

The Twenty-sixth Session of the Scientific Advisory Committee (SAC26)
on the Acid Deposition Monitoring Network in East Asia
20-22 October 2026, Kuala Lumpur, Malaysia (Hybrid)

Adoption of the Report of the Inter-laboratory Comparison Project 2025

I. INTRODUCTION

1. The Acid Deposition Monitoring Network in East Asia (EANET) was established as an initiative for regional cooperation among the participating countries, creation of a common understanding on the state of both air concentration and acid deposition problems and for providing useful inputs to policy makers at various levels. Monitoring activities started during the preparatory phase activities of EANET from March 1998 to December 2000. Regular air concentration and acid deposition monitoring started in January 2001 with 10 participating countries, namely China, Indonesia, Japan, Malaysia, Mongolia, Philippines, Republic of Korea, Russia, Thailand, and Vietnam. Cambodia, Lao PDR, and Myanmar joined EANET in 2001, 2002 and 2005, respectively.
2. Air concentration and acid deposition monitoring activities of EANET consist of five environmental items – dry deposition (air concentration), wet deposition, soil and vegetation, inland aquatic environment, and catchment-scale monitoring. Monitoring for dry and wet deposition is implemented to measure atmospheric concentrations and to evaluate fluxes of acidic substances to the land surface, while monitoring for soil and vegetation, inland aquatic environment and catchment-scale is carried out to assess adverse impacts on terrestrial and aquatic ecosystems. These monitoring data are used to evaluate the state of air concentration and acid deposition as well as impacts on ecosystems. Therefore, it is essential to provide accurate and reliable data that is comparable across regions.
3. The Inter-laboratory Comparison (ILC) Project was conducted among the analytical laboratories in participating countries of the 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 dry deposition (filter pack method), wet deposition, 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. Dry deposition
- b. Wet deposition
- c. Soil
- d. Inland aquatic environment

4. The participating countries are required to submit the reports of analytical results based on the report forms and the manuals prepared by the NC. The NC prepares a draft Report of the ILC Project based on its evaluation of the analytical results reported by participating laboratories and discussions with QA/QC managers from participating countries at the Senior Technical Managers' Meeting (STM). The draft Report of the ILC is submitted to the session of Scientific Advisory Committee (SAC), and the Report of the ILC Project is adopted. Following the comments and guidance at the SAC, the NC elaborated and finalized the report.

II. REPORT of THE ILC PROJECT 2025 AND THE REVISION OF THE STRUCTURE OF THE REPORT OF THE ILC PROJECT

5. As indicated in the document of Twenty-sixth Session of the Science Advisory Committee (SAC26) for the Data Report 2025 (EANET/SAC26/6), the priority of EANET has been shifted from acid deposition to air pollution and atmospheric deposition, and the importance of air concentration monitoring has increased. Therefore, the rearrangement of the chapters was made in the Report of the ILC Project 2025 the same as for the Data Report 2025 as follows (No changes were made to the detailed structure other than changing the order of the chapters):

Report of the ILC Project 2024	Report of the ILC Project 2025
1. Introduction	1. Introduction
2. 27th ILC Project on Wet Deposition	2. 21st ILC Project on Dry Deposition
3. 20th ILC Project on Dry Deposition	3. 28th ILC Project on Wet Deposition
4. 26 th ILC Project on Soil	4. 27 th ILC Project on Soil
5. 25 th ILC Project on Inland Aquatic Environment	5. 26 th ILC Project on Inland Aquatic Environment

III. ACTIONS REQUIRED

6. The SAC26 Meeting is invited to consider the adoption of the Report of the ILC Project 2025

(Attachment 1), with modification, including changes to its structure (switching the order of Chapter 2 and 2: Chapter 2, 21st ILC Project on Dry Deposition, and Chapter 3, 28th ILC Project on Wet Deposition).

Attachment 1

The Twenty-sixth Session of the Scientific Advisory Committee
on the Acid Deposition Monitoring Network in East Asia
20-22 October 2026, Kuala Lumpur, Malaysia (Hybrid)

Draft Report of the Inter-laboratory Comparison Project 2025

28th Inter-laboratory Comparison Project on Wet Deposition

21st Inter-laboratory Comparison Project on Dry Deposition

27th Inter-laboratory Comparison Project on Soil

26th Inter-laboratory Comparison Project

on Inland Aquatic Environment

October 2026
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 dry deposition (filter pack method), wet deposition, 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. Dry deposition
- b. Wet deposition
- c. Soil
- d. Inland aquatic environment

This report presented the results of the 21st Inter-laboratory Comparison Project on dry deposition, 28th Inter-laboratory Comparison Project on wet deposition, 27th Inter-laboratory Comparison Project on soil, and 26th 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.

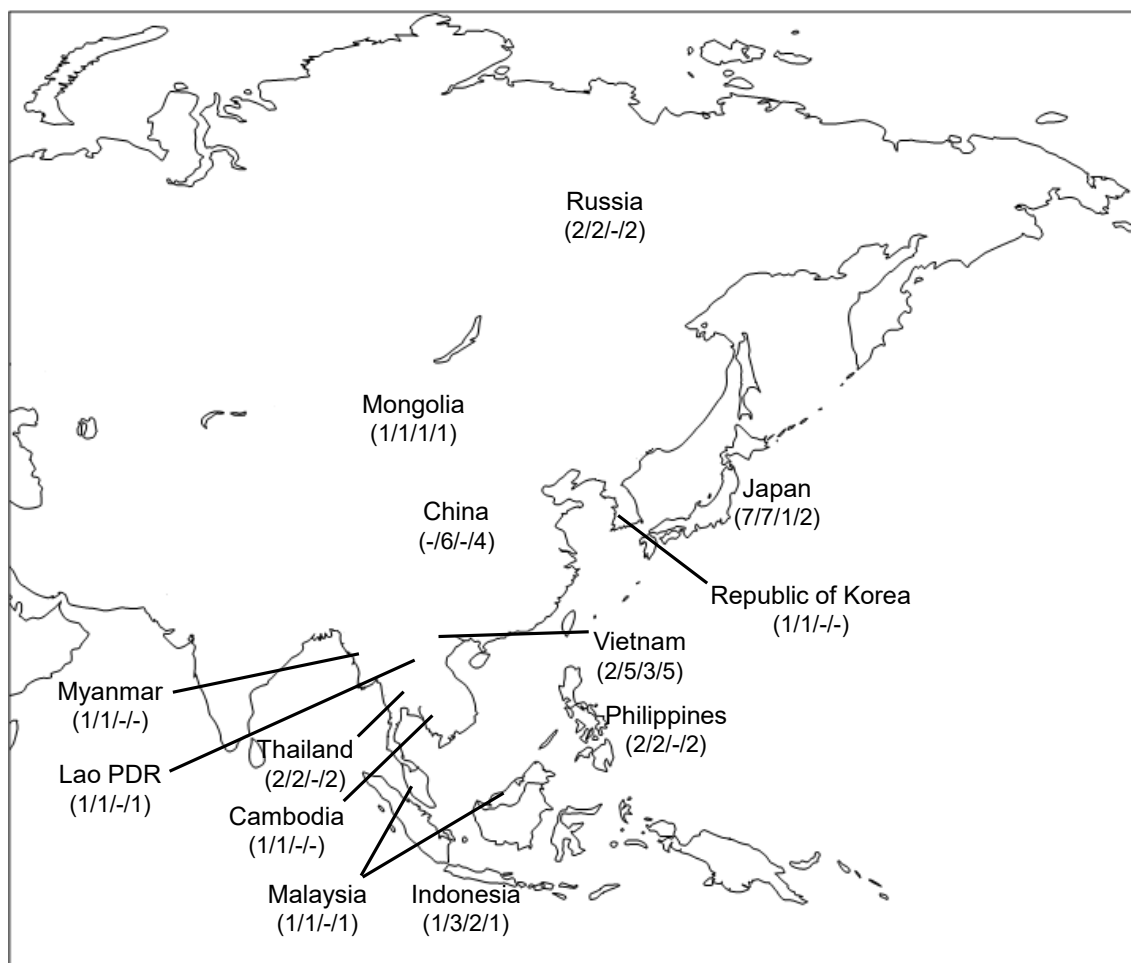


Figure 1.1 Number of participating laboratories in 2025

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

Table 1.1 Participating laboratories and data submission status

Participating laboratories	Code	Data submission			
		Dry	Wet	Soil	IAE
<u>Cambodia</u>					
General Directorate of Environmental Protection (GDEP), Ministry of Environment	KH01				
<u>China</u>					
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		✓		
<u>Indonesia</u>					
Center for Environmental Management Facility, Ministry of Environment/Environmental Protection Agency (CEMF)	ID01		✓	✓	✓
Climatology, Meteorological and Geophysical Agency (BMKG)	ID02		✓		
National Research and Innovation Agency	ID03	✓	✓		
Indonesian Soil and Fertilizer Engineering and Testing Institute (ISOFETI)	ID04			✓	
<u>Japan</u>					
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		✓		
Ishikawa Prefectural Institute of Public Health and Environmental Science	JP13			✓	
<u>Lao PDR</u>					
Environmental Quality Analysis center, Biotechnology and Ecosystem Institute	LA01				
<u>Malaysia</u>					
Environmental Quality Division, Department of Chemistry Malaysia (DOC)	MY01	✓	✓		✓
<u>Mongolia</u>					
Central Laboratory of Environment and Metrology (CLEM)	MN01	✓	✓	✓	✓
<u>Myanmar</u>					
Department of Meteorology and Hydrology (DMH)	MM01	✓	✓		
<u>Philippines</u>					
Environmental Management Bureau - Central Office (EMB-CO)	PH01	✓	✓		✓
Environmental Management Bureau - Cordillera Administrative Region (EMB-CAR)	PH02	✓	✓		✓
<u>Republic of Korea</u>					
Aerosol research Lab. in National Institute of Environment Research	KR01	✓	✓		
<u>Russia</u>					
Limnological Institute, Russian Academy of Sciences, Siberian Branch (LI/RAS/SB)	RU01	✓	✓		✓
Primorsky Center for Environmental Monitoring, Roshydromet (PCEM)	RU02		✓		✓
<u>Thailand</u>					
Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MONRE)	TH01	✓	✓		✓
Climate Change and Environmental Research Center (CERC), Department of Climate Change and Environment (DCCE)	TH02	✓	✓		✓
<u>Vietnam</u>					
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(SIHYMECC)	VN03	✓	✓		✓
Center for Hydro-Meteorological and Environmental Networks, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN04		✓	✓	✓
Southern Region Hydro-Meteorological Center, National Hydro-Meteorological Service of Vietnam (NHMS), MoNRE	VN05		✓	✓	✓
Total number of submitted data :		19	31	7	20

Table 1.2 Laboratories in charge of the analysis of each monitoring site in EANET (2025)

Country	Site for deposition monitoring	Code	Plot for soil and vegetation monitoring	Code	Site for monitoring on inland aquatic environment	Code	Laboratory code			
							Dry (FP*)	Wet	Soil	IAE
Cambodia	Phnom Penh	<i>KHA001</i>			Sras Srang Lake	<i>KHI002</i>	KH01	KH01		KH01
China	Chingqing - Haifu - Jinyunshan Xi'an - Shizhan - Jiwozi Xiamen - Hogwen - Xiaoping Zhuhai - Xiang Zhou - Zhuxiandong - Haibin-Park 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 CN03 CN02 CN02 CN01 CN01 CN05 CN06	CN04 CN03 CN03 CN02 CN02 CN01 CN01	CN04 CN03 CN03 CN02 CN02 CN01 CN01
Indonesia	Jakarta Kototabang Maros Jembrana Lombok	<i>IDA001</i> <i>IDA003</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 ID02 ID02 ID02 ID02	ID02 ID02 ID02 ID04 ID01	ID04 ID04	ID01
Japan	Rishiri Ochiishi Sado-seki Happo Ijira Okii Yusuhara Hedo Ogasawara Tokyo 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>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>IPI006</i>	JP01 JP09 JP02 JP03 JP04 JP09 JP09 JP08 JP10 JP10 JP09	JP01 JP09 JP09 JP03 JP04 JP09 JP09 JP08 JP10 JP10 JP14	JP13 JP13 JP04 JP04	JP15 JP04
Lao PDR	Vientiane	<i>LAA001</i>			Nam Houm Lake	<i>LAI001</i>	LA01	LA01		LA01
Malaysia	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>MYI103</i> <i>MYI006</i>	MY01 MY01 MY01 MY01 MY01	MY01 MY01 MY01 MY01 MY01		MY01
Mongolia	Khan-Uul Terelj	<i>MNA004</i> <i>MNA002</i>	Bogdkhan Mountain Terelj Mountain	<i>MNS001</i> <i>MNS002</i>	Terelj River	<i>MNI002</i>	MN01 MN01	MN01 MN01	MN01 MN01	MN01
Myanmar	Yangon Mandalay	<i>MMA001</i> <i>MMA002</i>					MM01	MM01		
Philippines	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 Research Site	<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 PH02		PH01 PH02
Republic of Korea	Ganghwa Jeju Imsil	<i>KRA001</i> <i>KRA002</i> <i>KRA003</i>					KR01 KR01 KR01	KR01 KR01 KR01		
Russia	Listvyanka Irkutsk Primorskaya	<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 RU01 RU01 RU02	RU01 RU01 RU01 RU01	RU01 RU02
Thailand	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 TH02 TH01	TH01 TH02 TH01		TH01
Vietnam	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 VN03 VN03 VN03 VN01	VN01 VN01 VN04 VN02 VN03 VN03 VN01	VN01 VN01 VN01	VN01

* FP: Filter pack method

2. 21st INTER-LABORATORY COMPARISON PROJECT ON DRY DEPOSITION

2.1 Introduction

For the Inter-laboratory Comparison on dry deposition, impregnated filters containing either SO_4^{2-} and Cl^- , or NH_4^+ , were prepared by the Network Center (NC) and distributed to the participating laboratories in December 2024. Most EANET laboratories that use the filter pack method participated in this activity and submitted their analytical results to the NC. The submitted results were compared with the corresponding prepared values and statistically analyzed.

2.2 Procedures

2.2.1 Participating Laboratories

A total of 22 laboratories responsible for EANET dry deposition monitoring participated in this 21st activity, and 18 laboratories submitted their results to the NC. The participating laboratories and their data submission status are shown in Table 1.1.

2.2.2 Description of Samples

Two types of filter samples were prepared and distributed to the laboratories: one containing two ions (SO_4^{2-} and Cl^-) and the other containing one ion (NH_4^+). Blank filters, which were impregnated with K_2CO_3 or H_3PO_4 but did not contain SO_4^{2-} , Cl^- , or NH_4^+ , were also prepared and distributed. Details of the filter samples are provided in Table 2.1. The analytical precision and accuracy for each analyte were summarized through statistical calculations using the analytical results submitted by each participating laboratory.

Table 2.1 Outline of filter samples

Name	Details	Container	Number of filters	Note
No.251d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.
No.251d-2	Acid (H_3PO_4) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions.
No.252d-1	Alkali (K_2CO_3) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of sulfate and chloride ions.

Table 2.1 Outline of filter samples (continued)

Name	Details	Container	Number of filters	Note
No.252d-2	Acid (H ₃ PO ₄) impregnated filter	Polyethylene centrifuge tube	3	Each filter contains a known quantity of ammonium ions
No.253d-1	Alkali (K ₂ CO ₃) impregnated filter	Polyethylene centrifuge tube	3	Blank
No.253d-2	Acid (H ₃ PO ₄) impregnated filter	Polyethylene centrifuge tube	3	Blank

2.2.3 Analytes

All participating laboratories were expected to analyze these filter samples and to submit their values as the net quantity of each ion (SO₄²⁻, Cl⁻ and NH₄⁺) in microgram (µg).

2.2.4 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.251d-1, No.252d-1, No.253d-1

Add 20 mL of H₂O₂ solution (0.05% v/v) as an extracting solvent into each centrifuge tube, then shake them for 20 minutes.

(2) Sample No.251d-2, No.252d-2, No.253d-2

Add 20 mL of pure water (EC<0.15 mS m⁻¹) 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 2.2.

Table 2.2 Analytical methods specified in the Technical Manual

Analyte	Analytical method
SO ₄ ²⁻ , Cl ⁻	Ion Chromatography (preferably with suppressor)
	Spectrophotometry
NH ₄ ⁺	Ion Chromatography
	Spectrophotometry (Indophenol Blue)

2.2.5 Data Check Procedures

All participating laboratories were requested to report as the net quantity of each ion (SO₄²⁻, Cl⁻ and NH₄⁺) 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⁻¹);

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.251d-1, No.251d-2, No.252d-1 and No.252d-2;

$M_{sol, Blank}$: the median quantity (μg) in the filtrate from blank sample No.253d-1 and No.253d-2.

3.3 Results

The NC distributed the filter samples to 22 laboratories in the participating countries of EANET and received their results from 18 laboratories. The results compared to the prepared values are summarized in Table 2.3. 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 2.3 and three results were rejected this time.

As shown in Table 2.3, the deviations ($\Delta V/V_p$) for SO_4^{2-} in Sample No.251d and Sample No.252d were -7.9 % and -5.2%. The deviations for Cl^- in Sample No.251d and Sample No.252d were -11.7% and -5.6%. The deviations for NH_4^+ in Sample No.251d and Sample No.252d were 4.3% and -1.5%.

The Data Quality Objectives (DQOs) of EANET are specified that determined values are expected to fall within $\pm 15\%$ deviation from the prepared values in *Technical Manual for Air Concentration Monitoring in East Asia* (2013). Each laboratory analyzed each sample 3 times, 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.251d and No.252d is described in 2.3.1 Evaluation of Laboratories' Performance (by sample). The comparison of the results for each analyte is described in 2.3.2 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 2.3.3 Information on Laboratories.

Table 2.3 Summary of analytical results of the filter samples

Analyte	Prepared* (V_p) (μg)	Average (V_a) (μg)	$\Delta V/V_p^*$ (%)	S.D. (μg)	Number (N)	Minimum (μg)	Maximum (μg)
<u>Sample No.251d</u>							
SO_4^{2-}	8.25	7.60	-7.9	0.68	17	5.77	8.74
Cl^-	5.83	5.15	-11.7	1.36	18	1.32	6.90
NH_4^+	23.0	24.0	4.3	2.73	18	20.1	31.7
<u>Sample No.252d</u>							
SO_4^{2-}	27.1	25.7	-5.2	2.75	18	20.1	31.2
Cl^-	14.0	13.2	-5.6	1.70	17	9.08	16.3
NH_4^+	57.1	56.2	-1.5	4.73	17	45.3	64.3

* Prepared: Prepared values

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

2.3.1 Evaluation of Laboratories' Performance (by sample)

Samples No.251d-1, No.251d-2

For Sample No.251d, 6 analytical data in 54 results were flagged E, and 6 analytical data were flagged X. The total percentage of the flagged samples was 22.2% (Figure 2.1, Table 2.4 and 2.5).

Table 2.4 Number of flagged data for Sample No.251d

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	3	1	2	6
Flag X *	2	3	1	6
Data within DQOs	13	14	15	42
Ratio of Flagged (%)	27.8	22.2	16.7	22.2

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

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

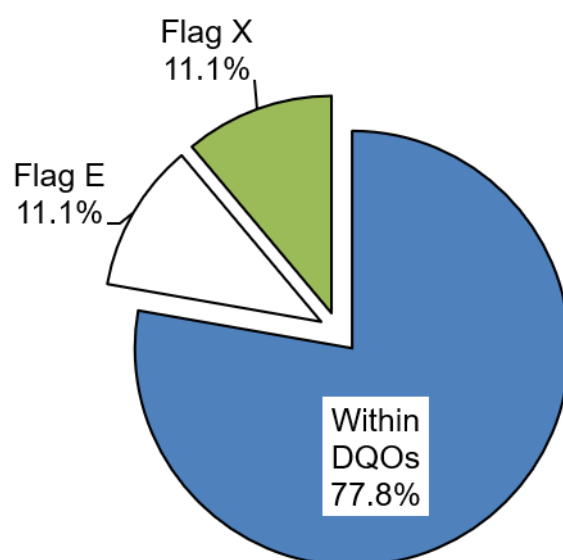


Figure 2.1 Percentage of flagged data for Sample No.251d

Table 2.5 Average analytical results of Sample No.251d

Lab. Code	SO ₄ ²⁻ (µg)		Cl ⁻ (µg)		NH ₄ ⁺ (µg)	
KH01						
ID03	6.92	E	2.05	X	31.7	X
JP01	7.52		5.23		23.1	
JP02	8.7		5.67		22.6	
JP03	8.18		5.46		23.3	
JP04	7.98		5.56		23.0	
JP08	7.60		5.41		22.6	
JP09	8.07		5.53		22.3	
JP10	8.16		6.02		22.0	
LA01						
MY01	6.8	E	6.21		25.7	
MN01	7.90		5.20		29.0	E
MM01	4.04	X	5.06		20.1	
PH01	7.6		5.58		22.6	
PH02	7.96		4.06	X	23.5	
KR01	5.77	X	5.20		23.6	
RU01	6.84	E	1.32	X	21.1	
TH02	7.30		5.65		26.8	E
VN01	7.92		6.90	E	24.5	

VN03	7.86	6.52	24.3
Note:	Flag E:	$15\% < \text{Deviation} \leq 30\%$	
	Flag X:	$30\% < \text{Deviation} $	

Samples No.252d-1, No.252d-2

For Sample No.252d, 9 analytical data in 54 results were flagged E, and 3 analytical data were flagged X. The total percentage of the flagged samples was 22.2% (Figure 2.2, Table 2.6 and 2.7).

Table 2.6 Number of flagged data for Sample No.252d

	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Total
Flag E *	5	2	2	9
Flag X *	0	2	1	3
Data within DQOs	13	14	15	42
Ratio of Flagged (%)	27.8	22.2	16.7	22.2

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

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

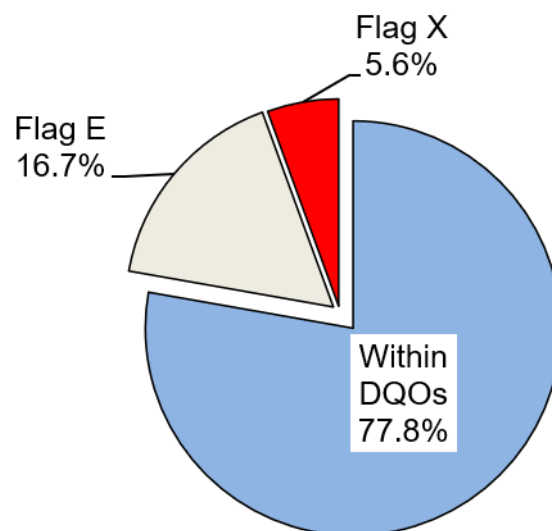


Figure 3.2 Percentage of flagged data for Sample No.252d

Table 3.7 Average analytical results of Sample No.252d

Lab. Code	SO ₄ ²⁻ (μg)		Cl ⁻ (μg)		NH ₄ ⁺ (μg)	
KH01						
ID03	22.0	E	9.1	X	55.8	
JP01	25.3		13.2		57.3	
JP02	26.8		13.6		57.5	
JP03	26.9		13.2		56.5	
JP04	26.4		13.6		56.8	
JP08	26.0		13.3		55.7	
JP09	26.4		13.7		56.9	
JP10	27.4		14.2		57.4	
LA01						
MY01	24.7		14.2		60.4	
MN01	25.6		12.6		64.3	
MM01	20.1	E	12.0		53.5	
PH01	27.1		13.5		58.2	
PH02	24.2		10.0	E	57.0	
KR01	21.6	E	12.7		55.0	
RU01	24.5		4.0	X	90.5	X
TH02	25.1		13.7		62.9	
VN01	31.2	E	16.3	E	45.3	E
VN03	31.2	E	15.9		45.5	E

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

Flag X: 30% < | Deviation |

Blank Sample (No.253d)

Each quantity of SO₄²⁻, Cl⁻, and NH₄⁺ was determined for blank sample No.253d-1 and No.253d-2. Their obtained values are shown in Table 2.8. Blank values were detected in a wide range, including 0 μg.

Table 2.8 Analytical results of Blank Sample No.253d

Lab. Code	SO ₄ ²⁻ (μg)	Cl ⁻ (μg)	NH ₄ ⁺ (μg)
KH01			
ID03	0.25	1.92	2.94
JP01	0.22	0.91	0.25
JP02	0.00	0.90	0.42
JP03	0.50	1.13	0.30

JP04	0.36	0.90	0.00
JP08	0.30	0.98	0.22
JP09	0.49	0.89	0.45
JP10	0.08	0.75	0.19
LA01			
MY01	1.21	1.79	0.22
MN01	0.01	1.19	0.89
MM01	1.10	2.48	4.14
PH01	0.59	0.95	0.84
PH02	0.00	1.44	0.58
KR01	1.20	1.58	0.30
RU01	0.00	0.00	0.17
TH02	0.43	1.60	1.92
VN01	0.00	0.19	0.08
VN03	1.28	1.28	1.25
Average	0.45	1.16	0.84
Median	0.33	1.06	0.36
Minimum	0.00	0.00	0.00
Maximum	1.28	2.48	4.14
Standard deviation	0.44	0.58	1.08

2.3.2 Comparison of Laboratories' Performance (by analyte)

The overviews of their results are shown in the following figures and tables for each analyte (SO_4^{2-} , Cl^- and NH_4^+). The obtained values from each laboratory were evaluated for their deviations. The number of the flagged data is shown in Table 2.9, 2.10 and 2.11 for each analyte.

SO_4^{2-} (Sulfate)

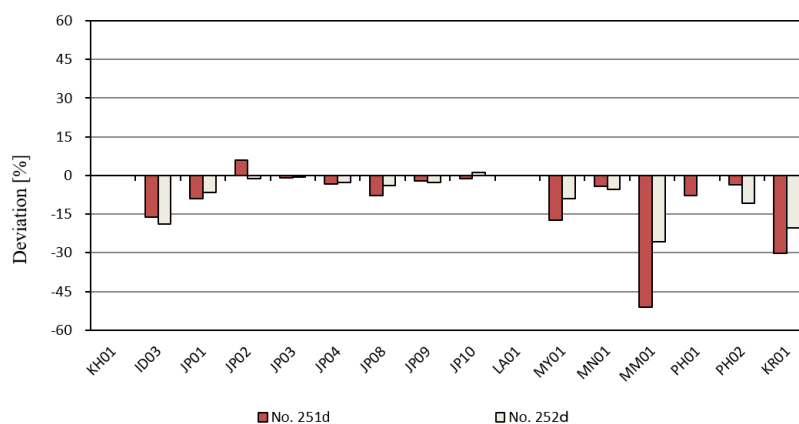


Figure 2.3 Deviation for SO_4^{2-}

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

Table 3.9 Flagged data of SO_4^{2-}

	Flag E	Flag X	Flagged (%)
Sample No.251d	3	2	27.8
Sample No.252d	5	0	27.8

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of SO_4^{2-} . The E flag was observed at three laboratories for Sample No. 251d and at five laboratories for Sample No. 252d. The X flag was observed at two laboratories for Sample No. 251d.

Cl⁻ (Chloride)

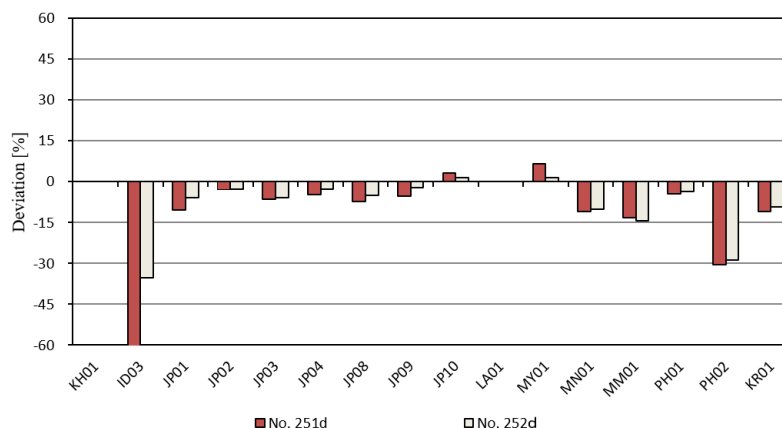


Figure 2.4 Deviation for Cl⁻

Table 3.10 Flagged data of Cl⁻

	Flag E	Flag X	Flagged (%)
Sample No.251d	1	3	22.2
Sample No.252d	2	2	22.2

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of Cl⁻. E flag was observed at three laboratories for Sample No.251d and No.252d. X flag was observed at five laboratories for Sample No.251d and No. 252d.

NH₄⁺ (Ammonium)

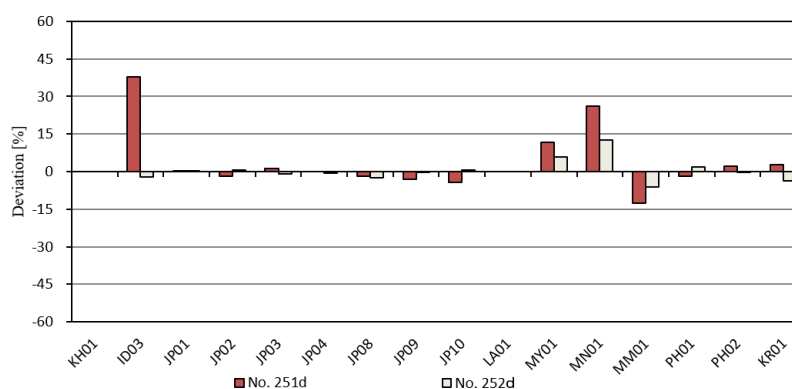


Figure 2.5 Deviation for NH₄⁺

Table 2.11 Flagged data of NH_4^+

	Flag E	Flag X	Flagged (%)
Sample No.251d	2	1	16.7
Sample No.252d	2	1	16.7

One laboratory used the spectrophotometry method. The other laboratories used Ion Chromatography for the determination of NH_4^+ . E flag was observed four laboratories for Sample No.251d and Sample No. 252d. X flag was observed two laboratories for Sample No.251d and Sample No. 252d.

3.3.3 Information on Laboratories

Years of staff experience

Years of staff experience are summarized in Table 2.12. 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 2.12 Years of staff experience

Lab. Code	SO_4^{2-}	Cl^-	NH_4^+
KH01			
ID03	18		18
JP01	22	22	22
JP02	6	6	6
JP03	2	2	2
JP04	4	4	4
JP08	4	4	4
JP09	11	11	11
JP10	8	8	8
LA01			
MY01	7	7	7
MN01	22	22	22
MM01	4	4	4
PH01	4	4	4
PH02	3	3	3
KR01	20	20	20

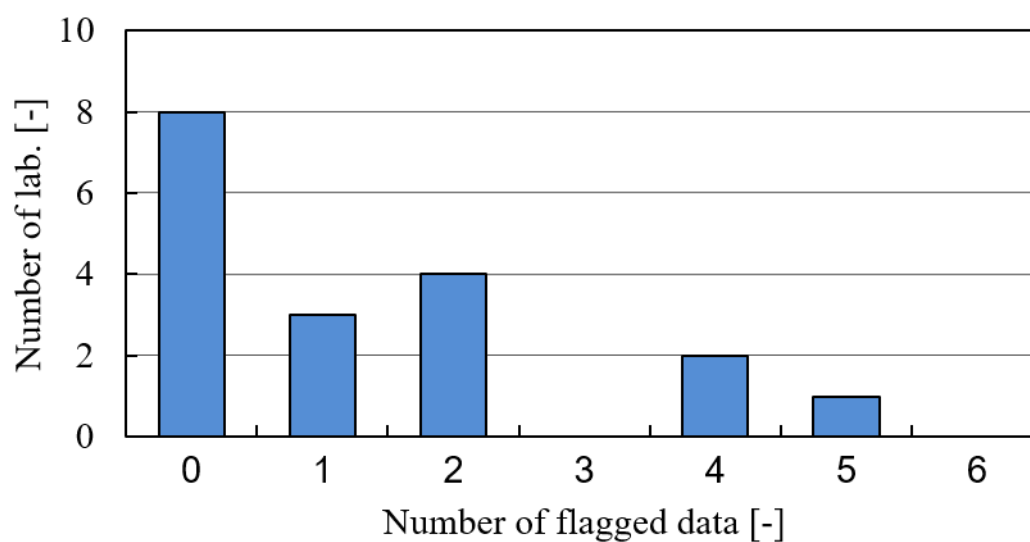
RU01	26	26	26
TH02	26	26	26
VN01	12	12	12
VN03	12	12	12

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

Flagged Data

In the results of Sample No.251d and No.252d, the total number of the flagged data was 24 (E: 15, X: 9) in the whole values (108). The number of the flagged data in each laboratory is shown in Figure 2.6. Night laboratories met DQOs (44.4%).

