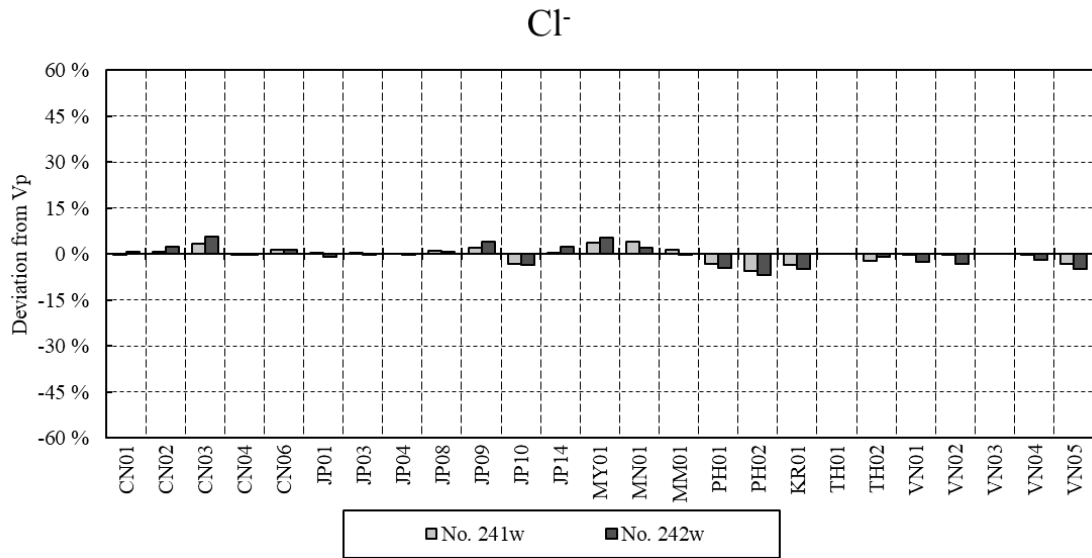


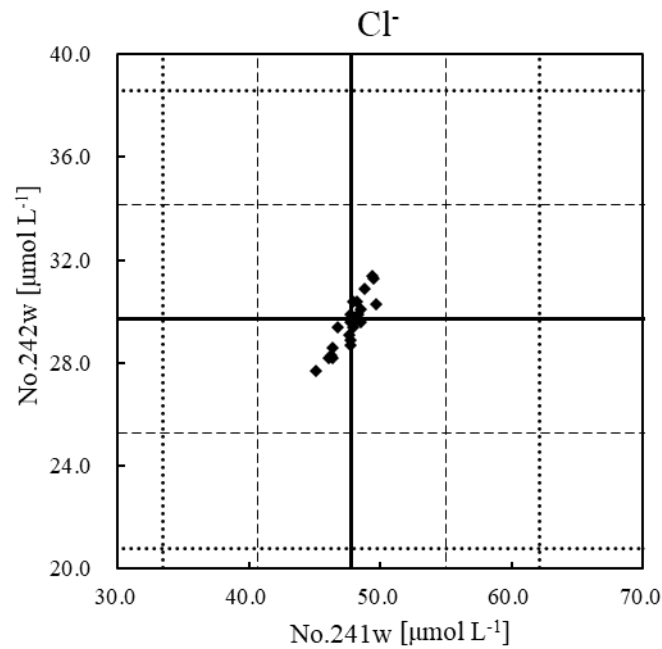
Figure 2.12 Scatter diagram for  $\text{NO}_3^-$

## 5) Cl<sup>-</sup>

None of the data was marked with flag “E” nor “X”.



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



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

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

None of the data was marked with flag “E” nor “X”.

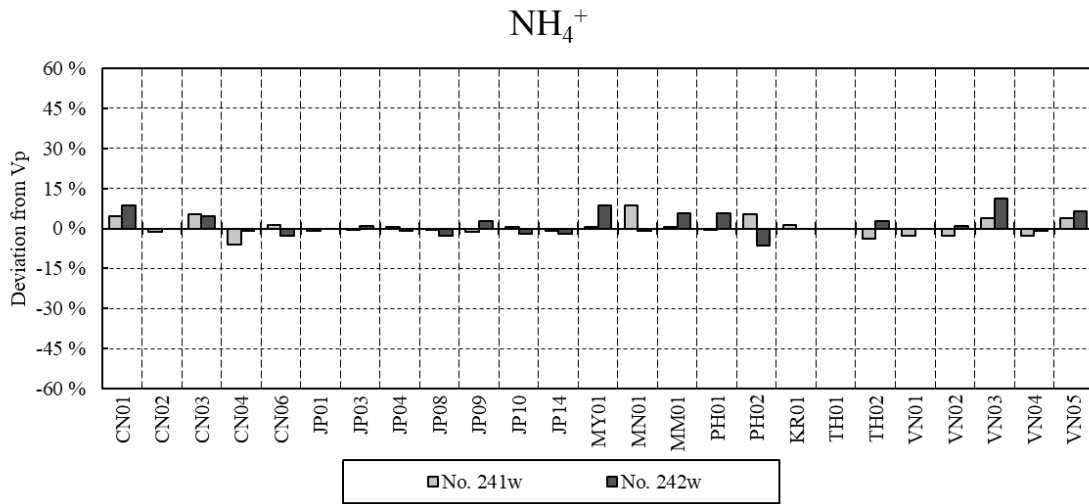


Figure 2.15 Deviation from prepared value for  $\text{NH}_4^+$  (normalized by prepared value)

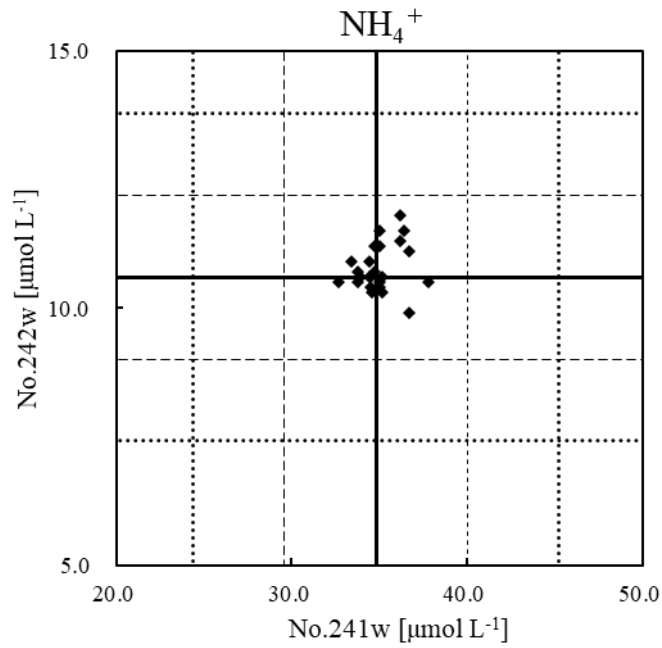
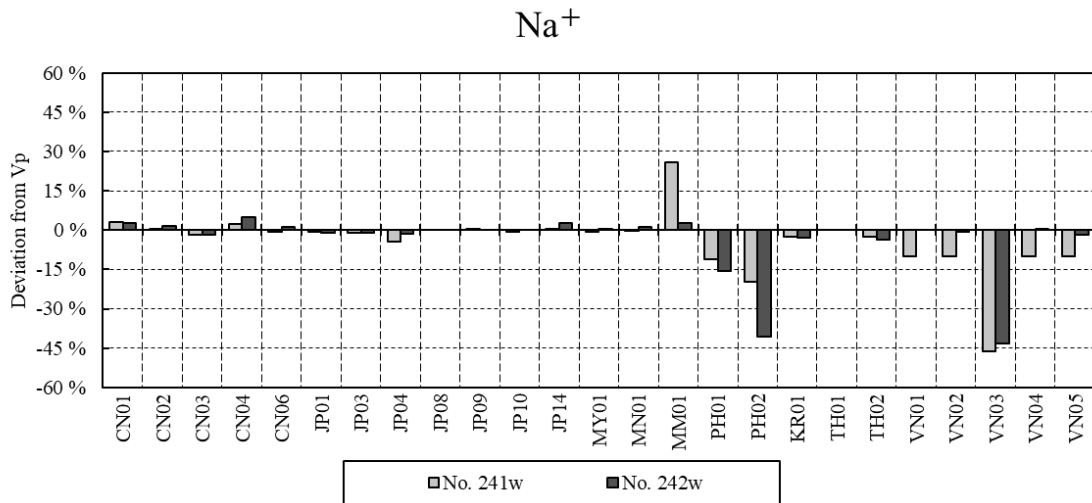


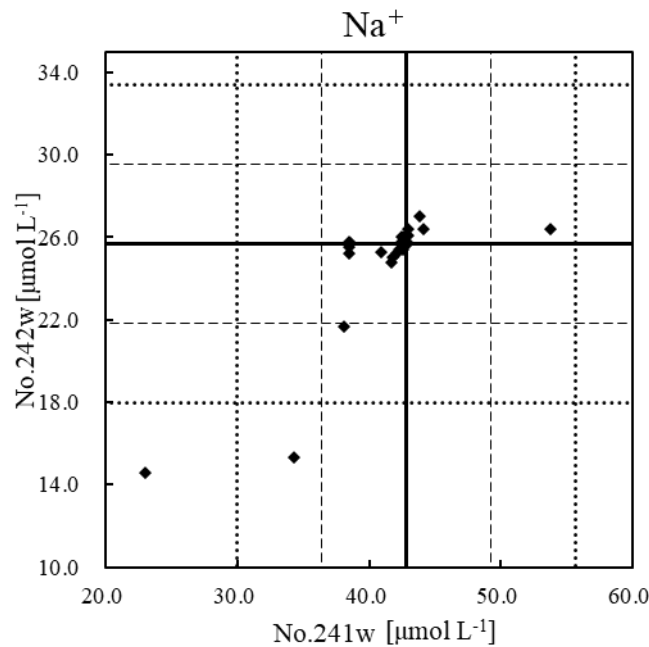
Figure 2.16 Scatter diagram for  $\text{NH}_4^+$

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

The data of sample No. 241w from 2 laboratories (MM01 and PH02) and sample No.242w from PH01 were marked with flag “E”. Additionally, the data of sample No.241w from VN03 and sample No. 242w from 2 laboratories (PH02 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<sup>+</sup>

The data of sample No. 241w from 5 laboratories (JP04, PH01, PH02, VN02 and VN03) and sample No.242w from 4 laboratories (PH01, PH02, VN01 and VN03) were marked with flag “E”. Additionally, the data of sample No. 242w from 4 laboratories (CN03, CN04, VN02 and VN05) were marked with flag “X”.

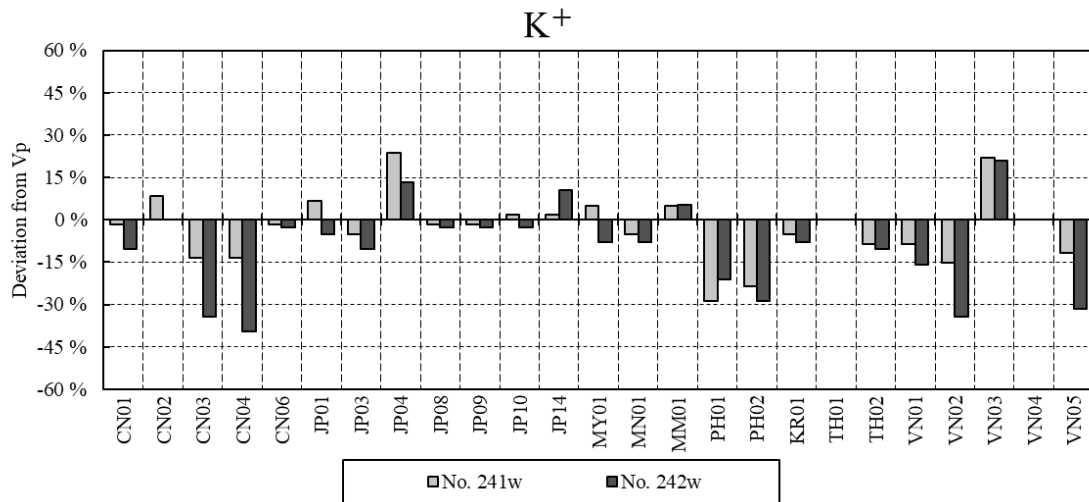


Figure 2.19 Deviation from prepared value for K<sup>+</sup> (normalized by prepared value)

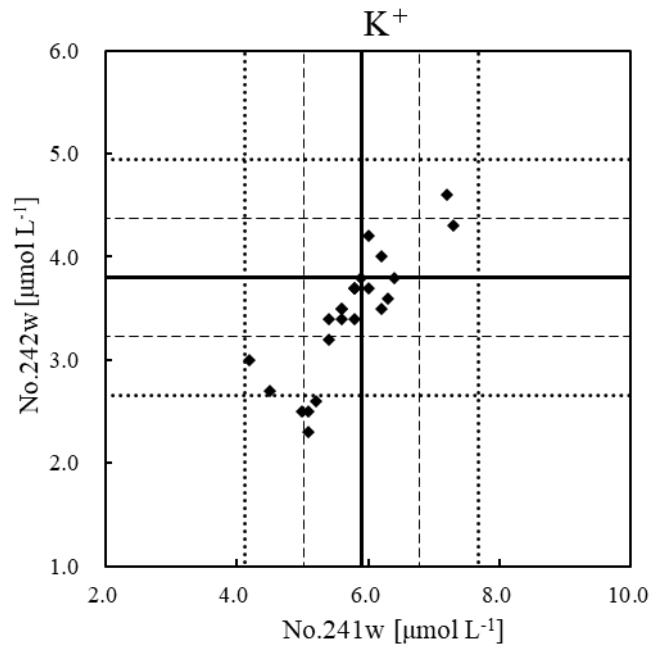


Figure 2.20 Scatter diagram for K<sup>+</sup>

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

The data of sample No. 241w from VN05 and sample No. 242w from 3 laboratories (MN01, MM01 and PH02) were marked with flag “E”. Additionally, the data of sample No.241w from VN03 and No.242w from VN03 were marked with flag “X”.

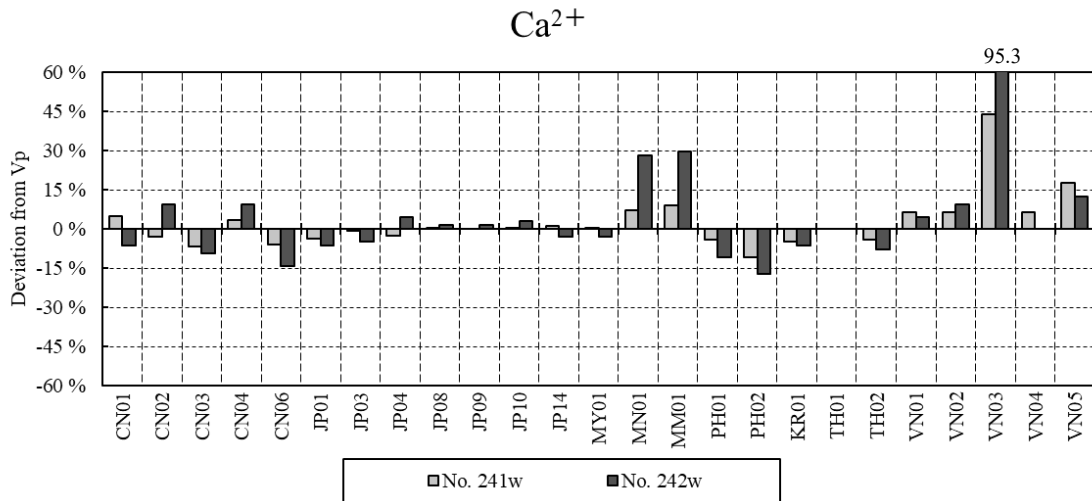


Figure 2.21 Deviation from prepared value for Ca<sup>2+</sup> (normalized by prepared value)

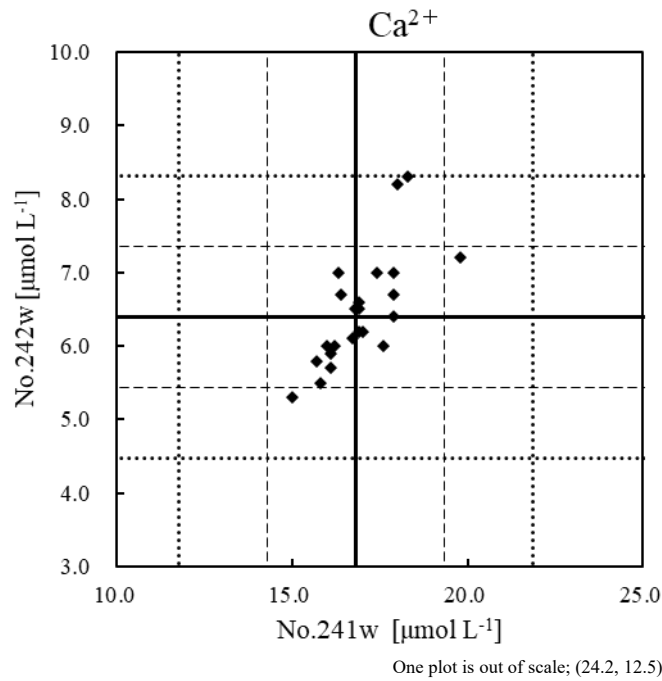


Figure 2.22 Scatter diagram for Ca<sup>2+</sup>

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

The data of sample No. 242w from 2 laboratories (CN06 and MY01) were marked with flag “E”. Additionally, the data of sample No.242w from 5 laboratories (VN01, VN02, VN03, VN04 and VN05) were marked with flag “X”.

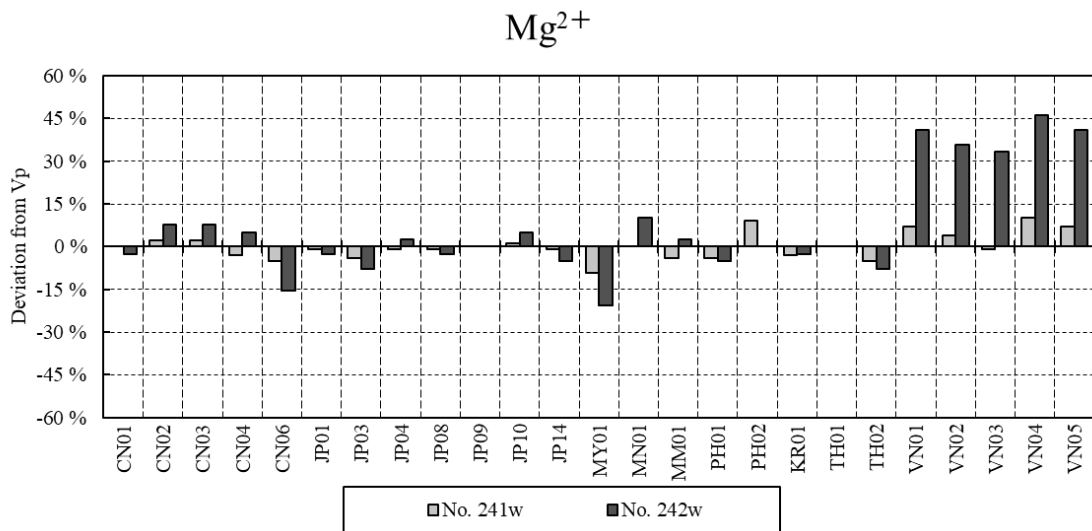


Figure 2.23 Deviation from prepared value for Mg<sup>2+</sup> (normalized by prepared value)

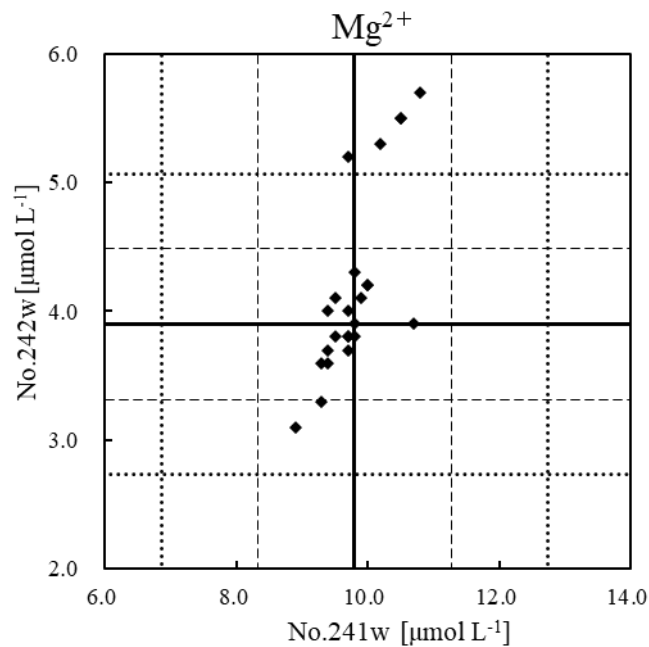


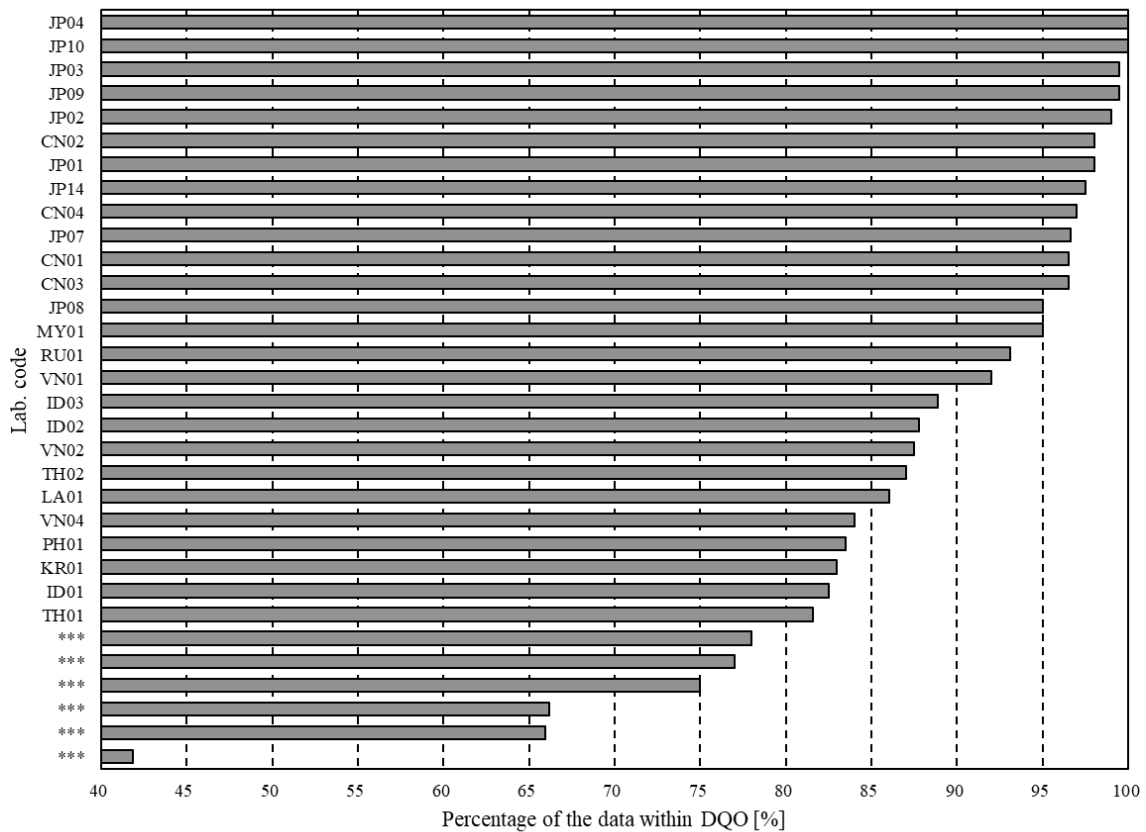
Figure 2.24 Scatter diagram for Mg<sup>2+</sup>

## 11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 241w and 242w. It suggested that systematic error could be the reason for the deviation of results in many of laboratories.

## 12) Percentage of the data within DQO

Figure 2.25 shows the percentage of the data within DQO for each participating laboratory from 2015 to 2024. All the analytical data of 2 laboratories (JP04 and JP10) met DQO, while the percentage of the data within DQO in 6 laboratories was below 80%.



Note: Lab. code is indicated as "\*\*\*\*" in case that percentage of the data within DQO is below 80%.

**Figure 2.25 Percentage of the data within DQO for each participating laboratory (2015-2024)**

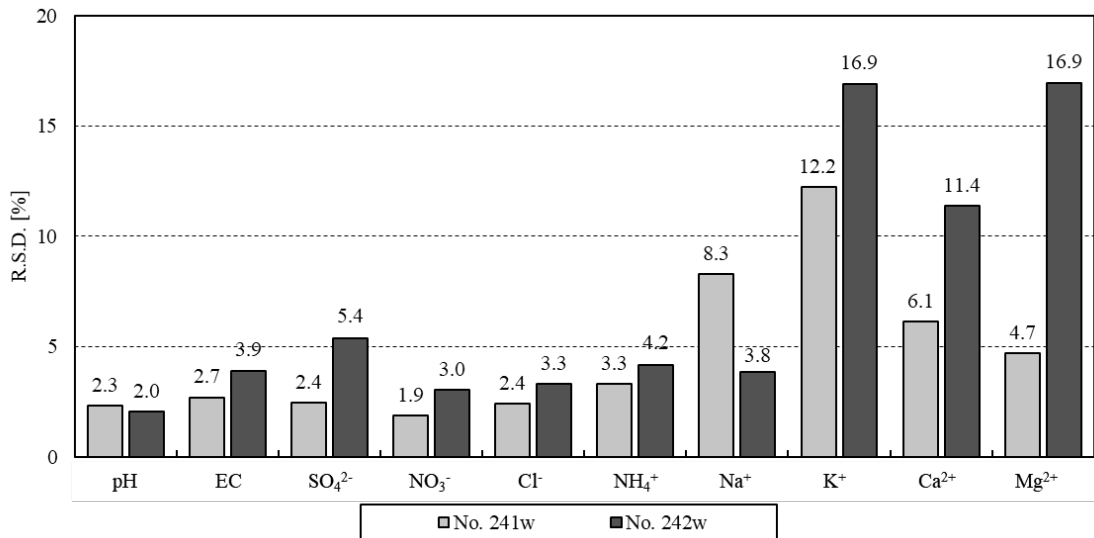
### 2.3.3 Sample and analysis evaluation

The concentrations of the analytical parameters in the samples for this survey were determined based on actual EANET monitoring data of wet deposition. Two samples were not distinguished

as high or low concentration samples when they were distributed to participating laboratories. Each ion (including pH as H<sup>+</sup>) concentrations of sample No. 241w were higher than those of No. 242w.