Figure 2.6 Number of flagged data and laboratories



Calibration standard solution

The ranges of the calibration standard solution in each laboratory are shown in Figure 2.7 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.

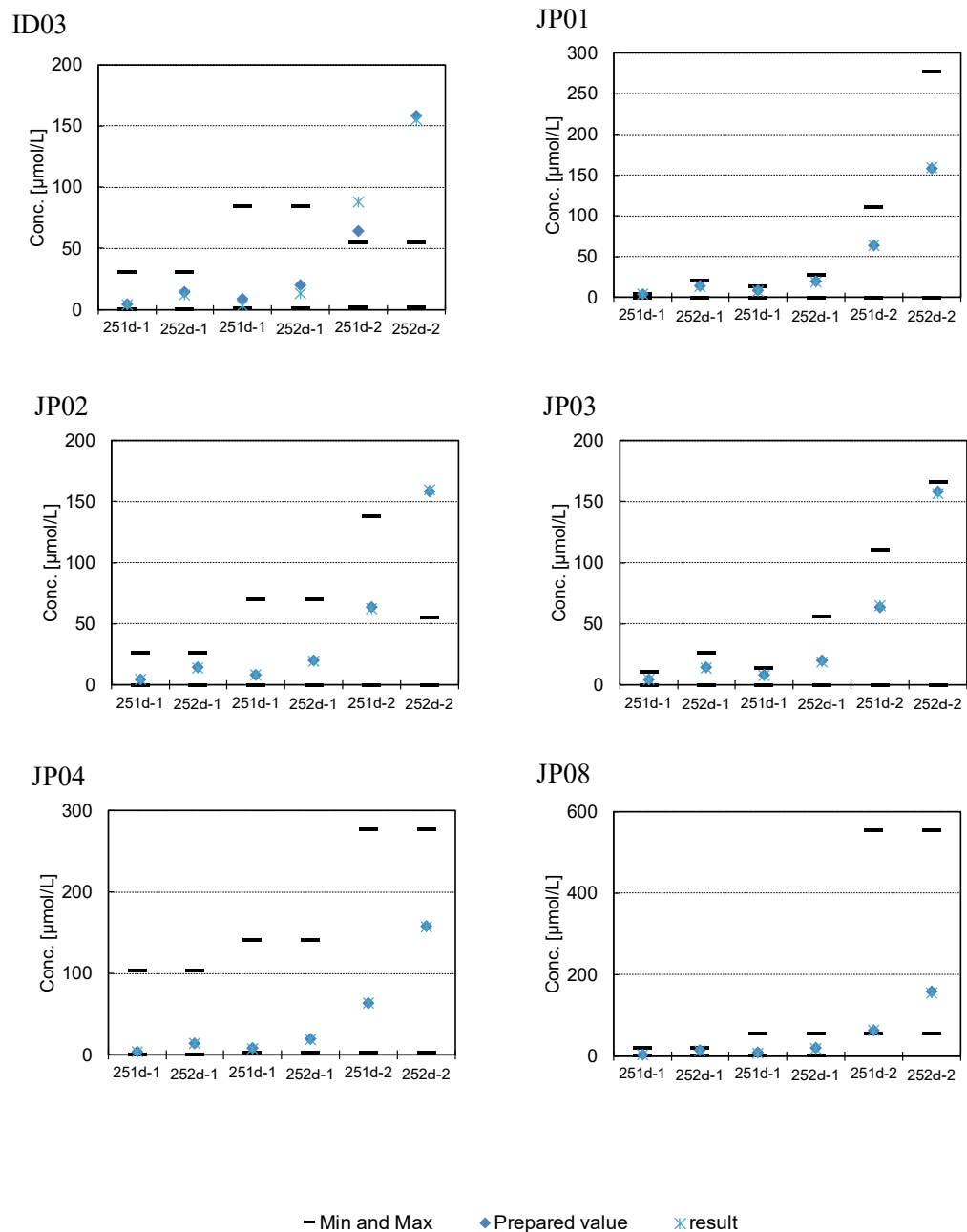
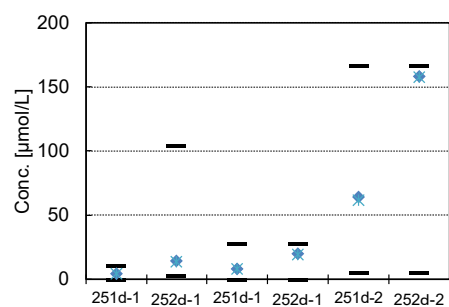
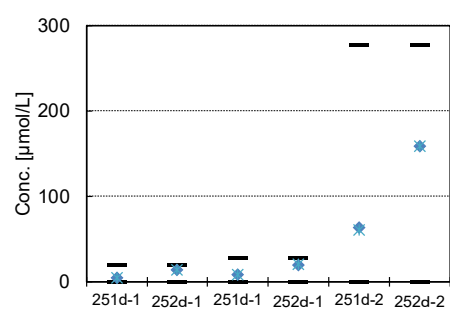


Figure 2.7 Ranges of the calibration standard solution in each laboratory

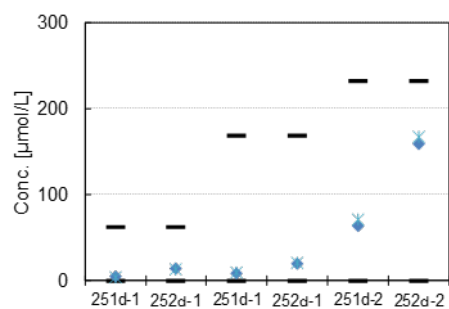
JP09



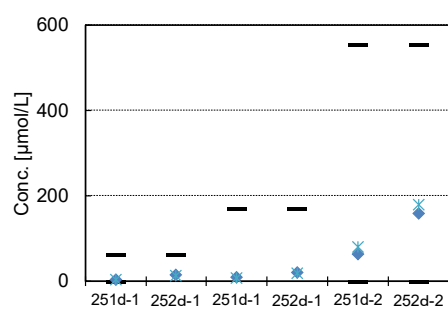
JP10



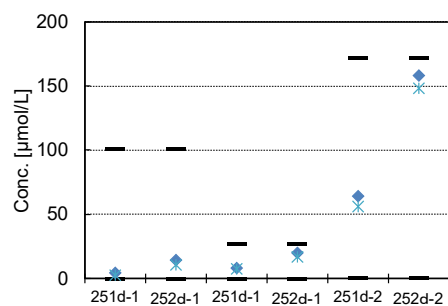
MY01



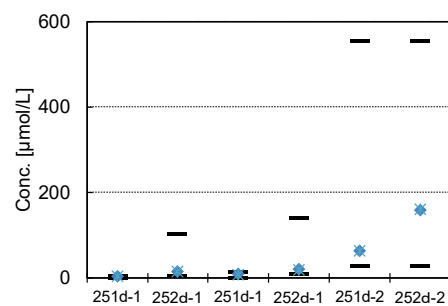
MN01



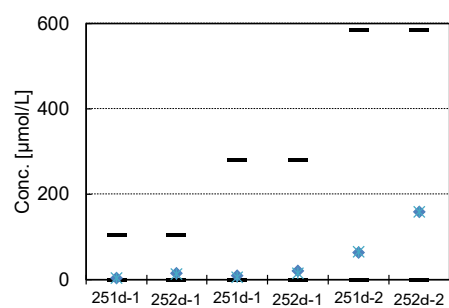
MM01



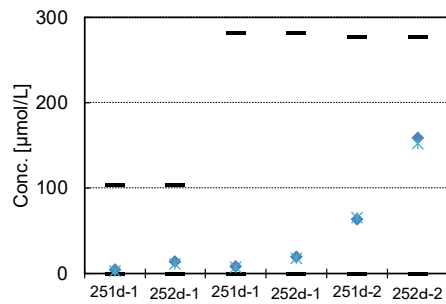
PH01



PH02



KR01



— Min and Max ◆ Prepared value ✕ result

Figure 2.7 Ranges of the calibration standard solution in each laboratory (continued)

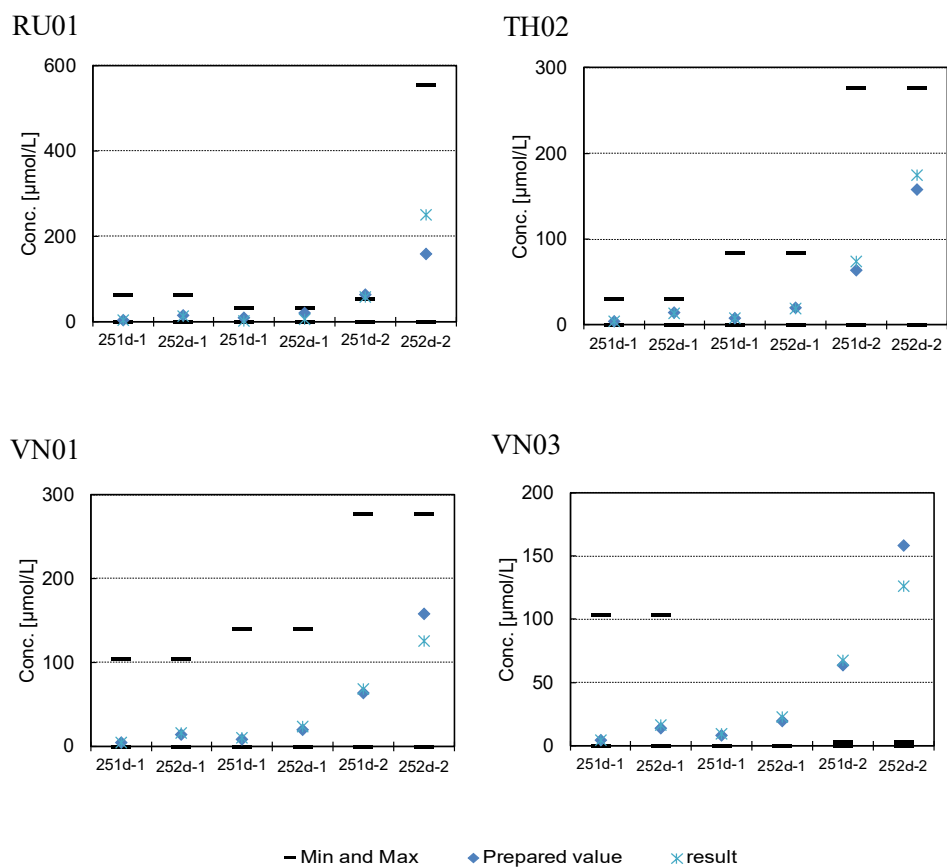


Figure 2.7 Ranges of the calibration standard solution in each laboratory (continued)

2.4 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 data meeting the DQOs were shown in Figure 2.8.

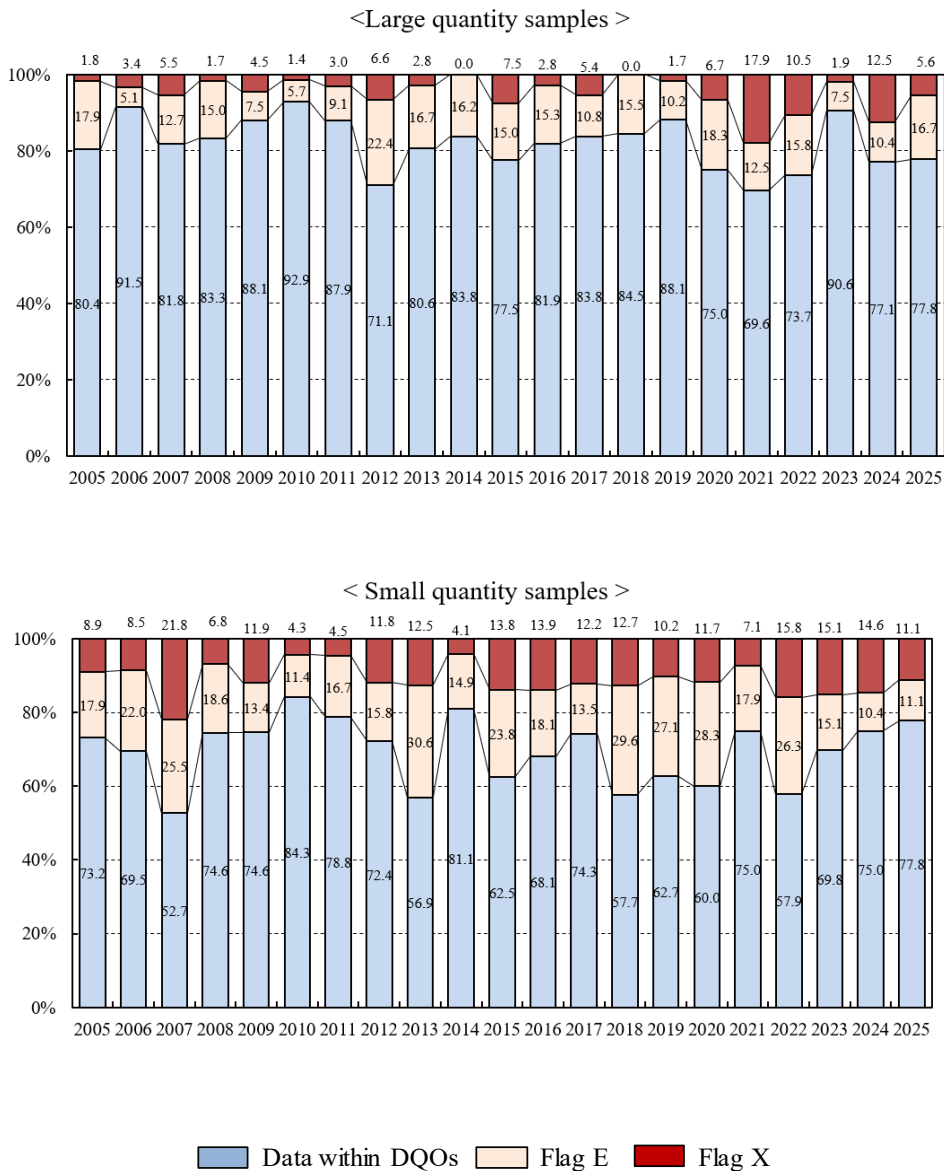


Figure 2.8 Comparison of DQOs' results for the past years

The comparison for each analyte in Inter-laboratory Comparison on dry deposition year-by-year is shown in Figure 2.9.

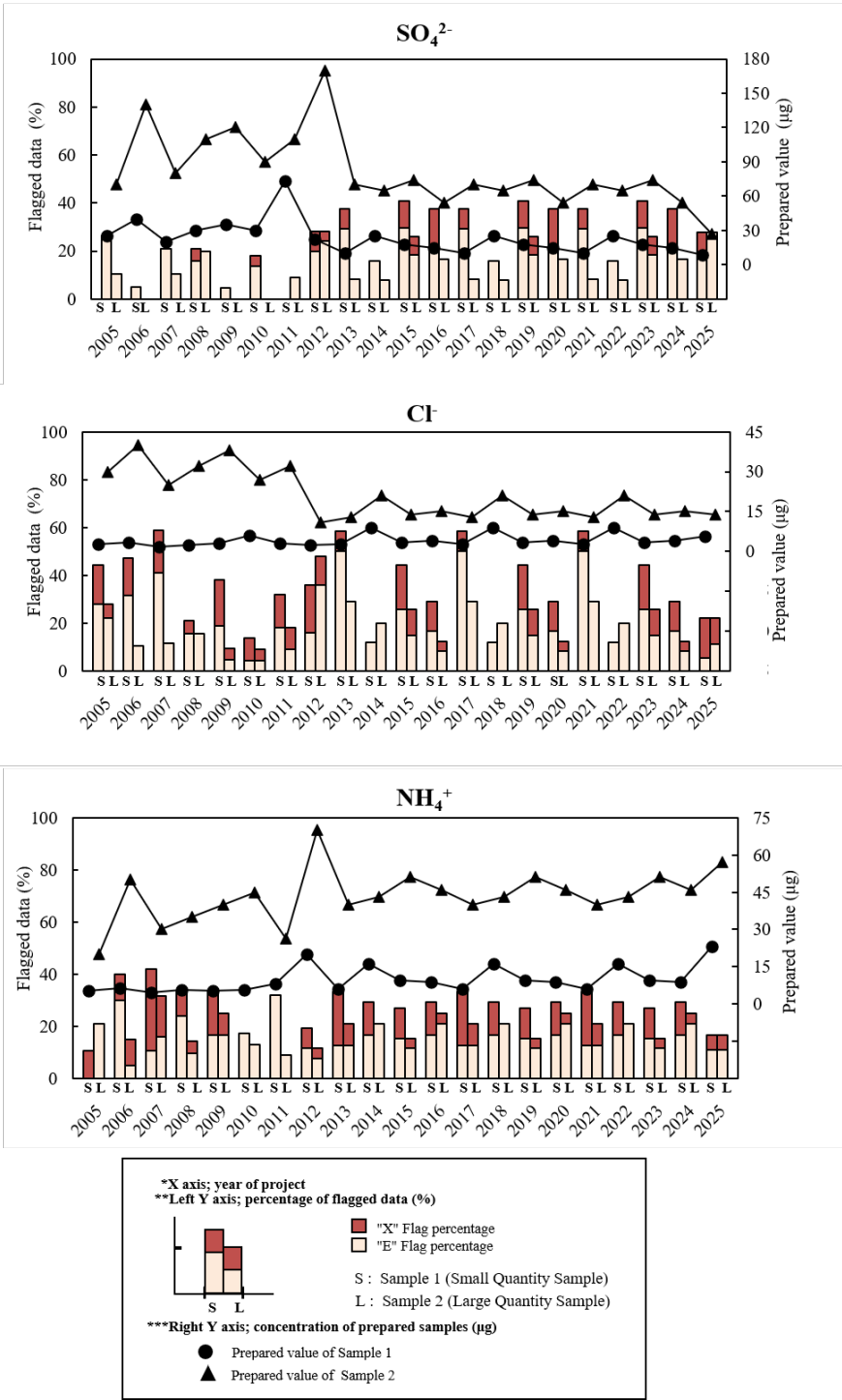


Figure 2.9 Comparison for each parameter in Inter-laboratory comparison project

2.5 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”

2.5.1 Measurement and Analyses

- ▶ Before placing the tubes in a shaker and start shaking for 20 minutes, shake each tube thoroughly by hand.
- ▶ Samples should not be diluted even if the concentration of the extract exceeds that of the highest standard solution prepared. Instead, add one or two higher-concentration standard solutions to extend the calibration curve, and measure the sample within the calibration range.
- ▶ Extraction, filtration, and analyses should be performed on the same day after the bag is opened. In particular, special care is needed for NH_4^+ determination. (Be aware that sample solutions may be contaminated by ammonia in the laboratory. Even if each sample is placed in an autosampler with a cap, the sample may still be contaminated by ammonia during analysis.)
- ▶ It is strongly recommended that only the interlaboratory samples be analyzed consecutively to minimize contamination during analysis. Regular samples should not be analyzed together 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.

3. 28th INTER-LABORATORY COMPARISON PROJECT ON WET DEPOSITION

3.1 Introduction

In the 28th 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 November 2025. Their analytical results were required to be submitted to the NC by 28 February 2026.

3.2 Procedures

3.2.1 Participating laboratories

The NC distributed the artificial rainwater samples to 33 laboratories in charge of chemical analysis in 13 countries of EANET. 31 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.

3.2.2 Description of samples

Two kinds of artificial rainwater samples were distributed to the laboratories. A description of the samples is given in Table 3.1.

Table 3.1 Description of artificial rainwater samples

Artificial rain-water sample	Quantity of sample	Container	Number of samples	Note
No. 251w No. 252w	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 3.2 are not added

The prepared values of analytical parameters in the artificial rainwater samples are described in Table 3.2. These parameters are calculated based on the quantity of reagents.

Table 3.2 Prepared values/concentrations of analytical parameters*

	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
	-	mS m ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹	μmol L ⁻¹
No. 251w	4.74	2.49	32.9	37.5	40.4	33.3	39.4	4.9	16.3	7.8
No. 252w	5.30	1.01	15.1	14.6	18.1	15.1	17.1	2.0	7.6	4.3

* For 100 times diluted samples.

3.2.3 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⁻¹) 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 SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺.

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 3.3.

Table 3.3 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 ₄ ²⁻ NO ₃ ⁻ Cl ⁻	Ion Chromatography (preferably with suppressor) Spectrophotometry
NH ₄ ⁺	Ion Chromatography Spectrophotometry (Indophenol Blue Method)
Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺	Ion Chromatography Atomic Absorption Spectrometry Atomic Emission Spectrometry

Checking analytical results was performed using the calculation of ion balance (R₁) and total electric conductivity agreement (R₂).

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 [$\mu\text{mol L}^{-1}$]).

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

n, c_{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 [$\mu\text{mol L}^{-1}$]).

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

n, c_{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 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 3.4. If R_1 was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 3.4 Allowable ranges for R_1 in different concentration ranges

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

Comparison between calculated and measured values of electrical conductivity (R₂)

(1) Total electrical conductivity (Λ 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 (R₂) was calculated as follows;

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

Λ meas : measured conductivity

(3) R₂ calculated by the above equation was compared with allowable ranges specified in the Technical Manual which are shown in Table 3.5. If R₂ was out of the range, re-measurement, check with standard solutions, and/or inspection of calibration curves were required.

Table 3.5 Allowable ranges for R₂ in different ranges of EC

Λ meas [mS m^{-1}]	R ₂ [%]
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9

3.3 Results

The NC received the analytical results from 31 laboratories in the participating countries of EANET.

Basic statistics of submitted data summarized in Table 3.6 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 3.6, the range of $\Delta V/V_p$ was between -3.5% to 5.5% for sample No. 251w, and -2.6% to 8.7% for sample No. 252w.

**Table 3.6 Summary of analytical results of the artificial rainwater samples
(Reported data after removing outliers)**

Sample No. 251w							
Constituents	Prepared (Vp)	Average (Va)	$\Delta V/V_p$ *1 %	S.D.	N	Min.	Max.
pH	4.74	4.84	2.0	0.13	31	4.60	5.18
EC [mS m ⁻¹]	2.49	2.40	-3.5	0.10	30	2.10	2.55
SO ₄ ²⁻ [μmol L ⁻¹]	32.9	32.8	-0.4	1.22	29	28.3	35.1
NO ₃ ⁻ [μmol L ⁻¹]	37.5	38.0	1.3	1.86	29	33.6	43.5
Cl ⁻ [μmol L ⁻¹]	40.4	40.4	-0.1	2.89	29	32.4	44.6
NH ₄ ⁺ [μmol L ⁻¹]	33.3	33.8	1.4	2.00	29	30.9	40.7
Na ⁺ [μmol L ⁻¹]	39.4	39.2	-0.5	1.81	29	35.9	46.4
K ⁺ [μmol L ⁻¹]	4.9	4.9	0.3	0.57	29	3.5	5.7
Ca ²⁺ [μmol L ⁻¹]	16.3	16.8	3.0	1.47	30	12.9	20.0
Mg ²⁺ [μmol L ⁻¹]	7.8	8.2	5.5	1.01	29	7.0	12.0
Sample No. 252w							
Constituents	Prepared (Vp)	Average (Va)	$\Delta V/V_p$ *1 %	S.D.	N	Min.	Max.
pH	5.30	5.29	-0.2	0.14	31	4.99	5.70
EC [mS m ⁻¹]	1.01	1.03	1.7	0.07	30	0.82	1.17
SO ₄ ²⁻ [μmol L ⁻¹]	15.1	14.7	-2.6	1.34	30	11.0	18.6
NO ₃ ⁻ [μmol L ⁻¹]	14.6	14.8	1.1	0.94	29	13.3	17.5
Cl ⁻ [μmol L ⁻¹]	18.1	18.3	1.0	2.17	29	11.9	22.2
NH ₄ ⁺ [μmol L ⁻¹]	15.1	16.0	6.2	1.82	30	14.1	21.4
Na ⁺ [μmol L ⁻¹]	17.1	17.0	-0.8	1.23	29	13.3	19.8
K ⁺ [μmol L ⁻¹]	2.0	2.2	8.7	0.59	30	0.8	3.8
Ca ²⁺ [μmol L ⁻¹]	7.6	7.8	2.6	0.76	29	6.7	10.6
Mg ²⁺ [μmol L ⁻¹]	4.3	4.5	5.3	0.65	29	3.6	6.7

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 3.2.3. 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. 251w and No. 252w,
- ii) Comparison of individual parameters,
- iii) Comparison of circumstances of chemical analysis in each participating laboratory.

Evaluation of analytical data on both sample No. 251w and No. 252w is presented in 3.3.1 Evaluation of laboratories’ performance (by sample), evaluation of analytical data for each constituent is presented in 3.3.2. 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 3.3.4 Information on laboratories.

3.3.1 Evaluation of laboratories' performance (by sample)

1) Sample No. 251w

The number and percentage of the flagged data for sample No. 251w are shown in Table 3.7. 25 analytical data out of 301 were flagged by "E". And 6 analytical data out of 301 were flagged by "X". Data flagged by "E" and "X" shared 10.3 percent of all the submitted data for sample No. 251w.

The data normalized by prepared value in each parameter are shown in Figure 3.1.

Table 3.7 Number of flagged data for the Sample No. 251w

Charactarization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total
Data within DQO	31	29	29	28	27	27	28	24	25	22	270
Data with flag E ^{*1}	0	1	1	2	2	2	1	5	5	6	25
Data with flag X ^{*2}	0	1	0	0	0	1	1	1	0	2	6
Flagged data [%]	0.0	6.5	3.3	6.7	6.9	10.0	6.7	20.0	16.7	26.7	10.3

(Total data = 301)

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

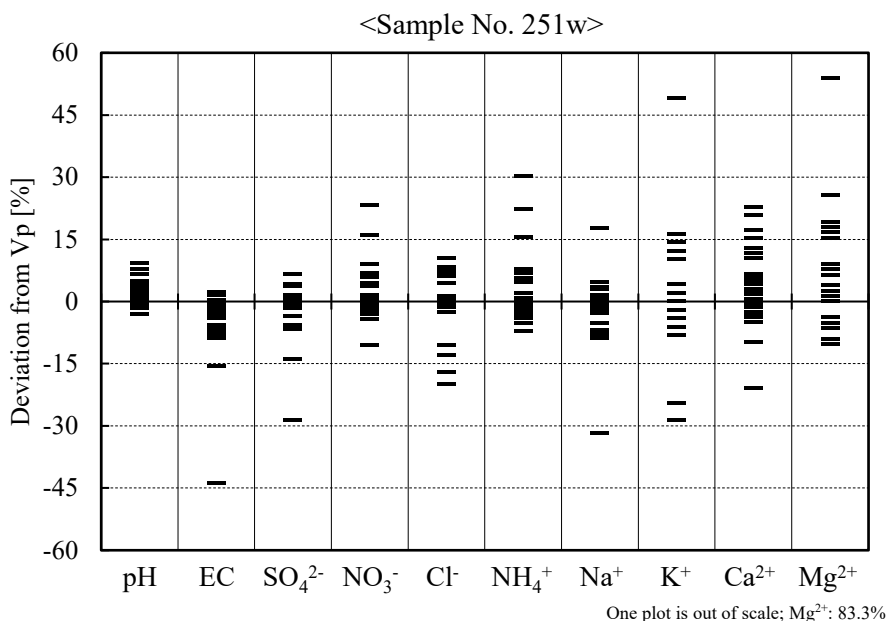


Figure 3.1 Distribution of the data normalized by prepared value in each parameter for sample No. 251w

The parameter which had the most flags was Mg²⁺. The analytical data submitted by the participating laboratories are shown in Table 3.8 with flags.

Table 3.8 Analytical Results of Sample No. 251w

Lab. ID	pH	EC mS m ⁻¹	SO ₄ ²⁻ μmol L ⁻¹	NO ₃ ⁻ μmol L ⁻¹	Cl ⁻ μmol L ⁻¹	NH ₄ ⁺ μmol L ⁻¹	Na ⁺ μmol L ⁻¹	K ⁺ μmol L ⁻¹	Ca ²⁺ μmol L ⁻¹	Mg ²⁺ μmol L ⁻¹	R ₁ %	R ₂ %
CN01	4.71	2.48	33.3	38.1	40.7	35.2	40.8	4.9	16.3	8.1	1.3	1.9
CN02	4.77	2.47	33.1	38.9	40.3	33.3	38.7	5.4	16.8	8.3	-0.3	0.1
CN03	4.97	2.29	32.8	39.2	40.6	35.0	39.1	5.1	16.8	9.2 E	-1.2	-0.3
CN04	4.80	2.40	33.3	38.9	40.3	32.2	40.0	5.1	17.0	7.8	-1.1	0.7
CN05	4.78	2.51	34.3	41.0	38.8	33.6	39.9	4.8	14.9	7.5	-3.0	-1.1
CN06	4.97	2.29	32.8	40.1	44.6	38.5 E	39.0	4.9	16.2	9.3 E	-2.1	0.9
ID01	4.67	2.46	31.7	36.5	35.2	43.4 X	26.9 X	3.5 E	12.9 E	7.8	0.5	0.8
ID02	4.82	2.31	35.1	39.9	43.0	30.9	40.6	4.7	16.8	7.9	-4.2	3.0
ID03	4.77	2.40	31.0	46.2 E	33.5 E	40.7 E	38.5	5.0	16.6	7.9	2.9	1.7
JP01	4.83	2.47	33.2	37.1	39.4	34.0	40.0	4.9	16.4	8.1	-0.1	-1.8
JP03	4.78	2.49	32.9	37.2	40.1	33.5	38.9	4.7	16.1	7.3	-0.9	-1.4
JP04	4.78	2.44	32.5	37.0	39.9	33.6	38.6	4.9	15.8	7.5	-0.6	-0.6
JP08	4.81	2.39	32.7	37.6	40.9	33.5	39.6	4.9	16.2	7.8	-0.8	0.2
JP09	4.84	2.40	32.8	36.7	40.0	33.1	39.5	4.9	16.3	7.8	-0.8	-1.0
JP10	4.79	2.53	34.1	39.7	42.2	32.3	39.6	4.8	18.4	8.4	-1.2	-0.7
JP14	4.87	2.40	33.1	37.4	40.6	33.0	38.9	4.9	16.1	7.1	-2.7	-1.7
MY01	4.81	2.49	32.8	36.8	40.4	34.9	41.3	5.6	17.4	7.0	1.1	-1.4
MN01	4.60	2.27	34.3	40.9	40.8	34.9	36.3	4.6	18.2	8.0	1.0	10.5
MM01	4.73	1.40 X	33.4	36.6	43.1	33.6	38.3	4.8	17.2	7.5	-0.6	28.8 C
PH01	4.66	2.29	33.3	35.9	40.5	31.6	38.7	5.5	15.7	7.4	0.3	6.2
PH02	4.93	2.48	23.5 E	33.6	32.4 E	32.0	35.9	3.5 E	18.8 E	14.3 X	13.9 I	-8.5
KR01	4.76	2.42	32.4	37.2	40.3	35.6	39.1	4.9	15.9	7.9	0.8	0.9
RU01	4.79	2.50	30.7	36.4	43.8	35.9	36.7	3.7 E	16.7	8.5	0.5	-1.7
RU02	5.05	2.10 E	28.3	43.5 E	36.2	32.3	46.4 E	7.3 X	14.7	12.0 X	4.2	1.8
TH01	4.79	2.46	---	---	---	---	---	---	---	---	---	---
TH02	4.81	2.55	32.8	37.5	40.0	32.7	39.1	4.5	15.5	7.3	-2.0	-3.6
VN01	4.96	2.33	32.5	37.5	43.3	32.4	38.8	5.5	19.7 E	9.3 E	0.0	-0.5
VN02	4.92	2.34	32.4	37.6	43.4	32.5	38.7	5.6	19.1 E	9.0 E	-0.3	-0.1
VN03	5.18	2.42	33.4	37.7	---	33.4	39.2	5.7 E	17.1	9.1 E	---	---
VN04	5.11	2.32	32.7	37.4	42.9	32.2	39.0	5.5	20.0 E	9.8 E	-0.6	-2.6
VN05	4.89	2.35	33.0	37.8	43.8	33.3	37.4	5.7 E	18.0	8.0	-2.2	0.1
Vp	4.74	2.49	32.9	37.5	40.4	33.3	39.4	4.9	16.3	7.8	0.1	0.1
N of data	31	31	30	30	29	30	30	30	30	30		
Within DQO	31	29	29	28	27	27	28	24	25	22		
Flag E	0	1	1	2	2	2	1	5	5	6		
Flag X	0	1	0	0	0	1	1	1	0	2		

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

"I", Poor ion balance (R₁); "C", Poor conductivity agreement (R₂); "---", 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. 252w

The number and percentage of the flagged data for sample No. 252w are shown in Table 3.9. 28 analytical data out of 301 were flagged by "E". 21 analytical data out of 301 were flagged by "X". Data marked with flags shared up to 16.3 percent of all the submitted data for sample No. 252w.

The normalized data by prepared value in each parameter are shown in Figure 3.2.

Table 3.9 Number of flagged data for the sample No. 252w

Characterization of data	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total
Data within DQO	31	28	26	27	21	25	26	17	27	24	252
Data with flag E ^{*1}	0	3	4	2	7	3	3	3	1	2	28
Data with flag X ^{*2}	0	0	0	1	1	2	1	10	2	4	21
Flagged data [%]	0.0	9.7	13.3	10.0	27.6	16.7	13.3	43.3	10.0	20.0	16.3

(Total data = 301)

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

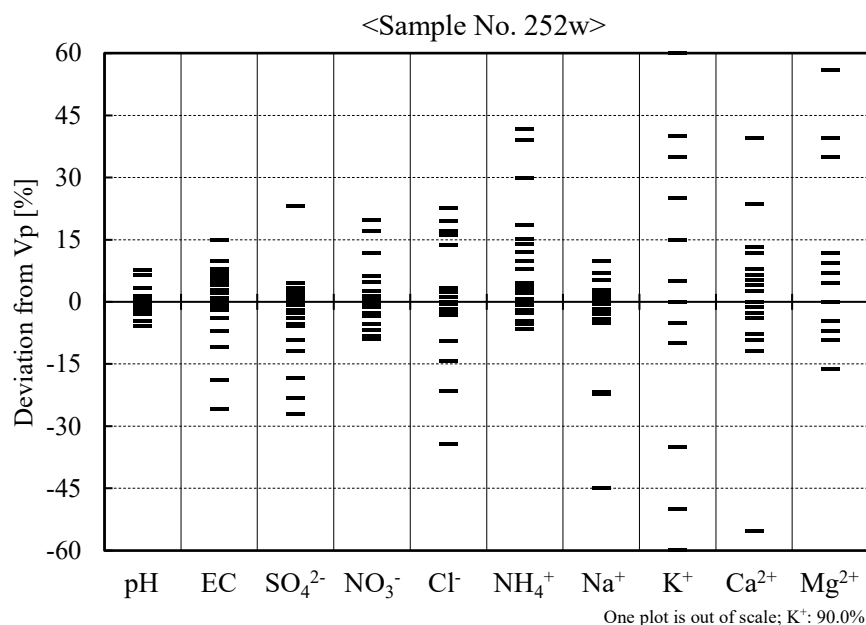


Figure 3.2 Distribution of the data normalized by prepared value for each parameter for sample No. 252w

The parameter which had the most flags was K⁺. The analytical data submitted by the participating laboratories are shown in Table 3.10 with flags.

Table 3.10 Analytical Results of Sample No. 252w

Lab. ID* ¹	pH	EC mS m ⁻¹	SO ₄ ²⁻ μmol L ⁻¹	NO ₃ ⁻ μmol L ⁻¹	Cl ⁻ μmol L ⁻¹	NH ₄ ⁺ μmol L ⁻¹	Na ⁺ μmol L ⁻¹	K ⁺ μmol L ⁻¹	Ca ²⁺ μmol L ⁻¹	Mg ²⁺ μmol L ⁻¹	R ₁ %	R ₂ %
CN01	5.21	1.02	15.0	15.0	18.5	16.6	18.0	2.1	8.0	4.7	3.6	2.7
CN02	5.26	1.02	15.0	14.4	18.3	14.4	17.4	2.1	7.5	4.6	0.7	0.1
CN03	5.35	1.03	15.5	16.3	21.1 E	15.6	17.3	2.8 X	8.0	5.8 X	-0.5	1.4
CN04	5.28	1.03	14.7	14.4	17.5	14.4	17.4	2.0	8.0	4.1	1.6	-1.4
CN05	5.08	1.17 E	15.6	15.5	16.9	15.1	19.8 E	1.9	7.9	4.6	4.9	-1.0
CN06	5.35	1.03	14.8	15.5	21.2 E	17.9 E	16.8	2.5 E	7.8	6.7 X	3.2	1.6
ID01	5.24	0.82 E	11.6 E	13.4	14.2 E	21.4 X	9.4 X	1.0 X	3.4 X	3.9	1.3	3.8
ID02	5.15	0.94	18.6 E	17.5 E	22.2 E	14.1	17.6	1.9	8.5	4.6	-7.0	12.0
ID03	5.33	1.09	13.7	17.1 E	16.4	21.0 X	17.2	1.9	8.1	4.8	7.4	-2.7
JP01	5.27	1.08	14.7	14.1	17.5	15.8	17.3	1.9	7.9	4.6	3.5	-3.0
JP03	5.20	1.06	15.3	14.7	17.6	15.4	16.6	1.8	7.3	4.0	-0.2	-0.8
JP04	5.32	1.02	15.1	14.5	18.0	15.5	16.8	2.0	7.9	4.3	0.6	-0.9
JP08	5.26	0.97	15.3	14.7	18.0	15.1	17.2	1.9	7.6	4.3	0.2	2.8
JP09	5.35	1.03	15.1	14.5	18.1	15.2	17.1	2.0	7.5	4.3	-0.3	-2.2
JP10	5.28	1.07	15.6	15.0	18.7	14.7	17.0	1.9	8.2	4.6	-0.3	-1.6
JP14	5.47	1.01	15.4	14.4	18.3	15.0	16.7	2.3	6.9	3.6 E	-4.2	-3.7
MY01	5.29	1.04	14.7	14.1	18.1	17.2	18.3	2.3	7.8	3.6 E	3.2	-1.0
MN01	5.06	1.05	15.1	15.3	17.6	15.8	16.2	1.9	9.4 E	4.6	5.6	5.0
MM01	4.99	0.75 E	14.8	14.4	21.0 E	15.5	18.8	2.5 E	10.6 X	4.6	8.7 I	25.3 C
PH01	5.36	0.94	15.8	13.6	18.0	14.1	16.4	2.5 E	7.6	4.0	-2.1	1.9
PH02	5.37	0.99	11.0 E	15.3	15.5	16.9	13.3 E	1.3 X	8.6	7.2 X	12.1 I	-3.0
KR01	5.15	1.04	14.5	13.3	17.8	17.4 E	16.8	2.1	7.4	4.5	5.6	1.6
RU01	5.23	1.03	14.3	13.8	18.1	16.3	13.4 E	0.8 X	7.3	4.3	-0.8	-1.6
RU02	5.64	0.90	12.3 E	24.9 X	11.9 X	19.6 E	16.2	3.8 X	6.7	6.0 X	4.6	2.3
TH01	5.27	1.04	---	---	---	---	---	---	---	---	---	---
TH02	5.31	1.07	15.1	14.6	18.1	15.7	17.1	2.0	7.0	4.0	-1.0	-3.5
VN01	5.27	1.02	15.1	14.6	20.6	15.4	17.1	2.7 X	7.4	4.5	-0.8	1.2
VN02	5.22	1.05	15.2	14.8	21.6 E	15.5	17.0	2.7 X	7.3	4.6	-1.3	1.4
VN03	5.70	1.16	13.3	14.4	---	14.3	17.5	3.2 X	6.9	4.3	---	---
VN04	5.48	1.00	15.0	14.6	18.0	15.2	17.1	2.7 X	7.5	4.5	-0.2	-2.5
VN05	5.19	1.11	14.2	14.2	21.1 E	14.8	16.4	2.7 X	7.6	4.3	0.4	-2.2
Vp	5.30	1.01	15.1	14.6	18.1	15.1	17.1	2.0	7.6	4.3	0.1	-0.2
N of data	31	31	30	30	29	30	30	30	30	30		
Within DQO	31	28	26	27	21	25	26	17	27	24		
Flag E	0	3	4	2	7	3	3	3	1	2		
Flag X	0	0	0	1	1	2	1	10	2	4		

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

"I", Poor ion balance (R₁); "C", Poor conductivity agreement (R₂); "---", 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. 251w and 252w are shown in Figure 3.3. The percentage of the data within the DQO for sample No. 251w and 252w were 89.7% and 83.7%, respectively. The difference between both samples was 6.0%. In this project, the total number of flagged data was 80 (E: 53, X: 27) out of all the 602 data.

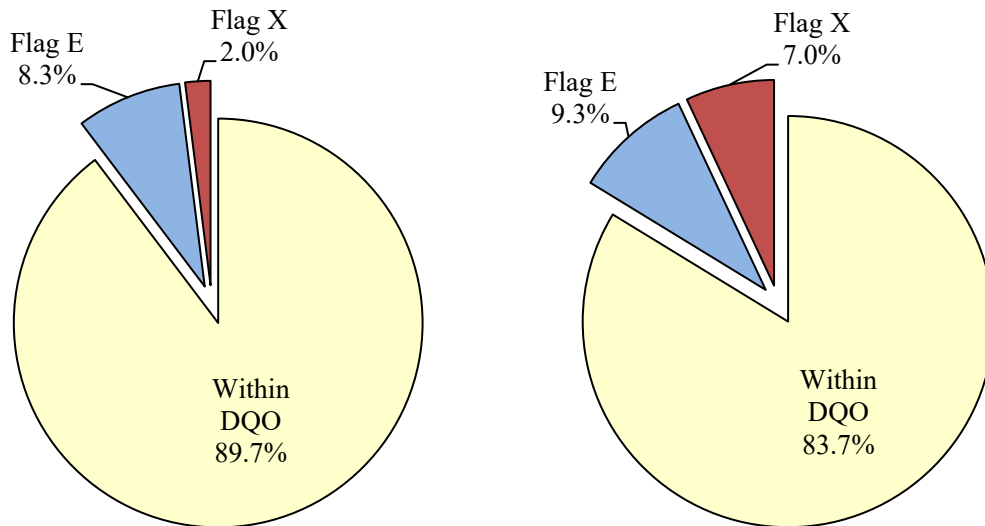


Figure 3.3 Percentage of flagged data for sample No. 251w and No. 252w (Left: No. 251w, Right: No. 252w)

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

The number of laboratories by number of flags is shown in Figure 3.4. The number of laboratories without flagged data was 11, which corresponds to 35.5% of all the participating laboratories.

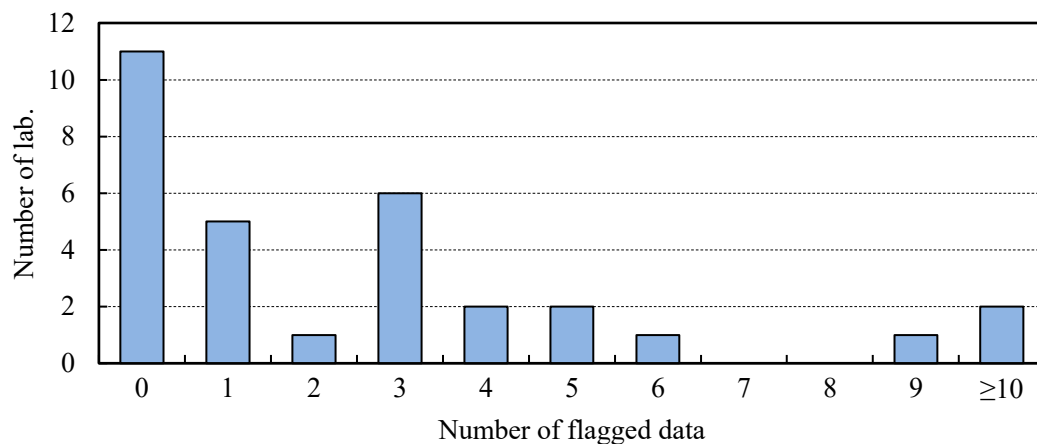


Figure 3.4 Distribution of the number of laboratory (by number of flags)

2.3.2 Evaluation of laboratories' performance (by analytical parameter)

The data normalized by V_p are shown in Figures 3.5 through 3.24 for each parameter. In scatter diagrams (lower figures), bold line means the prepared values of sample No. 251w and 252w, 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".

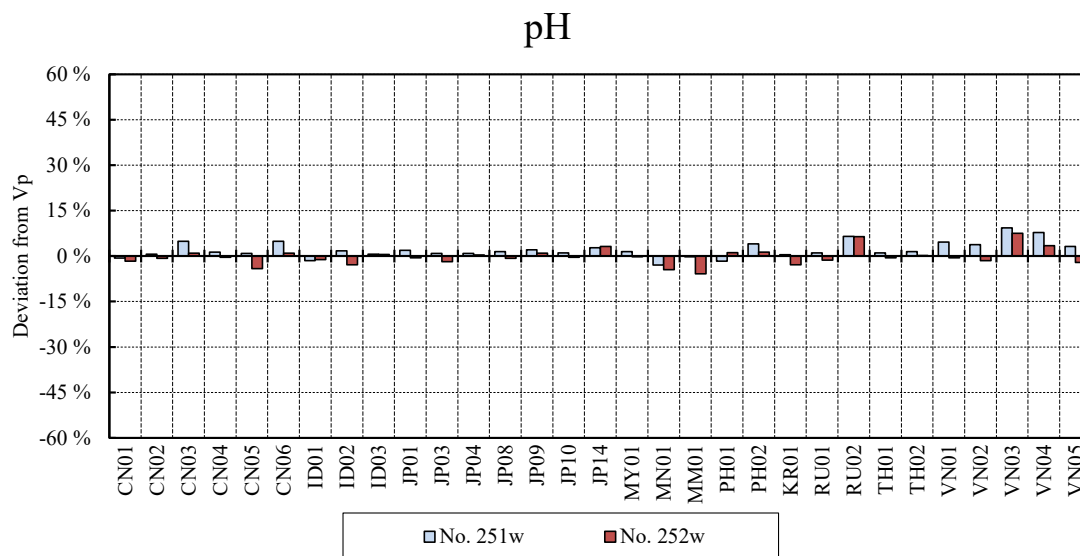


Figure 3.5 Deviation from prepared value for pH (normalized by prepared value)

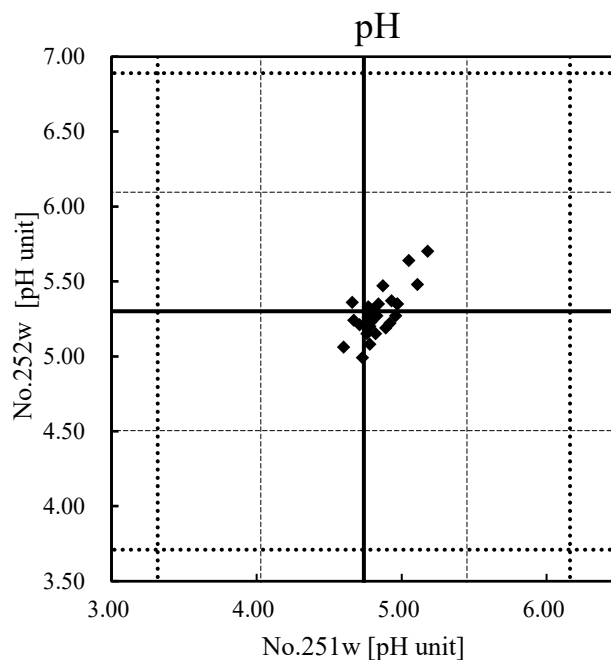


Figure 3.6 Scatter diagram for pH

2) EC

All participating laboratories used conductivity cell method for the measurement of EC.

The data of sample No. 251w from RU02 and sample No.252w from 3 laboratories (CN05, ID01 and MM01) were marked with flag “E”. Additionally, the data of sample No.251w from MM01 were marked with flag “X”.

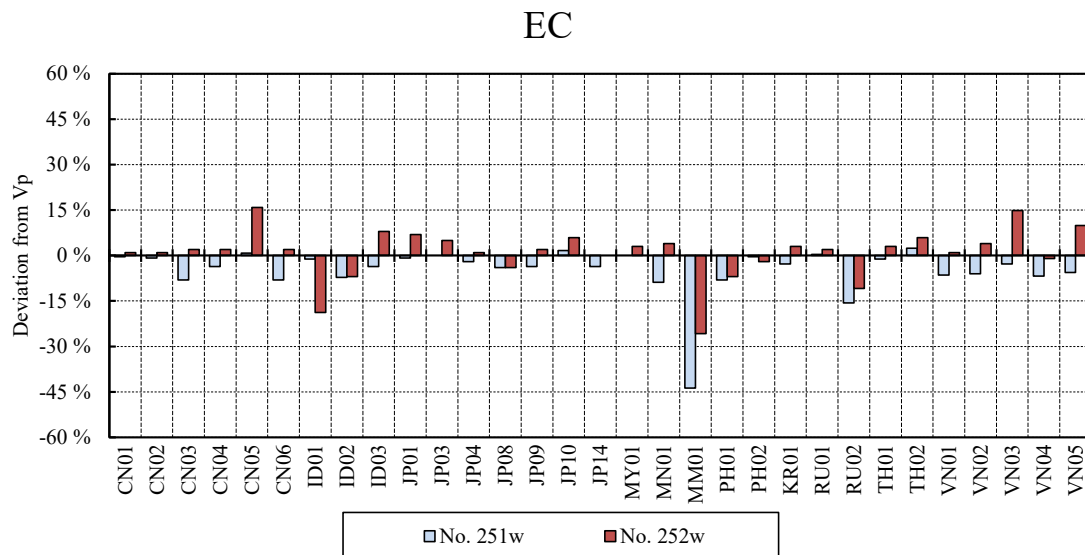


Figure 3.7 Deviation from prepared value for EC (normalized by prepared value)

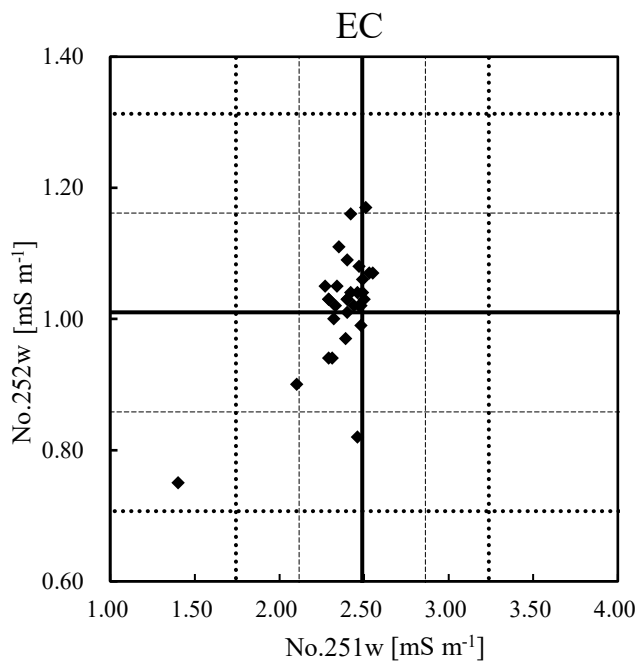


Figure 3.8 Scatter diagram for EC

3) SO_4^{2-}

The data of sample No. 251w from PH02 and sample No.252w from 4 laboratories (ID01, ID02, PH02, and RU02) were marked with flag “E”.

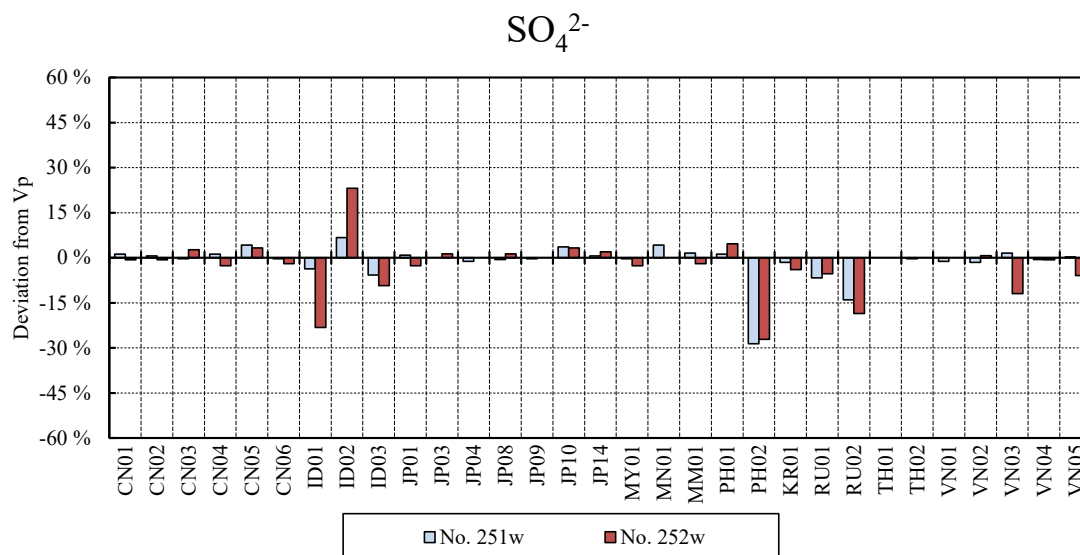


Figure 3.9 Deviation from prepared value for SO_4^{2-} (normalized by prepared value)

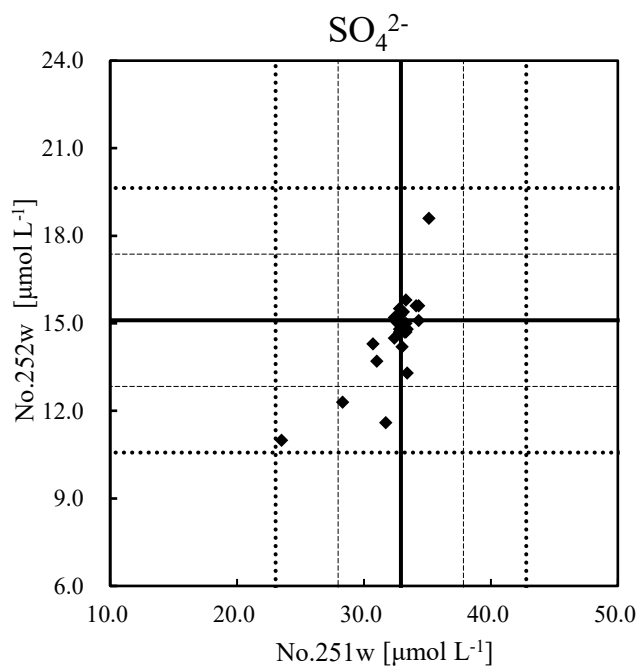


Figure 3.10 Scatter diagram for SO_4^{2-}

4) NO_3^-

The data of sample No. 251w from 2 laboratories (ID03 and RU02) and sample No.252w from 2 laboratories (ID02 and ID03) were marked with flag “E”. Additionally, the data of sample No.252w from RU02 were marked with flag “X”.

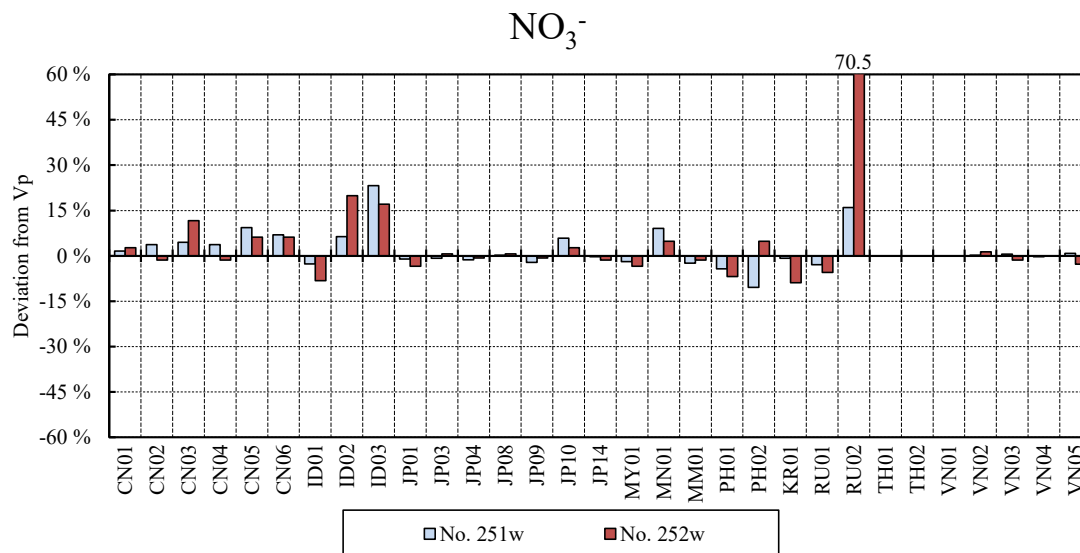


Figure 3.11 Deviation from prepared value for NO_3^- (normalized by prepared value)

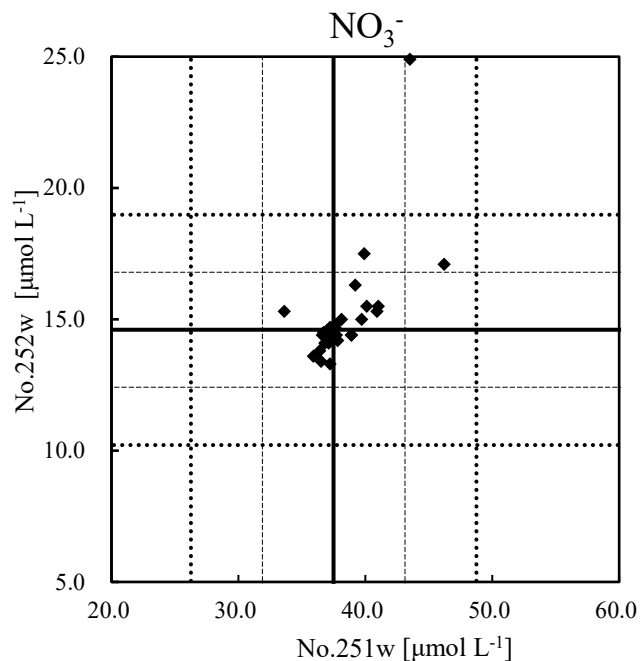


Figure 3.12 Scatter diagram for NO_3^-

5) Cl^-

The data of sample No. 251w from 2 laboratories (ID03 and PH02) and sample No.252w from 7 laboratories (CN03, CN06, ID01, ID02, MM01, VN02, and VN05) were marked with flag “E”. Additionally, the data of sample No.252w from RU02 were marked with flag “X”.

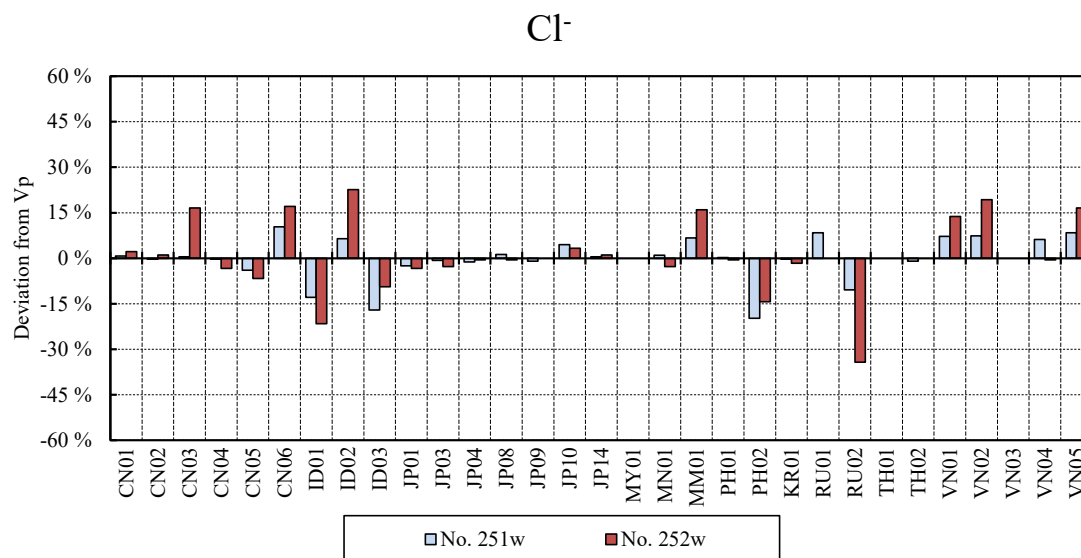


Figure 3.13 Deviation from prepared value for Cl^- (normalized by prepared value)

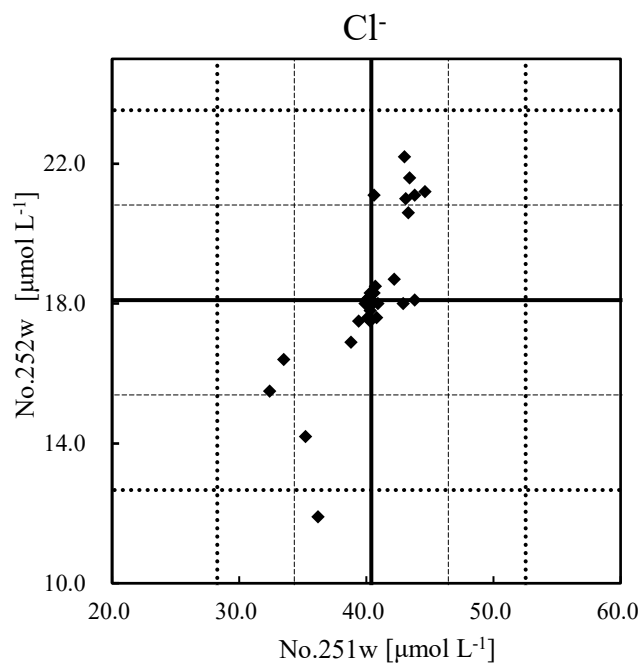


Figure 3.14 Scatter diagram for Cl^-

6) NH_4^+

The data of sample No. 251w from 2 laboratories (CN06 and ID03) and sample No.252w from 3 laboratories (CN06, KR01, and RU02) were marked with flag “E”. Additionally, the data of sample No. 251w from ID01 and sample No.252w from 2 laboratories (ID01 and ID03) were marked with flag “X”.