The relative standard deviations (R.S.D.) of each parameter for sample No. 241w and No. 242w are shown in the Figure 2.26. The R.S.D. values of sample No. 242w were higher than sample No.241w except for Na<sup>+</sup>. Mg<sup>2+</sup> had the largest R.S.D. value difference between sample No.241w and No. 242w. The R.S.D. of K<sup>+</sup> and Mg<sup>2+</sup> for sample No. 242w was the largest in this survey.

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



**Figure 2.26 Relative standard deviations (R.S.D.) of each parameter**

### 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”, “C” and “D” refer to individual analysts in each laboratory who carried out analyses. In 11 laboratories, single analyst carried out the analyses for all parameters. No clear relationship between the number of analysts and flagged data was 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	2	A	A	B	B	B	B	B	B	B	B
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
CN06	4	A	B	C	C	C	C	C	D	D	D
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
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
JP14	2	A	A	B	B	B	B	B	B	B	B
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B	B	B	B	B	B	B	B
MM01	1	A	A	A	A	A	A	A	A	A	A
PH01	4	A	A	B	B	B	A	C	C	D	D
PH02	1	A	A	A	A	A	A	A	A	A	A
KR01	1	A	A	A	A	A	A	A	A	A	A
TH01	2	A	B	---	---	---	---	---	---	---	---
TH02	1	A	A	A	A	A	A	A	A	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	2	A	A	B	A	---	A	B	B	B	B
VN04	2	A	A	B	B	B	B	B	B	B	B
VN05	2	A	A	B	B	B	B	B	B	B	B

Note: Light mesh, Analytic data of sample No. 241w or No. 242w was marked with flag "E" or "X";

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

"---", Not measured

180 data out of all the submitted data (482), were analyzed by the analysts whose experience was less than 5 years, and they account for 37.3%. No clear relationship between the years of experience and flagged data was suggested.

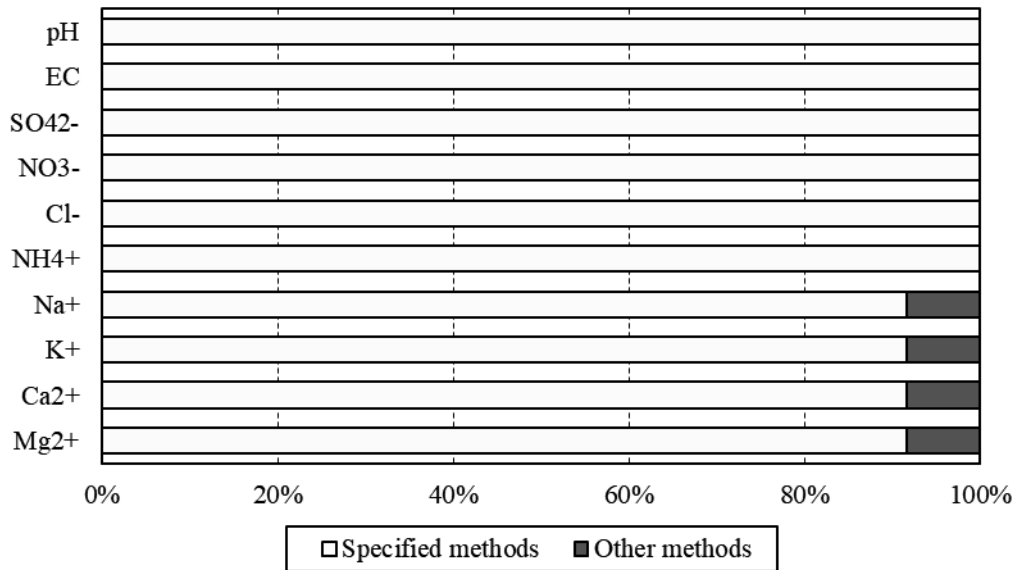
**Table 2.12 Years of experience**

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	6	6	6	6	6	6	6	6	6	6
CN03	12	12	26	26	26	26	26	26	26	26
CN04	16	16	16	16	16	16	16	16	16	16
CN06	1	6	6	6	6	6	6	6	6	6
JP01	21	21	21	21	21	21	21	21	21	21
JP03	1	1	1	1	1	1	1	1	1	1
JP04	7	7	7	7	7	7	7	7	7	7
JP08	3	3	3	3	3	3	3	3	3	3
JP09	2	2	2	2	2	2	2	2	2	2
JP10	5	5	5	5	5	5	5	5	5	5
JP14	2	2	2	2	2	2	2	2	2	2
MY01	11	11	3	3	3	3	3	3	3	3
MN01	17	17	21	21	21	21	21	21	21	21
MM01	3	3	3	3	3	3	3	3	3	3
PH01	1	1	4	4	4	1	5	5	1	1
PH02	1	1	1	1	1	1	1	1	1	1
KR01	19	19	19	19	19	19	19	19	19	19
TH01	1	10	---	---	---	---	---	---	---	---
TH02	25	25	25	25	25	25	25	25	25	25
VN01	8	8	11	11	11	11	11	11	11	11
VN02	15	15	11	11	11	11	11	11	11	11
VN03	10	10	13	10	---	10	13	13	13	13
VN04	1	1	20	20	20	20	20	20	20	20
VN05	12	12	17	17	17	16	17	17	17	17

Note: Light mesh, Analytic data of sample No. 241w or No. 242w was marked with flag "E" or "X";  
 Dark mesh, Analytic data of both samples were marked with flag "E" or "X";  
 "---", Not measured

## 2) Analytical instruments

As shown in Figure 2.27, all the participating laboratories used the recommended methods described in *Technical Manual for Wet Deposition Monitoring in East Asia -2010*. The method list is shown in Table 2.3. Analytical methods used for the measurement in the participating laboratories are shown in Table 2.13. No clear relationship between analytical methods and flagged data was suggested.



**Figure 2.27 Percentage of laboratories that use the recommended 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>
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
CN06	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
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
JP14	IC	IC	IC	IC	IC	IC	IC	IC
MY01	IC	IC	IC	IC	IC	IC	IC	IC
MN01	IC	IC	IC	IC	IC	IC	IC	IC
MM01	IC	IC	IC	IC	IC	IC	IC	IC
PH01	IC	IC	IC	SP	ICP-OES	ICP-OES	ICP-OES	ICP-OES
PH02	IC	IC	IC	SP	ICP-OES	ICP-OES	ICP-OES	ICP-OES
KR01	IC	IC	IC	IC	IC	IC	IC	IC
TH01	---	---	---	---	---	---	---	---
TH02	IC	IC	IC	IC	IC	IC	IC	IC
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	IC	IC	IC	IC	IC	IC	IC

Note: "---" Not measured

IC: Ion Chromatography

AES: Atomic Emission Spectrometry

SP\*: Spectrophotometry(Others)

ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry

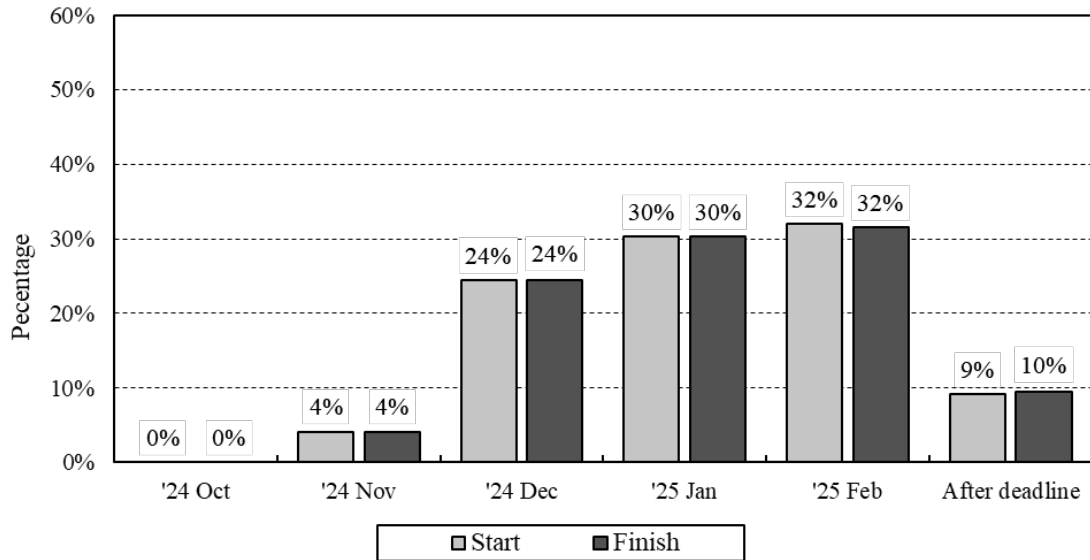
AAS: Atomic Absorption Spectrometry

SP: Spectrophotometry(Indophenol)

TI: Titrimetry

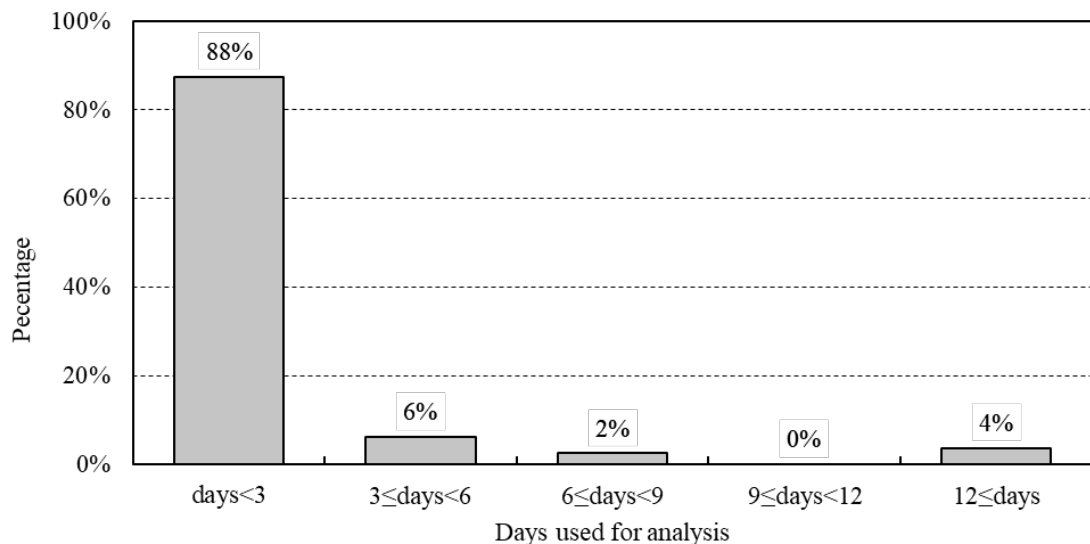
### 3) Date of analysis

Figure 2.28 shows the distribution of “Start date” and “Finish date” of analysis at the participating laboratories. In total, 28% of all the submitted data was determined by the end of 2024, and 10% was determined later than the submission deadline of this project.



**Figure 2.28 Distribution of start date and finish date of analysis**

Figure 2.29 shows the number of days required to determine the analytical data at the participating laboratories. Most analytical data were obtained within less than 3 days.



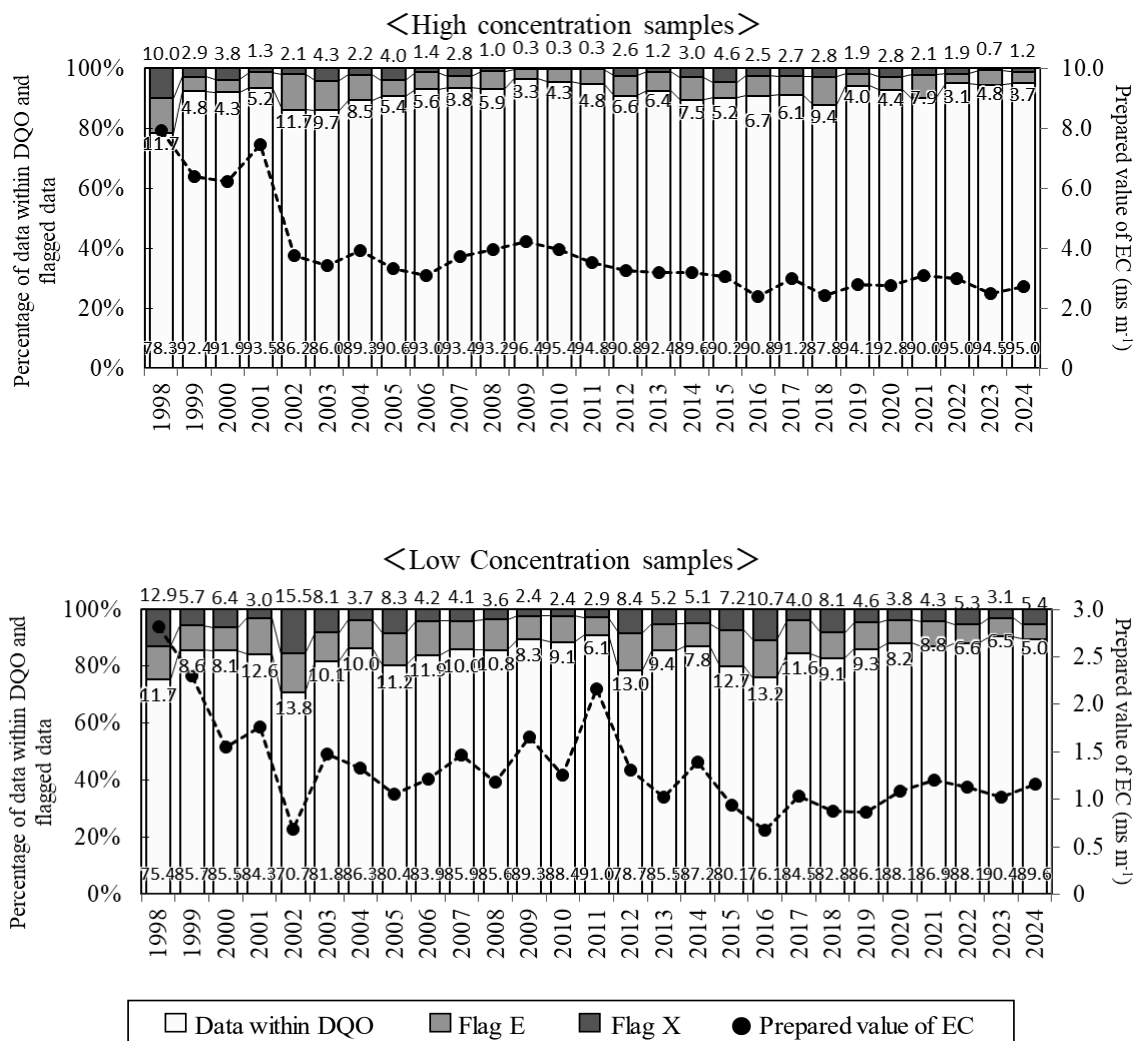
**Figure 2.29 Distribution of days used for analysis**

No clear relationship between date of analysis and flagged data was suggested, however, it is recommended analyzing the samples as soon as possible once they arrive at each laboratory.

## 2.4 Comparison with past surveys

Since the beginning of EANET, the inter-laboratory comparison on wet deposition has reached the 27<sup>th</sup> survey. The percentages of data within DQO and prepared value of EC are shown in Figure 2.30. Hereafter, sample No. 241w and No. 242w are treated as high and low concentration samples, respectively.

The percentage of data within DQO for the sample No. 241w and No. 242w were 95.0% and 89.6%, respectively. As shown in this figure, low concentration samples show a tendency that the percentages of data within DQO are dependent on the prepared values of EC.



**Figure 2.30 Comparison of results from the inter-laboratory comparison projects**

Figure 2.31 shows the trend of the prepared values and the percentage of the flagged data. There is a tendency that cations have more flagged data than anions throughout the series of survey.

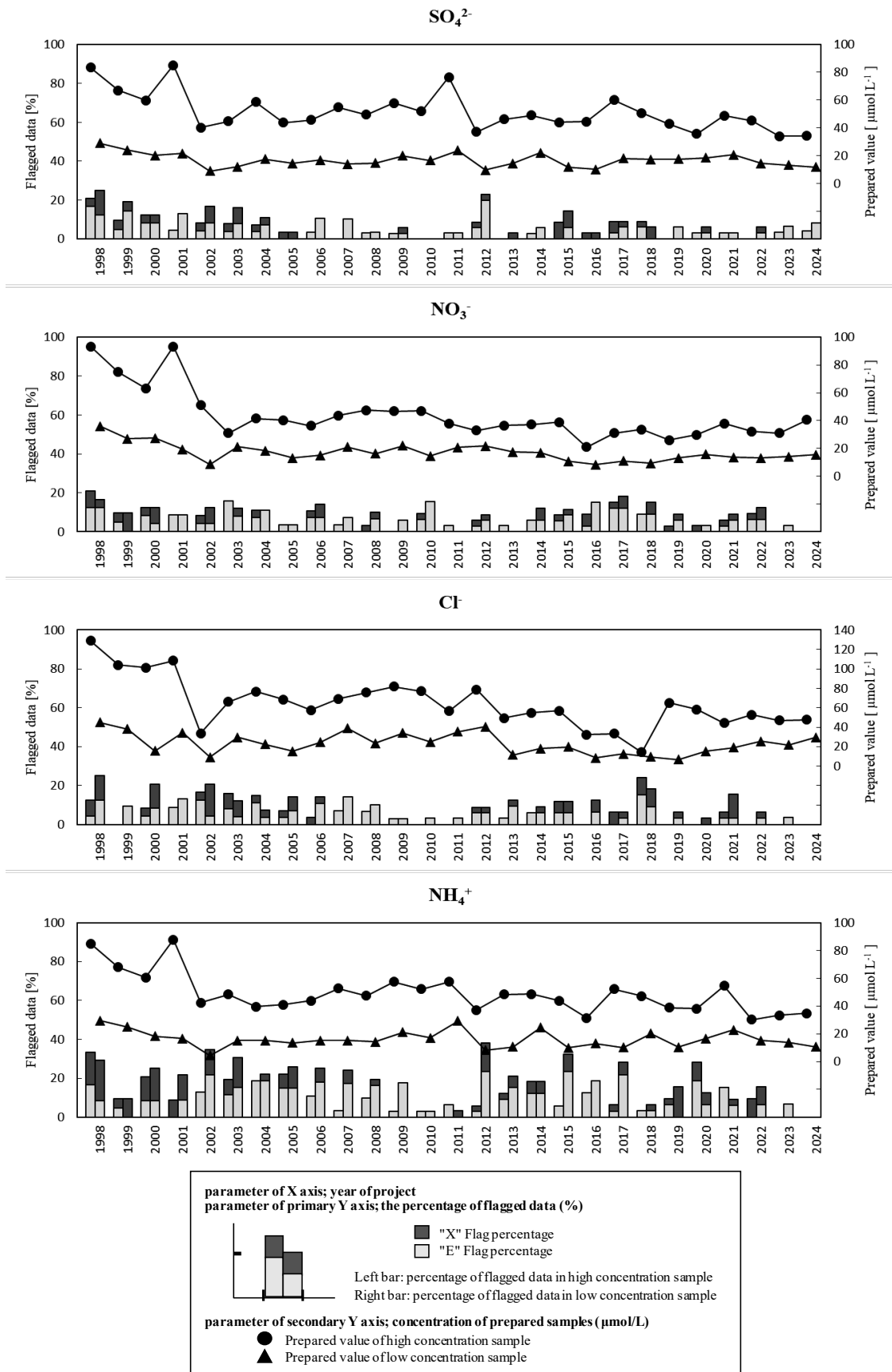


Figure 2.31 Comparison for each parameter in inter-laboratory comparison (ILC) project

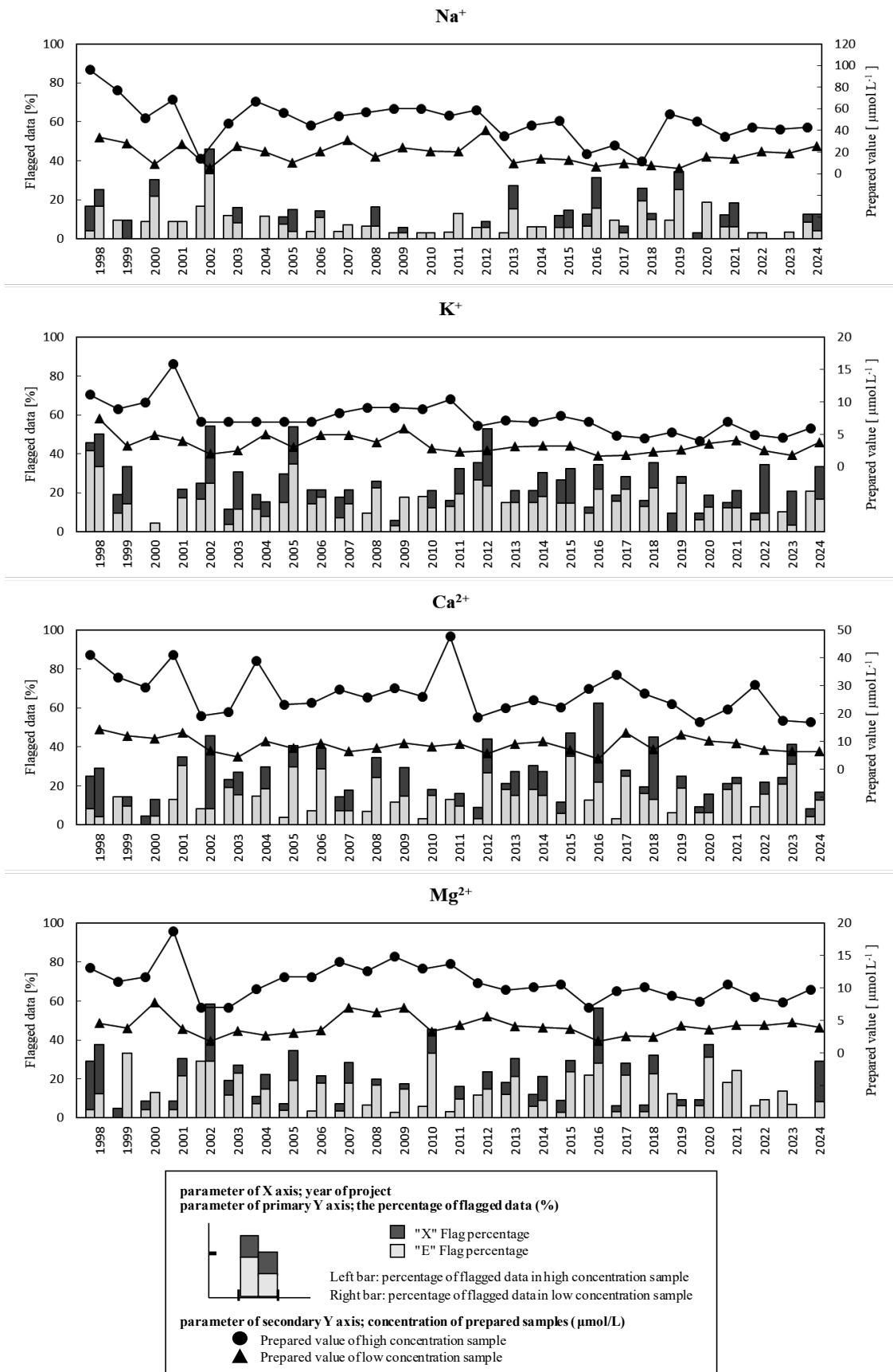
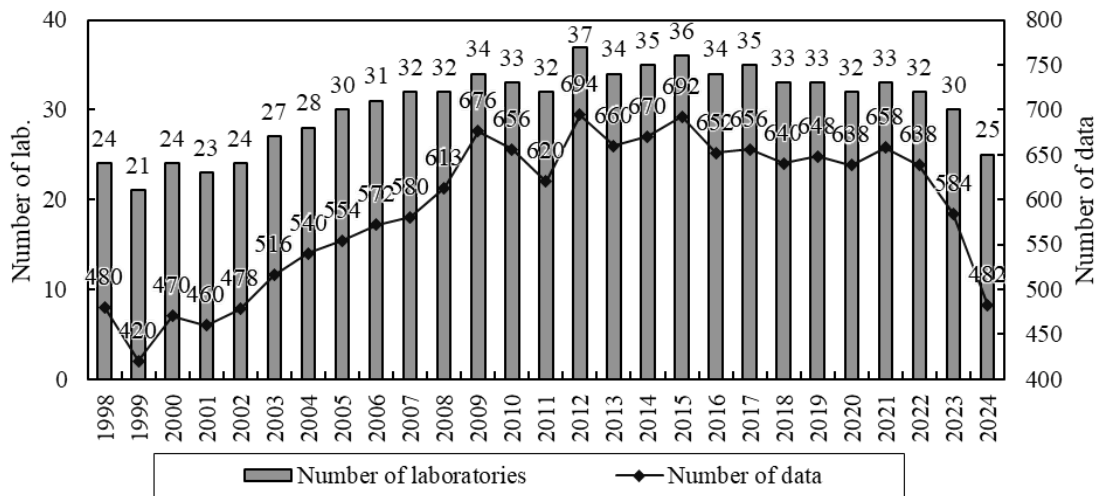


Figure 2.31 Comparison for each parameter in ILC project (continued)

As shown in figure 2.32, the total number of data in this survey was 584.



**Figure 2.32 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.

► Before analysis, it is important to make sure that every experimental instrument is kept clean. Otherwise, contamination would be likely to occur, which leads to increase the blank values. High blank values could adversely affect the quality of analytical data, so careful and diligent cleaning is strongly recommended from the point of view of QA/QC.

### 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  $R_2$  must 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 parameters to indicate precision, is defined by the equation below.

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

$\sigma$ : standard deviation of result

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. There is a tendency that each constituent of higher concentration sample (No. 241w) shows better R.S.D. than that of lower concentration sample (No. 242w). This suggests that R.S.D. are greatly affected by sample concentrations.