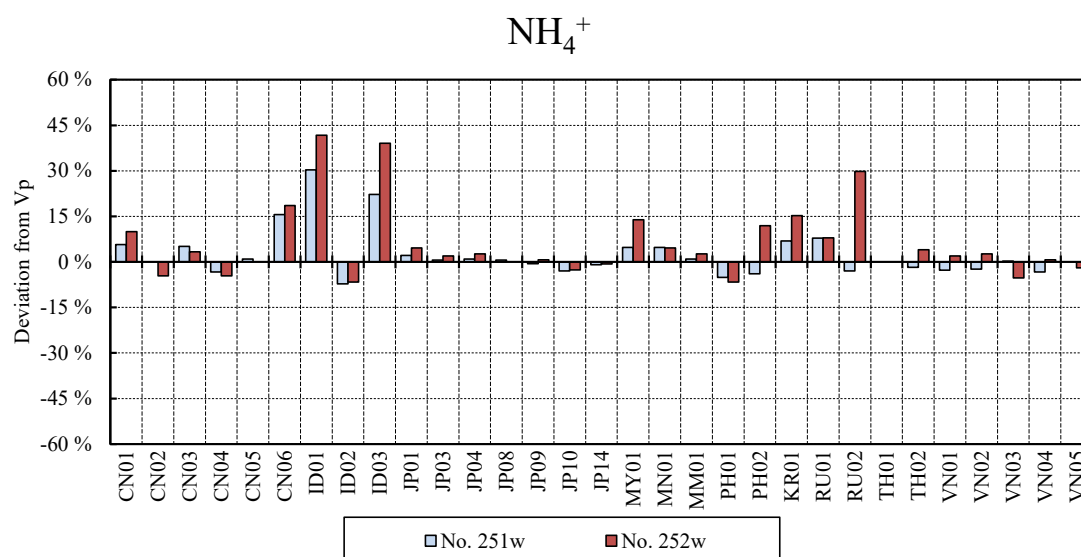


Figure 3.15 Deviation from prepared value for NH_4^+ (normalized by prepared value)

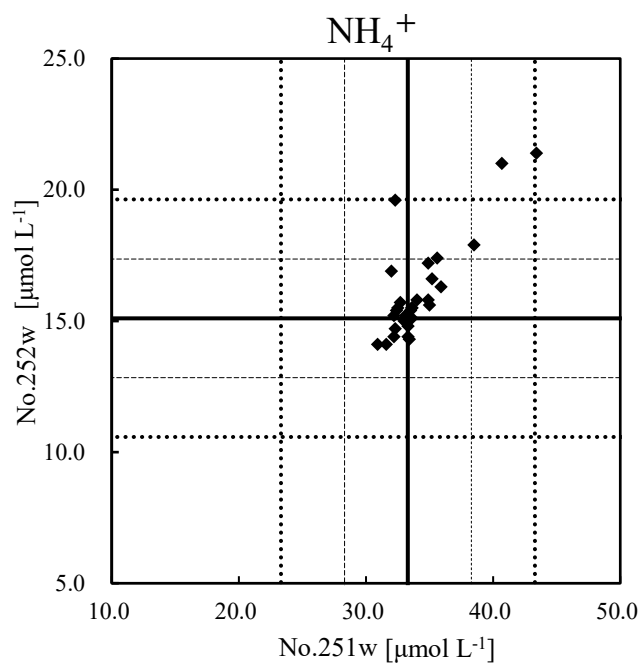


Figure 3.16 Scatter diagram for NH_4^+

7) Na⁺

The data of sample No. 251w from RU02 and sample No.252w from 3 laboratories (CN05, PH02 and RU01) were marked with flag “E”. Additionally, the data of sample No.251w and No. 252 from ID01 were marked with flag “X”.

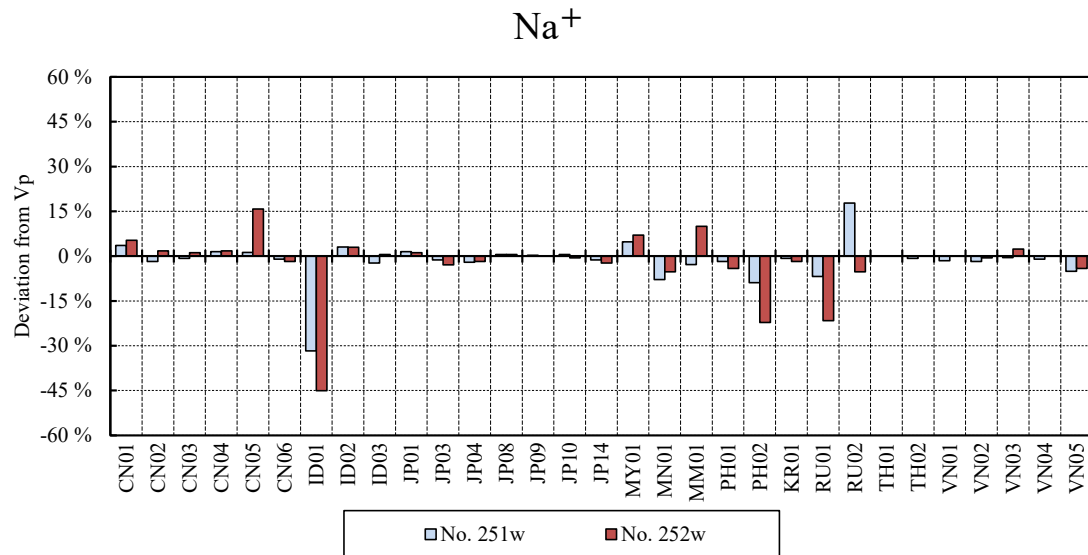


Figure 3.17 Deviation from prepared value for Na⁺ (normalized by prepared value)

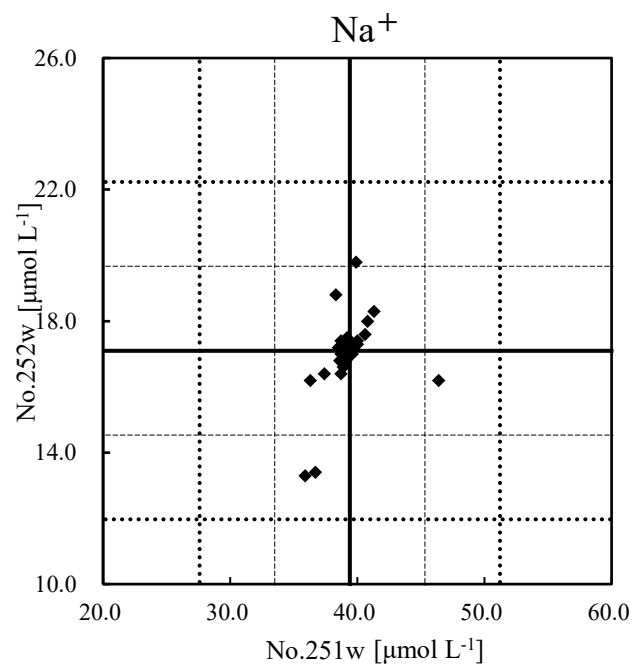


Figure 3.18 Scatter diagram for Na⁺

8) K^+

The data of sample No. 251w from 5 laboratories (ID01, PH02, RU01, VN03, and VN05) and sample No.252w from 3 laboratories (CN06, MM01, and PH01) were marked with flag “E”. Additionally, the data of sample No. 251w from RU02 and sample No. 252w from 10 laboratories (CN03, ID01, PH02, RU01, RU02, VN01, VN02, VN03, VN04, and VN05) were marked with flag “X”.

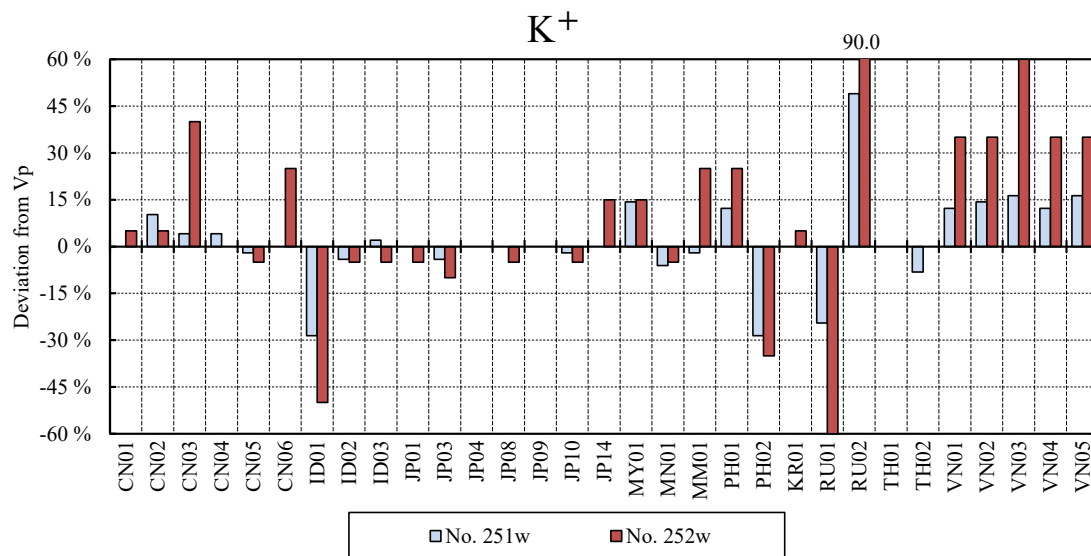


Figure 3.19 Deviation from prepared value for K^+ (normalized by prepared value)

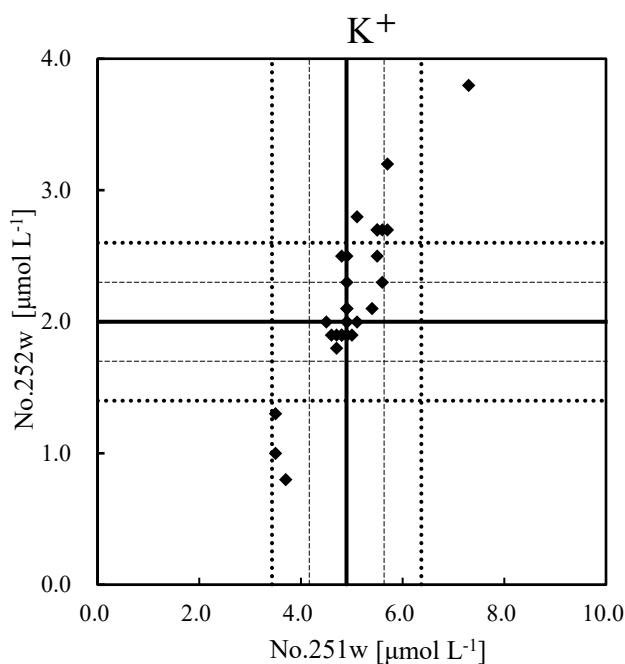


Figure 3.20 Scatter diagram for K^+

9) Ca^{2+}

The data of sample No. 251w from 5 laboratories (ID01, PH02, VN01, VN02, and VN04) and sample No. 252w from MN01 were marked with flag “E”. Additionally, the data of sample No.252w from 2 laboratories (ID01 and MM01) were marked with flag “X”.

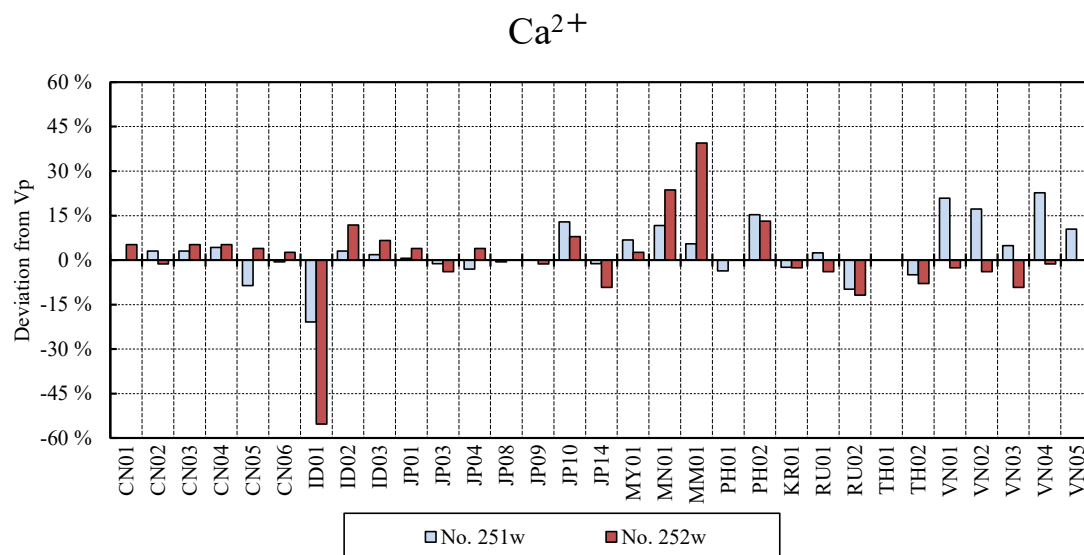


Figure 3.21 Deviation from prepared value for Ca^{2+} (normalized by prepared value)

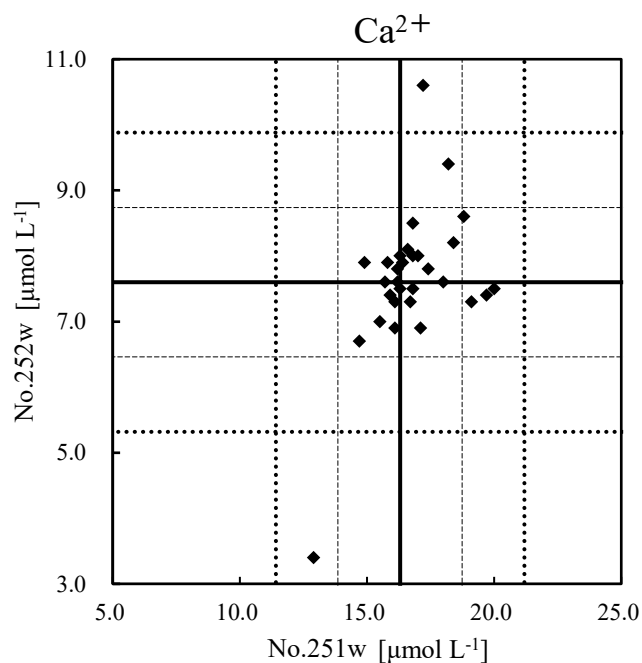


Figure 3.22 Scatter diagram for Ca^{2+}

10) Mg^{2+}

The data of sample No. 251w from 6 laboratories (CN03, CN06, VN01, VN02, VN03, and VN04) and sample No.252w from 2 laboratories (JP14 and MY01) were marked with flag “E”. Additionally, the data of sample No. 251w from 2 laboratories (PH02 and RU02) and sample No. 252w from 4 laboratories (CN03, CN06, PH02, and RU02) were marked with flag “X”.

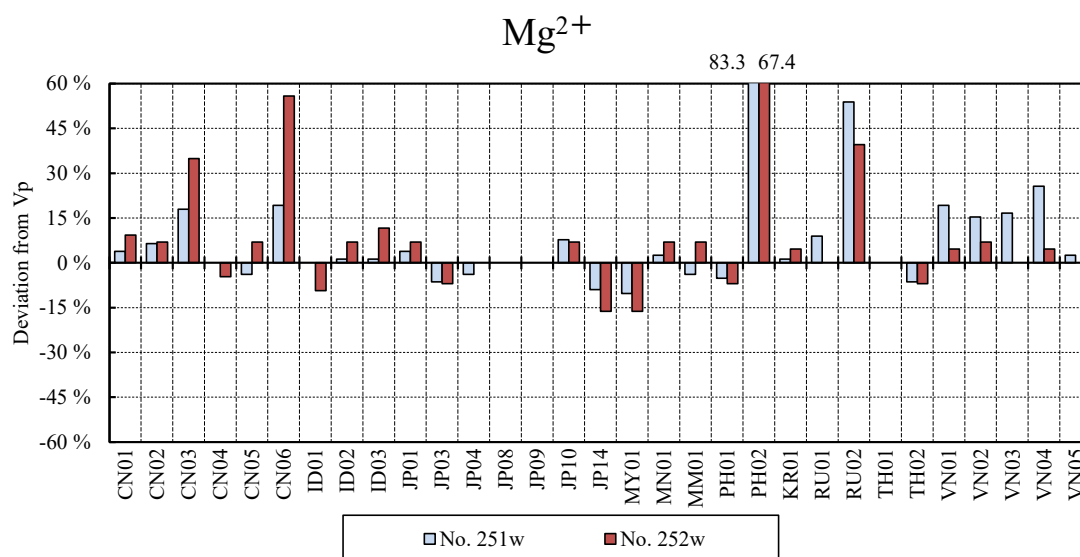


Figure 3.23 Deviation from prepared value for Mg^{2+} (normalized by prepared value)

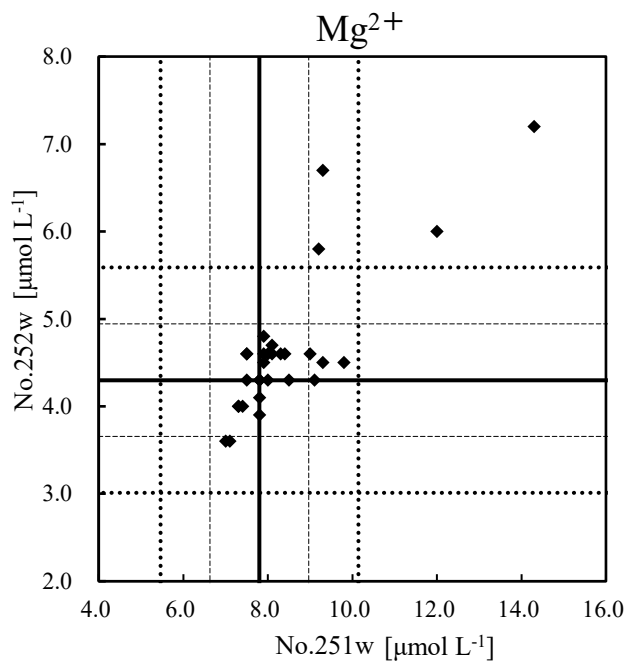


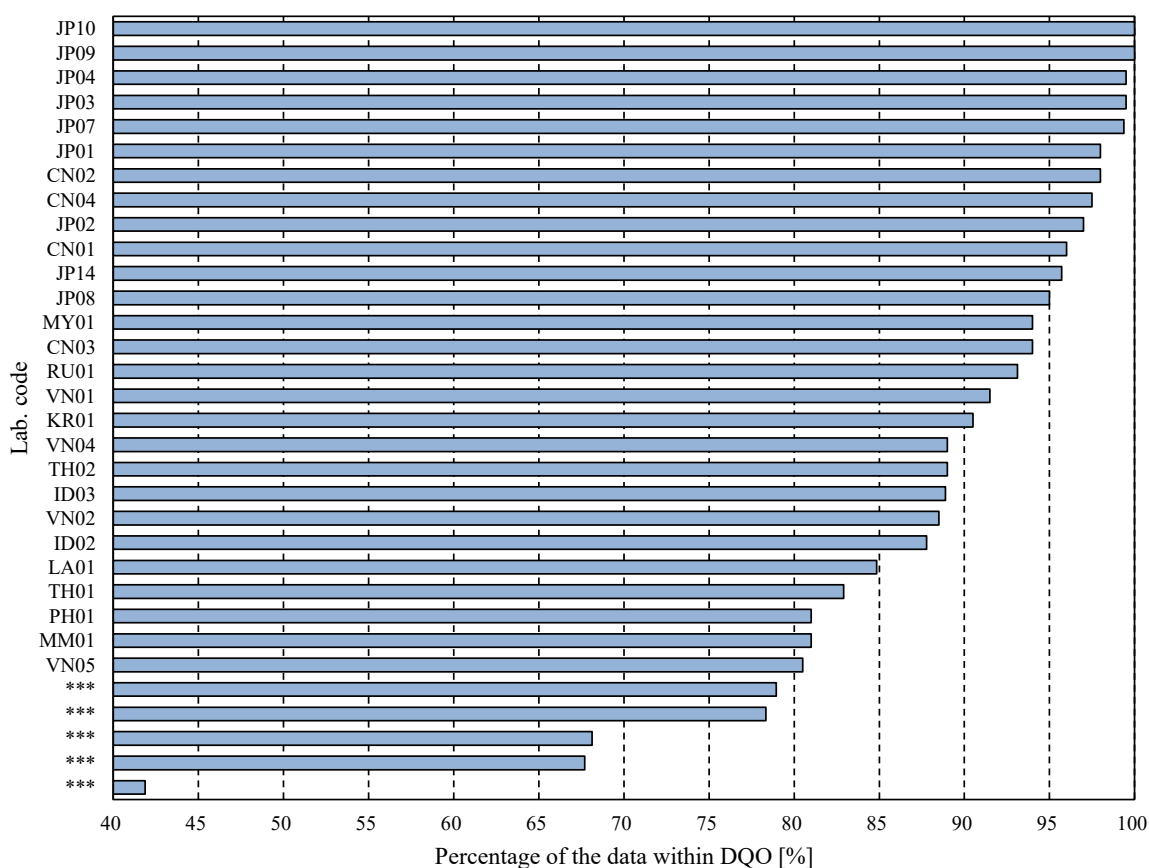
Figure 3.24 Scatter diagram for Mg^{2+}

11) Scatter diagrams

Most of constituents showed positive correlation between the submitted pairs of results of sample No. 251w and 252w. It suggested that systematic error could be the reason for the deviation of results in most laboratories.

12) Percentage of the data within DQO

Figure 3.25 shows the percentage of the data within DQO for each participating laboratory from 2016 to 2025. All the analytical data of 2 laboratories (JP09 and JP10) met DQO, while the percentage of the data within DQO in 5 laboratories was below 80%.



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

Figure 3.25 Percentage of the data within DQO for each participating laboratory (2016-2025)

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^+) concentrations of sample No. 251w were higher than those of No. 252w.

The relative standard deviations (R.S.D.) of each parameter for sample No. 251w and No. 252w are shown in the Figure 3.26. Of all items, the R.S.D. values of sample No. 252w were higher than those of sample No.251w. K^+ had the largest R.S.D. value difference between sample No.251w and No. 252w. The R.S.D. of K^+ for sample No. 252w was the largest in this survey.

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

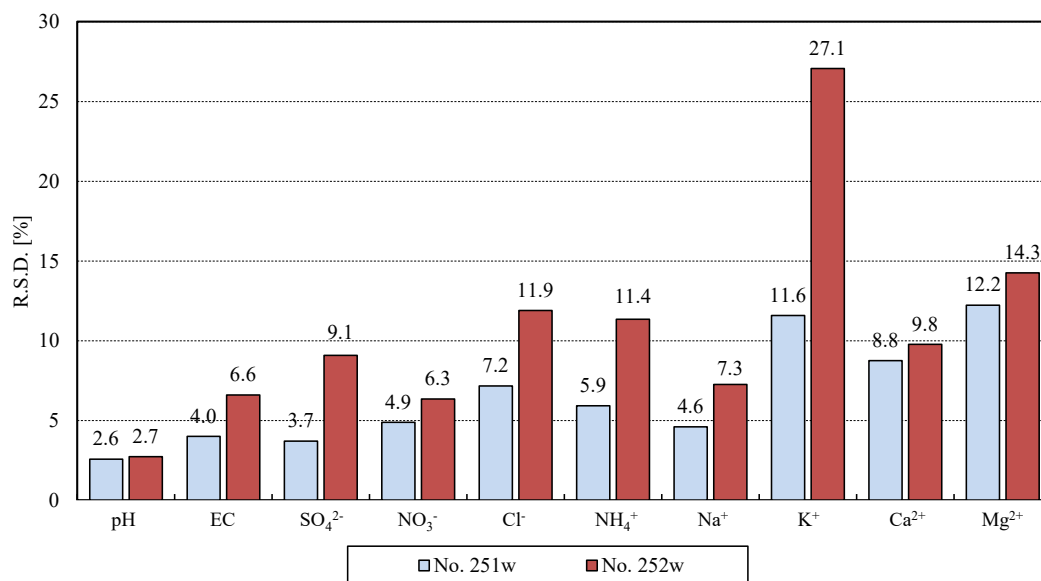


Figure 3.26 Relative standard deviations (R.S.D.) of each parameter

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 3.11 and Table 3.12, respectively. In Table 3.11, the letters of “A”, “B”, “C” and “D” refer to individual analysts in each laboratory who carried out analyses. In 15 laboratories, single analyst carried out the analyses for all parameters. No clear relationship between the number of analysts and flagged data was suggested.

Table 3.11 Number of analysts

Lab. ID	Total	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
CN01	3	A	A	B	B	B	C	C	C	C	C
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
CN05	1	A	A	A	A	A	A	A	A	A	A
CN06	3	A	B	C	C	C	C	C	C	C	C
ID01	1	A	A	A	A	A	A	A	A	A	A
ID02	4	A	B	C	C	C	D	D	D	D	D
ID03	1	A	A	A	A	A	A	A	A	A	A
JP01	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A
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	2	A	B	B	B	B	B	B	B	B	B
JP14	1	A	A	A	A	A	A	A	A	A	A
MY01	3	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	B	B	B	B	B	B	B	B
MM01	1	A	A	A	A	A	A	A	A	A	A
PH01	1	A	A	A	A	A	A	A	A	A	A
PH02	2	A	A	B	B	B	B	B	B	B	B
KR01	1	A	A	A	A	A	A	A	A	A	A
RU01	3	A	A	B	B	B	A	C	C	C	C
RU02	3	A	A	A	B	A	A	C	C	C	C
TH01	1	A	A	---	---	---	---	---	---	---	---
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. 251w or No. 252w was marked with flag "E" or "X";

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

"---", Not measured

238 data out of all the submitted data (602), were analyzed by the analysts whose experience was less than 5 years, and they account for 39.5%. No clear relationship between the years of experience and flagged data was suggested.

Table 3.12 Years of experience

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
CN01	2	2	2	2	2	2	2	2	2	2
CN02	7	7	7	7	7	7	7	7	7	7
CN03	13	13	27	27	27	27	27	27	27	27
CN04	17	17	17	17	17	17	17	17	17	17
CN05	5	5	5	5	5	5	5	5	5	5
CN06	2	3	7	7	7	7	7	7	7	7
ID01	0	0	0	0	0	0	0	0	0	0
ID02	4	6	20	20	20	20	20	20	20	20
ID03	20	20	20	20	20	20	20	20	20	20
JP01	22	22	22	22	22	22	22	22	22	22
JP03	2	2	2	2	2	2	2	2	2	2
JP04	4	4	4	4	4	4	4	4	4	4
JP08	4	4	4	4	4	4	4	4	4	4
JP09	11	11	11	11	11	11	11	11	11	11
JP10	8	8	8	8	8	8	8	8	8	8
JP14	3	3	3	3	3	3	3	3	3	3
MY01	1	1	4	4	4	4	4	4	4	4
MN01	2	2	22	22	22	22	22	22	22	22
MM01	4	4	4	4	4	4	4	4	4	4
PH01	4	4	4	4	4	4	4	4	4	4
PH02	1	1	3	3	3	3	3	3	3	3
KR01	20	20	20	20	20	20	20	20	20	20
RU01	26	26	26	26	26	26	26	26	26	26
RU02	1	1	1	1	1	1	1	1	1	1
TH01	1	1	---	---	---	---	---	---	---	---
TH02	26	26	26	26	26	26	26	26	26	26
VN01	9	9	12	12	12	12	12	12	12	12
VN02	16	16	12	12	12	12	12	12	12	12
VN03	11	11	14	11	---	11	14	13	14	14
VN04	2	2	21	21	21	21	21	21	21	21
VN05	10	10	18	18	18	18	18	18	18	18

Note: Light mesh, Analytic data of sample No. 251w or No. 252w 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 3.27, 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 3.3. Analytical methods used for the measurement in the participating laboratories are shown in Table 3.13. No clear relationship between analytical methods and flagged data was suggested.

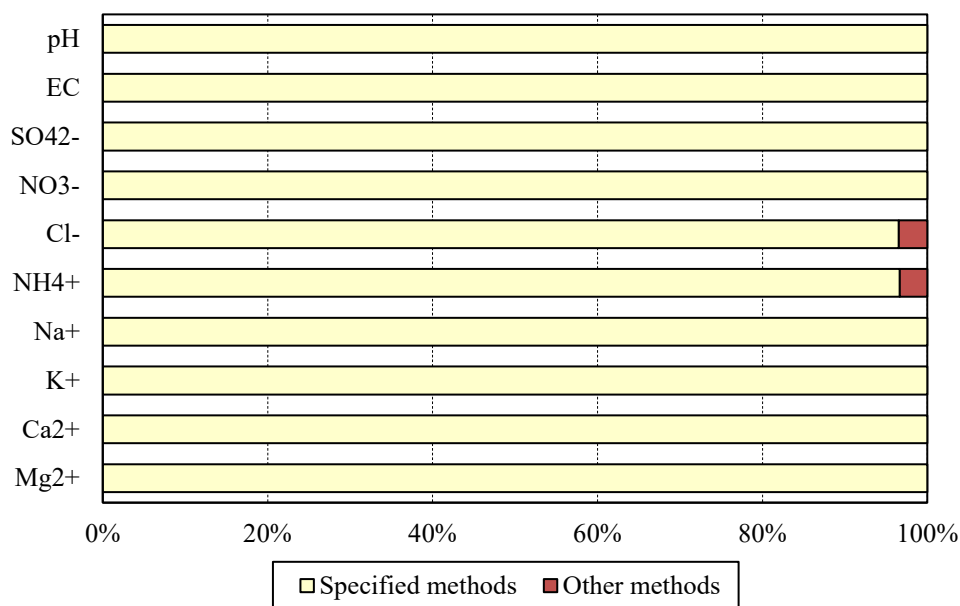


Figure 3.27 Percentage of laboratories that use the recommended methods

Table 3.13 Analytical method used for the measurement in the participating laboratories

Lab. ID	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
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
CN05	IC	IC	IC	IC	IC	IC	IC	IC
CN06	IC	IC	IC	IC	IC	IC	IC	IC
ID01	IC	IC	IC	IC	IC	IC	IC	IC
ID02	IC	IC	IC	IC	IC	IC	IC	IC
ID03	IC	IC	IC	IC	IC	IC	IC	IC
JP01	IC	IC	IC	IC	IC	IC	IC	IC
JP03	IC	IC	IC	IC	IC	IC	IC	IC
JP04	IC	IC	IC	IC	IC	IC	IC	IC
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	IC	IC	IC	IC	IC
PH02	IC	IC	IC	IC	IC	IC	IC	IC
KR01	IC	IC	IC	IC	IC	IC	IC	IC
RU01	IC	IC	IC	SP	AAS	AAS	AAS	AAS
RU02	SP	SP	TI	SP*	AES	AES	AAS	AAS
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 3.28 shows the distribution of “Start date” and “Finish date” of analysis at the participating laboratories. In total, 45% of all the submitted data was determined by the end of 2025, and 10% was determined later than the submission deadline of this project.

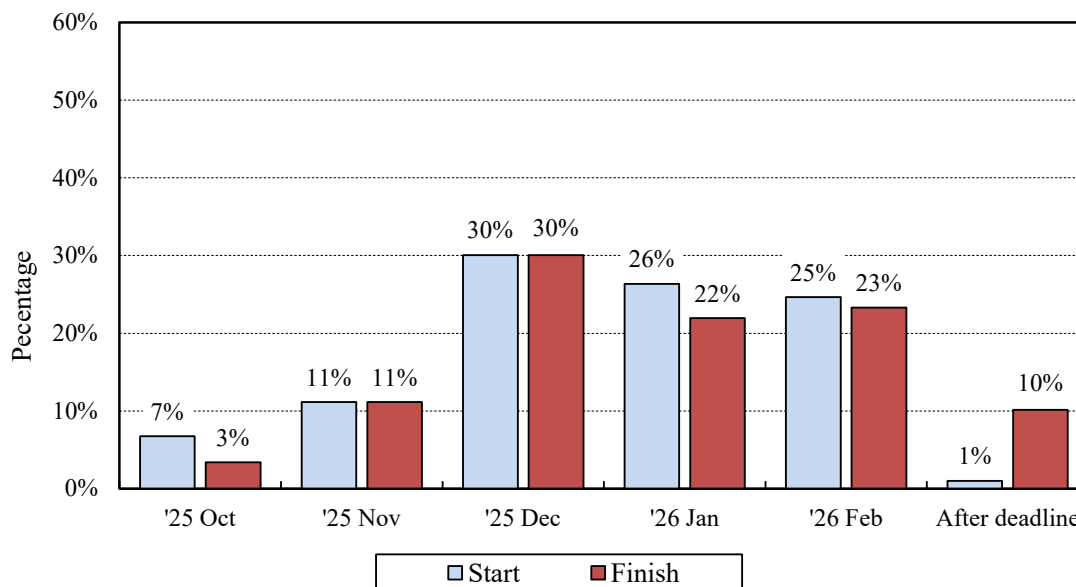


Figure 3.28 Distribution of start date and finish date of analysis

Figure 3.29 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.

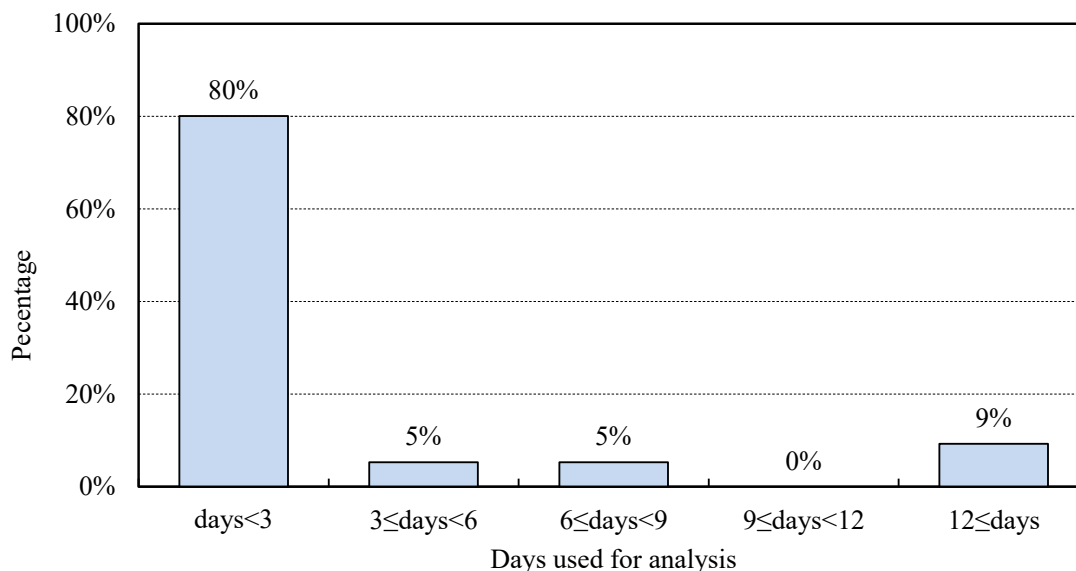


Figure 3.29 Distribution of days used for analysis

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 28th survey. The percentages of data within DQO and prepared value of EC are shown in Figure 3.30. Hereafter, sample No. 251w and No. 252w are treated as high and low concentration samples, respectively.

The percentage of data within DQO for the sample No. 251w and No. 252w were 89.7% and 83.7%, 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.

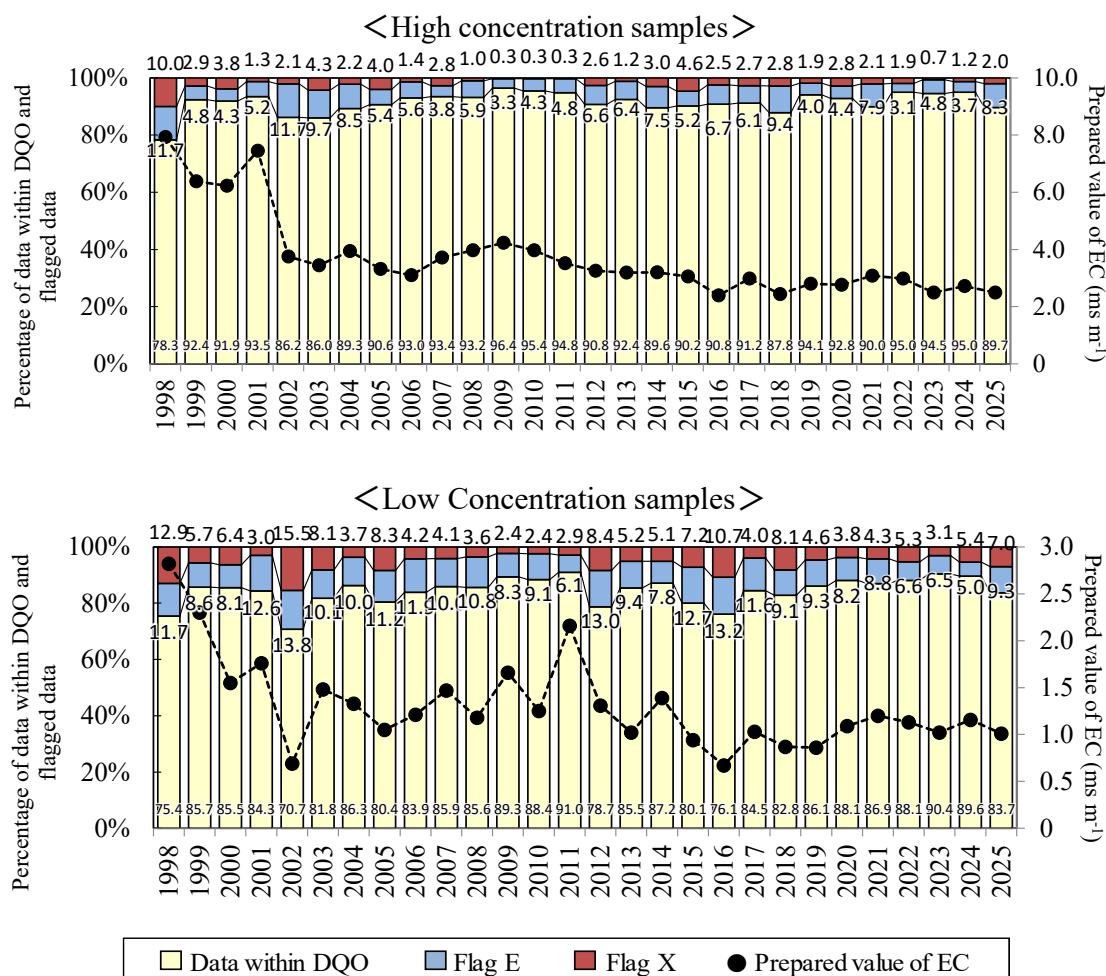


Figure 3.30 Comparison of results from the inter-laboratory comparison projects

Figure 3.31 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.

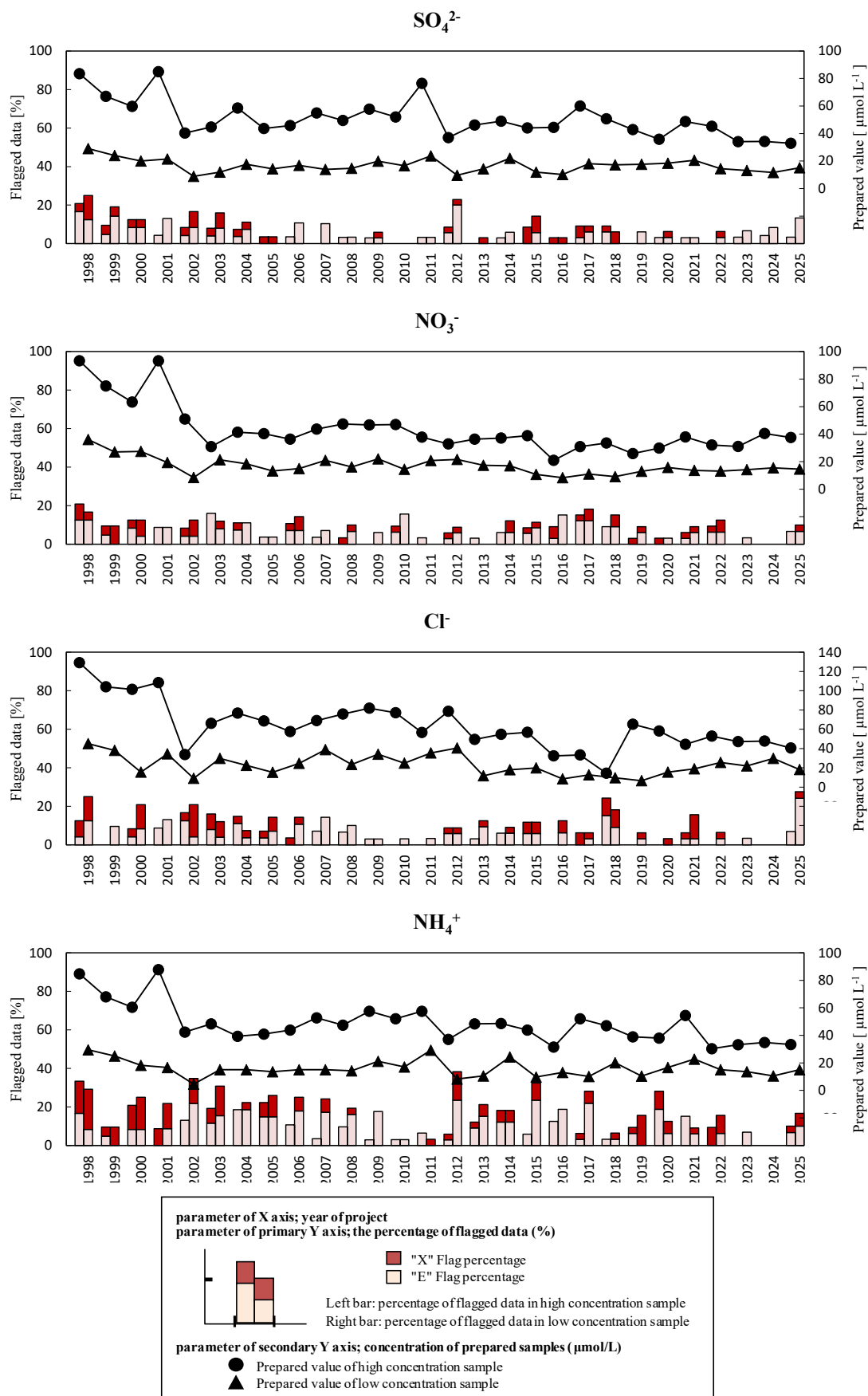


Figure 3.31 Comparison for each parameter in inter-laboratory comparison (ILC) project

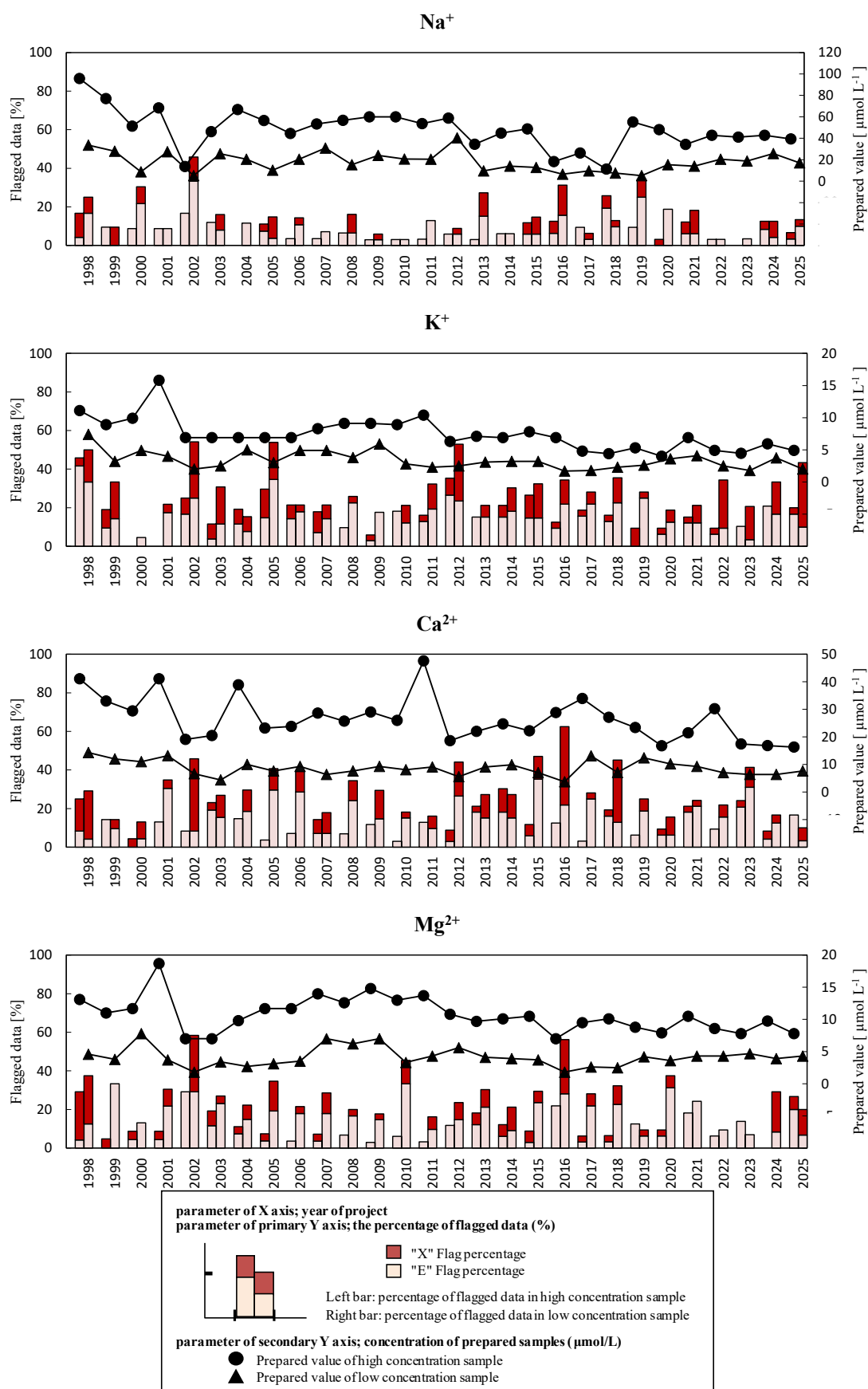


Figure 3.31 Comparison for each parameter in ILC project (continued)

As shown in Figure 3.32, the total number of data in this survey was 602.

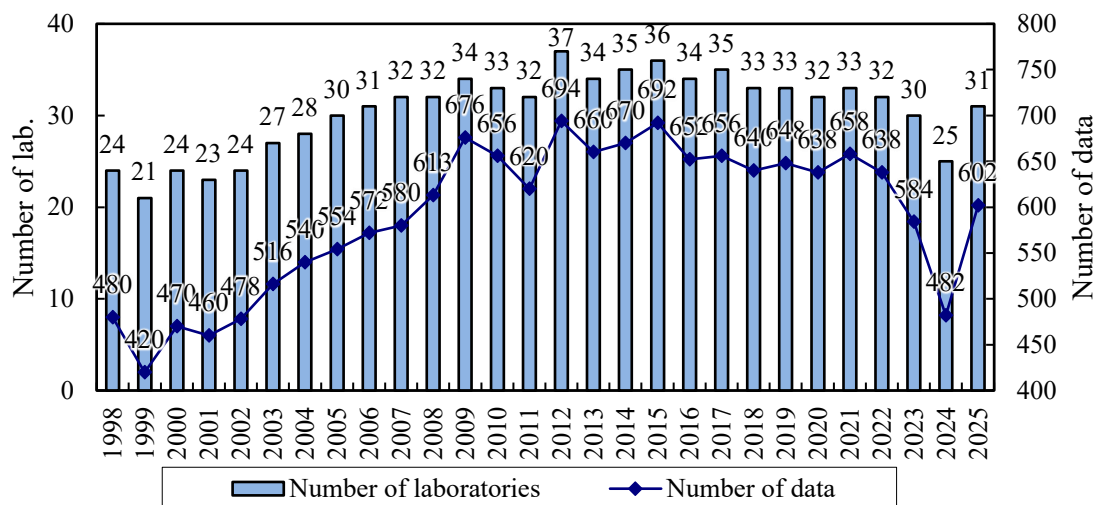


Figure 3.32 The number of participating laboratories and data in the inter-laboratory comparison projects on wet deposition

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.

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

σ : standard deviation of result

V_a : average of result

In Appendix Table 3.1.1 and Appendix Table 3.1.2, data precisions calculated from the submitted results are shown. There is a tendency that each constituent of higher concentration sample (No. 251w) shows better R.S.D. than that of lower concentration sample (No. 252w). 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 3.1.1 Data precision (R.S.D.) of sample No. 251w

Lab. ID	pH as H ⁺ %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
CN01	1.0	0.1	0.3	0.3	0.2	0.6	0.2	0.7	0.7	0.6
CN02	1.3	0.2	0.2	0.1	0.1	0.2	0.1	0.8	0.3	0.9
CN03	2.3	0.3	0.9	0.2	0.8	0.3	0.2	1.0	0.5	0.9
CN04	5.8	0.9	0.6	0.9	1.0	2.2	1.9	1.3	1.9	3.1
CN05	1.7	0.2	0.8	0.7	1.0	0.9	1.4	2.7	2.0	0.0
CN06	1.5	0.5	0.5	2.2	1.4	1.0	0.6	1.4	0.5	1.8
ID01	3.1	1.3	2.5	1.2	2.4	2.2	3.1	10.0	3.7	2.6
ID02	2.1	1.9	0.5	0.3	0.3	0.8	0.0	0.0	0.0	0.0
ID03	7.3	2.0	1.9	1.6	2.6	1.1	0.9	3.0	1.9	3.4
JP01	3.7	1.6	0.6	0.7	0.5	1.6	0.6	1.4	1.4	0.5
JP03	2.6	0.6	0.2	0.3	0.3	0.3	0.1	1.1	0.3	0.6
JP04	2.2	0.4	0.2	0.1	0.1	0.2	0.5	1.2	0.5	0.7
JP08	8.6	1.2	0.2	0.1	0.1	0.2	0.2	0.9	1.8	2.9
JP09	7.3	0.9	0.2	0.2	0.1	0.1	0.3	0.0	0.2	0.0
JP10	1.9	0.4	0.5	0.3	0.3	0.2	0.1	0.0	0.3	0.5
JP14	4.6	0.8	0.9	0.4	0.4	0.8	0.3	6.5	0.4	0.7
MY01	2.5	0.9	0.3	0.5	0.6	0.1	1.5	5.2	0.7	0.7
MN01	1.4	3.6	0.5	0.7	0.5	3.7	1.9	1.5	2.0	0.9
MM01	8.2	4.0	4.2	4.6	6.6	3.6	2.0	3.3	3.0	4.5
PH01	11.5	1.0	0.3	0.5	0.3	0.7	0.8	2.4	3.0	2.5
PH02	26.0	3.0	5.6	2.7	3.0	4.1	2.0	5.2	13.1	22.8
KR01	2.9	0.5	0.3	0.6	0.2	0.1	0.1	0.0	0.5	0.0
RU01	3.1	0.6	31.4	2.3	1.8	1.0	1.3	7.5	2.6	1.0
RU02	3.9	0.4	0.6	0.6	1.8	1.1	7.6	2.3	1.1	2.8
TH01	1.9	0.0	--	--	--	--	--	--	--	--
TH02	2.7	0.6	1.5	0.8	0.7	0.6	0.4	4.9	2.5	1.4
VN01	2.7	1.3	0.2	0.1	0.1	0.2	0.2	1.2	0.3	0.8
VN02	4.9	0.7	0.8	0.9	0.4	1.9	0.4	3.4	1.3	2.2
VN03	0.7	0.0	0.2	0.2	--	0.6	0.5	2.2	0.5	1.0
VN04	5.3	0.4	0.5	1.1	1.1	1.0	1.1	2.2	0.8	1.2
VN05	1.2	0.1	1.9	1.8	3.3	0.7	2.1	2.6	5.0	1.8
Number of data	31	31	30	30	29	30	30	30	30	30
Minimum	0.7	0.0	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0
25% value	1.9	0.4	0.3	0.3	0.3	0.2	0.2	1.0	0.5	0.6
Median	2.7	0.6	0.5	0.6	0.5	0.7	0.6	1.8	0.9	1.0
75% value	5.1	1.2	0.9	1.1	1.4	1.1	1.5	3.2	2.0	2.4
Maximum	26.0	4.0	31.4	4.6	6.6	4.1	7.6	10.0	13.1	22.8

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

R.S.D for "pH as H⁺" was calculated after pH value was converted to H⁺ concentration;

"--", Not measured

Appendix Table 3.1.2 Data precision (R.S.D.) of sample No. 252w

Lab. ID	pH as H ⁺ %	EC %	SO ₄ ²⁻ %	NO ₃ ⁻ %	Cl ⁻ %	NH ₄ ⁺ %	Na ⁺ %	K ⁺ %	Ca ²⁺ %	Mg ²⁺ %
CN01	0.8	0.3	0.0	0.9	0.9	1.2	0.6	0.0	0.6	1.1
CN02	1.0	0.5	0.3	0.3	0.5	0.3	0.3	2.4	0.9	1.5
CN03	1.6	0.9	0.5	0.6	1.0	0.8	0.7	3.1	1.0	1.5
CN04	5.2	1.1	0.7	1.6	1.0	2.7	2.1	6.3	2.1	3.3
CN05	1.5	0.0	0.4	2.1	3.6	1.3	5.1	7.9	1.3	0.0
CN06	1.1	0.5	3.2	2.5	2.4	0.6	1.1	3.1	0.8	2.1
ID01	9.4	0.6	4.1	3.1	4.2	1.5	4.5	0.0	5.1	8.2
ID02	5.4	2.4	0.5	0.6	0.6	2.2	0.0	0.0	0.5	0.0
ID03	1.4	4.7	1.7	1.7	1.2	3.7	1.5	11.2	2.8	0.9
JP01	2.5	0.7	0.7	1.3	1.8	1.0	1.1	2.6	2.8	1.4
JP03	6.4	0.9	0.5	0.8	0.3	0.2	0.2	0.0	0.0	0.0
JP04	8.0	1.2	0.2	0.0	0.2	0.9	0.5	2.5	2.9	1.2
JP08	4.6	0.9	0.2	0.4	0.2	0.7	0.2	1.8	0.8	1.9
JP09	8.1	1.1	0.5	0.3	0.3	0.3	0.0	0.0	0.4	0.8
JP10	3.2	0.4	0.3	0.3	0.3	0.5	0.2	0.0	1.9	0.0
JP14	8.6	0.8	1.0	0.7	0.5	1.4	1.4	19.4	1.0	0.9
MY01	5.9	0.7	0.7	0.5	0.4	0.3	0.8	12.6	2.7	2.9
MN01	7.6	4.9	1.3	0.7	0.4	1.5	3.4	7.7	0.9	1.1
MM01	6.7	5.0	5.7	8.3	5.9	2.6	1.7	6.1	14.6	4.2
PH01	63.7	1.2	0.5	1.0	0.9	1.3	1.9	4.8	2.8	4.4
PH02	19.4	0.5	10.4	5.2	2.0	16.0	6.5	46.6	14.5	16.3
KR01	9.7	1.0	0.8	1.2	1.0	0.5	0.3	0.0	1.1	0.0
RU01	2.3	1.0	--	4.2	5.3	1.0	3.1	16.1	3.3	5.9
RU02	3.4	1.1	1.1	0.6	11.5	5.1	4.7	0.0	3.5	3.5
TH01	1.6	0.0	--	--	--	--	--	--	--	--
TH02	8.7	0.5	1.7	0.5	0.6	0.7	1.6	9.4	3.1	1.9
VN01	8.1	2.9	0.2	0.3	0.3	0.3	0.3	1.9	0.7	1.0
VN02	5.0	1.2	1.4	1.1	1.4	1.4	1.7	8.0	2.2	4.8
VN03	13.3	0.0	1.1	1.1	--	0.6	1.4	1.7	2.3	1.9
VN04	6.2	0.5	1.0	1.4	2.1	1.4	0.8	5.0	1.9	1.7
VN05	0.8	0.4	2.0	1.4	2.1	2.0	2.2	6.1	1.4	4.3
Number of data	31	31	29	30	29	30	30	30	30	30
Minimum	0.8	0.0	0.0	0.0	0.2	0.2	0.0	0.0	0.0	0.0
25% value	2.0	0.5	0.5	0.5	0.4	0.6	0.4	0.4	0.9	0.9
Median	5.4	0.9	0.7	0.9	1.0	1.1	1.2	3.1	1.9	1.6
75% value	8.1	1.2	1.4	1.6	2.1	1.5	2.0	7.8	2.8	3.5
Maximum	63.7	5.0	10.4	8.3	11.5	16.0	6.5	46.6	14.6	16.3

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

R.S.D for "pH as H⁺" was calculated after pH value was converted to H⁺ concentration;

"--", Not measured

Appendix 2.2 Deviation% from prepared values

Appendix Table 3.2.1 Deviation% from prepared values of sample No. 251w

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
	%	%	%	%	%	%	%	%	%	%
CN01	-0.6	-0.4	1.2	1.6	0.7	5.7	3.6	0.0	0.0	3.8
CN02	0.6	-0.8	0.6	3.7	-0.2	0.0	-1.8	10.2	3.1	6.4
CN03	4.9	-8.0	-0.3	4.5	0.5	5.1	-0.8	4.1	3.1	17.9
CN04	1.3	-3.6	1.2	3.7	-0.2	-3.3	1.5	4.1	4.3	0.0
CN05	0.8	0.8	4.3	9.3	-4.0	0.9	1.3	-2.0	-8.6	-3.8
CN06	4.9	-8.0	-0.3	6.9	10.4	15.6	-1.0	0.0	-0.6	19.2
ID01	-1.5	-1.2	-3.6	-2.7	-12.9	30.3	-31.7	-28.6	-20.9	0.0
ID02	1.7	-7.2	6.7	6.4	6.4	-7.2	3.0	-4.1	3.1	1.3
ID03	0.6	-3.6	-5.8	23.2	-17.1	22.2	-2.3	2.0	1.8	1.3
JP01	1.9	-0.8	0.9	-1.1	-2.5	2.1	1.5	0.0	0.6	3.8
JP03	0.8	0.0	0.0	-0.8	-0.7	0.6	-1.3	-4.1	-1.2	-6.4
JP04	0.8	-2.0	-1.2	-1.3	-1.2	0.9	-2.0	0.0	-3.1	-3.8
JP08	1.5	-4.0	-0.6	0.3	1.2	0.6	0.5	0.0	-0.6	0.0
JP09	2.1	-3.6	-0.3	-2.1	-1.0	-0.6	0.3	0.0	0.0	0.0
JP10	1.1	1.6	3.6	5.9	4.5	-3.0	0.5	-2.0	12.9	7.7
JP14	2.7	-3.6	0.6	-0.3	0.5	-0.9	-1.3	0.0	-1.2	-9.0
MY01	1.5	0.0	-0.3	-1.9	0.0	4.8	4.8	14.3	6.7	-10.3
MN01	-3.0	-8.8	4.3	9.1	1.0	4.8	-7.9	-6.1	11.7	2.6
MM01	-0.2	-43.8	1.5	-2.4	6.7	0.9	-2.8	-2.0	5.5	-3.8
PH01	-1.7	-8.0	1.2	-4.3	0.2	-5.1	-1.8	12.2	-3.7	-5.1
PH02	4.0	-0.4	-28.6	-10.4	-19.8	-3.9	-8.9	-28.6	15.3	83.3
KR01	0.4	-2.8	-1.5	-0.8	-0.2	6.9	-0.8	0.0	-2.5	1.3
RU01	1.1	0.4	-6.7	-2.9	8.4	7.8	-6.9	-24.5	2.5	9.0
RU02	6.5	-15.7	-14.0	16.0	-10.4	-3.0	17.8	49.0	-9.8	53.8
TH01	1.1	-1.2	---	---	---	---	---	---	---	---
TH02	1.5	2.4	-0.3	0.0	-1.0	-1.8	-0.8	-8.2	-4.9	-6.4
VN01	4.6	-6.4	-1.2	0.0	7.2	-2.7	-1.5	12.2	20.9	19.2
VN02	3.8	-6.0	-1.5	0.3	7.4	-2.4	-1.8	14.3	17.2	15.4
VN03	9.3	-2.8	1.5	0.5	---	0.3	-0.5	16.3	4.9	16.7
VN04	7.8	-6.8	-0.6	-0.3	6.2	-3.3	-1.0	12.2	22.7	25.6
VN05	3.2	-5.6	0.3	0.8	8.4	0.0	-5.1	16.3	10.4	2.6
Number of data	31	31	30	30	29	30	30	30	30	30
Average	2.0	-4.8	-1.3	2.0	-0.1	2.4	-1.6	1.9	3.0	8.1
Minimum	-3.0	-43.8	-28.6	-10.4	-19.8	-7.2	-31.7	-28.6	-20.9	-10.3
Maximum	9.3	2.4	6.7	23.2	10.4	30.3	17.8	49.0	22.7	83.3

Note: "---", Not measured

Appendix Table 3.2.2 Deviation% from prepared values of sample No. 252w

Lab. ID	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
	%	%	%	%	%	%	%	%	%	%
CN01	-1.7	1.0	-0.7	2.7	2.2	9.9	5.3	5.0	5.3	9.3
CN02	-0.8	1.0	-0.7	-1.4	1.1	-4.6	1.8	5.0	-1.3	7.0
CN03	0.9	2.0	2.6	11.6	16.6	3.3	1.2	40.0	5.3	34.9
CN04	-0.4	2.0	-2.6	-1.4	-3.3	-4.6	1.8	0.0	5.3	-4.7
CN05	-4.2	15.8	3.3	6.2	-6.6	0.0	15.8	-5.0	3.9	7.0
CN06	0.9	2.0	-2.0	6.2	17.1	18.5	-1.8	25.0	2.6	55.8
ID01	-1.1	-18.8	-23.2	-8.2	-21.5	41.7	-45.0	-50.0	-55.3	-9.3
ID02	-2.8	-6.9	23.2	19.9	22.7	-6.6	2.9	-5.0	11.8	7.0
ID03	0.6	7.9	-9.3	17.1	-9.4	39.1	0.6	-5.0	6.6	11.6
JP01	-0.6	6.9	-2.6	-3.4	-3.3	4.6	1.2	-5.0	3.9	7.0
JP03	-1.9	5.0	1.3	0.7	-2.8	2.0	-2.9	-10.0	-3.9	-7.0
JP04	0.4	1.0	0.0	-0.7	-0.6	2.6	-1.8	0.0	3.9	0.0
JP08	-0.8	-4.0	1.3	0.7	-0.6	0.0	0.6	-5.0	0.0	0.0
JP09	0.9	2.0	0.0	-0.7	0.0	0.7	0.0	0.0	-1.3	0.0
JP10	-0.4	5.9	3.3	2.7	3.3	-2.6	-0.6	-5.0	7.9	7.0
JP14	3.2	0.0	2.0	-1.4	1.1	-0.7	-2.3	15.0	-9.2	-16.3
MY01	-0.2	3.0	-2.6	-3.4	0.0	13.9	7.0	15.0	2.6	-16.3
MN01	-4.5	4.0	0.0	4.8	-2.8	4.6	-5.3	-5.0	23.7	7.0
MM01	-5.8	-25.7	-2.0	-1.4	16.0	2.6	9.9	25.0	39.5	7.0
PH01	1.1	-6.9	4.6	-6.8	-0.6	-6.6	-4.1	25.0	0.0	-7.0
PH02	1.3	-2.0	-27.2	4.8	-14.4	11.9	-22.2	-35.0	13.2	67.4
KR01	-2.8	3.0	-4.0	-8.9	-1.7	15.2	-1.8	5.0	-2.6	4.7
RU01	-1.3	2.0	-5.3	-5.5	0.0	7.9	-21.6	-60.0	-3.9	0.0
RU02	6.4	-10.9	-18.5	70.5	-34.3	29.8	-5.3	90.0	-11.8	39.5
TH01	-0.6	3.0	---	---	---	---	---	---	---	---
TH02	0.2	5.9	0.0	0.0	0.0	4.0	0.0	0.0	-7.9	-7.0
VN01	-0.6	1.0	0.0	0.0	13.8	2.0	0.0	35.0	-2.6	4.7
VN02	-1.5	4.0	0.7	1.4	19.3	2.6	-0.6	35.0	-3.9	7.0
VN03	7.5	14.9	-11.9	-1.4	---	-5.3	2.3	60.0	-9.2	0.0
VN04	3.4	-1.0	-0.7	0.0	-0.6	0.7	0.0	35.0	-1.3	4.7
VN05	-2.1	9.9	-6.0	-2.7	16.6	-2.0	-4.1	35.0	0.0	0.0
Number of data	31	31	30	30	29	30	30	30	30	30
Average	-0.2	0.9	-2.6	3.4	1.0	6.2	-2.3	8.7	0.7	7.4
Minimum	-5.8	-25.7	-27.2	-8.9	-34.3	-6.6	-45.0	-60.0	-55.3	-16.3
Maximum	7.5	15.8	23.2	70.5	22.7	41.7	15.8	90.0	39.5	67.4

Note: "---", Not measured

4. 27th 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.