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. 241w**

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	1.1	0.2	0.4	0.3	0.3	1.0	0.6	1.5	1.0	0.5
CN02	1.3	0.2	0.3	0.3	0.3	0.3	0.1	1.4	0.5	0.8
CN03	1.6	0.3	0.8	0.2	0.2	0.2	0.2	1.4	0.5	0.7
CN04	2.7	0.4	0.3	0.7	0.6	1.7	1.1	4.7	2.5	2.1
CN06	0.7	0.5	0.5	1.0	0.0	1.2	0.5	3.4	1.1	2.3
JP01	3.2	0.6	0.2	0.3	0.3	0.7	0.7	0.8	0.7	0.5
JP03	1.5	0.4	0.4	0.4	0.2	0.7	0.2	2.5	0.3	0.5
JP04	3.9	0.7	0.4	0.1	0.3	1.2	0.0	12.4	0.4	0.5
JP08	4.1	0.7	0.1	0.1	0.1	0.1	0.1	0.0	0.4	1.0
JP09	4.2	0.4	0.2	0.2	0.3	0.1	0.0	0.6	0.3	0.0
JP10	0.7	0.2	0.1	0.2	0.2	0.3	0.2	0.8	0.4	0.7
JP14	6.6	1.1	0.1	0.3	0.2	0.5	0.7	5.0	0.3	0.5
MY01	3.0	0.3	1.0	0.5	1.4	0.2	0.1	6.6	1.2	0.9
MN01	4.0	1.1	0.5	3.3	0.5	2.0	1.6	2.2	1.4	0.9
MM01	48.6	8.6	0.6	0.6	0.8	1.7	0.2	4.1	1.6	6.4
PH01	3.1	0.6	1.6	0.5	0.4	1.3	2.5	4.8	0.8	0.9
PH02	13.0	2.2	3.3	2.1	2.4	1.8	12.1	17.5	3.4	2.3
KR01	6.3	0.4	1.5	1.5	1.6	1.5	1.5	0.9	1.5	1.6
TH01	2.5	0.5	--	--	--	--	--	--	--	--
TH02	47.0	1.4	4.0	3.8	3.9	1.8	0.3	1.3	0.3	1.3
VN01	7.6	1.0	1.2	0.9	0.7	0.6	0.5	3.4	1.5	1.1
VN02	3.4	0.7	0.9	0.6	0.4	0.6	0.4	3.5	1.2	1.9
VN03	2.1	0.0	1.1	0.6	--	0.2	2.0	2.5	0.7	3.3
VN04	7.8	0.4	0.4	1.9	0.3	0.5	0.4	1.4	1.4	2.6
VN05	2.0	0.2	0.3	1.3	0.6	0.5	0.6	1.4	0.6	3.3
Number of data	25	25	24	24	23	24	24	24	24	24
Minimum	0.7	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.3	0.0
25% value	2.0	0.3	0.3	0.3	0.2	0.3	0.2	1.3	0.4	0.6
Median	3.2	0.5	0.4	0.6	0.3	0.7	0.5	2.3	0.7	0.9
75% value	6.3	0.7	1.0	1.1	0.6	1.3	0.8	4.2	1.4	2.1
Maximum	48.6	8.6	4.0	3.8	3.9	2.0	12.1	17.5	3.4	6.4

Note: R.S.D was calculated from three reported measurement.

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. 242w**

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	1.2	0.4	0.3	0.7	0.4	2.2	0.6	0.0	1.1	1.2
CN02	1.6	0.4	0.8	0.5	0.4	0.6	0.5	0.9	0.7	1.4
CN03	2.2	0.7	0.6	0.5	0.3	0.6	0.3	2.9	1.2	0.8
CN04	3.5	0.9	1.1	1.7	0.3	2.6	3.8	10.9	3.3	5.9
CN06	0.0	0.8	0.4	0.0	0.7	2.4	1.4	2.8	4.8	0.0
JP01	5.5	0.3	0.4	0.6	0.3	1.1	0.4	2.0	1.5	0.0
JP03	3.8	0.5	0.8	0.9	0.6	0.7	0.2	0.0	0.5	1.2
JP04	3.6	0.8	0.0	0.7	0.3	1.0	3.1	7.9	3.0	1.9
JP08	3.7	0.4	0.3	0.4	0.3	0.5	0.1	1.2	1.8	1.8
JP09	5.0	0.3	0.4	0.4	0.5	0.7	0.2	0.0	0.0	0.0
JP10	1.1	0.3	0.4	0.2	0.5	0.6	0.0	0.0	0.8	0.0
JP14	6.8	0.9	0.6	0.5	0.2	0.7	0.7	5.6	0.0	1.2
MY01	2.7	0.0	0.6	0.9	2.1	0.4	0.4	2.2	5.1	1.4
MN01	5.7	0.5	1.0	2.1	1.1	2.8	4.6	2.0	7.7	4.8
MM01	30.2	10.2	1.1	1.4	0.9	2.9	0.7	1.9	4.0	4.5
PH01	19.1	1.0	0.9	1.1	0.4	11.7	1.4	4.0	0.9	1.9
PH02	31.9	1.6	4.1	2.4	2.7	6.3	12.5	21.1	15.7	5.4
KR01	3.6	1.4	1.6	1.6	1.5	1.7	1.8	2.2	1.9	1.3
TH01	4.7	2.1	--	--	--	--	--	--	--	--
TH02	6.6	0.3	1.8	0.3	0.4	0.6	0.4	1.5	0.9	1.4
VN01	5.8	2.6	5.4	2.1	0.6	2.0	0.6	6.4	4.7	2.6
VN02	4.7	1.4	1.5	1.3	0.6	2.4	0.7	6.2	2.8	3.6
VN03	1.3	0.0	1.4	1.7	--	1.9	2.0	5.7	2.9	2.7
VN04	0.0	0.8	4.5	3.0	1.1	0.8	0.5	1.8	3.3	6.5
VN05	0.8	0.4	2.1	2.0	0.4	3.8	2.4	1.9	1.1	5.0
Number of data	25	25	24	24	23	24	24	24	24	24
Minimum	0.0	0.0	0.0	0.0	0.2	0.4	0.0	0.0	0.0	0.0
25% value	1.6	0.4	0.4	0.5	0.4	0.7	0.4	1.4	0.9	1.2
Median	3.7	0.7	0.8	0.9	0.5	1.4	0.7	2.1	1.8	1.6
75% value	5.7	1.0	1.6	1.7	0.8	2.5	1.8	5.6	3.5	3.8
Maximum	31.9	10.2	5.4	3.0	2.7	11.7	12.5	21.1	15.7	6.5

Note: R.S.D was calculated from three reported measurement.

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 Deviation% from prepared values

**Appendix Table 2.2.1 Deviation% from prepared values of sample No. 241w**

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	-1.1	-4.4	0.9	0.0	-0.2	4.6	3.0	-1.7	4.8	0.0
CN02	0.6	-1.5	1.5	-0.5	0.8	-1.1	0.5	8.5	-3.0	2.0
CN03	0.2	-6.3	3.2	-0.5	3.3	5.5	-1.6	-13.6	-6.5	2.0
CN04	0.4	0.0	0.9	0.0	-0.2	-6.0	2.3	-13.6	3.6	-3.1
CN06	0.9	-7.4	0.3	-2.5	1.5	1.1	-0.7	-1.7	-6.0	-5.1
JP01	1.1	-0.4	1.8	0.0	0.2	-0.9	-0.5	6.8	-3.6	-1.0
JP03	0.2	-1.5	0.3	-0.2	0.4	-0.3	-1.2	-5.1	-0.6	-4.1
JP04	-0.2	-1.8	-0.6	-0.5	0.0	0.6	-4.4	23.7	-2.4	-1.0
JP08	1.5	-7.0	-0.3	0.0	1.0	-0.6	0.0	-1.7	0.6	-1.0
JP09	2.1	-2.9	1.8	2.0	2.1	-1.1	0.5	-1.7	0.0	0.0
JP10	0.4	0.0	0.3	-0.5	-3.1	0.6	-0.5	1.7	0.6	1.0
JP14	1.7	-1.8	1.5	1.0	0.2	-0.9	0.5	1.7	1.2	-1.0
MY01	1.3	-0.4	1.5	0.7	3.6	0.6	-0.7	5.1	0.6	-9.2
MN01	4.7	-6.6	9.1	9.2	4.0	8.6	-0.2	-5.1	7.1	0.0
MM01	8.1	-46.7	0.3	-2.7	1.5	0.6	25.7	5.1	8.9	-4.1
PH01	1.9	-3.3	-1.8	-4.0	-3.3	-0.3	-11.0	-28.8	-4.2	-4.1
PH02	1.5	-4.0	-21.9	-5.2	-5.6	5.5	-19.9	-23.7	-10.7	9.2
KR01	-0.6	-3.3	-2.0	-2.7	-3.6	1.1	-2.3	-5.1	-4.8	-3.1
TH01	1.3	-5.5	---	---	---	---	---	---	---	---
TH02	7.0	-8.1	-2.3	-2.2	-2.3	-4.0	-2.6	-8.5	-4.2	-5.1
VN01	4.7	-2.9	0.0	-0.7	-0.2	-2.6	-9.8	-8.5	6.5	7.1
VN02	2.1	1.1	0.0	-1.0	-0.2	-2.9	-10.0	-15.3	6.5	4.1
VN03	2.3	-4.0	-3.2	-5.0	---	4.0	-46.3	22.0	44.0	-1.0
VN04	7.0	-6.3	0.3	-0.5	-0.4	-2.9	-10.0	0.0	6.5	10.2
VN05	2.3	-1.5	-3.2	-3.2	-3.1	4.0	-10.0	-11.9	17.9	7.1
Number of data	25	25	24	24	23	24	24	24	24	24
Average	2.1	-5.1	-0.5	-0.8	-0.2	0.6	-4.1	-3.0	2.6	0.0
Minimum	-1.1	-46.7	-21.9	-5.2	-5.6	-6.0	-46.3	-28.8	-10.7	-9.2
Maximum	8.1	1.1	9.1	9.2	4.0	8.6	25.7	23.7	44.0	10.2

Note: "---", Not measured

**Appendix Table 2.2.2 Deviation% from prepared values of sample No. 242w**

Lab. ID	pH	EC	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
	%	%	%	%	%	%	%	%	%	%
CN01	-0.2	-2.6	-0.9	-1.3	0.7	8.5	2.7	-10.5	-6.3	-2.6
CN02	2.2	-2.6	3.4	-2.6	2.4	0.0	1.6	0.0	9.4	7.7
CN03	2.4	-1.7	6.8	-4.5	5.7	4.7	-1.9	-34.2	-9.4	7.7
CN04	2.5	-1.7	0.0	-1.9	-0.3	-0.9	5.1	-39.5	9.4	5.1
CN06	3.3	-4.3	2.6	-3.8	1.3	-2.8	1.2	-2.6	-14.1	-15.4
JP01	0.4	2.6	0.9	1.3	-1.0	0.0	-1.2	-5.3	-6.3	-2.6
JP03	-0.4	0.0	0.9	0.6	-0.3	0.9	-1.2	-10.5	-4.7	-7.7
JP04	-0.4	0.0	-0.9	-1.3	-0.3	-0.9	-1.6	13.2	4.7	2.6
JP08	1.4	-12.9	16.2	0.0	0.7	-2.8	0.0	-2.6	1.6	-2.6
JP09	1.6	0.0	2.6	3.2	4.0	2.8	0.0	-2.6	1.6	0.0
JP10	-0.2	2.6	-0.9	-0.6	-3.7	-1.9	0.0	-2.6	3.1	5.1
JP14	2.4	-1.7	3.4	0.6	2.4	-1.9	2.7	10.5	-3.1	-5.1
MY01	1.0	2.6	-2.6	-2.6	5.4	8.5	0.4	-7.9	-3.1	-20.5
MN01	3.1	-2.6	6.8	5.1	2.0	-0.9	1.2	-7.9	28.1	10.3
MM01	3.3	-32.8	-0.9	-3.8	-0.3	5.7	2.7	5.3	29.7	2.6
PH01	2.7	-6.9	-0.9	2.6	-4.7	5.7	-15.6	-21.1	-10.9	-5.1
PH02	3.1	-1.7	-24.8	3.2	-6.7	-6.6	-40.5	-28.9	-17.2	0.0
KR01	-3.9	1.7	-6.0	-5.1	-5.1	0.0	-2.7	-7.9	-6.3	-2.6
TH01	2.0	-7.8	---	---	---	---	---	---	---	---
TH02	1.8	-6.0	-6.0	-3.2	-1.0	2.8	-3.5	-10.5	-7.8	-7.7
VN01	4.3	-5.2	11.1	-3.2	-2.7	0.0	0.0	-15.8	4.7	41.0
VN02	2.5	1.7	9.4	-4.5	-3.4	0.9	-0.8	-34.2	9.4	35.9
VN03	2.4	-3.4	4.3	-6.4	---	11.3	-43.2	21.1	95.3	33.3
VN04	7.8	-7.8	12.8	-1.9	-2.0	-0.9	0.4	0.0	0.0	46.2
VN05	2.0	0.0	5.1	-5.1	-5.1	6.6	-1.9	-31.6	12.5	41.0
Number of data	25	25	24	24	23	24	24	24	24	24
Average	1.9	-3.6	1.8	-1.5	-0.5	1.6	-4.0	-9.4	5.0	6.9
Minimum	-3.9	-32.8	-24.8	-6.4	-6.7	-6.6	-43.2	-39.5	-17.2	-20.5
Maximum	7.8	2.6	16.2	5.1	5.7	11.3	5.1	21.1	95.3	46.2

Note: "---", Not measured

### 3. 20<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 December 2024. Most of the laboratories which use 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 19 laboratories in charge of EANET dry deposition monitoring participated in this 20<sup>th</sup> activity and 16 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.241d-1	Alkali ( $\text{K}_2\text{CO}_3$ ) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.
No.241d-2	Acid ( $\text{H}_3\text{PO}_4$ ) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions.
No.242d-1	Alkali ( $\text{K}_2\text{CO}_3$ ) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.

**Table 3.1 Outline of filter samples (continued)**

Name	Details	Container	Number of filters	Note
No.242d-2	Acid (H <sub>3</sub> PO <sub>4</sub> ) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions
No.243d-1	Alkali (K <sub>2</sub> CO <sub>3</sub> ) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.243d-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 microgram (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.241d-1, No.242d-1, No.243d-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.241d-2, No.242d-2, No.243d-2

Add 20 mL of pure water (EC<0.15 mS m<sup>-1</sup>) as an extracting solvent into each centrifuge tube, then shake 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) 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
SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup>	Ion Chromatography (preferably with suppressor)
	Spectrophotometry
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography
	Spectrophotometry (Indophenol Blue)

### 3.2.5 Data Check Procedures

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

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

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

where  $M_{sol}$  : quantity of each component in the filtrate (μg);

$C_{sol}$  : concentration of each component in the filtrate (mg L<sup>-1</sup>);

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

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

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

where  $netM_{sol}$  : net quantity of each ion on the filter;

$M_{sol, Sample}$  : quantity (μg) of each component in the filtrate from sample No.241d-1, No.241d-2, No.242d-1 and No.242d-2;

$M_{sol, Blank}$  : the median quantity (μg) in the filtrate from blank sample No.243d-1 and No.243d-2.

### 3.3 Results

The NC distributed the filter samples to 19 laboratories in the participating countries of EANET and received their results from 16 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. Outliers, defined as those results exceeding three standard deviations, excluded from the summary calculation shown in

Table 3.3 and all results were not rejected this time.

As shown in Table 3.3, the deviations ( $\Delta V/V_p$ ) for  $\text{SO}_4^{2-}$  in Sample No.241d and Sample No.242d were -10.8% and -0.9%. The deviations for  $\text{Cl}^-$  in Sample No.241d and Sample No.242d were -13.7% and -10.2%. The deviations for  $\text{NH}_4^+$  in Sample No.241d and Sample No.242d were -8.3% and -4.1%.

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, and these average values were evaluated based on the deviation from the corresponding prepared values. 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.241d and No.242d 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* ( $V_p$ ) ( $\mu\text{g}$ )	Average ( $V_a$ ) ( $\mu\text{g}$ )	$\Delta V/V_p^*$ (%)	S.D. ( $\mu\text{g}$ )	Number (N)	Minimum ( $\mu\text{g}$ )	Maximum ( $\mu\text{g}$ )
<u>Sample No.241d</u>							
SO <sub>4</sub> <sup>2-</sup>	16.0	14.3	-10.8	2.15	16	9.57	18.0
Cl <sup>-</sup>	7.61	6.57	-13.7	1.51	16	3.35	8.37
NH <sub>4</sub> <sup>+</sup>	26.0	23.8	-8.3	5.15	16	10.8	31.3
<u>Sample No.242d</u>							
SO <sub>4</sub> <sup>2-</sup>	37.8	37.5	-0.9	7.62	16	20.3	53.3
Cl <sup>-</sup>	16.9	15.2	-10.2	2.36	16	10.1	17.4
NH <sub>4</sub> <sup>+</sup>	56.0	53.7	-4.1	4.77	16	44.6	65.3

\* Prepared: Prepared values

\*  $\Delta V/V_p$ : (Average result ( $V_a$ ) - Prepared value ( $V_p$ )) / Prepared value ( $V_p$ )  $\times$  100 (%)

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

#### Samples No.241d-1, No.241d-2

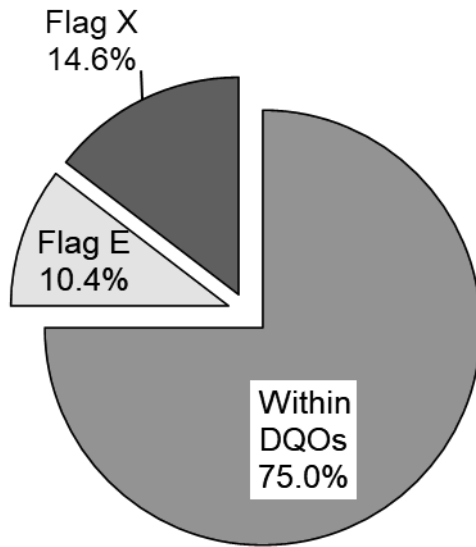
For Sample No.241d, 5 analytical data in 48 results were flagged E, and 7 analytical data were flagged X. The total percentage of the flagged samples was 25% (Figure 3.1, Table 3.4 and 3.5).

**Table 3.4 Number of flagged data for Sample No.241d**

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Flag E *	3	1	1	5
Flag X *	2	3	2	7
Data within DQOs	11	12	13	36
Ratio of Flagged (%)	31.3	25.0	18.8	25.0

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

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



**Figure 3.1 Percentage of flagged data for Sample No.241d**

**Table 3.5 Average analytical results of Sample No.241d**

Lab. Code	SO <sub>4</sub> <sup>2-</sup> (µg)	Cl <sup>-</sup> (µg)	NH <sub>4</sub> <sup>+</sup> (µg)
JP01	15.7	7.69	25.7
JP02	16.8	7.34	25.9
JP03	16.3	7.31	25.2
JP04	15.8	7.47	25.6
JP08	15.1	6.85	25.2
JP09	14.8	7.26	25.9
JP10	14.5	7.69	24.8
MY01	14.1	7.65	23.2
MN01	18.0	8.37	31.3 E
MM01	14.1	4.03 X	23.6
PH01	15.0	6.81	26.2
PH02	9.57 X	5.99 E	26.8
KR01	12.9 E	7.00	23.5
TH02	12.9 E	6.79	26.5
VN01	12.0 E	3.46 X	11.3 X
VN03	10.7 X	3.35 X	10.8 X

Note: Flag E: 15% < | Deviation | ≤ 30%  
 Flag X: 30% < | Deviation |

**Samples No.242d-1, No.242d-2**

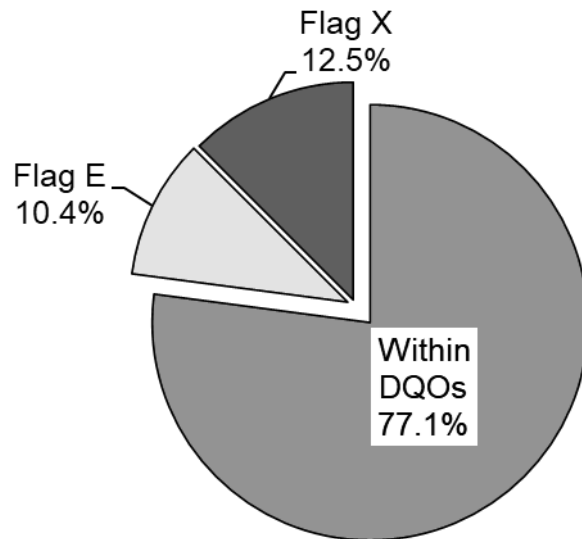
For Sample No.242d, 5 analytical data in 48 results were flagged E, and 6 analytical data were flagged X. The total percentage of the flagged samples was 22.9% (Figure 3.2, Table 3.6 and 3.7).

**Table 3.6 Number of flagged data for Sample No.242d**

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Total
Flag E*	2	1	2	5
Flag X*	3	3	0	6
Data within DQOs	11	12	14	37
Ratio of Flagged (%)	31.3	25.0	12.5	22.9

\*Flag E: 15% < | Deviation | ≤ 30%

\*Flag X: 30% < | Deviation |



**Figure 3.2 Percentage of flagged data for Sample No.242d**

**Table 3.7 Average analytical results of Sample No.242d**

Lab. Code	SO <sub>4</sub> <sup>2-</sup> (µg)	Cl <sup>-</sup> (µg)	NH <sub>4</sub> <sup>+</sup> (µg)
JP01	37.8	16.5	54.6
JP02	38.6	16.3	56.8
JP03	37.7	16.0	54.5
JP04	37.7	16.9	54.3
JP08	37.3	15.9	53.8
JP09	35.4	15.9	56.4

JP10	35.5		17.0		52.6
MY01	36.0		17.1		56.2
MN01	44.7	E	17.4		65.3 E
MM01	29.5	E	13.6	E	48.8
PH01	35.8		16.5		47.8
PH02	20.3	X	11.4	X	44.6 E
KR01	33.4		15.9		49.3
TH02	33.9		15.9		59.8
VN01	53.3	X	10.1	X	52.6
VN03	52.4	X	10.3	X	51.6

Note: Flag E: 15% < | Deviation | ≤ 30%  
Flag X: 30% < | Deviation |

### **Blank Sample (No.243d)**

Each quantity of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NH}_4^+$  was determined for blank sample No.243d-1 and No.243d-2. Their obtained values are shown in Table 3.8. Blank values were detected in a wide range, including 0  $\mu\text{g}$ .

**Table 3.8 Analytical results of Blank Sample No.243d**

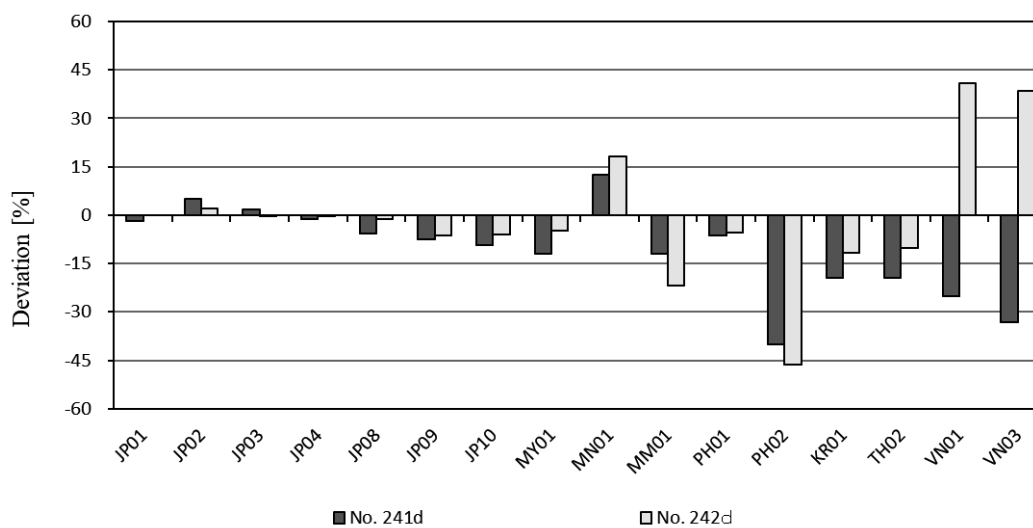
Lab. Code	$\text{SO}_4^{2-}$ ( $\mu\text{g}$ )	$\text{Cl}^-$ ( $\mu\text{g}$ )	$\text{NH}_4^+$ ( $\mu\text{g}$ )
JP01	0.38	1.29	0.38
JP02	0	1.19	0.55
JP03	0	1.22	0.27
JP04	0.27	1.18	0.21
JP08	0.44	1.50	0.60
JP09	0	1.16	0.77
JP10	0.12	0.80	0.23
MY01	1.35	1.94	1.55
MN01	0.03	1.24	1.21
MM01	1.72	1.74	2.66
PH01	1.05	2.10	2.11
PH02	3.34	3.24	1.30
KR01	0.76	1.44	3.05
TH02	0.47	2.11	4.29
VN01	0.13	0.17	0.09
VN03	3.90	1.21	1.00

Average	0.87	1.47	1.27
Median	0.41	1.27	0.88
Minimum	0.00	0.17	0.09
Maximum	3.90	3.24	4.29
Standard deviation	1.15	0.65	1.16

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

The overviews of their results are shown in the following figures and tables for each analyte ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$ ). The obtained values from each laboratory were evaluated for their deviations. The number of the flagged data is shown in Table 3.9, 3.10 and 3.11 for each analyte.

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



**Figure 3.3** Deviation for  $\text{SO}_4^{2-}$

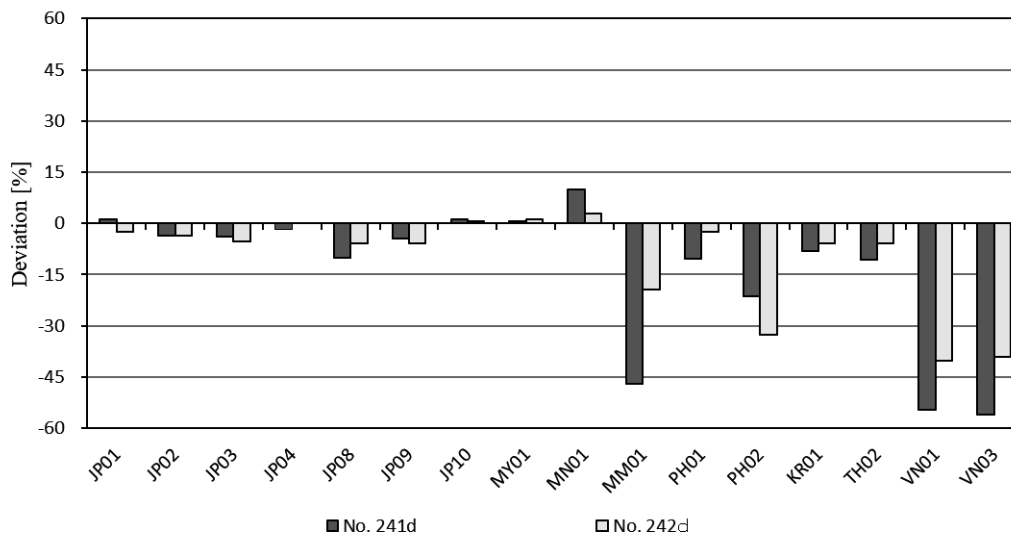
$$\text{Deviation (\%)} = (\text{Determined value} - \text{Prepared value}) / \text{Prepared value} \times 100 (\%)$$

**Table 3.9** Flagged data of  $\text{SO}_4^{2-}$

	Flag E	Flag X	Flagged (%)
Sample No.241d	3	2	31.3
Sample No.242d	2	3	31.3

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of  $\text{SO}_4^{2-}$ . The E flag was observed at three laboratories for Sample No. 241d and at two laboratories for Sample No. 242d. The X flag was also observed at two laboratories for Sample No. 241d and at three laboratories for Sample No. 242d.

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



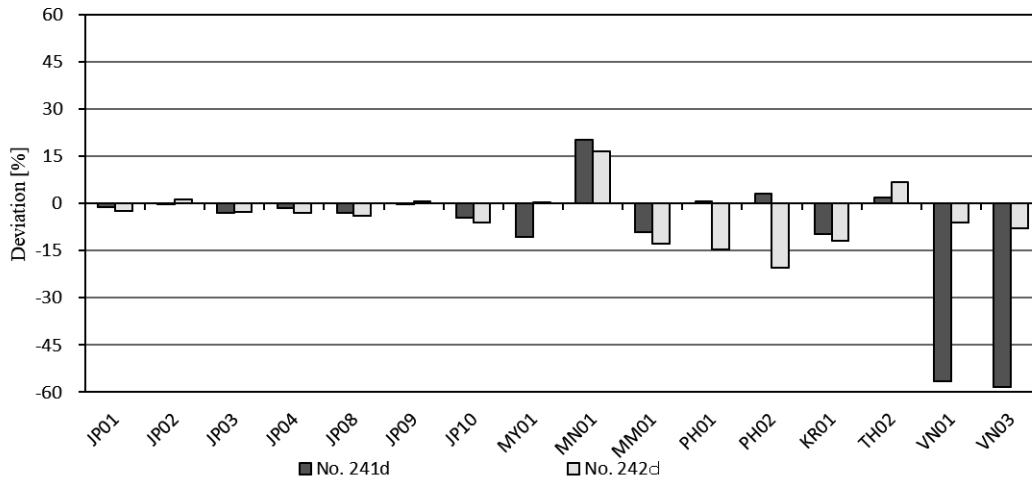
**Figure 3.4 Deviation for Cl<sup>-</sup>**

**Table 3.10 Flagged data of Cl<sup>-</sup>**

	Flag E	Flag X	Flagged (%)
Sample No.241d	1	3	25.0
Sample No.242d	1	3	25.0

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of Cl<sup>-</sup>. E flag was observed at one laboratory for Sample No.241d and No.242d. X flag was observed at 3 laboratories for Sample No.241d and No. 242d.

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



**Figure 3.5 Deviation for NH<sub>4</sub><sup>+</sup>**

**Table 3.11 Flagged data of NH<sub>4</sub><sup>+</sup>**

	Flag E	Flag X	Flagged (%)
Sample No.241d	1	2	18.8
Sample No.242d	2	0	12.5

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of NH<sub>4</sub><sup>+</sup>. E flag was observed 1 laboratory for Sample No.241d and 2 laboratories for Sample No. 242d. X flag was observed 2 laboratories for No.241d.



### 3.3.3 Information on Laboratories

#### Years of staff experience

Years of staff experience are summarized in Table 3.12. A light gray color cell indicates that there is a flag for Sample No.241d or No.242d. A dark gray color cell indicates the flagged data in both Sample No.241d and No.242d.

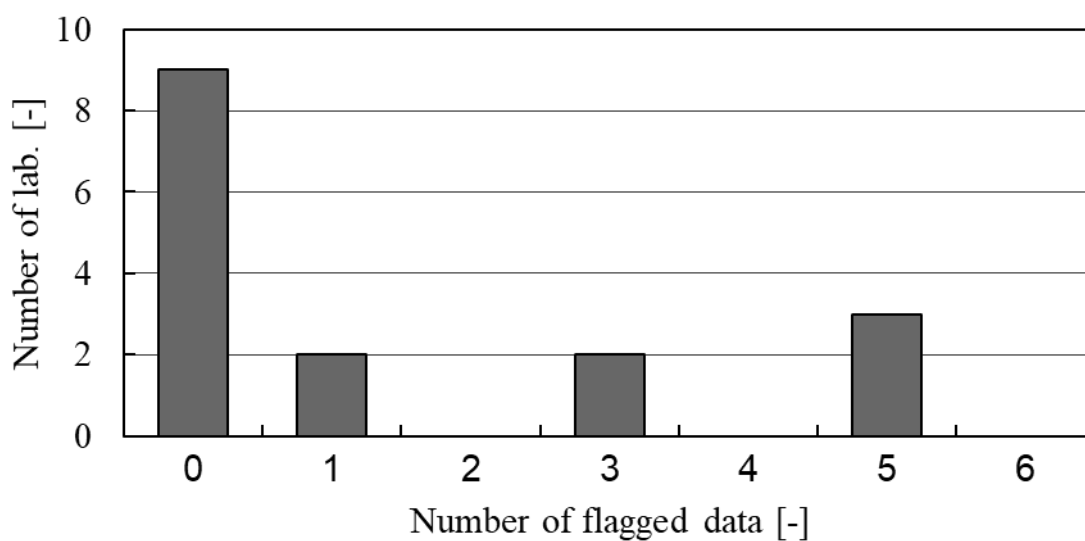
**Table 3.12** Years of staff experience

Lab. Code	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
JP01	21	21	21
JP02	5	5	5
JP03	1	1	1
JP04	7	7	7
JP08	3	3	3
JP09	2	2	2
JP10	5	5	5
MY01	6	6	6
MN01	21	21	21
MM01	3	3	3
PH01	4	4	4
PH02	1	1	1
KR01	18	18	18
TH02	25	25	25
VN01	11	11	11
VN03	11	11	11

 : One sample is flagged.  
 : Two samples are flagged.

#### Flagged Data

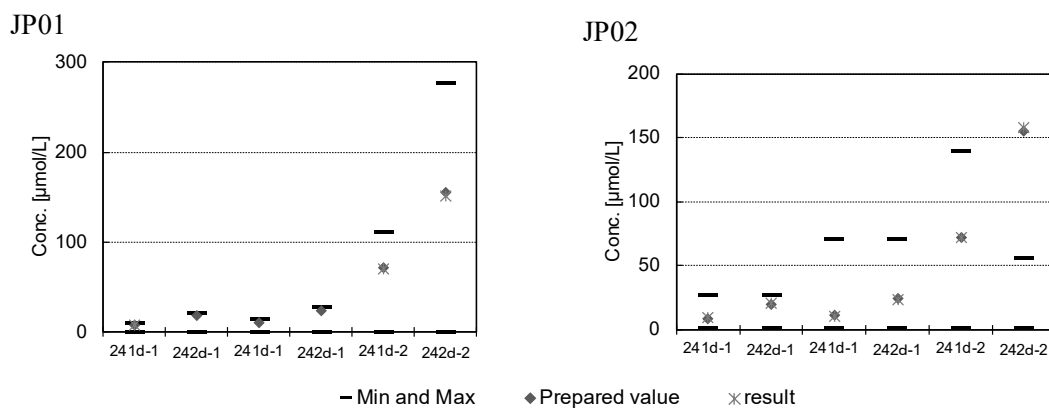
In the results of Sample No.241d and No.242d, the total number of the flagged data was 23 (E: 10, X: 13) in the whole values (96). The number of the flagged data in each laboratory is shown in Figure 3.6. Night laboratories met DQOs (56.3%).



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

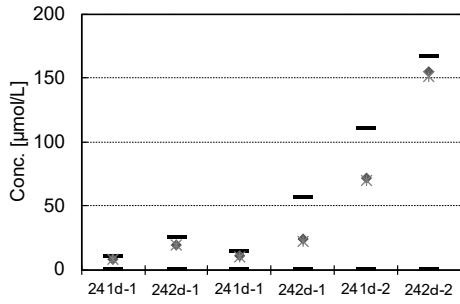
**Calibration standard solution**

The ranges of the calibration standard solution in each laboratory are shown in Figure 3.7 with the prepared values and their laboratory results, which were converted in  $\mu\text{mol L}^{-1}$ . Each concentration of the prepared values was expected within the range of both concentrations of lowest and highest standard solutions. 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.

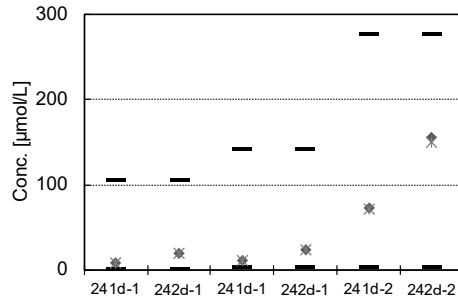


**Figure 3.7** Ranges of the calibration standard solution in each laboratory

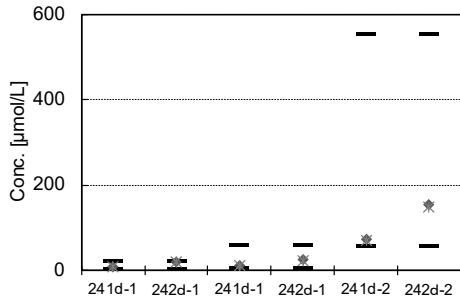
JP03



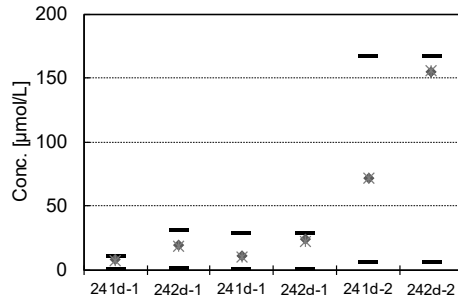
JP04



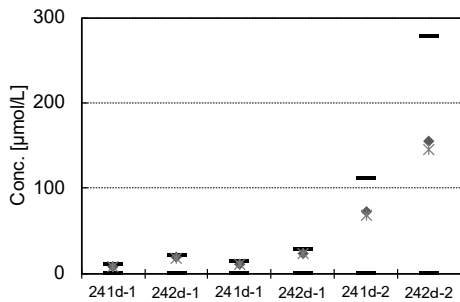
JP08



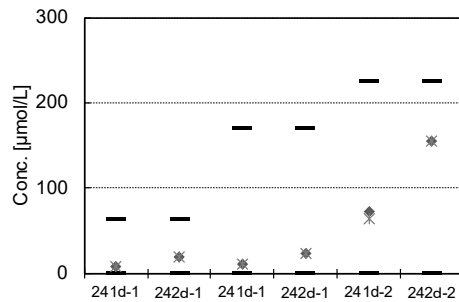
JP09



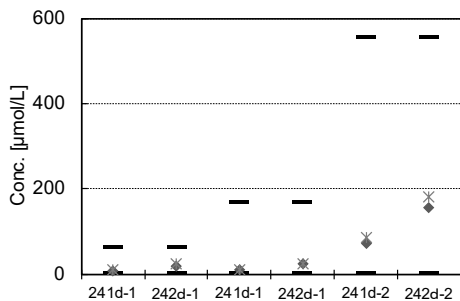
JP10



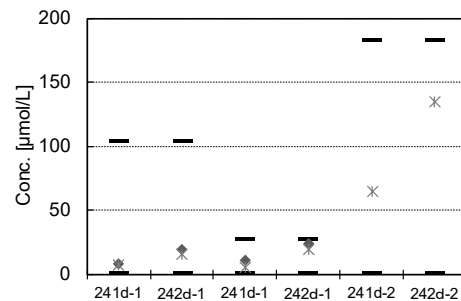
MY01



MN01

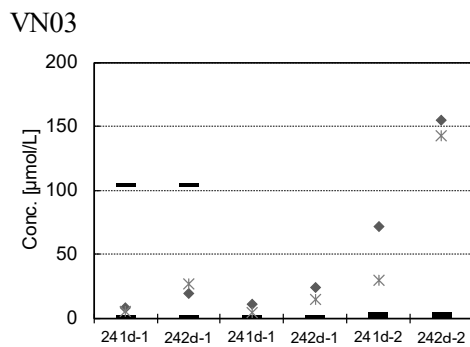
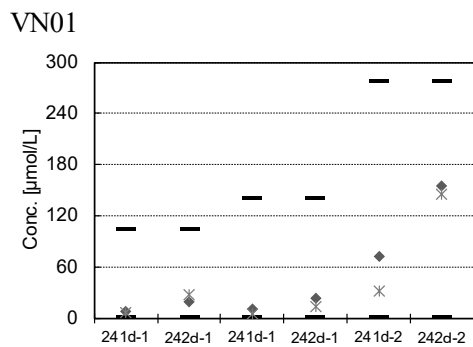
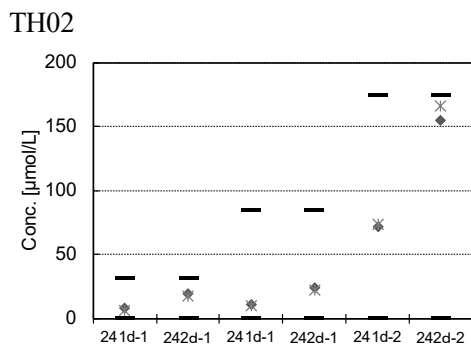
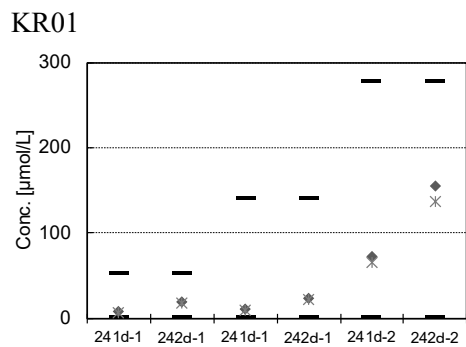
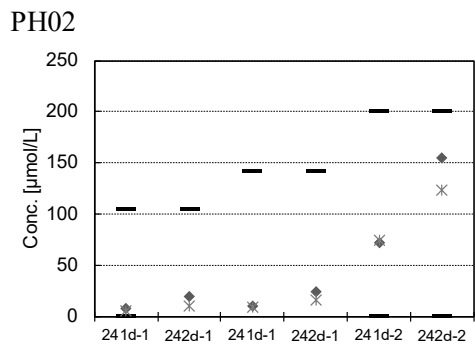
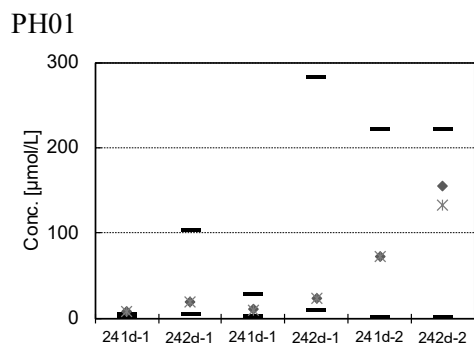


MM01



— Min and Max    ◆ Prepared value    ✕ result

Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

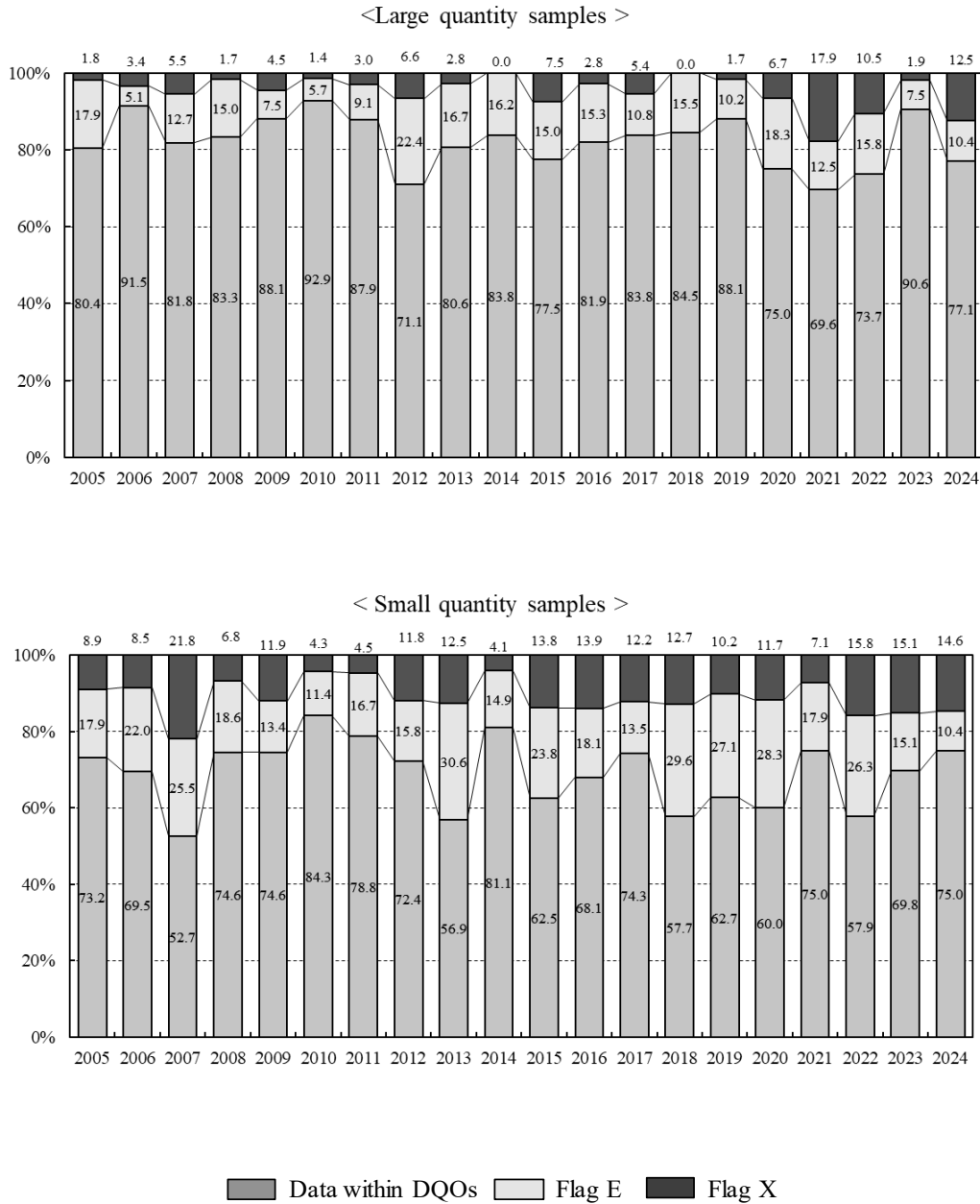


— Min and Max    ◆ Prepared value    ✕ result

Figure 3.7 Ranges of the calibration standard solution in each laboratory (continued)

### 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 3.8.



**Figure 3.8 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 3.9.

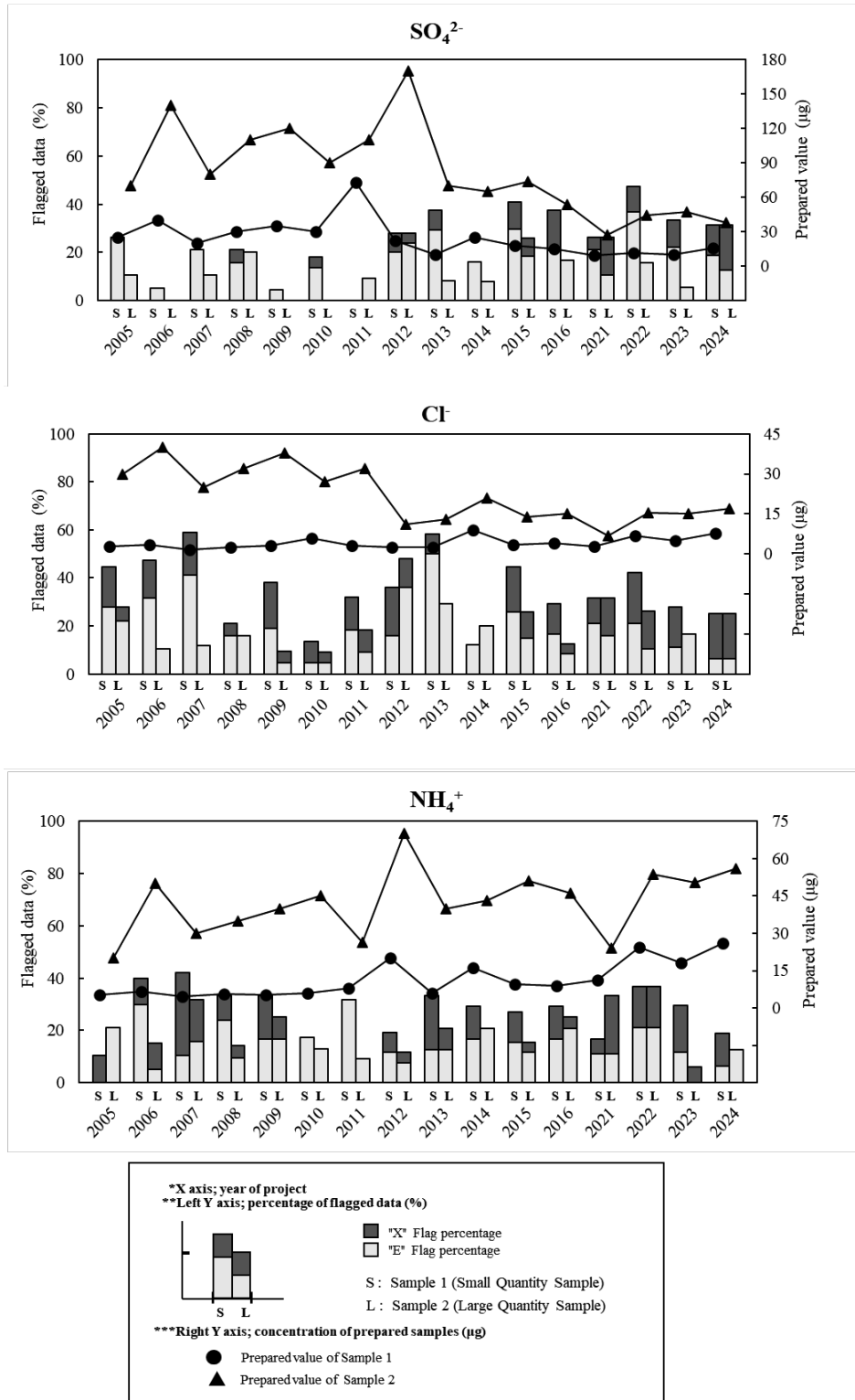


Figure 3.9 Comparison for each parameter in Inter-laboratory comparison project

### 3.5 Recommendations for improvement

Filter samples are put in centrifuge tubes, and then the extracting solvents are directly added into the tubes. The extraction and filtration procedures are specified in the “Technical Manual for Air Concentration Monitoring in East Asia, December 2013”

#### 3.5.1 Measurement and Analyses

- ▶ Before setting a shaker and start shaking for 20 minutes, shake each tube by hand sufficiently.
  
- ▶ Samples should not be diluted even though the concentration of the analytical sample exceeds that of the highest standard solution you prepared. Instead, add one or two higher standard solutions during analyses and measure its values within the calibration curve range.
  
- ▶ Extraction, filtration, and analyses should be done on the same day once you open the bag. In particular, special care for  $\text{NH}_4^+$  determination. (Be aware that sample solutions may be contaminated by ammonia in a laboratory. Even each sample sets in an autosampler with a cap may be possibly contaminated by ammonia during analyses.)
  
- ▶ It is strongly recommended that only the interlaboratory samples should be analyzed in sequence to minimize contamination during analyses. Regular samples should not be analyzed simultaneously with the interlaboratory samples.

#### 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. 26<sup>th</sup> INTER-LABORATORY COMPARISON PROJECT ON SOIL**

### **4.1 Introduction**

The Inter-Laboratory Comparison (ILC) Project on Soil began in 1999 as part of the QA/QC program for Soil and Vegetation Monitoring. The project aims to clarify inter-laboratory precision, as well as within-laboratory and repeatability precision, to enhance the analytical quality of laboratories participating in EANET. Potential factors affecting analytical precisions have been discussed in previous projects.

Compared to environmental water, soil analysis involves more complex procedures and multiple steps. Variability among laboratories may arise from specific stages of the analysis, such as extraction, instrumental analysis, and/or titration. Results from the first three projects (1999 to 2001) suggested that instrumental analysis has a relatively large impact on the overall precision of soil analysis. In addition, the following analytical conditions were identified as influential:

- Addition of La or Sr solution for AAS analysis for Ex-Ca and Ex-Mg
- Preparation methods for standard solution
- Instruments used for Ex-K and Ex-Na analysis

Participating laboratories have shared information on these factors to improve analytical precision.

In the 26<sup>th</sup> project, the Network Center (NC) provided two soil samples (No.241s and No.242s) to the laboratories to support standardization and improve inter-laboratory precision. The submitted data were statistically evaluated in accordance with the QA/QC program for soil monitoring. These results are expected to contribute to the assessment of inter-laboratory variation and offer insights into improving the analytical precision of soil monitoring EANET.

### **4.2 Procedures**

#### **4.2.1 Participating Laboratories**

Six laboratories from three countries participated in the 26<sup>th</sup> ILC Project on Soil. The data submitted by these laboratories were statistically analyzed by the NC as part of the QA/QC program. The names of the participating laboratories are listed in Table 1.1.

#### **4.2.2 Description of Samples**

The characteristics of the soil samples are as follows:

### Sample No.241s: Cambisols

### Sample No.242s: Cambisols

Soil samples 241s and 242s were collected from beneath Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*), respectively, in Niigata Prefecture, Japan. Both samples were taken from the B-horizon, which primarily composed of mineral soil. The soils were air-dried and sieved to obtain particles smaller than 2 mm (i.e., fine soil). To ensure complete homogeneity, the bulk samples were repeatedly divided into two portions, thoroughly mixed, recombined, and this process was repeated fifteen times. Subsequently, 400-500 g of each homogenized soil sample was placed into 500 mL plastic bottles and sterilized using gamma irradiation (50 kGy) prior to distribution to participating countries.

#### 4.2.3 Parameters Analyzed

All participating laboratories were expected to measure the parameters listed in Table 4.1.

**Table 4.1 Parameters to be measured**

Parameters	Unit	Mandatory or not
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

Note: All parameters were mandatory (M).

In this report, “Exchangeable” is abbreviated as “Ex-”; for example, Ex-Ca, Ex-Mg, etc.

#### 4.2.4 Analytical Methodologies

All chemical analysis were conducted in accordance with the *Technical Manual for Soil and Vegetation Monitoring in East Asia* (EANET, 2000). In each laboratory, all parameters were analyzed three times under repeatability conditions (i.e., using the same analyst, time, and instrument). The procedures were then repeated twice under within-laboratory reproducibility conditions, involving different analysts, times, and instruments.