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. Potential factors affecting analytical precisions have been discussed in previous projects. 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 27th project, the Network Center (NC) provided two soil samples (No.251s and No.252s) 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

Seven laboratories from four countries participated in the 27th 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.251s: Cambisols (Brown Forest Soil, B_D)

Sample No.252s: Cambisols (Brown Forest Soil, B_D)

Soil samples 251s and 252s were collected in Japanese cedar (*Cryptomeria japonica*) and Japanese cypress (*Chamaecyparis obtusa*) plantations in the Field Museum Oyasan of the University Forest, Tokyo University of Agriculture and Technology (TUAT), 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 ₂ O)	-	M
c) pH(KCl)	-	M
d) Exchangeable Ca ²⁺	cmol _c kg ⁻¹	M
e) Exchangeable Mg ²⁺	cmol _c kg ⁻¹	M
f) Exchangeable K ⁺	cmol _c kg ⁻¹	M
g) Exchangeable Na ⁺	cmol _c kg ⁻¹	M
h) Exchangeable acidity	cmol _c kg ⁻¹	M
i) Exchangeable Al ³⁺	cmol _c kg ⁻¹	M
j) Exchangeable H ⁺	cmol _c kg ⁻¹	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 analyses 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 CH₃COONH₄ (pH 7.0)** for the analysis of Ex-Ca, Ex-Mg, Ex-K, and Ex-Na. This same 1 M CH₃COONH₄ (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 CH₃COONH₄ (pH 7.0) solution.
- (2) Pipette an appropriate aliquot of the soil extract into a volumetric flask and add 100 g-Sr L⁻¹ solution to achieve a final concentration of 1000 mg-Sr L⁻¹ (SrCl₂ solution helps eliminate matrix interference). Then bring to volume with 1 M CH₃COONH₄ (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 CH₃COONH₄ (pH 7.0).
- (5) Add 100 g-Sr L⁻¹ 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⁻¹)

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_{NaOH} = Volume of 0.025 M NaOH used for sample percolate (mL)

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

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

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

M_{NaOH} = Molarity of NaOH (mol L⁻¹)

M_{HCl} = Molarity of HCl (mol L⁻¹)

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 21st 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⁻¹]) 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 2nd 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 27th inter-laboratory project, sample 252s had higher concentrations of Ex-Ca, Ex-Mg Ex-acidity, and Ex-Al than sample 251s, whereas soil pH values [pH(H₂O) and pH(KCl)] were almost same. We observed considerable variation in the analyzed data, with coefficients of variation (CVs) ranging from approximately 8-51% for Ex-base cations, 43% and 61% for Ex-acidity, and 30-98% for acid cations in both samples. In contrast, the CVs for pH(H₂O) and pH(KCl) were relatively low (< 10%) in both samples.

Table 4.2 Basic statistics of the entire dataset

Table 4.2 Basic statistics of the entire dataset									
Statistics	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol kg ⁻¹						
No. 251s									
Number of Laboratories	7	7	5	5	5	5	6	6	6
Total average	4.7	4.1	0.61	0.17	0.10	0.07	2.16	1.99	0.47
Median	4.7	4.1	0.76	0.12	0.10	0.09	2.06	1.66	0.45
Maximum	4.9	4.2	0.81	0.26	0.12	0.10	3.20	2.98	0.65
Minimum	4.4	4.0	0.07	0.11	0.08	0.03	0.77	1.28	0.32
Standard deviation	0.2	0.1	0.31	0.07	0.01	0.03	0.92	0.77	0.14
CV (%) ^{*1}	4.3	1.9	51.3	44.0	11.8	44.3	42.7	38.9	29.8
No. 252s									
Number of Laboratories	7	7	5	5	5	5	6	6	6
Total average	4.8	4.1	1.92	0.43	0.29	0.25	3.25	2.44	0.63
Median	4.6	4.4	2.19	0.44	0.29	0.26	3.59	2.08	0.43
Maximum	5.4	4.5	2.71	0.46	0.35	0.27	5.28	4.75	1.76
Minimum	4.2	3.6	0.24	0.38	0.22	0.22	0.80	0.51	0.01
Standard deviation	0.5	0.4	0.96	0.03	0.06	0.02	1.97	2.12	0.62
CV (%) ^{*1}	10.3	10.2	50.3	7.9	20.1	6.9	60.7	86.7	97.6

*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.251s and 252s 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.

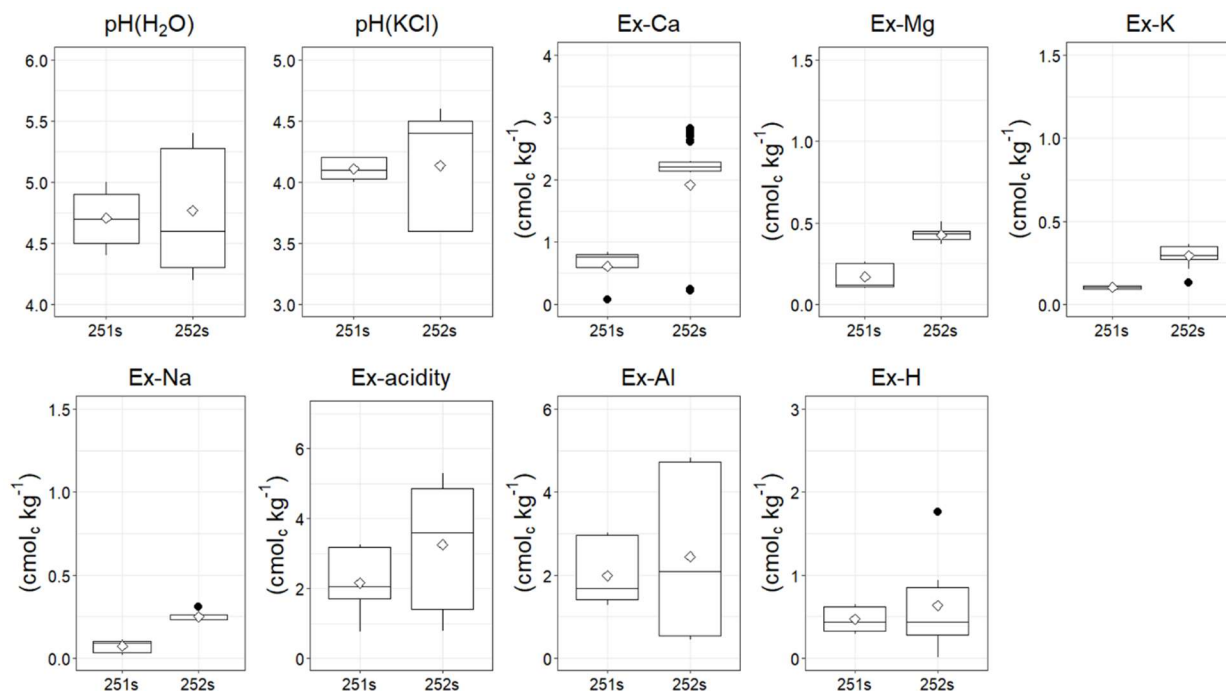


Figure 4.1 Data variability of No.251s and No.252s

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 “JP13” for Ex-acidity in sample 251s. 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 example, a “g” mark was assigned to laboratory “ID01” and “JP13” for Ex-Ca in sample 252s. The Cochran-Grubbs test identified several outliers across different items. After excluding these outliers, the “verified” dataset—consisting of 5-7 laboratories for pH(H₂O) and pH(KCl), 2-5 laboratories for Ex-base cations, and 3-6 laboratories for Ex-acidity, Al, and H—was used for further analysis in the following section.

**Table 4.3 Data verification by Cochran-Grubbs tests
No. 251s**

Country	Lab.	Repeat analysis	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
					cmol _c kg ⁻¹						
Indonesia	ID01	1st	4.9	4.1	0.07 g	0.12	0.11	0.05	0.77	1.68	0.65
		2nd	4.8	4.2	0.07 g	0.12	0.12	0.05	0.77	1.68	0.65
	ID04	1st	4.9	4.2	0.61 g	0.12	0.09	0.09	2.03	1.40 c	0.62
		2nd	4.9	4.2	0.60 g	0.11	0.10	0.10	2.02	1.40 c	0.62
Japan	JP13	1st	5.0	4.2	0.76 g	0.11	0.08	0.03	2.13 c	1.68 c	0.45 c
		2nd	4.9	4.2	0.77 g	0.11	0.08	0.03	2.08 c	1.60 c	0.48 c
Mongolia	MN01	1st	4.5	4.1	NA	NA	NA	NA	1.71	1.28	0.43
		2nd	4.4	4.1	NA	NA	NA	NA	1.71	1.28	0.43
Vietnam	VN01	1st	4.6	4.0	0.80	0.25	0.10	0.10	3.19	2.97 c	0.33
		2nd	4.6	4.0	0.81	0.26	0.11	0.10	3.21	3.00 c	0.33
	VN04	1st	4.5	4.1	0.79	0.24	0.10	0.09	3.19	2.96	0.32
		2nd	4.5	4.1	0.82	0.25	0.11	0.09	3.17	2.96	0.32
	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. 252s**

Country	Lab.	Repeat analysis	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
					cmol _c kg ⁻¹						
Indonesia	ID01	1st	5.3	4.5	0.23 g	0.38	0.23 c	0.25	2.35	0.64	0.01
		2nd	5.3	4.5	0.24 g	0.39	0.29 c	0.26	2.35	0.64	0.01
	ID04	1st	5.1	4.5	2.26	0.44	0.29	0.24	1.39	0.52 c	0.87
		2nd	5.1	4.5	2.28	0.44	0.29	0.24	1.39	0.52 c	0.88
Japan	JP13	1st	5.4	4.5 c	2.69 g	0.39	0.22	0.23	0.80	0.50 c	0.31
		2nd	5.4	4.5 c	2.73 g	0.40	0.21	0.22	0.80	0.51 c	0.29
Mongolia	MN01	1st	4.6 c	4.4	NA	NA	NA	NA	5.28	3.52	1.76
		2nd	4.5 c	4.4	NA	NA	NA	NA	5.28	3.52	1.76
Vietnam	VN01	1st	4.3	3.6	2.18	0.45	0.35	0.27	4.86	4.75 c	0.43
		2nd	4.3	3.6	2.19	0.46	0.35	0.27	4.86	4.75 c	0.42
	VN04	1st	4.2	3.6	2.17	0.47	0.35	0.26	4.84	4.73	0.43
		2nd	4.2	3.6	2.18	0.45	0.36	0.26	4.83	4.73	0.43
	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 251s and 252s is presented in Table 4.4. 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.

For Ex-Ca and Ex-Al, the number of laboratories remaining after the Cochran-Grubbs test was limited to only two or three, owing to the relatively large number of detected outliers. Accordingly, the ANOVA results for these items, including estimates of within-laboratory and inter-laboratory variation, should be regarded as reference information only.

Table 4.4 Basic statistics of the verified^{*2} dataset

Statistics	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
			cmol _c kg ⁻¹						
			No. 251s						
Number of Laboratories	7	7	2	5	5	5	5	3	5
Total average	4.7	4.1	0.80	0.17	0.10	0.07	2.18	1.97	0.47
Median	4.7	4.1	0.80	0.12	0.10	0.09	2.02	1.68	0.43
Maximum	4.9	4.2	0.81	0.26	0.12	0.10	3.20	2.96	0.65
Minimum	4.4	4.0	0.80	0.11	0.08	0.03	0.77	1.28	0.32
Standard deviation	0.2	0.1	0.00	0.07	0.01	0.03	1.03	0.88	0.16
CV (%) ^{*1}	4.3	1.9	0.1	44.0	11.8	44.3	47.5	44.5	33.2
No. 252s									
Number of Laboratories	5	6	3	5	4	5	6	3	6
Total average	4.9	4.1	2.21	0.43	0.30	0.25	3.25	2.96	0.63
Median	5.1	4.1	2.19	0.44	0.32	0.26	3.59	3.52	0.43
Maximum	5.4	4.5	2.27	0.46	0.35	0.27	5.28	4.73	1.76
Minimum	4.2	3.6	2.18	0.38	0.22	0.22	0.80	0.64	0.01
Standard deviation	0.6	0.4	0.05	0.03	0.06	0.02	1.97	2.10	0.62
CV (%) ^{*1}	11.7	10.4	2.4	7.9	21.5	6.9	60.7	70.9	97.6

*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(H₂O) and pH(KCl), with CVs of 1.0% or less, indicating consistent triplicate measurements. For Ex-base cations, Ex-acidity, Ex-Al, and Ex-H, CVs were below 18%, 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-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-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 12% for pH(H₂O) and pH(KCl). However, for the other parameters except for Ex-Ca, CVs ranged from 8 to 98%. 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 0.2-1.6 for pH(H₂O) and pH(KCl), 0.03-0.18 cmol_c kg⁻¹ for Ex-base cations except for Ex-Ca, 0.4-5.9 cmol_c kg⁻¹ for Ex-acidity, Ex-Al, and Ex-H.

Table 4.5 Analysis of variance for the verified dataset

Statistics	No. 251s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	7	7	2	5	5	5	5	3	5
Total sum of square	39000	30000	93	26	9.2	4.8	4300	1300	200
ST/lmd	930	710	7.8	0.86	0.31	0.16	140	70	6.6
Number of Laboratories	7	7	2	5	5	5	5	3	5
Number of Data	42	42	12	30	30	30	30	18	30
Total sum	200	170	9.7	5.1	3.0	2.2	65	36	14
Total average	4.7	4.1	0.80	0.17	0.10	0.07	2.18	1.97	0.47
Sum of square inter-laboratories (S _R)	1.5	0.2	0.00	0.13	0.00	0.03	25.63	9.24	0.59
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)	0.1	0.0	0.00	0.00	0.00	0.00	0.01	0.00	0.01
Total sum of square (S _T)	1.5	0.3	0.01	0.13	0.00	0.03	25.64	9.24	0.60
Inter-laboratories degree of freedom (φ _R)	6	6	1	4	4	4	4	2	4
Within-laboratory degree of freedom (φ _{RW})	7	7	2	5	5	5	5	3	5
Repeatability degree of freedom (φ _r)	28	28	8	20	20	20	20	12	20
Total degree of freedom (φ _T)	41	41	11	29	29	29	29	17	29
Inter-laboratories variance (V _R = S _R /φ _R)	0.2	0.0	0.00	0.03	0.00	0.01	6.41	4.62	0.15
Within-laboratory variance (V _{RW} = S _{RW} /φ _{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 /φ _r)	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Laboratory component of variance (s _b ² = (V _R -V _{RW})/(2×3))	0.0	0.0	0.00	0.01	0.00	0.00	1.07	0.77	0.02
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	0.00	0.00	0.00
Inter-laboratories standard deviation (s _R = SQRT(s _b ² /(2×3) + s _c ² /2 + s _b ²))	0.2	0.1	0.00	0.07	0.01	0.03	1.03	0.88	0.16
Within-laboratory standard deviation (s _{RW} = SQRT(s _r ² /3 + s _c ²))	0.0	0.0	0.01	0.00	0.01	0.00	0.01	0.00	0.00
Repeatability standard deviation (s _r = SQRT(s _r ²))	0.0	0.0	0.02	0.01	0.01	0.01	0.02	0.00	0.02
Inter-laboratories precision CV (%)	4.3	1.9	0.15	43.99	11.76	44.25	47.49	44.47	33.20
Within-laboratory precision CV (%)	0.7	0.5	1.67	2.92	6.00	4.79	0.34	0.00	0.00
Repeatability precision CV (%)	1.0	0.8	2.78	3.41	5.11	17.86	0.94	0.00	4.92
Reproducibility limit (R = D(2, 0.95)×s _R)	0.6	0.2	0.00	0.21	0.03	0.09	2.89	2.46	0.44
Within-laboratory-reproducibility limit (R _W = D(2, 0.95)×s _{RW})	0.1	0.1	0.04	0.01	0.02	0.01	0.02	0.00	0.00
Repeatability limit (r = D(3, 0.95)×s _r)	0.2	0.1	0.07	0.02	0.02	0.04	0.07	0.00	0.08

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

Statistics	No. 252s								
	pH(H ₂ O)	pH(KCl)	Ex-Ca	Ex-Mg	Ex-K	Ex-Na	Ex-acidity	Ex-Al	Ex-H
Number of Laboratories	5	6	3	5	4	5	6	3	6
Total sum of square	21000	21000	1600	160	52	56	14000	2800	520
ST/lmd	710	600	88	5.4	2.2	1.9	380	160	14
Number of Laboratories	5	6	3	5	4	5	6	3	6
Number of Data	30	36	18	30	24	30	36	18	36
Total sum	150	150	40	13	7.2	7.5	120	53	23
Total average	4.9	4.1	2.21	0.43	0.30	0.25	3.25	2.96	0.63
Sum of square inter-laboratories (S_R)	7.7	5.4	0.03	0.03	0.08	0.01	116.87	52.97	11.47
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	0.01	0.00	0.00	0.01	0.00	0.00	0.03
Total sum of square (S_T)	7.8	5.4	0.05	0.03	0.08	0.02	116.87	52.97	11.50
Inter-laboratories degree of freedom (ϕ_R)	4	5	2	4	3	4	5	2	5
Within-laboratory degree of freedom (ϕ_{RW})	5	6	3	5	4	5	6	3	6
Repeatability degree of freedom (ϕ_r)	20	24	12	20	16	20	24	12	24
Total degree of freedom (ϕ_T)	29	35	17	29	23	29	35	17	35
Inter-laboratories variance ($V_R = S_R/\phi_R$)	1.9	1.1	0.02	0.01	0.03	0.00	23.37	26.49	2.29
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	0.00	0.00	0.00
Laboratory component of variance ($s_b^2 = (V_R - V_{RW})/(2 \times 3)$)	0.3	0.2	0.00	0.00	0.00	0.00	3.90	4.41	0.38
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	0.00	0.00	0.00
Inter-laboratories standard deviation ($s_R = \text{SQRT}(s_b^2/(2 \times 3) + s_c^2/2 + s_r^2)$)	0.6	0.4	0.05	0.03	0.06	0.02	1.97	2.10	0.62
Within-laboratory standard deviation ($s_{RW} = \text{SQRT}(s_r^2/3 + s_c^2)$)	0.0	0.0	0.01	0.01	0.01	0.00	0.00	0.00	0.01
Repeatability standard deviation ($s_r = \text{SQRT}(s_r^2)$)	0.0	0.0	0.03	0.02	0.01	0.02	0.01	0.00	0.04
Inter-laboratories precision CV (%)	11.7	10.4	2.36	7.95	21.46	6.86	60.69	70.90	97.58
Within-laboratory precision CV (%)	0.0	0.0	0.46	2.00	1.71	1.34	0.11	0.00	0.97
Repeatability precision CV (%)	1.0	0.8	1.49	3.64	3.03	8.32	0.40	0.00	5.74
Reproducibility limit ($R = D(2, 0.95) \times s_R$)	1.6	1.2	0.15	0.09	0.18	0.05	5.53	5.88	1.73
Within-laboratory-reproducibility limit ($R_W = D(2, 0.95) \times s_{RW}$)	0.0	0.0	0.03	0.02	0.01	0.01	0.01	0.00	0.02
Repeatability limit ($r = D(3, 0.95) \times s_r$)	0.2	0.1	0.11	0.05	0.03	0.07	0.04	0.00	0.12

4.3.5 Inter-laboratory variations in each parameter

To assess precision for each laboratory and property, scatter plots comparing samples 251s and 252s are presented in Figure 4.2. Outliers have been removed to improve readability.

1) pH

A linear and positive correlation was observed between samples 251s and 252s for pH(H₂O), 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.

2) Base cations

Due to the limited number of participating laboratories, no significant correlations were observed between samples 251s and 252s for exchangeable base cations. 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

No linear correlations were observed between samples 251s and 252s for Ex-acidity, Ex-Al, and Ex-H. In general, 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.

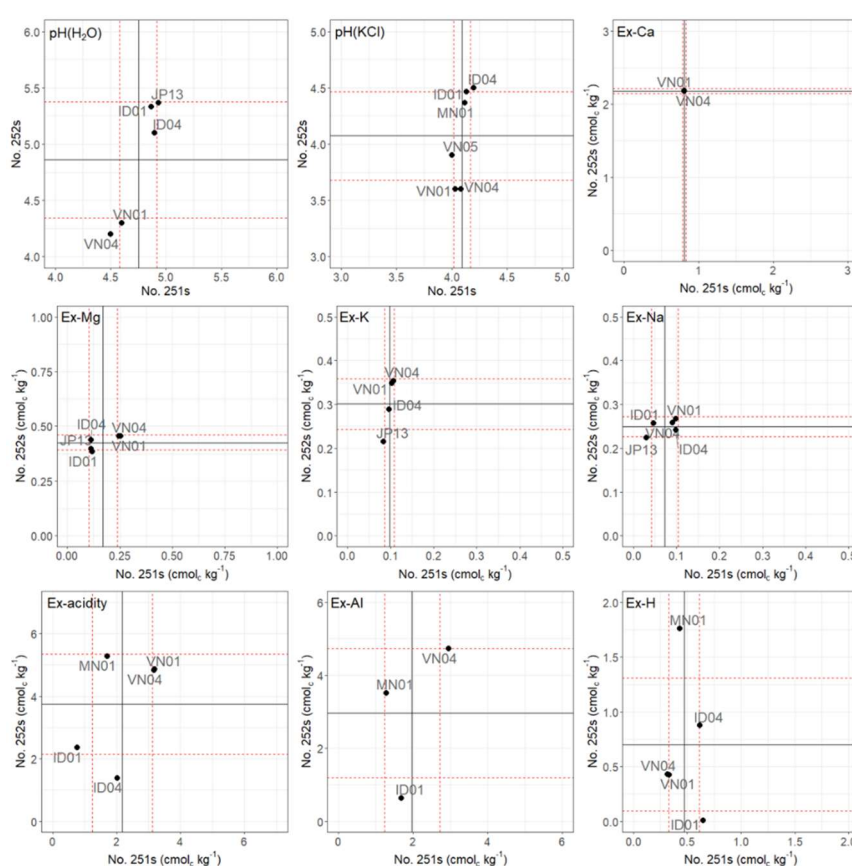


Figure 4.2 Scatter plots of each soil chemical property between No.251s and No.252s
Solid and dotted lines indicate mean and mean $\pm$ S.D. of verified datasets, respectively.
The outliers are excluded from the plots.

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	
ID01	1	3	0	1	3	0	s
ID04	1	3	3	1	3	3	d
JP13	1	22	0	1	3.5	0	d
MN01	-	-	-	1	21	14	-
VN01	1	12	12	1	9	9	d
VN04	1	19	18	1	20	19	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, two laboratories, and one laboratories used the Percolation tube procedure, the Buchner funnel method, and the Centrifuge procedure, respectively. No significant differences were observed among these procedures. Regarding burette sizes used for the titration of Ex-acidity, capacities ranged from 10 to 50 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 relationship was found between the analysis date and the analytical results. The duration of analysis ranged from 1 to 13 days, and the interval between the first and second measurements in repeat analyses varied from 0 days (same day) to 12 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*	Instrument	Years	Instrument	Years	Instrument	Years	Instrument	Years		method	Size of burette (mL)
ID01	251s	Centrifuge procedure	AAS	6	AAS	6	6	+	AAS	6	AAS	6	6	+	Titration	50
	252s		AAS	6	AAS	6	6	+	AAS	6	AAS	6	6	+	Titration	50
ID04	251s	Percolation tube procedure	AAS	11	AAS	11	11	+	AAS	11	AAS	11	11	+	Titration	25
	252s		AAS	11	AAS	11	11	+	AAS	11	AAS	11	11	+	Titration	25
JP 13	251s	Percolation tube procedure	ICP-AES	6.5	ICP-AES	6.5	6.5	+	ICP-AES	6.5	ICP-AES	6.5	6.5	+	Titration	25
	252s		ICP-AES	6.5	ICP-AES	6.5	6.5	+	ICP-AES	6.5	ICP-AES	6.5	6.5	+	Titration	25
MN01	251s	-												Titration	25	0.1
	252s													Titration	25	0.1
VN01	251s	Buchner funnel	AAS	18	AAS	18	18	-	AAS	18	AAS	18	18	-	Titration	10
	252s		AAS	18	AAS	18	18	-	AAS	18	AAS	18	18	-	Titration	10
VN04	251s	Buchner funnel	AAS	19	AAS	19	19	na	AAS	19	AAS	19	19	na	Titration	10
	252s		AAS	19	AAS	19	19	na	AAS	19	AAS	19	19	na	Titration	10
VN05	251s	-												-		0.01
	252s													-		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; +, 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	Start Date	Finish Date	AD	ID	Start Date	Finish Date	AD	ID	Start Date	Finish Date
ID01	1st	2025/12/11	2025/12/11	1	7	2025/12/18	2025/12/22	5	11	2025/12/18	2025/12/22	5	11	2025/12/22	2025/12/22
	2nd	2025/12/18	2025/12/18	1	1	2025/12/29	2025/12/31	3	3	2025/12/29	2025/12/31	3	3	2025/12/29	2025/12/29
ID04	1st	2025/12/12	2025/12/12	1	10	2025/12/12	2025/12/12	1	10	2025/12/12	2025/12/12	1	10	2025/12/12	2025/12/12
	2nd	2025/12/22	2025/12/22	1	1	2025/12/22	2025/12/22	1	1	2025/12/22	2025/12/22	1	1	2025/12/22	2025/12/22
JP 13	1st	2025/12/17	2025/12/18	2	5	2025/12/24	2026/1/5	13	12	2025/12/24	2026/1/5	13	12	2025/12/15	2025/12/18
	2nd	2025/12/22	2025/12/23	2	2	2026/1/5	2026/1/8	4	4	2026/1/5	2026/1/8	4	4	2025/12/19	2025/12/24
MN01	1st	2026/1/5	2026/1/15	11	0		NA				NA			2026/1/5	2026/1/15
	2nd	2026/1/5	2026/1/15	11	1		NA				NA			2026/1/5	2026/1/15
VN01	1st	2026/1/7	2026/1/7	1	2	2026/1/6	2026/1/7	2	2	2026/1/6	2026/1/7	2	2	2026/1/6	2026/1/7
	2nd	2026/1/9	2026/1/9	1	1	2026/1/8	2026/1/9	2	2	2026/1/8	2026/1/9	2	2	2026/1/8	2026/1/9
VN04	1st	2026/1/5	2026/1/5	1	0	2026/1/5	2026/1/5	1	1	2026/1/5	2026/1/5	1	1	2026/1/1	2026/1/1
	2nd	2026/1/5	2026/1/5	1	1	2026/1/6	2026/1/6	1	1	2026/1/6	2026/1/6	1	1	2026/1/3	2026/1/3
VN05	1st	2026/2/2	2026/2/5	4	0		NA				NA				NA
	2nd	2026/2/2	2026/2/5	4	4		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 21st 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 0.01 to 0.073 mg/L, 0.002 to 0.076 mg/L, 0.003 to 0.132 mg/L, and 0.001 to 0.0455 mg/L, respectively. Similarly, the quantification limits for Ex-Ca, Ex-Mg, Ex-K, and Ex-Na ranged from 0.003 to 0.242 mg/L, 0.007 to 0.254 mg/L, 0.01 to 0.441 mg/L, and 0.003 to 0.1516 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 ID04—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
ID01	0.001	0.004	mg L ⁻¹	0.002	0.007	mg L ⁻¹	0.132	0.441	mg L ⁻¹	0.026	0.086	mg L ⁻¹
ID04	0.027	0.0899	mg L ⁻¹	0.0066	0.0221	mg L ⁻¹	0.0226	0.0752	mg L ⁻¹	0.0455	0.1516	mg L ⁻¹
JP13	0.001	0.003	mg L ⁻¹	0.003	0.008	mg L ⁻¹	0.003	0.01	mg L ⁻¹	0.001	0.003	mg L ⁻¹
MN01	-	-	-	-	-	-	-	-	-	-	-	-
VN01	0.07	0.21	mg L ⁻¹	0.04	0.12	mg L ⁻¹	0.03	0.09	mg L ⁻¹	0.03	0.09	mg L ⁻¹
VN04	0.073	0.242	mg L ⁻¹	0.076	0.254	mg L ⁻¹	0.015	0.05	mg L ⁻¹	0.015	0.05	mg L ⁻¹
VN05	-	-	-	-	-	-	-	-	-	-	-	-

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

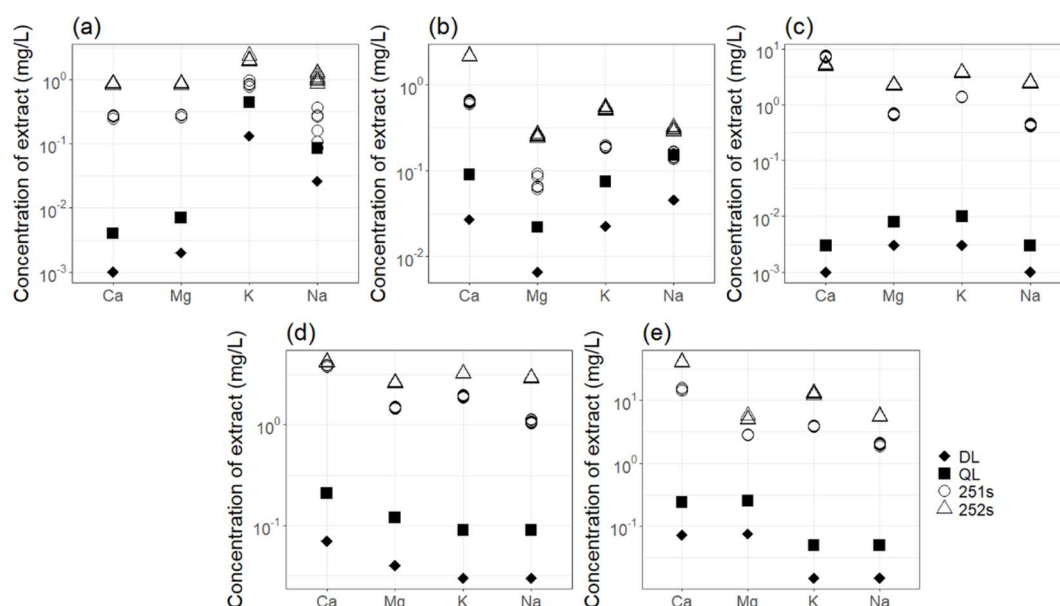


Figure 4.3 Detection limit, quantification limit and concentrations of soil extracts for Ex-base cations in the participating laboratories, (a) ID01, (b) ID04, (c) JP13, (d) VN01, and (e) VN04
DL, detection limit; QL, quantification limit

4.4 Needs for improvement of soil analysis

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 2025. The number of laboratories peaked in the late 2000s to early 2010s, with up to 18 laboratories from 10 countries involved. However, in 2024, participation dropped to only 6 laboratories from 3 countries, reducing the project's scale to one-third of its peak. In 2025, only seven laboratories from 4 countries participated in the project.

Although the outlier ratio has decreased since the initial experiment in 2002, it has remained relatively high (10-25%) between 2003 and 2025. In 2025, the outlier ratios for both samples 251s and 252s (i.e., 2025_1 and 2025_2, respectively) were higher than the average outlier ratio from 2003 to 2024. In addition, 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.