##### 4.2.4.1 Standardization of methods

All chemical analysis procedures should be conducted in accordance with the *Technical Documents for Soil and Vegetation Monitoring in East Asia* (March 2000, adopted at the Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia). Furthermore, the following analytical procedures have been standardized:

- (1) **Atomic Absorption Spectrometry (AAS)** should be used for the analysis of Ex-Ca, Ex-Mg, Ex-K, and Ex-Na. If AAS is not available, the flame emission photometry method is acceptable for Ex-K and Ex-Na.
- (2) The **titration method** should be used for the analysis of Ex-acidity, Ex-Al, and Ex-H.
- (3) The **calibration curve method** should be used for the determination of Ex-Ca, Ex-Mg, Ex-K, and Ex-Na.
- (4) Soil samples should be extracted and diluted with **1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0)** for the analysis of Ex-Ca, Ex-Mg, Ex-K, and Ex-Na. This same 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0) solution should also be used as the solvent for preparing standard solutions.
- (5) **Sr solution** should be added to the samples and standard solutions to eliminate interference during the analysis of Ex-Ca and Ex-Mg. If Sr is not available, La may be used as an alternative.

#### 4.2.4.2 Procedures for Exchangeable Base Cations

- (1) Extract the air-dried soil sample with 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0) solution.
- (2) Pipette an appropriate aliquot of the soil extract into a volumetric flask and add 100 g-Sr L<sup>-1</sup> solution to achieve a final concentration of 1000 mg-Sr L<sup>-1</sup> (SrCl<sub>2</sub> solution helps eliminate matrix interference). Then bring to volume with 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0). This solution is referred to as the prepared sample.
- (3) Prepare three prepared samples for each soil extract.
- (4) Prepare each standard solution by diluting 1 M CH<sub>3</sub>COONH<sub>4</sub> (pH 7.0).
- (5) Add 100 g-Sr L<sup>-1</sup> solution to each standard solution to match the Sr concentration of the prepared samples.
- (6) Analyze both the standard solutions and the prepared samples using AAS.
- (7) Store the calibration curves securely and submit them along with the reporting forms.
- (8) Repeat steps 1-7 twice to assess within-laboratory reproducibility.
- (9) Calculation of Exchangeable Cation Content in Soil

The content of exchangeable base cations in the soil can be calculated using the following formulas:

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

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

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

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

Where:

*A* = Concentration of the prepared (diluted) sample (mg L<sup>-1</sup>)

*B* = Dilution factor (e.g., *B* = 2, if 25 mL is diluted to 50 mL)

$V$  = Volume of extract (mL)  
 $mcf$  = Moisture correction factor  
 $S$  = Weight of the air-dried sample (g)

#### 4.2.4.3 Procedures for Exchangeable Acidity

- (1) Perform extraction and titration in accordance with the *Technical Documents for Soil and Vegetation Monitoring in East Asia*.
- (2) Prepare three samples and analyze each along with at least one blank.
- (3) Repeat the entire procedure twice to ensure reproducibility.
- (4) Calculation of exchangeable acidity in soil

The following formulas are used to calculate the content of exchangeable acidity components in the soil:

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

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

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

Where:

$A_{\text{NaOH}}$  = Volume of 0.025 M NaOH used for sample percolate (mL)

$A_{\text{HCl}}$  = Volume of 0.02 M HCl used for sample percolate (mL)

$bl_{\text{NaOH}}$  = Volume of 0.025 M NaOH used for blank (mL)

$bl_{\text{HCl}}$  = Volume of 0.02 M HCl used for blank (mL)

$M_{\text{NaOH}}$  = Molarity of NaOH (mol L<sup>-1</sup>)

$M_{\text{HCl}}$  = Molarity of HCl (mol L<sup>-1</sup>)

$c$  = Aliquot factor (e.g.,  $c = 2$  if 50 mL out of 100 mL percolate is used)

$mcf$  = Moisture correction factor

$S$  = Weight of air-dried soil sample (g)

#### 4.2.4.4 Detection and Quantification Limits for Ex-base Cation Analysis

Starting from the 21<sup>st</sup> project, it has been recommended that detection limits and quantification limits for Ex-base cations be reported. In general, these limits are calculated as follows:

- (1) A standard solution with the lowest concentration (Std-1 [mg L<sup>-1</sup>]) should be measured at least five times, and the standard deviation (s.d.) of Std-1 should be calculated.
- (2) The detection and quantification limits are then determined using the following formulas:

$$\text{Detection limit} = 3 * \text{s.d. [mg L}^{-1}\text{]}$$

$$\text{Quantification limit} = 10 * \text{s.d. [mg L}^{-1}\text{]}$$

#### 4.2.4.5 Reporting

- (1) Report Preparation

Participating laboratories are provided with digital templates (Microsoft Excel) that include built-in formulas to automatically calculate the chemical properties of soil samples.

## (2) Report Submission

The completed templates, along with supporting information such as calibration curves, are submitted via email.

### 4.2.4.6 Data Checking Procedures

The data were statistically evaluated following the procedures described in the *Technical Manual for Soil and Vegetation Monitoring in East Asia* (approved at the 2<sup>nd</sup> ISAG, 2000). For the statistical analysis, pH values were rounded to one decimal place, and concentrations of Ex-cation and Ex-acidity were rounded to two decimal places.

#### 1) General Description of Data Variability

The Mean, median, variance and coefficient variation (CV) were calculated for the entire dataset from the inter-laboratory project. Box-and-whisker plots were also used to visually assess data variability and detect outliers.

#### 2) Outlier Detection and Preparation of Verified Datasets

Within-laboratory precision (variation within each laboratory) and inter-laboratory precision (variation among laboratories) were evaluated using Cochran and Grubbs tests, respectively. “Verified” means, medians, and other statistical summaries were then calculated from the verified datasets. In this inter-laboratory comparison project, the “verified mean” serves as a useful reference for assessing each laboratory’s analytical values.

#### 3) Analysis of Variance

Total variation among laboratories includes within-laboratory and inter-laboratory variations. As shown in the following equation, the total sum of squares ( $S_T$ ) comprises the sum of squares inter-laboratories ( $S_R$ ), the sum of squares within-laboratory ( $S_{RW}$ ), and the sum of squares repeatability ( $S_r$ ):

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

Based on this equation, variances for inter-laboratory differences, within-laboratory reproducibility, and repeatability were calculated, and analytical precision was estimated.

#### 4) Calculation of Permissible Tolerance

Permissible tolerances were calculated based on the estimated precision: 1) repeatability limit, 2) within-laboratory reproducibility limit, and 3) inter-laboratory reproducibility limit. These permissible tolerances are valuable for determining a “5% significant difference” in actual monitoring data. For example, significant temporal changes at a single site or notable differences between two laboratories can be identified if the changes or exceed the within-laboratory or inter-laboratory reproducibility limits.

## 4.3 Results

### 4.3.1 General Description of Data Variability

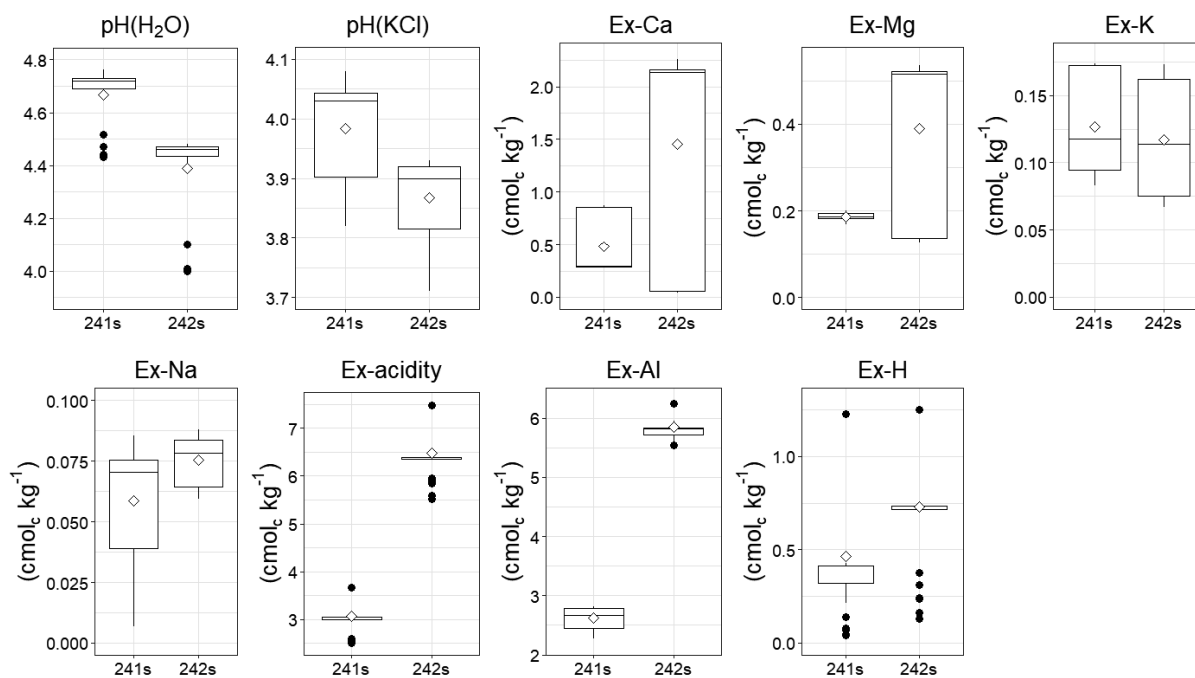
The statistical summary is presented in Table 4.2. In the 26<sup>th</sup> inter-laboratory project, sample 242s had higher concentrations of Ex-Ca, Ex-Mg, Ex-acidity, and Ex-Al than sample 241s, whereas 241s showed higher soil pH values [pH(H<sub>2</sub>O) and pH(KCl)]. We observed considerable variation in the analyzed data, with coefficients of variation (CVs) ranging from approximately 2-84% for Ex-base cations, around 10% for Ex-acidity, and 4-94% for acid cations in both samples. In contrast, the CVs for pH(H<sub>2</sub>O) and pH(KCl) were relatively low (< 4%) in both samples.

**Table 4.2 Basic statistics of the entire dataset**

Statistics	pH(H <sub>2</sub> O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
<b>No. 241s</b>									
Number of Laboratories	6	6	3	3	3	3	5	5	5
Total average	4.7	4.0	0.48	0.19	0.13	0.06	3.06	2.62	0.47
Median	4.7	4.0	0.29	0.18	0.12	0.06	3.02	2.75	0.34
Maximum	4.7	4.1	0.86	0.19	0.17	0.08	3.67	2.76	1.22
Minimum	4.4	3.8	0.29	0.18	0.09	0.04	2.54	2.40	0.10
Standard deviation	0.1	0.1	0.33	0.01	0.04	0.02	0.40	0.18	0.44
CV (%) <sup>*1</sup>	2.4	2.3	68.8	2.8	33.4	35.1	13.1	6.8	93.6
<b>No. 242s</b>									
Number of Laboratories	6	6	3	3	3	3	5	5	5
Total average	4.4	3.9	1.46	0.39	0.12	0.08	6.48	5.85	0.73
Median	4.5	3.9	2.14	0.52	0.11	0.08	6.38	5.77	0.72
Maximum	4.5	3.9	2.18	0.52	0.17	0.09	7.49	6.24	1.25
Minimum	4.1	3.7	0.05	0.13	0.07	0.06	5.78	5.69	0.24
Standard deviation	0.2	0.1	1.22	0.22	0.05	0.01	0.62	0.22	0.36
CV (%) <sup>*1</sup>	3.8	1.9	83.7	57.5	40.5	15.5	9.5	3.8	48.7

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

We also provide an overview of the data using box-and-whisker plots (Figure 4.1) for samples No.241s and 242s analyzed by 6 laboratories. Each plot displays six-number summaries: the overall mean indicated by an open diamond; the lower quartile, median, and upper quartile presented by the box and bold line; and the minimum and maximum values shown as error bars, defined as the range between the lower quartile minus 1.5 times the interquartile range and the upper quartile plus 1.5 times the interquartile range. Values outside this range are shown as outliers and are considered non-parametric outliers. Several such outliers were observed for each item. These may have resulted from calculation errors, procedural issues, or irregular contamination. Therefore, in the following section, these outliers were removed using a parametric statistical method to obtain reference values closer to the true values.



**Figure 4.1 Data variability of No.241s and No.242s**

### 4.3.2 Detection of Outliers

Detection of outliers using the Cochran-Grubbs test is summarized in Table 4.3. Laboratories showing significantly large differences in repeated analyses—identified using the Cochran test, which evaluates within-laboratory precision—were flagged as outliers. For example, a “c” mark was assigned to laboratory “VN01” for Ex-Al in sample 241s. Subsequently, the remaining data were assessed using the Grubbs test, which examines the average values reported by each laboratory. In this test, laboratories with significantly high or low average values were also identified as outliers. For instance, a “g” mark was assigned to “MN01” for pH(H<sub>2</sub>O) in sample 241s. The Cochran-Grubbs test identified several outliers across different items. After excluding these outliers, the “verified” dataset—consisting of 5-6 laboratories for pH(H<sub>2</sub>O) and pH(KCl), 3 laboratories for Ex-base cations, and 4-5 laboratories for Ex-acidity, Al, and H—was used for further analysis in the following section (Table 4.4).

**Table 4.3 Data verification by Cochran-Grubbs tests  
No. 241s**

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 kg <sup>-1</sup>		
Mongolia	MN01	1st	4.4 g	3.8	NA	NA	NA	NA	3.67	2.45	1.22
		2nd	4.4 g	3.8	NA	NA	NA	NA	3.67	2.45	1.22
Philippines	PH01	1st	4.7	3.9	0.86	0.17	0.09	0.03	2.54	2.40	0.10
		2nd	4.7	3.9	0.86	0.20	0.09	0.04	2.55	2.41	0.10
Vietnam	VN01	1st	4.7	4.1	0.29	0.19	0.12	0.07	3.02	2.74 c	0.34
		2nd	4.7	4.1	0.29	0.19	0.11	0.08	3.03	2.78 c	0.35
	VN02	1st	4.7	4.0	NA	NA	NA	NA	3.03	2.75	0.32
		2nd	4.7	4.0	NA	NA	NA	NA	3.03	2.75	0.32
	VN04	1st	4.7	4.1	0.29	0.18	0.17	0.07	3.01	2.75	0.32 c
		2nd	4.7	4.0	0.29	0.18	0.17	0.05	3.03	2.75	0.36 c
	VN05	1st	4.7	4.0	NA	NA	NA	NA	NA	NA	NA
		2nd	4.7	4.0	NA	NA	NA	NA	NA	NA	NA

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

**Table 4.3 Data verification by Cochran-Grubbs tests (continued)  
No. 242s**

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 kg <sup>-1</sup>		
Mongolia	MN01	1st	4.1 g	3.8	NA	NA	NA	NA	7.49	6.24 g	1.25
		2nd	4.0 g	3.7	NA	NA	NA	NA	7.49	6.24 g	1.25
Philippines	PH01	1st	4.4	3.8	0.04	0.13	0.07	0.06	5.78	5.70	0.24
		2nd	4.4	3.8	0.05	0.13	0.07	0.06	5.79	5.68	0.25
Vietnam	VN01	1st	4.5	3.9	2.18	0.52	0.17	0.09	6.41 c	5.77	0.74
		2nd	4.5	3.9	2.17	0.53	0.16	0.09	6.36 c	5.78	0.72
	VN02	1st	4.5	3.9	NA	NA	NA	NA	6.39	5.76	0.72
		2nd	4.5	3.9	NA	NA	NA	NA	6.39	5.76	0.72
	VN04	1st	4.5	3.9	2.14	0.51	0.12	0.08	6.38	5.75	0.71
		2nd	4.5	3.9	2.14	0.52	0.11	0.08	6.38	5.79	0.71
	VN05	1st	4.5	3.9	NA	NA	NA	NA	NA	NA	NA
		2nd	4.5	3.9	NA	NA	NA	NA	NA	NA	NA

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

### 4.3.3 Statistical Summary for Verified Data

The statistical summary for the verified datasets of samples 241s and 242s is presented in Table 4.4. This year, zero to one laboratory were excluded as outliers for each measured item, resulting in only slight changes to the overall averages. However, the data variability (CVs) for most items decreased compared to the full dataset. Nevertheless, the remaining variability is still too large for accurate comparison of regular monitoring data among participating countries. The variation may reflect errors arising from repeated measurements under the same conditions (repetition), differences in personnel, timing, or instruments within a laboratory (within-laboratory variation), or differences across laboratories (inter-laboratory variation). We will further examine these sources of variation in the next section.

**Table 4.4 Basic statistics of the verified<sup>\*2</sup> dataset**

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>						
<b>No. 241s</b>									
Number of Laboratories	5	6	3	3	3	3	5	4	4
Total average	4.7	4.0	0.48	0.19	0.13	0.06	3.06	2.59	0.50
Median	4.7	4.0	0.29	0.18	0.12	0.06	3.02	2.60	0.33
Maximum	4.7	4.1	0.86	0.19	0.17	0.08	3.67	2.75	1.22
Minimum	4.7	3.8	0.29	0.18	0.09	0.04	2.54	2.40	0.10
Standard deviation	0.0	0.1	0.33	0.01	0.04	0.02	0.40	0.19	0.50
CV (%) <sup>*1</sup>	0.5	2.3	68.8	2.8	33.4	35.1	13.1	7.2	99.8
<b>No. 242s</b>									
Number of Laboratories	5	6	3	3	3	3	4	4	5
Total average	4.5	3.9	1.46	0.39	0.12	0.08	6.51	5.75	0.73
Median	4.5	3.9	2.14	0.52	0.11	0.08	6.38	5.76	0.72
Maximum	4.5	3.9	2.18	0.52	0.17	0.09	7.49	5.78	1.25
Minimum	4.4	3.7	0.05	0.13	0.07	0.06	5.78	5.69	0.24
Standard deviation	0.0	0.1	1.22	0.22	0.05	0.01	0.71	0.04	0.36
CV (%) <sup>*1</sup>	0.4	1.9	83.7	57.5	40.5	15.5	10.9	0.7	48.7

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

\*2: Outliers determined by Cochran-Grubbs tests and obvious calculation mistakes were removed.

#### 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 high for pH(H<sub>2</sub>O) and pH(KCl), with CVs below 0.9%, indicating consistent triplicate measurements. For Ex-base cations, Ex-acidity, Ex-Al, and Ex-H, CVs were below 28%, though this level of variability suggests potential challenges in maintaining consistency across replicates. Overall, participating laboratories conducted the analyses using their own standard procedures and instruments, but improvements in repeatability for certain items may be necessary.

##### 2) Within-laboratory Precision

For all parameters except for Ex-Mg and K, the CVs for within-laboratory precision were smaller than those for repeatability precision. This suggests that the average of triplicate analyses under repeatability conditions can serve as a representative value for a laboratory’s analysis. However, the relatively high variability in Ex-Mg and K may reflect greater sensitivity to procedural inconsistencies or instrumental limitations. It is assumed that participating laboratories were able to effectively analyze the parameters using their own standard procedures.

##### 3) Inter-laboratories Precision

CVs for inter-laboratories precision were less than 3% for pH(H<sub>2</sub>O) and pH(KCl). However, for the other parameters, CVs ranged from 1 to 100%. These results indicate that, in this inter-laboratory

comparison, most of the variability in each parameter can be attributed to differences between laboratories. Possible factors contributing to the relatively high inter-laboratory CVs will be discussed in the following section.

#### 4) Calculation of Permissible Tolerance

The repeatability limit and within-laboratory reproducibility limit were sufficiently small to serve as reference values for repeated instrumental analyses within individual laboratories. Participating laboratories can detect significant temporal changes in pH at each site if the differences exceed 0.1 pH units. Furthermore, the reproducibility limit (i.e., inter-laboratory reproducibility limit) indicates that participating laboratories can detect significant differences between monitoring sites if the differences exceed approximately 0.1-0.3 for pH(H<sub>2</sub>O) and pH(KCl), 0.01-3.41 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-base cations, 2.0 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-acidity, 0.5 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-Al, and 1.39 cmol<sub>c</sub> kg<sup>-1</sup> for Ex-H.

**Table 4.5 Analysis of variance for the verified dataset**

Statistics	No. 241s								
	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	5	6	3	3	3	3	5	4	4
Total sum of square	20000	21000	75	11	5.2	1.1	8400	3900	140
ST/lmd	670	570	4.2	0.63	0.29	0.062	280	160	5.9
Number of Laboratories	5	6	3	3	3	3	5	4	4
Number of Data	30	36	18	18	18	18	30	24	24
Total sum	140	140	8.7	3.4	2.3	1.1	92	62	12
Total average	4.7	4.0	0.48	0.19	0.13	0.06	3.06	2.59	0.50
Sum of square inter-laboratories (S <sub>R</sub> )	0.0	0.3	1.31	0.00	0.02	0.01	3.87	0.62	4.44
Sum of square within-laboratory (S <sub>RW</sub> )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of square repeatability (S <sub>r</sub> )	0.0	0.0	0.00	0.00	0.00	0.00	0.02	0.07	0.03
Total sum of square (S <sub>T</sub> )	0.0	0.3	1.31	0.00	0.02	0.01	3.88	0.69	4.47
Inter-laboratories degree of freedom (φ <sub>R</sub> )	4	5	2	2	2	2	4	3	3
Within-laboratory degree of freedom (φ <sub>RW</sub> )	5	6	3	3	3	3	5	4	4
Repeatability degree of freedom (φ <sub>r</sub> )	20	24	12	12	12	12	20	16	16
Total degree of freedom (φ <sub>T</sub> )	29	35	17	17	17	17	29	23	23
Inter-laboratories variance (V <sub>R</sub> = S <sub>R</sub> /φ <sub>R</sub> )	0.0	0.1	0.66	0.00	0.01	0.00	0.97	0.21	1.48
Within-laboratory variance (V <sub>RW</sub> = S <sub>RW</sub> /φ <sub>RW</sub> )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability variance (V <sub>r</sub> = S <sub>r</sub> /φ <sub>r</sub> )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Laboratory component of variance (s <sub>b</sub> <sup>2</sup> = (V <sub>R</sub> -V <sub>RW</sub> )/(2×3))	0.0	0.0	0.11	0.00	0.00	0.00	0.16	0.03	0.25
Within-laboratory component of variance (s <sub>c</sub> <sup>2</sup> = (V <sub>RW</sub> -V <sub>r</sub> )/3)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability component of variance (s <sub>r</sub> <sup>2</sup> = V <sub>r</sub> )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Inter-laboratories standard deviation (s <sub>R</sub> = SQRT(s <sub>r</sub> <sup>2</sup> /(2×3) + s <sub>c</sub> <sup>2</sup> /2 + s <sub>b</sub> <sup>2</sup> ))	0.0	0.1	0.33	0.01	0.04	0.02	0.40	0.19	0.50
Within-laboratory standard deviation (s <sub>RW</sub> = SQRT(s <sub>r</sub> <sup>2</sup> /3 + s <sub>c</sub> <sup>2</sup> ))	0.0	0.0	0.00	0.01	0.00	0.01	0.01	0.00	0.00
Repeatability standard deviation (s <sub>r</sub> = SQRT(s <sub>r</sub> <sup>2</sup> ))	0.0	0.0	0.00	0.01	0.00	0.02	0.03	0.07	0.04
Inter-laboratories precision CV (%)	0.5	2.3	68.78	2.79	33.44	35.10	13.12	7.17	99.82
Within-laboratory precision CV (%)	0.1	0.2	0.91	4.81	3.75	14.83	0.27	0.18	0.73
Repeatability precision CV (%)	0.9	0.3	0.89	2.78	1.61	28.04	0.96	2.63	8.00
Reproducibility limit (R = D(2, 0.95)×s <sub>R</sub> )	0.1	0.3	0.93	0.01	0.12	0.06	1.12	0.52	1.39
Within-laboratory-reproducibility limit (R <sub>w</sub> = D(2, 0.95)×s <sub>RW</sub> )	0.0	0.0	0.01	0.03	0.01	0.02	0.02	0.01	0.01
Repeatability limit (r = D(3, 0.95)×s <sub>r</sub> )	0.1	0.0	0.01	0.02	0.01	0.05	0.10	0.22	0.13

**Table 4.5 Analysis of variance for the verified dataset (continued)**

Statistics	No. 242s								
	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	5	6	3	3	3	3	4	4	5
Total sum of square	18000	19000	690	49	4.4	1.8	24000	19000	480
ST/lmd	600	540	38	2.7	0.25	0.10	1000	790	16
Number of Laboratories	5	6	3	3	3	3	4	4	5
Number of Data	30	36	18	18	18	18	24	24	30
Total sum	130	140	26	7.0	2.1	1.4	160	140	22
Total average	4.5	3.9	1.46	0.39	0.12	0.08	6.51	5.75	0.73
Sum of square inter-laboratories ( $S_R$ )	0.0	0.2	17.81	0.61	0.03	0.00	9.08	0.03	3.04
Sum of square within-laboratory ( $S_{RW}$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum of square repeatability ( $S_r$ )	0.0	0.0	0.04	0.00	0.00	0.00	0.16	0.18	0.04
Total sum of square ( $S_T$ )	0.0	0.2	17.85	0.61	0.03	0.00	9.25	0.21	3.08
Inter-laboratories degree of freedom ( $\phi_R$ )	4	5	2	2	2	2	3	3	4
Within-laboratory degree of freedom ( $\phi_{RW}$ )	5	6	3	3	3	3	4	4	5
Repeatability degree of freedom ( $\phi_r$ )	20	24	12	12	12	12	16	16	20
Total degree of freedom ( $\phi_T$ )	29	35	17	17	17	17	23	23	29
Inter-laboratories variance ( $V_R = S_R/\phi_R$ )	0.0	0.0	8.90	0.30	0.01	0.00	3.03	0.01	0.76
Within-laboratory variance ( $V_{RW} = S_{RW}/\phi_{RW}$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability variance ( $V_r = S_r/\phi_r$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Laboratory component of variance ( $s_b^2 = (V_R - V_{RW})/(2 \times 3)$ )	0.0	0.0	1.48	0.05	0.00	0.00	0.50	0.00	0.13
Within-laboratory component of variance ( $s_c^2 = (V_{RW} - V_r)/3$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repeatability component of variance ( $s_r^2 = V_r$ )	0.0	0.0	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Inter-laboratories standard deviation ( $s_R = \text{SQRT}(s_b^2/(2 \times 3) + s_c^2/2 + s_r^2)$ )	0.0	0.1	1.22	0.22	0.05	0.01	0.71	0.04	0.36
Within-laboratory standard deviation ( $s_{RW} = \text{SQRT}(s_r^2/3 + s_c^2)$ )	0.0	0.0	0.01	0.01	0.00	0.00	0.00	0.02	0.01
Repeatability standard deviation ( $s_r = \text{SQRT}(s_r^2)$ )	0.0	0.0	0.06	0.01	0.00	0.00	0.10	0.10	0.05
Inter-laboratories precision CV (%)	0.4	1.9	83.70	57.48	40.47	15.52	10.91	0.67	48.73
Within-laboratory precision CV (%)	0.2	0.4	0.46	1.59	3.59	1.63	0.06	0.27	0.70
Repeatability precision CV (%)	0.2	0.2	3.90	1.32	1.89	2.38	1.56	1.82	6.25
Reproducibility limit ( $R = D(2, 0.95) \times s_R$ )	0.0	0.2	3.41	0.63	0.13	0.03	1.99	0.11	1.00
Within-laboratory-reproducibility limit ( $R_w = D(2, 0.95) \times s_{RW}$ )	0.0	0.0	0.02	0.02	0.01	0.00	0.01	0.04	0.01
Repeatability limit ( $r = D(3, 0.95) \times s_r$ )	0.0	0.0	0.19	0.02	0.01	0.01	0.33	0.35	0.15

### 4.3.5 Inter-laboratory Variations in Each Parameter

To assess precision for each laboratory and property, scatter plots comparing samples 241s and 242s are presented in Figure 4.2. Extreme outliers have been removed to improve readability.

#### 1) pH

A linear and positive correlation was observed between samples 241s and 242s for pH(KCl), suggesting the presence of systematic errors in inter-laboratory variation. These errors may result from factors such as the purity of water, standard solutions, or the condition of the glass electrode. In addition, factors affecting stabilization time—such as carbon dioxide pressure, leakage of KCl solution from the electrode, and settling of clay particles in the sample tube—could influence ion balance in the soil suspension and contribute to variation. For pH(H<sub>2</sub>O), the limited number of participating laboratories may have affected the clarity of the observed relationships.

#### 2) Base Cations

Due to the limited number of participating laboratories this year, no significant correlations were observed for exchangeable base cations. No laboratory was excluded from the analysis because only three laboratories participated—fewer than the minimum required to apply the Cochran-Grubbs test. To improve analytical precision, analysts should pay attention to factors such as the purity of water, standard

solutions, and other procedural details. In the analysis of base cations, higher concentrations or higher pH levels of the extraction solution may lead to increased base cation concentrations. It is important to prepare appropriate standard solutions that span a wide range of concentrations—from low to high—to fully cover the range of unknown sample concentrations and reduce potential errors. Using the same extraction solution to dilute the standards can also help minimize matrix effects.

### 3) Acidity

Weak but positive linear correlations were observed for Ex-acidity and Ex-H. To minimize errors, analysts should pay attention to titration procedures, which can be easily affected by factors such as the accuracy of volumetric solutions and end-point detection. By definition, Ex-acidity is the sum of Ex-Al and Ex-H. It is strongly recommended to verify that each parameter falls within the expected range of this relationship before submitting results.

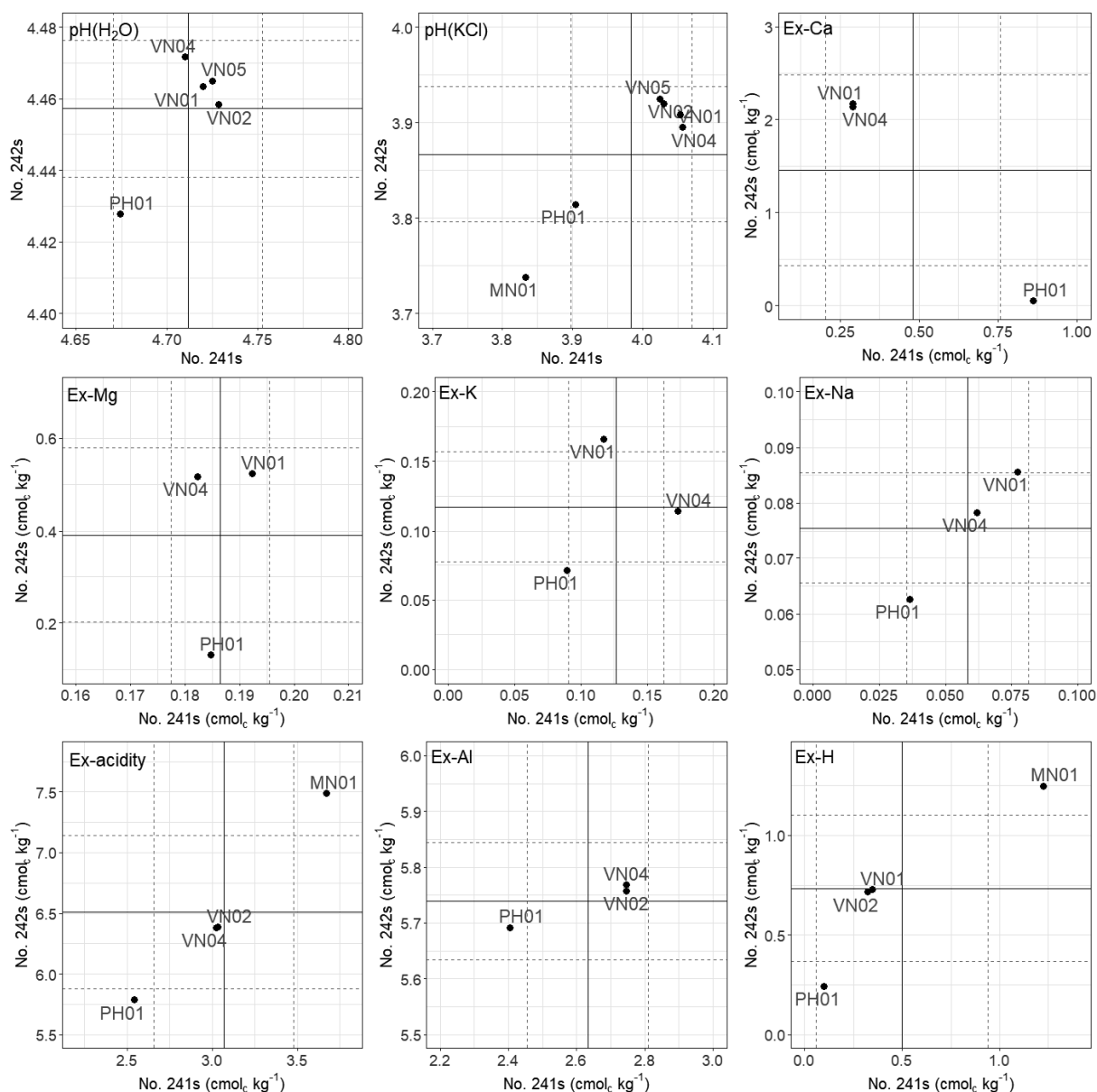


Figure 4.2 Scatter plots of each soil chemical property between No.241s and No.242s

Solid and dotted lines indicate mean and mean  $\pm$  S.D. of verified datasets, respectively.  
The outliers are excluded from the plots.

#### 4.3.6 Comparison with Information on Laboratories

##### 1) Number of Analysts and Their Experience

Table 4.6 presents the number of analysts and their years of experience. Specialization in analytical tasks—where different analysts are assigned depending on the type of analysis—is becoming common. No clear relationship was found between the number of analysts, their years of experience, and the occurrence of outliers.

**Table 4.6 Number of analyst and years of experience**

Lab.	Ex-base cations			Ex-acidity			Analyst
	Number of analyst	Years of experience		Number of analyst	Years of experience		
		Chemical	Soil		Chemical	Soil	
MN01	-	-	-	1	20	13	-
PH01	1	5	5	2	3, 1	3, 1	d
VN01	1	11	11	1	8	8	d
VN02	-	-	-	1	20	16	-
VN04	1	18	17	1	19	18	d
VN05	-	-	-	-	-	-	-

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

##### 2) Analytical Instruments and Condition of Instruments

Table 4.7 presents the analytical instruments used for measurement, the extraction procedures for Ex-base cations, and the burette sizes used in the titration method for Ex-acidity. Ex-base cations were analyzed using either AAS or ICP-AES/OES. These instruments have been in use for 11 to 17 years. For extraction procedures, two laboratories used the Buchner funnel method, while one used a centrifugation method. No significant differences were observed among these procedures. Regarding burette sizes used for the titration of Ex-acidity, capacities ranged from 10 to 25 mL, with minimum graduations varying from 0.01 to 0.1 mL.

##### 3) Date of Analysis

Table 4.8 presents the dates of analysis conducted at each laboratory and the number of days required for the analysis. No significant correlation was found between the analysis date and the analytical results. The duration of analysis ranged from 1 to 18 days, and the interval between the first and second measurements in repeat analyses varied from 0 days (same day) to 20 days. To accurately estimate within-laboratory reproducibility, it is recommended that repeat analyses be conducted at intervals of several days (preferably three days or more). This recommendation is based on discussions held at SAC 3 (the Third Session of the Scientific Advisory Committee on EANET).

**Table 4.7 Analytical instruments and their conditions for Ex- cations**

Lab.	Sample	Procedures for extraction of Ex-base cations		Ex-Ca		Ex-Mg		Interference depressant for Ca and Mg		Ex-K		Ex-Na		Interference depressant for K and Na		Ex-Acidity, Al and H	
		Instrument	Years <sup>*1</sup>	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years	method	Capacity
MN01	241s 242s														Titration	25	0.1
PH01	241s 242s	Centrifuge	ICP-AES ICP-AES	11 11	ICP-AES ICP-AES	11 11	na na	ICP-AES ICP-AES	11 11	ICP-AES ICP-AES	11 11	na na	ICP-AES ICP-AES	11 11	Titration	25	0.03, 0.05
VN01	241s 242s	Buchner funnel	AAS AAS	17 17	AAS AAS	17 17	+ +	AAS AAS	17 17	AAS AAS	17 17	+ +	AAS AAS	17 17	Titration	10	0.05
VN02	241s 242s														Titration	10	0.05
VN04	241s 242s	Buchner funnel	AAS AAS	18 18	AAS AAS	18 18	na na	AAS AAS	18 18	AAS AAS	18 18	na na	AAS AAS	17 17	Titration	10	0.01
VN05	241s 242s														Titration	10	0.01

\*1, years in use of instrument; -, not measured; AAS, Atomic Absorption Spectrometry; ICP-AES, Inductively Coupled Plasma-Atomic Emission Spectrometry; na, not added; +, not reported.

**Table 4.8 Date of analysis**

Lab.	Repeat	pH			Ex-Ca and Mg			Ex-K and Na			Ex-acidity, Al and H					
		Start Date	Finish Date	AD ID Days	Start Date	Finish Date	AD ID Days	Start Date	Finish Date	AD ID Days	Start Date	Finish Date	AD ID Days			
MN01	1st 2nd	2025/1/27 2025/1/27	2025/1/31 2025/1/31	5 5	0 0	NA	NA	NA	NA	NA	2025/1/27 2025/1/27	2025/1/31 2025/1/31	5 5	0 0		
PH01	1st 2nd	2025/2/18 2025/3/10	2025/2/18 2025/3/10	1 1	20 1	2025/3/12 2025/3/17	2025/3/12 2025/3/17	1 1	5 1	2025/3/12 2025/3/17	2025/3/12 2025/3/17	1 1	5 1	2025/3/25 2025/4/7	16 18	
VN01	1st 2nd	2025/1/15 2025/1/17	2025/1/15 2025/1/17	1 1	2 1	2025/1/14 2025/1/16	2025/1/15 2025/1/17	2 2	2 2	2025/1/14 2025/1/16	2025/1/15 2025/1/17	2 2	2 2	2025/1/16 2025/1/17	2 2	1 1
VN02	1st 2nd	2025/1/15 2025/1/16	2025/1/15 2025/1/16	1 1	1 1	NA	NA	NA	NA	NA	2025/1/15 2025/1/16	2025/1/15 2025/1/16	1 1	1 1	2025/1/15 2025/1/16	1 1
VN04	1st 2nd	2025/1/1 2025/1/3	2025/1/1 2025/1/3	1 1	2 1	2025/1/1 2025/1/3	2025/1/1 2025/1/3	1 1	2 1	2025/1/1 2025/1/3	2025/1/1 2025/1/3	1 1	2 1	2025/1/1 2025/1/3	1 1	2 1
VN05	1st 2nd	2025/2/19 2025/2/19	2025/2/19 2025/2/19	1 1	0 0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

AD, days for analysis; ID; interval between the repeat analyses; +, not reported; NA, not analyzed.

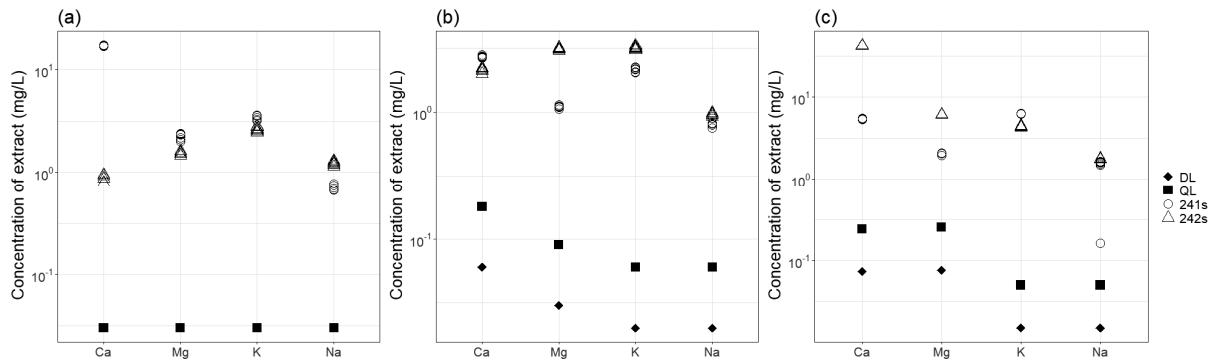
### 4.3.7 Detection Limit and Quantification Limit

Since the 21<sup>st</sup> project, reporting the detection and quantification limits for Ex-base cations has been required. All laboratories that analyzed Ex-base cations submitted these values (Table 4.9). The detection limits for Ex-Ca, Ex-Mg, Ex-K, and Ex-Na ranged from 0.03 to 0.073 mg/L, 0.03 to 0.076 mg/L, 0.015 to 0.03 mg/L, and 0.015 to 0.03 mg/L, respectively. Similarly, the quantification limits for Ex-Ca, Ex-Mg, Ex-K, and Ex-Na ranged from 0.18 to 0.242 mg/L, 0.03 to 0.254 mg/L, 0.03 to 0.06 mg/L, and 0.03 to 0.06 mg/L, respectively. Figure 4.3 compares these limit values with the measured concentrations in the soil extracts. For almost all analytes and laboratories—except for Na in VN04—the concentrations exceeded the quantification limits by at least one order of magnitude, indicating that the analyses of Ex-base cations were conducted with a sufficient margin of capacity.

**Table 4.9 Detection limit and quantification limit of each laboratory**

Lab.	Ex-Ca			Ex-Mg			Ex-K			Ex-Na		
	DL	QL	unit	DL	QL	unit	DL	QL	unit	DL	QL	unit
MN01	-	-	-	-	-	-	-	-	-	-	-	-
PH01	0.03	0.03	mg/L	0.03	0.03	mg/L	0.03	0.03	mg/L	0.03	0.03	mg/L
VN01	0.06	0.18	mg/L	0.03	0.09	mg/L	0.02	0.06	mg/L	0.02	0.06	mg/L
VN02	-	-	-	-	-	-	-	-	-	-	-	-
VN04	0.073	0.242	mg/L	0.076	0.254	mg/L	0.015	0.05	mg/L	0.015	0.05	mg/L
VN05	-	-	-	-	-	-	-	-	-	-	-	-

DL, detection limit; QL, quantification limit; -, not reported or not analyzed.



**Figure 4.3 Detection limit, quantification limit and concentrations of soil extracts**

(a) PH01, (b) VN01, (c) VN04

DL, detection limit; QL, quantification limit

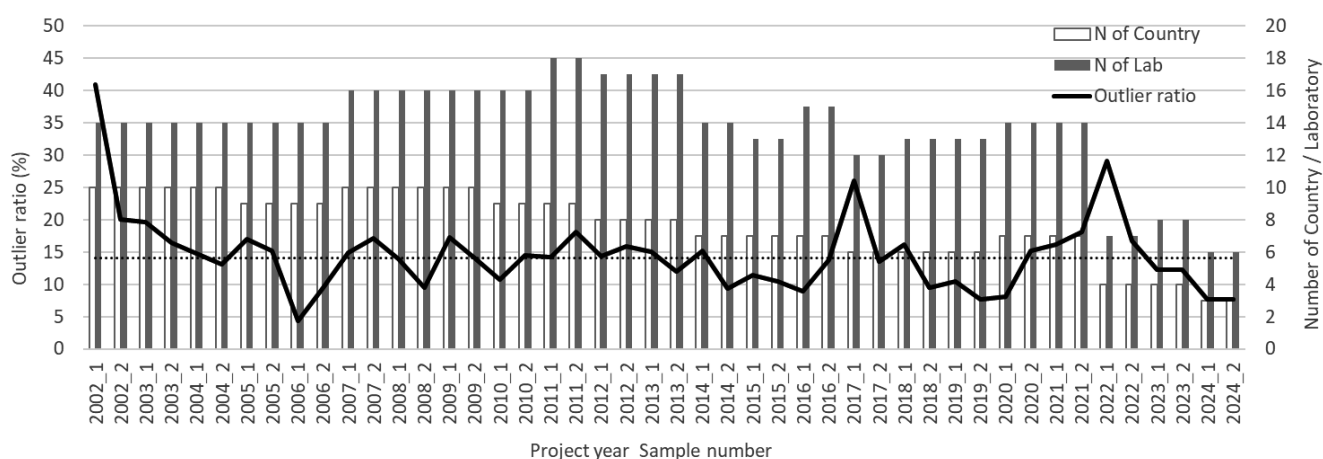
## 4.4 Needs for Improvement of Soil Analyses

Figure 4.4 illustrates the changes in the number of participating countries and laboratories, as well as the outlier ratios for all items and laboratories, from 2002 to 2024. The number of participants peaked in the late 2000s to early 2010s, with up to 10 countries and 18 laboratories involved. However, in 2024, participation dropped to only three countries and six laboratories, reducing the project's scale to one-third of its peak.

Although the outlier ratio has decreased since the initial experiment in 2002, it has remained relatively

high (10-25%) between 2003 and 2024. In 2024, the outlier ratios for both samples 241s and 242s (i.e., 2024\_1 and 2024\_2, respectively) were lower than the average outlier ratio from 2003 to 2023. Nevertheless, the reduced number of participating laboratories—fewer than the minimum required number for statistical assessments—poses increasing challenges in sustaining the evaluation framework of the ILC Soil project.

Outliers can distort the evaluation and interpretation of actual monitoring data. Therefore, reducing the occurrence of outliers remains a key objective for future inter-laboratory comparison projects on soil. To minimize the presence of extreme values identified as outliers, it is essential to review and improve the use of standard solutions, extraction methods, dilution procedures, and calculations.



**Figure 4.4 Change in outlier ratios in all items and laboratories from 2002 to 2024.**

$$\text{Outlier ratio} = \{(N \text{ of entire dataset}) - (N \text{ of verified dataset})\} / (N \text{ of entire dataset}).$$

The suffixes ‘\_1’ and ‘\_2’ denote the two types of the samples analyzed each year (e.g., 241s and 242s).

Outlier ratios from 2002 to 2023 were obtained from the *Report of Inter-Laboratory Comparison Project 2000-2023* (<https://monitoring.eanet.asia/document/public/index>).

The dotted line indicates the average outlier ratio from 2003 to 2023.

#### 4.5 Recommendations for improvement

Priority should be given to reducing outliers in the analysis of Ex-base and acid cations. In addition, efforts should be made to improve precision, particularly for samples with low concentrations. This requires careful evaluation of standard solutions, extraction methods, dilution rates, calculation procedures, and instrument operation. Analysts should work toward enhancing procedural consistency within each laboratory. It is also essential to thoroughly review not only analytical procedures but also data reporting practices.

#### References

EANET (2000). *Technical Documents for Soil and Vegetation Monitoring in East Asia: Acid Deposition and Oxidant Research Center*, Niigata, Japan.

**Appendix Table 4.1 Results submitted by the laboratories (sample No. 241s)**

Lab	pH(H <sub>2</sub> O)			pH(KCl)			Ex-Ca (nmol kg <sup>-1</sup> )			Ex-Mg (nmol kg <sup>-1</sup> )			Ex-K (nmol kg <sup>-1</sup> )			Ex-Na (nmol kg <sup>-1</sup> )			Ex-Acidity (nmol kg <sup>-1</sup> )			Ex-Al (nmol kg <sup>-1</sup> )			Ex-H (nmol 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			
	4.4 (0.0)	4.4 (0.0)	4.4 (0.0)	3.8 (0.0)	3.8 (0.0)	3.9 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		
MN01	4.4 (0.0)	4.4 (0.0)	4.4 (0.0)	3.8 (0.0)	3.8 (0.0)	3.9 (0.0)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		
PH01	4.7 (0.1)	4.7 (0.1)	4.5 (0.0)	3.9 (0.0)	3.9 (0.0)	3.9 (0.0)	0.86 (0.01)	0.86 (0.01)	0.86 (0.01)	0.17 (0.01)	0.17 (0.01)	0.17 (0.01)	0.09 (0.01)	0.09 (0.01)	0.09 (0.01)	0.04 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	
VN01	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.29 (0.01)	0.29 (0.01)	0.29 (0.01)	0.19 (0.00)	0.19 (0.00)	0.19 (0.00)	0.12 (0.00)	0.12 (0.00)	0.12 (0.00)	0.08 (0.01)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	
VN02	4.7 (0.0)	4.7 (0.0)	4.7 (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	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
VN04	4.7 (0.0)	4.7 (0.0)	4.7 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.29 (0.00)	0.29 (0.00)	0.29 (0.00)	0.18 (0.01)	0.18 (0.01)	0.18 (0.01)	0.17 (0.00)	0.17 (0.00)	0.17 (0.00)	0.06 (0.03)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	
VN05	4.7 (0.0)	4.7 (0.0)	4.7 (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	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

**Appendix Table 4.2 Results submitted by the laboratories (sample No. 242s)**

Lab	pH(H <sub>2</sub> O)			pH(KCl)			Ex-Ca (nmol kg <sup>-1</sup> )			Ex-Mg (nmol kg <sup>-1</sup> )			Ex-K (nmol kg <sup>-1</sup> )			Ex-Na (nmol kg <sup>-1</sup> )			Ex-Acidity (nmol kg <sup>-1</sup> )			Ex-Al (nmol kg <sup>-1</sup> )			Ex-H (nmol 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
	(0.1)	(0.1)	4.1	3.7	3.8	3.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
MN01	4.1 (0.1)	4.1 (0.1)	4.1	3.7 (0.0)	3.8 (0.0)	3.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PH01	4.4 (0.0)	4.4 (0.0)	4.4	3.8 (0.0)	3.8 (0.01)	3.8	0.05 (0.01)	0.04 (0.00)	0.04 (0.00)	0.13 (0.00)	0.13 (0.00)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.08 (0.00)	0.06 (0.00)	0.06 (0.18)	0.06 (0.17)	5.78 (0.17)	5.78 (0.21)	5.60 (0.21)	5.60 (0.09)	5.60 (0.09)	5.60 (0.09)	5.70 (0.09)	5.70 (0.09)	5.95 (0.09)
	4.4 (0.0)	4.4 (0.0)	4.4	3.8 (0.0)	3.8	3.8	0.05	0.05	0.05	0.13	0.14	0.08	0.08	0.08	0.06	0.06	0.07	0.07	5.79 (0.24)	5.79 (0.15)	5.95 (0.15)	5.95 (0.12)	5.95 (0.12)	5.95 (0.12)	5.68 (0.12)	5.68 (0.12)	5.84 (0.12)
VN01	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9 (0.09)	3.9	2.18 (0.09)	2.22 (0.04)	2.18 (0.04)	0.51 (0.01)	0.52 (0.01)	0.17 (0.00)	0.17 (0.00)	0.17 (0.00)	0.17 (0.00)	0.09 (0.00)	0.09 (0.04)	0.09 (0.05)	6.38 (0.04)	6.44 (0.05)	6.44 (0.05)	6.44 (0.02)	6.44 (0.02)	6.44 (0.02)	5.77 (0.05)	5.77 (0.05)	5.76 (0.05)
	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9	3.9	2.14	2.22	2.14	0.53 (0.01)	0.53 (0.01)	0.16 (0.00)	0.16 (0.00)	0.16 (0.00)	0.09 (0.00)	0.09 (0.00)	0.09 (0.03)	0.09 (0.03)	6.36 (0.03)	6.36 (0.03)	6.39 (0.03)	6.39 (0.02)	6.39 (0.02)	6.39 (0.02)	5.78 (0.05)	5.78 (0.05)	5.82 (0.05)
VN02	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9	3.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	6.39 (0.00)	6.39 (0.05)	6.39 (0.05)	6.39 (0.00)	6.39 (0.00)	6.39 (0.00)	5.76 (0.06)	5.76 (0.06)	5.72 (0.06)
	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9	3.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	6.39 (0.00)	6.39 (0.05)	6.39 (0.05)	6.39 (0.00)	6.39 (0.00)	6.39 (0.00)	5.76 (0.06)	5.76 (0.06)	5.72 (0.06)
VN04	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9 (0.01)	3.9	2.14 (0.01)	2.14 (0.02)	2.14 (0.02)	0.51 (0.00)	0.51 (0.00)	0.12 (0.00)	0.12 (0.00)	0.12 (0.00)	0.12 (0.00)	0.08 (0.00)	0.08 (0.00)	0.08 (0.06)	6.38 (0.00)	6.38 (0.06)	6.38 (0.06)	6.38 (0.00)	6.38 (0.00)	6.38 (0.00)	5.75 (0.06)	5.75 (0.06)	5.72 (0.06)
	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9	3.9	2.14	2.14	2.13	0.52	0.52	0.12	0.12	0.12	0.08	0.08	0.08	0.08	6.38 (0.00)	6.38 (0.06)	6.38 (0.06)	6.38 (0.00)	6.38 (0.00)	6.38 (0.00)	5.72 (0.06)	5.72 (0.06)	5.72 (0.06)
VN05	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9	3.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	6.38 (0.00)	6.38 (0.06)	6.38 (0.06)	6.38 (0.00)	6.38 (0.00)	6.38 (0.00)	5.82 (0.06)	5.82 (0.06)	5.82 (0.06)
	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9	3.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	6.38 (0.00)	6.38 (0.06)	6.38 (0.06)	6.38 (0.00)	6.38 (0.00)	6.38 (0.00)	5.82 (0.06)	5.82 (0.06)	5.82 (0.06)

## 5. 25<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 25<sup>th</sup> Project, the NC shipped an artificial inland water sample to 19 laboratories involved in the EANET activities on December 2, 2024, and most of them submitted their analytical data to the NC by February 28 2025. Participating laboratories and their identification codes are listed in Table 1.1.