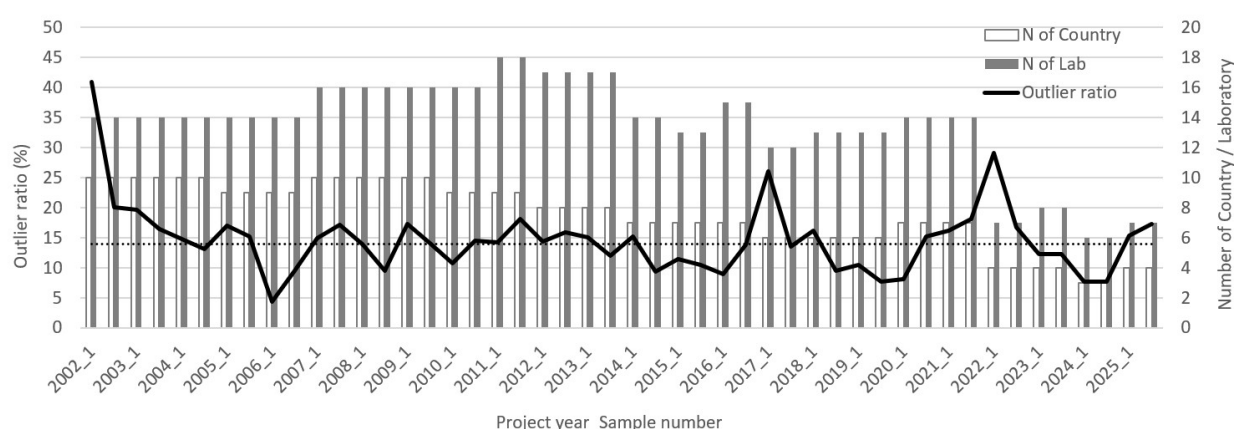


Figure 4.4 Change in outlier ratios in all items and laboratories from 2002 to 2025.

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., 251s and 252s).

Outlier ratios from 2002 to 2024 were obtained from the *Report of Inter-Laboratory Comparison Project 2000-2024* (<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. 251s)

Lab	pH(H ₂ O)			pH(KCl)			Ex-Ca (mmol.kg ⁻¹)			Ex-Mg (mmol.kg ⁻¹)			Ex-K (mmol.kg ⁻¹)			Ex-Na (mmol.kg ⁻¹)			Ex-Acidity (mmol.kg ⁻¹)			Ex-Al (mmol.kg ⁻¹)			Ex-H (mmol.kg ⁻¹)		
	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
ID01	4.9 (0.1)	4.9 (0.0)	4.9 (0.0)	4.1 (0.1)	4.1 (0.0)	4.1 (0.0)	0.07 (0.00)	0.07 (0.00)	0.07 (0.00)	0.12 (0.01)	0.12 (0.00)	0.12 (0.00)	0.11 (0.00)	0.11 (0.00)	0.11 (0.00)	0.05 (0.02)	0.05 (0.02)	0.06 (0.02)	0.77 (0.00)	0.77 (0.00)	0.77 (0.00)	1.68 (0.00)	1.68 (0.00)	1.68 (0.00)	1.68 (0.00)	0.65 (0.00)	0.65 (0.00)
ID04	4.9 (0.0)	4.9 (0.0)	4.9 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.61 (0.02)	0.61 (0.02)	0.61 (0.02)	0.12 (0.01)	0.12 (0.01)	0.12 (0.01)	0.09 (0.00)	0.09 (0.00)	0.09 (0.01)	0.09 (0.01)	0.09 (0.01)	0.09 (0.01)	2.02 (0.02)	2.03 (0.02)	2.04 (0.02)	1.40 (0.02)	1.40 (0.02)	1.39 (0.02)	1.41 (0.02)	0.62 (0.04)	0.63 (0.04)
JPI3	4.9 (0.1)	5.0 (0.1)	5.0 (0.0)	4.2 (0.0)	4.2 (0.0)	4.2 (0.0)	0.75 (0.04)	0.75 (0.04)	0.75 (0.04)	0.11 (0.01)	0.11 (0.01)	0.11 (0.01)	0.08 (0.01)	0.08 (0.01)	0.09 (0.00)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)	2.10 (0.05)	2.13 (0.05)	2.14 (0.05)	1.64 (0.08)	1.64 (0.08)	1.62 (0.06)	1.71 (0.06)	0.45 (0.07)	0.44 (0.07)
MN01	4.4 (0.1)	4.5 (0.1)	4.5 (0.0)	4.1 (0.1)	4.1 (0.1)	4.1 (0.1)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.71 (0.00)	1.71 (0.00)	1.71 (0.00)	1.28 (0.00)	1.28 (0.00)	1.28 (0.00)	1.28 (0.00)	0.43 (0.00)	0.43 (0.00)
VN01	4.6 (0.0)	4.6 (0.0)	4.6 (0.1)	4.0 (0.1)	4.0 (0.1)	4.0 (0.1)	0.80 (0.02)	0.80 (0.02)	0.78 (0.01)	0.25 (0.01)	0.26 (0.01)	0.25 (0.01)	0.10 (0.00)	0.10 (0.00)	0.10 (0.00)	0.10 (0.01)	0.10 (0.01)	0.09 (0.00)	3.20 (0.03)	3.19 (0.03)	3.20 (0.03)	2.98 (0.03)	2.97 (0.04)	2.97 (0.04)	3.01 (0.05)	0.33 (0.05)	0.29 (0.05)
VN04	4.5 (0.0)	4.5 (0.0)	4.5 (0.0)	4.1 (0.0)	4.1 (0.0)	4.1 (0.0)	0.79 (0.04)	0.79 (0.04)	0.76 (0.03)	0.24 (0.01)	0.25 (0.01)	0.24 (0.01)	0.10 (0.01)	0.10 (0.01)	0.11 (0.00)	0.09 (0.00)	0.09 (0.00)	0.09 (0.00)	3.18 (0.02)	3.19 (0.03)	3.17 (0.03)	2.96 (0.00)	2.96 (0.00)	2.96 (0.00)	3.01 (0.05)	0.32 (0.05)	0.32 (0.05)
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	3.17 (0.00)	3.17 (0.00)	3.17 (0.00)	2.96 (0.00)	2.96 (0.00)	2.96 (0.00)	2.96 (0.00)	0.32 (0.00)	0.32 (0.00)

Appendix Table 4.2 Results submitted by the laboratories (sample No. 252s)

Lab	pH(H ₂ O)			pH(KCl)			Ex-Cu (cmol.kg ⁻¹)			Ex-Mg (cmol.kg ⁻¹)			Ex-K (cmol.kg ⁻¹)			Ex-Na (cmol.kg ⁻¹)			Ex-Acidity (cmol.kg ⁻¹)			Ex-Al (cmol.kg ⁻¹)			Ex-H (cmol.kg ⁻¹)		
	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
ID01	5.3 (0.1)	5.3 (0.1)	5.3	4.5 (0.1)	4.5 (0.1)	4.5	0.24 (0.01)	0.23 (0.01)	0.24	0.38 (0.01)	0.38 (0.01)	0.38	0.26 (0.07)	0.23 (0.08)	0.23	0.26 (0.04)	0.25 (0.03)	0.24	2.35 (0.00)	2.35 (0.00)	2.35	0.64 (0.00)	0.64 (0.00)	0.64	0.01 (0.00)	0.01 (0.00)	0.01
			5.4			4.5			0.22			0.37		0.13	0.29			0.29			2.35			0.64		0.01	
			5.2			4.5			0.24			0.39		0.29	0.27			0.26			2.35			0.64		0.01	
			5.4			4.4			0.24			0.40		0.03	0.33	0.31			2.35			0.64			0.01		
ID04	5.1 (0.0)	5.1 (0.0)	5.1	4.5 (0.0)	4.5 (0.0)	4.5	2.27 (0.02)	2.26 (0.02)	2.24	0.44 (0.01)	0.44 (0.01)	0.43	0.29 (0.01)	0.29 (0.02)	0.30	0.24 (0.02)	0.24 (0.02)	0.24	1.39 (0.02)	1.39 (0.04)	1.37	0.52 (0.05)	0.50 (0.05)	0.50	0.88 (0.04)	0.87 (0.02)	0.87
			5.1			4.5			2.28			0.45		0.27	0.23			1.42			0.57			0.85		0.85	
			5.1			4.5			2.28			0.44		0.28	0.26			1.39			0.52			0.88		0.85	
			5.1			4.5			2.28			0.45		0.01	0.29	0.24			1.38			0.53			0.85		0.85
JP13	5.4 (0.1)	5.4 (0.1)	5.3	4.5 (0.0)	4.5 (0.0)	4.5	2.71 (0.09)	2.69 (0.09)	2.77	0.40 (0.01)	0.39 (0.01)	0.38	0.22 (0.01)	0.22 (0.01)	0.21	0.22 (0.01)	0.23 (0.01)	0.23	0.80 (0.02)	0.80 (0.02)	0.82	0.51 (0.05)	0.50 (0.05)	0.44	0.30 (0.07)	0.31 (0.06)	0.38
			5.4			4.5			2.60			0.41		0.21	0.22			0.82			0.51			0.29		0.38	
			5.3			4.5			2.74			0.40		0.01	0.21	0.22			0.79			0.57			0.22		
			5.4			4.6			2.83			0.40		0.21	0.22	0.22			0.80			0.53			0.28		
MN01	4.6 (0.1)	4.6 (0.0)	4.6	4.4 (0.1)	4.4 (0.1)	4.4				NA	NA	NA	NA	NA	NA	NA	NA	NA	5.28 (0.00)	5.28 (0.00)	5.28	3.52 (0.00)	3.52 (0.00)	3.52	1.76 (0.00)	1.76 (0.00)	1.76
			4.6			4.4						NA		NA	NA			5.28			3.52			1.76		1.76	
			4.5			4.4						NA		NA	NA			5.28			3.52			1.76		1.76	
			4.5			4.3						NA		NA	NA			5.28			3.52			1.76		1.76	
VN01	4.3 (0.0)	4.3 (0.0)	4.3	3.6 (0.0)	3.6 (0.0)	3.6	2.19 (0.02)	2.18 (0.04)	2.15	0.46 (0.01)	0.45 (0.01)	0.45	0.35 (0.00)	0.35 (0.00)	0.35	0.27 (0.01)	0.27 (0.01)	0.27	4.86 (0.02)	4.75 (0.04)	4.87	4.75 (0.02)	4.75 (0.02)	4.74	0.43 (0.03)	0.43 (0.02)	0.42
			4.3			3.6			2.22			0.46		0.35	0.27			4.86			4.78			0.42		0.42	
			4.3			3.6			2.20			0.46		0.35	0.26			4.84			4.69			0.42		0.46	
			4.3			3.6			2.19			0.46		0.01	0.34	0.27			4.86			4.82			0.42		0.42
VN04	4.2 (0.0)	4.2 (0.0)	4.2	3.6 (0.0)	3.6 (0.0)	3.6	2.18 (0.04)	2.17 (0.05)	2.21	0.46 (0.03)	0.47 (0.04)	0.45	0.35 (0.01)	0.35 (0.02)	0.35	0.26 (0.00)	0.26 (0.01)	0.26	4.84 (0.00)	4.73 (0.00)	4.84	4.73 (0.00)	4.73 (0.00)	4.73	0.43 (0.00)	0.43 (0.00)	0.43
			4.2			3.6			2.12			0.44		0.36	0.26			4.84			4.73			0.43		0.43	
			4.2			3.6			2.13			0.45		0.36	0.26			4.83			4.73			0.43		0.43	
			4.2			3.6			2.23			0.44		0.00	0.36	0.26			4.83			4.73			0.43		0.43
VN05	4.5 (0.0)	4.5 (0.0)	4.5	3.9 (0.0)	3.9 (0.0)	3.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
			4.5			3.9			NA			NA		NA	NA			NA			NA			NA		NA	
			4.5			3.9			NA			NA		NA	NA			NA			NA			NA		NA	
			4.5			3.9			NA			NA		NA	NA			NA			NA			NA		NA	

5. 26th 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 SO_4^{2-} , NO_3^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and 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

The NC distributed the artificial inland water samples to 21 laboratories in charge of chemical analysis in 10 countries of EANET. 20 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.

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 ⁻¹
Alkalinity	milli equivalent per liter	meq L ⁻¹
SO ₄ ²⁻	milli gram per liter	mg L ⁻¹
NO ₃ ⁻	milli gram per liter	mg L ⁻¹
Cl ⁻	milli gram per liter	mg L ⁻¹
Na ⁺	milli gram per liter	mg L ⁻¹
K ⁺	milli gram per liter	mg L ⁻¹
Ca ²⁺	milli gram per liter	mg L ⁻¹
Mg ²⁺	milli gram per liter	mg L ⁻¹
NH ₄ ⁺	milli gram per liter	mg L ⁻¹

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 ⁺	1 – 10 mg L ⁻¹
EC	1.5 – 15 mS m ⁻¹	K ⁺	0.2 – 2 mg L ⁻¹
Alkalinity	0.05 – 0.5 meq L ⁻¹	Ca ²⁺	0.5 – 5 mg L ⁻¹
SO ₄ ²⁻	2 – 20 mg L ⁻¹	Mg ²⁺	0.2 – 2 mg L ⁻¹
NO ₃ ⁻	0.1 – 5 mg L ⁻¹	NH ₄ ⁺	0.05 – 0.5 mg L ⁻¹
Cl ⁻	1 – 10 mg L ⁻¹		

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 ₄ ²⁻ NO ₃ ⁻	Ion Chromatography or Spectrophotometry
Cl ⁻	
Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺	Ion Chromatography or Atomic Absorption / Flame (emission) photometry
NH ₄ ⁺	
	Ion Chromatography or Spectrophotometry (Indophenol blue)

5.2.4 Data Checking Procedures

a) Calculation of ion balance (R_1)

- (1) Total anion 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 (HCO_3^-).

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

n, c_{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 [$\mu\text{mol L}^{-1}$]).

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

n, c_{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_{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 (HCO_3^-).

(2) Ratio (R_2) of calculations (A_{calc}) to measurements (A_{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_{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_{meas} [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	7.20	6.97	0.14	19	6.70	7.18
EC (mS m ⁻¹)	3.86	3.73	0.14	19	3.39	4.04
Alkalinity (meq L ⁻¹)	0.132	0.129	0.01	20	0.099	0.153
SO ₄ ²⁻ (mg L ⁻¹)	4.57	4.56	0.22	18	3.97	4.96
NO ₃ ⁻ (mg L ⁻¹)	0.65	0.65	0.05	18	0.58	0.73
Cl ⁻ (mg L ⁻¹)	3.04	3.05	0.18	18	2.69	3.42
Na ⁺ (mg L ⁻¹)	3.91	3.88	0.18	19	3.46	4.38
K ⁺ (mg L ⁻¹)	0.52	0.52	0.02	17	0.47	0.55
Ca ²⁺ (mg L ⁻¹)	1.55	1.56	0.14	19	1.33	1.90
Mg ²⁺ (mg L ⁻¹)	0.53	0.52	0.03	18	0.45	0.55
NH ₄ ⁺ (mg L ⁻¹)	0.32	0.31	0.04	19	0.24	0.40

(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 ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Total	Ratio
E	1	1	3	0	0	1	0	1	2	1	3	13	6.1%
X	0	0	0	0	1	0	0	0	0	0	0	1	0.5%
Data within DQOs	19	19	17	19	18	18	19	18	17	18	16	198	93.4%
Flagged(%)	5.0	5.0	15.0	0.0	5.3	5.3	0.0	5.3	10.5	5.3	15.8	6.6	

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

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

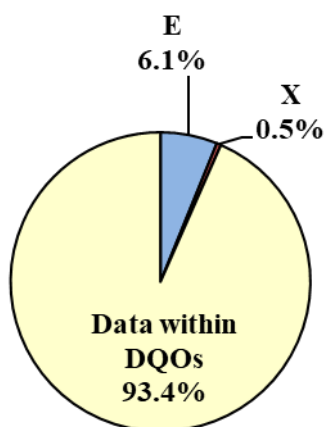


Figure 5.1 Percentage of flagged data

The data flagged by "E" shared 6.1% of all reported data, and the data flagged by "X" shared 0.5% of all reported data of samples. The NH₄⁺ result was flagged most, and the percentage was 15.8%.

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	11	55%
1	6	30%
2	2	10%
3	0	0%
4	1	5%
5	0	0%
6	0	0%
7	0	0%
8	0	0%
9	0	0%
Total	20	100%

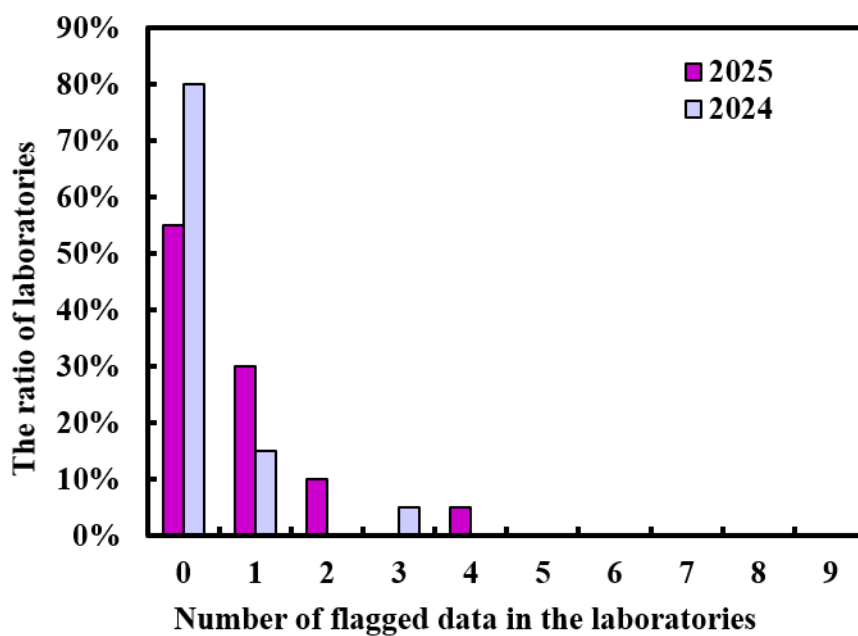


Figure 5.2 Distribution of laboratories with the number of flagged data

The percentage of the laboratories without flagged data was 55% in this attempt, while that in the last attempt was 80%. The maximum number of flagged data was four, 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.25Ii (artificial inland aquatic environment sample : EANET in 2025)

Lab. ID	pH	EC mS m ⁻¹	Alkalinity meq L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	NO ₃ ⁻ mg L ⁻¹	Cl ⁻ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	NH ₄ ⁺ mg L ⁻¹	R1 %	R2 %
CN01	7.08	3.87	0.134	4.52	0.63	2.98	3.98	0.52	1.53	0.52	0.28	-0.21	-0.56
CN02	6.98	3.81	0.133	4.46	0.65	2.94	3.91	0.53	1.50	0.54	0.30	0.04	0.00
CN03	7.08	3.87	0.131	4.36	0.70	2.91	4.01	0.53	1.54	0.52	0.28	1.31	-0.97
CN04	6.90	3.72	0.133	4.55	0.68	2.97	3.91	0.53	1.60	0.54	0.28	0.26	1.76
ID01	6.92	4.04	0.105 E	4.52	0.67	2.86	3.72	0.53	1.33	0.45	0.40 E	1.81	-5.98
JP03	7.12	3.67	0.130	4.96	0.70	3.33	3.80	0.53	1.46	0.50	0.24 E	-5.04	2.76
JP04	7.12	3.69	0.136	4.56	0.64	3.01	3.89	0.52	1.60	0.53	0.30	-0.56	2.32
MY01	7.10	3.77	0.137	4.53	0.61	3.03	3.92	0.47	1.54	0.53	0.31	-0.90	1.02
MN01	6.94	3.39	0.133	4.95	0.73	3.22	3.86	0.50	1.74	0.53	0.26 E	-2.01	8.09
PH01	6.73	3.79	0.131	4.55	0.62	2.97	3.98	0.54	1.90 E	0.49	0.28	2.81	1.73
PH02	6.97	4.67 E	0.153 E	4.38	0.71	2.89	3.78	0.49	1.83 E	0.64 E	0.33	0.24	-7.83
RU01	7.07	3.80	0.099 E	4.82	0.58	2.69	3.46	0.55	1.56	0.52	0.30	2.97	-3.29
RU02	7.11	3.91	0.127	3.97	0.61	3.91 E	4.05	0.40 E	1.63	0.53	0.35	0.15	0.62
TH01	7.18	3.53	0.136									(-)	(-)
TH02	6.10 E	3.66	0.130	4.59	0.62	3.00	4.38	0.49	1.39	0.48	0.31	1.50	3.05
VN01	6.85	3.67	0.125	4.60	0.72	3.19	3.80	0.50	1.50	0.54	0.32	-1.19	2.22
VN02	6.95	3.68	0.125	4.63	0.63	3.15	3.81	0.52	1.48	0.52	0.32	-1.10	1.66
VN03	6.83	3.72	0.128	4.56	0.60	3.42	3.85	0.51	1.45	0.51	0.34	-2.37	1.95
VN04	6.70	3.64	0.126	4.37	0.99 X	3.24	3.79	0.49	1.51	0.55	0.33	-1.29	2.79
VN05	6.88	3.70	0.123	4.68	0.62	3.07	3.84	0.51	1.54	0.55	0.32	0.46	1.74
Expected value	7.20	3.86	0.132	4.57	0.65	3.04	3.91	0.52	1.55	0.53	0.32	-	-

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.

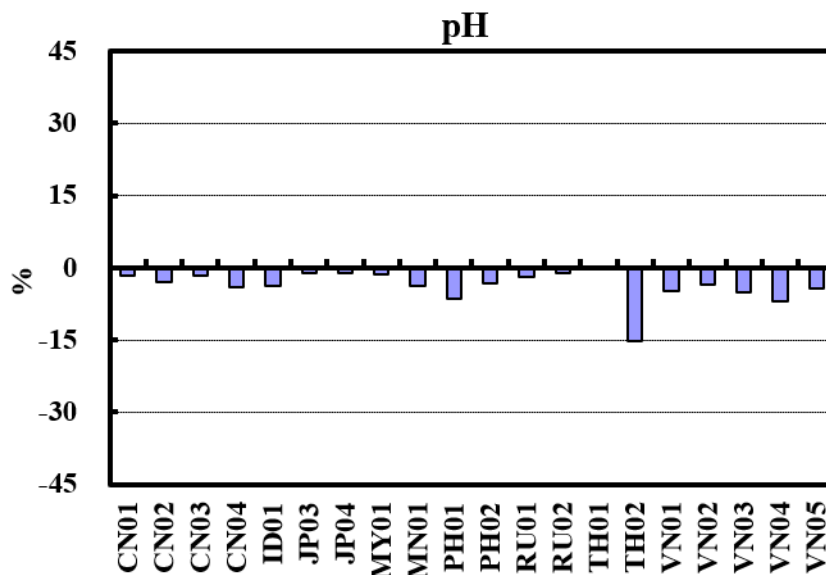


Figure 5.3 Distribution of results for pH (normalized by the prepared value)

Except for TH02, all the submitted data of pH were within DQOs.

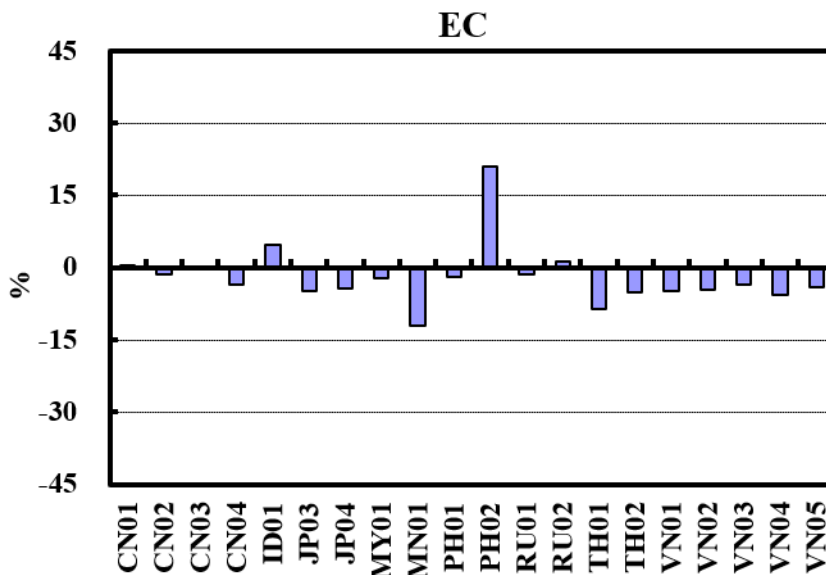


Figure 5.4 Distribution of results for EC (normalized by the prepared value)

Except for PH02, all the submitted data of EC were within DQOs.

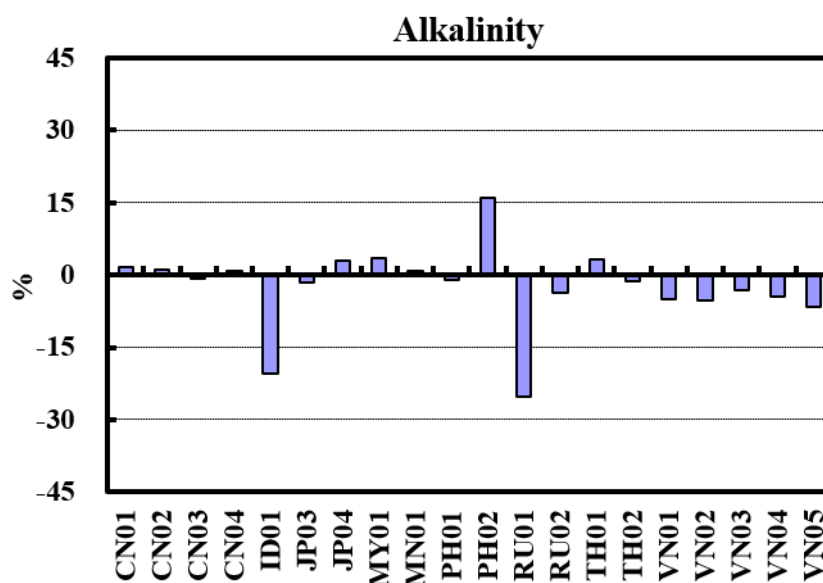


Figure 5.5 Distribution of results for alkalinity (normalized by prepared concentration)

Except for ID01, PH02 and RU01, all the submitted data of Alkalinity were within DQOs.

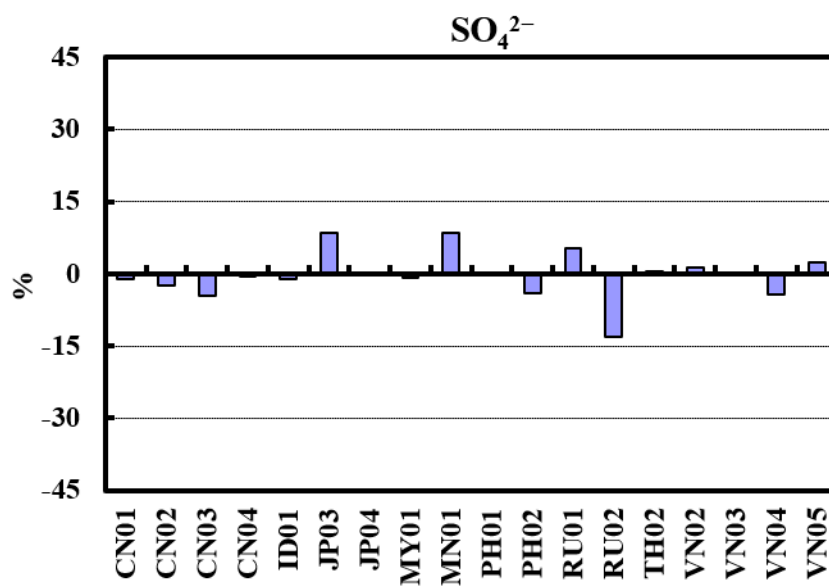


Figure 5.6 Distribution of results for SO₄²⁻ (normalized by prepared concentration)

All the submitted data of SO₄²⁻ were within DQOs.

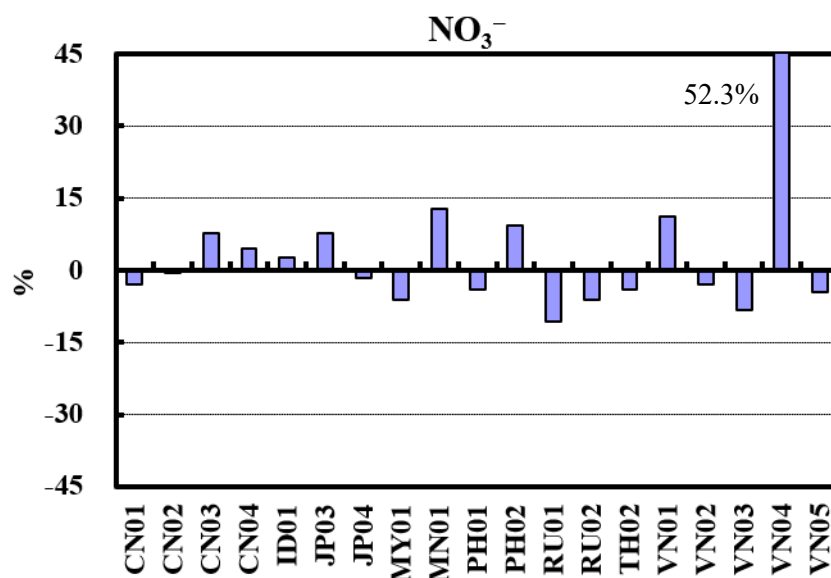


Figure 5.7 Distribution of results for NO_3^- (normalized by prepared concentration)

Except for VN04, all the submitted data of NO_3^- were within DQOs.

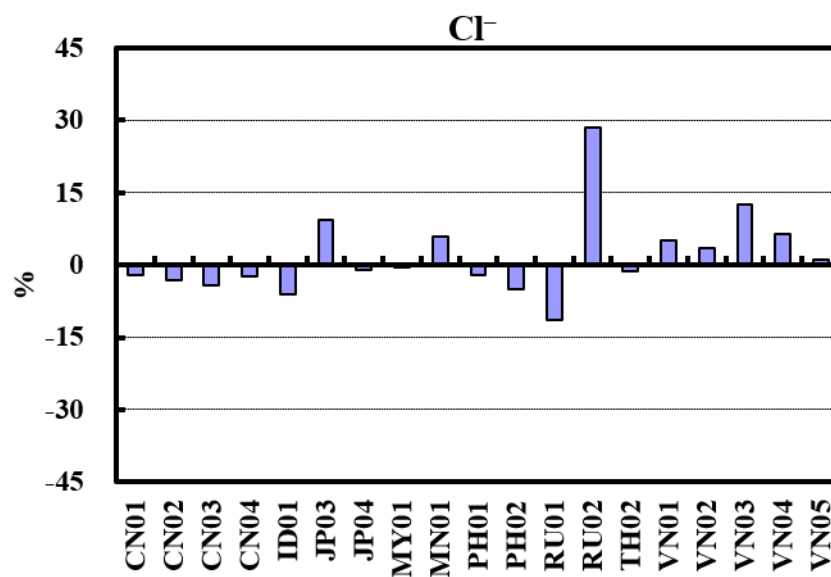


Figure 5.8 Distribution of results for Cl^- (normalized by prepared concentration)

Except for RU02, all the submitted data of Cl^- were within DQOs.

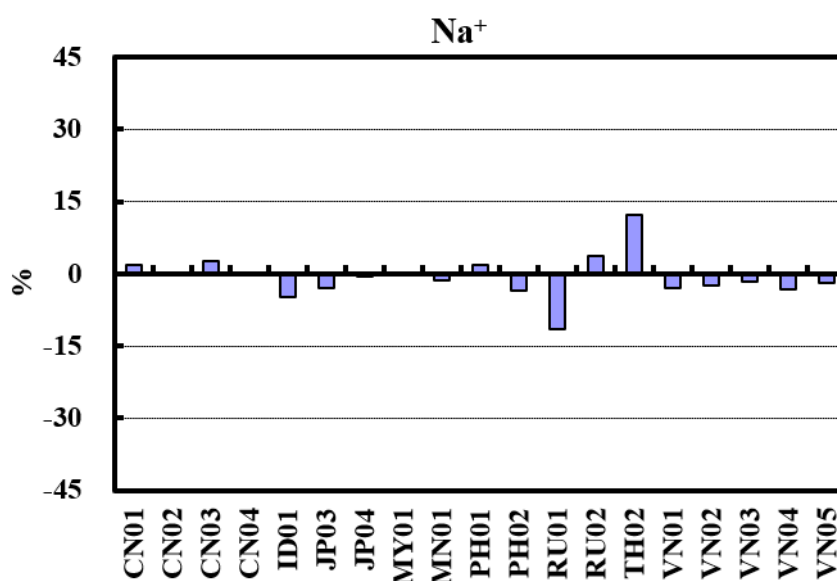


Figure 5.9 Distribution of results for Na⁺ (normalized by prepared concentration)

All the submitted data of Na⁺ were within DQOs.