#### 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 1 L	Poly-ethylene bottle 1 L	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>	0.1 – 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 pH 4.8)
SO <sub>4</sub> <sup>2-</sup> NO <sub>3</sub> <sup>-</sup>	Ion Chromatography or Spectrophotometry
Cl <sup>-</sup>	Ion Chromatography or Titration
Na <sup>+</sup> K <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup>	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH <sub>4</sub> <sup>+</sup>	Ion Chromatography or Spectrophotometry (Indophenol blue)

#### 5.2.4 Data Checking Procedures

##### a) Calculation of ion balance ( $R_1$ )

(1) Total anion equivalent concentration ( $A$  [ $\mu\text{eq L}^{-1}$ ]) was calculated by summing the concentrations of all anions ( $c$  [ $\mu\text{mol L}^{-1}$ ]) and alkalinity ( $ALK$ :  $\mu\text{eq L}^{-1}$ ). Alkalinity was considered to be corresponded to bicarbonate ions ( $\text{HCO}_3^-$ ).

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

$n, c_{\text{Ai}}$ : electric charge and concentration [ $\mu\text{mol L}^{-1}$ ] of anion "i".

(2) Total cation equivalent concentration ( $C$  [ $\mu\text{eq L}^{-1}$ ]) was calculated by summing the concentrations of all cations ( $c$  [ $\mu\text{mol L}^{-1}$ ]).

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

$n, c_{\text{Ci}}$ : electric charge 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 allowable ranges 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;

$$A_{\text{calc}} (\text{mS m}^{-1}) = \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2C (\text{SO}_4^{2-}) + 71.4 \times C (\text{NO}_3^-) + 76.3 \times C (\text{Cl}^-) + 73.5 \times C (\text{NH}_4^+) + 50.1 \times C (\text{Na}^+) + 73.5 \times C (\text{K}^+) + 59.8 \times 2C (\text{Ca}^{2+}) + 53.0 \times 2C (\text{Mg}^{2+}) + 44.5 \times (ALK)\} / 10000$$

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

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

$A_{\text{meas}}$  : measured conductivity

(3)  $R_2$ , which is calculated using the above equation, is compared with allowable ranges 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

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. Original data from the laboratories are shown in Table 5.10 and APPENDIX table 5.1.

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

Constituents	Prepared	Average	S.D.	N	Min.	Max.
pH	7.04	6.92	0.29	17	6.11	7.24
EC (mS m <sup>-1</sup> )	3.84	3.73	0.16	17	3.40	3.97
Alkalinity (meq L <sup>-1</sup> )	0.126	0.130	0.01	16	0.113	0.141
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	4.22	4.23	0.19	15	3.98	4.82
NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	0.61	0.61	0.04	16	0.56	0.70
Cl <sup>-</sup> (mg L <sup>-1</sup> )	3.50	3.49	0.14	16	3.29	3.89
Na <sup>+</sup> (mg L <sup>-1</sup> )	4.20	4.14	0.19	16	3.78	4.54
K <sup>+</sup> (mg L <sup>-1</sup> )	0.47	0.47	0.04	15	0.40	0.55
Ca <sup>2+</sup> (mg L <sup>-1</sup> )	1.42	1.45	0.15	16	1.23	1.71
Mg <sup>2+</sup> (mg L <sup>-1</sup> )	0.46	0.47	0.03	16	0.41	0.52
NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	0.30	0.29	0.02	16	0.26	0.32

(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  $\pm 30\%$ .

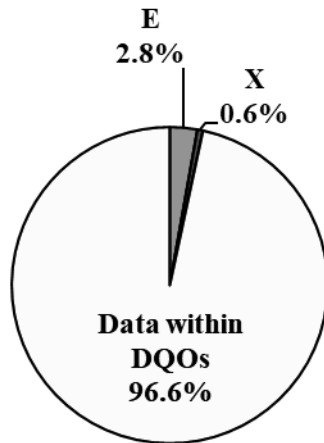
Table 5.8 shows the number of flagged data for each parameter and Figure 5.1 shows the percentage of flagged data.

**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	0	1	1	0	0	1	2	0	0	5	2.8%
X	0	0	0	0	0	0	0	1	0	0	0	1	0.6%
Data within DQOs	17	17	16	15	15	16	16	14	14	16	16	172	96.6%
Flagged(%)	0.0	0.0	0.0	6.3	6.3	0.0	0.0	12.5	12.5	0.0	0.0	3.4	

Flag E: 15% < |Deviation| ≤ 30%

Flag X: 30% < |Deviation|



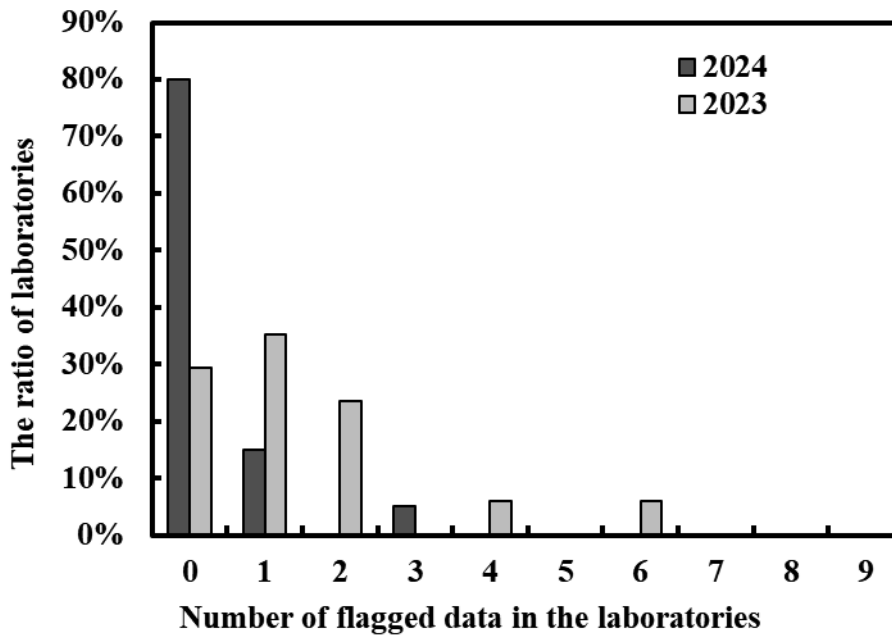
**Figure 5.1 Percentage of flagged data**

The data flagged by "E" shared 2.8% of all reported data, and the data flagged by "X" shared 0.6% of all reported data of samples. The K<sup>+</sup> and Ca<sup>2+</sup> results were flagged most (E and X), and their percentage was 12.5%.

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	16	80%
1	3	15%
2	0	0%
3	1	5%
4	0	0%
5	0	0%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	20	100%



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

The percentage of the laboratories without flagged data was 80% in this attempt, while that in the last attempt (2023) was 29%. The maximum number of flagged data was three, 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.241i (artificial inland aquatic environment sample : EANET in 2024)**

Lab. ID	pH	EC mS m <sup>-1</sup>	Alkalinity meq L <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> mg L <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> mg L <sup>-1</sup>	Cl <sup>-</sup> mg L <sup>-1</sup>	Na <sup>+</sup> mg L <sup>-1</sup>	K <sup>+</sup> mg L <sup>-1</sup>	Ca <sup>2+</sup> mg L <sup>-1</sup>	Mg <sup>2+</sup> mg L <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> mg L <sup>-1</sup>	R1 %	R2 %
CN01	7.03	3.64	0.130	4.21	0.59	3.50	4.29	0.47	1.28	0.43	0.27	-2.01	2.27
CN02	6.95	3.77	0.137	4.17	0.61	3.35	4.05	0.44	1.58	0.47	0.28	-1.18	1.14
CN03	6.98	3.68	0.137	4.27	0.60	3.51	4.08	0.42	1.71 E	0.50	0.30	-0.40	3.75
CN04	6.34	3.85	0.139	4.16	0.56	3.46	3.91	0.40	1.68 E	0.48	0.28	-1.88	0.55
JP03	7.10	3.70	0.136	4.34	0.65	3.66	3.78	0.47	1.37	0.44	0.26	-6.94	1.44
JP04	6.99	3.73	0.130	4.22	0.62	3.49	4.09	0.47	1.46	0.47	0.26	-1.56	1.38
MY01	7.24	3.56	0.133	4.37	0.59	3.56	4.27	0.46	1.49	0.46	0.30	-1.19	5.06
MN01	7.09	3.72	0.124	4.82	0.70	3.89	4.54	0.52	1.61	0.48	0.26	-0.01	5.63
PH01	7.07	3.90	0.121	4.14	0.59	3.44	4.45	0.46	1.46	0.46	0.27	2.70	-0.81
PH02	7.00	3.73	0.141	3.18 E	0.70 E	3.29	4.15	0.27 X	1.23	0.49	0.27	-1.08	-1.78
TH01	7.14	3.40	0.140										
TH02	6.11	3.52	0.113	4.20	0.59	3.49	4.18	0.45	1.25	0.41	0.26	-0.73	2.53
VN01	6.88	3.85	0.126	4.19	0.60	3.45	4.05	0.46	1.34	0.48	0.32	-1.32	-0.91
VN02	6.98	3.90	0.125	4.19	0.62	3.51	4.08	0.47	1.38	0.48	0.32	-0.75	-1.07
VN03	7.01	3.94	0.130	4.03	0.60	3.41	4.23	0.55 E	1.58	0.52	0.32	2.66	-0.37
VN04	6.70	3.61	0.126	4.19	0.57	3.39	4.01	0.47	1.30	0.48	0.32	-1.48	1.89
VN05	7.00	3.97	0.126	3.98	0.57	3.51	4.10	0.48	1.53	0.47	0.32		
Expected value	7.04	3.84	0.126	4.22	0.61	3.50	4.20	0.47	1.42	0.46	0.30	-	-

Flag E: 15% < |Deviation| ≤ 30%

Flag X: 30% < |Deviation|

I: Poor ion balance (R1)

C: Rich Conductivity agreement (R2)

blank: not analyzed

### 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.

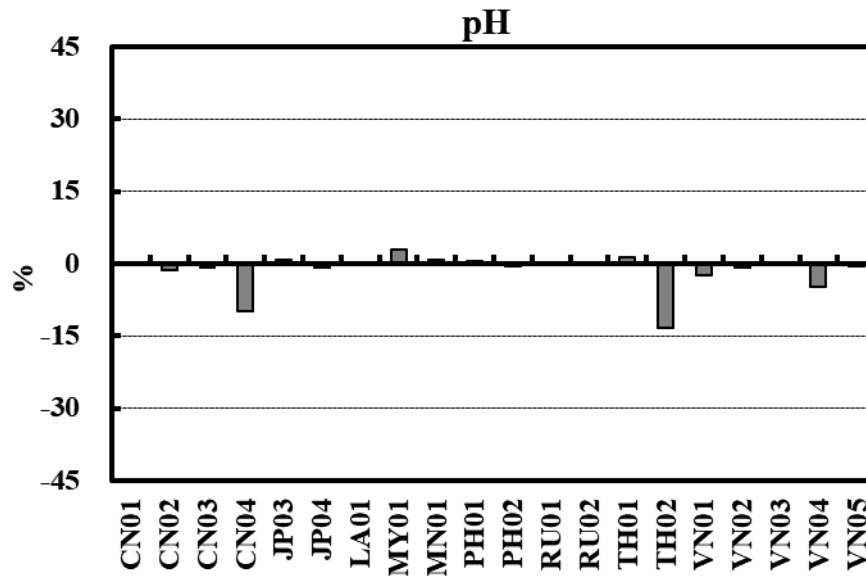


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

All the submitted data of pH were within DQOs.

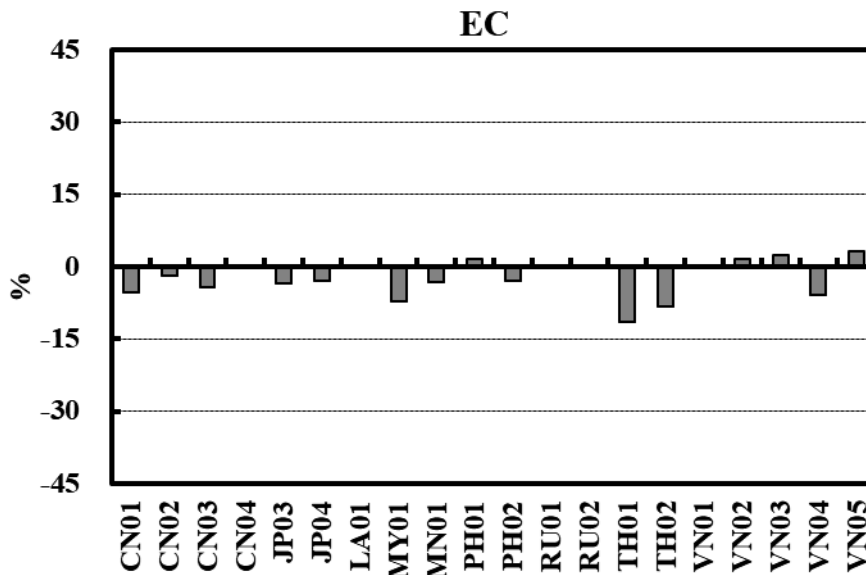


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

All the submitted data of EC were within DQOs.

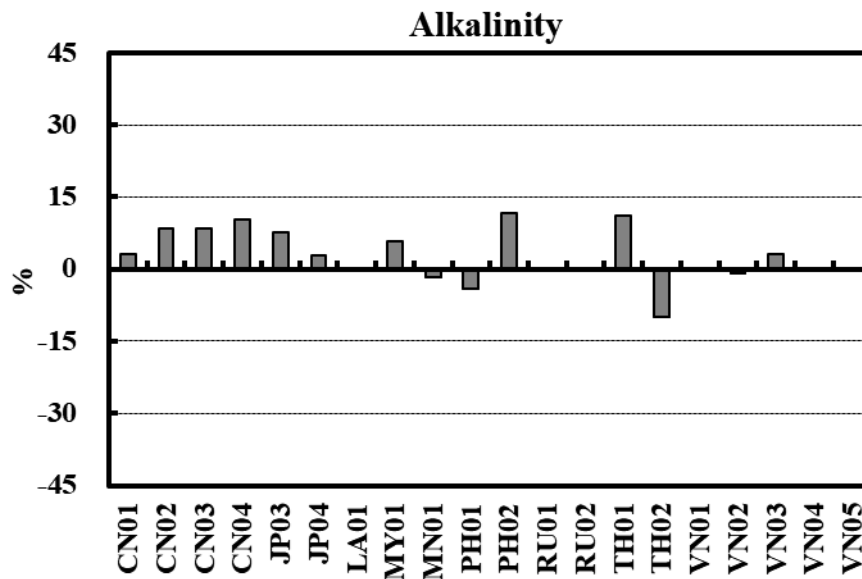


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

All the submitted data of Alkalinity were within DQOs.

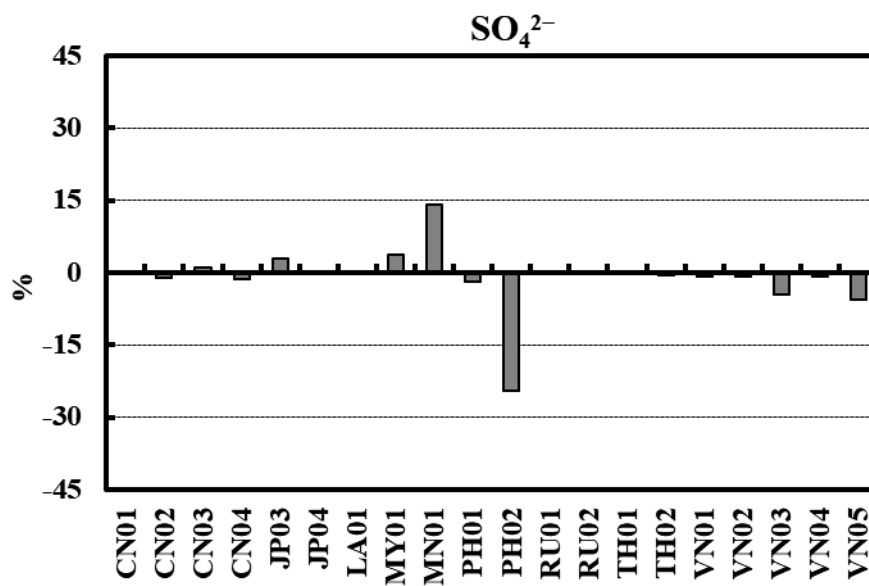


Figure 5.6 Distribution of results for SO<sub>4</sub><sup>2-</sup> (normalized by prepared concentration)

Except for PH02, all the submitted data of SO<sub>4</sub><sup>2-</sup> were within DQOs.

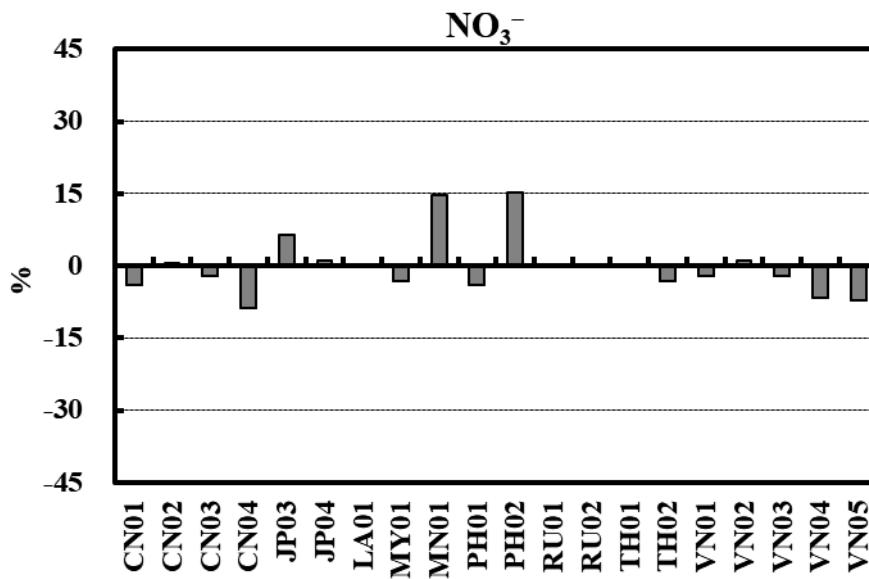


Figure 5.7 Distribution of results for NO<sub>3</sub><sup>-</sup> (normalized by prepared concentration)

Except for PH02, all the submitted data of NO<sub>3</sub><sup>-</sup> were within DQOs.

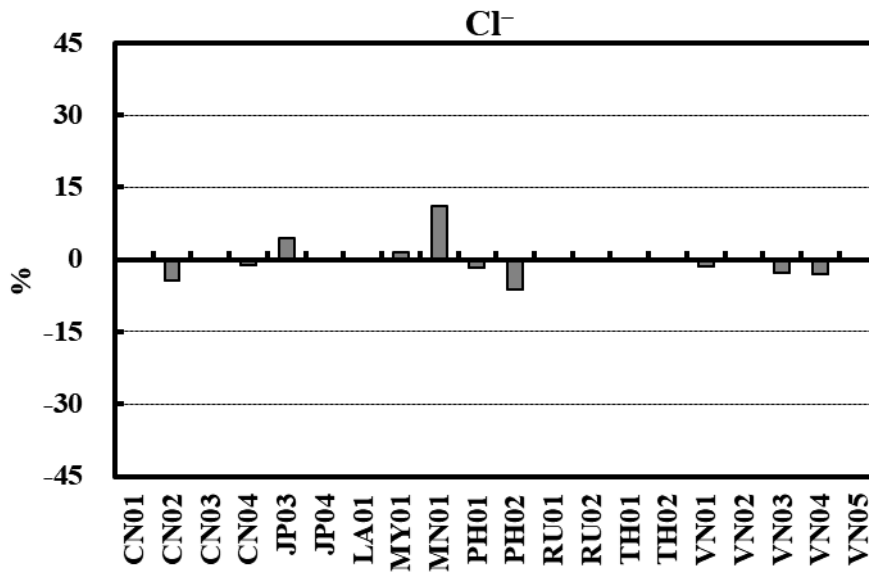


Figure 5.8 Distribution of results for Cl<sup>-</sup> (normalized by prepared concentration)

All the submitted data of Cl<sup>-</sup> were within DQOs.

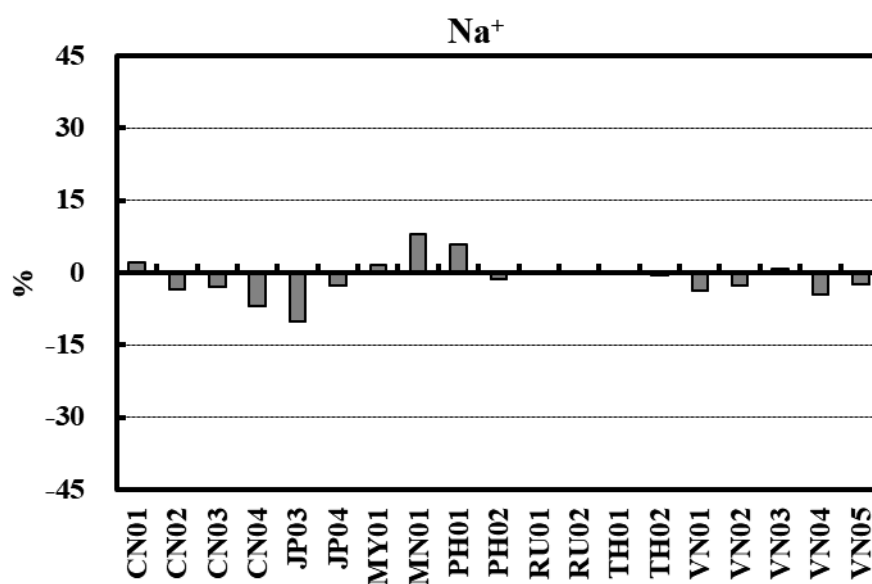


Figure 5.9 Distribution of results for Na<sup>+</sup> (normalized by prepared concentration)

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

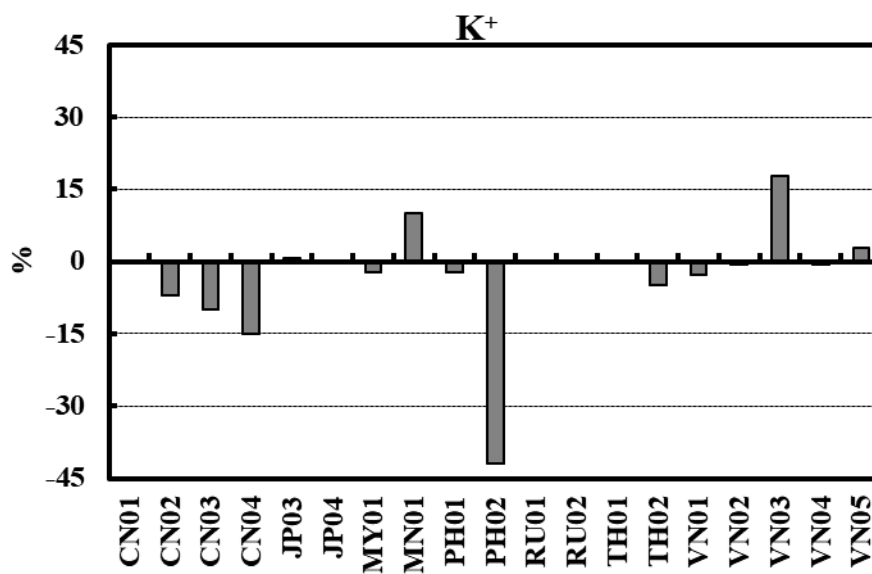


Figure 5.10 Distribution of results for K<sup>+</sup> (normalized by prepared concentration)

Except for PH02 and VN03, all the submitted data of K<sup>+</sup> were within DQOs.

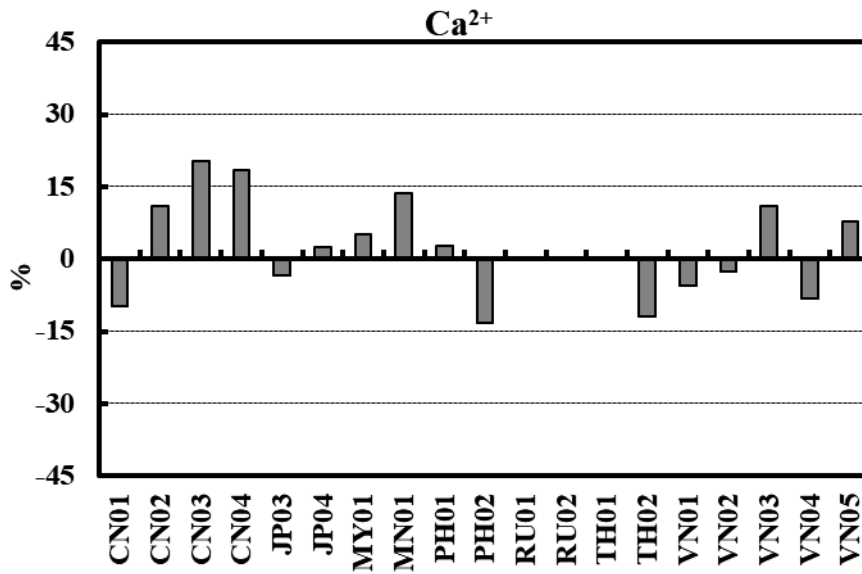


Figure 5.11 Distribution of results for Ca<sup>2+</sup> (normalized by prepared concentration)

Except for CN03 and CN04, all the submitted data of Ca<sup>2+</sup> were within DQOs.

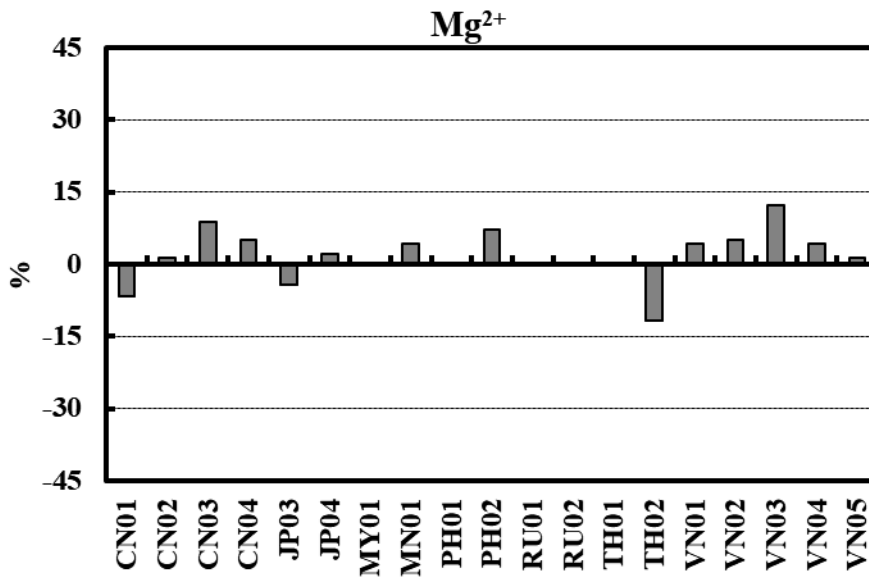


Figure 5.12 Distribution of results for Mg<sup>2+</sup> (normalized by prepared concentration)

All the submitted data of Mg<sup>2+</sup> were within DQOs.