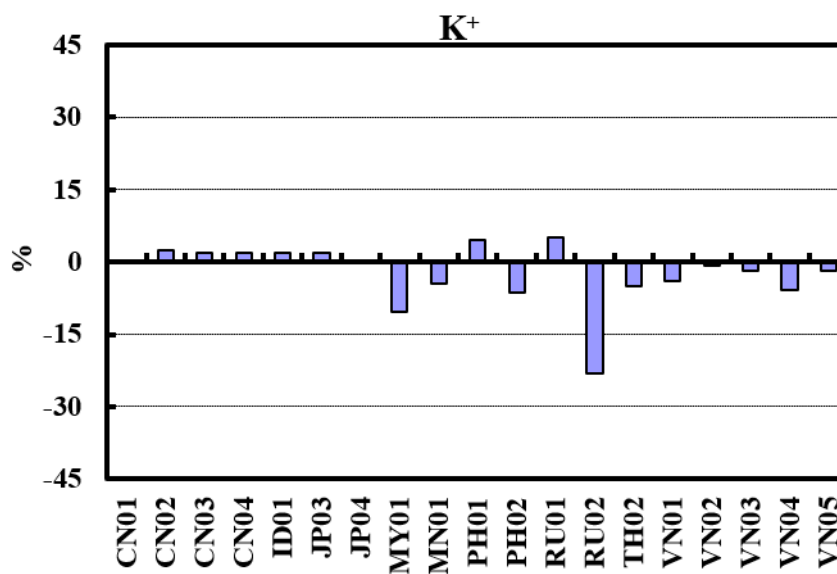


Figure 5.10 Distribution of results for K⁺ (normalized by prepared concentration)

Except for RU02, all the submitted data of K⁺ were within DQOs.

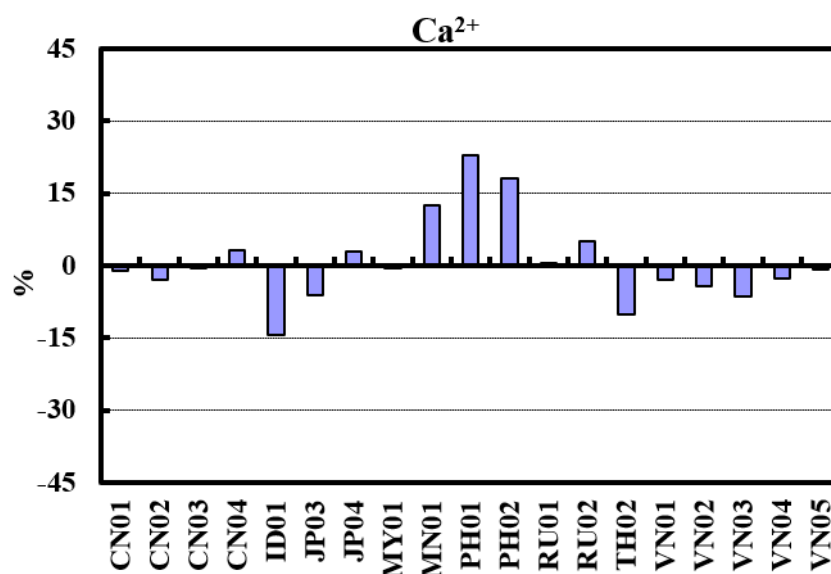


Figure 5.11 Distribution of results for Ca^{2+} (normalized by prepared concentration)

Except for PH01 and PH02, all the submitted data of Ca^{2+} were within DQOs.

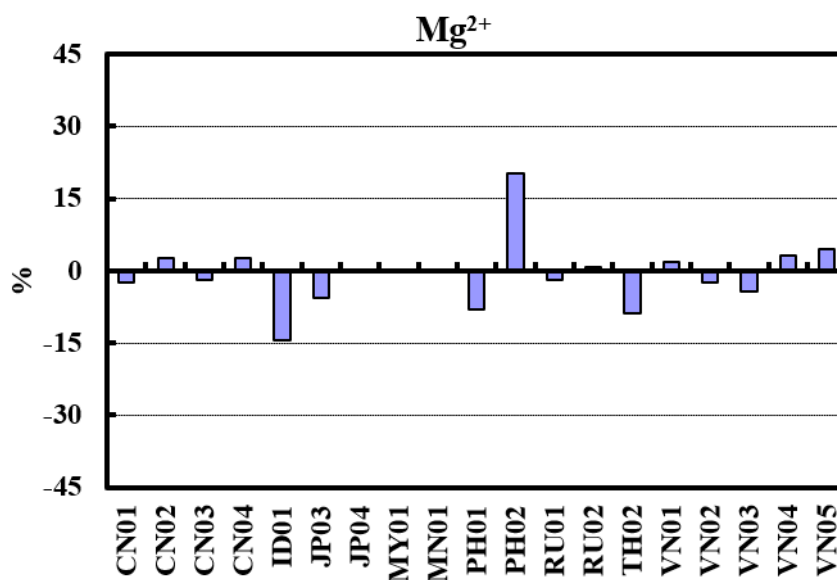


Figure 5.12 Distribution of results for Mg^{2+} (normalized by prepared concentration)

Except for PH02, all the submitted data of Mg^{2+} were within DQOs.

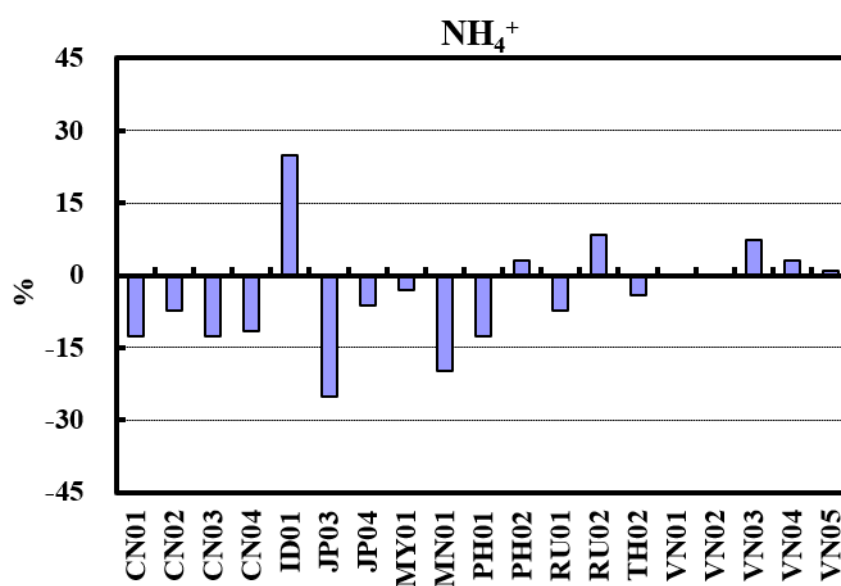


Figure 5.13 Distribution of results for NH_4^+ (normalized by prepared concentration)

Except for ID01 and JP03 and MN01, all the submitted data of NH_4^+ 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.

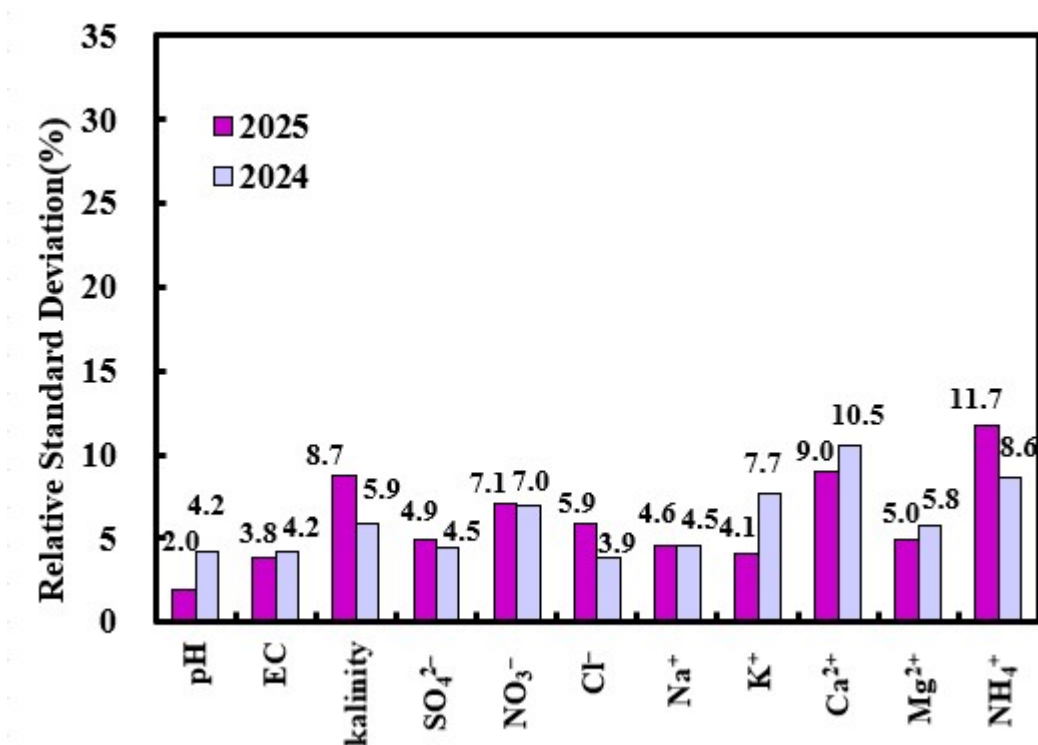


Figure 5.14 Relative standard deviation of each constituent

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

The relative standard deviation (RSD) of pH, EC, K⁺, Ca²⁺ and Mg²⁺ were lower than those in the last attempt. In particular, K⁺ showed a substantial reduction in RSD. On the other hand, the RSDs of Alkalinity, SO₄²⁻, NO₃⁻, Cl⁻, Na⁺ and NH₄⁺ were higher than those of the last 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.

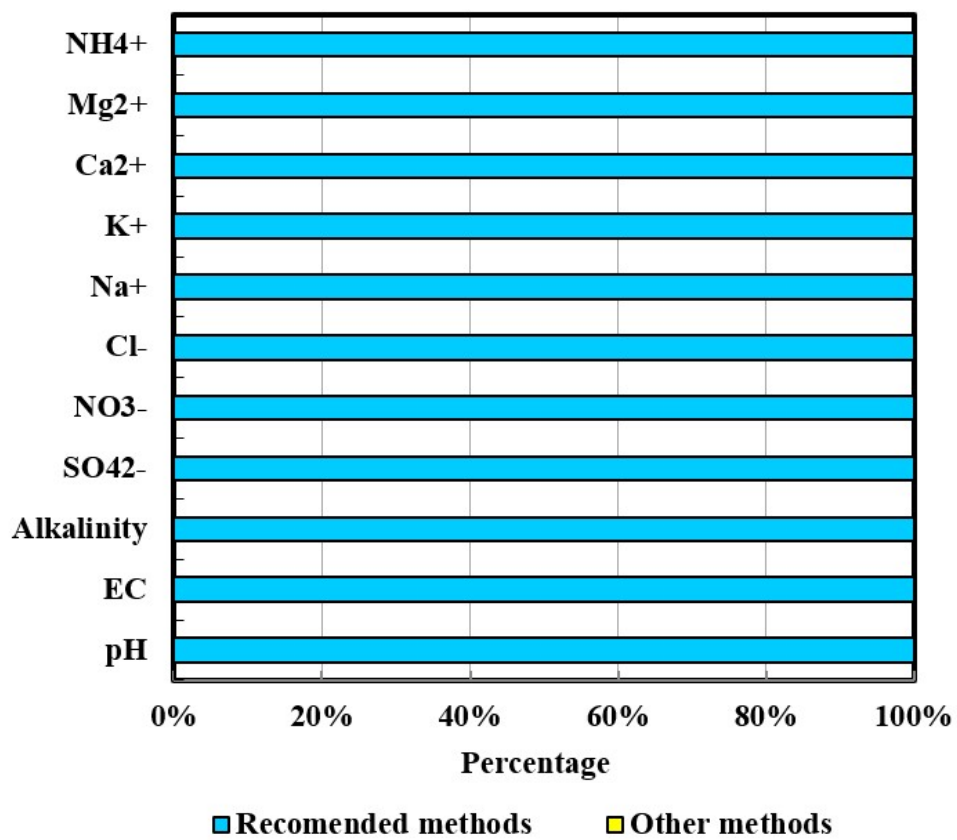


Figure 5.15 Percentage of laboratories using the recommended methods

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	y	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
0	20(1)										
1		20(1)									
2			20(3)			2(1)					
3							4	4(1)	4(1)	4	
4				17	17(1)	17	14	14	14	14	15(3)
5							1*	1*	1(1)*	1(1)*	
6											
7				2	2						
8											4
9											
10											
Flagged E	1	1	3	0	0	1	0	1	2	1	3
Flagged X	0	0	0	0	1	0	0	0	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 ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
CN01	7	A,B	A,B	C,D	E,F	E,F	E,F	E,G	E,G	E,G	E,G	E,G
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
ID01	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	3	A	A	A	B	B	B	C	C	C	C	C
MN01	2	A	A	A	B	B	B	B	B	B	B	B
PH01	1	A	A	A	A	A	A	A	A	A	A	A
PH02	2	A	A	B	B	B	B	B	B	B	B	B
RU01	3	A	A	A	B	B	B	C	C	C	C	A
RU02	7	A	B	C	D	E	C	F	F	F	F	G
TH01	1	A	A	A	A	A	A	A	A	A	A	A
TH02	1	A	A	A								
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	3	A	A	B	C	C	C	C	C	C	C	C

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	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
CN01	7,15	7,15	1,13	7,13	7,13	7,13	7,16	7,16	7,16	7,16	7,16
CN02	7	7	7	11	11	11	11	11	11	11	11
CN03	13	13	13	27	27	27	27	27	27	27	27
CN04	19	19	19	19	19	19	19	19	19	19	19
ID01	3	3	3	3	3	3	3	3	3	3	3
JP03	6	6	24	22	22	22	22	22	22	22	22
JP04	13	13	13	13	13	13	13	13	13	13	13
MY01	1	1	1	12	12	12	12	12	12	12	12
MN01	3	3	3	27	27	27	27	27	27	27	27
PH01	6	6	6	5	5	6	6	6	6	6	6
PH02	0.8	0.8	6	6	6	6	6	6	6	6	6
RU01	32	32	32	30	30	30	40	40	40	40	33
RU02	3	10	50	1	1	50	1	1	1	1	45
TH01	26	26	26	26	26	26	26	26	26	26	26
TH02	19	19	19								
VN01	9	9	9	12	12	12	12	12	12	12	12
VN02	19	19	21	21	21	21	21	21	21	21	21
VN03	11	11	14	14	11	11	14	14	14	14	11
VN04	13	13	21	22	22	22	22	22	22	22	22
VN05	16	16	16	21	21	21	21	21	21	21	21

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

1 year means experienced with one year or less.

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

5.4. Comparison with past surveys

The inter-laboratory comparison projects of the EANET have been carried out 26 times, and the results showing the percentage of flagged data and the percentage of data that satisfied the DQOs are shown in Figure 5.16.

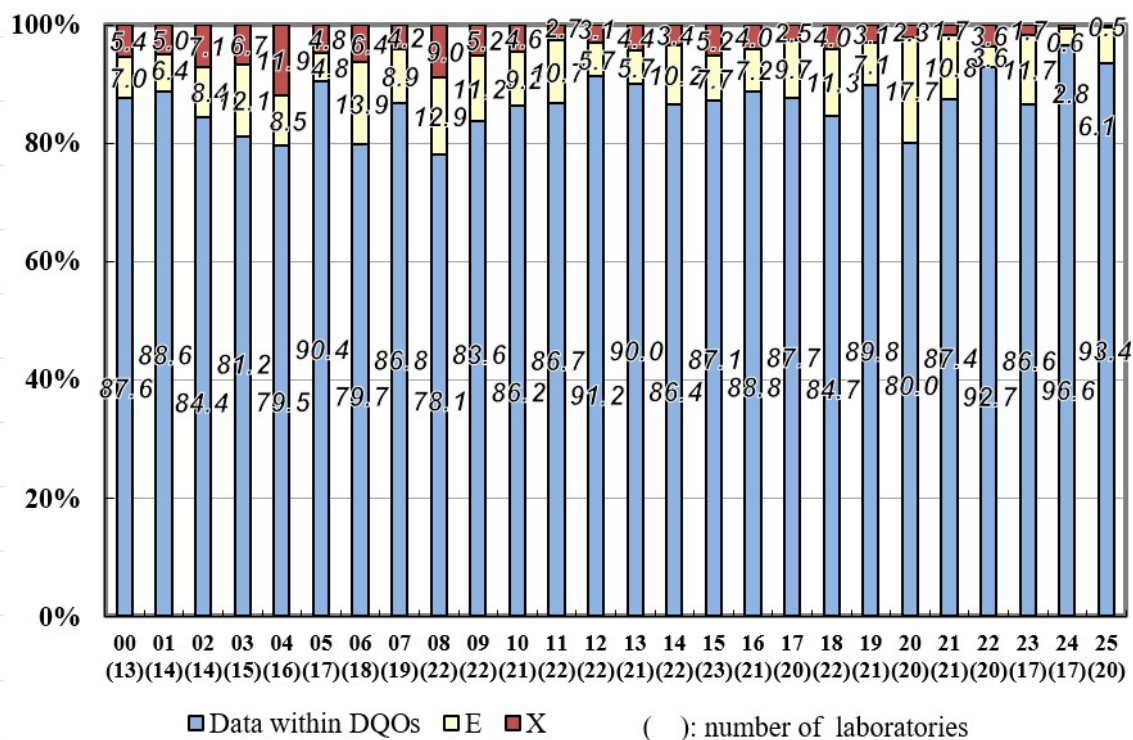


Figure 5.16 Comparison of the results from the inter-laboratory comparison projects

The percentage of data satisfied the DQOs decreased from the last attempt.

The values/concentrations for each parameter from the 1st to 26th projects were compared with the percentage of flagged data in Figure 5.17.

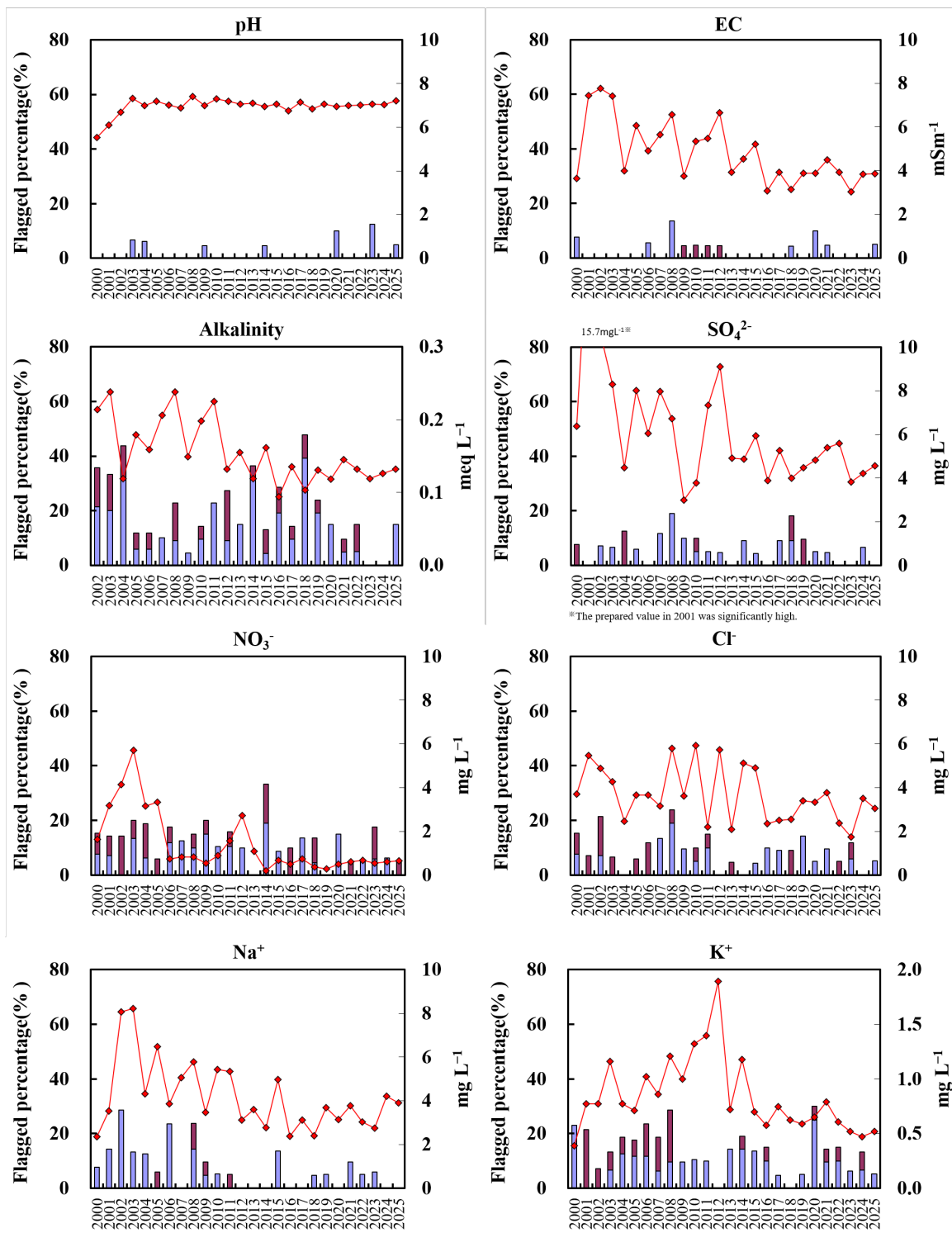


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects

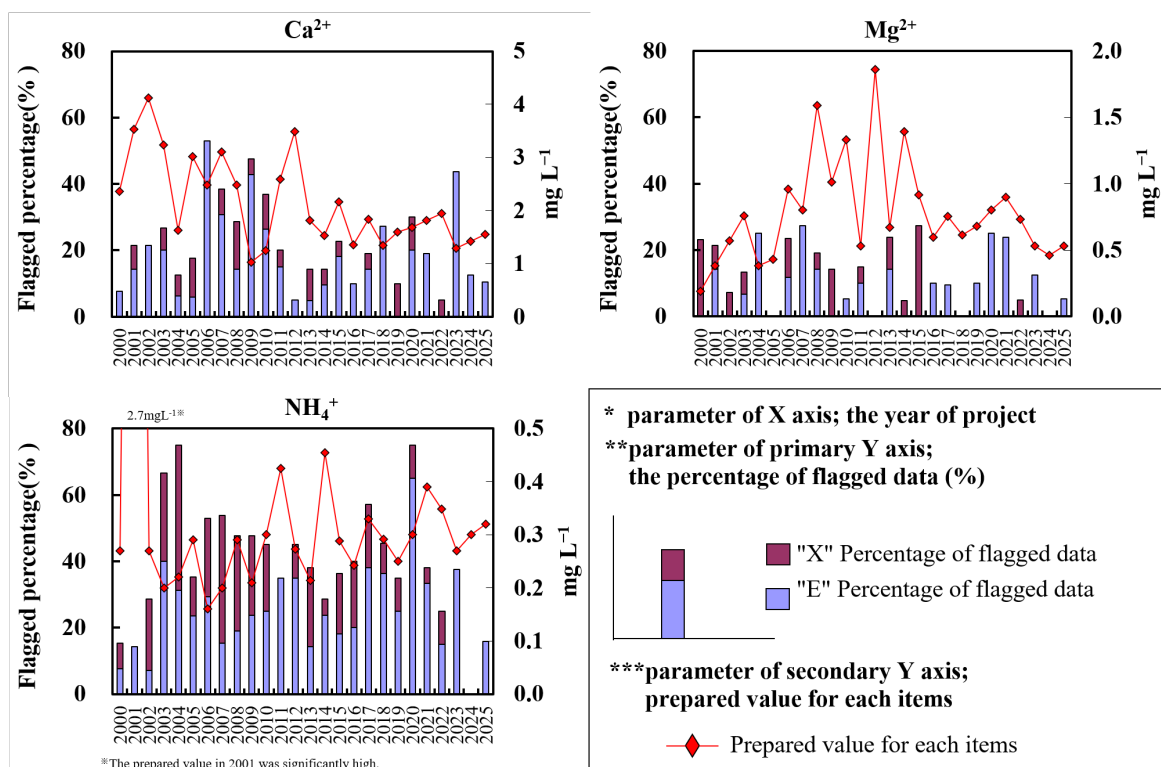


Figure 5.17 Concentrations and the percentage of flagged data for each parameter in inter-laboratory comparison projects (Continued)

There was no flagged data in SO_4^{2-} and Na^+ in this attempt.

The analysis of K^+ and Ca^{2+} were improved.

In this attempt, flagged percentages of pH, EC, Alkalinity, Cl^- , Mg^{2+} and NH_4^+ became higher than the last attempt.

Furthermore, the percentage of flagged data was higher for NH_4^+ than for other parameters in all surveys except the 1st, 2nd, and 25th projects. Therefore, special attention should be paid to NH_4^+ in inland water analysis.

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 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.

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Appendix Table 5.1 Results submitted by the laboratories

Lab. ID	pH	EC - mS m ⁻¹	Alkalinity (meq L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	NH ₄ ⁺ (mg L ⁻¹)
CN01	7.08	3.87	0.134	4.52	0.63	2.98	3.98	0.52	1.53	0.52	0.28
CN02	6.98	3.81	0.133	4.46	0.65	2.94	3.91	0.53	1.50	0.54	0.30
CN03	7.08	3.87	0.131	4.36	0.70	2.91	4.01	0.53	1.54	0.52	0.28
CN04	6.90	3.72	0.133	4.55	0.68	2.97	3.91	0.53	1.60	0.54	0.28
ID01	6.92	4.04	0.105	4.52	0.67	2.86	3.72	0.53	1.33	0.45	0.40
JP03	7.12	3.67	0.130	4.96	0.70	3.33	3.80	0.53	1.46	0.50	0.24
JP04	7.12	3.69	0.136	4.56	0.64	3.01	3.89	0.52	1.60	0.53	0.30
LA01	0.00	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MY01	7.10	3.77	0.137	4.53	0.61	3.03	3.92	0.47	1.54	0.53	0.31
MN01	6.94	3.39	0.133	4.95	0.73	3.22	3.86	0.50	1.74	0.53	0.26
PH01	6.73	3.79	0.131	4.55	0.62	2.97	3.98	0.54	1.90	0.49	0.28
PH02	6.97	4.67	0.153	4.38	0.71	2.89	3.78	0.49	1.83	0.64	0.33
RU01	7.07	3.80	0.099	4.82	0.58	2.69	3.46	0.55	1.56	0.52	0.30
RU02	7.11	3.91	0.127	3.97	0.61	3.91	4.05	0.40	1.63	0.53	0.35
TH01	7.18	3.53	0.136								
TH02	6.10	3.66	0.130	4.59	0.62	3.00	4.38	0.49	1.39	0.48	0.31
VN01	6.85	3.67	0.125	4.60	0.72	3.19	3.80	0.50	1.50	0.54	0.32
VN02	6.95	3.68	0.125	4.63	0.63	3.15	3.81	0.52	1.48	0.52	0.32
VN03	6.83	3.72	0.128	4.56	0.60	3.42	3.85	0.51	1.45	0.51	0.34
VN04	6.70	3.64	0.126	4.37	0.99	3.24	3.79	0.49	1.51	0.55	0.33
VN05	6.88	3.70	0.123	4.68	0.62	3.07	3.84	0.51	1.54	0.55	0.32
Expected value	7.20	3.86	0.132	4.57	0.65	3.04	3.91	0.52	1.55	0.53	0.32
Number of data	20	20	20	19	19	19	19	19	19	19	19
Average	6.93	3.78	0.13	4.55	0.67	3.09	3.88	0.51	1.56	0.53	0.31
Minimum	6.10	3.39	0.10	3.97	0.58	2.69	3.46	0.40	1.33	0.45	0.24
Maximum	7.18	4.67	0.15	4.96	0.99	3.91	4.38	0.55	1.90	0.64	0.40

blank: not analyzed

Appendix Table 5.2 Data normalized by the prepared value

(Original data / Expected Value – 1) × 100 (%)

Lab. ID	pH (%)	EC (%)	Alkalinity (%)	SO ₄ ²⁻ (%)	NO ₃ ⁻ (%)	Cl ⁻ (%)	Na ⁺ (%)	K ⁺ (%)	Ca ²⁺ (%)	Mg ²⁺ (%)	NH ₄ ⁺ (%)
CN01	-1.7	0.3	1.5	-1.0	-3.1	-2.0	1.8	0.0	-1.1	-2.5	-12.5
CN02	-3.0	-1.4	1.0	-2.5	-0.5	-3.2	-0.1	2.6	-3.0	2.5	-7.3
CN03	-1.7	0.3	-0.8	-4.6	7.7	-4.3	2.6	1.9	-0.4	-1.9	-12.5
CN04	-4.1	-3.6	0.8	-0.5	4.6	-2.4	0.0	1.9	3.2	2.5	-11.5
ID01	-3.9	4.7	-20.5	-1.1	2.6	-6.0	-4.9	1.9	-14.4	-14.5	25.0
JP03	-1.2	-4.8	-1.5	8.5	7.7	9.4	-2.9	1.9	-6.0	-5.7	-25.0
JP04	-1.2	-4.4	3.0	-0.3	-1.5	-1.0	-0.5	0.0	3.0	0.0	-6.3
LA01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MY01	-1.4	-2.3	3.5	-0.9	-6.2	-0.4	0.3	-10.3	-0.6	0.0	-3.1
MN01	-3.7	-12.1	0.8	8.4	12.8	6.0	-1.3	-4.5	12.5	0.0	-19.8
PH01	-6.5	-1.8	-1.0	-0.4	-4.1	-2.2	1.9	4.5	22.8	-8.2	-12.5
PH02	-3.2	21.0	15.9	-4.2	9.2	-4.9	-3.4	-6.4	18.1	20.1	3.1
RU01	-1.8	-1.5	-25.3	5.4	-10.8	-11.5	-11.4	5.1	0.4	-1.9	-7.3
RU02	-1.2	1.3	-3.8	-13.2	-6.2	28.6	3.6	-23.1	4.9	0.6	8.3
TH01	-0.3	-8.5	3.3								
TH02	-15.2	-5.2	-1.3	0.4	-4.1	-1.2	12.1	-5.1	-10.1	-8.8	-4.2
VN01	-4.9	-4.9	-5.1	0.7	11.3	5.0	-2.9	-3.8	-3.0	1.9	0.0
VN02	-3.5	-4.6	-5.3	1.2	-3.1	3.5	-2.6	-0.6	-4.3	-2.5	0.0
VN03	-5.1	-3.6	-3.0	-0.3	-8.2	12.5	-1.5	-1.9	-6.5	-4.4	7.3
VN04	-6.9	-5.7	-4.5	-4.3	52.3	6.5	-3.2	-5.8	-2.6	3.1	3.1
VN05	-4.4	-4.1	-6.6	2.4	-4.6	1.0	-1.8	-1.9	-0.9	4.4	1.0
Minimum	-15.2	-12.1	-25.3	-13.2	-10.8	-11.5	-11.4	-23.1	-14.4	-14.5	-25.0
Maximum	-0.3	21.0	15.9	8.5	52.3	28.6	12.1	5.1	22.8	20.1	25.0
Average	-3.7	-2.1	-2.4	-0.3	2.9	1.8	-0.7	-2.3	0.6	-0.8	-3.9

blank: not analyzed

6. ACKNOWLEDGEMENT

Soil samples were collected in Japanese cedar (*Cryptomeria japonica*) and Japanese cypress (*Chamaecyparis obtusa*) plantations in the Field Museum Oyasan of the University Forest, Tokyo University of Agriculture and Technology (TUAT).

7. CONTACT INFORMATION

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