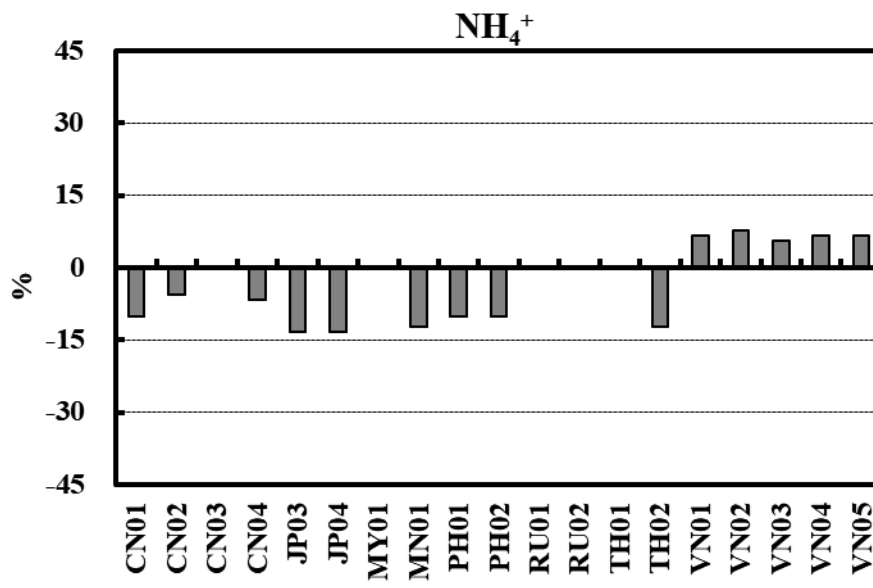
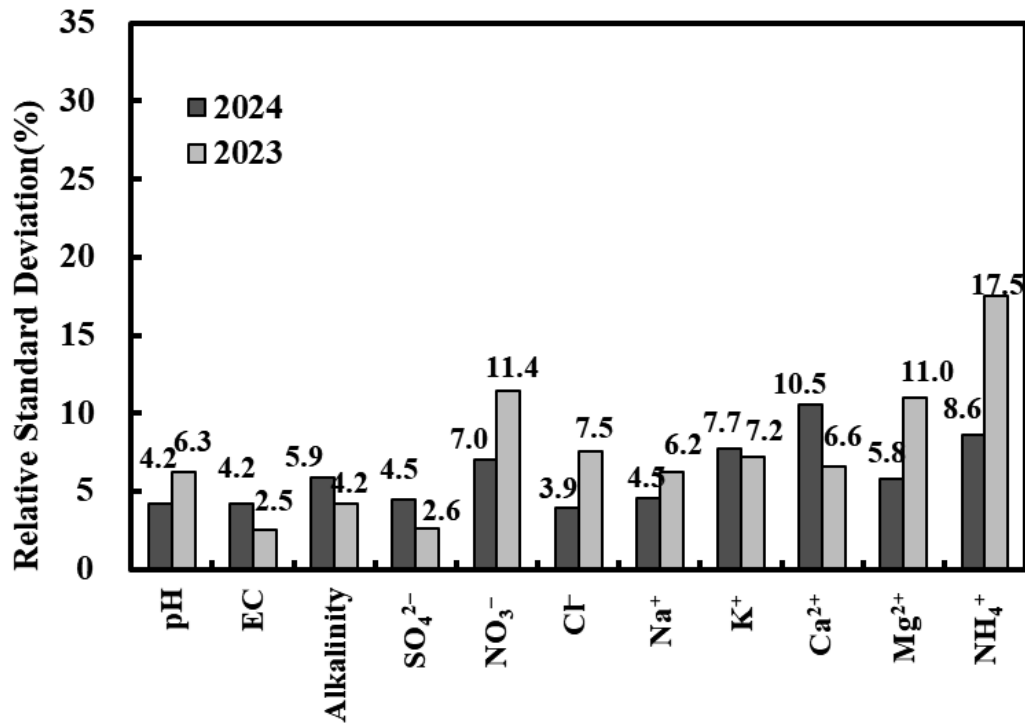


Figure 5.13 Distribution of results for NH<sub>4</sub><sup>+</sup> (normalized by prepared concentration)

All the submitted data of NH<sub>4</sub><sup>+</sup> were within DQOs.

### 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 (2023).



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

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

The relative standard deviation (RSD) of NO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> in 2024 was particularly lower than the last attempt (2023). On the other hand, the RSDs of Ca<sup>2+</sup> was increased in this attempt.

### 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.

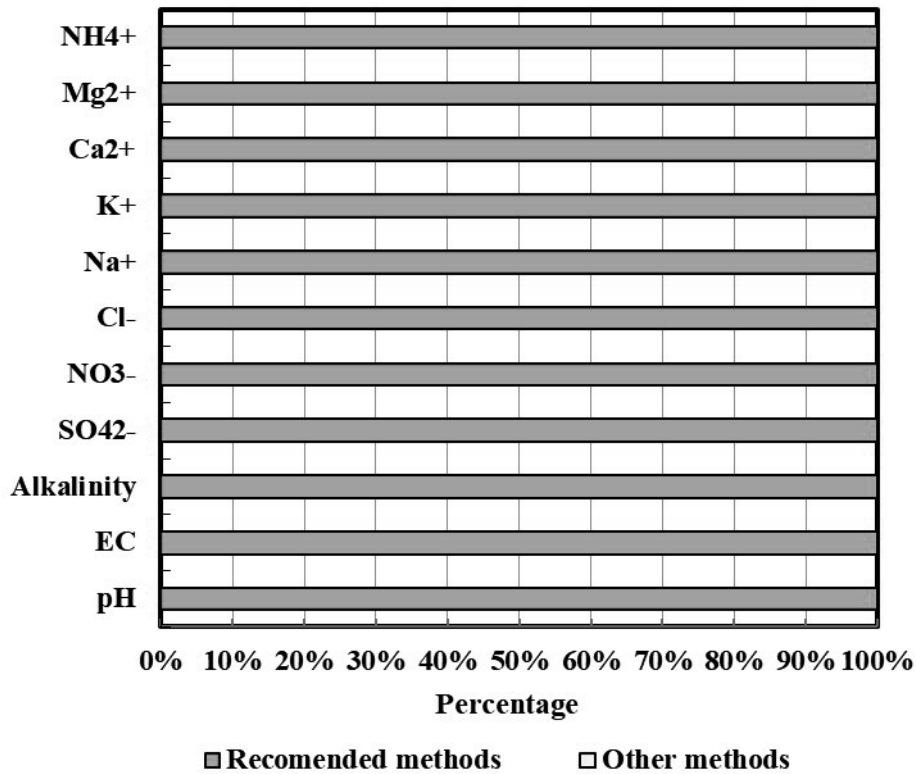


Figure 5.15 Percentage of laboratories using the recommended methods

**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	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	17										
1		17									
2			16			1					
3							2	2(1)	2	2	
4				15(1)	15(1)	15	13	13	13(2)	13	14
5							1*	1(1)*	1*	1*	
6											
7				1	1						
8											2
9											
10											
Flagged E	0	0	0	1	1	0	0	1	2	0	0
Flagged X	0	0	0	0	0	0	0	1	0	0	0

Recommended methods       Other methods

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

\* : Although not included in the manual, this method is recommended in this report due to its high accuracy.

The participating laboratories used recommended methods of the EANET.

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 <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>
CN01	3	A,B	A,B	A,B	C	C	C	C	C	C	C	C
CN02	2	A	A	A	B	B	B	B	B	B	B	B
CN03	2	A	A	A	B	B	B	B	B	B	B	B
CN04	1	A	A	A	A	A	A	A	A	A	A	A
JP03	3	A	A	B	C	C	C	C	C	C	C	C
JP04	1	A	A	A	A	A	A	A	A	A	A	A
MY01	4	A	A	B	C	C	C	D	D	D	D	D
MN01	3	A	A	B	C	C	C	C	C	C	C	C
PH01	3	A	A	A	A	A	A	B	B	C	C	A
PH02	1	A	A	A	A	A	A	A	A	A	A	A
TH01	1	A	A	A								
TH02	2	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B	A,B
VN01	2	A	A	A	B	B	B	B	B	B	B	B
VN02	3	A	A	B	C	C	C	C	C	C	C	C
VN03	2	A	A	B	B	A	A	B	B	B	B	A
VN04	3	A	A	B	C	C	C	C	C	C	C	C
VN05	2	A	A		B	B	B	B	B	B	B	B

The letters of A,B,C...mean individuals of staff in each laboratory who are in charge of measurement.

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

In many laboratories, 2 or 3 persons analyzed the sample, and usually 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	Unit : year							
				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	7,15	7,15	2,12	6	6	6	6	6	6	6	6
CN02	6	6	6	10	10	10	10	10	10	10	10
CN03	12	12	12	26	26	26	26	26	26	26	26
CN04	18	18	18	18	18	18	18	18	18	18	18
JP03	5	5	23	21	21	21	21	21	21	21	21
JP04	22	22	22	22	22	22	22	22	22	22	22
MY01	11	11	12	12	12	18	18	18	18	18	18
MN01	23	23	2	26	26	26	26	26	26	26	26
PH01	3	3	3	3	3	3	5	5	4	4	3
PH02	5	5	5	5	5	5	5	5	5	5	5
TH01	18	18	18								
TH02	25	25	25	25	25	25	25	25	25	25	25
VN01	8	8	8	11	11	11	11	11	11	11	11
VN02	18	18	20	20	20	20	20	20	20	20	20
VN03	10	10	13	13	10	10	13	13	13	13	10
VN04	12	12	20	21	21	21	21	21	21	21	21
VN05	19	19		20	20	20	19	19	19	19	19

Data were Flagged by “E” or “X” in sample

1 year means experienced with one year or less.

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 24 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.

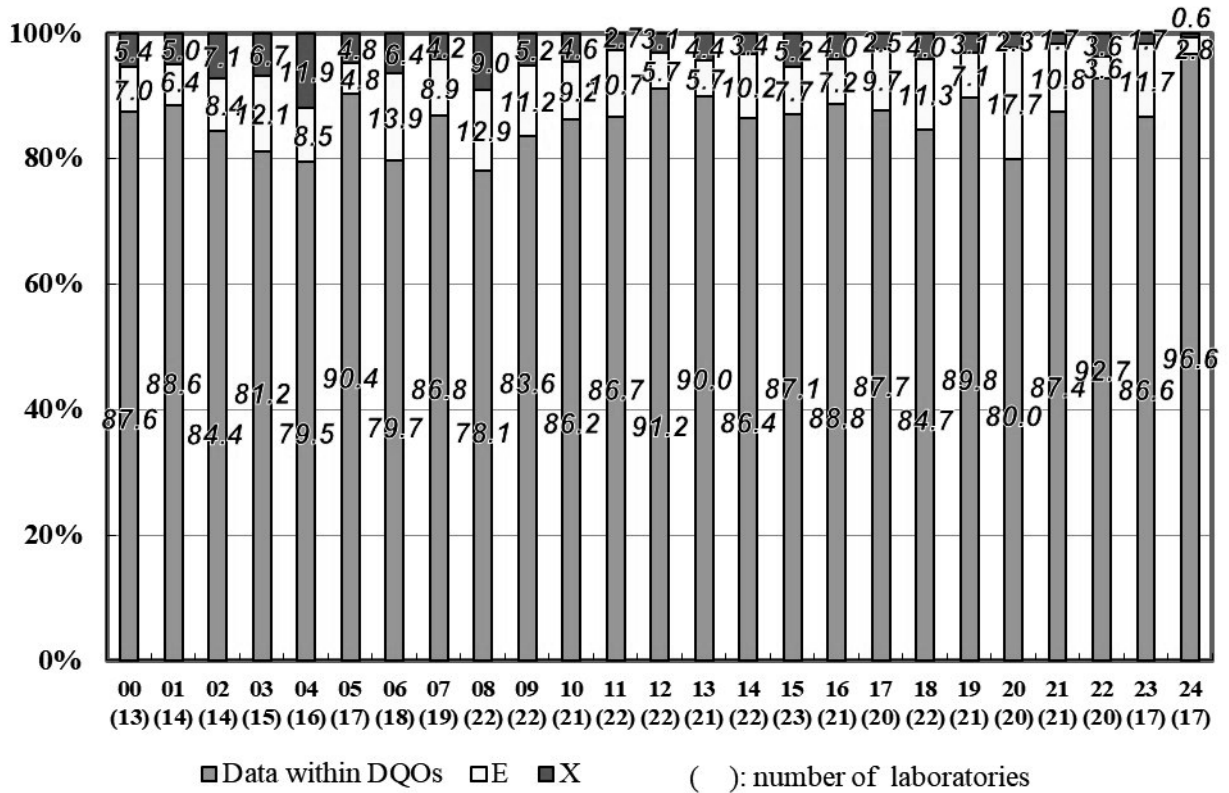


Figure 5.16 Comparison of the results from the inter-laboratory comparison projects

The percentage of data satisfied the DQOs increased from the last attempt (2023).

The values/concentrations for each parameter from the 1<sup>st</sup> to 25<sup>th</sup> projects were compared with the percentage of flagged data in Figure 5.17.

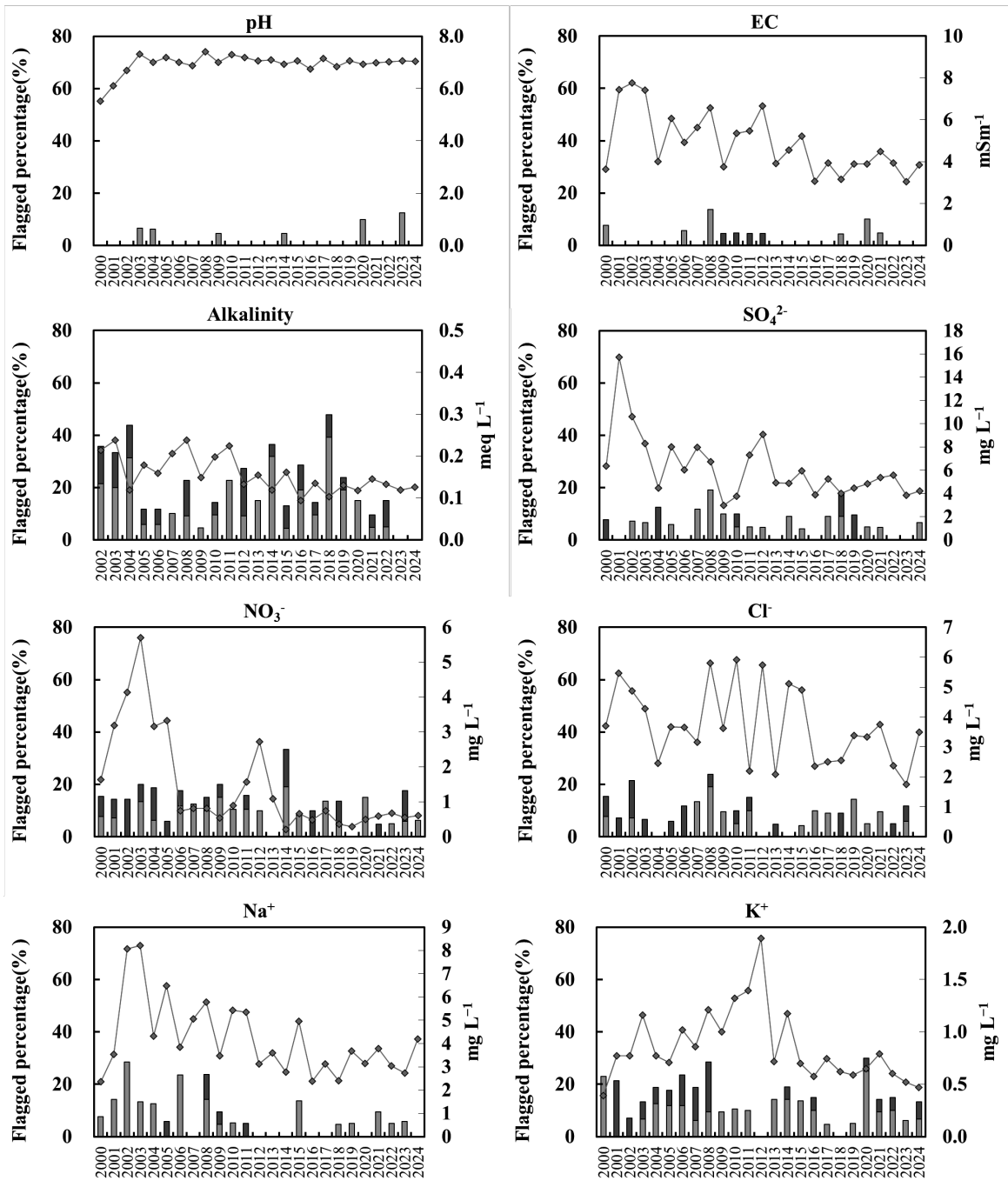
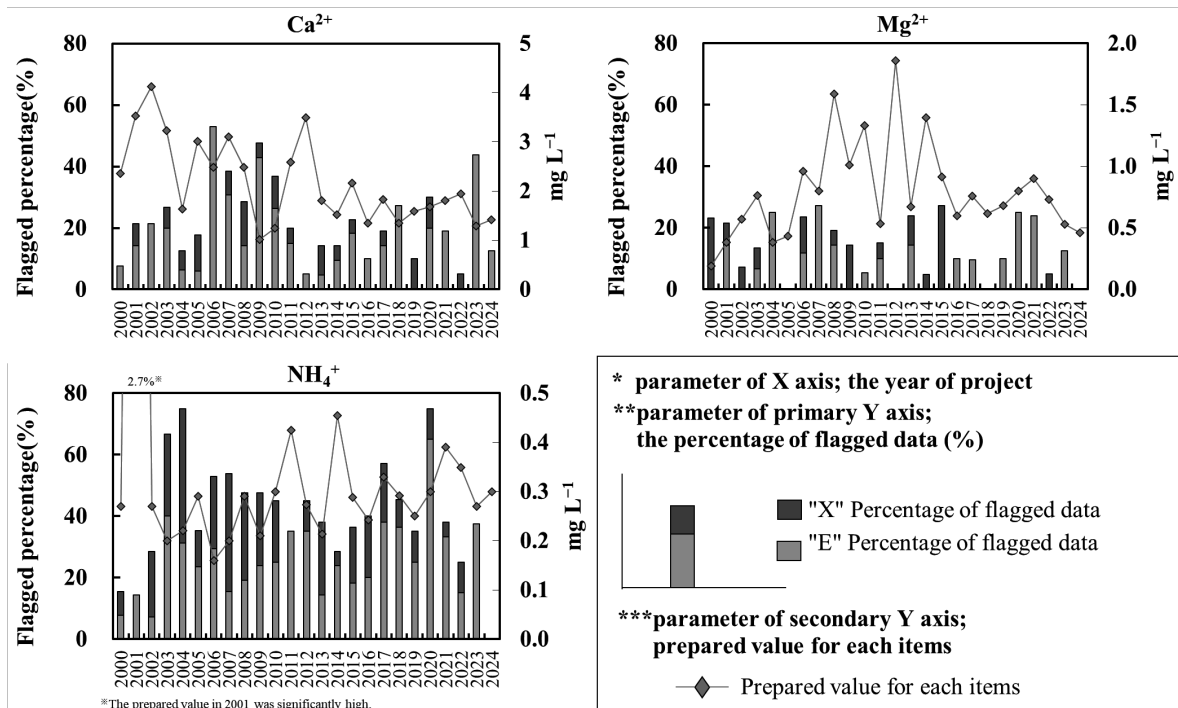


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects



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

There was no flagged data in pH, EC, Alkalinity, Cl<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> in this attempt. The analysis of NO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> was improved. In this attempt, flagged percentages of SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup> became higher than the last attempt.

Regarding NH<sub>4</sub><sup>+</sup>, which had been a recurring issue in previous years, no flags were assigned this time. This is the first occurrence since the start of the project. The improvement is attributed to enhanced measurement skills in the participating countries, and further advancements in analytical methods are expected in the future.

## **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 of measured results of samples and certified materials.
- ▶ In order to assure the reliability of measurements, the certified solutions and materials should be used as much as possible.

#### **4) Pretreatment of samples at analytical laboratory**

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

#### **5) Calibration of analytical instruments**

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

## 5.5.2 Evaluation of reliability

### 1) Sensitivity fluctuation of analytical instruments

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

For example, in ion chromatography

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

## 5.5.3 Data control

### 1) Data checks by the analytical laboratories

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

## References

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, 124.

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

Lab. ID	pH	EC - (mS m <sup>-1</sup> )	Alkalinity (meq L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	Cl <sup>-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	K <sup>+</sup> (mg L <sup>-1</sup> )	Ca <sup>2+</sup> (mg L <sup>-1</sup> )	Mg <sup>2+</sup> (mg L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )
CN01	7.03	3.64	0.130	4.21	0.59	3.50	4.29	0.47	1.28	0.43	0.27
CN02	6.95	3.77	0.137	4.17	0.61	3.35	4.05	0.44	1.58	0.47	0.28
CN03	6.98	3.68	0.137	4.27	0.60	3.51	4.08	0.42	1.71	0.50	0.30
CN04	6.34	3.85	0.139	4.16	0.56	3.46	3.91	0.40	1.68	0.48	0.28
JP03	7.10	3.70	0.136	4.34	0.65	3.66	3.78	0.47	1.37	0.44	0.26
JP04	6.99	3.73	0.130	4.22	0.62	3.49	4.09	0.47	1.46	0.47	0.26
MY01	7.24	3.56	0.133	4.37	0.59	3.56	4.27	0.46	1.49	0.46	0.30
MN01	7.09	3.72	0.124	4.82	0.70	3.89	4.54	0.52	1.61	0.48	0.26
PH01	7.07	3.90	0.121	4.14	0.59	3.44	4.45	0.46	1.46	0.46	0.27
PH02	7.00	3.73	0.141	3.18	0.70	3.29	4.15	0.27	1.23	0.49	0.27
TH01	7.14	3.40	0.140								
TH02	6.11	3.52	0.113	4.20	0.59	3.49	4.18	0.45	1.25	0.41	0.26
VN01	6.88	3.85	0.126	4.19	0.60	3.45	4.05	0.46	1.34	0.48	0.32
VN02	6.98	3.90	0.125	4.19	0.62	3.51	4.08	0.47	1.38	0.48	0.32
VN03	7.01	3.94	0.130	4.03	0.60	3.41	4.23	0.55	1.58	0.52	0.32
VN04	6.70	3.61	0.126	4.19	0.57	3.39	4.01	0.47	1.30	0.48	0.32
VN05	7.00	3.97		3.98	0.57	3.51	4.10	0.48	1.53	0.47	0.32
Expected value	7.04	3.84	0.126	4.22	0.61	3.50	4.20	0.47	1.42	0.46	0.30
Number of data	17	17	16	16	16	16	16	16	16	16	16
Average	6.92	3.73	0.13	4.17	0.61	3.49	4.14	0.45	1.45	0.47	0.29
Minimum	6.11	3.40	0.11	3.18	0.56	3.29	3.78	0.27	1.23	0.41	0.26
Maximum	7.24	3.97	0.14	4.82	0.70	3.89	4.54	0.55	1.71	0.52	0.32

blank: not analyzed

Appendix Table 5.2 Data normalized by the prepared value

Lab. ID	(Original data / Expected Value - 1) × 100 (%)												
	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	-0.1	-5.2	3.2	-0.2	-3.8	0.0	2.2	0.0	-9.9	-6.5	-10.0		
CN02	-1.2	-1.9	8.5	-1.1	0.5	-4.4	-3.6	-7.1	11.0	1.4	-5.6		
CN03	-0.9	-4.2	8.5	1.1	-2.2	0.3	-2.9	-9.9	20.4	8.7	0.0		
CN04	-9.9	0.3	10.3	-1.3	-8.7	-1.1	-6.9	-14.9	18.5	5.1	-6.7		
JP03	0.9	-3.6	7.7	2.8	6.6	4.5	-10.0	0.7	-3.5	-4.3	-13.3		
JP04	-0.7	-3.0	2.9	-0.1	1.1	-0.4	-2.6	0.0	2.6	2.2	-13.3		
MY01	2.9	-7.2	5.8	3.6	-3.3	1.6	1.6	-2.1	5.2	0.0	0.0		
MN01	0.8	-3.2	-1.6	14.1	14.8	11.1	8.0	9.9	13.6	4.3	-12.2		
PH01	0.5	1.6	-4.0	-2.0	-3.8	-1.8	5.9	-2.1	2.8	0.0	-10.0		
PH02	-0.6	-3.0	11.6	-24.6	15.3	-6.1	-1.3	-41.8	-13.4	7.2	-10.0		
TH01	1.4	-11.4	11.1										
TH02	-13.2	-8.3	-10.1	-0.5	-3.3	-0.3	-0.6	-5.0	-12.0	-11.6	-12.2		
VN01	-2.3	0.3	0.0	-0.7	-2.2	-1.3	-3.7	-2.8	-5.6	4.3	6.7		
VN02	-0.8	1.6	-0.8	-0.8	1.1	0.3	-2.8	-0.7	-2.6	5.1	7.8		
VN03	-0.4	2.5	3.2	-4.5	-2.2	-2.7	0.8	17.7	11.0	12.3	5.6		
VN04	-4.8	-5.9	0.0	-0.8	-6.6	-3.0	-4.5	-0.7	-8.2	4.3	6.7		
VN05	-0.6	3.3		-5.6	-7.1	0.3	-2.3	2.8	7.7	1.4	6.7		
Minimum	-13.2	-11.4	-10.1	-24.6	-8.7	-6.1	-10.0	-41.8	-13.4	-11.6	-13.3		
Maximum	2.9	3.3	11.6	14.1	15.3	11.1	8.0	17.7	20.4	12.3	7.8		
Average	-1.7	-2.8	3.5	-1.3	-0.2	-0.2	-1.4	-3.5	2.4	2.1	-3.7		

blank: not analyzed



## **6. ACKNOWLEDGEMENT**

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## **7. CONTACT INFORMATION**

Please address all inquiries, comments, and suggestions to:

Dr. Jun-ichi KUROKAWA

Head, Data Management Department

Asia Center for Air Pollution Research (ACAP)

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

Tel: +81 25-263-0562

Fax: +81 25-263-0567

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

URL: <https://www.eanet.asia>